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hnical Report **R600**

NUCLEATION OF STEAM BUBBLES FROM LARGE-DIAMETER PREPARED SITES

October 1968

NAVAL FACILITIES ENGINEERING COMMAND

U. S. NAVAL CIVIL ENGINEERING LABORATORY
Port Hueneme, California

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1968

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NUCLEATION OF STEAM BUBBLES FROM LARGE-DIAMETER PREPARED SITES

Technical Report R-600

Z-R011-01-01-109

by

E. J. Beck

ABSTRACT

The Naval Facilities Engineering Command has, through the Naval Civil Engineering Laboratory, been active for some time in the development of improved desalination equipment to provide potable water at advanced bases. A review of the current literature on the physics of boiling disclosed a consensus that (1) nucleation is necessary for boiling, (2) nucleation is accomplished by sites of certain sizes only, and (3) the amount of superheat above the boiling point that is necessary for bubble formation is a function of site orifice diameter.

Because no supporting theory accompanied the latter two observations, a study was made to determine why these limiting factors should apply—if in fact they do. A simple theory derived by the author indicated, on the contrary, that for a given wetting angle at the solid-vapor-liquid interface, the superheat necessary should be a function of the effective radius of vapor bubbles as determined by the wetting angle and the angle formed by the site's walls. This hypothesis was tested using a small copper hot plate with several relatively large sites (on the order of 1 to 2 mm in diameter); nucleation proved possible with superheats of only a few degrees Fahrenheit. Although steam would form a bubble, the emergence and growth of the bubble was inhibited by the thickness of the boundary layer, because a large radius bubble would penetrate to the area in which the covering layer was at or below the boiling point. The vapor within the bubble would therefore be condensed by this relatively cooler water. The appendixes describe future experiments to study long-time boiling histories of similar sites, the depletion of adsorbed gases, scaling, and the effects of additives which change the contact angle.

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INTRODUCTION

Heterogeneous Nucleation and Phase Change

The Naval Facilities Engineering Command has, through the Naval Civil Engineering Laboratory, for some time been active in the development of improved desalination equipment to provide potable water at advanced bases. The development of improved and more efficient water distillation equipment depends upon a better understanding of nucleation, which appears to limit the useful distillation processes.

The consensus of current literature on the physics of boiling is that for a substance (water, for example) to change from its liquid phase to its gaseous phase, one of two conditions probably must exist: either some of the gas phase or nuclei of a compatible material must be present on which the gas phase can form. This is the concept of heterogeneous nucleation, which will be discussed in this report.

A large number of industrial and geophysical processes are nucleation limited. In the latter class are precipitation of snow and rain, and the initial formation of ice on the ocean's surface.

So long as heat transfer rates are kept low, a closed container of very pure water with steam above it can exist in essentially complete thermal equilibrium over a wide temperature and saturation pressure range without these nucleation sites because phase change can take place at the water-gas interface—all of which is essentially, in this case, a large nucleator. If heat is added at the bottom at a very high rate, the fluid becomes locally superheated at the container-liquid interface, but boiling cannot occur in the absence of nucleation sites.

Not only does the water in a thin boundary layer become superheated, but the solid surface assumes a temperature, ΔT, above the fluid's boiling temperature at the local pressure. Because the surfaces of ordinary materials are imperfect and in the absence of special treatment hold adsorbed gases, at pressures near atmospheric distilled water will usually boil at a metal surface temperature some 8 to $10^{O}F$ above the local saturation temperature, but boiling is not observed at a lower surface temperature. Because a very thin layer of fluid is in intimate contact with the metal and the conductivity of water is relatively high, an infinitesimal layer is superheated to the same temperature as the metal surface. For specially polished surfaces, high superheating can occur; this has frequently been observed in flame polished, outgassed glassware.

The importance of adsorbed gases is demonstrated by the fact that the temperature necessary to boil a fluid increases as nucleation sites' properties change with continued boiling. As the boiling progresses, presumably each bubble takes away some of the adsorbed air or other gas. Whether a particular surface discontinuity can nucleate in the absence of an adsorbed gas film, irrespective of the superheat temperature imposed, is not known. As will be discussed later, there are good reasons why it may not be practicable to obtain the experimental evidence necessary to prove the point.

The obtaining of curiously high supersaturation conditions in freezing, evaporation by boiling, and condensing is scientifically important, and some work along these lines is being considered for later efforts within this work unit. Industrially, there are many reasons for working in the opposite direction—avoiding extremes in superheating, supersaturation, supercooling, etc. An example in nature of very active nucleation of the type which might be useful in industrial processes is found in first formation stages of sea ice. In polar summers, a condition in which the sun is shining, the ocean is at its freezing temperature (usually having been recently covered with or largely covered with sea ice), and a cold wind is blowing. From on board ship, for instance, one can observe within a few hours the supercooling of the top fraction of an inch of seawater by a cold wind and the forming of multitudes of small ice crystals, which are first visible as areas resembling oil slicks. If clouds obscure the sun for some time and the chill winds blow steadily for an hour or so, the crystalite bed grows to a thickness of perhaps 1/8 to 1/4 inch. The hydrodynamic action of gentle waves frequently agglomerates these crystals into plate-sized discs, and interaction of the discs cause piling up of crystalites at the edges. The net effect causes formations resembling lily pads, thus the common name "lily pad ice." Eventually the soft ice bed may disappear in the event that solar insolation increases or the wind dies down. A continuous sheet of ice may be formed under prolonged cold winds. The important point so far as nucleation is concerned is that there are obviously sufficient impurities in arctic seawater that nucleation readily occurs on a microscopic but widespread scale. For lack of better information it is satisfactory to assume that dust and other small particles form the nuclei necessary for rapid crystal formation. In the improbable situation that the seawater did not contain the nuclei, supercooling of a large but thin layer would occur, and eventually a nucleus for freezing would become active because of a local disturbance; for example, ice formation through the supercooled layer then would progress rapidly until the lack of sensible heat of fusion was overcome by freezing. These processes have recently received considerable study in connection with desalting of seawater by freezing, a highly advantageous process thermodynamically if the mechanical problems could be overcome. The ice crystals formed are very small, are of freshwater, and are surrounded by a layer of brine. It is the removal of brine without melting the freshwater ice which makes the process difficult.

In spite of its cost, water purification is most often done by some form of distillation, but the high costs of superheating to achieve a phase change are not generally appreciated. It is not the high latent heat of water (970 Btu's per pound at 1 atmosphere of pressure) that controls the cost. (Equipment has been devised which largely uses the heat transferred upon condensation to supply this heat in the cycle.) Rather, it is the total temperature drop between the boiling or evaporation* side and the condensing side necessary to effect the heat transfer that largely determines the total cost. In all equipment, but especially in multieffect evaporators, the requirement for a superheat in the metal significantly above the saturation boiling point directly determines the surface area which needs to be constructed, cleaned and fed brine. This in turn limits the practical number of stages in typical equipment.

If this required superheat value could be halved (e.g., reduced from $10^{o}F$ to $5^{o}F$) the number of stages and product output could be almost doubled in a given useful temperature range. A similar but even more cogent argument for reducing the required superheat is found in the vapor compression distillation cycle, the temperature–entropy curve for which is shown in Figure 1 (from Beck, 1967). Here, saturated steam at approximately atmospheric pressure (point 1) is compressed (point 3) and is then condensed at the higher pressure and temperature. The enthalpy change from point 1 to 3 is supplied as premium mechanical work of compression. If the necessary boiling or evaporation can be accomplished with a lower temperature difference (e.g., along the dotted line), then the premium power input can be reduced to the difference in enthalpy (h_{fg}) between points 1 and 2. Even more remarkable economies than this example have been achieved in the laboratory using bench models of reboilers and thin-film evaporation. With the latter method, if the brine or evaporating film can be maintained thin enough, it approaches the thickness of the boundary layer, and evaporation is possible without boiling, that is, without nucleation, Beck (1965a, 1965b, 1967). Practical devices await industrial engineering development of appropriately large units.

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* Boiling here refers to evaporation by release of bubbles at the superheated solid-liquid interface. Evaporation of a fluid at a free surface by kinetic escape of individual molecules would not require nucleation.

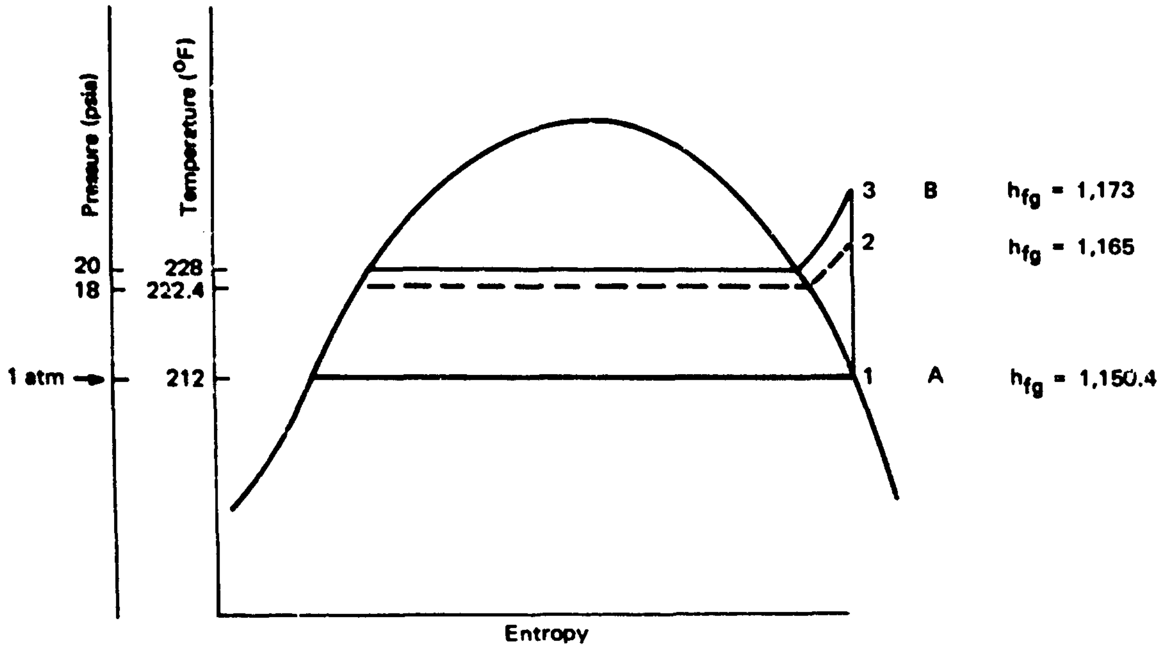

Figure 1. Dimensionless temperature-entropy diagram for a vapor-compression still.

Not all surfaces require the same superheat to achieve boiling. In addition to gas adsorption, physical dimensions of the openings of surface imperfections and surface tension in the fluid establish the superheat of the heat transfer surface necessary to support a given bubble. The picture is greatly complicated by the fact that the thickness, δ, of the useful superheated boundary layer is usually less than the principal vertical dimension of the bubble upon detachment (Figure 2). This usually will not be the same as the radius, r, of the bubble, which is important in predicting the superheat, the equivalent boundary layer saturation temperature, and the pressure within the bubble according to the following equation:*

$$\Delta P = \frac{\sigma}{2r} \qquad (1)$$

The relationship between the height, h, of the bubble and dimension δ is important in a complicated way to bubble growth and detachment, because that portion of the bubble within the superheated boundary-layer

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* See foldout list of symbols for values.

thickness will receive heat, and evaporation will take place at the vapor—liquid interface. The part of the bubble above δ will "see" cold water relative to the saturation temperature within the bubble, so condensation will occur there. Once the bubble is detached, it rises through a turbulent world and its future is immeasurably complicated.

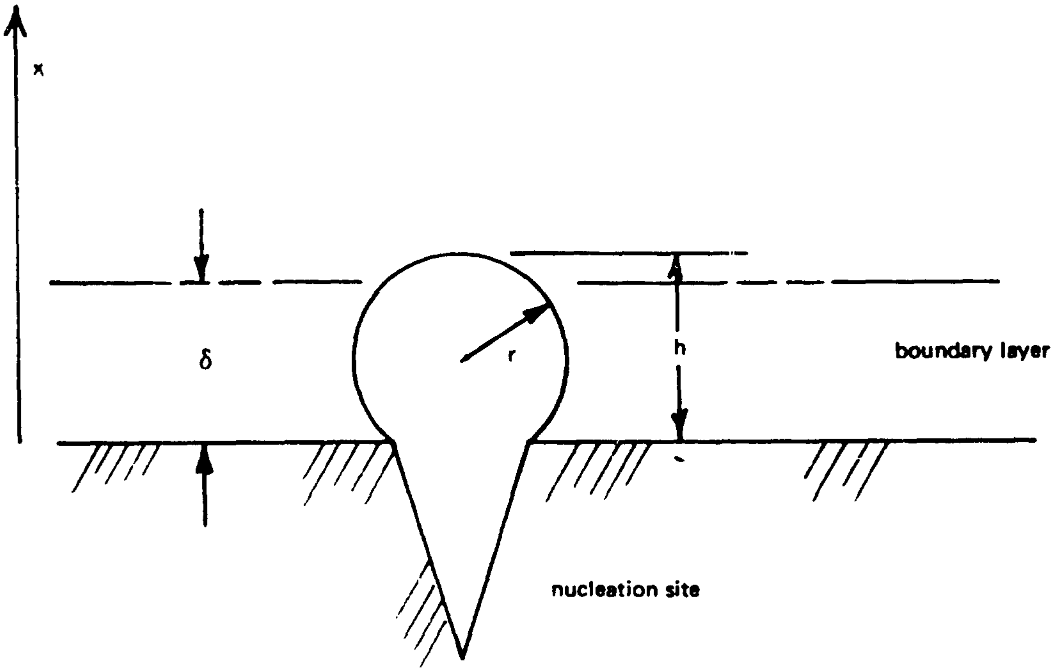


Figure 2. Relation of bubble to nucleation site and boundary layer.

An early account of the simpler aspects of the bubble's progress in a paper by Scorah (1951) is interesting background for what is to follow here. However, it is the prior history of the bubble's formation which will be discussed in detail in this report.

Not all useful boiling surfaces are parallel to the earth's surface, and the gravity and buoyancy forces acting on a vertical bubble on a horizontal surface will obviously be different from those acting on a horizontal bubble on a vertical surface. Most of the experimental work has dealt with a bubble on a horizontal surface; this idealization will be used here, since buoyancy probably has little if anything to do with formation of the bubble within a nucleation cavity before it emerges, when surface tension effects would be preeminent.

Griffith (1966), Rohsenow (1964), and McAdams (1942) consider the birth of the bubble as that time when a definite radius has been established which can be related to the cavity opening. There is considerable evidence that a large cavity with a specific opening behaves very much like a small cavity with an opening of the same size and shape. That is, the history of a bubble would be essentially the same from any of the nucleation cavities illustrated in Figure 3.

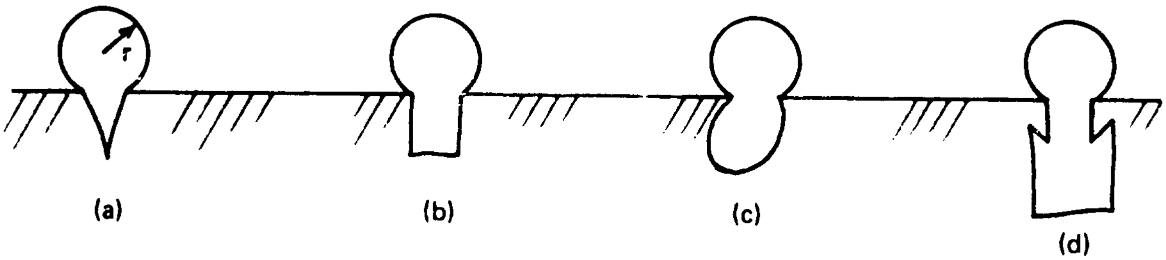


Figure 3. Four shapes of nucleation sites, all with the same opening shape. According to existing theories, all would require the same superheat in the surface to sustain the same size of vapor bubble.

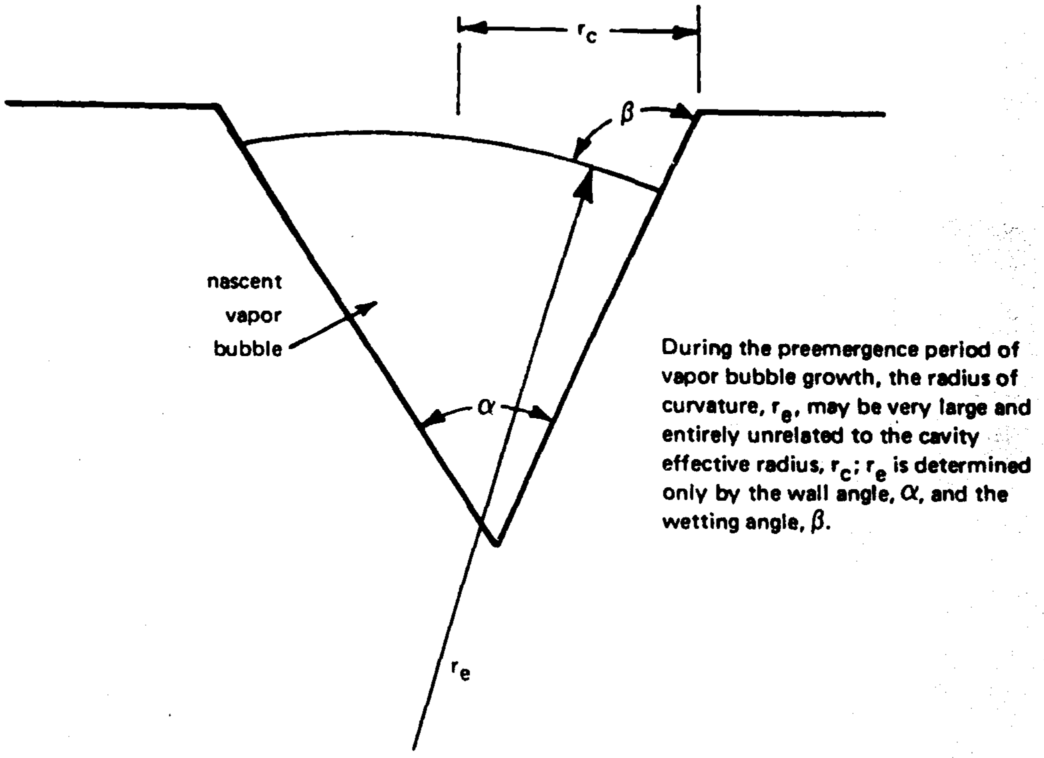
A neglected aspect of nucleation research is the manner in which the cavity, whatever its shape and volume, is filled with steam to form a bubble. The remainder of this report will discuss a hypothesis for the formation of bubbles and describe the results of a crucial experiment substantiating the hypothesis.

Bubble Formation at Nucleation Sites

Whereas the bulk of the literature on boiling discusses the growth, detachment, and destruction of bubbles after they achieve a certain size and shape (as shown in Figure 2) and can be described approximately (Equation 1 and its variations), it is the intention here to proceed in the opposite direction.

The starting point in this discussion is the one usually taken: the characteristics of bubbles represented at Figure 2. Equation 1 is applicable here if we can neglect the problems associated with the variation in temperature through the boundary layer, since this variation affects point-to-point condensation or evaporation within the bubble. Every child knows that a balloon is hard to "start," and he frequently hands it to an adult for partial inflation. Once a satisfactory radius is established, he can proceed to blow it up and cause it to burst, in spite of an increasing tension in the rubber material. He does not seem to have the same difficulty with soap bubbles, which ostensibly would pose a similar problem at small diameters. Soap bubble tension would, however, be more nearly constant.

In Figure 4, the bubble is seen at an earlier stage for which the radius is seen to be not a function of cavity dimensions, depth, or volume, but of cavity angle and wetting angle, β. The term $\mathbf{r_e}$ is dependent on $\mathbf{x}$, which is directly



During the preemergence period of vapor bubble growth, the radius of curvature, r_e, may be very large and entirely unrelated to the cavity effective radius, r_c; r_e is determined only by the wall angle, α, and the wetting angle, β.

Figure 4. The geometry of vapor bubble growth.

related to cavity dimensions although not to any angle dimension of the cavity. Here, r_e is relatively large compared with any of these dimensions. Receding one step further in the argument, a visualization of possible bubble (or more accurately, vapor) volume and configuration is shown in Figure 5, with a possible early situation at c. The earliest concept of our growing bubble in an undefined cavity is shown sketched at b. Here, the first fluid layer on the solid surface within the site is adsorbed gas.

An alternative description of the formation of a bubble which does not require an adsorbed film has been suggested by Griffith (1966), but he does not elaborate. He suggests that when a dry surface is flooded with a fluid, trapped gas in a cavity forms the nucleus for vapor bubbles. To extend this theory, the first bubble to be released according to this model would be a mixture of noncondensable vapor and vapor formed from the fluid. Heat would transfer through the fluid boundary layer film after the fluid is superheated upon contact with the solid surface.* Because there would be nothing to keep the steam formed from mixing with the air, the vapor would diffuse into the air and early bubbles would contain air. The second bubble would contain less air, the third less, etc. by successive dilutions. So long as the wall (and therefore laminar film of fluid) remained at a superheat above the

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* Presumably heat transferred to the vapor from the cavity walls would be trivial, as it would be transferred to a gas with relatively low conductivity.

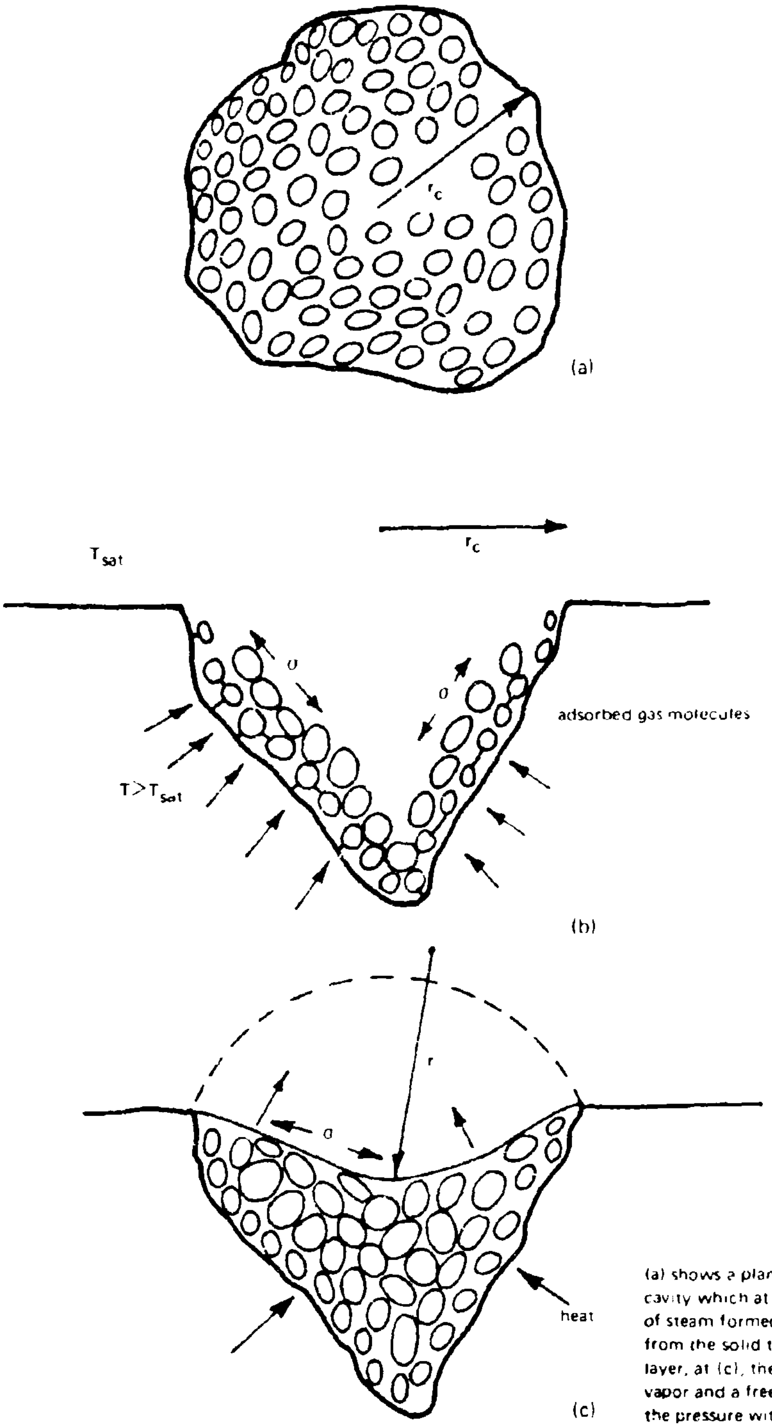
local saturation temperature, each departing bubble would leave a nucleus of vapor. If the system wall temperature and laminar film were allowed to drop below the saturation temperature, heat transfer would occur in the opposite direction, the residual vapor would condense and the nucleation site would become dormant. Unless a critical amount of air had somehow been retained, it would be necessary to reintroduce a noncondensable vapor to the cavity before the site could become effective. This amazingly simple explanation of the functioning of a nucleation site is probably the correct one.

The experiments described below are designed to select the correct explanation for nucleation or suggest an alternative capable of demonstration. The theoretical considerations for growth of a bubble after emergence should be the same for any mixture of gases. However, because the ratio of condensables to noncondensables changes with time, the contact angle might vary systematically, and the superheat necessary to achieve nucleation might change with time.

Homogeneous Nucleation

Work now planned will investigate the concept of homogeneous nucleation—bubble formation without specific, advantageous nucleation sites or particles. This and other problems of potential interest are discussed at some length in Appendixes A and B. To save the casual reader the time of pursuing this in detail, it might be said here that there probably is no such thing as homogeneous nucleation, but that it will exist in the minds of its originators for a long while for the same reason as will the concept of evolution. The definitive experiments to disprove homogeneous nucleation will not be conclusive and it is an attractive alternative to the hypotheses observed derived from phenomena. It also forms the basis for some elegant mathematical exercises, and on that basis it should be retained in accordance with the best principles of scientific investigation as so eloquently laid down by Chamberlin (1890). A poor alternative hypothesis is better than none at all.

In support of this position against homogeneous nucleation it should be said that most of the beautiful mathematical work on surface energies, etc., necessary for the development of the homogeneous nucleation theories was done before general use was made of bubble chambers. Nucleation on high energy particle tracks could probably account for some bubble formation that was then inexplicable. So might imperfect containers. In any event, the crucial experiment for demonstration of truly homogeneous nucleation probably awaits a laboratory free of both cosmic and terrestrial gamma rays, which may be difficult to locate and build. It certainly would be deep within the earth or a body of very pure water.



(a) shows a plan view of the hypothetical cavity which at (b) is accumulating a layer of steam formed by the heat transferring from the solid through the absorbed gas layer, at (c), the cavity is largely filled with vapor and a free surface is actually reducing the pressure within the forming bubble.

Figure 5. Schematic representation of vapor forming in a cavity at very low superheat.

EQUIPMENT

The prepared nucleation sites that were investigated and for which the data and discussion are given later were formed in the horizontal, upper surface of a right circular cylinder of copper (Figure 6) previously described for boiling experiments (Beck, 1967). It was heated from a point near its lower face by two electric cartridge heaters, the input to which was varied by means of an autotransformer. The upper surface temperature was measured with fine constantan thermocouples, one of which was buried about 1/64 inch below the surface. The solid copper cylinder formed one leg of the thermocouple pair, and the junction could thus be located precisely and soldered in place. The lead was brought out horizontally just below the surface and the milled grooved peened over the constantan lead. The small residual groove was smoothed with dental amalgam and the entire surface polished with a 200-grit Carborundum paper. The second thermocouple was filed to a sharp point and used as a cat whisker in a manner similar to the old crystal detector technique. The cat whisker probe was used for most of the temperature measurements and the buried couple was used as an occasional check. Because the temperature gradient through the copper cylinder was high, the buried couple usually read from 0.8 to 1.0°F above that measured by the surface probe.

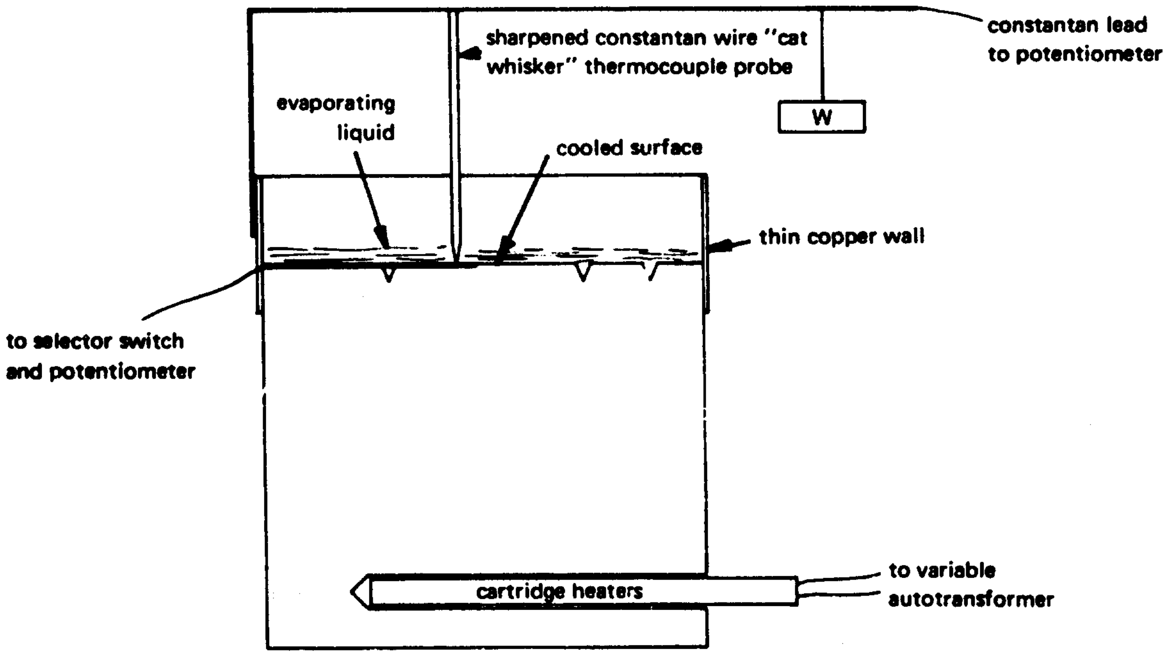


Figure 6. Diagram of small heated copper block used for nucleation experiments. Prepared conical sites were formed in horizontal surface in center area.

All temperatures were measured directly using one of two hand-balanced potentiometers, a Leeds and Northrup Model 8662 Precision or a direct-reading Rubicon Model 46804. The Leeds and Northrup was capable of reading to 0.1°F, while the Rubicon could be read to 1°F and estimated with some certainty to 1/2°F. The more precise but slower Leeds and Northrup was used for those tests with surface temperatures very near to 212°F only. Both instruments were frequently checked against a thermocouple exposed to a 212°F source of wet steam, a small boiler (Figure 7) which conformed to the requirements for such a temperature reference, Condon and Odishaw (1958). The Naval Civil Engineering Laboratory is located immediately adjacent to the Pacific Ocean and the experiment was at an elevation of about 12 feet above sea level. Deviations in atmospheric pressure introduced by this small elevation and by variations in barometric pressure were both neglected; the experimental temperature thus varied a fraction of a degree with variations in the local barometric pressure. This introduces no significant error, as all of the physical properties and important thermodynamic properties of water and steam are essentially linear with temperature over a small temperature range. All of the important temperatures recorded lay between 212°F and 220°F.

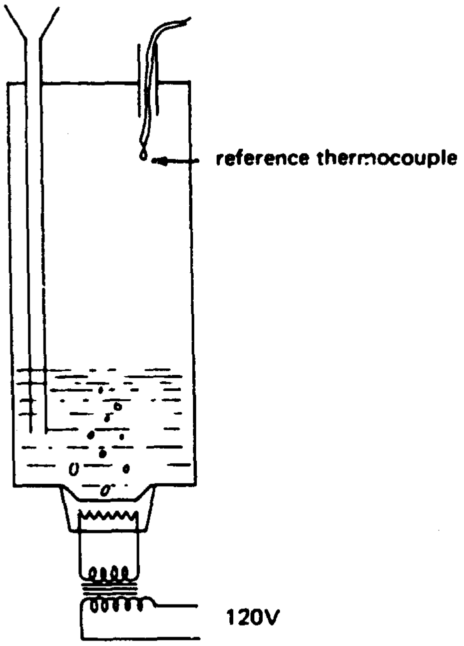


Figure 7. Small electric boiler used as reference junction and cold junction (212°F)—served as cold junction for use with Leeds and Northrup potentiometer.

The experiment was "open face" in that such evaporation as occurred, produced steam which was not condensed and retained. It was, therefore, necessary to replenish the water over the prepared sites (Figure 8) periodically. This was done from the small reference boiler. Except for a few special cases, the water was boiled for at least 1/2 hour to remove dissolved air. All water used in the experiments was essentially mineral-free water purified in a dual-bed ion exchanger.

RESULTS

The following discussion is an abbreviated account of tests of the simple copper block apparatus shown in Figure 6. Various prepared nucleation sites were tested at different heat inputs. The surface was flooded with water to a depth of 1/4 to 3/8 inch and brought to, or slightly above 212°F. The surface of the whole appartus was initially cleaned with 200-grit Carborundum cloth. The prepared sites were places near the center and away from the edge, where minor convection and conduction losses would cause only a small temperature discontinuity. The four sites made by penetration of a sharpened steel point were large (Figure 8), and bubbles forming at these sites were easily distinguishable with the naked eye from any formed at naturally occurring sites on the surface. The temperature at which a bubble could first be seen was recorded. The heat input was varied electrically to achieve the desired history of change in nucleation characteristics for each nucleation site. So sensitive was this technique that a bubble just emerging could be systematically retracted (condensed within the site) or released as a free bubble by changing the electrical heat input slightly. It was also possible to visibly shrink a bubble by introducing a piece of metal at room temperature to the region of the bubble; the cold metal probe would initially draw heat from the water adjacent to the bubble, which would then be momentarily reduced in diameter, again by local condensation. Once warmed to the water temperature, the probe would have no such cooling effect. Usually the bubble's surface would be visible at the surface as indicated schematically in Figure 2 once the metal surface had been heated to a fraction of a degree Fahrenheit above 212°F and the overlying water had had time to be similarly warmed to the boiling point.

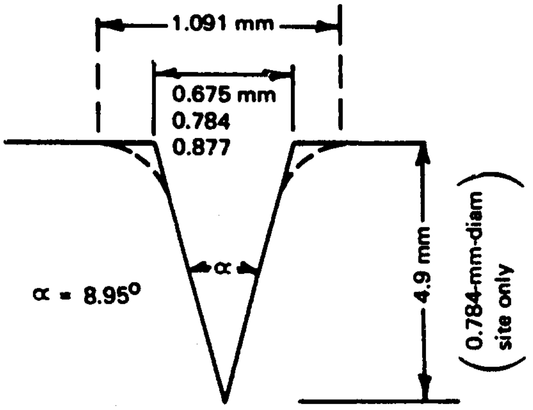


Figure 8. **Geometry of four prepared sites. The angle was the same in each case, but one site had rounded opening, shown dotted.**

Griffith (1966) states that the history of a nucleation site begins with the last time it was dry. The first tests of a prepared conical site, shown schematically in Figure 8, were to determine the validity of this hypothesis. Beginning from a dry surface, the warm but not hot surface was flooded with aerated, deionized water, and the surface gradually brought above the boiling point. A typical temperature history of the surface is shown in Figure 9. This procedure was varied by starting from a dry, warm surface but flooding with deaerated, deionized water at 212°F, the local boiling point. The effect was the same in each case: nucleation at a metal temperature of just above 212°F.

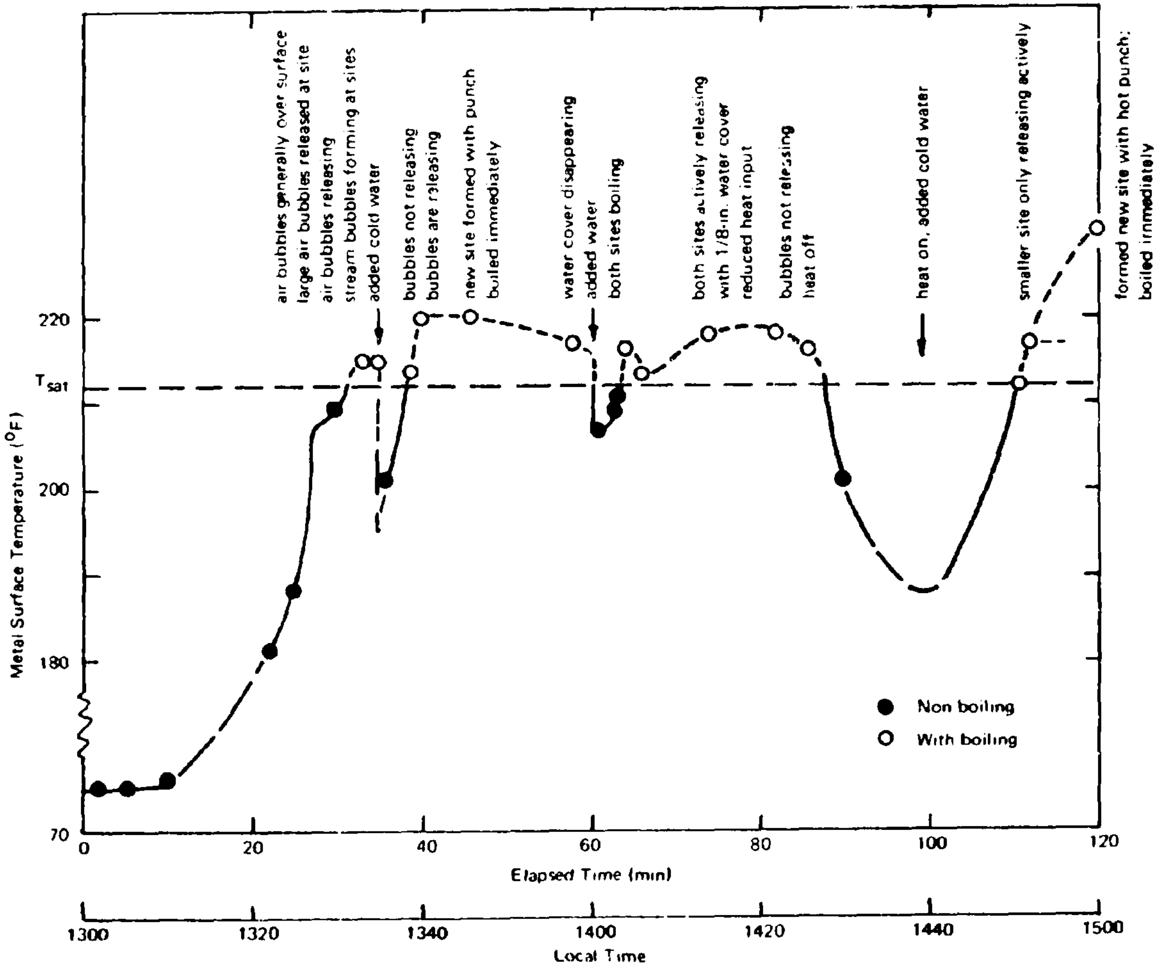


Figure 9. Typical time--temperature history during boiling experiments using two large sites formed by punching.

A second aspect of the first test was subjecting the prepared site to prolonged boiling, which caused the eventual loss of nucleation after the release of many bubbles. Many observers have recorded the increase in temperature necessary to sustain bubbling from a surface over a prolonged period and the eventual loss of the ability to nucleate by certain sites. Several tests were run in which a single site was subjected to boiling until it would no longer produce bubbles. The surface and overlying deionized water layer were then allowed to cool to below 212°F—as low as 70°F in one case. In none of these trials did the site again produce bubbles on reheating to above 212°F, even though other locations on the surface at which boiling had been observed did again become active.

This aging phenomenon was varied by allowing the deactivated site to cool overnight to ambient temperature. Upon reheating, the site would usually begin to produce bubbles at a metal surface temperature of about 216°F (Figure 10). Obviously, the deaerated water was, upon being allowed to stand and cool, absorbing air from the atmosphere which then would come out on the metal surface upon heating. The site had not, however, been dry. Whether the activating layer of gas thus evolved (in this case in the prepared conical site as well as over the surface at large) was in the form of a very thin adsorbed layer or a bubble at the apex of the site cone as shown schematically in Figure 10 is conjectural and was not determined in these experiments. Certainly the volume of gas was small, as it must have come from the liquid held by the site, approximately 0.55 ml.

Having activated one "drowned" site which had a wet history, alternative methods were sought for forming nucleation sites having no dry history. The site discussed above was produced by driving a hard steel point into soft copper in air at room temperature. The apparently necessary gas load in the site, whatever its physical form, was available at all steps in the forming operation. The same steel point was allowed to lie on the heated, submerged copper surface for some time near a drowned, or deactivated site. The surface temperature was well above 212°F—between 218° and 220°F. The system was allowed to cool to about 212°F metal temperature and a new site was produced by driving the steel point into the surface without having removed the point from the water; the point was, in fact, kept in contact with the copper surface. Upon withdrawal of the steel point from the newly prepared site, a bubble immediately appeared. Here was a second method of making a nucleation site to order, one with no dry history.

Upon the chance that the degassing of the steel point by heat transfer only from the copper surface might not be complete, and that the necessary gas might still be adsorbed after lengthy heating, the experiment was repeated with the point heated in a previously prepared, aged and drowned site. Two significant facts were observed. First, the aged, drowned site was not reactivated by the steel point, even when the point was pressed in and rotated, which should have transferred some of any gas layer remaining on the point. Second, the new site was active immediately upon removal of the point.

From the above it was concluded that the necessary gas phase probably came from the gas in the body of the copper; this would appear as an adsorbed layer on the newly revealed surfaces. Very little gas is obviously necessary, and its form is probably not important. It can be a gas bubble or an adsorbed layer.

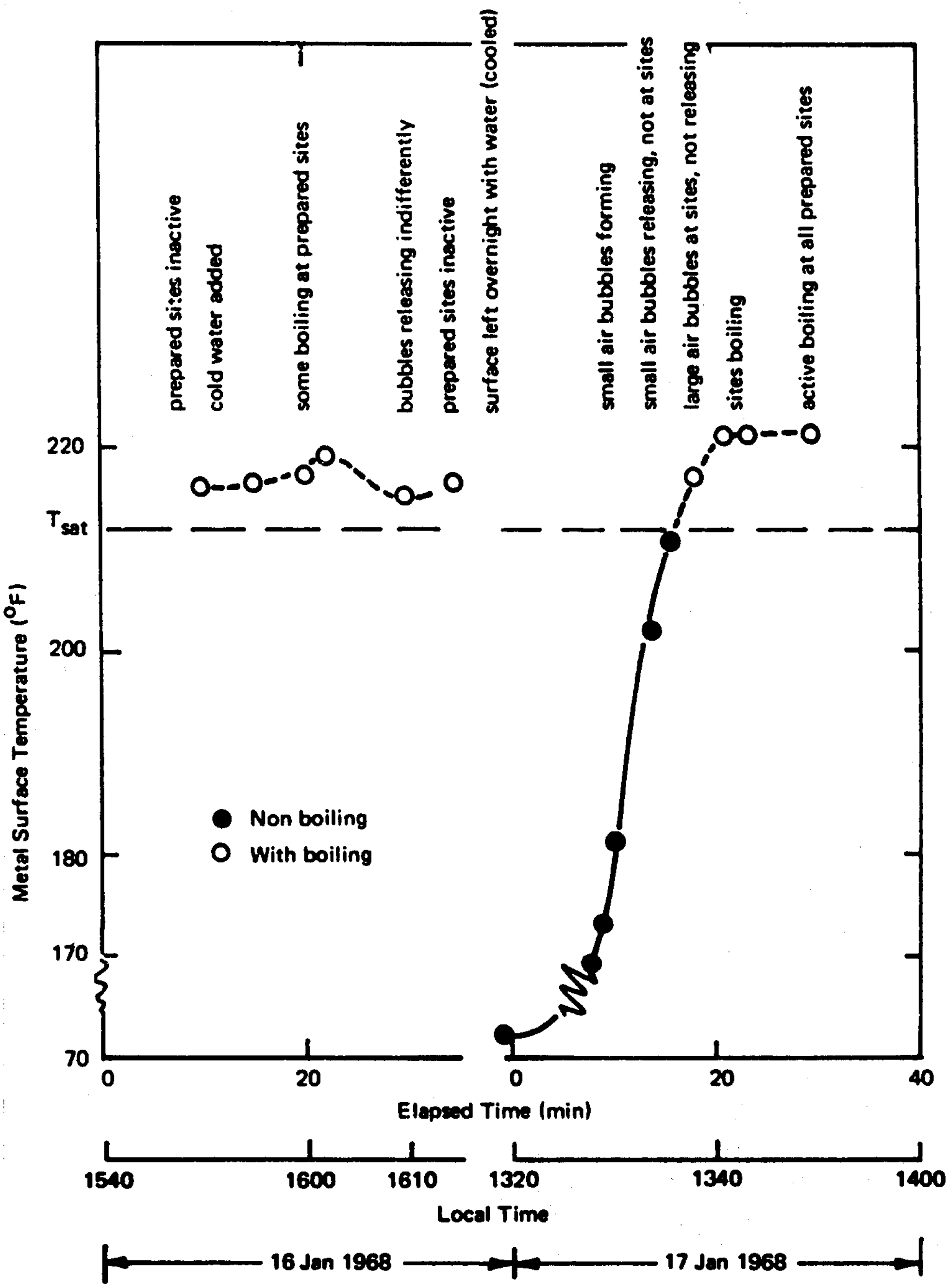
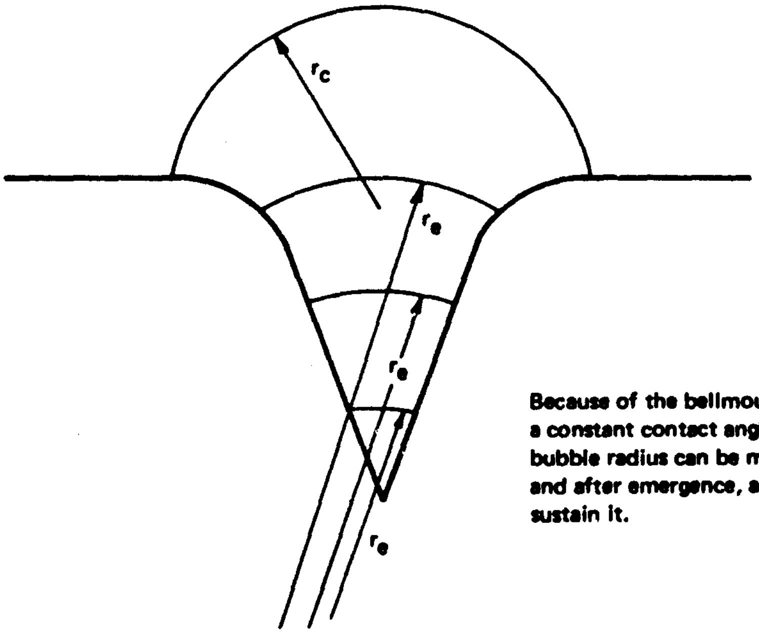


Figure 10. Activation of prepared sites by letting stand cold under water overnight after having been deactivated by boiling previous day.

A mathematical appreciation for deactivation of a site can be obtained from the following analysis. Starting with a dry, conical site of known geometry, water flows in upon submergence of the surface. A small amount of air remains at the apex of the cone in the form of a bubble which, because surfaces are large and surface tension forces are great compared with buoyant forces, does not move from the site in spite of its low density. Upon heating, a small amount of additional dissolved air, which will soon be shown to be insignificant, is probably added to that in the site. This air comes out of solution upon heating and diffuses into the residual air bubble at the apex.

When the metal surface is heated, heat is transferred by conduction to the water layer immediately adjacent to the metal; a lesser path for heat is found through the small residual air bubble. Depending upon the contact angle of the metal-liquid-vapor interface (Figure 11), the pressure necessary to sustain the bubble (opposed by surface tension) may be very great, or if as pictured, very small. The metal superheat necessary to heat the boundary layer to a comparable saturation temperature is, therefore, quite low. It is thus possible to fill even a large conical site with steam at just above the saturation point of the liquid, if the conical angle, α, is small and the contact angle approximately 90 degrees. The important point here is that heat can evaporate the superheated water at the liquid–vapor interface very rapidly. This slightly cools the boundary layer of liquid, and heat is transferred by conduction, convection, or a combination of the two from the still hot superheated boundary layer adjacent to the nucleation site. There are no major barriers to rapid heat transfer.



Because of the bellmouth configuration (assuming a constant contact angle of about 90°) a very large bubble radius can be maintained prior to, during, and after emergence, and a low wall superheat can sustain it.

Figure 11. Schematic concept of a highly idealized nucleation cavity.

However, if the surface temperature is raised well above the saturation temperature, a large bubble radius is not necessary; the necessary pressure can be sustained, the bubble emerges and finally releases under buoyant forces. The volume of vapor (steam in this instance) which has been added to this original small amount of air is large. The air and water vapor are free to rapidly mix by diffusion and convection. so the steam bubble released would carry some air with it, and the site's air supply would be depleted. The large-mouthed sites studied here produce large steam bubbles compared with those produced by naturally occurring microscopic sites, so depletion could be expected to be rapid. It was. Probably only firm attachment of a thin adsorbed layer of noncondensables prevents essentially complete stripping of the site of air within a few hundred bubble releases. The depletion rate for the bulk gas can be approximated by:

$$\frac{dn}{dt} = -K n_o \qquad (2)$$

Separating the variables,

$$\int \frac{dn}{n} = K \int dt, \quad \text{or} \ln n = -Kt + \ln c$$

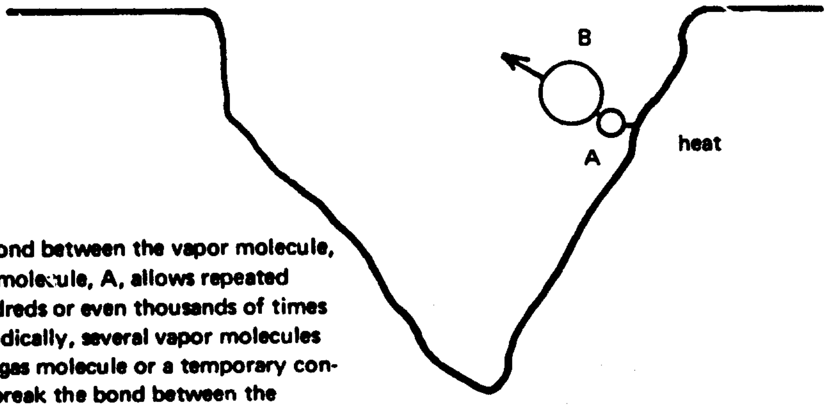
or

$$n = n_o e^{-Kt} \qquad (3)$$

where **n** is the number of noncondensable gas molecules in the site at a particular time, n_o is the number before the first vapor bubble is released, **K** is a constant which depends upon the frequency of bubble release and the ratio of the bubble volume at release to the total site volume, and **c** is an arbitrary constant.

To get some idea of the probable rate of depletion it is necessary to evaluate **K** in Equation 2. This would require observing the volume of air in the site after each of a succession of bubbles—obviously not practicable. However, the large conical sites under study have known volumes. The approximate volume of the bubbles they produce is also known. For the largest site, 0.877-mm diameter at the opening, the bubbles formed usually had a diameter of about 2 mm (Figure 8). The site has a calculated volume of about 0.55 mm^3 and the steam bubble about 4.19 mm^3, for a total volume of about 4.74 mm^3. At standard conditions the maximum volume of air that could be trapped (less than this was actually trapped, because water entered the site) would be about 0.5 mm^3, or some 1.5×10^{16} molecules of air. Assuming that the site was filled with steam upon dislodging of a bubble during boiling, the residual of steam would be about 1/10th of that in the site and bubble. At least during the early period of boiling, the air remaining would be mixed with the steam. Only 17* steam bubbles would have to escape to reduce the trapped air molecules to 1, if they were not adsorbed on the metal surface or otherwise held. This would still not be a firm argument for retention of air, if nucleation can occur on the residual steam—the vapor in the nucleation site that is not condensed when the metal temperature drops below the saturation temperature. However, it has been observed that very small, naturally occurring nucleation sites have remained active for long periods and still functioned after a cooling cycle. This would rule out residual steam as the only possible source of nucleation.

A possible explanation is that initially an air-filled site nucleates bubbles and loses most of its air. It still continues to function so long as there is an adequate (perhaps one-molecule thick) layer of adsorbed gas in the site surface (schematically illustrated, Figure 5b). Eventually this layer is apparently dislodged (Figure 12) after prolonged boiling and the thermal and mechanical agitation caused by the bubble release. Such a process would be consistent with all the observations made here.



A comparatively weak bond between the vapor molecule, B, and the adsorbed gas molecule, A, allows repeated bubble formation—hundreds or even thousands of times a minute for days. Periodically, several vapor molecules may act on an adsorbed gas molecule or a temporary concentration of heat may break the bond between the surface and A. The vapor molecule carries away in the steam bubble, and eventually the nucleation site fails to nucleate additional bubbles.

Figure 12. Schematic representation of proposed mechanism for outgassing.

Most of the above discussion has dealt with sharp-edged sites, which obviously have a problem nucleating after the liquid–vapor interface is displaced from the conical interior to the surface. When there is a large wetting angle, further bubble growth leads to a decrease in effective bubble radius (Figure 13) and an increase in the superheat above the saturation temperature necessary to sustain a bubble (Equation 1).

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* Many more than this might be released in 1 second in a natural site boiling at an elevated metal temperature.

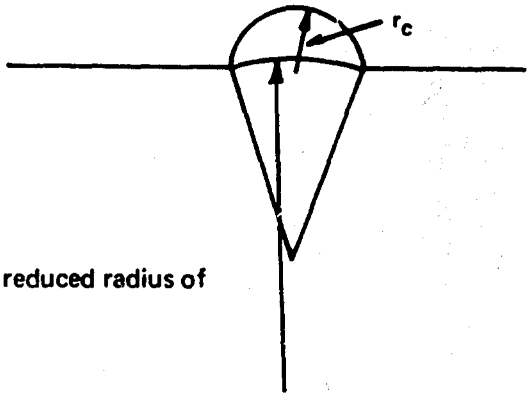

Figure 13. Small-angle conical site showing reduced radius of bubble curvature on emergence.

Two obvious approaches to securing further bubble growth outside the cavity without raising the metal temperature will be considered. First, the fluid's surface tension can be modified to change the wetting angle by introducing surface-active chemical agents. The second approach, and that tried in this investigation, was rounding of the edges of a site, shown schematically in Figure 11. A large radius can thus be maintained for a given superpressure (equivalent to a larger metal superheat), and the larger radius bubble should release more readily because the buoyant forces would be greater.

One of the prepared sites was reamed with a series of sharp, tapered points to give a radius similar to that in Figure 11. The major diameter at the flat surface was 1.091 mm, as determined with a precision optical comparator; this is some 50% greater than the largest diameter of the undisturbed cone portion.

Within the accuracy that could be obtained by close inspection, the bubbles produced by this larger diameter site appeared to be about 3 mm across, or some 50% larger in diameter than the typical bubble formed by sites of comparable diameter but without the bellmouthed rounding. As predicted, it was possible to consistently and regularly secure release at a lower metal temperature from the bellmouthed site than from a sharp-edged site. Both types of sites formed bubbles at the same elapsed time (same metal temperature) upon gradual heating, but it was possible to hold a surface temperature at which the bellmouth would release its bubble, but sharp-edged site would not.

While the details of functioning of nucleation sites in boiling at low metal supertemperatures has received little attention in the heat transfer field, similar considerations have been given great study in metallurgy. The heat transfer fraternity has been largely preoccupied with obtaining maximum rates of heat transfer without excessive temperatures. which would destroy the metal surface. They have largely neglected the low end of the boiling curve.

Nucleation and growth kinetics are, on the other hand, the heart and soul of obtaining desired physical properties of metals. The work of Hirth and Pound (1963) was examined for leads which might prove productive in the present study. Several sections suggested that during rapid cooling of alloys, especially with the presence of impurities, irregular crystal formations on the surface would be expected, and especially numerous would be various types of dislocations. In a single exploratory attempt at randomly developing particularly effective nucleation sites for boiling, an area of the experimental apparatus used here was tinned with a thick layer of 50% tin and 50% lead solder. It was quenched with water droplets, producing a dull, fine-grained, diffuse surface. One edge of the chilled area was thickened and had an overhung or return area similar to that shown at A in Figure 14.

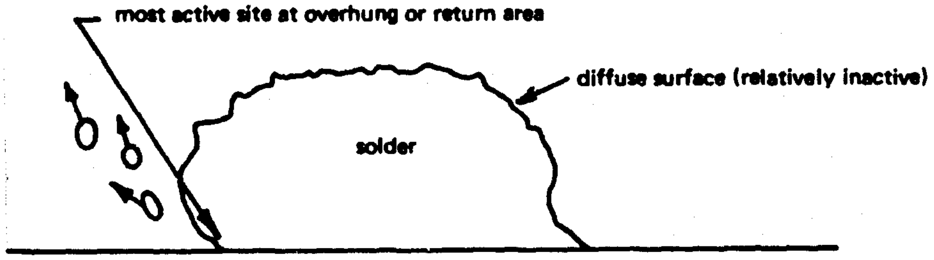

Figure 14. Location of active nucleating site in chilled solder blob.

The diffuse surface proved ineffective as a nucleation area, but this return area did not. Active release of bubbles from a single point in the crevice could be repeatedly obtained with a metal superheat of only 2.9°F. Whether this clearly superior performance is due to a peculiar crystal imperfection or to the gross arrangement of the site near a large radius is problematical, but it is believed the latter is the correct explanation. Nucleation without bubble release at very low superheat temperatures can routinely be accomplished in the prepared conical sites. Bubble release at lower temperatures than for the conical sites can be obtained by breaking the sharp edges.

It is believed that the effective nucleation site located in a crevice had two desirable characteristics: first, its large radius allowed the emergence of a bubble with a large radius—similar to the bubbles from the bellmouth site discussed previously; second, the protected area beneath the solder shelf in which the site was located heated the surrounding water uniformly, so the bubble was not subjected to a strong temperature gradient through a thin boundary layer as it might be on a horizontal surface. This would suggest the possibility of increasing the effective thickness of, or reducing the temperature gradient through boundary layers by breaking up a heat transfer surface through gross mechanical roughening.

A final observation was made quite by accident. In the course of the experiments a lead pencil was used to mark certain sites on the smooth copper surface in which the prepared sites were formed. Immediately, a series of bubbles would form tangent to the edges of the graphite track. If the metal surface was above about 218°F, these bubbles would release. If the metal was only a few degrees above the saturation temperature, standing bubbles would form. With rapidly releasing bubbles, the superior ability of the graphite trace to nucleate disappeared within some 5 to 8 seconds, repeatedly. There is so far no suitable explanation for the phenomenon, but the obvious first place for investigation will be to discover if a broken trace of graphite produces an unusual wetting angle. It may be possible to do this with compressed air or other nonthermal techniques. No obvious practical application can be seen for this phenomenon unless (a) the effect can be made persistent and (b) nucleation and bubble release can be effected with lower superheats by using a graphite or other prepared surface. Nevertheless, such nontypical performances should be investigated for the insights they may yield.

All of these experiments have been performed with very pure (deionized) water in the interest of maintaining continuity of the experiments in time. To have used a less pure fluid (e.g., seawater) would have caused surface changes from scale deposition which would have prevented comparison of the series of experiments. Because of obvious practical application to the distillation of nonpure liquids, there is a need for repeating at least part of these experiments (and some alternatives suggested above) using solutions, especially salt water.

From these exploratory experiments, it can be seen that boiling need not necessarily be controlled by random defects in industrially finished metal for heat transfer surfaces. There is real basis for expecting to be able eventually to produce superior nucleating surfaces mechanically.

CONCLUSIONS

The exploratory work to date has shown that:

1. For a given fluid, the threshold surface temperature above saturation necessary to accomplish the formation of a bubble on a given heat transfer surface has not yet been established.

2. Growth of a bubble from a surface defect (nucleation site) is inhibited by the projection of the bubble into or through the boundary layer. With a large bubble and small boundary layer (good convection) the heat in the upper part of the bubble is dissipated and the bubble cannot grow to the point where it is released under buoyance forces.

3. Large prepared nucleation sites can effectively initiate nucleation, subject to the limitations on bubble release.

4. A nucleation site need not have been at one time dry and in contact with air to be effective. However, an adsorbed layer of gas within a site must be available to make it active.

5. Selective shaping of a nucleation site may provide for an increasing bubble radius with a constant wetting angle, so that bubble growth and release may be enhanced without an excessive temperature difference.

6. Local inhibiting of forced or natural convection will significantly increase the effective thickness of the boundary layer, thus reducing the thermal gradient from the hot metal surface to the cooler bulk of the liquid. This will in turn facilitate bubble growth and release at a small metal-to-fluid temperature difference (Appendix A).

FUTURE PLANS

Investigation of these areas, by means of the approach discussed in Appendix A, is planned:

1. Inhibition of local convection cells to increase the thickness of the boundary layer and thus promote bubble release.

2. Long-term boiling of aqueous solutions from a prepared, optimum site to investigate scaling and its effects on nucleation.

Appendix A

PROMOTION OF BUBBLE RELEASE

The usual water purification equipment in which boiling occurs such as vapor compression machines, multieffect evaporators, and reboilers typically have smooth heat transfer surfaces. Nucleation sites at which vapor bubbles form consist of microscopic discontinuities in the surface accumulations of impurities. The work discussed in the body of this report indicated that nucleation per se is essentially independent of site orifice size, but that large sites nucleate large bubbles. Since these large bubbles would project through the typical boundary layer, heat transfer to the vapor cannot occur in the upper part of a large, attached bubble; the bubble would not release and might collapse. Contrary to the practice in the typical heat transfer case, it may be desirable to inhibit turbulence, flow, and severe natural convection, all of which will act to reduce the boundary layer thickness, δ. A thick boundary layer would promote bubble release, or active boiling. A useful application of nucleation will require both bubble release and acceptable heat transfer rates to be economically attractive.

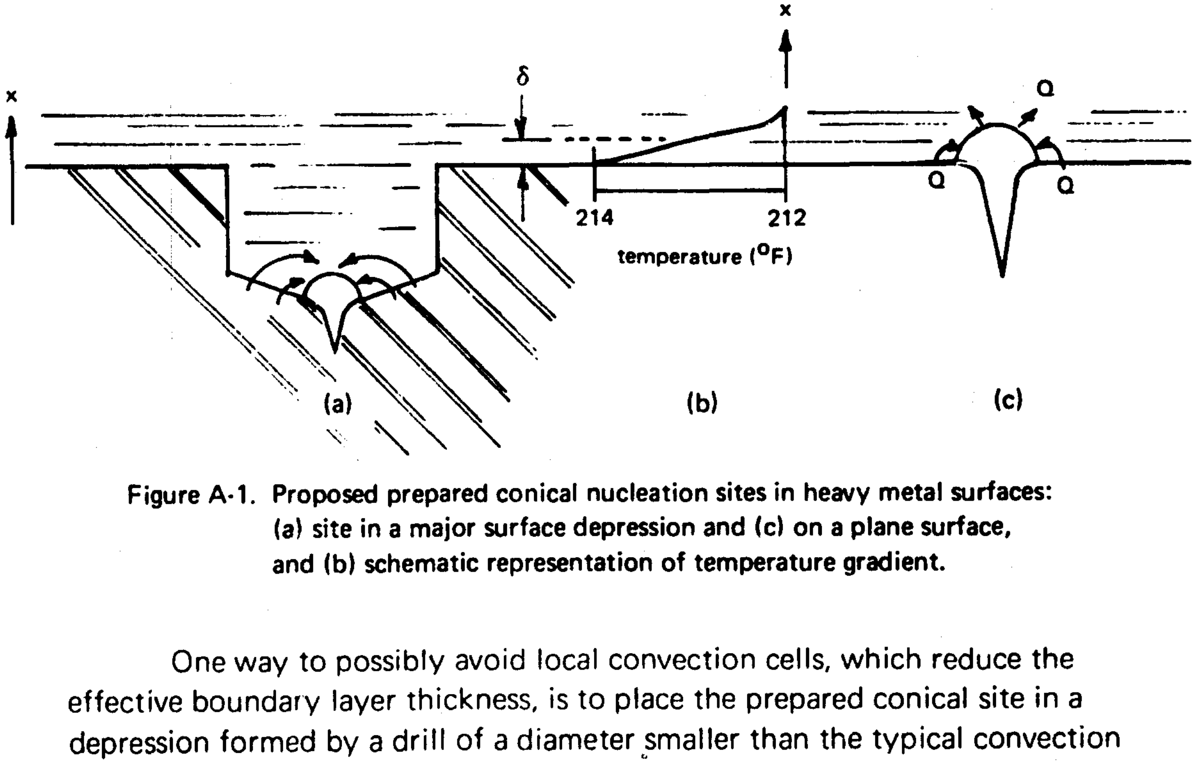

Figure A-1. Proposed prepared conical nucleation sites in heavy metal surfaces: (a) site in a major surface depression and (c) on a plane surface, and (b) schematic representation of temperature gradient.

One way to possibly avoid local convection cells, which reduce the effective boundary layer thickness, is to place the prepared conical site in a depression formed by a drill of a diameter smaller than the typical convection cell in shallow water. Such a cell would have a diameter of about 1/4 to 3/8 inch. A drilled site **a** is shown schematically in Figure A-1, and at **c** the prepared site is shown formed in a plane, horizontal metal surface. The temperature scale common to the two sites (on a plane surface or in a depression) is shown in Figure A-1. In each case the site will be exposed to fluid at about the temperature of the metal surface.

The site shown schematically at **a** in Figure A-1 will be suitable for the present copper block surface. Because there will be a finite albeit small temperature gradient through the copper (in the **x** direction, Figure A-1), an auxiliary experiment using the type of site shown at **a** in Figure A-2 may be necessary. Here, the site would be formed in a thin metal surface and heated from below by condensing steam; the metal surface would be located in the upper end of what has recently been termed a "heat pipe," in which heat is transferred from a lower boiling area to an upper condensing area without significant temperature drop.

A possible alternative location of the nucleation sites in a major depression is shown at **b** in Figure A-2. In addition to allowing multiple sites in a single major depression, there should prove some advantage in having the bubble released adjacent to a vertical surface, because it would thus grow largely inside the boundary layer.

Scaling is the bane of most distillation processes. With microscopic nucleation sites, it is fairly certain that scale fills the original sites and new sites are formed in the scale. The presently planned experiment should allow observation of the larger sites during scaling. These sites should have a longer active life than small natural sites, with slower loss of heat transfer capability and less need for cleaning. It is planned to conduct at least part of the proposed tests with a saline solution and to arrange the equipment so that the vapor can be condensed and returned to the solution; the brine will thus stay at essentially one concentration, except for the small loss of solids to form scale.

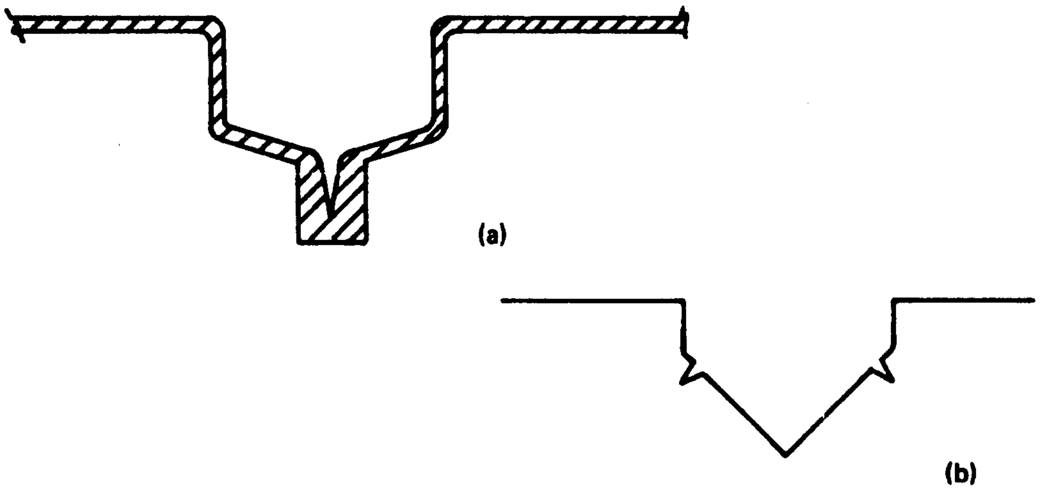

Figure A-2. Proposed prepared sites for nucleation: (a) recess in a thin metal surface (b) multiple sites in a single recess.

Appendix B

THE ROLE OF NUCLEATION IN PHASE CHANGE

Melting, evaporation, condensation, and freezing are such common phenomena in everyday life that it is not obvious at first that a change in phase is essentially a forbidden transaction when you are dealing with pure materials and uncontaminated containers. Ice melts when you add heat, and water evaporates if you add heat at a high enough temperature. Boiling is of special interest because of its importance in cooking, distillation, etc. Nevertheless, the first definitive experiment on which a vast technology of boiling heat transfer is based was made as recently as 1934. Because boiling is the process considered in this report and because the experiment was relatively simple, it is worth describing.

A heated wire was held horizontally in a container of water at the local boiling temperature, approximately 212°F. The wire's surface temperature was measured and it was found that heat was transferred to the fluid by the heated wire without visible bubble formation until the wire's temperature reached some 8° to 10°F above the water temperature. Boiling was first observed at one or two points until the heat input was increased, when additional boiling sites appeared. Unbelievably high heat transfer was achieved when boiling was general over the wire's length at a temperature about 45°F above the saturation temperature of the water. This temperature, the highest point of stable boiling, has been the subject of a great deal of engineering speculation and investigation. It must not be exceeded in typical engineering applications, the most notable of which are the heat transfer surfaces in nuclear reactors.

The interesting point for discussion here is why no boiling was observed until the wire had been heated well above the saturation temperature, and why it occurred first at a particular point on the surface which appeared no different from any other.

The single site phenomena had long since been recognized, and a physical description of a boiling site been made. A description is omitted here because of the detail with which it is discussed in the body of this report.

Statistical mechanics, the theoretical treatment of energy of particles in interaction and the basis of modern thermodynamics, considers a fluid as a group of randomly moving molecules of discrete velocities and, therefore, discrete kinetic energies. Staticical mechanics also is the basis for the definition of temperature.

Not all the molecules in a fluid have the same energy (Montroll in Condon and Odishaw, 1958, and Sommerfeld, 1956). This was recognized by Maxwell, who gave:

$$c_w = \left(\frac{2kT}{m}\right)^{1/2} \tag{B-1}$$

as the most probable molecular velocity, where T is the absolute temperature, m is the molecular mass, and k is Boltzmann's constant. The average kinetic energy, on the other hand is

$$<\frac{1}{2}\,m v^2>_{av} = \frac{3}{2}\,kT \tag{B-2}$$

The resulting distribution frequency versus absolute energy of discrete molecules is a skewed curve which decays exponentially at the higher energies because of relativistic effects (Figure B-1). The important implication of this is that fluids of a given temperature do not consist of a collection of molecules all at the same temperature and therefore all with the same energy or heat content. If, for instance, the average kinetic energy were approximately the most probable, it would be correct to say that the energy at the peak (Figure B-1) represented a temperature. If we were somehow able to sort out these peak-energy molecules we would have a hot gas at a uniform thermodynamic temperature. If we could then segregate the slow (cold) molecules, we would have a small amount of very cold fluid and another small amount of very warm fluid. In the extreme case these fluids might be in the solid and the gaseous phases, respectively.

In a single-phase substance, there would seem to be a possibility, however remote, that sufficient fast or slow molecules might get together and at least momentarily form a small inclusion of a different phase. This is not known to have happened.

However, if we slowly heat water, for instance we can increase its temperature to the well-understood saturation temperature for a given pressure (212°F at sea level, standard atmosphere). At that point we still have a single phase (liquid), although the kinetic energy of the most energetic molecules would be very high. Many of them would, in fact, be escaping from a free surface. Upon further heating, the total internal energy would be increasing, the fluid would be superheated. Even though the more energetic molecules have far in excess of the energy expected for a liquid at that temperature, there would be no obvious change in phase, except for the gradual evaporation from a free surface. There would be a metastable condition. Water has been known to have been heated to well over 100°F above its saturation temperature without boiling.

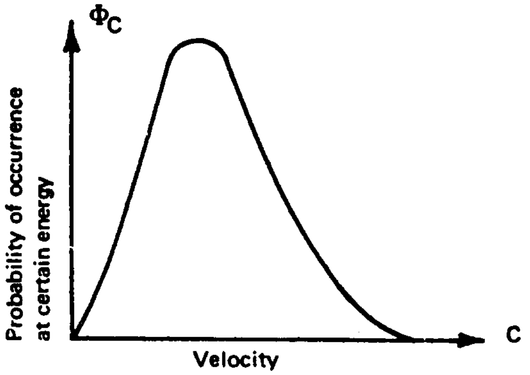

Figure B-1. Maxwellian distribution for molecular energies (dimensionless).

How would it be possible to systematically isolate some of these molecules from the bulk of the fluid to obtain some steam? Conceivably, by chance a fair number of these more energetic molecules might meet, forming a pocket of steam. To develop a cavity to hold the steam requires work to displace the fluid; but more important, if the group of molecules is small, surface tension will prevent cavity formation—the free energy required to do so for a very small group will not be available. Beyond a certain minimum (critical) radius, the adding of an additional energetic molecule would not require as much free energy as an energetic molecule supplies. The steam bubble (cavity) can thus grow. This is the argument in favor of homogeneous nucleation, widely held and believed in, as an explanation for evaporation of liquids and melting or freezing of solids. There is an elegant mathematical theory, but there are no experiments other than those mathematically linking certain treatments of freezing rates with similar treatments designed to cause homogeneous nucleation. The observed and predicted rates are similar.

How then, can evaporation occur in the body of a fluid (in distinction to evaporation occurring at the fluid–vapor interface)? It probably does not. The key to the problem probably lies in the adsorption of noncondensable gases on solid surfaces. When a solid surface prepared in one environment is placed in a different gaseous environment, two things happen. Depending upon the materials, the fineness of subdivision of the solid surface, and on properties of the gas, a certain amount of the gas is immediately adsorbed in a layer generally considered to be no more than a few molecules thick. The bonds are weak and the gas can be desorbed by heating the surface or reducing the total pressure. The second thing that is observed is that the adsorption process is exothermic; the heat released is roughly equivalent to that which would be expected from condensing the gas.

Exactly how this quasi-gaseous adsorbed layer functions in a nucleation site for boiling from a solid surface is not clear, but two aspects are evident. The adsorbed layer has sufficient gaseous characteristics that it can perform the function of a free surface in allowing a vapor layer to escape from the superheated fluid to form the nucleus of a bubble. Its bond to the solid surface is such that moderately high temperatures and pressures do not allow its rapid removal by diffusion to a gas-poor area—the vapor bubble. Further, it appears that the radius of curvature of the site plays a critical role in the early stages of bubble formation—otherwise bubble formation could occur at large on any solid surface with an adsorbed layer of gas. It is possible that because of surface energy considerations the gas layer is many molecules thick in the nucleation site, but only a few molecules thick on a flat surface.

The adsorption of, say, nitrogen and probably all common atmospheric gases is probably due to this physical bond discussed above. Oxygen, if it reacts with certain metals, forms a compound and loses its vaporlike qualities. Other gases are known to chemically bond, and the resulting adsorption is called chemisorption. The bonds are stronger, and greater energy and temperature must be supplied to desorb the layer. It might prove important to investigate chemisorbed layers for their ability to nucleate, as boiling surfaces are known to become ineffective after prolonged use. A chemically bonded layer might delay or prevent the aging of nucleation sites.

If homogeneous nucleation (boiling without the intervention of a second phase, imperfection, or other discontinuity to act as a nucleation site) is to ever be demonstrated, the conditions for the tests will be severe. The cleanliness of both the container and the fluid to be placed in a metastable condition will have to be virtually perfect. Further, it is known that high energy radiation, which produces ions when it traverses matter, can cause nucleation. This is the basis for operation of both cloud chambers and bubble chambers; the large number of ions formed serve as nucleation sites and the resulting condensed vapor or bubble tracks can be photographed. There is some speculation whether it is the ionic charge or the thermal energy released that causes nucleation. However, it would appear that if the arguments regarding the Maxwellian energy distribution (Figure B-1) are extended, a thermal spike with a sudden and high concentration of very energetic molecules could produce what the homogeneous nucleation theory would allow. Both the required energy and localization are apparently present. This adequately explains the operation of the bubble chamber, but it is not quite so clear how introduction of energy spikes into a supercooled vapor in the case of the cloud chamber can produce a concentration of very-low-energy water vapor molecules or droplets—fog. It would be easier to argue that the energy released would cause a local concentration of molecules of high-energy vapor or even superheated gas. In any case, the effect should disappear very rapidly by diffusion and energy transfer with successive molecular collisions. It does not; the fog produced is usually quite persistent and a strong electric field is necessary to collect the charged water droplets at a fluid interface so that successive particle tracks can be observed.

Clearly, if homogeneous nucleation is to be observed experimentally under conditions controlled sufficiently closely that this type of nucleation can be repeated and unequivocally identified, it will be necessary to eliminate all naturally occurring radiation. This means going at least 50 feet underground in an area where there is no natural gamma ray radioactivity.

One final objection should probably be voiced against the existence of homogeneous nucleation. Following Boltzmann's early work, statistical mechanics (Montroll in Condon and Odishaw 1958) had as its basis the probability of collision of two molecules. This well-developed and proven theory admits a negligible probability for the simultaneous collision of three or more molecules. Inasmuch as at least 50 molecules of diatomic gases are necessary to form a mass with a critical radius, and by definition they must have higher than average energy, it would appear improbable that homogeneous nucleation occurs frequently.

While homogeneous nucleation cannot be categorically ruled out on the basis of the above arguments, it does seem that more probable but as yet unsuspected or unrevealed explanations for nucleation should be sought. Less reliance should be placed on the unsupported but popular mathematical arguments on the nature of homogeneous nucleation. This will allow more time for consideration of the very useful and practical heterogeneous nucleation, the subject of this report.

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LIST OF SYMBOLS

C	Particle energy
c	An arbitrary constant
c_w	Molecular velocity as used by Maxwell
h	Height of bubble, linear units
h_{fg}	Enthalpy, units of heat energy per unit weight of fluid
K	A constant which depends upon the frequency of bubble release and the ratio of the bubble volume at release to the total site volume
k	Boltzmann's constant
m	Molecular mass
n	Number of noncondensable gas molecules in the site at a particular time
n_o	Number of noncondensable gas molecules in the site before the first vapor bubble is released
ΔP	Pressure above atmospheric within a bubble, equivalent to average T_{sat} for an adiabadic or constant size bubble
Q	Heat transfer per unit area, time (heat units per unit area, hour)
r	Radius of bubble or nucleation site, linear units
r_e	Effective radius of curvature of bubble, linear units
r_c	Radius of site and hemispherical bubble with 90-degree contact angle; generally, minimum bubble radius, linear units
T	Absolute temperature, $^{\circ}$F, as used in Maxwell's equation
T	Temperature, $^{\circ}$F
ΔT	Surface metal superheat above saturation temperature, $^{\circ}$F
T_{sat}	Saturation, or boiling, temperature at local atmospheric pressure, $^{\circ}$F
t	Time
v^2	Particle velocity
x	Vertical distance from horizontal boiling surface, linear units
α	Cone angle of nucleation site, degrees
β	Wetting angle at solid-liquid-vapor interface, degrees
δ	Effective boundary layer thickness, linear units (in x direction)
σ	Surface tension, dynes/cm
Φ_C	Relative frequency of particle of energy C, dimensionless

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13. ABSTRACT

The Naval Facilities Engineering Command has, through the Naval Civil Engineering Laboratory, been active for some time in the development of improved desalination equipment to provide potable water at advanced bases. A review of the current literature on the physics of boiling disclosed a consensus that (1) nucleation is necessary for boiling, (2) nucleation is accomplished by sites of certain sizes only, and (3) the amount of superheat above the boiling point that is necessary for bubble formation is a function of site orifice diameter.

Because no supporting theory accompanied the latter two observations, a study was made to determine why these limiting factors should apply—if in fact they do. A simple theory derived by the author indicated, on the contrary, that for a given wetting angle at the solid-vapor-liquid interface, the superheat necessary should be a function of the effective radius of vapor bubbles as determined by the wetting angle and the angle formed by the site's walls. This hypothesis was tested using a small copper hot plate with several relatively large sites (on the order of 1 to 2 mm in diameter); nucleation proved possible with superheats of only a few degrees Fahrenheit. Although steam would form a bubble, the emergence and growth of the bubble was inhibited by the thickness of the boundary layer, because a large radius bubble would penetrate to the area in which the covering layer was at or below the boiling point. The vapor within the bubble would therefore be condensed by this relatively cooler water. The appendixes describe future experiments to study long-time boiling histories of similar sites, the depletion of adsorbed gases, scaling, and the effects of additives which change the contact angle.

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14. KEY WORDS	LINK A		LINK B		LINK C	
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Homogeneous nucleation						
Heterogeneous nucleation						
Adsorbed gases						
Water purification						
Superheat						
Enthalpy						

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