

DETERMINATION OF THE HETEROGENEOUS NUCLEATION FACTOR DURING A TRANSIENT LIQUID EXPANSION

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(Received 15 September 1990; in revised form 1 November 1991)

Abstract—Analysis of a wide range of data obtained from very fast depressurization experiments for water and freon has demonstrated that the heterogeneous nucleation factor correlates very strongly with the ratio of the initial liquid temperature and the critical temperature of the fluid.

Key Words: blowdown, heterogeneous nucleation, metastable liquid

1. INTRODUCTION

During rapid pressure decreases of a subcooled or saturated liquid the phenomenon of nucleation dominates the phase transition process. The time available is usually insufficient for any equilibrium vaporization to occur and the liquid becomes superheated. Following a constant temperature path the system dips into the metastable region, where it is liable to flash at any pressure between the saturation value and the pressure at the spinodal limit. Early nucleation prevents the pressure from going too low and reduces the explosive character of flashing. Delayed nucleation has the opposite effect. For commercial storage tanks and liquids of low purity it is well-documented (Van den Akken 1986) that homogeneous nucleation is negligible and the effects of wall cavities and any impurities in the bulk of the liquid are dominant in determining the nucleation rate. This heterogeneous nucleation depends on the prevailing thermodynamic conditions of the liquid and an empirical factor ϕ ; ϕ is a geometric factor which reflects the percentage of the bubble surface exposed to the liquid and it is well-defined for an isolated bubble, but for swarms of bubbles it is statistical in nature and difficult to determine analytically.

Hunt (1970), Edwards & O'Brien (1970), Malnes (1975), Pohatgi & Reshotko (1975) and Riznic & Ishii (1989) have attempted to include nucleation in two-phase modelling in order to predict the metastable region of a liquid, but have usually had to rely on unjustified empirical factors in order to obtain agreement with experiments. To progress further better estimates of ϕ are required.

In order to quantify ϕ , Alamgir & Lienhard (1981) conducted carefully controlled depressurization experiments and correlated ϕ with the rate of depressurization and initial temperature. Their method of analysis was based on the integration of the expression for the rate of nucleation along the depressurization path from the binodal line to the pressure minimum. It was later suggested by Deligiannis & Cleaver (1990) that a potentially more reliable determination of ϕ could be achieved by matching the results from unsteady thermal non-equilibrium model calculations with the position of the minimum pressure.

A comparison of values of ϕ obtained by the above methods is presented. However, because of the complexity associated with these analyses, a simpler method of determining ϕ is given and correlated with the initial temperature. The resulting correlations are based on experiments using water (Alamgir & Lienhard 1981) and freon-12 (Winters 1978; Deligiannis 1990; Friedel 1986).

2. DETERMINATION OF THE HETEROGENEOUS FACTOR ϕ

Prior to nucleation the wave action in a suddenly depressurized vessel of modest size is sufficiently fast for any spatial changes to be small. Thus, a quasi-steady model can be considered. In addition, during this period little liquid will be expelled and thus any changes in the volume of vapour arising

from nucleation will be translated into pressure changes given by the liquid compressibility equation

$$dp = -\frac{E}{V} dV, \quad [1]$$

where E is the liquid compressibility coefficient and V is the volume of the liquid.

The rate of decrease of the liquid volume per unit volume of the vessel is

$$\frac{1}{V} \frac{dV}{dt} = NV_b \phi, \quad [2]$$

where N is the rate of nucleation events and V_b is the bubble volume. Blander & Katz (1975) show that N is given by

$$N = \frac{\rho_L N_A B}{MW} \exp\left(-\frac{W_{cr} \phi}{T_i K}\right), \quad [3]$$

where ρ_L is the liquid density, T_i is the initial temperature, N_A is the Avogadro number, MW is the molecular weight, K is the Boltzman constant and B is the number of molecular interactions per second which Skripov (1974) suggests that can be assumed constant and equal to 10^{12} s^{-1} . W_{cr} is the energy barrier for nucleation,

$$W_{cr} = \frac{16\pi\sigma^3}{3\Delta p_{sat}^2}, \quad [4]$$

where σ is the surface tension and $\Delta p_{sat} = p(T_i) - p_{min}$.

If nucleation is assumed to be dominant in the region where the pressure gradient is zero, the rate of depressurization associated with nucleation can be approximated by $\Delta p_{sat}/\Delta t$, where $\Delta t = t(p_{min}) - t(p_s(T_i))$. With the above assumption, ϕ can be obtained from

$$\frac{1}{E} \frac{\Delta p_{sat}}{\Delta t} = \frac{\rho_L N_A B V_b \phi}{MW} \exp\left(-\frac{W_{cr} \phi}{KT_i}\right), \quad [5]$$

provided that $\Delta p_{sat}/\Delta t$ can be obtained from experimental data.

It can be readily shown that heterogeneous nucleation prevents the system from penetrating deeply into the metastable region. It is therefore reasonable to assume that all physical properties involved in this study are equal to their saturation values. The surface tension, modulus of elasticity and density exhibit very small changes as the pressure reduces towards the spinodal limit. Since the temperature is almost constant during depressurization, this implies that these additional properties can also be considered constant. For freon, the property variations were taken from Rogers & Mayhew (1980). For water the surface tension is taken from Lienhard & Karim (1981) and the saturation values of the physical properties were extracted from Alamgir *et al.* (1980).

3. CORRELATION OF THE EXPERIMENTAL DATA

Depressurization experiments have been carried out by a number of workers but for the purposes of the present analysis the data of Alamgir & Lienhard (1981) for water and that of Winters (1978), Friedel (1986) and Deligiannis (1990) for freon-12 contain sufficient detail for ϕ to be determined from [5].

The calculated value of ϕ has been statistically correlated with the initial temperature of the liquid, the mean rate of pressure reduction $\Delta p_{sat}/\Delta t$ and the time to the minimum pressure and Δp_{sat} . ϕ was found to be mainly dependent on the liquid superheat Δp_{sat} and T_i , as shown in figures 1 and 2. This is not entirely surprising since both parameters affect the size of the critical cluster, characterized by

$$r_{cr} = \frac{2\sigma}{\Delta p_{sat}}. \quad [6]$$

Here it is assumed that the pressure within the critical bubble is the saturated pressure of the initial state of the liquid and that the surrounding pressure is the minimum pressure in the vessel.

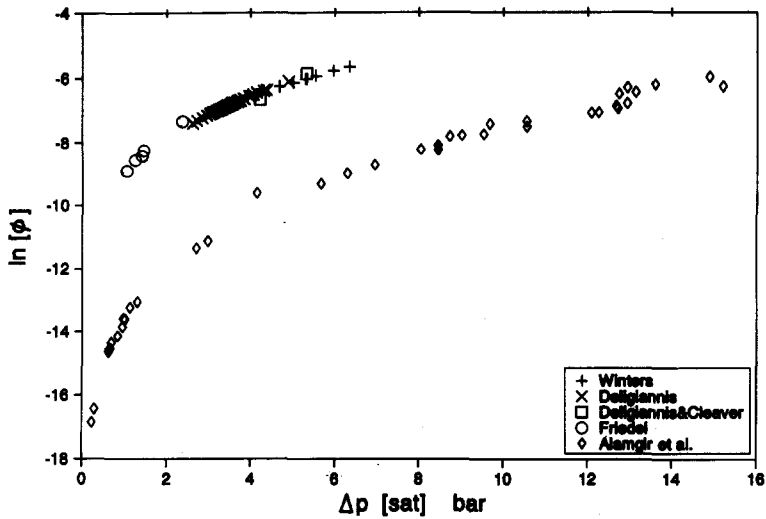


Figure 1. Correlation of the heterogeneous factor ϕ with respect to the liquid's superheat (for water and R12).

The temperature dependence arises through the surface tension and the molecular energy. Since ϕ is a geometric factor associated with the contact angle between the critical bubble and the surface (Blander & Katz 1975), it is clear that as r_{cr} changes so will ϕ . Hence, the averaged value of ϕ for all the wall nuclei in the vessel should not depend on the rate of pressure release in the vessel, but only on the pressure and temperature at the point where nucleation is most dominant; in this case where the pressure is a minimum. For very rapid discharges the temperature of the liquid at this point varies little from the initial temperature. Of course for very slow releases of pressure these approximations would not be adequate and ϕ , as calculated from [5], would show an increasing dependence on Δt which is mainly a function of the exit opening time and the size of the exit compared with the cross-section of the vessel.

For both the water and freon tests p_{min} shows a close correlation with T_i , as shown in figure 3. For the water data, the correlation is quite good and probably reflects the similar opening times for all the tests. This is not true for the freon tests. While the data of Winters (1978) and Deligiannis (1990) show similar values of Δt , that of Friedel (1986) shows a much slower rate of release of pressure, as can be seen in figure 4. The degree of scatter within each data set probably reflects the inconsistency of the vessel opening mechanism. Since the degree of superheat in a system, prior

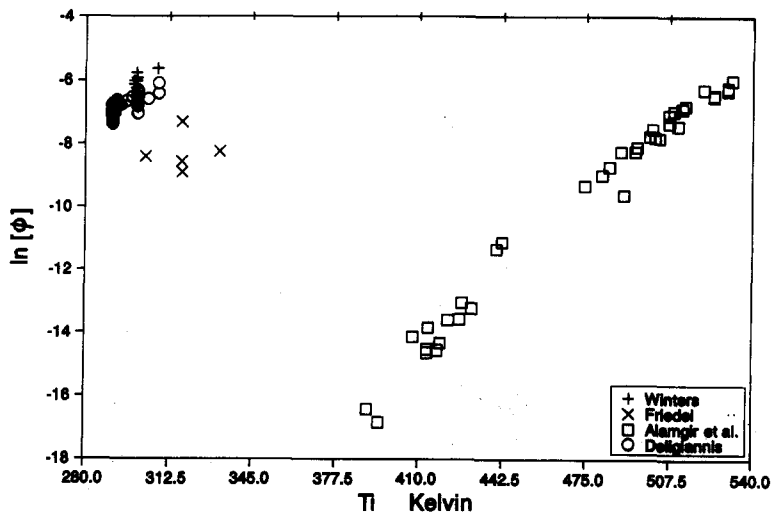


Figure 2. Correlation of the heterogeneous factor ϕ with respect to T_i (for water and R12).

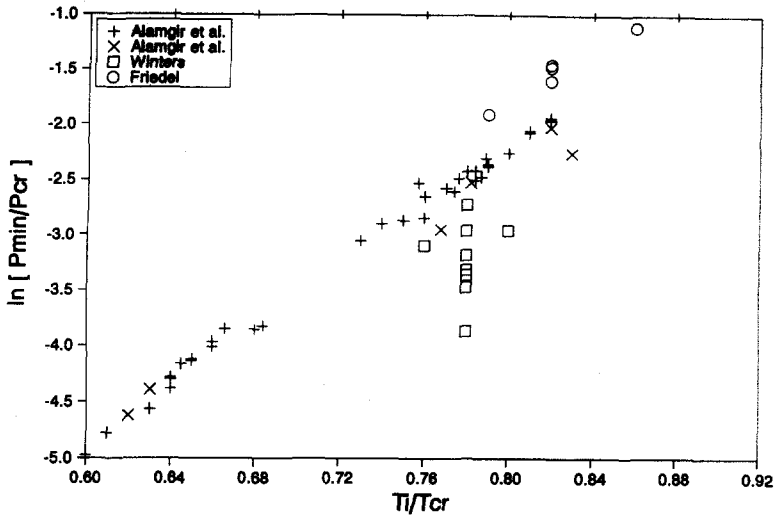


Figure 3. The temperature dependence of the minimum pressure (for water and R12).

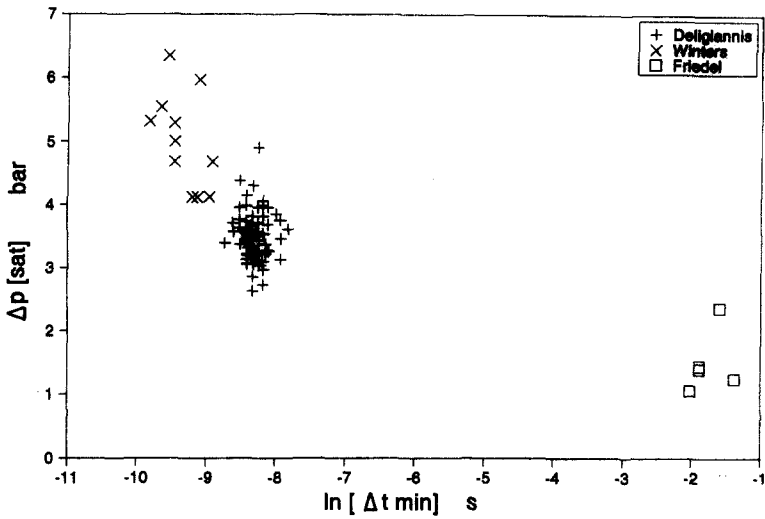


Figure 4. Dependence of Δp_{sat} on Δt_{min} (for R12).

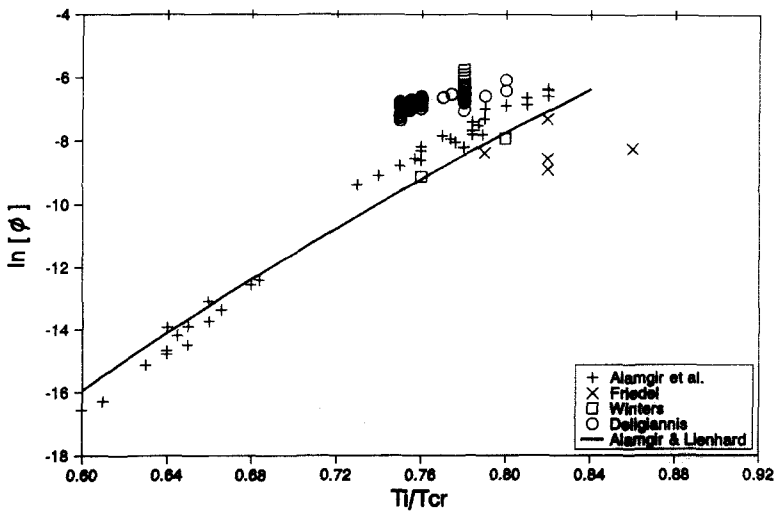


Figure 5. Correlation of the heterogeneous factor ϕ with respect to T_i/T_{cr} (for water and R12 experiments).

to nucleation, is mainly determined by the rate at which the pressure is reduced, it is convenient to distinguish between experiments which experience fast or slow depressurization rates. Whilst these are relative descriptions of the process, in the present context a fast depressurization is one for which $\Delta p/\Delta t_{\min} > 2000$ bar/s.

The fact that p_{\min} is a function of T_i suggests that ϕ should only be a function of T_i . This is indeed the case, as shown in figures 2 and 5 where T_i is presented relative to the critical temperature T_{cr} .

If the slow depressurization data of Friedel (1986) is neglected, both the water and freon data give remarkably consistent values of ϕ as a function of T_i/T_{cr} . The strong correlation of ϕ with Δp_{sat} arises since it contains both temperature and opening time effects. However, from a practical point of view this is of less value since Δp_{sat} cannot be obtained *a priori*.

The value of ϕ obtained by Alamgir & Lienhard (1981) is also shown in figure 5 and it is encouraging to note the similarity between the two methods. The method suggested by Deligiannis & Cleaver (1990) for obtaining ϕ is also given and once again broad agreement is found.

The correlation of ϕ with T_i/T_{cr} , shown in figure 5, suggests that very fast discharges provide a robust method of attempting to quantify the heterogeneous nucleation factor. Since T_L hardly changes from T_i during the nucleation process, the functional relation of ϕ with T_L may be of value in modelling non-equilibrium two-phase flows in which nucleation is known to play an important role.

4. CONCLUSIONS

A quasi-steady model of the initial depressurization of a saturated or subcooled liquid has allowed the heterogeneous nucleation factor to be evaluated from data obtained from blowdown tests in water and freon-12. For very fast discharges ϕ is shown to be only a function of T_L/T_{cr} .

Acknowledgement—P. Deligiannis gratefully acknowledges the support of the Onassis Public Benefit Foundation.

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