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LETTERS TO THE EDITORS

COMMENTS ON THE PAPER "ON THE MECHANISM OF BOILING HEAT TRANSFER (VAPOUR BUBBLES GROWTH RATE IN THE PROCESS OF BOILING OF LIQUIDS, SOLUTIONS AND BINARY MIXTURES)"

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In a recent paper, Tolubinsky and Ostrovsky [1] make the statement, that systematic data on the rate of bubble growth in boiling aqueous binary mixtures and solutions are obtained "for the first time". Apparently, these workers have overlooked a number of previous papers in the literature, in which similar experimental results have been presented. Reference is made here to the publications by Van Wijk and Van Stralen [2, 3], Benjamin and Westwater [4] and Van Stralen [5, 6]. In some cases, not only the growth of free or released bubbles after departure [2, 3, 5, 6] has been studied both theoretically and experimentally, but the behaviour of adhering bubbles in binary mixtures has also been investigated [2–7]. The nomenclature of [6, 7] is adopted in this comment.

Tolubinsky and Ostrovsky make restriction to a determination of the average growth rate during a complete bubble cycle, which explains their peculiar experience, "that the photography speed up to 10^3 pictures per second was sufficient to obtain reliable data on the growth rate of vapour bubbles at normal boiling of the liquid". Actually, much higher speeds (10^4–10^5 p.p.s.) are necessary to obtain adequate information on the very high initial growth rates of adhering bubbles generated on an approximately 20 degC superheated wall supporting nucleate boiling.

The final paragraph of [1] states, that "the theoretical considerations describing the laws of vaporization in binary mixtures and experimental data reported in this paper make it possible to explain qualitatively the character of intensity changes in boiling heat transfer depending on the composition of binary mixtures". Neither this dependence (i.e. the nucleate boiling peak flux density $q_{w,\max}$ is showing a maximum at a certain small fraction x_0 of the more volatile component, at least on relatively small heating areas, cf. [2, 3, 5, 7–12]*), nor the way in which the "boiling paradox" [7] can be explained, are pointed out in [1].

The curious boiling paradox states, that a coincidence occurs at the same x_0 of the maximal peak flux (which is due to a maximal bubble frequency) and a minimal bubble growth rate and departure radius (which results in a minimal heat flux to individual bubbles).

In addition, also no reference has been made to previous papers [2, 3, 5–7, 9–12], in which bubble growth rates in mixtures are related to the relative volatility of the more volatile component. This can be done by means of a (graphical) deduction of the concentration of maximal slowing down of bubble growth from equilibrium data showing $T(x)$, $T(x_0)$ and $T(y)$ at constant pressure. Curiously, a similar diagram (ΔC vs. C', i.e. $y - x_0$ vs. x_0) has been drawn in Fig. 8 of [1].

Most of the experimental results of Tolubinsky and Ostrovsky are in good agreement with those obtained previously by other workers, and can be explained quantitatively in terms of recent bubble growth theories [6] or in terms of Van Stralen's "relaxation microlayer" theory for the mechanism of nucleate boiling. The merits of [1] are not originating from the original design of the experiments, but from the elaborate work of studying indeed a very large number of isolated bubbles generated on various nuclei. This finds expression in the possibility of presenting probability distribution curves of the departure radius R_1, of the bubble frequency ν and of the product $w = 2\nu R_1$. Similar curves (which show also normal or Gaussian distributions) are obtained recently by Sanders [14].

A more comprehensive discussion follows now.

1. *The average bubble growth rate during adherence.* In [1] the average growth rate of adhering vapour bubbles is defined by $w = fd_0$, i.e. $2\nu R_1$, where d_0 (or $2R_1$) denotes the departure diameter and f (or ν) the bubble frequency. A more reliable definition should be $\overline{\dot{R}}(t) = R_1/t_1$, where t_1 denotes the instant of breaking away from the heating surface. One has then to make use of very high camera speeds to determine the instants $t = 0$ and $t = t_1$ accurately, as the unavoidable inaccuracy corresponds to one picture.

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* Fastowsky and Artym [13] repeated the experiments described in [9]. Their results, which were published in a Russian journal, are in quantitative agreement with those of Van Wijk, Vos and Van Stralen. Even the nomenclature of [9] concerning a preliminary theoretical treatment of the occurrence of minimal bubble growth rates in mixtures, was adopted by these workers.

2. *The reduction of the bubble growth constant in water–ethanol mixtures.* In Fig. 8 of [1] d_0 (C'), i.e. $2R_{1,m}$ (x_0), for the binary system water–ethanol shows a maximal reduction to a factor of 0·45 at 20 wt (?)% ethanol in comparison with the corresponding value for water. This will be shown to be in good agreement with Van Stralen's equations (12) of part I of [7] and (27) of [6] for the bubble growth constant $C_{1,m}$.

This constant is proportional to $R_{1,m}$ according to equation (16) of part I of [7], and is reduced in the ratio 0·67 in comparison with water:

$$C_{1,m} = \left(\frac{12}{\pi}\right)^{\frac{1}{2}} \frac{a^{\frac{1}{2}}}{(\rho_2/\rho_1)\{l/c + (a/D)^{\frac{1}{2}}\,\Delta T/G_d\}} \tag{1}$$

$C_{1,p} = 24 \times 10^{-4}$ m/(s$^{\frac{1}{2}}$. degC) for water, $C_{1,p} = 9 \times 10^{-4}$ m/(s$^{\frac{1}{2}}$. degC) for ethanol, $C_{1,m} = 16 \times 10^{-4}$ m/(s$^{\frac{1}{2}}$. degC) for $x_0 = 0{\cdot}20$. In the equation (45) of part I of [7] for the departure radius:

$$R_{1,m} = 0{\cdot}26\; C_{1,m}\theta_0 t^{\frac{1}{2}}_{1,m} \tag{2}$$

the factor $t^{\frac{1}{2}}_{1,m}$ is reduced in the ratio 0·90 as $d_{w,co} \sim k^{\frac{3}{4}}$ and $d_0 \sim k/k^{\frac{3}{4}} = k^{\frac{1}{4}}$ at constant θ_0 follows from the convection region of the boiling curves for $x_0 = 0{\cdot}20$, cf. [11, 12], equation (16) of [15] and Section 1.5 of part II of [7]. Theoretically, the total decrease in the departure radius amounts thus to a factor of 0·60.

3. *Equilibrium data.* The diagram $\Delta C(C')$, which is also shown in Fig. 8 of [1], is similar to $y(x_0) - x_0 = x_0\{K(x_0) - 1\}$ vs. x_0. According to Van Stralen [11, 12, 6, 7]:

$$\frac{\Delta T}{G_d} \approx -\,x_0\{K(x_0) - 1\}\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)_{x=x_0} \tag{3}$$

is independent of θ_0 and of G_d and x for relatively small values of G_d, i.e. $\Delta T/G_d$ is proportional to ΔC only for small fractions x_0 of the more volatile component, as only then the boiling-point curve has a constant slope.

4. *The bubble frequency in water–ethanol.* The theoretical increase at $x_0 = 0{\cdot}20$ of the bubble frequency in comparison with the corresponding value in water follows from equation (9) of part II of [7] to:

$$\frac{\nu_m}{\nu_p} = \frac{t_{1,p} + 3t_{1,p}}{t_{1,m} + 3(C_{1,m}/C_{1,p})^2\, t_{1,m}} = \frac{4t_{1,p}}{2{\cdot}33t_{1,m}} = \frac{4}{2{\cdot}33(0{\cdot}90)^2} = 2{\cdot}1, \tag{4}$$

in reasonably good agreement with the experimental value of 1·7 in Fig. 8 of [1]. The average value of $\nu_p = 67$/s in water agrees good with Van Stralen's value of 70/s, cf. Section 4.3 of part II of [7]. The experimental independence of $\nu_m/\nu_p = 2{\cdot}0$ of x_0 in the range $x_0 = 0{\cdot}30$–$1{\cdot}00$ may partly be due to the gradually decreasing value of $t_{1,m}$, according to equation (4); cf. also Sections 5 and 9.

5. *The product $2\nu R_1$ for water–ethanol at $x_0 = 0{\cdot}20$.* The experimental increase in comparison to water follows from the values of Sections 2 and 4, i.e. $0{\cdot}45 \times 1{\cdot}7 = 0{\cdot}76$. Figure 8 of [1] shows a different ratio of 0·53. The theoretical prediction amounts to $0{\cdot}60 \times 2{\cdot}1 = 1{\cdot}26$. According to Van Stralen [7] νR_1^2 is independent of t_1, but this product has a constant value at constant θ_0 only. The theoretical ratio of this product for $x_0 = 0{\cdot}20$ in comparison with the value for $x_0 = 0$ amounts then to: $(4/2{\cdot}33)\,(16/24)^2 = 0{\cdot}76$. Unfortunately, a comparison with experimental data in [1] is impossible, as boiling curves and values of θ_0 are not recorded.

As mentioned in Section 4, the experimental ν_m is independent of x_0 in the range $x_0 = 0{\cdot}30$–$1{\cdot}00$. The theory predicts a slightly different behaviour, which is partly caused by a corresponding decrease in the convective contribution. Generally, the geometrical configuration of the heating element may possibly cause an increase in $t_{1,m}$, i.e. bubbles adhere (at nearly constant size) to the heating strip during a larger time. Results of Sanders [14] show the same behaviour for a similarly constructed heating element, cf. Section 9.

6. *The system benzene–ethanol.* The results for this binary system are very interesting and confirm the theoretical predictions very well. Two relative minima (at both sides of the azeotrope) occur in R_1; this behaviour is similar to that of the system water–1-butanol [11, 12, 6, 7]. In turn, both components are the more volatile, one for $x_0 < x_{0,\,\mathrm{azeotrope}}$ and the other for the remaining compositions. The minima in $C_{1,m}$ should correspond with maxima in $q_{w,\max}$, but, unfortunately, this quantity has not been measured by Tolubinsky and Ostrovsky.

7. *The influence of viscosity on C_1.* This effect is shown to be insignificant [1] in accordance with previous results of Van Stralen [16, 17] on skimmilk and whey and on solutions of lactose in water, boiling at subatmospheric pressures.

8. *Water at elevated pressures.* Highly interesting results are shown in Figs. 4 and 5 of [1]. Roughly speaking, it follows from equations (1) and (2), that the theoretical equation for the departure radius in dependence on the pressure p can be simplified, in case of a pure component ($\Delta T = 0$), to:

$$\frac{R_{1,p}(p)}{R_{1,p}(1)} \sim \frac{C_{1,p}(p)}{C_{1,p}(1)} \sim \frac{\rho_2(1)}{\rho_2(p)} \sim \frac{1}{p}, \tag{5}$$

if the effect of temperature on the quantities k, ρ_1, c and l has been neglected. The experimental decrease in R_1 amounts to a factor of fifteen as the pressure is increased by a factor of ten.

The reader is referred to the final paragraph of Section 5 for a possible explanation of the experimental pressure-independence of ν. In contradistinction to this result, Séméria [18] observed a gradually increasing frequency (up to a factor of 4–6) of isolated vapour bubbles generated on horizontal platinum heating wires in water at increasing pressure (up to a factor of 50–100).

9. *Effect of the geometry of the heating element on v.* Our argument, that v depends on the geometrical configuration of the heating element, is reinforced hereby. A favourable effect caused by the upward flow of the convection currents arising from a heated bottom plate of the boiling vessel or from the bottom side of the heating element used by Tolubinsky and Ostrovsky [1] and by Sanders [14] are partially or completely eliminated at the upper side, on which the investigated vapour bubbles are generated.

In addition, recent preliminary experiments by Van Stralen, Sluyter and Boreas show, that the peak flux ratio at atmospheric pressure $q_{w,\max,m}/q_{w,\max,p}$ in 4·1 wt % methylethylketone in comparison with water is decreased from the value 2·5, cf. [2, 3, 7–12] for horizontal platinum wires of circular cross-section with a diameter of 0·02 cm—and from the value 1·9, cf. Fig. 28 of [11], for horizontal oxidized nichrome-V wires of circular cross-section with a diameter of 0·08 cm—is decreased to 1·2 for various flat heating strips (of rectangular cross-section with dimensions of 0·15 cm × 0·02 cm). It is striking, that the ratio of the bubble departure radii was unaffected. This ratio amounts approximately to a factor of 3·0 for individual bubbles. The time $t_{1,m}$ was increased considerably, resulting in a corresponding decrease in v_m and hence also in $q_{w,\max,m}$, cf. part II of [7].

As a consequence, one has to take in general for $t_{1,m}$ in Van Stralen's relaxation microlayer theory [7] the growth time at the heating surface, and not the (sometimes larger) adherence time of the bubbles.

10. *The behaviour of NaCl-solutions.* The interpretation given in Section 9 may also explain the discrepancy between the results on NaCl-solutions by Tolubinsky and Ostrovsky [1] and those by Samuel [19]. Samuel observed an increase in the peak flux of water to a factor of 2·05 due to the addition of NaCl at saturation concentration. This worker made use of vertical platinum heating wires with a diameter of 0·05 cm.

11. *The Marangoni-effect.* We regret, that in [1] no observations are made of a possible influence of the Marangoni-effect, which results in a diminished tendency for coalescence of touching vapour bubbles at certain concentrations of "positive" systems, cf. [20, 7], e.g. in water–ethanol.

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