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Mechanical nonequilibrium considerations in homogeneous bubble nucleation for unsteady-state boiling

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Abstract

With thermal and mechanical nonequilbrium taken into consideration, the classical kinetic theory of boiling is modified to study unsteady-state homogeneous nucleation processes. Based on this newly developed model, the degree of superheat and the maximum nucleation rate corresponding to different rates of temperature rise in water are calculated and presented. For the first time, the initial nonequilibrium vapor pressure and the initial growth rate of bubble nuclei with different initial embryo sizes and different rates of temperature rise are accurately modeled. The resulting algorithm provides a method by which the details of bubble nucleation in a superheated liquid can be predicted, leading to a better understanding of the kinetics of boiling. Model validation, accuracy and application are also presented and discussed.

Keywords: Homogeneous nucleation; Bubble nucleation; Unsteady-state process; Boiling; Kinetics

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1. Introduction

Bubble nucleation in homogeneous liquids can take place in a variety of applications, ranging from ink jet printers to microelectronic cooling devices and microbubble actuators in MEMS devices. This fundamental phenomenon is also involved in the development of technologies required for the operation of nuclear reactors, the storage and transportation of liquefied natural gas, acoustic cavitations and laser-assisted phase-change phenomena. In all of these applications, bubble nucleation in a liquid (homogeneous nucleation) is directly related to boiling incipience. As a result, control of this nucleation has been of considerable interest to researchers and practitioners for nearly four decades, and considerable effort has been devoted to a better understanding of the fundamental science and governing phenomena of nucleation.

Homogeneous bubble nucleation has been investigated in detail, both experimentally and theoretically [1–9]. However, the fundamental mechanisms of bubble nucleation are not well understood, especially during the initial stages of unsteady-state boiling.

Although classical kinetic theory of boiling can be used to explain the causes and some of the fundamental mechanisms occurring in the explosive boiling in liquids, theoretical results are not always in good agreement with experimental data and much of the experimental

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Nomenclature

A	surface area of bubble
b	linear fitting factor in Eq. (1)
B	coefficient in Eq. (8), $B \approx 1 - \frac{1}{3}\left(1 - \frac{P_{\mathrm{l}}}{P_{\mathrm{e}}}\right)$
C_P	thermal capacity per molecule of liquid
f	factor of nucleation frequency
G_b	Gibbs number
h_{fg}	latent heat
J	nucleation rate
k	Boltzmann constant
m	mass evaporated
M_0	molecular mass
n	molecular number evaporated
N	number of liquid drop; bubble number per unit volume
N_0	number density of liquid
N_{total}	initial number of liquid drop
P	Pressure
P_{e}	equilibrium vapor pressure with flat interface
P_{l}	bulk pressure
P_{v}	hydrostatic vapor pressure with curved interface
r	initial size of bubble
r_{ij}	distance between two molecules
$\dot{r}$	initial velocity of bubble surface
$\ddot{r}$	initial acceleration of bubble surface
R	gas constant
t	time
T	temperature
T_{c}	temperature at critical point of phase diagram
T_{l}	liquid temperature of bulk
T_0	reference temperature where $J(T_0) = 1$
V	volume of bubble
V_0	volume of superheated liquid
v_{l}	molecular volume of liquid
W_{min}	minimum possible work to form a bubble

Greek symbols

δ	correction factor for the departure of vapor pressure from equilibrium
δ_{c}	critical value of δ_λ
δ_λ	factor in Eq. (18)
ΔH_{fg}	enthalpy of evaporation per molecule
$\bar{\varepsilon}$	representative scale of energy
λ	heat conductivity of liquid
ν	viscosity of liquid
ρ	density
σ	surface stress
σ'	representative scale of length
ζ	nucleation probability

Subscripts and superscripts

$'$	parameters in vapor bubble
c	parameters in critical bubble
e	equilibrium
f	fluid
interface	parameters at the interface of bubble
l	liquid phase
ne	nonequilibrium
v	vapor phase

data reported in the literature are inconsistent [1–9]. Furthermore, as summarized by Delale et al. [10], classical homogeneous nucleation theory ignores the effects of curvature on the surface free energy. As a result, the classical theory is unable to accurately predict the finite limit at which the spinodal is approached.

Observation of the boiling phenomena from the perspective of homogeneous nucleation at constant pressure and the second law of thermodynamics, indicates that the experimental data of the superheat should be lower than the superheat at which the process would occur reversibly. As a result, the nonequilibrium work of formation of a bubble becomes greater than the minimum work of formation for the ideal case, in which the process occurs reversibly, as assumed in classical nucleation theory. This shortcoming has limited the application of classical theory in correctly predicting values other than the superheat, and forced the assumption of a case specific nucleation rate.

However, the classical theory of homogeneous bubble nucleation may represent the best way to study of the mechanisms that govern the formation of clusters of the vapor phase in a metastable liquid, over a range extending from the molecular level to the macroscale. As pointed out by Delale et al. [10], using the stochastic techniques, or methods of nonequilibrium thermodynamics to describe homogeneous nucleation, is too complicated to be used in practice, however, classical nucleation theory can be used to predict the bubble size and steady-state nucleation rates. In the classical theory, most of the attention has been focused on the formation of the critical bubble nuclei, which is in mechanical, thermal, and chemical equilibrium with the surroundings [11]. Thus, the growth rate of the critical nuclei is zero and the bubbles will remain at a constant size, provided the environmental conditions do not change. However, this is not what would happen in the actual phase change process, no matter how slow the temperature rise rate is in the liquid. This implies that in reality, a process that may appear to be steady-state from a macroscopic point of view, is in fact unsteady-state from a microscopic perspective. Another important reason for studying these processes is that there are many questions remaining to be answered, such as initial growth rate of vapor bubbles and initial vapor pressure in the bubbles during the nucleation process.

A number of assumptions have been made to ease the difficulties associated with the mathematical formulation of bubble growth heretofore and solvability of the problem in classical bubble dynamics. These include the assumptions of the initial bubble size and the thermodynamic process, i.e., isobaric or isothermal, neglecting the complex interactions of heat and mass transfer between the two phases during bubble growth, and ignoring the transient process i.e., assuming constant bulk temperatures [12–14]. In addition, while Kagan [15] has investigated the nonequilibrium vapor pressure in the bubble embryo from a mechanical nonequilibrium nucleation theory perspective and Okumura and Ito [16] have done so from a nonequilibrium molecular dynamics simulation perspective, classical bubble dynamics typically assumes an arbitrary initial nonequilibrium vapor pressure to drive the nucleated bubble growth, due to a lack of information on the nonequilibrium vapor pressure in the bubble embryo.

The process of initial bubble nucleation in a superheated liquid is a key stage in the generation of vapor in the boiling process. In the following analysis, the initial bubble nucleation during an unsteady boiling process will be investigated and analyzed based on a modification of classical kinetics of boiling developed by Kagan [15] by taking into consideration the thermal and mechanical nonequilibrium. Here, it is assumed that the local transient maximum vapor pressure in the bubble embryo is a function of time [13], which has been demonstrated by nonequilibrium molecular dynamics simulations [16,17]. The initial nonequilibrium pressure in the vapor phase and the bubble growth rates for different initial bubble sizes and different rates of temperature rise in liquids are computed and discussed, and then compared with the experimental results available in the literature. The possible limits of superheat and maximum number of bubbles in the liquid are calculated and discussed, and then combined with the phenomenological nucleation barrier employed by Delale et al. [10].

The results of the present analysis provide a quantitative description of the initial bubble nucleation process, which is critically important for both the fundamental understanding and industrial applications, e.g., to calculate the bubble growth with bubble dynamics and to predict the behavior of microbubbles as actuators in MEMS.

2. Classical homogeneous nucleation theory in superheated liquids

In most situations, impurities (gas or vapor) trapped in the cavities of even a "smooth" surface become the nuclei where the incipience of *heterogeneous* nucleation is initiated. However, under the circumstances of intense pulsed heating or the case of a volatile liquid droplet immersed in an immiscible, nonvolatile, hot liquid, the fluctuation nucleation in liquid becomes the driving force for the incipience of *homogeneous* boiling. As described in molecular kinetics, molecules of the liquid are considered to have a distribution of energy, such that only a very small fraction has an energy level that is considerably greater than the average. While small in number, these 'activated' molecules are presumed to initiate the phase change process. Owing to the collisions occurring among molecules, some regions have a denser collection of these molecules, while in neighboring regions they are relatively sparse. Such a region with a sparse collection of molecules is formed by those activated molecules that scatter the neighboring nonactivated molecules [16]. The initial nucleus of the nucleate bubbles is formed in these regions [11].

In his pioneering work, Gibbs [18] developed the fundamental formulation that outlines and defines the minimum work to form a bubble nucleus, with which the classical theory of homogeneous nucleation was originated by Volmer and Weber [19] and later Doring [20]. More quantitative treatments were later developed by Zel'dovich [21], Frenkel [1], Kagan [15], and Blander and Katz [4]. Some excellent pedagogical reviews on homogeneous nucleation in a superheated liquid are given by Skripov [2], Blander and Katz [4], Avedisian [5] and Debenedetti [3].

Classical homogeneous nucleation theory suggests that the largest nucleation rate J corresponding to the minimum possible value of the critical work [2,11, 22] is,

$$J = N_0 \cdot f \cdot \exp\left(-\frac{W_{\min}}{kT_1}\right) \tag{1}$$

where f can be interpreted as the factor of nucleation frequency. Eq. (1) is the general form for the nucleation rate, related to the possible maximum velocity of phase transition for the possible minimum work required to form a critical embryo.

According to Gibbs [18] and other researchers [3], the minimum work, $W_{\min}$, required to form a bubble in the homogeneous liquid phase of a single component can be described as

$$W_{\min} = \sigma A + n\lfloor \mu'(P') - \mu_1(P_1) \rfloor - (P' - P_1)V \tag{2}$$

where the superscript '′' refers to the newly formed phase. In the current work, the superscript '′' specifically refers to the nonequilibrium state of vapor phase. The above equation implies that within an existing phase with a fixed mass, $W_{\min}$ is the minimum work required to form a new, enclosed phase. As such, Eq. (2) serves as the fundamental equation in nucleation theory.

If the vapor phase is regarded as a perfect gas, replacing the chemical potential of the liquid by the equal chemical potential of the vapor in a critical bubble, the chemical potential difference between vapor phase and liquid phase becomes [3,4,15]

$$\mu'(P') - \mu_l(P_l) = kT_l \ln \frac{P'}{P_c} \tag{3}$$

where P_c is the vapor pressure in the critical bubble and comes from $\mu_l = \mu_v$,

$$P_c = P_e(T_l) \exp\left[(P_l - P_e(T_l))v_l/kT_l\right] \tag{4}$$

with v_l being the volume per molecule of liquid and P_e being the saturation vapor pressure in an equilibrium thermodynamic system.

Noting that $A = 4\pi r^2$ and $V = \frac{4}{3}\pi r^3$ for spherical bubbles with radius r and substituting Eq. (3) into Eq. (2) yields

$$W_{\min} = 4\pi r^2 \sigma + nkT_l \ln \frac{P'}{P_c} - \frac{4}{3}\pi r^3 (P' - P_l) \tag{5}$$

In order to compute $W_{\min}$ from Eq. (5), a relation between r and P' in the bubbles is required.

Doring [20] assumed that the vapor pressure satisfies the hydrostatic equation or Young–Laplace equation

$$P_v - P_l = 2\sigma/r \tag{6}$$

If we invoke the Young–Laplace equation and define the radius of the critical embryo to be $r_c = 2\sigma/(P_c - P_l)$ and assume that it is in thermal, chemical potential and mechanical equilibrium with the liquid, where P_c is the vapor pressure in the critical bubble, the work of formation of such an embryo can be determined from Eq. (5) as

$$W_{\min} = \frac{4}{3}\pi r_c^2 \sigma \tag{7}$$

which is widely accepted as the minimum reversible work required to form a critical bubble embryo based upon classical nucleation theory. If this critical embryo is in thermal, mechanical and chemical equilibrium with the bulk liquid, it is well known that the minimum work $W_{\min}$ exhibits a maximum value at the critical radius, r_c, given by $\partial W_{\min}/\partial r|_{r=r_c} = 0$ and $\partial W_{\min}/\partial P|_{P=P_c} = 0$.

For small departures from equilibrium, Eq. (5) can be expanded using a Taylor series for the critical bubble (r_c, P_c). Restricting the discussion here to the first two orders of expansion yields

$$\begin{aligned} W_{\min}(r, P') \approx{}& W_{\min}(r_c, P_c) + \left.\frac{\partial W_{\min}}{\partial r}\right|_{r=r_c} \Delta r \\ &+ \left.\frac{\partial W_{\min}}{\partial P}\right|_{P=P_c} \Delta P + \frac{1}{2}\left.\frac{\partial^2 W_{\min}}{\partial r^2}\right|_{r=r_c} \Delta r^2 \\ &+ \frac{1}{2}\left.\frac{\partial^2 W_{\min}}{\partial P^2}\right|_{P=P_c} \Delta P^2 \\ &+ \left.\frac{\partial}{\partial P}\left(\frac{\partial W_{\min}}{\partial r}\right)\right|_{r=r_c, P=P_c} \Delta r \Delta P \end{aligned} \tag{8}$$

Though P' is related to r and is not independent, here it can be regarded as another variable. Since the first-order derivatives $\partial W_{\min}/\partial r|_{r=r_c}$ and $\partial W_{\min}/\partial P|_{P=P_c}$ are zero, substituting the critical parameters into the equation above yields

$$W_{\min}(r, P') \approx \frac{4\pi r_c^2 \sigma}{3} - 4\pi\sigma(r - r_c)^2 + \frac{2\pi r_c^3}{3p_c}(P' - P_c)^2 \tag{9}$$

Kagan [15] pointed out the inaccuracy of using Eq. (6) for the calculation of vapor pressure during the nucleation process, and introduced the following hydrodynamic equation (the mechanical nonequilibrium equation) into the homogeneous nucleation theory:

$$P' = P_l + \rho_l\left(r\ddot{r} + \frac{3}{2}\dot{r}^2\right) + \frac{2\sigma}{r} + 4v\frac{\dot{r}}{r} \tag{10}$$

which is the well-known Rayleigh–Plesset equation relating the vapor pressure in the bubble with the velocity and acceleration of the bubble growth. Eq. (10) is the governing equation in classical bubble dynamics [12], which reduces to Eq. (6) when $\dot{r} = \ddot{r} = 0$.

In order to calculate the vapor pressure in Eq. (9) with Eq. (10), Kagan [15] focused his attention on obtaining the velocity and acceleration of the bubbles having a critical radius. To this end, he considered the thermal balance between the vapor in the bubble and the liquid outside of the bubbles. He argued that when there is a net flux of molecules evaporating into the bubble, there must be a net flux of enthalpy across the interface of the bubble. Also, there must be an equal enthalpy flux to the interface from the bulk liquid at steady-state, so that

$$\lambda\left(\frac{\partial T_l}{\partial r}\right)_{r=R} A = \frac{dn}{dt}\Delta H_{fg} \tag{11}$$

where dn/dt is the net rate of vaporization of molecules into the bubble, which can be obtained based on the difference between the chemical potentials of the liquid and vapor and with the assumption that the vapor behaves as an ideal gas to give [2–4,15]

$$\frac{dn}{dt} \cong \frac{A}{(2\pi M_0 kT_l)^{1/2}}\left[P_c(T_{\text{interface}}) - P'\right] \tag{12}$$

where $T_{\mathrm{interface}}$ is unknown and can be found by solving the energy balance equation.

After the minimum work is determined from Eq. (5), (7) or (9) respectively, the bubble size distribution at steady-state can be computed according to the Boltzmann equation

$$N(r) = N_0 \exp\left(-\frac{W_{\min}}{kT_{\mathrm{l}}}\right) \tag{13}$$

Using Eqs. (10)–(13) and the steady-state equation for an ideal gas ($P'V = nkT'$) to calculate $(\mathrm{d}\dot{n}/\mathrm{d}r)_{r=r_c}$, and recognizing that at the point $n = n_c$, the power of the exponential in the integration part has an extremum, the complicated relationship between P', $\dot{r}$, and $\ddot{r}$ can be avoided by mathematical manipulation. Using this process, Kagan [15] obtained the following equation to determine the degree of superheat for the nucleation process controlled by vaporization. This was later modified by Blander et al. [4] to arrive at the following expression:

$$J = N_0 \frac{\left(\frac{2\sigma}{\pi M_0 B}\right)^{1/2}}{1+\delta_c} \exp\left[-\frac{16\pi\sigma^3}{3kT_{\mathrm{l}}(P_e - P_{\mathrm{l}})^2\delta^2}\right] \tag{14}$$

where $B \approx 1 - (1 - P_{\mathrm{l}}/P_c)/3$ and $\delta \cong 1 - \rho_v/\rho_{\mathrm{l}} + (\rho_v/\rho_{\mathrm{l}})^2/2$. Here δ is the correction factor for the departure of the vapor pressure P_c in critical bubbles from the vapor saturation pressure P_e with a flat liquid–vapor surface at a given liquid temperature $P_c - P_{\mathrm{l}} = (P_e - P_{\mathrm{l}})\delta$. The expression of δ_c will be given in Section 3.3.

Eq. (2) can be calculated not only along a reversible path (which is widely used in classical nucleation theory), but it can also be calculated along an irreversible path for real unsteady-state processes, as pointed out by Delale et al. [10]. In order to obtain a direct solution and compensate for the loss of work in an irreversible case, and to be consistent with the second law of thermodynamics, Delale et al. [10] employed a phenomenological nucleation barrier that utilized the superheat threshold achieved in experiments to revise the classical theory of homogeneous bubble nucleation. Considering the second law of thermodynamics and attempting to be consistent with traditional nucleation theory, Delale et al. [10] proposed the following expression for the minimum work to form of a critical bubble

$$W_{\min} = \frac{4}{3}\pi r_c^2 \sigma(1 - 2\alpha) \tag{15}$$

where $0 \leqslant \alpha < 1/2$. For $\alpha = 0$, the above expression reduces to Eq. (7) given by the classical theory. In principle, the value of α can be obtained either by comparison with experimental data (as will be discussed in Section 3.1 or with other theoretical calculations (e.g., density functional method).

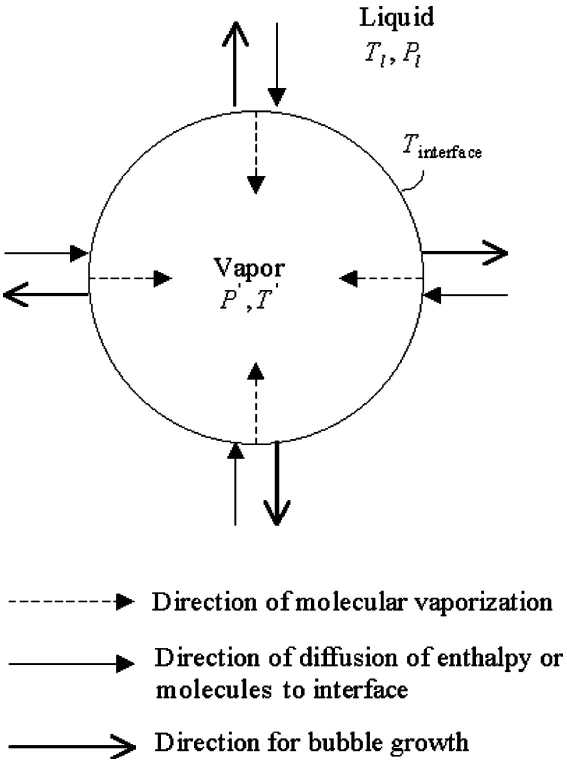

Fig. 1. Bubble nucleation and growth process (adapted from Blander and Katz [4]).

As will be pointed out later in this paper, the sensible heat of the evaporated molecules is neglected in Eq. (11) if the vapor phase is in thermal nonequlibrium with the bulk liquid, and appears to apply for both steady and nonsteady-state process (see Fig. 1). For a steady-state process, however, the analysis of Kagan developed to obtain the velocity and the acceleration of the bubble surface, may not be entirely appropriate, and will be discussed later. Furthermore, from the analysis of Kagan, it is not possible to obtain the initial nonequilibrium pressure in vapor for different bubble sizes in a transient process even though their departure from the equilibrium values is very small. In fact, it is this small departure from equilibrium that causes the initial bubble to grow or collapse, and it is this small departure that is the source of the small disturbance in nonequilibrium bubble dynamics.

In the following, transient bubble nucleation with thermal and mechanical nonequilibrium taken into consideration will be analyzed to obtain the initial bubble pressure and its initial growth rate with different initial bubble sizes at different rates of temperature rise in a superheated liquid. Based on this analysis, some fundamental relations in nonequilibrium nucleation and nonequilibrium bubble dynamics can be established.

3. Further considerations of unsteady-state homogeneous bubble nucleation

In the previous discussion, the limitations of the classical theory of bubble nucleation in a superheated liquid have been examined, and based on this examination a number of observations can be made. First, it is clear that the nucleation rate in the classical theory is strongly dependent on the nucleation rate of the critical bubble nuclei, which is assumed to be in thermal, force, and chemical potential equilibrium with the surroundings; second, the nucleation process has been assumed to be a steady-state process. Thus, the classical theory is unable to answer the following questions: (i) how far from the equilibrium state is the vapor pressure in a noncritical bubble nuclei? (ii) how fast will the bubbles grow in an unsteady process? and (iii) what is the relationship between the nonequilibrium state and the rate of temperature rise in the liquid?

To answer these questions, it is necessary to obtain the initial nonequilibrium vapor pressure and the initial growth rate of the bubble nuclei. This can be done as follows:

(i) Initially, the possible nucleation temperature at different rates of temperature rise in a superheated liquid is determined. Thus, properties of the liquid and the parameters of the critical bubble nuclei can be calculated (Section 3.1);
(ii) Once this has been accomplished, the variation of the vapor pressure at the moment of bubble nucleation will be determined (Section 3.2);
(iii) After the nonequilibrium thermodynamic relationship between the mass flux at the interface and the vapor pressure in a bubble nucleus has been determined (Section 3.3), the relationship between the mass flux at the interface and the bubble growth rate at the moment of bubble nucleation can be derived (Section 3.4). It will be shown that the mass flux at the interface is a bridge that connects the nonequilibrium vapor pressure and the bubble growth rate (Section 3.5).

It should be noted that two other assumptions used in the classical work will also be used in the present work:

(i) While it is well known from molecular dynamics simulations that there exist interfacial ambiguities in a microbubble [23], the shape of the bubbles will be assumed to remain spherical at all times. The shape of the embryo with a radius of 1–10 nm usually deviates slightly from that of a sphere and thus has some size ambiguities;
(ii) The liquid is a continuum. Note that Eq. (10) is based on the incompressible Navier–Stokes equations. Although the Navier–Stokes equations failed to model some existing experimental results of liquid flow in nano-scale, it is known that the classical model is still valid as long as the thickness of the liquid film exceeds 10 molecular layers [24]. Note that the typical size of a bubble nuclei in water is about 5 nm and the molecular distance is approximately 1 Å. Thus, the traditional continuum model for water is applicable here, but the continuum model is not valid for the vapor phase because the bubble size is comparable to the mean free path of molecules. Thus,all of the properties of vapor should be regarded as statistically averaged.

3.1. Initial nucleation temperature

It has been shown previously [2–4] that a liquid with volume V_0, heated at a rate of $\mathrm{d}T_l/\mathrm{d}t$, may remain in a liquid state to a temperature T_l, which may be higher than the equilibrium nucleation temperature. Assuming that the nucleation probability is defined as $\zeta = 1-N/N_{\text{total}}$, where N/N_{total} is the probability that the liquid with volume V_0 will survive to a temperature T_l, Blander and Katz [4] developed the following expression relating ζ to the rate of temperature rise in liquid and the nucleation rate

$$\ln(1-\zeta) \approx -\frac{V_0 J(T_l)}{b\left(\frac{\mathrm{d}T_l}{\mathrm{d}t}\right)}, \tag{16}$$

where V_0 can be regarded as the volume of superheated liquid in question, e.g., the volume of superheated liquid droplets or the volume of superheated liquid films; and b is the *fitting factor* if the reversible work of bubble formation is linearized at a reference temperature T_0 where T_0 is the temperature calculated from Eq. (1) at which $J(T_0) = 1$ [2],

$$b = -\left.\frac{\mathrm{d}(W_{\min}/kT_l)}{\mathrm{d}T_l}\right|_{T_l=T_0} \tag{17}$$

At a pressure close to atmospheric and moderate nucleation rates, b is approximately 6–8 $\deg^{-1}$ and the linearization for $W_{\min}$ is acceptable from $J = 10^{-10}/\mathrm{cm}^3$ s to $10^{10}/\mathrm{cm}^3$ s [2]. For the current investigation, $b = 7 \deg^{-1}$ was chosen based upon the work presented in Ref. [2]. Rewriting Eq. (16) in the following form

$$J(T_l) \approx -\frac{1}{V_0}\cdot b\cdot\left(\frac{\mathrm{d}T_l}{\mathrm{d}t}\right)\cdot\ln(1-\zeta) \tag{18}$$

allows the computation of the nucleation rate for different rates of temperature rise in a small volume of superheated liquid (where $V_0 = 10^{-5}\mathrm{cm}^3$).

As mentioned earlier, Delale et al. [10] gave a phenomenological correction to the minimum work for a vapor bubble of critical size which is given by Eq. (15). Thus, we have a corrected fitting factor $b' = b(1-2\alpha)$ and Eq. (18) becomes

$$J(T_1) \approx -\frac{1}{V_0} \cdot b(1-2\alpha) \cdot \left(\frac{\mathrm{d}T_1}{\mathrm{d}t}\right) \cdot \ln(1-\zeta) \tag{19}$$

Also combining Eq. (14) and (15) yields,

$$J(T_1) = N_0 \frac{\left(\frac{2\sigma}{\pi M_0 B}\right)^{1/2}}{1+\delta_c} \times \exp\left[-\frac{16\pi\sigma^3}{3kT_1(P_e - P_1)^2\delta^2}(1-2\alpha)\right] \tag{20}$$

As a first step, α can be estimated from experimental measurements for a specific rate of temperature increase using Eqs. (19) and (20). Then, the superheat limit of water, T_1, at different rates of temperature rise, can be calculated from Eqs. (19) and (20). By comparing with the experimental results, Delale et al. [10] found that for a quasi steady-state process, an assigned value of $\alpha = 7/16$ yields good agreement between the theoretical and experimental results. However, it appears that such a simple correction is not adequate for an unsteady-state analysis, especially for high rates of temperature rise. After a detailed comparison with the existing experimental data, we propose the following expression with an exponential correction factor for a transient process:

$$\alpha = \frac{7}{16}\exp(-\mathrm{d}T_1/\mathrm{d}t) \tag{21}$$

Note that when $\mathrm{d}T_1/\mathrm{d}t \to 0$ for steady-state, the above equation gives $\alpha = 7/16$ as assigned by Delale et al. [10], and when $\mathrm{d}T_1/\mathrm{d}t \to \infty$, the above equation gives $\alpha = 0$ to which classical theory applies. Here, the probability of nucleation is chosen to be $\zeta = 0.5$. The results of the ensuing calculations are presented in Table 1, where P_c is the critical pressure calculated from Eq. (4), r_c is the critical radius calculated from Eq. (6) with P_v replaced by P_c, and $T_c = 647.3$ K is the critical temperature of the water. A comparison of the theoretical results of the superheat limit for different rates of temperature increase, with experimental data presented or cited in Refs. [2,6,8,25,26] is presented in Fig. 2, which shows a good agreement of the nucleation temperature between the theoretical prediction from Eqs. (19)–(21) and the experimental results for a large change in the temperature rise rate.

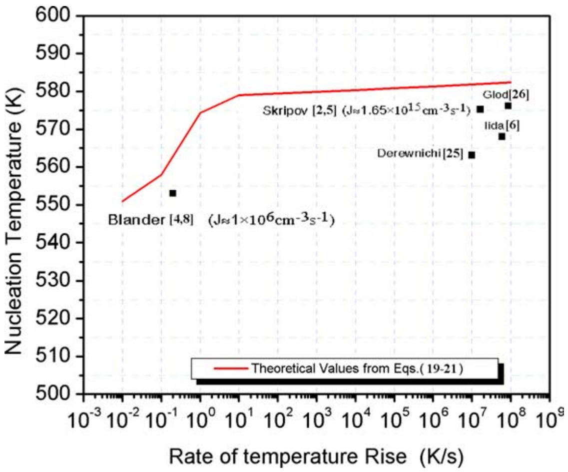

Fig. 2. Comparison of the theoretical results of the superheat limit and experimental data at different temperature rise rates in water at atmospheric pressure (the rate of temperature rise in the experiments carried out by Blander [4,8] was estimated according to the rising velocity of liquid droplets and the elapsed time).

The temperature rise in a liquid when the first bubble embryo is formed after the temperature of the liquid has reached the required superheat can be estimated simply from $\Delta T_1 \approx (1/J \cdot V_0)\mathrm{d}T_1/\mathrm{d}t$ and Eq. (19). For example, it can be found from Eq. (19) that at atmospheric pressure, when nucleation may occur ($\zeta = 0.5$), the nucleation rate, J, is approximately $5 \times 10^{12}/\mathrm{cm}^3$ s for $\mathrm{d}T_1/\mathrm{d}t = 10^7$ K/s,

Table 1
Superheat limit and the critical parameters in water with different temperature rise rates ($\zeta \to 0.5$, $T_c = 647.3$ K)

$\frac{\mathrm{d}T_1}{\mathrm{d}t}$ (K/s)	J (cm^{-3} s^{-1})	T_1 (K)	$\frac{T_1}{T_c}$	r_c (nm)	δ_c	P_c (MPa)	P_e (MPa)
10^{-2}	600	550.9	0.851	7.27	1.37	5.85	6.09
0.1	1×10^4	557.9	0.862	6.05	1.18	6.44	6.76
1	3×10^5	574.3	0.887	3.83	0.81	7.99	8.51
10	4.85×10^6	579.0	0.895	3.28	0.64	8.68	9.34
10^2	4.85×10^7	579.5	0.895	3.22	0.63	8.73	9.40
10^3	4.85×10^8	579.9	0.896	3.18	0.62	8.77	9.46
10^4	4.85×10^9	580.4	0.897	3.13	0.61	8.82	9.51
10^5	4.85×10^{10}	580.8	0.897	3.09	0.60	8.87	9.57
10^6	4.85×10^{11}	581.3	0.898	3.04	0.59	8.93	9.64
10^7	4.85×10^{12}	581.9	0.899	2.99	0.58	8.98	9.70
10^8	4.85×10^{13}	582.4	0.900	2.94	0.57	9.04	9.77

and the temperature rise in the liquid will only be 0.2 K higher than the superheat when the first occurrence of bubble nucleation takes place. As a first approximation, it can be assumed that as the moment of bubble nucleation approaches and the bulk temperature of the liquid reaches the superheat limit, the transient process can be considered to be a constant temperature process (quasi-steady state process) for a very short period of time and the classical kinetics of nucleation are therefore applicable for prediction of the nucleation temperature and the determination of the thermophysical properties of the fluid.

3.2. Initial variation of vapor pressure in bubble nuclei

It is difficult to determine the nonequilibrium vapor pressure in initially nucleated bubbles because the physical process is not well understood at the present time. It is, however, well known that while the vapor pressure in a homogeneous nucleate bubble embryo is much higher than the ambient liquid pressure [2], the vapor pressure will decrease with an increase in the volume of the bubble as observed by many researchers [12–14]. Asai [13] obtained the following expression for the vapor pressure in bubbles during the early period of growth in a vapor explosion by an exponential function of the form:

$$P' = P_{\mathrm{v}} \exp\left[-(1+t/\tau_1)(1+t/\tau_2)^{1/2}\right] \tag{22}$$

where P_{v} was assumed as the initial pressure in bubble nuclei, and τ_1 and τ_2 are time-scale parameters from the experiments. Eq. (22) satisfies the condition that $\mathrm{d}P'/\mathrm{d}t = 0$ at $t = 0$. Thus, it would appear that the vapor pressure inside the bubble may be an extremum at the moment of the formation of a bubble nuclei in a bulk liquid.

From molecular dynamics [27], the statistically exerted pressure, which comes from n evaporated molecules moving from the liquid state to the vapor state in a bubble nucleation process for a constant N_0, P_{l}, T_{l}, can be calculated by the virial representation

$$P = \frac{nkT}{V} - \frac{1}{3V}\left\langle \sum_i \sum_{i<j} \mathbf{r}_{ij}\frac{\mathrm{d}\phi(r_{ij})}{\mathrm{d}r_{ij}} \right\rangle \tag{23a}$$

where ϕ is the potential given by

$$\phi(r_{ij}) = 4\bar{\varepsilon}\left[\left(\frac{\sigma'}{r_{ij}}\right)^{12} - \left(\frac{\sigma'}{r_{ij}}\right)^{6}\right] \tag{23b}$$

Eq. (23b) is the Lennard-Jones (LJ) 12-6 potential. In Eq. (23a) the first term in the right-hand side is for the momentum flux caused by molecular motion and the second term is caused by intermolecular forces. The term $r_{ij}\mathrm{d}\phi(r_{ij})/\mathrm{d}r_{ij}$ in Eq. (23a) is negative and increases with an increase of r_{ij}, and then once it reaches its positive maximum, decreases with the increase in the molecular distance, r_{ij}, to approach zero. This means that the pressure exerted by the evaporated molecules n will increase before the bubble embryo is formed. After a vapor bubble is formed, the second term in Eq. (23a) will approach zero and the pressure in the vapor bubble will decrease with bubble growth similar to that occurring in an ideal gas. This concept has been previously discussed in the literature [7,13,14]. Okumura and Ito [16] used a molecular dynamics simulation approach to study unsteady-state bubble nucleation and collapse. In their investigation, 80 atoms in a bulk liquid were selectively heated and the resultant scattering of the neighboring nonheated atoms was observed. This scattering resulted in bubble formation and then the bubble was cooled and compressed by the surrounding liquid. The bubble dynamics were observed to be in good agreement with the classical Rayleigh–Plesset equation given by Eq. (10). In their study, the number of atoms constituting the bubble surface was estimated and the pressure contribution from these atoms was calculated. It was found that the pressure increased for a very short time because the heated and accelerated atoms approach each other and the virial term became large, as discussed previously, and then the pressure decreased after the pressure reached its extremum and later relaxed to the equilibrium value. Wu and Pan [17] presented the time evolution of pressure and temperature during homogeneous bubble nucleation under heating, using a molecular dynamic simulation approach. In this investigation, it was found that at the moment of bubble nucleation the pressure approaches the extremum.

In the current work, this extremum is interpreted such that the nonequilibrium vapor pressure in the initially formed bubble nucleus is an extremum during the entire bubble nucleation and growth process (even if this is not true, the initial nonequilibrium vapor pressure should be very close to this extremum). The intermolecular forces will decrease during the evolution from a bubble nucleus to a stable bubble as discussed previously. Consequently, the vapor pressure will be decreasing during the evolution, as described by Asai [13] and Okumura and Ito [16]. This means that during homogeneous nucleation, the pressure in the bubble nucleus will be at a local maximum at the moment of the bubble nucleus formation, such that $\mathrm{d}P'/\mathrm{d}t = 0$, $\mathrm{d}^2P'/\mathrm{d}t^2 \leqslant 0$ regardless of its size. Based upon the preceding discussions, this assumption is quite reasonable, and while a rigorous proof of this assumption is beyond the scope of the current investigation, the accuracy can be verified and confirmed through analysis of the initial bubble growth and comparison with the published experimental results, which follows herein. A rigorous proof could be obtained from a combined nonequilibrium statistical thermodynamics and molecular dynamics perspective.

It should be noted that the hypothesis $\mathrm{d}P'/\mathrm{d}t = 0$ is reasonable only at the moment of the formation of a bubble nucleus. In fact, the variation of the vapor pressure in the bubbles is still not well understood at the present time. This is especially true for situations involving rapid transient phase change processes induced by pulsed heating or rapid depressurization of a liquefied gas, where the vapor pressure in an initially nucleated bubble, may or may not be at the maximum during the whole process.

As mentioned previously, the nonequilibrium hydrodynamic relationship between the vapor pressure, P', in a bubble and the motion of the bubble surface is given by Eq. (10) in terms of r and $\dot{r}$, $\ddot{r}$. Other relationships between $r, \dot{r}, \ddot{r}$ and P' are required in order to solve the above equation. These relationships are obtained in the following sections based on energy and mass conservation.

3.3. Initial mass flux at interface

During the formation of a bubble nucleus, there exists a continuous energy and mass transfer at the bubble interface. Focusing attention on the mass in the vapor bubble and the mass that will be evaporated, the energy conservation for an open thermodynamic system yields $\delta Q = \mathrm{d}H - V\mathrm{d}P'$, which gives

$$\underset{\substack{\uparrow\\ \text{Heat flux at}\\ \text{the interface}}}{\lambda\left(\frac{\partial T_l}{\partial r}\right)_{r=R}} A = \underset{\substack{\uparrow\\ \text{Latent heat of}\\ \text{the evaporated}\\ \text{molecules}}}{\frac{dn}{dt}}[\Delta H_{fg} + C_P(T' - \underset{\substack{\uparrow\\ \text{Sensible heat of}\\ \text{the evaporated}\\ \text{molecules}}}{T_{interface}})] + \underset{\substack{\uparrow\\ \text{Enthalpy increase of}\\ \text{molecules in bubble}}}{nC_P}\frac{dT'}{dt} - V\frac{dP'}{dt} \tag{24}$$

where the term $\mathrm{d}n/\mathrm{d}t$ is also given by Eq. (12) with $T_{\text{interface}}$ being an unknown quantity. The first two terms on the right-hand side of the above equation, with C_P denoting the thermal capacity per molecule, are the enthalpy increase of the controlled mass under consideration. With the aid of the Clausius–Clapeyron equation

$$\frac{\mathrm{d}T}{\mathrm{d}P} = \frac{T}{h_{\text{fg}} \cdot \rho_{\text{v}}} \tag{25}$$

and under the assumption of $\mathrm{d}P'/\mathrm{d}t = 0$ during the initial period of bubble formation, the last two terms of Eq. (24) would disappear. A comparison of Eq. (11) and Eq. (24) without the last two terms shows that the heat sensitive terms in Eq. (24) were overlooked in Kagan's analysis, even for a steady-state process.

Integrating Eq. (24) with respect to r, from r to $r \to \infty$, and with the aid of Eq. (25) and with the assumption of $\mathrm{d}P'/\mathrm{d}t = 0$, we obtain $T_{\text{interface}} - T_{\text{l}}$ as

$$\begin{aligned} T_{\text{interface}} - T_{\text{l}} &= -\frac{\dfrac{C_P}{4\pi\lambda r}\dfrac{\mathrm{d}n}{\mathrm{d}t}(T' - T_{\text{l}}) + \dfrac{\Delta H_{\text{fg}}}{4\pi\lambda r}\dfrac{\mathrm{d}n}{\mathrm{d}t}}{1 - \dfrac{C_P}{4\pi\lambda r}\dfrac{\mathrm{d}n}{\mathrm{d}t}} \\ &\approx -\frac{C_P}{4\pi\lambda r}\frac{\mathrm{d}n}{\mathrm{d}t}(T' - T_{\text{l}}) - \frac{\Delta H_{\text{fg}}}{4\pi\lambda r}\frac{\mathrm{d}n}{\mathrm{d}t} \end{aligned} \tag{26}$$

where $\frac{C_P}{4\pi\lambda r}\frac{\mathrm{d}n}{\mathrm{d}t} \ll 1$ and $T_{\text{interface}}$ is unknown. Substituting Eq. (26) and $P'V = nkT'$ into Eq. (25) gives,

$$\frac{P_{\text{c}}(T_{\text{interface}})}{P_{\text{c}}(T_{\text{l}})} = 1 - \frac{\frac{\mathrm{d}n}{\mathrm{d}t}[\Delta H_{\text{fg}}^2 + C_P\Delta H_{\text{fg}}(T' - T_{\text{l}})]}{4\pi k T_{\text{l}}^2 \lambda r} \tag{27}$$

Substituting Eq. (27) into Eq. (12) yields,

$$\frac{\mathrm{d}n}{\mathrm{d}t} \approx \frac{A}{(2\pi M_0 k T_{\text{l}})^{1/2}(1 + \delta_\lambda)}(P_{\text{c}}(T_{\text{l}}) - P') \tag{28a}$$

where

$$\begin{aligned} \delta_\lambda(r, T') &= P_{\text{c}}(T_{\text{l}})\left[\frac{\Delta H_{\text{fg}}^2 + \Delta H_{\text{fg}} C_P(T' - T_{\text{l}})}{k^2 T_{\text{l}}^2}\right] \\ &\quad \times \left(\frac{k}{2\pi M_0 T_{\text{l}}}\right)^{1/2}\frac{r}{\lambda} \end{aligned} \tag{28b}$$

Letting $r = r_{\text{c}} = 2\sigma/[P_{\text{c}}(T_{\text{l}}) - P_{\text{l},\infty}]$ and $T' = T_{\text{l}}$ for the critical bubble nuclei and substituting these into Eq. (28b), δ_λ is reduced to δ_{c}

$$\delta_{\text{c}} = \left[\frac{\Delta H_{\text{fg}}}{kT_{\text{l}}}\right]^2 \left(\frac{2k}{\pi M_0 T_{\text{l}}}\right)^{1/2} \frac{\sigma}{\lambda}\left(\frac{P_{\text{c}}}{P_{\text{c}} - P_{\text{l}}}\right) \tag{29}$$

which is the factor that appears in Eq. (14) and was first derived by Kagan [15]. The typical values of δ_{c} for water are presented in Table 1, which show that δ_{c} is not sensitive to the initial nucleation temperature and the temperature rise rate.

3.4. Initial bubble growth rate

In order to calculate the initial pressure of the bubbles from Eq. (10), it is necessary to obtain expressions for the initial bubble growth rate and the interface acceleration. As discussed previously, Kagan used a combination of Eqs. (10) and (12) and the state equation of ideal gas, $P'V = nkT'$, to calculate $(\mathrm{d}\dot{n}/\mathrm{d}r)_{r=r_{\text{c}}}$ and in this way the complicated relationship between P' and $\dot{r}, \ddot{r}$ can be avoided. In Kagan's derivation, the vapor temperature was assumed to be the same as the liquid temperature and constant for a steady-state process and thus, the sensitive heat terms in Eq. (24) were overlooked in Kagan's analysis, Eq. (11). It is apparent from the derivations of the expressions developed in the previous section that the vapor temperature is different from the liquid bulk temperature, otherwise the derivation of the relationship between the bubble surface temperature and the bulk temperature for different temperature increase rates would not make sense. A similar paradox exists in Kagan's derivation.

From mass conservation (see Fig. 1) and taking the entire mass in the bubble as the control mass, yields

$$\frac{\mathrm{d}m}{\mathrm{d}t} \equiv \frac{\mathrm{d}}{\mathrm{d}t}(\rho_{\text{v}} V) \tag{30}$$

It follows that the initial bubble growth rate is

$$\dot{r} \equiv \frac{1}{\rho_v A}\frac{dm}{dt} - \frac{r}{3\rho_v}\frac{d\rho_v}{dt} \tag{31}$$

With the assumptions, $dP'/dt = 0$ and the assumption that Eq. (25) is valid at the moment of the initial formation of a bubble nucleus, the variation of the vapor density with respect to time can be neglected (i.e., $d\rho_v/dt = 0$) if the vapor is assumed to behave as an ideal gas ($P' = \rho_v RT'$). Consequently, Eq. (31) becomes

$$\dot{r} \cong \frac{M_0}{\rho_v A}\frac{dn}{dt} \tag{32}$$

Eq. (32) gives the relationship between the rate of molecular evaporation, dn/dt, and the velocity of the surface of the initial nucleate bubble. Substituting Eq. (28a) into Eq. (32) yields

$$\dot{r} \cong \frac{M_0^{1/2}}{\rho_v(2\pi kT_l)^{1/2}(1+\delta_\lambda)}(P_c(T_l) - P') \tag{33}$$

Differentiating the above equation with respect to t, the initial acceleration of the bubble surface can be expressed as

$$\ddot{r} = \frac{d}{dt}(\dot{r}) \cong \frac{d}{dt}\left[\frac{M_0^{1/2}}{\rho_v(2\pi kT_l)^{1/2}(1+\delta_\lambda)}(P_c(T_l) - P')\right] \tag{34a}$$

If P_l = constant and δ_λ is regarded as a constant, with the assumption that $dP'/dt = 0$ and the assumption that Eq. (25) is valid, it follows from Eq. (34a) that

$$\ddot{r} = \frac{d}{dt}(\dot{r}) = \frac{M_0^{1/2}}{(2\pi kT_l)^{1/2}(1+\delta_\lambda)}\frac{h_{fg}\delta}{T_l}\frac{dT_l}{dt} - \frac{M_0^{1/2}}{(2\pi kT_l)^{1/2}(1+\delta_\lambda)}\frac{1}{2\rho_v T_l}[P_c(T_l) - P']\frac{dT_l}{dt} \tag{34b}$$

Eq. (34b) describes the temperature variation in the liquid which causes the temperature variation at the interface and further affects the variation of the evaporation rate at the interface. This, in turn, affects the acceleration of the surface of the bubble. With $\dot{r}$ and $\ddot{r}$ given by Eqs. (33) and (34b), the value of P' can be calculated from Eq. (10).

3.5. Nonequilibrium initial nucleation in an unsteady process

From Eqs. (10) and (27a), it can be shown that

$$\frac{dn}{dt} = \frac{A}{(2\pi M_0 kT_l)^{1/2}(1+\delta_c)} \times \left[P_c(T_l) - P_l - \rho_l\left(r\ddot{r} + \frac{3}{2}\dot{r}^2\right) - \frac{2\sigma}{r} - 4v\frac{\dot{r}}{r}\right] \tag{35}$$

Eqs. (10), (32), (34), (35) and (25) are a set of equations for the complicated relationship between dn/dt and $\dot{r}$, $\ddot{r}$, P', T', which is the nonequilibrium model for the initial bubble nucleation in a superheated liquid during an unsteady process. These equations can be solved numerically to obtain the initial bubble growth rate, $\dot{r}$, the initial bubble acceleration, $\ddot{r}$, and the initial pressure in the bubble, P', at a specific rate of temperature increase for a specific bubble radius, taking into account the variations of properties with temperature. The procedure of the numerical solution is as follows:

(1) Initially, the superheated or the initial nucleation temperature, T_l required for homogeneous boiling in a liquid for a specific temperature rise rate (dT_l/dt) is obtained from Eqs. (19) and (20). The results of this calculation are listed in Table 1;
(2) Then, at these values of T_l and dT_l/dt, the convergent solutions of dn/dt, $\dot{r}$, $\ddot{r}$, P', T' for nucleated bubbles with different radii, r, are calculated by iterating Eqs. (10), (32), (34b), (35) and (25) to obtain the convergent solutions for dn/dt, $\dot{r}$, $\ddot{r}$, P', T' if an initial nonequilibrium vapor pressure (here $P' = P_c$ is initially assumed) is assumed for the first iteration. It should be noted here that all of the thermodynamic and hydrodynamic properties of the vapor and liquid are temperature-dependent and the properties are adopted from Ref. [28].

Homogeneous nucleation at different rates of temperature variation can be investigated following Kagan's nonequilibrium mechanics and thermodynamic approach [15]. Although the current analysis adopts the nonequilibrium mechanics aspect of the Kagan analysis, it differs from those of Kagan in the evaluation of the bubble velocity and the acceleration at the moment of bubble formation. While Kagan focused attention on the velocity and acceleration of bubbles having a critical radius, the current analysis obtains the velocity and acceleration of different sizes of bubbles based on energy and mass conservation at the bubble/liquid interface. The major assumptions used in the present analysis are: the pressure and temperature of the bubbles are at the local maximum when the bubble nuclei are formed, i.e., $dP'/dt = 0$ and $d^2P'/dt^2 \leqslant 0$. These assumptions are reasonable and the results of this analysis appear to be valid from a physical perspective.

4. Results and discussion

In order to identify how far the vapor pressure is from the equilibrium state in initially nucleated bubbles, a comparison between the nonequilibrium vapor pressure, P', given by Eq. (10) and the equilibrium vapor

Table 2
The initial pressure, velocity and acceleration with different initial bubble sizes at three different temperature rise rates in water

dT_l/dt (K/s)	r (nm)	$\dot{r}$ (m/s)	$\ddot{r}$ (m/s^2)	P' (Pa)	P_v (Pa)
10^{-2}	6.899	-1.580×10^{-24}	11.52	5910646.75203	5910646.75198
	6.906	8.524×10^{-25}	11.51	5904531.17946	5904531.17941
	7.270*	1.163×10^{-22}	11.44	5614354.70912	5614354.70907
	11.410	9.117×10^{-22}	10.96	3614929.05049	3614929.05041
10	2.962	-2.939×10^{-24}	1.33×10^4	8897502.28436	8897502.25683
	2.966	4.916×10^{-25}	1.33×10^4	8887804.33298	8887804.30543
	3.279*	3.008×10^{-22}	1.31×10^4	8046794.14443	8046794.11435
	4.882	1.220×10^{-21}	1.26×10^4	5438998.52093	5438998.47797
10^7	2.699	-1.095×10^{-24}	1.34×10^{10}	9225353.22227	9200175.69045
	2.703	2.449×10^{-24}	1.34×10^{10}	9215311.64692	9190110.05366
	2.990*	3.096×10^{-22}	1.32×10^{10}	8345067.19957	8317555.65591
	4.422	1.245×10^{-21}	1.27×10^{10}	5695520.42841	5656480.35168

* The critical size of bubble nuclei.

pressure, P_v, given by Eq. (6) are shown in Table 2, for three different rates of temperature increase. It should be noted that the vapor pressure decreases with the increase of the initial bubble size. This is because the smaller the bubble nucleus, the greater the effect of the surface tension on P' as indicated in Eq. (10). When the rate of temperature increase in the liquid is relatively low, as shown in Table 2 (i.e., in the range of $dT_l/dt = 10^{-2}$ K/s), the difference between the vapor pressure derived from the hydrostatic and hydrodynamic relationships is quite small, but when the rate of temperature increase in the liquid is high (i.e., in the range of $dT_l/dt = 10^7$ K/s), the difference between the vapor pressure derived from the hydrostatic and hydrodynamic relationships is quite noticeable, especially when the initial bubble size is larger than the critical value. The vapor pressure derived from the hydrodynamic relationship is somewhat greater than the vapor pressure derived from the hydrostatic relationship at the same bubble size according to Eq. (10), which provides the driving force for bubble growth. Fig. 3 shows that the initial nonequilibrium vapor pressure ($P'-P_v$) in bubble nuclei with different sizes at different rates of temperature increases in liquid.

Fig. 4 illustrates that the initial bubble velocity increases with the increase of the initial bubble size. At a given bubble size, the growth rate of the bubbles increases as the rate of the temperature rise increases. It is interesting to note that the velocity for bubble growth is negative for the bubble if its size is below the critical bubble size, while the velocity for bubble growth is positive if its size is above the critical value. The bubble growth velocity is zero if the bubbles are close to their critical values. This can be explained by observing that the net rate of vaporization of molecules into a bubble, dn/dt, increases with the increase of the initial bubble size or with the decrease of the initial bubble pressure, P', as shown in Eq. (12). These results help to explain why the initial bubble size must be greater than the critical size in order to grow and form a stable bubble. This result also agrees with the second law of thermodynamics, i.e., that the bubble with a size greater than critical size will grow spontaneously.

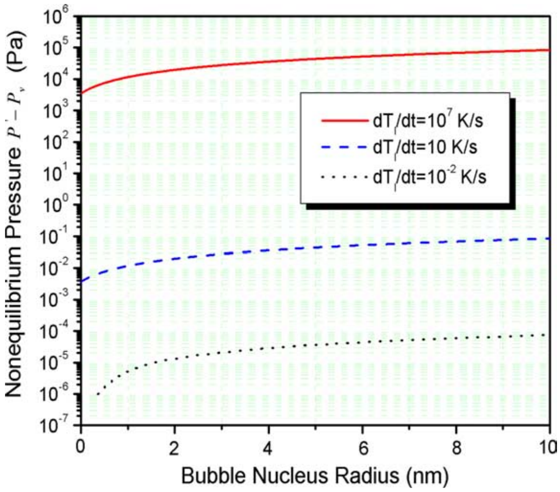

Fig. 3. Initial nonequilibrium pressure in a bubble with the different sizes at different temperature rise rates in a liquid.

Fig. 5 shows that the initial bubble acceleration increases drastically from about 10 m/s^2 to 1×10^{10} m/s^2 as the temperature rise rate increased from 10^{-2} K/s to 10^7 K/s. However, the initial acceleration rate of the bubble is relatively independent of the initial bubble radius when the bubble size is larger than the critical size. Iida and Okuyama [6] obtained an average acceleration of approximately 1.4×10^8m/s^2 for a temperature rise rate of 5.26×10^6 K/s in water on a smooth platinum microheater. It should be noted that in the experiments of Iida and Okuyama [6], the minimum time difference

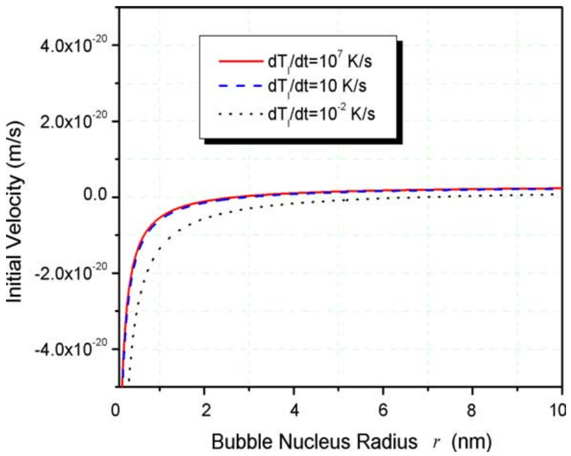

Fig. 4. Initial velocity of a bubble with different sizes at the different temperature rise rates in a liquid.

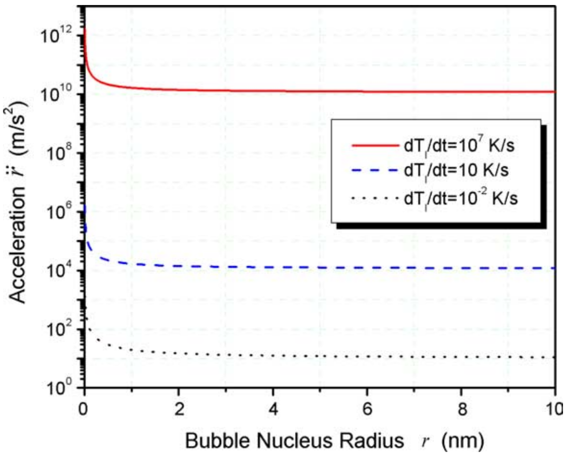

Fig. 5. Initial acceleration in a bubble with different sizes at different temperature rise rates in a liquid.

between the two photo frames was 0.4 μs, making it very difficult to identify the original moment of bubble nucleation, due to the rapid growth and speed of the video camera. Li and Peterson [29] obtained an acceleration of approximately 10 m/s^2 at the moment of boiling incipience for a quasi-steady state process on a smooth platinum microheater inferred from experiments when $t \to 0$. These experimental data can, however, provide initial verification of the model proposed here indirectly. It should also be noted that the results presented in Figs. 3–5 are meaningful only at the initial nucleation stage. After a stable bubble is formed, the variations of pressure, velocity and acceleration are different from those shown in Figs. 3–5 and are related to the bubble dynamics as noted in several previous theoretical and experimental investigations [6,13,26,29].

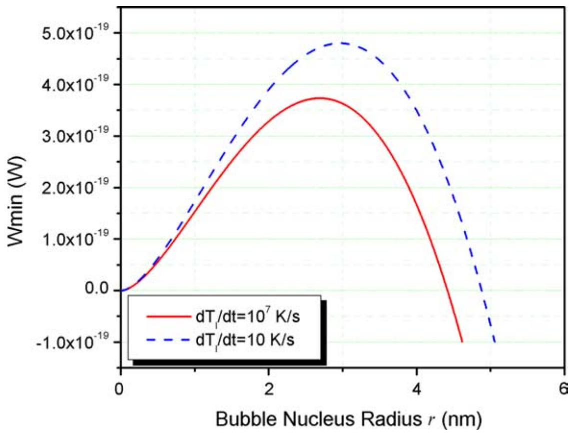

Fig. 6. Minimum work W required to form a bubble when $\mathrm{d}T_\mathrm{l}/\mathrm{d}t = 10^7$ K/s and $\mathrm{d}T_\mathrm{l}/\mathrm{d}t = 10$ K/s, respectively.

Fig. 6 illustrates the minimum work, W, required to form a bubble in a homogeneous liquid phase with a single component, when $\mathrm{d}T_\mathrm{l}/\mathrm{d}t = 10^7$ K/s and $\mathrm{d}T_\mathrm{l}/\mathrm{d}t = 10$ K/s, as calculated from Eq. (5) based on the non-equilibrium vapor pressure, P', presented in Fig. 3. The minimum work, W, is shown to be a maximum around the critical bubble size, which is consistent with the classical nucleation theory. The number distribution of bubbles with different sizes can be obtained from Eqs. (5), (10) and (13), and the results are presented in Fig. 7 for $\mathrm{d}T_\mathrm{l}/\mathrm{d}t = 10^7$ K/s and $\mathrm{d}T_\mathrm{l}/\mathrm{d}t = 10$ K/s, respectively.

Fig. 8 illustrates the minimum work, W, required to form a bubble and the number and distribution of bubbles with different sizes, when $\mathrm{d}T_\mathrm{l}/\mathrm{d}t = 10^{-2}$ K/s. In Fig. 8, the contributions from the bubbles with a size much greater than, or smaller than the critical value have the dominant role in bubble nucleation.

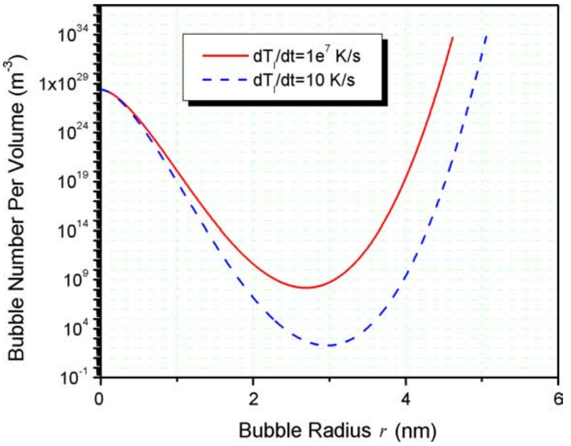

Fig. 7. The distribution of bubbles for different sizes when $\mathrm{d}T_\mathrm{l}/\mathrm{d}t = 10^7$ K/s and $\mathrm{d}T_\mathrm{l}/\mathrm{d}t = 10$ K/s, respectively.

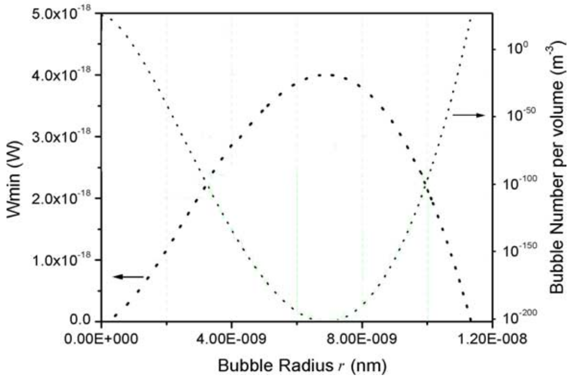

Fig. 8. The minimum work W required to form a bubble as a function of the bubble radius when $\mathrm{d}T_l/\mathrm{d}t = 10^{-2}$ K/s.

5. Nonequilibrium vapor pressure in bubble nuclei

The analysis of the initial nonequilibrium nucleation and bubble growth is very limited in classical bubble dynamics. Bornhorst et al. [30] were the first to introduce nonequilibrium thermodynamics into the study of bubble dynamics, and they considered almost all aspects of bubble growth. With the analysis of the noncontinuous pressure distribution between the vapor and liquid phases they determined the pressure difference between the actual pressure of the liquid at the interface, $P_{\mathrm{l,interface}}$, and the saturation pressure, $P_{\mathrm{e,interface}}$, at $T_{\mathrm{interface}}$

$$\begin{aligned}\delta_f P &\equiv P_{\mathrm{l,interface}} - P_{\mathrm{e,interface}} \\ &= [P_{\mathrm{e}}(T_{\mathrm{l}}) - P_{l,\infty}] + \frac{\rho_{\mathrm{v}} h_{\mathrm{fg}}}{T_{\mathrm{l}}}[(T_{\mathrm{l}} - T_{\mathrm{interface}}) - \Delta T_{\mathrm{s}}]\end{aligned} \tag{36}$$

where ΔT_{s} is the superheat of the liquid at infinity $\Delta T_{\mathrm{s}} = T_{\mathrm{l}} - T_{\mathrm{s}}(P_{\mathrm{l},\infty})$. If the liquid–vapor system is in equilibrium, $\delta_{\mathrm{f}}P$ is zero. Because of the difficulty involved in the determination of this nonequilibrium condition, Zeng et al. [14] and Lee et al. [31] assumed an arbitrary condition of $T' = T_{\mathrm{l}} + \Delta T_{\mathrm{disturbance}}$. By means of the analysis derived in the current work, this nonequilibrium disturbance can be fully derived.

The size of the bubble is clearly important in that once formed, the condition, $\dot{r} \geqslant 0$ must be true in order for the bubble to grow (i.e., the bubble will grow up spontaneously and satisfy the second law of thermodynamics) and also, $W_{\min} \geqslant 0$ (i.e., it must satisfy the first law of thermodynamics). Given these constraints, the average parameters for stable boiling may be established and can be modeled using statistical methods, e.g., the initial size, the initial velocity, the initial acceleration and the initial nonequilibrium vapor pressure.

From Fig. 4 and Table 2 it is apparent that around the critical bubble size, the velocity will change from negative to positive. Thus, statistically the average initial radius of a bubble under a given rate of bulk temperature rise, $\mathrm{d}T_{\mathrm{l}}/\mathrm{d}t$, can be obtained from

$$\bar{r} = \frac{\int_{r_{\mathrm{c}}}^{r_{\mathrm{W}}} r \cdot N(r)\mathrm{d}r}{\int_{r_{\mathrm{c}}}^{r_{\mathrm{W}}} N(r)\mathrm{d}r} \tag{37}$$

and

$$\overline{P'} = P'(\bar{r}) \tag{38}$$

where r_W is the bubble radius corresponding to $W_{\min} = 0$. According to Eqs. (37) and (38) and the results shown in Figs. 3, 7 and 8, the averaged parameters for the bubble nuclei which are most likely to appear in a given liquid for a certain transient boiling process with a given temperature rise rate, $\mathrm{d}T_{\mathrm{l}}/\mathrm{d}t$, can be obtained and will satisfy the conditions, $\dot{r} \geqslant 0$ and $W_{\min} \geqslant 0$. Some results are shown in Table 3.

To predict the initial bubble size in homogeneous nucleation in engineering applications, a relationship between the statistically averaged initial bubble radius and the temperature rise rate in the bulk liquid $\mathrm{d}T_{\mathrm{l}}/\mathrm{d}t$ can be obtained from the data shown in Table 3. Fitting the results yields

$$\bar{r}_{\mathrm{initial}} = r_{\mathrm{c}}(T_{\mathrm{l}}) + f\left(\frac{\mathrm{d}T_{\mathrm{l}}}{\mathrm{d}t}\right) \tag{39a}$$

where

$$\begin{aligned}f\left(\frac{\mathrm{d}T_{\mathrm{l}}}{\mathrm{d}t}\right) &= 2.10 \times 10^{-9} - 6.15 \times 10^{-10}\frac{\mathrm{d}T_{\mathrm{l}}}{\mathrm{d}t} \\ &\quad + 1.63 \times 10^{-10}\frac{\mathrm{d}T_{\mathrm{l}}}{\mathrm{d}t}^{2} - 1.29 \times 10^{-11}\frac{\mathrm{d}T_{\mathrm{l}}}{\mathrm{d}t}^{3}\end{aligned} \tag{39b}$$

The results from Eq. (39b) and the calculated data, $\bar{r}_{\mathrm{initial}} - r_{\mathrm{c}}$, are shown in Fig. 9. As shown, the error resulting from the curve fitting is very small and quite acceptable. Thus, the initial average radius can be obtained using Eq. (39) for a given temperature rise rate.

Table 3
Average initial bubble size and nonequilibrium vapor pressure for three different bulk temperature rise rates

$\mathrm{d}T_{\mathrm{l}}/\mathrm{d}t$ (K/s)	$\bar{r}_{\mathrm{initial}}$ (nm)	$\overline{P'}$ (MPa)	r_{c} (nm)	$r_{W_{\min>0}}$ (nm)	$\delta_{\mathrm{ne}}P = \overline{P'} - \overline{P}_{\mathrm{v}}$ (Pa)
10^{-2}	11.4	3.6311	7.27	11.4	9.42×10^{-5}
10	4.87	5.4538	3.28	4.88	4.29×10^{-2}
10^{7}	4.40	5.7196	2.99	4.42	3.89×10^{4}

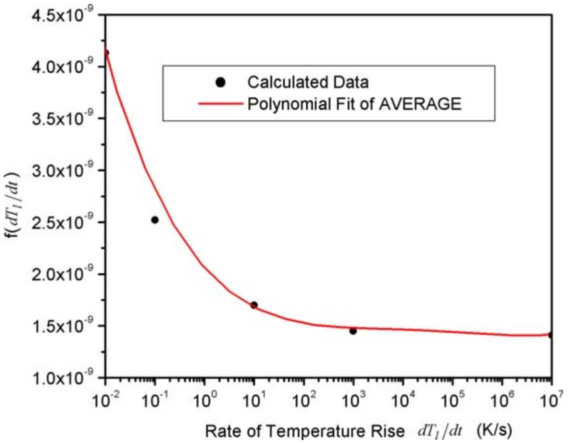

Fig. 9. The relationship between the statistically averaged initial bubble radius and the rate of temperature rise in bulk liquid dT_l/dt from the data shown in Table 3.

From Eq. (10)

$$\delta_{ne}P \equiv P' - P_v = \rho_l r\ddot{r} + \rho_l \frac{3}{2}\dot{r}^2 + 4v\frac{\dot{r}}{r} \tag{40}$$

where P_v is the hydrostatic pressure defined by Eq. (6). Combining Eqs. Eqs. (40), (33) and (34), and considering that the magnitude of the first term on the right-hand side of Eq. (40) is approximately 10^{-6}–10^{5} for different rates of temperature rise, and that the magnitudes of the second and third terms are approximately 10^{-40} and 10^{-20}, respectively, (the second term was also omitted in Kagan's derivation for the same reason, and also the effect of viscosity can be negligible in water nucleation), yields

$$\delta_{ne}P \equiv P' - P_v \approx \varepsilon\rho_l r\ddot{r} \tag{41}$$

Here ε is another adjustable parameter, similar to α in Section 3, where the value of ε can be obtained either from a comparison with the theoretical method as shown in the current work or estimated by comparison with experimental results available in the literature. With this, the nonequilibrium pressure disturbance in the vapor phase can be derived in terms of the rate of temperature rise in the liquid as,

$$\begin{aligned}\delta_{ne}P &\equiv P' - P_v \approx \varepsilon\rho_l r\ddot{r} \\ &= \varepsilon\rho_l r\left\{\frac{M_0^{1/2}}{(2\pi k T_l)^{1/2}(1+\delta_r)}\frac{h_{fg}\delta}{T_l}\frac{dT_l}{dt}\right. \\ &\quad \left. - \frac{M_0^{1/2}}{(2\pi k)^{1/2}(1+\delta_r)}\frac{1}{\rho_v T_l}[P_c(T_l) - P']\frac{dT_l}{dt}\right\}\end{aligned} \tag{42}$$

Rewriting $P_c(T_l) - P' = (P_c - P_v) - (P' - P_v)$ and after some algebraic manipulations, Eq. (42) becomes

$$\delta_{ne}P = \frac{c_1\rho_l r - c_2\rho_l r(P_c - P_v)}{1 - c_2\rho_l r\frac{dT_l}{dt}}\frac{dT_l}{dt} \tag{43a}$$

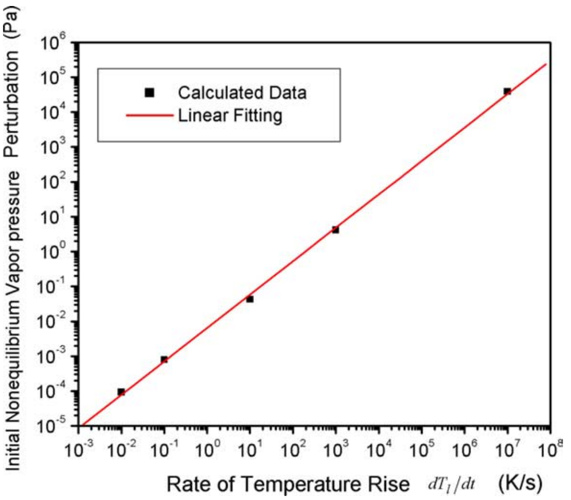

Fig. 10. Nonequilibrium pressure perturbation in vapor phase as a function of the temperature rise rate in a liquid.

where

$$\begin{aligned} c_1 &= \varepsilon\sqrt{\frac{M_0}{2\pi k T_l}}\frac{1}{1+\delta_r}\frac{h_{fg}\delta}{T_l} \\ c_2 &= \varepsilon\sqrt{\frac{M_0}{2\pi k T_l}}\frac{1}{1+\delta_r}\frac{1}{\rho_v T_l}\end{aligned} \tag{43b}$$

and ε is approximately unity for water. The results from Eq. (43) for different rates of temperature rise are shown in Table 3. These results are presented in a log–log plot as shown in Fig. 10, which can be represented as a straight line expressed as

$$\delta_{ne}P = 0.0064 \cdot \left(\frac{dT_l}{dt}\right)^{0.96} \tag{44}$$

Eq. (44) can be used to calculate the initial nonequilibrium pressure disturbance. Thus, the average nonequilibrium parameters, $\bar{r}_{initial}$, $\overline{P'}_{initial}$ and the nonequilibrium disturbance, $\delta_{ne}P$, can be determined for the initial bubble nucleation for a given temperature rise rate. With the equations proposed in the current work, the initial disturbance for bubble growth can be solved within an acceptable error range.

6. Conclusions

In this investigation, quantitative results for the vapor pressure, bubble interface velocity and the rate of bubble growth during the initial stage of bubble nucleation in a homogeneous liquid at different temperature rise rates are presented. These results can be used to obtain some missing information from classical bubble nucleation theory, such as the nonequilibrium vapor pressure in bubble nuclei and the initial interface acceleration for different rates of temperature rise in liquid. The assumption of $dP'/dt = 0$ at the bubble nucleation and two adjustable parameters α and ε are introduced from a theoretical perspective and experimental results, in order to avoid the complicated nonequilibrium thermodynamic analysis, and to demonstrate that the derived equation can be used for predicting the initial stage of the transient boiling process.

In this investigation, the initial vapor pressure and the initial growth rate of bubble nuclei with different bubble sizes at different rates of temperature rise are quantitatively analyzed in detail for the first time. In addition, the nonequilibrium pressure disturbance in the bubble nuclei is analyzed and computed. The following conclusions are obtained from the present analysis:

(1) The bubble growth velocity is negative if the bubble size is below the critical bubble size, while the growth velocity is positive if its size is above the critical value. These results explain why the initial bubble size must be greater than the critical size, in order to grow spontaneously and become a stable bubble.
(2) The vapor pressure derived from the hydrodynamic relationship is slightly greater than the vapor pressure derived from the hydrostatic relationship at the same bubble size, which provides the driving force for bubble growth from the initial size.
(3) The number of bubble nuclei, $N(r)$, computed from the Boltzmann equation, has a minimum value at the critical size, while most of the bubbles are distributed away from the critical size. Thus, the contributions from the bubbles with sizes different than the critical value play a dominant role, especially at low temperature increase rates.

Even though the kinetic theory presents some difficulties in dealing with nanoscale embryos [23], the theory is the only one that connects the phase change mechanism in microscale with the observed macroscale phenomena, making the results of the present analysis very useful in the theoretical analysis and design of microscale electro mechanical systems.

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