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Influence of surrounding bubbles on the rate of nucleation

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Abstract—It is demonstrated that the influence of surrounding bubbles may significantly affect the rate of nucleation. This arises through the wave action associated with the dynamic growth and the relative motion on the non-critical bubbles. Both affect the local liquid pressure and hence the critical work required by the classical nucleation theory for critical cluster formation.

1. INTRODUCTION

DISCHARGES of subcooled, or saturated liquids, from high pressure and enthalpy conditions is a commonly encountered problem in technological situations. In the initial phases of the expansion the liquid becomes metastable, and in consequence modelling of the flashing phenomena becomes very important. The process of flashing can be considered to occur in two stages. First, nucleation takes place, which results in the production of critical bubbles which partially relieve the liquid superheat. In practice, the rate of nucleation is found to be influenced by the liquid's initial condition, wall characteristics and the rate of depressurisation. During the second stage, the liquid continues to transfer energy through the bubbles' interface. As a consequence, the vapour void fraction increases and the two phase mixture pattern steadily evolves.

The process of nucleation as a means of relieving liquid superheat has been discussed by many authors and summaries of the work can be found in Skripov [1] and Blander and Katz [2]. Kagan [3] improved the classical theory of predicting the nucleation rate by allowing for the inertial effects of bubble growth, the role of viscosity and the thermal boundary layer surrounding critical cluster. Blander and Katz [2] further extended those concepts to include the effect of dissolved gases on the nucleation rate. In all cases the corrections were based on the analysis of the critical clusters developing in a superheated liquid medium of uniform state.

From classical nucleation theory the steady state rate of nucleation is given as

$$J = Bf_{\mathrm{cr}} = NB \exp Gb \tag{1}$$

where Gb is the Gibbs number, defined by

$$Gb = \frac{-16\pi\sigma^3\varphi}{3\Delta p_s^2 KT_{\mathrm{L}}} \tag{2}$$

In the above relationships, the pre-exponential factor B depends on the rate of transition of the bubbles from the critical to the next larger size. N is the number of 'liquid' molecules per unit volume of the system prior to nucleation, σ is the surface tension, K the Boltzmann constant, T_{L} the liquid temperature, f_{cr} the distribution function of the steady state nucleation and Δp_s the liquid superheat. Because of the exponential relation, any process which changes Δp_s will sensitively change J. φ is the so-called heterogeneous nucleation factor and is a function of the contact angle between a solid surface and the interface of the critical cluster which grows on it. In practice, φ indicates the percentage of the bubble exposed to the liquid, thus the type of nucleation is defined by

$\varphi = 1$ homogeneous nucleation

$1 > \varphi > 0$ heterogeneous nucleation.

Theoretical models of two phase flow which include the effect of nucleation have been described by Edwards and O'Brien [4], Riznic and Ishii [5], Deligiannis and Cleaver [6] and others. In these models, the thermodynamic properties needed for the calculation of the nucleation rate were assumed to be the locally averaged values. In particular the liquid superheat was taken as

$$\Delta p_s' = p_s(T_{\mathrm{L}}) - p \tag{3}$$

where T_{L} and p are the local averaged liquid temperature and mixture pressure, respectively. The usual assumption made in the above equation is that $p = p_{\mathrm{L}}$ since the correct liquid superheat in terms of pressure is represented by the liquid pressure difference between the stable condition with respect to T_{L} and the metastable one. As shown by Biesheuvel and van Wyngaarden [7], the presence of surrounding bubbles may invalidate the above assumption by virtue of their dynamic behaviour. This in turn affects the value of $\Delta p_s'$ and consequently in the complex motion associated with two phase flow, it is suggested that

NOMENCLATURE

a	thermal diffusivity
B	frequency of molecular interactions
f	distribution function (classical nucleation theory)
Ja	Jakob number
Gb	Gibbs number
N	number of molecules per unit volume
K	Boltzmann constant
T	temperature
p	pressure
r	local average bubble radius
u	local average velocity
N_b	bubble number density
J	theoretical rate of nucleation
J'	corrected rate of nucleation
S	slip velocity
Δp_s	correct liquid superheat, $p_s(T_L)-p_L$
$\Delta p'_s$	assumed liquid superheat, $p_{(T_L)}-p$
$\Delta p'_{sr}$	$\Delta p'_s/p_{cr}$
$\Delta\Delta p_s$	liquid superheat change, $\Delta p_s - p'_s$.

Greek symbols

α	void fraction
θ	critical bubble's constant angle
ρ	density
σ	surface tension
φ	heterogeneous nucleation factor.

Subscripts

cr	critical
G	vapour phase
L	liquid phase
s	saturation
sr	non dimensional saturation quantity.

nucleation may also be influenced by the motion and size of the already grown bubbles.

The present study proposes a way to avoid the aforementioned assumption and demonstrates the potentially important effect of bubble dynamics and slip on nucleation.

2. MACROMOTION CROWDED EFFECTS

When nucleation occurs concurrently with the dynamic growth of surrounding large bubbles, it may be affected by the pressure disturbances produced by the pulsation of the interface of these bubbles. The two main reasons for producing these pressure changes are (i) the change of the bubble radius, and (ii) the difference in the velocities between the bubble and the liquid. These two effects mainly influence the average local pressure in the bulk of the liquid.

The aforementioned pressure waves, arising through dynamic bubble growth, will not however affect the local average temperature of the incompressible liquid and hence for mechanical equilibrium of the critical bubble

$$\Delta p_s = p_s(T_L) - p_L = \frac{2\sigma}{r_{cr}} \tag{4}$$

where r_{cr} is the critical bubble radius. In order for the above equation to be valid, both the pressure and the temperature of the liquid have to be uniform. So the values used for these flow quantities are once again the average ones for the given locality. Furthermore, based on the large thermal diffusivity of the liquid, it was assumed that $T_{Li} = T_L$ and $P_{Li} = P_L$, so the liquid phase can be assumed to be of a uniform state in a given vicinity. It is a well known fact that the above equation only holds for the critical bubbles for which it can be assumed that their interior is of the same temperature as the bulk of the liquid, T_L, and since the critical cluster is in chemical equilibrium as well, the vapour inside the critical cavity is saturated with a pressure equal to $p_s(T_L)$.

The pressure waves associated with the growth of the non-critical bubbles will affect the local average liquid pressure. Biesheuvel and van Wyngaarden [7] took into account the void fraction and the size and growth of the predominant bubbles, and showed that the local average liquid pressure can be linked to the local average mixture pressure, p, by means of

$$p_L = p - \alpha\rho_L\left(\frac{3}{2}\left(\frac{dr}{dt}\right)^2 + r\left(\frac{d^2r}{dt^2}\right) - \frac{1}{4}(|u_G - u_L|)^2\right) \tag{5}$$

where u_G and u_L are the local average vapour and liquid velocities, ρ_L the liquid density and α the void fraction. Thus

$$\Delta p_s = p_s(T_L) - p + \alpha\rho_L\left(\frac{3}{2}\left(\frac{dr}{dt}\right)^2 + r\left(\frac{d^2r}{dt^2}\right) - \frac{1}{4}(|u_G - u_L|)^2\right). \tag{6}$$

Equation (6) can be written as $\Delta p_s = \Delta p'_s + \Delta\Delta p_s$, where $\Delta\Delta p_s$ is the superheat correction.

Most of the experimental and theoretical models of two phase flows assume that $p_L = p_G = p$, and that its value is predicted or measured by means of a very fast crystal quartz pressure transducer. The assumption accompanying the measured pressure is that the area of the sensor is sufficiently large so that it can be claimed that it is partially wetted, hence the measured pressure is an average between the liquid and the vapour one. Furthermore, based on the numerous bubbles that grow and move simultaneously at a given cross section area, it is assumed that the transverse effect of their motion is cancelled out, giving rise to a negligible transverse average pressure gradient.

Knowing the average mixture pressure, p, a correction has to be made for the dynamic bubble growth and slip effects. Hence using equation (5) the corrected value of Δp_s can be used with equation (1) to evaluate the rate of nucleation for the given conditions.

Using equation (1) it can be shown that

$$\frac{J}{J'} = \exp\left(\left(\left(\frac{\Delta p_s'}{\Delta p_s' + \Delta\Delta p_s}\right)^2 - 1\right) Gb\right) \qquad (7)$$

where J corresponds to the $\Delta p_s'$ superheat which is equal to $(p_s(T_L) - p)$ and J' to Δp_s which is equal to $\Delta p_s' + \Delta\Delta p_s$.

2.1. *The importance of* $\Delta\Delta p_s$ *on nucleation*

Making use of experimental data for rapid vessel depressurisation of water and Freon 12 Alamgir and Lienhard [8] and Deligiannis and Cleaver [9] analysed the nucleation phenomenon with respect to the heterogeneous nucleation factor, φ. It was evidenced from the measured liquid superheat that the only effective mode of nucleation was due to the rough wall surface. Heterogeneous nucleation is an extension of the classical nucleation theory which takes into account the effect of the nucleation sites on the critical work.

Based on the above studies, the two extreme limits for which experimental data exists for each of the two working fluids (water and Freon 12) is given in Table 1.

The last column of Table 1 shows the degree of superheat in the system, and Fig. 1 highlights the relationship that links the two variables. As can be seen from the experimental data, both water and Freon 12 working fluids show quite a close correlation between Gb and $\Delta p_{sr}'$. The above observation was expected since Gb and Δp_{sr} are related to the critical nucleation work based on $\Delta p_s'$.

Since KT is twice the molecular energy per degree of freedom of the molecule, Gb represents the number of molecules per critical bubble. Thus the higher the superheat the smaller the cluster and the fewer the molecules in it. It was stated by Skripov [1] that at high superheats the cluster is almost empty, and he suggested a typical experimental value of Gb equal to 11.

Table 1. Experimental data for nucleation of water and R12

$\Delta p_s'$ (bar)	T_L (K)	φ	W_{cr} (J)	Gb	$\Delta p_{sr}'$*
Freon 12					
3.13	290.30	0.89×10^{-3}	1.52×10^{-19}	37.8	0.076
6.34	308.0	3.54×10^{-3}	1.48×10^{-19}	34.7	0.1541
Water					
0.29	390.35	7.27×10^{-8}	2.48×10^{-19}	47.1	0.0013
12.66	512.55	1.04×10^{-3}	2.54×10^{-19}	35.8	0.0572

* $\Delta p_{sr}' = \Delta p_s'/p_{cr}$, p_{cr}: critical pressure.

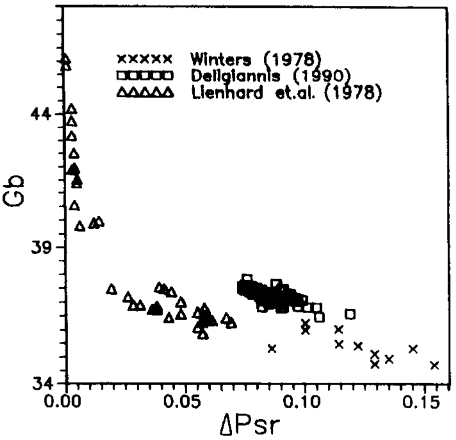

FIG. 1. The effect of the dimensionless pressure superheat on Gibbs number for water and Freon 12 experimental data.

Figure 1, which also includes data obtained by Winters [10] for Freon, suggests Gb depends on $\Delta p_{sr}'$ and since J/J' only depends on $\Delta\Delta p_{sr}$ and Gb, this allows J/J' to be calculated as a function of $\Delta\Delta p_{sr}$ for given conditions. Figure 2 displays the relationship between J/J' and $\Delta\Delta p_{sr}$ for the two cases in Table 1 and shows that the greater the superheat, i.e. smaller Gb, the smaller the effect of $\Delta\Delta p_s$ on the rate of nucleation. This means that for a system which nucleates vigorously the effect of the bubble growth and slip must be quite large in order to affect J. This may not apply to cases where Gb is directly related to $\Delta\Delta p_s$. For practical cases where the mode of nucleation is usually heterogeneous and the degree of superheat rather small, the effect described above seems to be quite important. The positive part of the $\Delta\Delta p_{sr}$ axis is related to a nucleation increase and the opposite occurs for a negative value of $\Delta\Delta p_{sr}$.

In overall terms, slip tends to reduce the nucleation rate whereas the dynamic effect of bubble growth increases the rate of nucleation.

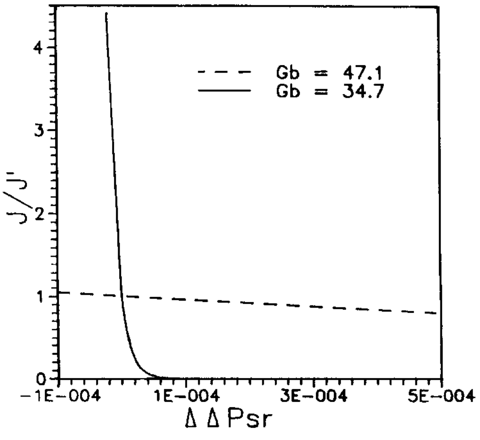

FIG. 2. Nucleation correction factor (J/J') vs liquid superheat change for two different values of Gb.

3. ASSESSMENT OF THE THEORY

The degree to which nucleation is affected by bubble growth and slip is specific to the process being considered. However, to give some broad indication of the effectiveness of the two competing mechanisms values of the nucleation rate are related to the case of a rapidly depressurised vessel.

In the case of superheated liquids flowing steadily through a pipe or transiently out of a pressurised vessel, nucleation first takes place to relieve the metastable system and then the inertia of the liquid layer adjacent to the critical bubble opposes any further growth. Slip and the system pressure variation are not important during this period (of order 10^{-8} s) since the bubbles are very small. The bubble growth (Hutcherson *et al.* [11]) is given as

$$r = \left(\frac{2}{3}\frac{\Delta p_{\mathrm{si}}}{\rho_{\mathrm{L}}}\right)^{1/2} t \tag{8}$$

where Δp_{si} is the initial undisturbed liquid superheat before any bubbles appear. Hence using equation (5) the inertially dominated bubble growth results in

$$\Delta\Delta p_{\mathrm{s}} = \alpha \Delta p_{\mathrm{si}}. \tag{9}$$

During the time which equation (8) is likely to be applicable the void fraction is given approximately as

$$\alpha = f_{\mathrm{c}} \frac{4\pi}{3} r^3. \tag{10}$$

For the smallest value of *Gb* (vigorous nucleation) of Table 1 and assuming that the critical bubbles have grown to only a size of the order of a few microns, equation (10) yields approximately $\alpha = 3\times10^{-3}$. This gives $\Delta\Delta p_{\mathrm{sr}} = 4.7\times10^{-4}$ with the result that $J/J' = 0.81$.

The effect increases as *r* increases and *Gb* decreases. It has been shown that for those systems which experience quite vigorous nucleation the initial rapid bubble growth, which is inertially controlled, may have a quite strong effect on further nucleation, and this is why the degree of superheat has to be corrected accordingly. Furthermore, this conclusion does not oppose the findings of Fig. 2 because α is exponentially related to *Gb* and through equation (9) is related to $\Delta\Delta p_{\mathrm{s}}$. From this it is obvious that the effect of *Gb* on $\Delta\Delta p_{\mathrm{s}}$ is larger than the effect of *Gb* on J/J'. This is why the initial bubble growth is important for smaller values of *Gb*. On the other hand, for large values of *Gb*, $\Delta\Delta p_{\mathrm{s}}$ is so small that the effect of a larger *Gb* on J/J' is negligible, cf. Fig. 2.

For longer time periods bubble growth is thermally controlled. A simple form of the bubble growth in a constant pressure field has been proposed by van Stralen [12]

$$r = \left(\frac{12}{\pi} a_{\mathrm{L}}\right)^{0.5} Ja\, t^{0.5}. \tag{11}$$

Neglecting slip, equation (5) gives

$$\Delta\Delta p_{\mathrm{s}} = \frac{1.5}{\pi} \alpha \rho_{\mathrm{L}} a_{\mathrm{L}} Ja^2 t^{-1} \tag{12}$$

which for longer times is usually negligibly small.

As the bubble grows, slip between the phases starts to become important, and according to equation (5)

$$\Delta\Delta p_{\mathrm{s}} = -\frac{\alpha\rho_{\mathrm{L}}}{4} |u_{\mathrm{G}} - u_{\mathrm{L}}|^2. \tag{13}$$

Measurements corresponding to Table 1 for Freon have indicated that the velocity of the liquid phase can typically be of order 5 m s^{-1}, for conditions where $\alpha \sim 0.2$. According to Crespo [13], the maximum value of the slip ratio $k = u_{\mathrm{G}}/u_{\mathrm{L}}$ is of order 3; thus for the present example $u_{\mathrm{G}} - u_{\mathrm{L}} = 10$ m s^{-1}. With $\rho_{\mathrm{L}} = 1300$ kg m^{-3} this gives $J/J' = 2.10$, which indicates a significant potential reduction in the nucleation rate.

4. CONCLUSIONS

It has been shown that the liquid superheat during two phase flow can be affected by the presence of surrounding bubbles. This is due to the wave action initiated by the growth of predominant bubbles and their relative motion with respect to the liquid. This affects the average liquid pressure which in turn changes the critical work as determined by classical nucleation theory.

The importance of these two effects is illustrated by reference to typical conditions likely to be experienced during the rapid depressurisation of a saturated liquid.

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REFERENCES

1. V. P. Skripov, *Metastable Liquids*. Wiley, New York (1974).
2. M. Blander and J. L. Katz, Bubble nucleation in liquids, *A.I.Ch.E. Jl* **21**, 833–848 (1975).
3. Yu Kagan, The kinetics of boiling of a pure liquid, *Russian J. Physical Chemistry*, **34**, 42–46 (1960).
4. A. R. Edwards and T. P. O'Brien, Studies of phenomena connected with the depressurisation of water reactors, *J. Br. Nuclear Energy* **9**, 125–135 (1970).
5. J. R. Riznic and M. Ishii, Bubble number density and vapour generation in flashing flow, *Int. J. Heat Transfer* **32**, 1821–1833 (1989).
6. P. Deligiannis and J. W. Cleaver, The role of nucleation in the initial phases of a rapid depressurisation of subcooled liquid, *J. Multiphase Flow* **16**, 975–984 (1990).
7. A. Biesheuvel and L. van Wyngaarden, Two phase flow equations for a dilute dispersion of gas bubbles in liquid, *J. Fluid Mech.* **148**, 301–318 (1984).
8. Md. Alamgir and J. H. Lienhard, Correlation of the pressure undershoot during hot water depressurisation, *J. Heat Transfer* **103**, 52–55 (1981).

9. P. Deligiannis and J. W. Cleaver, Determination of heterogeneous nucleation factor during a transient liquid expansion, *J. Multiphase Flow* **18**(2), 273–278 (1992).
10. W. S. Winters, Non-equilibrium blowdown in long pipes, Ph.D. Thesis, The University of Michigan, Ann Arbor (1978).
11. M. N. Hutcherson, R. E. Henry and D. E. Wollersheim, Two phase vessel blowdown of an initially saturated liquid—Part 2: analytical, *J. Heat Transfer* **105,** 694–699 (1983).
12. S. J. D. van Stralen, The growth rate of vapour bubbles in superheated pure liquids and binary mixtures—Part I: theory, *Int. J. Heat Mass Transfer* **11,** 1467–1489 (1968).
13. A. Crespo, Sound and shock waves in liquids containing bubbles, *Physics Fluids* **12**(11), 2274–2282 (1969).