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THE EFFECT OF CONTACT ANGLE ON BUBBLE NUCLEATION

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Abstract—The nucleation of gas bubbles from supersaturated solutions of nitrogen in water and ethanol–water mixtures has been studied on two metal surfaces. A decrease in contact angle decreases the population of bubble nucleation sites by reducing the effective radii of individual sites. The results are discussed briefly in relation to the prediction of vapour bubble nucleation from gas bubble nucleation experiments.

NOMENCLATURE

$n(r)$, cumulative site density of sites with radii $\geqslant r$;
P_A, initial saturation pressure;
P_{B1}, pressure before depressurisation;
P_{B2}, pressure after depressurisation;
ΔP, $(P_A - P_{B2})$, supersaturation;
ΔP_P, $(P_{B1} - P_A)$ or $(P_{\text{system}} - P_{\text{gas}})$, pre-pressurisation;
r_e, effective radius of nucleation site;
$1/r_p$, $-\Delta P_P/2\sigma$, precurvature.

Greek symbols
σ, surface tension;
θ, advancing contact angle.

1. INTRODUCTION

THE INFLUENCE of surface microgeometry and wetting characteristics on nucleate boiling heat transfer has long been a source of difficulty. Brown and Lorenz *et al.* have shown that bubble nucleation sites can be identified by experiments with supersaturated gas solutions [1, 2]. In two previous papers we have compared gas and vapour bubble nucleation [3, 4]. We have shown that the effect of initial subcooling on vapour bubble nucleation can be simulated by applying an initial excess pressure to a gas solution before depressurising it to cause supersaturation. However, quantitative comparison of gas and vapour bubble nucleation is complicated by the interference between sites which can occur in boiling because of the rapid growth of vapour bubbles to a size comparable with the distance between nucleation sites: this may take the form of thermal interference in which the activation of one site leads to less favourable conditions for nucleation at an adjacent site, or "seeding" of an inactive or unstable site by vapour from an active site [3, 4]. Another possible difficulty is that there may be differences in the wetting characteristics for liquid against gas at room temperature in one case, liquid against vapour at the boiling point in the other. More extreme changes in wettability occur when different liquids are boiled on the same surface: it has been shown that nucleation sites have much smaller effective radii in organic fluids than in water [5, 6].

In this study we have examined the effect of changes in wettability on the populations of gas bubble nucleation sites and on the effective radii of individual sites. The experiments were performed with solutions of nitrogen in water and ethanol–water mixtures. The surface materials were those used in the previous investigations [3, 4], rolled brass strip and rolled 18-8 stainless steel untreated except for careful cleaning in hot detergent solution followed by copious rinsing in double-distilled water. The wetting characteristics were determined by experimental measurement of the advancing contact angle for each surface-mixture combination. This is only a rough guide to wettability since contact angle hysteresis (differences between the advancing and receding values) might be expected to affect the penetration of a liquid–gas interface into a cavity and its subsequent re-emergence. Nevertheless we find a reasonably good correlation between advancing contact angle and the population of nucleation sites.

2. EXPERIMENTAL METHODS

2.1. *Gas bubble nucleation*

The experimental technique has been described in detail in [3]. Briefly, samples of the surface are mounted in a closed channel where they can be photographed through a window. The liquid is saturated with nitrogen in a large vessel A at pressure P_A. It is allowed to flow slowly into the channel, which is then isolated from vessel A and connected to a second vessel B containing nitrogen. Initially the pressure in B is $P_{B1} > P_A$. The difference $P_{B1} - P_A$ is the prepressurisation ΔP_P, which is equivalent to initial subcooling with $P > P_{\text{sat.}}$ in a boiling experiment. The pressure in B and the channel is maintained at P_{B1} for an immersion time of 20 min, then reduced to $P_{B2} < P_A$. This causes supersaturation by $\Delta P = P_A - P_{B2}$ and activates nucleation sites with effective radii:

$$r_e \geqslant 2\sigma/\Delta P. \tag{1}$$

The resulting bubbles within an area 10 mm × 15 mm marked on the surface are photographed when they have grown to a radius of 0.1 mm, after 1–2 min. The surface is then drained and dried by gentle heating in a stream of nitrogen ready for the next test. All experiments are performed at 25°C.

2.2. *Contact angle*

Advancing contact angles were measured by the sessile drop method. A sample of the surface 20 mm square was mounted horizontally in a vessel containing air saturated with the vapour of the liquid. The liquid was injected through a 0.5 mm diameter hole drilled in the surface, to form a drop approximately 10 mm in diameter. The drop was photographed with back illumination and the contact angle measured to $\pm 1\frac{1}{2}\%$ on an optical comparator at 20 × magnification. It was not possible to measure contact angles for pure ethanol: on brass the drop spread spontaneously, on stainless steel it did reach equilibrium but the contact angle was too small for accurate measurement.

The experimental results for the two surfaces are shown in Fig. 1. Both exhibit a local minimum in contact angle for the 11% ethanol mixture: similar behaviour has been reported for other systems [7]. Surface tension values for the mixtures were taken from [8].

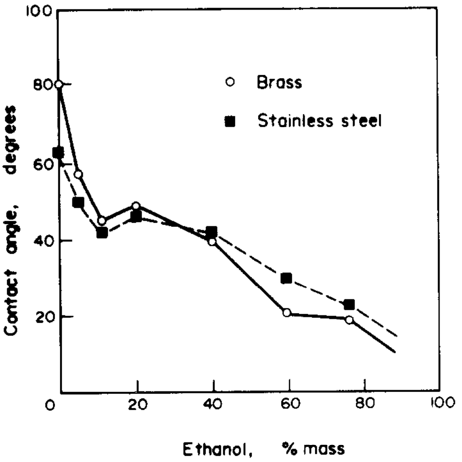


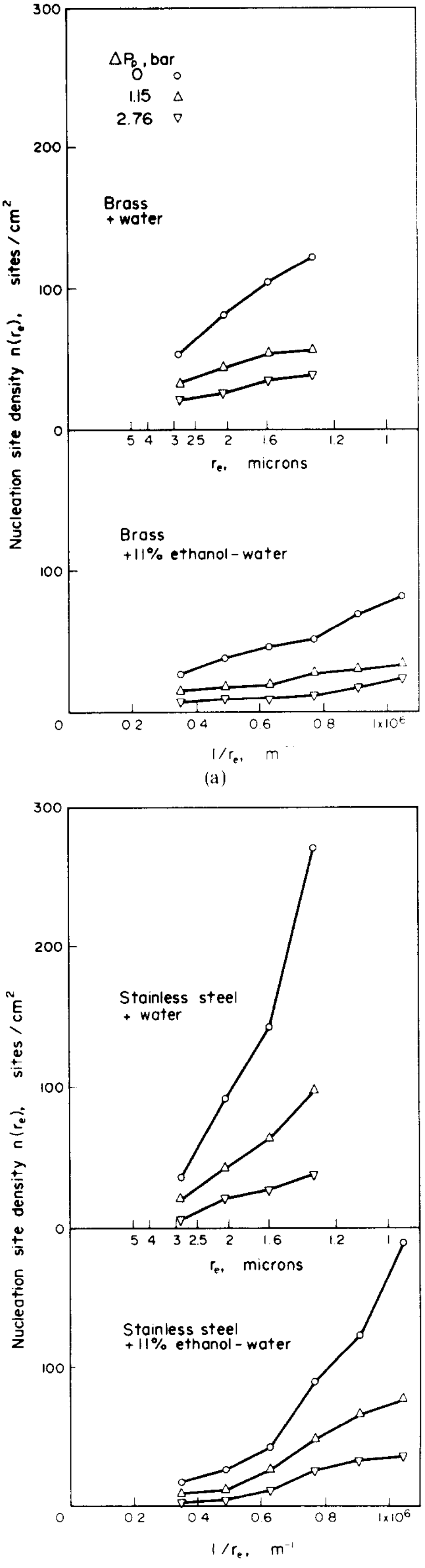
FIG. 1. Advancing contact angle measurements for ethanol–water mixtures at 25°C against nitrogen.

3. RESULTS

3.1. *Nucleation site densities*

Two types of test were performed for each material:

(a) Determinations of effective size distributions for water and 11% ethanol–water mixture (contact angles 81° and 45° respectively on brass, 63° and 42° on stainless steel). The pressure drops used for the two fluids were in the ratio of their surface tensions, so that they corresponded to the same values of r_e from equation (1). The cumulative site densities are presented in Fig. 2. For brass (Fig. 2a), the



(a)

(b)

FIG. 2. Cavity size distributions for water and 11% ethanol–water mixture on brass and stainless steel.

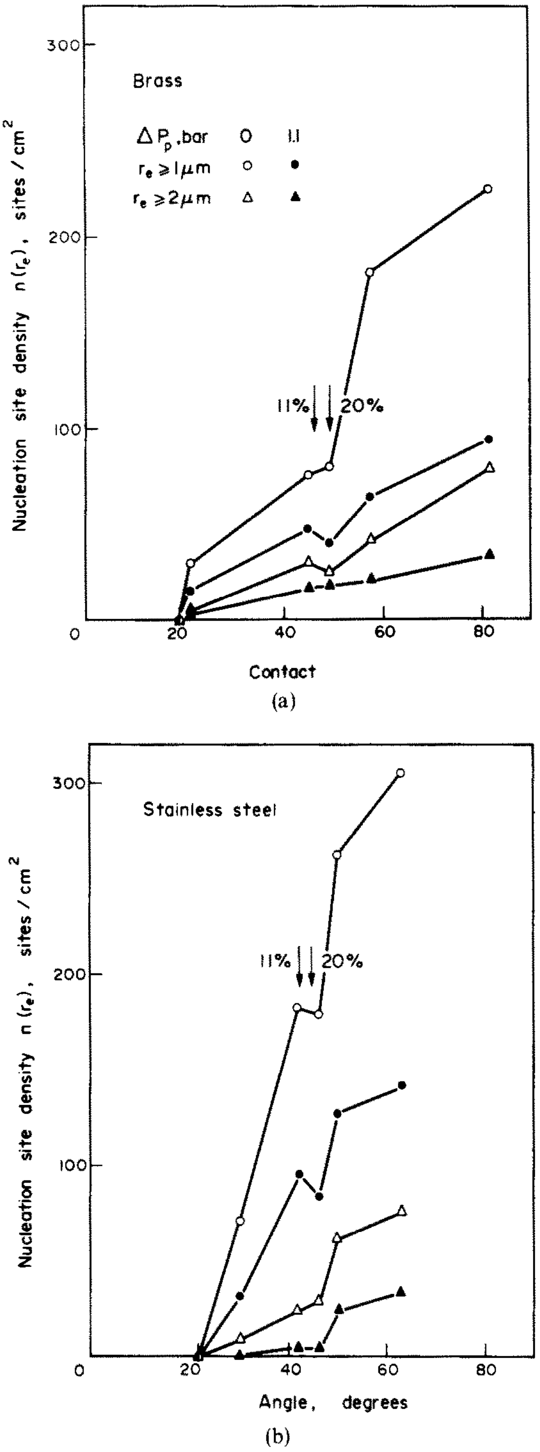


FIG. 3. Variation of nucleation site densities with contact angle.

distributions are approximately linear with ΔP (that is, with $1/r_e$) and the 36° decrease in contact angle reduces the populations by factors of 2 to 3, the largest reduction occurring at the highest prepressurisation. For stainless steel (Fig. 2b), the distributions are less linear; similar reductions in populations occur despite the smaller decrease in contact angle of 21°, but with no regular pattern in relation to ΔP_P or r_e.

(b) Determinations of site densities for $r_e > 2\,\mu m$ and $r_e > 1\,\mu m$ for the full range of contact angle variation. No sites with $r_e > 1\,\mu m$ were active on either material in pure ethanol or 76% ethanol–water mixture (contact angles $\leqslant 20°$). For increasing water content, the site densities increased approximately linearly with contact angle although with considerable scatter (Fig. 3). The relative positions of the points for the 11% and 20% mixtures (in the vicinity of the local minimum in contact angle, Fig. 1) suggest that advancing contact angle alone does not completely define the effect of wettability on nucleation.

It should be noted that tests (a) and (b) were performed with different specimens, so that some differences in site densities occur for comparable conditions. The two brass specimens were cut from the same strip of material and gave similar results; the stainless steel specimens were cut from different sheets in the same batch of material and differed considerably in the site densities for $r_e \geqslant 2\,\mu m$. Thus the tests only indicate the general trend for changing contact angle, which may be superimposed on further variations in nucleation characteristics between specimens of nominally the same material and finish.

In previous tests [3] gas bubble nucleation in water on brass was found to be reproducible to $\pm 6\%$ on populations, with 80% of individual sites reappearing in all four tests at nominally the same ΔP. These variations could be explained by the experimental uncertainty of ± 0.02 bar in ΔP. Consequently only a limited test on reproducibility was performed during the present set of experiments, for 60% ethanol–water on stainless steel (contact angle 30°). In three tests at a pressure drop corresponding to $r_e > 1.0\,\mu m$, $\Delta P_P = 0$, the numbers of sites activated were 99, 107, 10, again explicable by the uncertainty in ΔP. However, the reproducibility of individual sites was less good: a total of 136 sites were active, 79 in all three tests, 16 in two tests and 41 in one test only. Each of the 41 sites with poor reproducibility was subsequently examined by scanning electron microscope. In 8 cases a cavity of about the right size was present on the surface, in 17 cases possible nucleation sites (crevices of ill-defined shape) were identified but in the remaining 16 cases no surface cavity of sufficient size could be found. The reason for nucleation in the absence of cavities is unknown. One possibility is the carry-over of suspended nuclei from the saturating vessel and connecting pipework but this might be expected to give nucleation in the bulk of the liquid and on the glass window, which was not observed.

3.2. *Effective radii of individual sites*

Effective radii were determined for 359 sites which were active in both water and 11% ethanol–water mixture. Since the pressure drop ΔP is changed in finite steps the radius is known only to lie within a certain range: for this comparison it was assumed that all sites newly activated within a particular range had the radius corresponding to the mid-point of the range. Most sites exhibited a decrease in effective radius with decreasing contact angle so the pressure drops for the 11% mixture were extended to smaller radii. The ratios r_e (water): r_e (mixture) are given in Table 1. The distributions are distorted by the omission:

(a) Of sites with $r_e > 2.9\,\mu\text{m}$, for which the upper limit on r_e was not determined;

(b) Of sites active in water but not in the mixture at the maximum ΔP used, which might have large ratios.

It is commonly assumed that large cavities are more susceptible to deactivation than small ones but there was no correlation between r_e (water) in the range 1—3 μm and the r_e ratio for a reduction in contact angle to $\sim 40°$. However, it should be noted from tests 3.1 (b) that a further decrease to 20° virtually eliminated all sites in this size range.

Table 1. Effect of contact angle on site radius, water and 11% water–ethanol mixture

r_e (water): r_e (mixture)	% sites, brass	% sites, stainless steel
1.0–1.25	8	40
1.25–1.50	33	33
1.50–1.75	22	18
1.75–2.00	7	5
2.00–2.25	21	1
2.25–2.50	9	3

4. DISCUSSION AND CONCLUSIONS

Improved wetting (i.e. reduced contact angle) decreases the total number of bubble nucleation sites in the size range $1 \leqslant r_e \leqslant 3\,\mu\text{m}$. The decrease occurs through reductions in the effective radii of cavities, rather than complete flooding and deactivation. Individual sites vary greatly in their sensitivity to changes in contact angle: some are hardly affected at all, others are driven to radii 2 to 3 times smaller. The patterns of change for individual sites are significantly different for the two surfaces examined here (Table 1). This is not surprising in view of their differences in microgeometry and initial contact angle. From examination by scanning electron microscope, the stainless steel surface has mainly crevice sites with rather rounded edges; the brass surface [3] has a mixture of crevice sites and sharp-edged pits. Cornwell [9] reported a similar mixture of sites on a copper surface finished with emery paper. He commented on the inadequacy of the conventional conical and cylindrical cavity models, suggesting instead the idealised re-entrant cavity model. Even this would not describe those cavities which show a progressive change in radius with contact angle (or prepressurisation [3]), for which a "multiply re-entrant" model may be required so that the liquid–gas interface can reach equilibrium at a succession of positions.

From the above, it is to be expected that changes in overall site densities with contact angle will depend on the types of site present. In fact the stainless steel and brass surfaces exhibit rather similar behaviour for sites with $r_e > 1\,\mu\text{m}$, Fig. 3, with approximately linear variations in populations for contact angles exceeding 20°,

$$n(r) \propto (\theta - 20°). \qquad (2)$$

Differences between the surfaces become evident when the response to prepressurisation is considered. Since the penetration of an interface into a cavity at a specified contact angle is a geometrical problem, a more general definition of prepressurisation (or subcooling) is the interface precurvature,

$$1/r_p = -\Delta P_p/2\sigma. \qquad (3)$$

This definition can be applied throughout any variations in system temperature and pressure, liquid composition and dissolved gas content for which the surface tension and the total pressure in the gas phase are known. On this basis, the stainless steel surface is more sensitive to precurvature at large contact angle, while the brass surface shows little variation in response at 81 and 45°, Fig. 4.

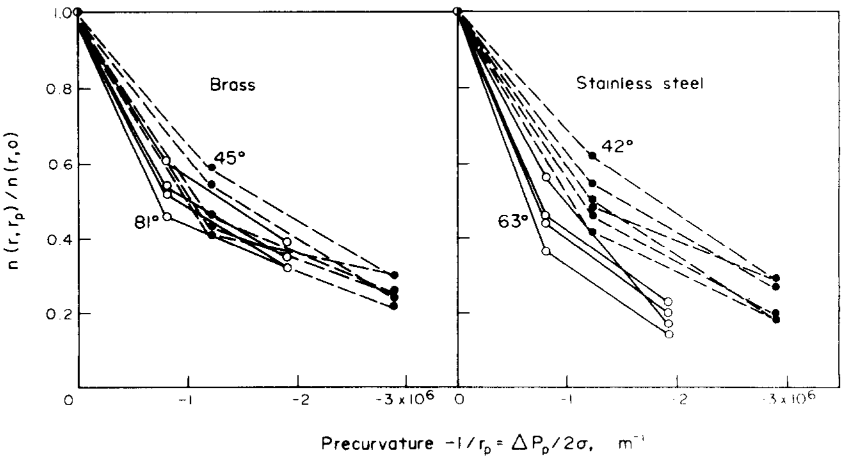


FIG. 4. Effect of precurvature on nucleation site densities.

This study was primarily aimed at determining the effect of small changes in contact angle on the analogy between gas bubble nucleation and boiling nucleation on metal surfaces in water, so attention was focussed on cavities in the micron size range and contact angles exceeding 40°. In this range it seems likely that correction to site populations determined by gas diffusion can be based on equation (2), provided the contact angle for liquid against its vapour at the saturation temperature is known. The use of the quasi-static advancing contact angle to characterise surface wettability is of course open to criticism: it ignores hysteresis in wetting, values may depend on dynamic effects and surface roughness which may not be the same within small cavities as on the external surface. However, it is at least a starting point for the possible prediction of boiling curves in industrial equipment, where the accuracy of prediction is in any case limited by the variations in nucleation characteristics over a large surface: recent measurements by Toral [10] for flow boiling of organic fluids in commercial-grade copper tubing have revealed reproducible axial variations in wall superheat of ±10–20%, which could be explained by local variations in nucleation site densities. We plan to use the gas bubble technique to investigate the range of variation which can occur inside tubing.

It has been shown that the gas bubble technique can be used with fluids other than pure water but in order to obtain information relevant to nucleate boiling in organic and cryogenic fluids the range of the present investigation must be extended to much smaller cavities with $r_e \sim 0.1\ \mu\text{m}$. The deactivation of all sites with $r_e > 1\ \mu\text{m}$ at $\theta \leqslant 20°$ is consistent with the large superheats observed at the inception of flow boiling in organic fluids [10–12]. Since boiling nucleation does occur at finite superheats, equation (2) cannot hold for very small sites but it is not yet clear how these sites can remain active after prepressurisation or subcooling (i.e. negative pre-curvature) at very small contact angles, when even re-entrant cavities might be expected to be completely filled with liquid. Whether activation still depends on a trapping process or on true nucleation from the liquid phase could perhaps be resolved by gas nucleation experiments with different levels of prepressurisation: by analogy with the larger sites, the effective radius of sites depending on trapping should be modified by prepressurisation, whereas a true nucleation process should be unaffected.

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EFFET DE L'ANGLE DE CONTACT SUR LA NUCLEATION DES BULLES

Résumé—On étudie la nucléation sur deux surfaces métalliques de bulles de gaz pour des solutions sursaturées d'azote dans l'eau et dans des mélanges eau–éthanol. Une diminution de l'angle de contact diminue la population des sites de nucléation en réduisant le rayon effectif des sites individuels. Les résultats sont discutés rapidement en relation avec la prédiction de la nucléation des bulles de vapeur à partir des expériences de nucléation des bulles de gaz.

DER EINFLUSS DES RANDWINKELS AUF DIE BLASEN-KEIMBILDUNG

Zusammenfassung—Die Keimbildung von Gasblasen aus übersättigten Lösungen von Stickstoff in Wasser und in Äthanol–Wasser-Gemischen wurde an zwei Metall-Oberflächen untersucht. Ein abnehmender Randwinkel verringert die Zahl der Blasenkeime durch Verkleinerung der effektiven Radien der einzelnen Keime. Die Ergebnisse werden kurz diskutiert im Hinblick auf die Möglichkeit, aus Gasblasen-Keimbildungs-Experimenten Aussagen über Dampfblasen-Keimbildung zu gewinnen.

ВЛИЯНИЕ УГЛА СМАЧИВАНИЯ НА ЗАРОЖДЕНИЕ ПУЗЫРЬКОВ

Аннотация — Исследовалось образование пузырьков газа в перенасыщенных водных растворах азота и в водно-этаноловых смесях на двух металлических поверхностях. Уменьшение угла смачивания ведет к уменьшению плотности центров образования пузырьков за счет снижения эффективных радиусов отдельных центров. Кратко рассмотрена возможность использования результатов экспериментов для расчета образования пузырьков пара.