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Publication Date

1971-04-01

Submitted to "Monatshefte fur Chemie"

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April 1, 1971

AEC Contract No. W-7405-eng-48

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THE FORMATION OF VAPOR PHASE NUCLEI IN NUCLEATE BOILING

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ABSTRACT

The conceptual bases of two analyses of vapor phase nucleation that share wide current acceptance are examined. Both consider a balance of pressure to be critical to the formation of stable nuclei. Because the concept of a pressure difference across curved interfaces has recently been shown faulty, a new analysis is required. Nucleation is formulated as a process governed by a free energy barrier. Critical radii for stable nuclei and vapor pressures in bubbles are calculated for water as functions of superheating.

This work was done under the auspices of the United States Atomic Energy Commission.

Introduction

The relationships of the vapor pressure inside bubbles to the vapor pressure of the liquid within which the bubbles form and to the ambient pressure are quantities of great importance to the theory of nucleate boiling. The required relationships have commonly been derived using as a starting point a theory developed by Young,¹ Laplace² and Kelvin³ and made rigorous by Gibbs.⁴ One of the authors⁵ has recently identified an error in an underlying assumption of Gibbs' analysis and has derived a new expression for the effect of surfaces on vapor pressure.

The purposes of this paper are to identify the conceptual bases of the two analyses of vapor phase nucleation in boiling which seem to share widest current acceptance and to present an alternate analysis in terms of a free energy barrier rather than a pressure barrier. The new analysis is analogous to that applied to the nucleation of condensed phases and is consistent with the new equation for the effect of surfaces on vapor pressures.

Pressure Barrier Model of Bulk Nucleation

The equation which is commonly stated to describe the variation of vapor pressures in drops, bubbles or capillaries with surface curvature is the Kelvin or Gibbs-Thomson equation

$$\ln \frac{P}{P_0} = \pm \frac{2\sigma}{r} \frac{V_l}{RT} \quad (1)$$

where P_0 is the vapor pressure outside a plane surface and P is that outside a curved surface, σ is the surface tension, V_l is the molal volume of the liquid, r is the radius of curvature (in this form of the

equation the two radii of curvature are assumed equal), R is the gas constant, and T is the absolute temperature. The negative sign is assigned when the liquid surface is concave as it is for a bubble.

The Kelvin equation predicts that vapor pressures in bubbles are lower than vapor pressures above plane surfaces. But nucleation of stable bubbles has been conceived^{6,7,8,9} to require that a pressure of vapor be generated inside the bubble that equals or exceeds the sum of the ambient pressure on the liquid (including any hydrostatic head) and the pressure change that in the Young-Laplace-Kelvin theory is supposed to exist across curved surfaces. According to the theory this pressure gradient is given for spheres by the Laplace equation¹⁰

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

and the phase on the concave side of the surface experiences the higher pressure. If the Kelvin equation is held to apply, however, this higher pressure is still lower than the vapor pressure over a plane surface at the same temperature and the pressure in the liquid may be a negative pressure. For plane surfaces, the pressure gradient disappears, so that the internal pressure P_i (an indirectly deduced property, discussed by Rice¹¹) of a liquid can be assumed equal to the ambient pressure on the liquid P_a . Then

$$P_v = P_a + \frac{2\sigma}{r} \quad (3)$$

represents the pressure which it is assumed that the vapor inside a bubble must achieve in order to resist collapse. The Clausius-Clapeyron equation can be used with Eq. (3) to calculate the superheating required for formation of bubbles of various radii. For water, bubbles of 10^{-3} cm diameter are calculated⁶ to be stable with 3.3° of superheating; bubbles of 10^{-5} cm diameter are calculated to require 76° superheating.

Plesset¹² and others^{13,14,15} have used Eq. (3) for interpretation of the kinetics of bubble growth in liquids, but have assumed different, in fact contradictory, boundary conditions. They did not assume $P_i = P_a$ but instead calculated a difference between these quantities which they assumed to be the driving force for bubble growth. They substituted temperatures of superheating of the order of those measured in the laboratory¹⁶ into the Clausius-Clapeyron equation to calculate P_v , and used $P_v - \frac{2\sigma}{r} = P_i$ to obtain the presumed internal pressure of the liquid at the bubble surface.

As indicated at the beginning of the next section, there is now good reason for rejection of the Laplace equation for bubbles. A formulation of the problem of vapor phase nucleation in terms of a balance of free energies rather than of pressures is required.

The Free Energy Barrier to Nucleation of Vapor Phase Bubbles

Gibbs⁴ assigned any surface free energy σA (where A is the area of the surface) to a dividing plane of negligible thickness. He assumed that σA and μ_i , the chemical potential of the system components, are mutually independent. In consequence, Gibbs deduced that the partial vapor pressures of a vapor phase in equilibrium with a condensed phase would be unchanged by the creation of plane surfaces.

It can be shown, however, that if work σA is introduced into a condensed phase subsystem of n_c molecules, equilibrium with a vapor phase can only be maintained at constant temperature and constant n_c by raising the molal free energy of the vapor phase by $\sigma A/n_c$. This increase in molal free energy of the vapor is accomplished by increasing the vapor pressure. If, as assumed by Gibbs, there were no increases in vapor pressure, the fundamental condition for equilibrium--that the free energy change for transfer of infinitesimal quantities of matter between the subsystems be zero--would be violated.

Analysis of the effects of added surfaces in terms of the fundamental condition of equilibrium shows that as long as the specific surface free energy (which may be a function of curvature but is always a positive quantity) is taken as that for the particular surface of interest, the effect of the added total surface free energy on the average molal free energy of the condensed phase is independent of whether the surface concerned is planar, convex, or concave. No directional effect such as is represented by the Laplace equation need be assigned to curved surfaces. Free energy barriers are already assumed to be crucial in condensed phase nucleation processes.^{9,17} We need only adapt the familiar model to adjust for the fact that the volume of a given quantity of gas is a sensitive function of temperature.

According to standard nucleation theory when strain energy terms can be neglected, the formation of a daughter phase that becomes stable when a parent phase is heated to above the equilibrium transition temperature is opposed by the unfavorable free energy of formation of an interface between the parent and daughter phases. For very small particles of

the daughter phase, the ratio of surface to volume is large and this surface free energy contribution exceeds the favorable free energy of the bulk reaction.

Suppose G_g is the free energy content of the vapor phase formed into a bubble of volume V and G_l is the free energy of the molecules before they vaporized. The free energy change per unit volume of the bulk reaction is then

$$\Delta G_v = \frac{G_g - G_l}{V} \quad (4)$$

where we assume that the first step in the formation of a bubble is the transformation of the liquid into vapor at the ambient pressure (which also includes any hydrostatic head). For this step we have a free-energy change of $\frac{4}{3} \pi r^3 \Delta G_v$, where r is the radius of the bubble. To this must now be added the free energy of formation of the interface, $4\pi r^2 \sigma$. The total free energy change ΔG_r when a bubble is formed is

$$\Delta G_r = \frac{4}{3} \pi r^3 \Delta G_v + 4\pi r^2 \sigma. \quad (5)$$

The role played by Eq. (5) when a free energy barrier is assumed critical is analogous to that played by Eq. (3) when a pressure barrier is assumed critical. Equation (5) must have a maximum at any temperature of superheat because the first term of the right hand side of Eq. (5) is then a negative function of r^3 and the second term is a positive function of r^2 . The radius at the maximum, called the critical radius, is given by

$$r_c = - \frac{2\sigma}{\Delta G_v} \quad (6)$$

A bubble with radius r_c has an equal probability of growing (through the addition of one molecule of gas, which makes $\frac{d\Delta G}{dr}$ negative and thus leads to spontaneous further growth) or collapsing (through loss of one molecule of gas). Several other forms of the relations between the various quantities involved can be immediately derived. Thus using Eq. (6) to eliminate G_v in Eq. (5) we obtain for the free energy of formation of a nucleus

$$\Delta G_{r_c} = \frac{4}{3} \pi r_c^2 \sigma = \frac{1}{3} A \sigma. \quad (7)$$

We can now write

$$\Delta G_{r_c} = nRT_0 \ln \frac{f_1}{f_0}, \quad (8)$$

where R is the ideal gas constant, f_0 is the fugacity of the superheated liquid, f_1 the final fugacity of the bubble and n the number of moles of vapor per bubble. (In what follows we assume that fugacity can be replaced by pressure.) If we now denote by V_{st} the volume of one mole of vapor under standard conditions of temperature ($T_{st} = 273^\circ\text{K}$) and pressure ($f_{st} = 1 \text{ Atm.}$), we obtain

$$n = \frac{4\pi r_c^3}{3} \cdot \frac{1}{V_{st}} \cdot \frac{T_{st}}{T_0} \cdot \frac{f_1}{f_{st}} = \frac{4\pi r_c^3}{3} \frac{f_1}{RT_0} \quad (9)$$

where T_0 is the temperature of the superheated liquid. Substituting Eqs. (8) and (9) in Eq. (7), we have

$$f_1 \ln \frac{f_1}{f_0} = \frac{\sigma}{r_c} \quad (10)$$

The value of r_c still has to be deduced. We can write for ΔG_v

$$\Delta G_v = \Delta H_v - T_0 \Delta S_v, \quad (11)$$

where ΔH_v and ΔS_v are the enthalpy and entropy changes per unit volume corresponding to ΔG_v . Close to the normal boiling point T_b we have

$$\Delta S_v = \frac{\Delta H_v}{T_b} \quad (12)$$

and

$$\Delta G_v = - \Delta H_v \left(\frac{T_0 - T_b}{T_b} \right) = - \frac{2\sigma}{r} \quad (13)$$

Following the definition of ΔG_v we have

$$\Delta H_v = \frac{\Delta H_b}{V_{st}} \frac{T_{st}}{T_0} \frac{f_a}{f_{st}} = \Delta H_b \cdot \frac{f_a}{RT_0} \quad (14)$$

where ΔH_b is the heat of vaporization at the normal boiling point and f_a the ambient pressure. Equations (13) and (14) give

$$r_c = \frac{2\sigma}{\Delta H_b} \cdot \frac{RT_0 T_b}{f_a (T_0 - T_b)} \quad (15)$$

We thus obtain the critical radius as a function of superheating. If the vapor pressure of the liquid at the temperature of superheating, f_0 , is known, we can also write

$$\Delta G_v = \left(RT_0 \ln \frac{f_a}{f_0} \right) \cdot \frac{T_{st}}{T_0} \cdot \frac{1}{V_{st}} \cdot \frac{f_a}{f_{st}} \quad (16)$$

$$= f_a \ln \frac{f_a}{f_0} \quad (17)$$

In this manner we obtain

$$r_c = \frac{2\sigma}{f_a \ln \frac{f_0}{f_a}} \quad (18)$$

Values of r_c as a function of the superheating $\Delta T = T_0 - T_b$ are given in Table I. The values of σ used correspond to the surface tension of liquid water in equilibrium with its own vapor.¹⁸ The superheating $\Delta T = 170^\circ$ is the highest reached in the experiments of Kenrick, Gilbert and Wismer.¹⁹ Values for the smaller superheat temperatures are identical with those found by Plesset and Zwick. While, however, in the case of Plesset and Zwick the driving force responsible for bubble expansion is zero at the critical radius and grows to a constant value, we find that the driving force $f_l - f_a$ has a positive value at the critical radius

and decreases with increasing radius. (See Eq. (19) below.) Table I also gives the fugacity of superheated water, f_0 , and the difference between f_0 and the fugacity of the bubble f_1 . It is seen that the pressure inside the critical bubble is a few percent higher than the normal vapor pressure of the superheated water.

Finally, bubble pressures for other than critical radii can be derived from Eq. (5). If we substitute in this equation the Eqs. (8), (9) (with $r_c = r$), and (18), we obtain the equation

$$f_1 \ln \frac{f_1}{f_0} = \frac{3\sigma}{r} + f_a \ln \frac{f_a}{f_0} \quad (19)$$

Table II gives values of f_1 as a function of r calculated by means of this equation. Beyond a certain value of r the right-hand side of Eq. (19) becomes negative and f_1 smaller than f_0 . Physically, this means that beyond a certain radius f_1 remains constant and assumes a value close to f_0 .

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Table I. Bubble nucleus formation in superheated water
at 1 atm. ambient pressure

Superheating ΔT , °K	Critical radius r_c , cm.	Normal vapor pressure of water f_0 , atm.	Excess pressure of bubble $f_1 - f_0$ atm.
1	3.23×10^{-3}	1.036	0.018
2	1.61	1.074	0.035
3	1.06	1.112	0.052
5	6.43×10^{-4}	1.192	0.084
10	3.20	1.414	0.161
170	4.15×10^{-5}	7.84	0.95

Table II. Bubble pressure as function of radius

Radius r , cm.	Bubble pressure f_1 , atm. ($T_0 = 374^\circ\text{K}$)	Bubble pressure f_1 , atm. ($T_0 = 383^\circ\text{K}$)
10^{-5}	8.28	8.40
10^{-4}	2.20	2.40
10^{-3}	1.16	*
10^{-2}	*	*

* f_1 smaller than f_0

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