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The rate of bubble growth and the critical size of a nucleus are evaluated from an analysis of the dynamic equilibrium between vaporization and condensation.

It is known from statistical physics that in a superheated liquid vapor phase nuclei occur as a result of heterophase fluctuations with probability

$$\varphi \sim \exp\left(-\frac{\Delta\Phi_{mp}}{kT}\right). \quad (1)$$

For a slightly superheated liquid with pool boiling the following relation [1] holds:

$$\Delta\Phi_{mp} = 16 \pi \sigma^3 T_\infty^2 v''^2 / 3 \Delta T^2 X^2. \quad (2)$$

If it is assumed, in accordance with [2], that

$$N_c = N \exp(-\Delta\Phi_{mp}/kT), \quad (3)$$

calculation shows this quantity to be vanishingly small, for example, for

$$P = 147 \cdot 10^5 \text{ n/m}^2, \quad \Delta T = 5^\circ\text{K}, \quad N_c \approx 10^{-60} \text{ cm}^{-3}.$$

This means that tremendous superheat would be required for pool boiling, if impurities and dissolved gases were not present in the water. In actual conditions, however, even a small degree of superheating proves sufficient. If we also take into account that boiling begins at the heating surface, it becomes clear that the reduction in superheat is connected with the presence of a surface.

From the statistical physics viewpoint, the influence of the heating surface should reduce to a drop in the thermodynamic potential increment. The thermodynamic potential increment of the system when a bubble forms at the surface is [3]

$$\Delta\Phi_{ms} = f''N'' + f'N' + (S - S_{cs})\sigma + \sigma_{vs}S_{cs} - f'(N' + N'') - S_{cs}\sigma_{ws}. \quad (4)$$

It may be seen from (4) that the relation between  $S$  and  $S_{cs}$  affects the value of  $\Delta\Phi_{ms}$ : For a given  $S$   $\Delta\Phi_{ms}$  decreases with increasing  $S_{cs}$ .

If the surface is flat, then from (4)

$$\Delta\Phi_{ms} = \frac{16 \pi \sigma^3 T_\infty^2 v''^2}{3 \Delta T^2 X^2} \left( \frac{1 + \cos \theta}{1} \right)^2 (2 - \cos \theta). \quad (5)$$

Hence

$$\frac{\Delta\Phi_{ms}}{\Delta\Phi_{mp}} = \left( \frac{1 + \cos \theta}{2} \right) (2 - \cos \theta). \quad (6)$$

It may be seen from (6) that the right hand side must be very small for boiling to begin. This is possible only if the liquid does not wet the heating surface; moreover,  $\theta$  must be close to  $\pi$ . We may conclude that at a smooth surface with moderate subcooling boiling can begin only if wettability is disturbed at certain points on the surface, which then

become active sites.

A somewhat different situation exists at a rough surface. Here, if the vapor phase nuclei are small, the onset of boiling must be determined by the microscopic contact angle which is larger than the macroscopic contact angle [4].

At a rough surface,  $\Delta\Phi_{ms}$  is affected not only by the contact angle, but also by the surface area of the cavities. According to [3], the larger the surface area of the cavity, the smaller  $\Delta\Phi_{ms}$ . Thus the superheat at a smooth surface is greater than at a rough one, which has been confirmed by experiment [5]. It follows that the number of vaporization centers simultaneously active at a rough surface will be greater than at a smooth surface, which has also been confirmed experimentally [5, 8]. But since the ratio of the surface area of a cavity to the total bubble surface cannot approach unity, the value of the contact angle is of primary importance.

In practice the ratio  $\Delta\Phi_{ms}/\Delta\Phi_{mp} \ll 1$  can be satisfied only for  $\theta$  close to  $\pi$ . This does not contradict the conclusions of [7], in particular that pores of a certain size may be centers of vaporization both where wetting occurs and in nonwetting conditions, since in [7] the cavity is assumed to be occupied by gas. In our case the nucleation conditions are different, since the potential barrier  $\Delta\Phi_{ms}$  does not have to be overcome for bubbles to form.

When there is no adsorbed gas, the superheat calculated from Frenkel's formula [2],

$$\Delta T = 2\sigma T_{\infty}''/r\gamma''R, \quad (7)$$

is not sufficient for the formation of a viable vapor nucleus. Moreover, it is difficult to use (7) to determine boiling conditions at the heating surface, since bubbles near the walls are in a region of variable temperature, and, even neglecting thermocapillary forces, we are not in a position to decide what superheat to substitute in (7). Replacing  $\Delta T_s$  by  $\Delta T_{min}$ , as proposed in [6], leads to better agreement with the experimental data, but is purely arbitrary.

The question of determining the critical size of a vapor nucleus can also be approached in another way. We shall assume that the nucleus is viable, if the number of molecules of vapor condensing on the bubble surface does not exceed the number of water molecules evaporating into the bubble in the same time.

Because the interface is curved, the work function for vaporization of a molecule of water will depend on the radius of curvature of the interface. Since only those molecules with kinetic energy in excess of the threshold energy can enter the vapor phase, assuming a Boltzmann velocity distribution for the water molecules, the following expression may be obtained for the flux of evaporating molecules

$$m_{wv} = n' \sqrt{kT/2\pi m} \exp(-U_0/kT). \quad (8)$$

The kinetic theory of gases gives the flux of vapor molecules as  $n'' \sqrt{kT''/2\pi m}$  and the flux of condensing molecules as

$$m_{vw} = fn'' \sqrt{kT''/2\pi m}. \quad (9)$$

Using the relation

$$(T - T_c)/(T_s - T_c) = \exp(-x/\delta) \quad (10)$$

for the temperature distribution in the boundary layer [5], and assuming the bubbles to be spherical, we obtain for the number of evaporating molecules the expression

$$M_{wv} = \int_0^s n' \sqrt{kT/2\pi m} \exp(-U_0/kT) dS, \quad (11)$$

$$dS = 2\pi R dx, \quad (12)$$

where  $x$  is the distance from the heating surface.

Introducing the new variable  $y^2 = 1/kT$ , we obtain, after various transformations,

$$M_{wv} = \frac{n'2\pi R\delta}{\sqrt{2\pi m}} \exp\left(-\frac{U_0}{kT_s}\right) \int_{\frac{1}{\sqrt{kT_s}}}^y \frac{\exp[-U_0(y^2 - 1/\sqrt{kT_s})]}{y^2(1 - kT_c y^2)} dy. \quad (13)$$

The integral is not taken in finite form, but expanded in series, retaining only the zero- and first-order terms since the exponent is small.

We finally obtain

$$\begin{aligned} M_{wv} = & \frac{n'2\pi R\delta}{\sqrt{2\pi m}} \exp\left(-U_0 \frac{1}{kT_s}\right) \left[ \left(1 + \frac{U_0}{kT_s}\right) (\sqrt{kT_s} - \sqrt{kT}) + \right. \\ & \left. + \sqrt{\frac{kT_c}{4}} \ln \left\{ \left(1 + \sqrt{\frac{T_c}{T}}\right) \left(1 - \sqrt{\frac{T_c}{T_s}}\right) \times \right. \right. \\ & \left. \left. \times \left[ \left(1 + \sqrt{\frac{T_c}{T_s}}\right) \left(1 - \sqrt{\frac{T_c}{T}}\right) \right]^{-1} \right\} \left(1 + \frac{U_0}{kT_s} - \frac{U_0}{kT_c}\right) \right]. \end{aligned} \quad (14)$$

The number of vapor molecules condensing into water is

$$M_{vw} = fn'' \sqrt{kT''/2\pi m} 2\pi R^2 (1 + \cos\theta). \quad (15)$$

The criticality condition may be written in the form

$$M_{wv}/M_{vw} = 1. \quad (16)$$

or

$$\begin{aligned} & \frac{8\delta}{R(1 + \cos\theta)} \frac{\gamma'}{\gamma''} \sqrt{\frac{T_s}{T''}} \exp\left(-\frac{U_0}{kT_s}\right) \times \\ & \times \left[ \left(1 + \frac{U_0}{kT_s}\right) \left(1 + \sqrt{\frac{T_c}{T_s}}\right) \ln \left\{ \left(1 + \sqrt{\frac{T_c}{T}}\right) \left(1 - \sqrt{\frac{T_c}{T_s}}\right) \times \right. \right. \\ & \left. \left. \times \left[ \left(1 + \sqrt{\frac{T_c}{T_s}}\right) \left(1 - \sqrt{\frac{T_c}{T}}\right) \right]^{-1} \right\} \left(1 + \frac{U_0}{kT_s} - \frac{U_0}{kT_c}\right) \right] = 4f. \end{aligned} \quad (17)$$

In contrast to (7), Eq. (17) gives two values of bubble radius for one value of  $\Delta T_s$ . Figure 1 shows graphs obtained from (17) and (7). The coefficient  $f$  is determined from the equilibrium condition for the two phases with a plane interface:

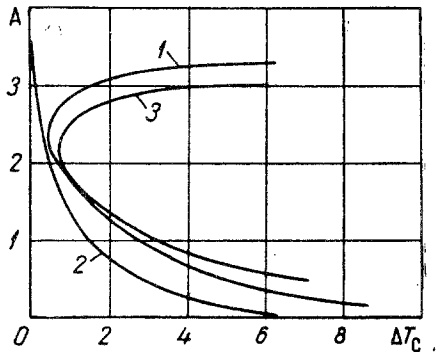


Fig. 1. Dependence of critical bubble radius  $(5 + 1gR) \equiv A$  on superheat  $P = 147 \cdot 10^5$  n/m<sup>2</sup>,  $\delta = 2 \cdot 10^{-3}$  cm; subcooling of flow core 5°K: 1), 2) from (17) and (7); 3) after [6].

$$\frac{\gamma'}{\gamma''} \exp\left(-\frac{U_0}{kT''}\right) = f. \quad (18)$$

All the viable vaporization centers are included in the region between the upper and lower branches of the curve of Fig. 1. The discrepancy between values of the radius obtained from (7) and (17) reaches 200% in the region of the lower branch. Thus, (17) gives not only a lower, but also an upper limit on the size of the nuclei. It should be noted that the upper branch of the curve also gives the maximum breakoff radius for surface boiling.

An expression for determining the rate of bubble growth for pool boiling is given in [10]:

$$\frac{dR}{dt} = \beta_0 \frac{\lambda c_p \gamma}{R} \left( \frac{\Delta T}{r \gamma''} \right)^2. \quad (19)$$

Noting correctly that this equation cannot be applied to surface boiling, the author of [3] gives a new expression for the bubble growth rate at a surface:

$$\frac{dR}{dt} = \beta \frac{\lambda \Delta T_s}{r \gamma'' R}. \quad (20)$$

It was assumed in deriving (20) that the heat reaches the bubble from the heating surface by conduction through the boundary layer. But in the case of channel boiling, when the bubble is exposed to a flow of water and may slip along the surface, the latter assumption is invalid and leads to an underestimate of the actual rate of bubble growth. Moreover, (20) is inapplicable to small bubbles (of the order of  $10^{-5}$  cm), since then the latent heat of vaporization depends on the bubble radius. The maximum bubble growth rate is observed when it is determined only by the kinetics of evaporation. This rate can be computed on the basis of the molecular balance:

$$M_{wv} - M_{vw} = \frac{d}{dt} \left( \frac{2}{3} \pi R^3 c n'' \right); \quad (21)$$

$$c = 1 + \frac{\cos \theta}{2} (3 - \cos \theta). \quad (22)$$

Hence

$$\frac{dR}{dt} = \frac{M_{wv} - M_{vw}}{2 \pi R^2 c n''}. \quad (23)$$

Using (14) and (15), we obtain

$$\begin{aligned} \frac{dR}{dt} &= \sqrt{\frac{kT''}{2 \pi m}} \left\{ \frac{n'}{n''} \frac{\delta}{Rc} \sqrt{\frac{T_s}{T''}} \exp\left(-\frac{U_0}{kT_s}\right) \left[ \left( \frac{U_0}{kT_s} + 1 \right) \left( \frac{T_s - T}{T_s} \right) + \right. \right. \\ &\quad \left. \left. + \frac{1}{2} \left( \frac{T_s + T_c}{T_s} \right) \left( 1 + \frac{U_0}{kT_c} - \frac{U_0}{kT} \right) \right] \times \right. \\ &\quad \left. \times \ln \frac{(3T + T_c)(T_s - T_c)}{(3T_s - T_c)(T - T_c)} \right] - f \frac{(1 + \cos \theta)}{c} \left. \right\}. \end{aligned} \quad (24)$$

To a good approximation this formula may be written

$$\begin{aligned} \frac{dR}{dt} &= \sqrt{\frac{kT''}{2 \pi m}} \left\{ \frac{\gamma'}{\gamma''} \frac{\delta}{Rc} \exp\left(-\frac{U_0}{kT_s}\right) \left[ \left( 1 + \frac{U_0}{kT_s} \right) \left( \frac{T_s - T}{T_s} \right) + \right. \right. \\ &\quad \left. \left. + \frac{R}{\delta} (1 + \cos \theta) \right] - \frac{f}{c} (1 + \cos \theta) \right\}. \end{aligned} \quad (25)$$

Somewhat inferior results are obtained by the approximate substitution

$$T \approx T_m = (T_s + T_c)/2. \quad (26)$$

In our case the formula takes the form

$$\frac{dR}{dt} = \sqrt{\frac{kT_m}{2\pi m}} \left\{ \frac{\gamma'}{\gamma''} \frac{\delta}{Rc} \times \right. \quad (27)$$

$$\left. \times \exp\left(-\frac{U_0}{kT_s}\right) - f \sqrt{\frac{T''}{T_m}} \frac{(1 + \cos \theta)}{c} \right\}.$$

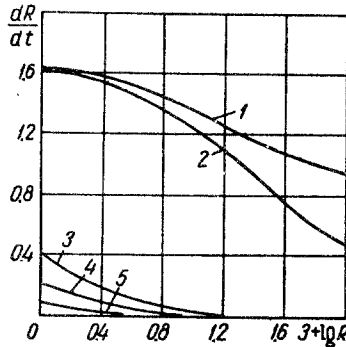


Fig. 2. Dependence of rate of bubble growth on radius,  $\delta = 2 \times 10^{-3}$  cm ( $\Delta T_s = 5^\circ\text{K}$ ): 1, 2)  $P = 78 \cdot 10^5$  n/m<sup>2</sup> from (24) and (19), respectively; 3, 4)  $P = 147 \cdot 10^5$  n/m<sup>2</sup> from (24) and (19), respectively; 5)  $P = 78 \cdot 10^5$  n/m<sup>2</sup> from pool boiling formula (20).

Figure 2 gives the results of calculations based on (19), (20) and (24). It may be seen from the graphs that for the high pressure region (19) gives a result that is distinctly too low.

As for the discrepancy in the values of  $dR/dt$  from (20) and (25), this is only to be expected, since in deriving (25)

we did not take into account the thermal resistance of the stationary layer of liquid surrounding the bubble. This is evidently incorrect for pool boiling, but corresponds to the boiling conditions where vapor bubbles "slip" along the heating surface (channel boiling).

#### NOTATION

$\Delta\Phi_{mp}$  — increment of thermodynamic potential of the liquid vapor system for bulk boiling;  $\Delta\Phi_{min}$  — increment of thermodynamic potential of the liquid vapor system for surface boiling;  $k$  — Boltzmann constant;  $T$  — absolute temperature;  $\sigma$  — surface tension at liquid vapor interface;  $T_\infty$  — saturation temperature above a plane surface;  $v$  — molecular volume of vapor;  $\Delta T$  — superheat of liquid;  $X$  — heat of vaporization per molecule;  $N$  — total number of possible vaporization centers;  $f''$ ,  $f'$  — thermodynamic potentials of vapor and liquid per molecule;  $P$  — pressure in system;  $S$  — total surface area of vapor bubble;  $S_{cs}$  — area of contact of bubble with solid;  $\sigma_{vs}$  and  $\sigma_{ws}$  — surface tension at vapor-solid and liquid-solid interfaces, respectively;  $N'$ ,  $N''$  — number of molecules of liquid and vapor in system;  $\theta$  — contact angle;  $\gamma'$ ,  $\gamma''$  — density of liquid and vapor;  $R$  — bubble radius;  $r$  — heat of vaporization;  $n''$ ,  $n'$  — concentration of vapor and liquid molecules;  $m$  — molecular weight;  $U_0$  — work function per molecule;  $T''$  — saturation temperature taking surface curvature into account;  $f$  — accommodation factor;  $m_{wv}$ ,  $m_{vw}$  — specific flux of molecules of liquid and vapor;  $\delta$  — thickness of superheated layer;  $T_c$  — temperature of core flow;  $T_s$  — superheat at heating surface;  $\Delta T_c$  — subcooling of core flow;  $c_p$  — specific heat of water;  $\lambda$  — thermal conductivity of water;  $\Delta T_{min}$  — superheat at top of bubble;  $\beta_0$  and  $\beta$  — constants;  $N_c$  — number of active vaporization centers.

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