American Jr. of Mathematics and Sciences
Vol. 1, No. 1, January 2012

www.journalshub.com

The Modeling homogeneous bubble nucleation in liquids : A probable mechanism

***A. K. Borah*[1] *and P.Goswami*[2]**

[1]**Department of Mathematics, R. G. Baruah College**
Fatasil Ambari , Guwahati-781025, India
E-mail: borah.arup@yahoo.com
[2]Research Associate, University Grants Commission
Bahadurshah Zafar Marg, New Delhi -110002, India.

Abstract

In this paper we studied rapid evaporation of a liquid at its superheat limit is one of the few aspects of boiling that is amenable to rigorous theoretical modeling. On the other hand the classical theory of bubble nucleation is reviewed and recent developments are presented that have been proposed for improving the treatment of the energy of forming bubble molecular dimensions. Application are discussed in which homogeneous nucleation is the most probable mechanism for initiating a phase transition, including thermal ink jet printing processes, rapid decompression of a two phase flow, and vapour explosion of liquids droplets.

Key words: Bubble nucleation, superheated liquids, two phase flow, density functional theory, rapid decompression, classical model.

1 *Introduction*

This paper deals the current understanding on modeling bubble nucleation within liquids, and a few applications under which it is likely to be important are studied. Bubbles form in a liquid by one of two mechanisms – from gases trapped in surface imperfections (*heterogeneous* nucleation) or by molecular activity in a liquid that is completely devoid of any pre-existing vapour phase (*homogeneous* nucleation). On the other hand, the former process prevalent if the liquid does not completely *wet* a surface, in the sense of its apparent contact angle being small as for some common fluids [1]. Bubble nucleation in this case involves the trapped gases being drawn out to the mouth of the cavities after which they detach from the surface as they continue growing [2]. The rising bubbles are the common occurrence of normal boiling. Several excellent reviews have been written on this process [3–5]. For homogeneous nucleation the bubbles do not exist *a priori* [6]. Furthermore, the process by which the bubbles are assumed to form in this latter situation is studied in two important treatises [7–8], and reviews the essential ideas behind the classical model of the kinetics of homogeneous nucleation and presents recent developments for the energetics of the process. Three applications in which homogeneous nucleation can be realized

(i) two-phase flows during rapid decompression within channels or tubes
(ii) vapour explosions
(iii) and ink-jet printing process

2 *Superheated liquids*

Liquid-to-vapour phase transitions occur at temperatures which are bounded on the lower end by the saturation or equilibrium vapour temperature, $T_S(P_0)$ corresponding the ambient pressure P_0 and at the upper end by the so called *spinodal* temperature or *thermodynamics limit of super heat* $T_t(P_0)$ corresponding to the given pressure. $T_t(P_0)$ is determined by the extremum principle of thermodynamics which asserts that the entropy of an isolates system is a maximum in a stable equilibrium state with respect to small variations of its natural variables. But for a single component liquid, $T_t(P_0)$ corresponds to $\partial P/\partial V = 0$ along an isotherm [9]. *Superheated* liquids refers to a liquid that is at a temperature in the range $T_S(P_0) < T(P_0) < T_t(P_0)$ or alternatively to a liquid which is under a pressure that is in the range $P_t(T) < P_0 < P_S(T)$. Fig. (1) shows the these temperatures $P–T$ and $P–V$ projections of a phase diagram for a single component liquid. But the thermodynamics state at which a phase transition is initiated depends on experimental conditions. If a liquid in contact with a solid with rapidly heated (along path $a \rightarrow c$ in Fig. (1)) at the rate of 10^6/s or higher, temperatures approaching T_t can be sustained before a phase transition occurs [7]. Moreover, if the liquid is heated at a rate which is many orders of magnitude less, then the phase transition typically occurs at temperatures close to T_S. Bubbles are the physical entity that forecasts a bulk phase transition. When they are spherical and in static mechanical equilibrium with the surrounding liquid, then

$$P - P_0 = \frac{2\sigma}{R} \tag{1}$$

Combining Eq.(1) with Clausius Clapeyron equation we obtain

$$T(P_0) - T_S(P_0) \approx T\,T_S R_g \frac{\ln\left(1 + \frac{2\sigma}{P_0 R}\right)}{hf_g} \tag{2}$$

Normal saturation states are conventionally based on equilibrium across a flat phase boundary, R→_. However, when a liquid is able to sustain some degree of superheat, any vapour present must be in the form of bubbles with R<_. The particular equilibrium bubble radius depends on the type of process under consideration. For *normal* boiling R is usually determined by the cavity size opening on a solid surface that traps vapour which is often of micron size dimensions. But for homogeneous nucleation, however, R is on the order of molecular dimensions so that the temperature above normal saturation a liquid can sustain is very large as shown by the tabulations of superheat limits liquids [10]. Similar ideas apply to the formation of liquid droplets within vapours that are at a pressure such that $P_0 > P_S$ a so called supersaturated vapour [11], though that situation is not of direct interest to this review.

3 *Modeling of kinetics of the bubble nucleation process*

The basic problem in *nucleation* theory is to predict the net rate of forming vapour nuclei-the *nucleation rate*- which is in equilibrium with the surrounding liquid. In addition the classical view of this problem [7-8][12-15]is that nuclei grow or decay isothermally in a unimolecular steady state process wherein molecule *evaporates* or *condenses* on the bubble surfaces. The process is visualized by drawing an analogy to the chemical reaction:

$$E_n + E_1 = E_{n+1} \tag{3}$$

Where $n = 1, 2, \ldots\ldots G$. E_G is some arbitrarily large nucleus containing G molecules and E_1denotes a single molecule. Eq.(3) such applies to every size nucleus containing n molecules. The last reaction in the set is irreversible to allow net conversion of molecules from the liquid to the vapour state: $E_G + E_1 \rightarrow E_{G+1}$. Moreover the forward and reverse rate constants are F_n and R_{n+1}, respectively. F_n are not known *a priori* [16] is determined and R_n is given by the condensation rate of molecules on a surface area S_n of a bubble containing n molecules and can be expressed in terms of molecular collision frequency β as

$$R_n = S_n\,\beta \tag{4a}$$

Where for am ideal gas

$$\beta = \frac{P}{\sqrt{2\pi\,m\,k\,T}} \tag{4b}$$

And for full spherical bubble

$$S_n = 4^1 R^2 \tag{5}$$

Here S_n depends on P and n through the ideal gas law, $PV = \underline{nRT}$ where $V = 4/3^1 R^3$

The rate of forming bubbles – the nucleation- rate $J$for the above reaction sequence [15]

$$J = F_n\,f_n - R_{n+1}\,f_{n+1} \tag{6}$$

Where $f_n$denotes the number density of nuclei that contain n molecules and the rate J is the same for all the reactions in the steady state approximation. In other words, the specific form of f_n is unknown. However, it is related to a constrained equilibrium distribution of nuclei, $N_n$in the superheated liquid by assuming a hypothetical situation where $J = 0$ in Eq. (6) so that we obtain $f_{\mathrm{n}} \rightarrow N_n$

$$F_n = R_{n+1}\left(\frac{N_{n+1}}{N_n}\right) \tag{7}$$

Combining Eqs.(6) and (7) we obtain

$$J = F_n\, N_n \left(\frac{f_n}{N_n} - \frac{f_{n+1}}{N_{n+1}}\right) \tag{8}$$

The unknown distributions in Eq. (8) are eliminated by summing Eq.(8) from $n = 1$ to $n = G - 1$ and assuming that $f_{\mathrm{n}} \rightarrow N_n$ as $N_n \rightarrow 1$ and $f_{\mathrm{n}} \rightarrow 0$ as $N \rightarrow G$ (there is no large nuclei present in the steady state $J = 0$ population)

$$J = \frac{1}{\sum_{i=1}^{G-1}\left(\frac{1}{F_n\, N_n}\right)} \tag{9}$$

Katz and Weidersich [17] showed that the equilibrium state at saturation conditions wherein $J = 0$ can be used to relate F_n to R_n. The saturation state is actually the more appropriate state in which equilibrium should be considered. It is necessary that the device of summing in Eq. (8) lead to a cancellation of all terms except the first and the last and [17] which showed such a cancellation can occur for the case of condensation of liquid droplets. An extension of this idea to the formation of vapour bubbles within a superheated liquid is not straightforward because of the dependence of surface area of a bubble on both the number of molecules it contains and on the internal vapour pressure. However, assuming that P Å $P_{\mathrm{S},}$ then $S_{\mathrm{n}}(P)$ Å $S_{\mathrm{n}}(P_S) \equiv S_{\mathrm{n}}$. We write N_{sn} for the distribution of nuclei at saturation ($f_n \rightarrow N_{\mathrm{sn}}$) in Eq. (7) when $J = 0$ yields $F_n = \mathrm{R}_{\,\mathrm{n+1}}(N_{\mathrm{sn+1}}/\, N_{\mathrm{sn})}$

Where the F_n are assumed to be independent of pressure. Combining the results with Eq. (8) multiplying both sides by γ^{n-1} where $\gamma \equiv \dfrac{\beta}{\beta_S}$ and summing, all terms cancel except the first and the last $J = \dfrac{1}{\sum_{i=1}^{G-1}\left(\dfrac{1}{F_n\, N_n\, \gamma^{1-n}}\right)}$ so that which differs from Eq. (9) by the presence of γ . However, the conceptual interpretation of the kinetic process is improved because the notion of a constrained equilibrium distribution of nuclei in a metastable fluid is now unnecessary in the development. Hence returning Eq. (9) by treating n as a continuous rather than discrete variables the summation in Eq. (8) is replaced by an integral:

$$J = \frac{1}{\int_{1}^{G-1} \frac{1}{F_n\, N_n}\, dn} \tag{10}$$

To evaluate the integral F_n and N_n must be known

On the other hand, the distribution of nuclei in a hypothetical constrained equilibrium state can be determined by assuming that the liquid/ nuclei system is an ideal dilute solution of vapour bubbles and single molecules. On minimizing the energy of mixing such a solution it can be shown that

$$N_n \approx N_0\, e^{\left(-\frac{\Delta\Omega}{kT}\right)} \tag{11}$$

Where $\Delta\Omega$ represents the energy to form a nucleus containing n molecules. Upon combining Eqs. (10) and (11) and integrating which gives

$$J = \Gamma S_{N} \beta^{N_{0} e^{\left(-\frac{\Delta\Omega^{*}}{kT}\right)}} \qquad (12)$$

Where

$$\Gamma = \sqrt{\frac{\frac{\left|d^{2}\,\Delta\Omega\right|_{n=n^{*}}}{dn^{2}}}{2\pi k T}} \qquad (13)$$

The *equilibrium* condition for a bubble in the metastable liquid is that $\frac{d(\Delta\Omega)}{dn}=0$ at $n = n^{*}$. Γ is a factor that accounts for the possibility that nuclei larger than the critical size may decay. If $\Gamma < 1$, not all nuclei that reach the critical size will ultimately continue growing. In Eq. (12) the terms of temperature as

$$T = \frac{\Delta\Omega^{*}}{k \ln\left(\frac{\Gamma S_{n}^{*} \beta N_{0}}{J}\right)} \qquad (14)$$

The quantities within the logarithm Eq. (14), such as, *J* have a minor influence on the nucleation temperature *T* so that Eq. (14) could also be written as the form

$$\frac{\Delta\Omega^{*}}{kT} \approx C \qquad (15)$$

Which is often useful for correlation phase change data that are believed to be governed by homogeneous nucleation. Experiments have shown that 10<*C*<75 for a wide range of applications [18] and for a rapid isothermal decompression produces *C* Å 28.5 [19]; nucleation at the interface between two immiscible liquids such as might exist within a dispersion of droplets in a field liquid (*i.e.* an *emulsion*) gives *C* Å 66 [20].

4 ***Modeling the energy of forming a critical size nucleus***

Classical electrodynamics of nucleation energetic

This approach assumes that bulk properties apply to the microscale of the nucleation process (dimensions of about 10^{-8} *cm*) and the relevant thermodynamic potential which determines the energy of forming a bubble with internal vapour pressure *P* is the change of the availability [21] between a homogeneous liquid system and a heterogeneous bubble or liquid system at the same ambient temperature *T* and pressure P_0:

$$\Delta\Omega = V\left(P_{0} - P\right) + W_{S} \qquad (16)$$

Where W_S denotes the surface energy of the bubble nucleus and for a spherical bubble gives

W_S Å$4^1\sigma$ R^2 (17)

For small departures from equilibrium the bubble nucleus is assumed to be chemical equilibrium [22] and combining Eqs. (16) and (17) then combine to yield [23]

$$\Delta\Omega = -kT\left(\frac{P^{*} - P_{0}}{P^{*}}\right)n + \sigma\left(36\pi\left(\frac{kT}{P^{*}}\right)^{2}\right)^{\frac{2}{3}} n^{\frac{2}{3}} \qquad (18a)$$

When $R \to 0$, or for a nucleus that contains a few molecules, Eq.(18a) will produce an inconsistent result since the meaning of the physical properties is lost. Considering n is treated as a continuous variable $(\Delta n = \pm 1 \to dn \, and \; n >> 1)$ Eq.(7) can be transformed to $F_n \approx R_n \exp\left(-\frac{d(\Delta\Omega)/dn}{kT}\right)$. Hence from Eq. (18a), $d(\Delta\Omega)/dn > 0$ when $n < n^{*}$ and vice versa when $n > n^{*}$. Thus, $F_n < R_n$ when $n < n^{*}$ and such nuclei degenerates because of the propensity for molecular condensation over evaporation. When $n > n^{*}$ nuclei will continue to grow. From Eq. (18a) we observe that $d(\Delta\Omega)/dn = 0$ for the critical nucleus state where Eq.(1) is also applicable. Furthermore,

$$\frac{d^{2}(\Delta\Omega)}{dn^{2}} = -\left(\frac{kT}{P^{*}}\right)^{2}\left(\frac{\left(P^{*} - P_{0}\right)^{2}}{32\pi\sigma^{3}}\right) < 0 \qquad (18b)$$

Where Eq. (18b) will be used to evaluate Γ in Eq.(13). On the other hand, from Eq. (18b) the energy of forming a *nucleus* is a maximum where $d(\Delta\Omega)/dn = 0$ which signifies the critical nucleus or metastable state. Now combining Eqs.(16) and (1) with the ideal gas law gives the well known result [25]

$$\Delta\Omega^{*} = \frac{16\pi\sigma^{3}}{3\left(P^{*} - P_{0}\right)^{2}} \qquad (19)$$

This shows the explicit dependence on bulk properties. Three important limits of Eq.(19) are the saturation state, critical point and the spinodal. In the first limit $(\Delta\Omega) \to$ _ and $J \to 0$ from Eq.(12) while in the second limit $\Delta\Omega^{*} = 0$ but since $\Gamma \to 0$ (as $\sigma = 0$ as $T \to T_c$ in Eqs.(13) and (18b)) then $J = 0$ as well at the critical point. On the spinodal curve (which is just another thermodynamic state as far as Eq.(1) is concerned), $\Delta\Omega^{*}$ _ 0.

Bubble nucleus as a collection of activated molecules

In this approach a nucleus is considered to be composed of *activated* molecules, where an activated molecules is one that has been separated from its z nearest neighbors (for a FCC structure $z = 12$) of distance d_m to a distance d_c the mean distance between molecules and the surface energy of *nucleus* is no longer given by Eq.(16). The energy of such a molecule is $\varepsilon_m z/2$ where ε_m denotes the *area* under the intermolecular potential curve between d_m and d_c and Lennard –Jones fluid and Kwak ans Panton [25] the *area* to be

$$\varepsilon_{m} = 4\varepsilon_{0}\left(1 - \left(\frac{\rho_{c}}{\rho_{m}}\right)^{2}\right)\left(\left(\frac{d_{s}}{d_{m}}\right)^{6} - \left(\frac{d_{s}}{d_{m}}\right)^{\delta}\right) \qquad (20)$$

and ε_0 Å $3/16\, E_i\, \gamma/d_s^{6}$, E_i, γ and d_s represents the ionization potential, polarizability and the hard sphere diameter of the fluid, respectively. If the energy required [26] overcoming the force holding molecules at the surface of a *spherical* nucleus is ½ $z\, \varepsilon_m$ and $n^{2/3}$ is the number of surface molecules [27], then the surface energy is [25]

$$W_S = n^{2/3}\left(\frac{1}{2}\varepsilon_m z\right) \qquad (21)$$

This replaces Eq. (17) of the capillarity approximation. Substituting Eq. (20) into Eq. (16);

$$\Delta\Omega = V\,(P_0 - P) + \frac{1}{2} z\,\varepsilon_m\, n^{\,2/3} \qquad (22)$$

Where now the cluster or *bubble* volume is V Å nV_m and for the critical nucleus state $d(\Delta\Omega)/\,dn = 0$ so that Eq.(21) transform to

$$\tau = -\frac{1}{n^{*1/3}}\left(\frac{z\,\varepsilon_m}{3V_m}\right) \qquad (23)$$

Where $n \to n*$ and $\tau \equiv \left(P_0 - P^*\right)$ is the tensile strength of the liquid and combining Eqs. (21) and (22) gives

$$\Delta\Omega^* = n^{*2/3} z\frac{\varepsilon_m}{6} \qquad (24)$$

It is determined by solving Eq. (12) for a give nucleation rate. Accurate values of J are not needed to determine the thermodynamic state for a critical nucleus because of the logarithmic dependence of

$\Delta\Omega^*$ on J in Eq. (12). Fig.(2) shows that how τ varies with nucleation rate for water at 283_K using Eqs.(12), (13), (22) and (23). The calculations are extended to $J = 10^{12}$ nuclei-cm^{3}-s^{-1} that has been conjectured by Lienhard and Karimi [28]. The results show that τ increases monotonically as J increases and also shown is a measurement of the tensile strength of water from Briggs [29]. Since the nucleation rate is not known *priori* for the experimental conditions of this measurement ─ it must be estimated independently.

Density functional theory

This approach is the proof that there exists a *grand* potential (given the symbol Ω) which is a functional whose minimum gives the equilibrium density profile, $\rho\,(r)$ within a metastable heterogeneous bubble/gas system Evans [30]. In addition, a functional is a quantity that takes on a specific numerical value of a function (ρ) on which it depends and is represented by $\Omega[\rho]$.

The difference in this potential between a system that contains a bubble and one that does not at the same far-field thermodynamic state (T, P_0) is the energy of forming the critical size bubble [20, 31]

$$\Delta\Omega^* = \Omega[\rho] - \Omega[\rho_0] \qquad (25)$$

Where ρ_0 represents the equilibrium density of the uniform far-field fluid and r denotes the bubble centre, $\Omega[\rho]$ denotes the Legendre transform of the internal energy and $U\,[T, \mu\,]$, Callen [32]

$$\Omega[\rho] = F[\rho] - \mu N \qquad (26)$$

where

$$N = \int_0^\infty \rho(r)\,d^3 r \qquad (27)$$

F[ρ] is evaluated by assuming it to be the sum of a hard-sphere repulsive term and an attractive tail w_2

$$F\,[\rho] = \int_0^\infty f_h\,[\rho(r)]\,d^3 r + \int_0^\infty \frac{1}{2}\rho(r)\rho(r')\,w_2\,(r)\,d^3 r'\,d^3 r \qquad (28)$$

Where f_h denoted Helmholtz free energy per unit volume ($f_h = F_h/V$) of a uniform hard sphere fluid the Yukawa form for w_2

$$w_2 = -\frac{\alpha \lambda^2 e^{-\lambda r}}{4\pi r} \qquad (29)$$

Where α denotes the integrated strength of the potential and λ (m^{-1}) is the range parameter and α is chosen to match phase equilibrium data λ being a free parameter to describe the effect of density gradients on the nucleation rate and combining Eqs.(25)-(27) gives

$$\Omega[\rho] = \int_0^\infty f_h\, \rho(r)\, d^3r - \mu \int_0^\infty \rho(r)\, d^3r + \frac{1}{2}\int_0^\infty \rho(r)\rho(r')\, w_2(r) d^3r'\, d^3r \qquad (30)$$

$\Omega[\rho_0]$ is determined from Eq.(30) by applying it to a fluid of uniform density ρ_0 (*independent of r*)

$$\Omega[\rho_0]/V = f_h(\rho_0) - \mu(\rho_0)\rho_0 - \frac{1}{2}\zeta\, \rho_0{}^2 \qquad (31)$$

Where $\zeta = -\int_0^\infty w_2\, d^3r$ (32)

And $N = \rho_0 V$ since ρ_0 is independent of r and the Euler equation for the Helmholtz free energy per unit volume [32] applied to a hard sphere fluid (subscript h) has been used

$$f_h(\rho_0) = -ph(\rho_0) + \mu h(\rho_0)\rho_0 \qquad (33)$$

Where $\mu h(\rho_0)$ *and* $ph(\rho_0)$ represents the hard sphere chemical potential and pressure, respectively both of which are obtained from a suitable equation of state [33] and evaluated at the density ρ_0, the equilibrium densities $\rho(r)$ *and* ρ_0 are determined from Eq. (29) for a homogeneous (liquid system / bubble) . For ρ_0 *and* $\delta\Omega/\delta\rho_0 = 0$ gives

$$\mu(\rho_0) = \mu h(\rho_0) - \zeta\, \rho_0 \qquad (34)$$

$$\mu(\rho) = \mu_h(\rho) - \phi \qquad (35)$$

Where now $\phi = -\int_0^\infty \rho(r') w_2(r') 4\pi r'^2\, dr'$ (36)

From Eqs. (31), (33) and (34), $\Omega(\rho_0) = -P_0 V$. Saturation properties (*liquid* or *vapour* density) are obtained from Eq.(32) by equating chemical properties for liquid and gas and solving iteratively. On the other hand, $\rho(r)$ is obtained by solving Eq. (35) iteratively. The solution is not *trivial* because Eq. (35) is an integral equation and solving Eqs.(34)-(36) Oxtoby and Evans [21] and Zeng and Oxtoby [34] and a typical result for $\rho(r)$ is shown in Fig.(3) for $\Delta\mu = -kT_c$ and $T / T_c = 0.6$. Now, for this calculation $\lambda = 1$ was used. Because the computed gas density at the centre of the bubble is twice the saturated vapour density the *error* involved assuming that the vapour density in the bubble is saturated is evident.

In addition, with the equilibrium densities determined from Eqs. (34)–(35), $\rho(r)$ and ρ_0 are introduced in Eqs.(31)-(32) to determine $\Delta\Omega^r$ Eq.(25):

$$\Delta\Omega^r = \int_0^\infty f_h[\rho(r)] d^3r - \mu \int_0^\infty \rho(r) d^3r + \frac{1}{2}\int_0^\infty \rho(r)\, \rho(r') w_2(r)\, d^3r'\, d^3r$$
$$-V\left[f_h(\rho_0) - \mu(\rho_0) - \frac{1}{2}\zeta\, \rho_0^2\right] \qquad (37)$$

Eq. (37) is the counterpart of Eqs.(19) and (24) to account for a density distribution across the bubble/liquid interface, and an interface that is not *sharp*. The variation of the barrier height to nucleation $\Delta\Omega^*/kT$ from Eq. (37) with the nondimensional gas density, ρ_g /ds^3 is shown in Fig.(4), [22] for the gas → liquid transition (nucleation of a liquid droplet in a supersurated vapour) for $T / T_c = 0.6$ and $\Delta\mu = -0.52kT_c$ to show how $\Delta\Omega^*/kT$ varies with supersaturation. Though our interest is in the opposite problem, the results for nucleation of liquid droplets provides an analogous framework to understand how the barrier height depends on the depth of penetration into the metastable state, now represented by the supersaturation, $S \equiv P^{*}/Ps$ ($S = 1$ coexistence) rather than the superheat. Since the temperature is constant for this calculation, the ordinate is essentially the supersaturation because $\rho_g / ds^3 = S\, P_S /(\mathrm{RT})\, ds^3$ and

P_S is a function of T. But, *t*wo curves are drawn –one calculated from density functional theory and other from the classical model with surface tension obtained from Eq. (38)

$$\sigma = (\Omega[\rho] - pV)/A \qquad (38)$$

For a planar interface using Eq.(30) for $\Omega(\rho)$, the bulk surface tension is not used in Eq.(19) as ρ_g / ds^3 increases, $\Delta\Omega^{*}/kT \rightarrow 0$ at the computed spinodal, $\left.\frac{\delta p}{\delta \rho}\right|_{T=0}$. Hence by contrast, $\Delta\Omega^{*}$ c_1/kT _0 at the spinodal. Moreover, at low supersaturation the capillarity approximation works well but differs increasingly as the supersaturation increases.

Discussion and future research direction In this paper from the different aspects we achieve the following:

(a) the capillarity approximation is most popular for predicting the onset of homogeneous nucleation in liquids and gives good results for many fluid sty stems.

(b) it works for a wide range of pure and single component liquids when a suitable estimate of the nucleation rate can be made and thermophysical properties can be accurately predicted.

(c) a notable exception is water, future works should resolve this issue

(d) density functional theory has so far not been applied to bubble nucleation in liquids to the same extent that the capillarity approximation has, and future works should seek to do so.

(e) the dynamic aspects of the phase change process at the superheat limit also appear to have received less attention and future work should strive to more clearly understand the dynamic aspects of a phase transition at the superheat limit.

References

[1] Adamson, A.W. 1982 “Physical Chemistry,” of Surfaces 4th edition, pp 349-350, New York, John Wiley.

[2] Lorenz, J. J., Mikie, B.B and Rohsenow, W.M “The effect of Surface Condition on Boiling Characetristics,” Proc.5th International heat Transfer Conference 4:35 (1974).

[3] Cole, R. “Boiling Nucleation,” Adv. Heat Trans. 10:85 1974.

[4] Van Stralen, S.J.D and Cole, R, 1979, “Boiling Phenomena,” Vol.(1)&(2) New York, Hemisphere.

[5] Collier, J.G. 1981, “Convective Boiling and Condensation,” Second edition, Chapter 4, New York McGraw- Hills

[6] Apfel, R.E., 1972, “The tensile Strength of Liquids,” Sci. American 227:58.

[7] Skripov, V.P., 1974, “Superheated Liquids,” New York, John Wiley.

[8] Debenedetti, P.G, 1996, “Metastable Liquids,” Princeton University Press, New Jersey

[9] Modell, M and Reid. R.C., 1983, “Thermodynamics and Its Applications,” Chapter 9 Englehood Cliffs, Prentice Hall.

[10] Avedisian, C.T., 1985, “The Homegeneous Nucleation Limits of Liquids,” J. Phys. Chem. Ref.data 14:695-720.

[11] Pound, G.M., 1972, “Selected Values of Critical Supersaturation for Nucleation of Liquids a from the Vapour , J. Phys. Chem. Ref. Data 1: 119.

[12] Volmer, M., 1939, “Kinetics of Phase Formation,” ATI No. 81935 (F-TS-7068-RE) from Clearinghouse for federal and Technical Information.

[13] Frenkel, J., “Kinetic Theory of Liquids,”1946, Chapter 3 pp. 6-9, Oxford University Press, Oxford.

[14] MacDonald, J.E., 1963, “Homogeneous Nucleation of Vapor Condensation II,” American Journal of Physics 31:31.

[15] Springer, G.S., 1978, “Homogeneous Nucleation,” Adv. Heat Trans. 14: 281.

[16] Reiss, H., 1977, “Adv. Coll. Interface. Sci,” 61:351.

[17] Katz, J.L and Weidersich, H., 1977, “Nucleation Theory without Maxwell Demons,” J. Coll Interface Sci, 61:351. .

[18] Apfel, R.E, 1971, “Vapour Nucleation at a Liquid-Liquid Interface J. Chem. Phys. 54:62.

[19] Alamgir, Md and Lienhard, J.H., 1981, “Correlation of Pressure Undershoot during Hot Water Depressurization,” J. Heat Trans. **103**:52

[20] Avedisian, C.T.,and Andres. R.P, 1978, “Bubble Nucleation within Superheated Liquid-Liquid Emulsion,” J. Coll. Interface. Sci 64:438.

[21] Oxtoby, D.W and Evans, R, 1988, “Nonclassical Nucleation Theory for the Gas-Liquid Transition, J. Chem. Phys. 89:7521-7530.

[22] Keenan, J.H, 1941, “Thermodynamics, “Chapter 17, New York: John Wiley.

[23] Pinnes, E.L and Mueller, W. K. 1979, “Homogeneous Vapour Nucleation and Superheat Limits of Liquid Mixtures, J.Heat Trans. 101:617-621.

[24] Avedisian, C.T, 1986, “Bubble Growth within Superheated Liquid Droplets,” Encyclopedia in Fluid Mechanics, Chapter 8, Gulf Publishing Co.

[25] Gibbs, J. W., 1961, “The Scientific papers of J. Willard Gibbs,” New York, Dover.

[26] Kwak, H and Panton. R.L., 1985, “The Tensile Strength of Simple Liquids Predicted by a Model of Molecular Interactions,” J. Phys. **D**. Appl. Phys 18:647-659.

[27] Feynman, R.P., 1972, “Statistical Mechanics,” pp.125-126, New York, Addison Wesley.

[28] Apfel. R. E., 1970, “Vapour Cavity Formation in Liquids,” Technical Memorandum 62, Harvard University, Acoustics Research Laboratory, Cambridge Mass.

[29] Lienhard, J.H and Karimi, A, 1981, “Homogeneous Nucleation and the Spinodal Line,” J. Heat.Trans. 103:61.

[30] Evans, R., 1979, “The Nature of the Liquid-Vapour Interface and Other Topics in the Statistical Mechanics of NonUniform, Classical Fluids, Adv. Phys. 28: 143-200.

[31] Rasmussen, D.H, 1992, “Homogeneous Nucleation or Spinodal Decomposition,” AICh Annual Meeting Symposium on the Thermodynamics on Nucleation.

[32] Callen, H.B., 1985, “Thermodynamics,” Second Edition p.148, New York: Wiley, 1985.

[33] Tarazona, P., and Evans, R,. 1983, “Wetting Transition in Models of a Solid-Gas Interface, Mol.Phys. 48:799-831.

[34] Zeng, X. C., and Oxtoby, D. W., 1991, “Gas-Liquid Nucleation in Lennard-Jones Fluids,” J.Chem.Phys. 94: 4472-4478.

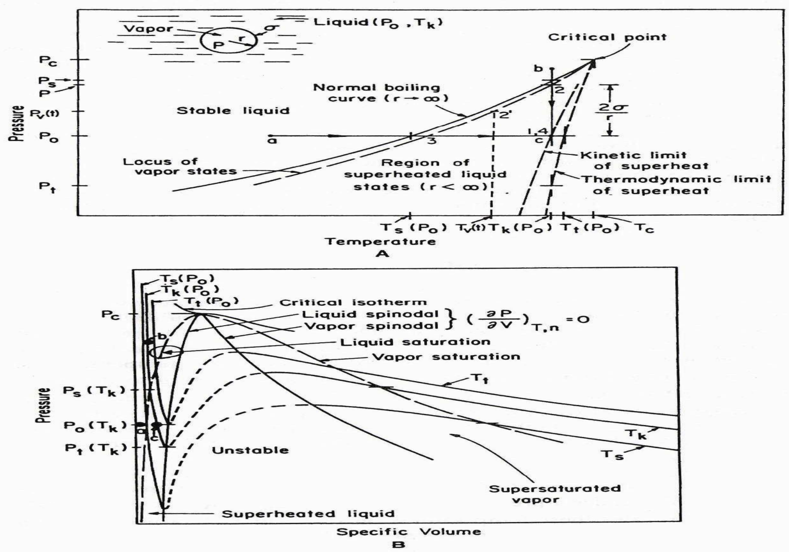

Fig.(1): Pressure/temperature (a) and pressure/volume (b) projections of a phase diagram for a pure substance illustrating stable, metastable, and unstable states.

Caption to the Fig.(1): Pressure/temperature (a) and pressure/volume (b) projections of a phase diagram for a pure substance illustrating stable, metastable and unstable states.

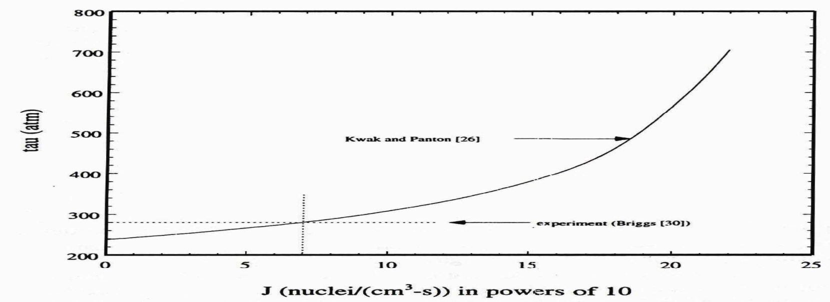

Fig.(2) : Predicted tensile strength, τ (atm), of water at 283 K for various nucleation rates (in powers of 10) using the model of Kwak and Panton [26] for $\Delta\Omega^*$ (eq. 24). The dotted line indicates a tensile strength measurment by Briggs [30] which is predicted by the model at a nucleation rate of approximately 10^7 nuclei/(cm^3-s).

Caption to the Fig. (2): Predicted tensile strength, τ (*atm*) of water at 283_K for various nucleation rates (in powers of 10) applying the model of Kwak and Panton and dotted line indicates a tensile strength which is predicted by the model at a nucleation rate of approximately 10^7 nuclei/(cm^3-s).

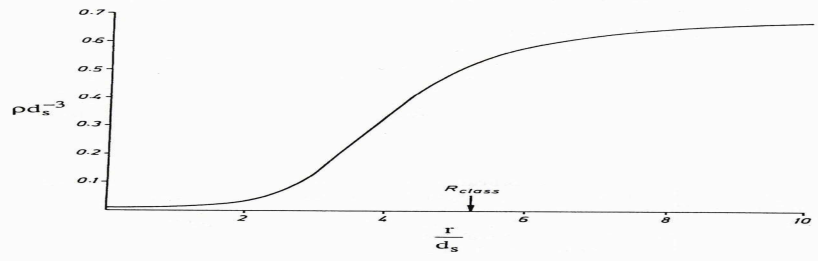

Fig. (3) : Predicted variation of density ($\rho d_S{}^3$) with radial distance (r/d_S) across the interface of a liquid droplet in a supersaturated vapor by solving Eq. [35] for $\rho(r)$ using the Yukawa potential (Eq. [29]) for $\Delta\mu = -0.52kT_c$ and $T/T_c = 0.60$ (after Oxtoby and Evans [21]). R_{class} is the radius of a critical size liquid droplet from Eq. [1].

Caption to the Fig. (3): Predicted variation density (ρd_S^3) with radial distance (r/d_S) across the interface of a liquid droplet in a supersaturated vapour by solving Eq. (35) for $\rho(r)$ using Yukawa potential for $\Delta\mu = -0.52kT_c$ and $T/T_c = 0.60$ and R_{class} represents the radius of the critical size liquid droplet from Eq. (1).

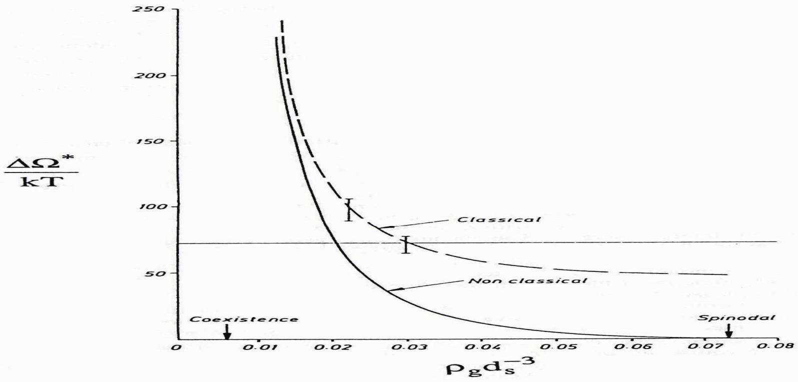

Fig.(4): Variation of energy of a critical size nucleus ($\Delta\Omega^*$) from Eq. [37] with ρ_g/d^3 for $\Delta\mu = -0.52kT_c$ and $T/T_c = 0.60$. The "classical" variation is from Eq. [19] with surface tension calculated using the grand potential from Eq. [30] (after Oxtoby and Evans [21]).

Caption to the Fig.(4): Variation of energy of a critical size nucleus $\left(\Delta\Omega^{r}\right)$ from Eq.(37) with ρ_g/d^3 for $\Delta\mu = -0.52kT_C$ and $T/T_C = 0.60$. The classical variation is from Eq.(19) with surface tension calculated using the grand potential from Eq.(30).