ON THE MECHANISM OF BOILING CENTERS ACTIVITY

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Established are the necessary and sufficient conditions for a depression (pore) in the heater surface to become a boiling center. Two modes of vapor generation in pores are revealed.

The characteristics of bubble boiling (number of centers, breakaway dimension and frequency, heat transfer rate, and acoustic noise level) are determined essentially by the mechanism of vapor center activity on the heater surface, i.e., by the dynamics of nucleation, buildup, and breakaway of the new phase.

As has been mentioned in [1] already, the basic source of active centers are depressions or pores in a solid surface as well as ready gas bubbles forming on poorly wetted horizontal areas of the hot body surface. After a few subsequent studies [2-18], the physical mechanism of boiling centers activity is still not quite well understood.

In this article the author analyzes the phenomena which occur in boiling centers often encountered in practice, namely in conical pores in a wetted surface.

1. We will determine the conditions of activity, i.e., the conditions under which vapor bubbles can form, build up to macroscopic dimension, and break away.

The role of pores in aiding the vapor generation process is that they contain already formed gas bubbles and thus eliminate the potential barrier of surface energy in a superheated liquid, which would otherwise impede the buildup of subcritical vapor nuclei [1]. Consequently, if a depression in the heater surface is completely filled with liquid, then the formation of a vapor bubble during boiling is not aided in any way. On the other hand, according to experimental evidence, macroscopic vapor bubbles do not emerge from all air-filled depressions in a hot solid surface. We must conclude, therefore, that the presence of some air in a pore next to the liquid is a necessary but not a sufficient condition which determines the vapor generating capability of the pore. (Pores which contain a gas phase separated from the liquid by a meniscus may be called potential boiling centers.)

In order to determine the supplementary conditions for a potential center to become active, we consider a conical pore in a heater surface, depth h and vertex angle φ , which contains insoluble gas and whose temperature can be varied at will (Fig. 1a).



Fig.1. Buildup of a bubble from a conical pore.

Before the gas makes contact with the liquid, let the gas pressure be $\mathbb{P}^{0}_{\mathbf{G}}$. After the plate has been immersed in the liquid, the latter will generally first penetrate into the pores, forming spherical menisci, and then evaporate into the air space underneath it. These processes come to an end when thermodynamic equilibrium is reached, i.e., when the temperatures as well as the pressures and the chemical potentials of both phases become respectively equal.

Let a vapor-gas bubble be formed in the lower part of the pore, its height x being the characteristic dimension here. Since the internal pressure inside the bubble P_i is equal to the sum of the gas pressure

Stavropolsk Pedagogical Institute, Stavropolsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 23, No. 1, pp. 51-58, July, 1972. Original article submitted March 13, 1972.

© 1974 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00. P_G and the saturated-vapor pressure P_V , while the external pressure P_e consists of the hydrostatic pressure P_L and the capillary pressure $2\sigma/R = 2\sigma/x \sin\varphi$, hence the net force $F = P_i - P_e$ per unit meniscus area is

$$F(x) = P_{\rm G} + P_{\rm V} - P_{\rm L} - \frac{2\sigma}{x\sin\phi} \,. \tag{1}$$

The gas pressure P_G and the surface tension σ are much less dependent on the temperature than the vapor pressure P_V , making it permissible to let

$$P_{G} = P_{G}^{0} \left(\frac{h}{x}\right)^{s} = \frac{A}{x^{3}}$$
$$\frac{2\sigma}{\sin\varphi} = C,$$
(2)

and

where A and C are constants.

Introducing $\Delta P = P_V - P_L$ and inserting (2) into (1), we have

$$F(x) = \frac{A}{x^3} + \Delta P - \frac{C}{x} . \tag{3}$$

When mechanical equilibrium is reached inside the pore, the net force vanishes and the following equation will yield the height of a bubble at equilibrium:

$$\frac{A}{x^2} = [C - \Delta P x. \tag{4}$$

The roots of this equation are most easily found by means of graphs, as the intersection points between the straight line $y_2 = C - \Delta Px$ and the curve $y_1 = A/x^2$ (Fig. 2). (One must remember that the curve $y_1(x)$ has two branches, in the first and in the second quadrant respectively. The interaction of the straight line $y_2(x)$ with the second branch yields negative values of x_2 and, therefore, these roots are of no significance to our problem.) The slope $\Delta P = P_V(T_1) - P_L$ of the straight line (4) characterizes the superheat $\Delta T = T_1 - T_s$ at the heater surface and may be called the vapor supersaturation.

As temperature T_1 rises, ΔP increases from the negative minimum possible value $\Delta P = -P_L$ in cold liquid $(T_1 \ll T_S)$ and approaches zero with increasing subheat $T_S - T_1$; $\Delta P = 0$ in saturated liquid $(T_1 = T_S)$ and becomes positive in superheated liquid $(T_1 > T_S)$. Thus, a rise in the heater temperature corresponds to a clockwise rotation of the straight line $y_2(x)$ about point C, as a result of which the conditions of its intersection with the curve $y_1(x)$ change (Fig. 2). For cold subheated and for saturated liquid Eq. (4) has only one positive root, i.e., there exists only one equilibrium height $x_0(T_1)$ for a bubble in the pore. When the bubble is purely gaseous, its height x_0 becomes minimum $x_0(0)$ in cold liquid (point K). (We note that, when $\Delta P = 0$, only one of the remaining two roots is negative and the other lies in infinity.)

For superheated liquid the straight line $y_2(x)$ intersects the curve $y_1(x)$ in the first quadrant (point M and N), i.e., there are two positive roots x_1 and x_2 . In other words, two equilibrium positions of a vaporgas bubble with respective height x_1 and x_2 are possible when the heater temperature becomes $T_1 > T_s(P_L)$. As the superheat ΔT increases, the absolute value of the negative slope of the straight line $y_2(x)$ increases while x_1 and x_2 come closer. At some limiting supersaturation level $\overline{\Delta P}$ the secant $y_2(x)$ becomes a tangent $y_2(x)$ and both roots merge into one: $\overline{x_1} = \overline{x_2} = x$. It is easy to prove that the abscissa of the point of tangency is

$$\bar{x} = \sqrt{\frac{3\bar{A}}{C}}$$

At a superheat above that a bubble in the pore cannot be in equilibrium with the liquid.

In order to completely interpret the mechanism of bubble buildup in a pore, we must still determine the stability characteristics of the equilibrium states. As is well known, an equilibrium is stable if the potential energy U at the given position is minimum, i.e., its second derivative d^2U/dx^2 is positive. Since the force is F = -dU/dx, the stability of an equilibrium state can also be characterized by the sign of the first derivative of the force dF/dx: namely, an equilibrium is stable when dF/dx < 0 and unstable when dF/dx > 0.



Fig. 2. Determining the equilibrium heights of a bubble in the pore.

Fig. 3. Net force (curve a) and potential energy (curve b) of a vapor-gas bubble as functions of the bubble height.

Differentiating Eq. (3) yields

$$\frac{dF}{dx} = \frac{1}{x^2} \left(\left| \mathcal{C} - \frac{3A}{x^2} \right| \right). \tag{5}$$

It follows from here that F'(x) is negative for small values of x and positive for large values of x. It becomes zero when $x = \sqrt{3A/C} = \overline{x}$, i.e., at the abscissa which corresponds to the point of tangency between lines $y_1(x)$ and $y_2(x)$.

Thus, in superheated liquid the vapor-gas bubbles are in a stable equilibrium and behave like gas bubbles when their height is $x_1 < \overline{x}$, but are unstable and behave like vapor bubbles when their height is $x_2 > \overline{x}$.

Knowing the derivative function F'(x), one can easily determine the general trend of the curve F(x) (Fig. 3). The potential energy $u = -\int F(x)dx + const$ of a bubble in a pore has been plotted in Fig. 3b as a function of the bubble height x.

2. We will now analyze the process of bubble buildup. Let the system be initially cold and, therefore, the bubble in the pore be a pure gas bubble with a height $x_0(0)$. As temperature T_1 rises, the liquid will evaporate and the bubble will thus become larger. As long as $T_1 \leq T_s$, however, the bubble remains absolutely stable and the pore remains passive. When the surface becomes so hot that $T_1 > T_s$, the vaporgas bubble in the pore reaches its first equilibrium state at the height $x_1(T_1)$ and becomes, unlike before, only relatively stable. Indeed, the height x_1 differs by a definite amount from the "critical" height x_2 beyond which the bubble will build up faster and faster. Only when the superheat $T_1 - T_s$ has become equal to $\overline{\Delta T}$ and the supersaturation $P_V - P_L$ has become equal to $\overline{\Delta P}$ at which the straight line $y_2(x)$ becomes a tangent, will the bubbles build up from pores unimpeded.

Thus, in order to make a potential center in superheated liquid active, the superheat ΔT must exceed $\overline{\Delta T}$ based on the pore geometry. While $0 < \Delta T < \overline{\Delta T}$, however, the pore remains subactive.

In order to determine $\overline{\Delta T}$, we will consider $\overline{\Delta P}$ to be the slope of the tangent to the curve $y_1(x)$ at point \overline{x} . Therefore, as one can easily see,

$$\overline{\Delta P} = 2 \sqrt{\frac{1}{A} \left(\frac{C}{3}\right)^3}.$$

Inserting here the values of A and C from (2), and expressing $h \sin \varphi$ in terms of the estuary radius r, we obtain

$$\overline{\Delta P} = \left(P_G^0\right)^{-1/2} \left(\frac{\sigma}{r}\right)^{3/2}.$$
(6)

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From here, with the aid of the Clapeyron-Clausius equation, we find the minimum superheat at which a conical pore becomes active:

$$\overline{MT} = \frac{T_s}{\lambda \rho'} \sqrt{\frac{\sigma^3}{r^3 P_G^0}} \,. \tag{7}$$

Considering that $r^2h\simeq V^0$ and $P^0_GV^0\simeq m_G^{}BT_s^{},$ one can rewrite (7) as

$$\overline{\Delta T} = \frac{G}{\sqrt{m_{\rm G} \sin \varphi}} \,. \tag{8}$$

Consequently, a conical pore with a vertex angle φ and containing m_G grams of gas becomes active when the surface superheat ΔT is not less than $\overline{\Delta T}$:

$$\Delta T \gg \overline{\Delta T} \,. \tag{9}$$

With the superheat ΔT and the initial gas pressure P_G^0 given, conversely, the condition for a conical depression to become active reduces to the requirement that its estuary radius r exceed r_{min} :

$$r \gg r_{\min},$$
 (10)

where

$$r_{\min} = \frac{D}{\sqrt[3]{(\Delta T)^2 P_G^0}}.$$
(11)

It is to be noted that, in addition to the preceding simplifications, we have also tacitly assumed a uniform temperature field in the pore. In reality, however, the heat transfer to the adjoining liquid produces a temperature gradient across the intermedia boundary on the heater:

$$\operatorname{grad} T = -\frac{\alpha}{k} (T_1 - T_0).$$

For this reason, the temperature and thus also the superheat ΔT in a pore increase with depth. The superheat inside a pore can be assumed $(1 + \alpha h/2k)$ times higher than at the surface. In view of this, the constant G in (8) must be replaced by G' = G/(1 + \alpha h/2k).

If condition (9) or the equivalent inequality (10) is satisfied, then the vapor-gas bubble will build up monotonically by first extracting liquid from the pore and then forming above the estuary a continually rising dome (Fig. 1b). When this dome becomes sufficiently large, it will form a neck which quickly narrows down to a point (Fig. 1c) and the upper part of the bubble will break away leaving a small segment above the pore (Fig. 1d).

3. As to the residual bubble in a pore after the main bubble has broken away, we note two possible situations.

If the bubble had built up slowly prior to its breakaway, quasistatically, then the thermodynamic equilibrium prevailed all the time. For this reason, the residual bubble in the pore (its volume is denoted by V*) is now in equilibrium. As a result of continuing evaporation of the liquid inside, it will build up to a volume V_{max} until again a new bubble with a volume $V_{max} - V^*$ breaks away and the entire process repeats. In this case the pore has become a permanent vapor generating center, then, even though the quantity of gas contained in the pore decreases after every breakaway.

An entirely different situation prevails in the case of a fast unbalanced bubble buildup from a pore, when the pore walls are locally cooled. As in the case of a bubble at a smooth solid surface [19-22], the temperature drops in the pore lower as the liquid-vapor interphase boundary moves faster. Since the velocity of the interphase boundary is determined mainly by the superheat ΔT , hence, according to (8), the cooling rate should be highest in narrow pores containing little gas.

The large temperature drop in pores after bubble breakaway results in a still larger drop of vapor pressure P_V and thus of the total internal pressure P_i . As a consequence, the mechanical equilibrium is disturbed and liquid penetrates into the pore. After some time, the temperature returns to its initial level T_i . The equilibrium height of a bubble in a pore $x'_1(T_i)$ is lower than $x_1(T_i)$ (on the other hand, $x'_1(T_i) > x_2(T_i)$), because P_G^0 has become lower and the curve $y_1(x)$ in Fig. 2 has shifted downward. In order now for a bubble to build up from height x'_i to the "critical" height x'_2 , it must overcome a large energy barrier.

As a consequence, the minimum superheat $\overline{\Delta T}$ at which the pore becomes active again will be higher after every breakaway: the boiling center operates periodically in bursts. This analysis has shown that boiling centers on the heater surface can, depending on the magnitude of $\overline{\Delta T}$, operate in two different modes. Namely, if the superheat $\overline{\Delta T}$ necessary for activating a surface depression is small (which is the usual case), then the mode is steady: it is sufficient for a bubble to exceed its critical height once, and the vapor generating process in the pore will continue as long as desired (even though the quantity of gas contained in the pore decreases fast).

If the conditions of breakaway are such that only a rather high superheat $\overline{\Delta T}$ can make the liquid boil, however, then the operation of pores is unsteady. An example of such a situation is the boiling of liquid metals on annealed and polished hot surfaces, especially under vacuum. Since in that case the saturation temperature T_s and the surface tension σ are both high, while the depression radius r and the gas pressure P_G are low, hence, according to (7), the initial superheat $\overline{\Delta T}$ becomes very high. This is the reason why periodic "spurts of activity" are observed here in the boiling centers, accompanied by strong acoustic signals and large temperature fluctuations.

4. We will briefly consider the problem of determining the activity density n in boiling centers.

According to the general principles of statistical physics, the probability of some defect (crack, depression, pore, etc.) appearing on a solid surface is a function of the work E necessary to produce it:

$$W = \operatorname{const} \exp\left(-\frac{E}{kT}\right). \tag{12}$$

One may assume, to the first approximation, that the work necessary to produce a pore of radius r is proportional to its cross-section area: $E = \epsilon r^2$. Coefficient ϵ is numerically equal to the energy necessary to produce a pore of unit radius, it characterizes the surface "strength" of the material.

It is reasonable to assume that there exists a dimensional distribution

$$dn(r) = a \exp\left(-\frac{\varepsilon r^2}{kT}\right) dr,$$
(13)

with $dn(\mathbf{r})$ denoting the number of pores per 1 cm² whose radii are from r to r + dr, and *a* denoting a constant of the same order of magnitude as the number of molecules per unit area.

Thus, we have for the activity density in boiling centers the following expression:

$$n = a \int_{r_{\min}}^{r_{\max}} \exp\left(-\frac{\varepsilon r^2}{kT}\right) dr, \qquad (14)$$

where r_{min} is determined from Eq. (7) and r_{max} is the largest radius with which a pore can still be considered capillary (r_{max} is usually about 1 mm).

As to the effect of surface treatment, it apparently contributes to the closing up of larger pores (whose radius is larger than some $r_0; r_0$ decreases with improved surface treatment). In this case the upper limit of integration in (14) must be replaced by r_0 .

In order to make formula (14) practically useful, one must first determine independently the coefficient ε and the critical radius r_0 for a given surface treatment.

NOTATION

r, h, φ	are the radius, depth, and vertex angle of conical pore;
h – x	is the depth of liquid penetration into the pore;
P _T	is the liquid pressure;
P_{G}^{L}	is the gas pressure;
P_{V}	is the vapor pressure;
Pi	is the internal pressure in a bubble in the pore;
P	is the external pressure on a bubble in the pore;
$\Delta \tilde{P} = P_V - P_L$	is the vapor supersaturation;

 ${}^{\mathrm{T}}_{\mathrm{T}_{1}}$ is the saturation temperature; is the heater temperature; T_{θ} is the liquid temperature; $\Delta T = T_1 - T_S$ is the superheat; is the heat transfer coefficient; α is the thermal conductivity of heater material; k is the specific heat of evaporation; λ ρ is the vapor density; is the potential energy; u $\mathbf{V}^{\mathbf{0}}$ is the pore volume: is the mass of gas contained in the pore; mG в is the specific gas constant; $G = \frac{\sigma}{\lambda \rho'} \sqrt{\frac{\overline{T_s}\sigma}{B}}$

and $D = \left(\frac{T_s}{\lambda \rho'}\right)^{2/3}$ are the constants which depend on the kind of liquid; $\mathbf{R} = x \sin \varphi$ is the curvature radius of meniscus; $\mathbf{A} = \mathbf{P}_{\mathbf{G}}^{\mathbf{0}} \mathbf{h}^{\mathbf{3}}$ is a constant.

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