ON THE WETTING BEHAVIOUR OF SURFACES IN BOILING

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ABSTRACT

Nucleate boiling heat transfer is strongly influenced by surface wettability as characterised by the Young’s contact angle, $\theta_Y$. The contact angle is usually obtained from measurements on sessile droplets on horizontal test surfaces, but in the case water at high temperatures and pressures, $\theta_Y$ values from droplet experiments appear to be typically 30-50 degrees higher than values needed to explain bubble departure sizes for similar surfaces and temperatures.

We explain the differences between $\theta_Y$ values for droplets and vapour bubbles by using the surface adsorption theory of Adamson. This theory suggests that in the case of bubble formation in high pressure boiling, as the non-wetted surface inside the bubble is in contact with a saturated vapour it will be covered by an adsorbed liquid layer of nanoscale thickness. Droplet experiments on the other hand generally use autoclaves pressurised by permanent gases in which the vapour pressure is far below saturation: in these relatively dry gases the adsorbed liquid nanolayer is expected to be absent. We suggest that the presence of the adsorbed layer in the case of vapour bubbles will increase the work of formation of new wetted surface by an amount comparable to the liquid surface tension, resulting in the significant reduction in $\theta_Y$. We show that by applying Adamson’s model with plausible choices for unknown parameters it is possible explain the magnitude of the differences in $\theta_Y$ in bubble and droplet experiments and to explain why $\theta_Y$ appears much less sensitive to surface material conditions in the case of departing vapour bubbles than in the case of sessile droplets.
We conclude that $\theta_f$ measurements for sessile droplets on heated surfaces in pressurised gas rather than saturated vapour environments may not be relevant to vapour bubbles and values should not be used directly in models of nucleate boiling.

1 NOTATION

- $a$: Decay constant in Equation (12)
- $A$: Area
- $\bar{A}$: Availability
- $B$: Constant in Equation (5)
- $Bo$: Bond number $= R^2 g (\rho_f - \rho_g)/\sigma$
- $C_D$: Drag coefficient
- $d_0$: Liquid molecular diameter
- $g$: Acceleration due to gravity
- $G$: Specific Gibbs function
- $h$: Specific enthalpy
- $h_{NB}$: Nucleate boiling heat transfer coefficient
- $k$: Boltzmann constant
- $n_c(R)$: Number density function of cavities on surface
- $N_c(R)$: Number of cavities /unit area with radius exceeding $R$
- $N_s$: Number of active nucleation sites/unit area
- $P$: Pressure
- $R$: Radius of curvature of surface of bubble or droplet
- $R_c$: Minimum radius of mouth of active cavity
- $R_D$: Bubble departure radius
- $s$: Distribution parameter in Equation (7)
$S$ Specific entropy
$T$ Temperature (deg K)
$T_{\text{crit}}$ Critical temperature
$T_R$ Ratio between temperature and critical temperature
$V$ Specific volume
$V_d$ Volume of droplet
$x$ Thickness of adsorbed liquid film on solid surface
$z_c$ Height of centroid of droplet above solid surface

$\alpha$ Decay constant in Equation (12)
$\beta$ Distortion potential in Equation (12)
$\beta_C$ Half cone angle at base of surface cavity
$\Delta I$ Spreading coefficient
$\Delta T$ Superheat
$\epsilon_0$ Potential in Equation (12)
$\epsilon(x)$ Molecular potential in adsorbed film
$\Gamma$ Number of molecules/unit area in adsorbed film
$\sigma$ Surface energy per unit area of vapour/liquid interface (Surface Tension)
$\sigma_k$ Surface energy per unit area of solid surface in contacting with bulk phase $k$
$\phi_1$, $\phi_2$ Geometric factors: $\phi_1 = 0.25(-\cos^3 \theta + 3 \cos \theta + 2)$ ; $\phi_2 = 0.5(1 + \cos \theta)$
$\rho$ Density
$\theta$ Dynamic contact angle at base of bubble or droplet
$\theta_Y$ Young’s contact angle $= \cos^{-1}\left[\frac{\epsilon_0 - \epsilon_f}{\sigma}\right]$

Subscripts

$b$ Property of base of droplet or bubble
$a$ Property of adsorbed liquid film
$c$ Property of cavity
$g$ Property of vapour phase
Increasing computer power has created the possibility of modelling nucleate boiling heat transfer and Departure from Nucleate Boiling (DNB) using Interface Tracking Methods (ITM) [1] in which the Navier Stokes equations are used to describe the growth of and departure of vapour bubbles at a boiling surface. The ITM approach requires accurate sub-models to describe surface phenomena that control the bubble departure size and the density of active nucleation sites on the surface, both of which depend strongly on surface wettability as characterised by the Young’s contact angle $\theta_Y$. The importance of $\theta_Y$ in controlling bubble departure diameter has been long established (Reference [2] provides an early example of a correlation for departure size that involves the contact angle). Furthermore, it is widely accepted that $\theta_Y$ strongly affects the number of active nucleation sites on a boiling surface due to its effect on the ability of surface cavities to entrap vapour [3, 4, 5, 6].

There is a good deal of evidence that in the case of water on metallic surfaces $\theta_Y$ decreases with increasing surface temperature, as predicted qualitatively by the surface adsorption model of Adamson [7, 8]. However, results of experiments to establish the magnitude of the temperature effect show wide scatter and apparently inconsistencies. In particular, observations of sessile water droplets on high temperature surfaces (see e.g. Refs [9] and [10]) suggest $\theta_Y$ values that are typically 30-50 degrees higher than those inferred from bubble departure data for similar surfaces and temperatures [11, 12]. Such contradictory results point to a lack of a fundamental understanding of surface wetting in boiling which is a potential impediment to moving forward with the ITM approach.

In this paper we propose a tentative explanation for the apparent differences between the contact angles inferred for bubbles on boiling surfaces and those from experimental observations of
sessile droplets. A correlation for $\theta_Y$ against temperature for vapour bubbles on metallic surfaces is first developed by fitting measured bubble departure diameter sizes to model predictions made with the energy minimisation approach of Ardron et al [11]. The $\theta_Y$ correlation is independently checked by applying it with previously established correlations for the size and cone-angle distributions of cavities on metallic surfaces to predict nucleation site densities in high pressure nucleate boiling. The good agreement with experimental data so obtained supports the validity of the $\theta_Y$ correlation.

When the $\theta_Y$ correlation inferred from the bubble departure data is used to predict contact angles measured for sessile water droplets for similar surfaces and temperatures it is found to underpredict the contact angles observed experimentally by 30-50°. The reason for the inconsistency is explained by applying the surface wetting theory of Adamson, which suggests that in the case of an attached bubble in boiling the unwetted surface is likely to be covered by a layer of adsorbed liquid due to its existing within a saturated vapour environment. In contrast, experiments carried out to date using sessile droplets have been carried out in permanent gas environments in which the water vapour pressure is likely to be far below $P_{sat}$. According to Adamson’s theory an adsorbed liquid layer cannot exist under these conditions. We argue that absence of the adsorbed liquid layer must result in a significant change in the surface energy of the surface exposed to the bulk gas phase and that this is the likely explanation for the higher $\theta_Y$ values observed in the droplet experiments. The conclusion reached is that $\theta_Y$ values measured for sessile droplets on heated surfaces in permanent gas rather than saturated vapour environments may not be applicable for vapour bubbles on similar surfaces at similar temperatures.

The paper is organised as follows. Section 3 describes the derivation of the $\theta_Y$ correlation using bubble departure size data in pool boiling reported in the literature: the application of the correlation to predict nucleation site densities in high pressure boiling is then discussed. Section 4 compares predictions of the $\theta_Y$ correlation with contact angle measurements for sessile droplets on high temperature surfaces and shows the measured values of $\theta_Y$ to be much greater than those predicted. The Adamson model of surface wetting is then applied, and it is shown that when the model is extended to the case of a surface in an unsaturated vapour environment (relevant to the
sessile droplet experiments) predicted contact angles may be much greater than for saturated vapour conditions and of a similar magnitude to those observed experimentally.

3 CONTACT ANGLE INFERRED FROM BUBBLE DEPARTURE AND NUCLEATION DATA

3.1 Bubble Departure

In previous studies of bubble departure in boiling by the authors [11, 12] an energy minimisation method was used to predict the dynamic contact angle $\theta$ at the base of a vapour bubble attached to a heated surface, in which the bubble geometry was approximated as a truncated sphere. For the case of a vapour bubble growing on a horizontal heated surface considered in [11] (illustrated in Figure 1a) the equation for $\theta$ contains three terms representing buoyancy forces, fluid drag forces due to the bubble growth, and surface adhesion forces related to the Young’s contact angle: the bubble departure radius $R_D$ is identified as the radius at which $\theta$ falls to zero, at which point the bubble is no longer in physical contact with the surface. For vapour bubbles formed in boiling of water at atmospheric pressure and above, the term due to growth forces is generally negligible compared with the other terms, and the departure radius at which $\theta = 0$ is expressed simply by:

$$R_D^* = 1.23(1 - \cos \theta_Y)^{1/2}$$

(1)

where $R^* = R/(\sigma/\rho_f g)^{1/2}$ is a non-dimensional bubble radius and $\theta_Y$ is Young’s contact angle which is a physical property of the fluid and solid surface. For contact angles below about 50°, $\cos \theta_Y$ can be approximated by $1 - \theta_Y^2/2$. Expressing $\theta_Y$ in degrees, Equation (1) then becomes:

$$D_D = 0.0152\theta_Y(\sigma/\rho_f g)^{1/2}$$

(2)

It is interesting that the above equation is the same as the well-known empirical correlation for bubble departure sizes proposed by Fritz [2] more than eighty years ago, except for the pre-multiplying constant that Fritz gave as 0.0208 rather than 0.0152. It can thus be seen the connection between bubble departure size in boiling and the surface contact angle $\theta_Y$ has been long established.

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1 It is important to note that in the theory the dynamic contact angle is to be regarded as a geometrical parameter that determines the ratio of the bubble base area to its curved surface area, rather than a microscopic contact angle measured along the triple contact line.
It is shown in Reference [11] that the energy minimisation approach is able to give a good prediction of bubble departure sizes in boiling of water over a wide range of pressures if the Young’s contact angle $\theta_Y$ is assumed to decrease with increasing surface temperature. For water at temperatures of $100^\circ C$ and above, the inferred correlation for $\theta_Y$ obtained in the present study by fitting to available bubble departure sizes for water (which covers the pressure range pressures 1-132 bar), is:

$$\theta_Y = 0.133T_R^{-0.95}$$  \hspace{1cm} (3)

where $\theta_Y$ is in degrees and $T_R$ is the ratio between the surface temperature and the critical temperature, both expressed in degrees absolute. Equation (3) indicates that $\theta_Y$ decreases sharply with increasing temperature (note that the equation gives $\theta_Y = 0.1^\circ$ at the critical temperature of water, rather than zero that would be expected, but this discrepancy is insignificant for predicting bubble departure sizes). Figure 2 shows a plot of Equation (3). The data points represent the ‘measured’ contact angle values $\theta_Y$ obtained for each data point by inserting the measured bubble departure radius into Equation (1). Denoting the estimated contact angle for each of the data points by $\hat{\theta}_Y$ (obtained from Equation (3)), the standard error of the correlation can be expressed as $\sqrt{\sum(\theta_Y - \hat{\theta}_Y)^2 / (N\hat{\theta}_Y^2)}$ where $N$ is the number of data points. The standard error is calculated as $\pm 40\%$, as represented by the shaded region in Figure 2. The uncertainty is believed due primarily to differences in the surface materials and finishes in the different experiments as discussed further below.

Figure 3 compares the experimental values of the bubble departure diameter with predictions of Equation (1) (using $\theta_Y$ values from (3)) for all the data points used to derive the correlation. The experimental database is seen to cover a wide range of metallic and non-metallic surfaces, including Indium-Tin Oxide (ITO) heaters [24] of around 1nm roughness [13], stainless steel heated wires, sheets and tubes [27], 8 $\mu m$ nickel sheets [14] and polished silicon wafers [22]. The tests reported from Reference [23] used a copper surface with 4 $\mu m$ mean roughness plated with a 10 $\mu m$ thick nickel layer and polished with a water-alumina paste before each boiling run.

In the Reference [25] experiments, different surface materials were tested to check the dependence of the measurements on surface wettability. The scatter in measured bubble
departure diameters in Figure 3 is believed mainly due to these widely ranging surface conditions.

Photographic observations of steam bubbles on horizontal surfaces in boiling show that the bubbles do indeed resemble truncated spheres, and that the contact angle $\theta$ at the bubble base does indeed fall dynamically to zero at the point of departure. Reference [11] also applied the energy minimisation method previously described to calculate the time variation of $\theta$ for bubbles growing in saturated pool boiling. Numerical results suggest that for fluid conditions and wall superheats characteristic of the boiling of water at atmospheric pressure and above, $\theta$ would be expected to remain close to $\theta_f$ for most of the growth period. Therefore, the dynamic contact angle measured at the bubble base midway through the growth period is expected to provide a reasonable approximation to $\theta_f$ and can potentially be used as a test of Equation (3).

Unfortunately, measurements of bubble dynamic contact angles in boiling are somewhat scarce, but Jung and Kim [13] provided photographs of isolated steam bubbles in the atmospheric pressure boiling of water on an electrically heated indium-tin-oxide film, which show a dynamic contact angle midway through the growth period (estimated from the photographs using $\theta = \sin^{-1}(R_b/R))$ of approximately 38°, which is reasonably close to the value of 32° obtained from Equation (3). Sakashita [14] also provided photographs of the growth of bubbles in pool boiling of water on a nickel ribbon at pressures up to 45 bars (surface temperatures up to 260°C). Photographs at 27 bars ($T = 227°C$) show that for a large part of the growth period the bubble is almost completely spherical with a very small base contact area. Due to the small value of $R_b/R$, $\theta$ cannot be estimated accurately, but measurements from photographs midway through the growth period suggest a value below 8° which is consistent with the value of $\theta_f = 1.7°$ predicted by Equation (3). Thus, these limited experimental data, though inconclusive, are consistent with Equation (3) and support the view that $\theta_f$ falls sharply with increasing surface temperature in the case of steam bubbles growing on metallic surfaces.

Adamson [7, 8] noted that contact angles decrease with increasing temperature in many liquid/vapour systems. He considered the wetting behaviour of such systems from a theoretical standpoint and attributed the reduction in $\theta_f$ to the effect of temperature on the molecular potential in the adsorbed liquid that exists on an unwetted surface when it is exposed to a near
saturated vapour. Adamson’s theoretical model is described further in Section 4 below, where it is used to explain the apparent differences in $\theta_Y$ values obtained from experiments on bubbles and droplets.

### 3.2 Nucleation Site Densities

Bubble nucleation in boiling occurs at microscopic surface cavities that are suitable both for inception of a bubble and retention of vapour following its departure. Theory shows that the density of these active nucleation sites on the boiling surface, $N_s$, is strongly affected by the contact angle, as the latter determines whether a surface cavity can entrap vapour after bubble departure and thus act as a viable nucleation site [3-6]. To provide an independent test of Equation (3) the correlation is applied below, with other established correlations for the size and cone-angle distributions of surface cavities, to predict $N_s$ for water at different pressures and wall superheats, and results compared with experimental data.

#### 3.2.1 Density of Active Cavities

To establish the density of active nucleation sites on a surface it is necessary to determine $R_C$, the minimum radius of a cavity that can act as a nucleation site. $R_C$ can be calculated by equating the over-pressure in the bubble due to surface tension with the vapour pressure inside the bubble at the point of maximum curvature when the bubble radius is equal to the radius of the cavity mouth. Use of the Clausius Clapeyron equation then results in the following approximate equation for $R_C$ that is widely used in nucleate boiling studies [15, 16]:

$$ R_C = \frac{2\sigma T_f}{\rho_g (h_g - h_f) \Delta T_f} $$  \hfill (4)

Several correlations are available relating the number of active cavities per unit area on a boiling surface, $N_C$, to the minimum active cavity radius, $R_C$. Mikic and Rosenhow [17] suggested a power law relationship of the form:

$$ N_C = \frac{B}{R_C^m} $$  \hfill (5)
where $B$ and $m$ are constants dependant on the boiling surface. Mikic and Rosenhow suggested using $m = 2.5$ for water based on the data of Brown [15]. Kocamustafagullari and Ishii [18] proposed an equation similar to Equation (5) but with $m = 4.4$ and $B$ specified as a function of physical properties of the fluid and boiling surface. It may be noted that Equation (5) implies that the cavity number density function $n_C(R)$ (where $n_C(R)dR$ is the number of cavities/unit area in size range $[R, R + dR]$) is $n_C(R) = Bm/R^{m+1}$, implying a mean active cavity radius of $\bar{R} = mR_C/(m - 1)$, which suggest that the mean radius of active cavities on a boiling surface is not very far from $R_C$.

Yang and Kim [3] measured the cavity size distribution $n_C(R)$ on a stainless-steel surface using a scanning electron microscope and concluded that it was best fitted by a Poisson distribution, $n_C(R) = \lambda \exp(-\lambda R)$, where $\lambda$ is a constant. Their data was later re-analysed by Hibiki and Ishii [6] who proposed using $n_C(R) = (\lambda'/R)\exp(-\lambda'/R)$. Yang and Kim’s data are plotted in Figure 4 where they are compared with the Poisson distribution, the power law distribution (5) and the Hibiki and Ishii distribution.

Yang and Kim observed that for a cavity to become an active nucleation site it is necessary for a pocket of vapour to remain trapped within it after the departure of each bubble. They invoked the analysis of Bankoff [19], who used simple geometrical arguments to show that a necessary condition for vapour entrapment in a groove or cavity with cone angle $2\beta_C$ is:

$$\theta_v > 2\beta_C$$

(6)

According to Equation (6) only cavities with half-cone angles less than $\theta_v/2$ are capable of becoming active nucleation sites. Yang and Kim measured the distribution of cavity cone angles on the surface of a stainless-steel heating element using a differential interference contrast microscope, and found that the pdf of the cavity half-cone angle, $f(\beta_C)$ could be fitted by a normal distribution:

$$f(\beta_C) = \frac{1}{s\sqrt{2\pi}}\exp\left[-(\beta_C - \bar{\beta}_C)^2/2s^2\right]$$

(7)

with $s = 0.285$, $\bar{\beta}_C = 0.374$. 

Combining Equations (5), (6) and (7) gives the following equation for the number of active nucleation sites per unit area on the boiling surface:

\[
N_s = \frac{B}{R_c^m} \int_0^{\theta/2} \frac{1}{s\sqrt{2\pi}} \exp\left[-\frac{(\beta_c - \bar{\beta}_c)^2}{2s^2}\right] d\beta_c
\]  

(8)

which on performing the integration simplifies to:

\[
N_s = BR_c^m \left[ \text{erf} \left( \frac{\theta/2 - \bar{\beta}_c}{s\sqrt{2}} \right) + \frac{\bar{\beta}_c}{s\sqrt{2}} \right]
\]

(9)

This equation was used as a test of the Equation (3) correlation, assuming \( s = 0.285 \) and \( \bar{\beta}_c = 0.374 \) as given by Yang and Kim, and calculating \( R_c \) from Equation (4). \( B \) and \( m \) were assumed to be constants for a given boiling surface and were chosen to give a best fit to data for a particular surface.

To use Equation (9) as a meaningful test of Equation (3) measurements are needed of \( N_s \) in the nucleate boiling of water over a range of pressures and temperatures. Unfortunately, actual counts of nucleation site numbers in high pressure boiling are presently unavailable but it is possible to follow the method of Kocamustafaogullari and Ishii [18] and infer likely nucleation site number densities in high pressure boiling by correlating measurements of the nucleate boiling heat transfer coefficient \( h_{NB} \) against \( N_s \) measurements in low pressure boiling (where data is available) and then applying the correlation to measured values of \( h_{NB} \) at high pressures to infer probable values of \( N_s \).

Figure 4 compares predictions of Equation (9) with values of \( N_s \) obtained in this way by Hibiki and Ishii [6] using the \( h_{NB} \) data of Borishanskii et al [20]. To compare with the experimental values, we assumed \( m = 3.0 \) (which is similar to the value of 2.5 suggested in [17]) and used \( B = 7 \times 10^{-12} /m \) which gave a best overall fit to data. It can be seen from Figure 5 that trends in the data are reasonably well predicted by Equation (9) with the overall quantitative agreement being essentially as good as that obtained with earlier correlations for \( N_s \) [18, 6] even though the
latter introduce additional temperature dependent parameters of uncertain physical origin to achieve a match to the data.

It is important to realise that predictions from Equation (9) are very sensitive to \( \theta_Y \) and without the introducing temperature dependence in \( \theta_Y \) implied by Equation (3) the effect of pressure on \( N_S \) would be grossly over-estimated. Therefore, the agreement obtained is considered to provide a meaningful test of the proposed correlation for the contact angle.

4 CONTACT ANGLE FROM SESSILE DROPLET EXPERIMENTS

4.1 Experimental Results

Numerous studies have used sessile droplets to study the wetting of solid surfaces by liquids, which is important in many industrial applications. As for attached gas bubbles, the equilibrium contact angle at the base of the stationary (sessile) droplet on a horizontal surface can be found by minimising the thermodynamic availability, \( \tilde{A} \). If the droplet is represented as a truncated sphere of fixed volume (as shown in Figure 1b) the availability is given by [21]:

\[
\tilde{A} = \sigma_A s + \sigma_f w - A_b + \sigma_g A_b + V_d g (\rho_f - \rho_g) z_c
\] (10)

where \( A_w \) is the total area of the solid substrate, \( A_s \) the liquid-gas contact area, \( A_b \) the droplet base area, \( V_d \) its volume and \( z_c \) the height of the droplet centroid C above the substrate.

In reality, the curved surface of a droplet on a horizontal surface is not perfectly spherical but is slightly flattened because of the hydrostatic pressure gradient in the liquid. However, a detailed analysis by Lubarda and Talke [21] shows that for droplet sizes typically encountered in sessile droplet experiments (\( Bo \leq 1 \)) the effect of gravity on sphericity is small, and the droplet geometry can be accurately predicted with gravity neglected. Ignoring the gravity term, and expressing \( V_d, A_s, \) and \( A_b \) as functions of \( R \) and \( \theta \) for a spherical cap geometry, the equilibrium contact angle can be found straightforwardly from (10) by minimising \( \tilde{A} \) with respect to \( R \) and \( \theta \) with \( V_d \) held constant, using the method of Lagrange multipliers. The result obtained is:

\[
\cos \theta = (\sigma_{gW} - \sigma_{fW})/\sigma = \cos \theta_Y
\] (11)
confirming that for sessile droplets of sizes typically studied experimentally, the base angle corresponds to the Young’s contact angle.

Bernardin et al [9] and Hirose et al [10] and Song et al [26] studied the effect of temperature on the contact angle for water on metallic surfaces by placing liquid droplets on a heated horizontal surface in a test cell that was pressurised with a permanent gas to suppress boiling. The droplet and surface temperature were the same. Photographic measurements were made of the base angle of the droplets when in a near-equilibrium state, which in accordance with Equation (11) is expected to correspond to $\theta_Y$.

The experiments of Bernardin et al studied water droplets on polished aluminium surfaces in the temperature range 25-170°C, with nitrogen gas used as a pressurising medium. Contact angles were found to depend on whether the liquid was advancing or receding on the surface and to vary significantly depending on the method of surface preparation, leading Bernardin et al to conclude that $\theta_Y$ was sensitive to chemical impurities that remained on the surfaces after chemical cleaning. Hirose et al reported similar data on contact angles for water droplets on stainless steel, zircaloy and aluminium surfaces over the temperature range 25-305°C, with nitrogen or argon gas used as a pressurising medium. Their data also show considerable scatter.

In a recent set of experiments, Song et al measured contact angles of water on 304 stainless steel surfaces at temperatures up to 250 °C and pressures between 0.1 and 15 MPa. Results showed a small tendency of contact angles to decrease with increasing applied pressure (and hence increasing droplet subcooling) but the effect was small compared with the effect of temperature.

Figure 6 shows a plot of $\theta_Y$ against $T_R$ for the experiments in the above three studies together with predictions of $\theta_Y$ from Equation (3) derived in the present work from the bubble departure sizes. The droplet contact angles are higher than the values inferred for bubbles by typically 30-50° which is well outside the uncertainty range of Equation (3). The droplet results show large scatter but do indicate a systematic reduction in $\theta_Y$ with increasing temperature.
4.2 Theoretical Analysis

To try to explain the differences between contact angles measured in sessile drop experiments and those inferred from bubble departure for similar surfaces and temperatures we used the theoretical approach of Adamson [7, 8] who considered contact angles in vapour/liquid systems close to saturation from a theoretical point of view. Adamson considered the contact angle was controlled by molecular forces in the adsorbed liquid layer that exists on a surface exposed to a vapour that is close to saturation. He argued that changes in the molecular potential in the liquid very close to the surface with increasing temperatures would cause the adsorbed layer to thicken and become more like the bulk liquid, resulting in the contact angle falling with temperature. We found that Adamson’s theory can give a plausible explanation for the differences between the contact angles observed in the experiments using bubbles and droplets, as described below.

Summary of Adamson’s model for saturated vapour/liquid systems

To model the adsorbed liquid film on a surface exposed to a saturated or near saturated vapour, Adamson assumed that:

1) the potential of molecules in the adsorbed liquid close to a surface, $\epsilon$, will be a function of the number of molecules per unit area $\Gamma$ ($= x/d_0^3$ where $x$ is the film thickness and $d_0$ is the molecular volume)

2) in equilibrium, the increase in molecular potential when a vapour molecule is brought to the film surface will be equal and opposite to the change in molecular free energy required to form the film, given by $\Delta G = kT \ln \left( (P_{\text{sat}}/P_g) \right)$ where $P_{\text{sat}}$ is the equilibrium vapour pressure at the surface of the film and $P_g$ is the partial pressure of vapour in the bulk gas.

3) the potential function for liquid molecules in the adsorbed film can be represented reasonably accurately as a sum of exponentials in $x$ described by the equation:

$$\epsilon(x) = k\Gamma \ln \left( P_{\text{sat}}/P_g \right) = \epsilon_0 e^{-ax} - \beta e^{-ax}$$

where $\epsilon_0, a, \beta$, and $\alpha$ are constants that can be found from surface adsorption experiments in which the thickness of the adsorbed layer is measured for different values of $P_g$.

Values of these constants for water on glass at 25°C given in Reference [7] are shown in Table 1.
The term in $\beta$ in Equation (12) was described by Adamson as a ‘potential distortion’ term and was introduced by him to account for the possible increase in $P_{\text{sat}}$ in the adsorbed film due to intermolecular forces: Adamson considered that it was the existence of this term that ‘allowed’ an adsorbed liquid film of finite thickness (and hence a non-zero contact angle) to exist on a solid surface when the vapour approaches saturation $P_g \rightarrow P_{\text{sat}}$. He speculated that the perturbation in molecular free energy due to the solid surface $\Delta G = \beta e^{-\alpha x}$ will consist of enthalpic and entropic components $\Delta G = V \Delta P - S \Delta T$ and that therefore $\beta$ will decrease with increasing absolute temperature: this effect explained why contact angles are observed to fall with increasing temperatures in many liquid-vapour systems.

Adamson used the potential function (12) to find the contact angle by applying Gibbs’ adsorption theory, which led him to propose the following equations for the surface energy/unit area in the bulk gas and bulk liquid regions:

$$\sigma_{\text{wa}} - \sigma_g = -J_2; \quad \sigma_{\text{wa}} - (\sigma_f + \sigma) = -J_1$$

where:

$$J_1 = \int_0^\infty \Gamma d\epsilon; \quad J_2 = \int_0^{x_0} \Gamma d\epsilon$$

In Equation (13) $x_0$ is the equilibrium film thickness, $\sigma_g$ and $\sigma_f$ are the surface energies in the bulk gas region and bulk liquid regions respectively, and $\sigma$ is the bulk liquid surface tension. The term $\sigma_{\text{wa}}$ is the surface energy in the limit when the adsorbed liquid layer has vanishingly small thickness $x_0 \rightarrow 0$.

By subtracting the first of Equations (13) from the second, and applying Young’s equation, Adamson derived the following equation for the contact angle:

$$\sigma_g - (\sigma_f + \sigma) = \sigma (\cos \theta_Y - 1) = J_2 - J_1 = \Delta I$$

$\Delta I$ is referred to as the equilibrium spreading coefficient and must be a negative quantity.
When the vapour is saturated so that $P_g = P_{sat}$, (12) gives the following equation for the equilibrium film thickness:

$$x_0 = \frac{1}{a-\alpha} \ln \left( \frac{\epsilon_0}{\beta} \right)$$

(15)

Using Equation (14) with $\epsilon(x)$ from Equation (12) and performing the integrations, results in the following equation for the contact angle when a bulk liquid and its saturated vapour co-exist on a surface:

$$\Delta l = \sigma (\cos \theta_Y - 1) = \frac{\epsilon_0}{\alpha \delta_0} e^{-\alpha x_0} \left( \frac{1}{a} - \frac{1}{\alpha} \right)$$

(16)

which on substituting $x_0$ from Equation (15) can be expressed as the following equation for $\theta_Y$:

$$\cos \theta_Y = 1 + \frac{\epsilon_0}{\alpha \delta_0} \left( \frac{1}{a} - \frac{1}{\alpha} \right) \left( \frac{\epsilon_0}{\beta} \right)^{-\frac{1}{a-\alpha}}$$

(17)

Adamson applied Equations (16) and (17) to water on glass at room temperature, using the coefficients in Table 1 and found that they gave a reasonable estimate of the contact angle.

Adamson [8] suggested that the constants $\alpha$ and $\epsilon_0$ should be nearly temperature-independent as they arise from Van der Waals forces, but that $\beta$ was likely to decrease strongly with increasing temperature for the reasons stated previously: he used (17) to develop an equation for the temperature dependence of the contact angle by postulating that $\beta$ falls linearly with temperature, with the other constants being fixed. However, the linearity assumption resulted in the predicted contact angle falling rapidly to zero at some pseudo-critical temperature below the actual critical temperature $T_{crit}$. This behaviour does not seem consistent with observations for water for either bubbles or droplets, which show contact angles remaining finite all the way to $T_{crit}$. Nonetheless it remains plausible that the temperature dependence of $\theta_Y$ is attributable to the variation of $\beta$ with temperature. Figure 7 shows the variation of $\beta$ with temperature that is needed to give the contact angle variation predicted by Equation (3), if Equation (17) applies, assuming the other constants $\epsilon_0, \alpha$, and $\alpha$ are fixed at the values in Table 1.
Extension to unsaturated vapour conditions

Adamson’s analysis implies that there may be a significant difference between the wetting behaviour of surfaces in saturated and unsaturated vapour conditions, as can be seen as follows. According to Equation (12) the maximum value of the potential function is approximately \((\varepsilon_0 - \beta)\) occurring when the adsorbed film has minimum thickness – i.e., it is simply a monolayer. This condition is achieved when the vapour pressure falls to \(P_{g,\text{min}}\) given by:

\[
kT \ln \left( \frac{P_{\text{sat}}}{P_{g,\text{min}}} \right) = \varepsilon_0 - \beta
\]

Using the constants in Table 1, Equation (18) implies that for water at 100°C, \(P_{g,\text{min}}/P_{\text{sat}} = 0.95\). Therefore, unless the vapour pressure in the bulk gas is at least 95% of the saturation pressure, the adsorbed liquid layer cannot exist. The physical interpretation of this limit is that for \(P_g < P_{g,\text{min}}\) the free energy required to bring a vapour molecule from the bulk gas to the saturation condition in the liquid film exceeds the reduction in molecular potential that occurs as the vapour molecules approach the film surface (noting that the potential is negative).

The condition that \(P_{g,\text{min}}/P_{\text{sat}} \geq 0.95\) is obviously met in the case of bubbles formed in boiling as the vapour inside the bubbles is saturated. However, it is not met in any of the sessile droplet experiments described in Section 4.1, when the vapour pressure in the bulk gas is likely to have been far below the saturation pressure.

Using Adamson’s analysis, it is possible to speculatively investigate differences in the wetting behaviour of surfaces with and without the absorbed liquid layer. It follows from Equations (13) that in the vapour bubble case, in which the adsorbed layer is present, the spreading coefficient is given by:

\[
\Delta I_{\text{bub}} = \sigma(\cos \theta_{r,\text{bub}} - 1) = I_2 - I_1
\]

Assuming the values of the constants for water in Table 1 apply, it is seen that \(I_1\) and \(I_2\) are both negative and that the spreading coefficient \(\Delta I_{\text{bub}}\) is also negative as it must be.
For the droplet case under similar conditions of temperature and pressure (but with \( p_g \ll p_{sat} \)) the second of Equations (13) should still apply, as \( I_1 \) is unaffected by the change in gas composition. In the bulk gas region, however, the adsorbed liquid layer will not be present, so \( I_2 = 0 \) and the surface energy \( \sigma_g \) will now take some value \( \sigma_{wg} \) that may be significantly different from \( \sigma_{wa} \). It then follows that subtracting the first of Equations (13) from the second in this case

\[
\sigma_{wa} - \sigma_{wg} + \sigma_f - (\sigma_f + \sigma) = -I_1
\]

(20)

and that the spreading coefficient will now be given by:

\[
\Delta I_{drop} = \sigma (\cos \theta_Y^{drop} - 1) = -I_1 - \Delta \sigma_w
\]

(21)

where \( \Delta \sigma_w = (\sigma_{wa} - \sigma_{wg}) \) is an excess surface energy required to form an initial film of adsorbed liquid of vanishingly small thickness. Subtracting (21) from (19) an equation can be obtained relating the contact angles in the bubble and droplet cases for similar conditions of pressure and temperature:

\[
\sigma (\cos \theta_Y^{bub} - \cos \theta_Y^{drop}) = I_2 + \Delta \sigma_w
\]

(22)

To see if Equation (22) could plausibly explain the differences between the \( \theta_Y \) values for bubbles and droplets we used it to calculate the variation of \( \theta_Y^{drop} \) with temperature, using \( \theta_Y^{bub} \) values from Equation (3): the integral \( I_2 \) (defined by Equations (13) and (15)) was calculated as a function of temperature using the constants in Table 1 but assuming the variation of \( \beta \) with temperature shown in Figure 7, obtained by fitting the Adamson equations to Equation (3). There seem to be no obvious means of finding \( \Delta \sigma_w \), but as this term involves the creation of a liquid surface it is reasonable to suppose that it is similar in magnitude to the bulk liquid surface tension, and that it falls with temperature along with \( \sigma \) and \( \rho_f \) as the liquid becomes more gas-like. It also seems likely that the term would be strongly affected by physical properties of the solid surface. In the current application we assumed \( \Delta \sigma_w = 0.018T^{-2} \) where the constant 0.018 was chosen to give a reasonable fit to measured values of \( \theta_Y^{drop} \) at around 100\(^\circ\)C.

Predictions of \( \theta_Y^{drop} \) versus temperature obtained from (22) by the above method are shown in Figure 8 together with predictions of \( \theta_Y^{bub} \) from Equation (3). Values of \( \theta_Y^{drop} \) are seen to be in reasonable agreement with the measurements for sessile droplets, although there is a large data
scatter. Interestingly, $\theta_{Y,\text{drop}}$ is predicted to initially fall with increasing $T_R$ and then to rise again when $T_R$ exceeds about 0.9 ($T \geq 300^\circ\text{C}$), this being due to the fall off with temperature of the surface tension term on the left-hand side of Equation (22). Such a recovery in $\theta_{Y,\text{drop}}$ above 300°C is suggested in data reported in Reference [10] although only a limited number of tests were reported at such high temperatures.

5 DISCUSSION

The above arguments imply that Young's contact angles $\theta_Y$ applicable to attached vapour bubbles are likely to be much smaller than those observed in experiments using sessile droplets in which the bulk gas phase is a pressurised gas containing water vapour at a partial pressure significantly below $P_{\text{sat}}$. The reason is that in the vapour bubble case, an adsorbed liquid layer is already present on the 'unwetted' surface inside the bubble, reducing the work required to form new bulk liquid surface and thus reducing $\theta_Y$. In our study, values of $\theta_Y$ for attached vapour bubbles have been derived from bubble departure sizes measured in surface boiling. As already pointed out, it is difficult to confirm these values by direct visual observations of bubble contact behaviour, as the tangent angle at the base of a bubble changes continuously up to the point of departure. However, our estimates of $\theta_Y$ are supported by the available observational evidence on the shape of attached bubbles as described in Section 3.1. In particular, it is very difficult to explain the near spherical shapes of bubbles observed in Sakashita's experiments in Ref [14] ($P = 30 \text{ bars}$), which suggest $\theta_Y$ values of a few degrees, if one accepts contact angle values for droplets observed in pressurised gas environments at similar temperatures (typically around 50 degrees). With such large values of $\theta_Y$ the bubble shapes would be expected to be much more like hemispheres than complete spheres.

Further support for the contact angle estimates comes from analysis of nucleation site densities in high pressure boiling, in which observed trends of increasing site densities with pressure are correctly predicted by using the proposed correlation for $\theta_Y$ against temperature. These pressure trends cannot be predicted satisfactorily if the higher contact angle values observed in droplet experiments are used.
It is possible to challenge the proposed correlation for $\theta_Y$ (Equation (3)) as it is based on a theoretical model for bubble departure size which itself may be questionable. The main assumptions of the model are that the shape of the attached bubble is a truncated sphere and that the bubble base is entirely in contact with saturated vapour. Photographs of attached bubbles in pool boiling on horizontal surfaces do seem to confirm the assumption of a truncated sphere geometry, but the assumption that the bubble base is in contact with vapour only could be questioned as there is evidence from many studies that a liquid layer of a few microns thickness (the microlayer) forms on the base of a growing bubble and may be an important source of vapour generation in nucleate boiling. If a microlayer is present, the departure size model might be invalidated as the surface energy at the bubble base would be miscalculated. This error does not seem likely to be significant, however, for the relatively slow growing bubbles found in nucleate boiling of water at atmospheric pressure and above. Jung and Kim [13] used an optical method to study the development of the microlayer in the growth of an isolated steam bubble in atmospheric pressure boiling. They found that the contribution of the microlayer to vapour generation was under 20%, and that the microlayer was fully evaporated significantly before the time of bubble departure. Thus, in the period immediately before departure the bubble base was in contact only with bulk vapour, in line with the assumptions of the model.

The proposed correlation for $\theta_Y$ for saturated vapour/liquid conditions (Equation (3)) is somewhat surprising in that it seems to be independent of the nature of the boiling surface. This seems at odds with the observations of water droplets, where contact angles appear to be strongly affected by the composition and finish of the test surface. However, it is important to realise that $\theta_Y$ predicted by Equation (3) is an average value which is subject to a significant uncertainty (±40%), probably resulting from variabilities between the surfaces used in the bubble departure tests used to derive it. Assuming Adamson’s theory (Equation (17)) is valid, and adopting the values of $\alpha$ and $\alpha$ in Table 1, $\theta_Y$ would be expected to vary with $\sim \varepsilon_0^{-0.4}$, where $\varepsilon_0$ is a molecular potential due to forces between molecules in the liquid and the solid surface that would be expected to be strongly surface dependent. If the variability in $\theta_Y$ is indeed due to $\varepsilon_0$, the 40% scatter in $\theta_Y$ suggest a variability in $\varepsilon_0$ of ×/÷ 2 across the test surfaces used in the bubble departure tests, which seems perfectly plausible. As $\varepsilon_0$ is believed to be independent of...
temperature, the uncertainty in $\theta_Y$ should be the same percentage of the mean value across the whole temperature range which is consistent with observations (see Figure 2).

In the extension of the Adamson model described above, $\theta_Y$ for the droplet case is given by Equation (21) and involves both $I_1$ and $\Delta \sigma_w$, both of which are expected to be strongly surface dependent. Sensitivity studies using Equation (21) show that at a surface temperature of $150^\circ$C, a 50% increase in $\varepsilon_0$ and $\Delta \sigma_w$ results in change in $\theta_Y$ of -11$^\circ$ and +26$^\circ$ respectively. At the same temperature, application of Equation (17) predicts a change in $\theta_Y$ of only -1.3$^\circ$ for a 50% increase in $\varepsilon_0$. Thus the sensitivity in $\theta_Y$ due to surface condition is expected to be much larger for sessile droplets in pressurised gas environments than for attached vapour bubbles in surface boiling. This appears consistent with observation.

6 CONCLUSIONS
The following correlation for the Young’s contact angle has been developed for saturated vapour/liquid conditions water by fitting bubble departure sizes in pool boiling to predictions of an energy minimisation model:

$$\theta_Y = 0.133 T^9 R^{-9.95}$$ \hspace{1cm} 1 \leq P \leq 132 \text{ bars}$$

where $\theta_Y$ is in degrees and $T_R$ is the ratio between the surface temperature and the critical temperature. The correlation is applicable to a wide range of metallic and non-metallic surfaces within an uncertainty range of (±40%).

Contact angles predicted by the proposed correlation have been found to be consistent with limited observational evidence for attached steam bubbles in nucleate boiling. When used with previously established models for the size and cone-angle distributions of surface cavities, the $\theta_Y$ correlation also successfully predicts the trends in nucleation site densities with pressure and temperature observed in nucleate boiling of water, further supporting its validity.

When compared with contact angles measured for sessile water droplets on high temperature surfaces, the correlation for $\theta_Y$ appears to grossly underpredict test results. The reason for the
discrepancy has been explained using the model of the surface wetting in solid/liquid/vapour systems developed by Adamson using surface adsorption theory. Adamson’s theory suggests that the non-wetted surface inside a vapour bubble is likely to be covered by an adsorbed liquid layer of nanoscale thickness. The adsorbed layer is unlikely to be present in any of the sessile droplet experiments carried out to date, as these have used pressurised gas environments with vapour partial pressures that are well below the saturation. Quantitative estimates of $\theta_Y$ obtained using Adamson’s equations with plausible choices for unknown parameters, are consistent with the magnitude of the differences in $\theta_Y$ obtained in experiments on bubbles and droplets and provide an explanation of why the sensitivity of $\theta_Y$ to surface conditions appears smaller for bubbles than seen in sessile droplet experiments.

It is concluded that contact angle values measured for sessile droplets on heated surfaces in pressurised gas rather than saturated vapour environments may not be relevant to contact angles applicable to attached vapour bubbles in boiling on similar surfaces and at similar temperatures.
Table 1: Values of constants from data on adsorption of water vapour on glass at 25C (data from Table 1 of Ref [7]).

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<table>
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<tbody>
<tr>
<td>α</td>
<td>$3.0 \times 10^8$ m$^{-1}$</td>
</tr>
<tr>
<td>α</td>
<td>$1.3 \times 10^8$ m$^{-1}$</td>
</tr>
<tr>
<td>ε₀</td>
<td>$3.5 \times 10^{-22}$ J</td>
</tr>
<tr>
<td>β</td>
<td>$1.1 \times 10^{-22}$ J</td>
</tr>
<tr>
<td>$d_0^3$</td>
<td>$6.4 \times 10^{-29}$ m$^3$</td>
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Figure 1a: Attached Vapour Bubble on Horizontal Heated Surface

Figure 1b: Sessile Liquid Droplet on Horizontal Surface
Figure 2: Plot of Equation (3) showing uncertainty spread due to experimental scatter.
Figure 3: Comparison of measured and predicted departure diameters in pool boiling of water on horizontal surfaces. Data of Sakashita $P=22-45$ bar [14]; Maity $P=1$ bar [22]; Siegel and Keshock $P=1$ bar [23]; Jung and Kim $P=1$ bar [13]; Duan et al $P=1$ bar [24]; Tolubinsky and Ostrovsky, $P=1-10$ bar [25], Semeria, $P=1-132$ bar [27].
Figure 4: Comparison of cavity number densities reported by Yang and Kim [3] with model predictions.
Figure 5: Comparison between predictions of Equation (9) and nucleation site densities for water inferred from heat transfer coefficients reported in Ref. [20].
Figure 6: Contact angles measured in sessile droplet experiments of Refs [9, 10, 26].
The solid line represents values computed with the correlation inferred from bubble data.
Figure 7: Variation of potential distortion term with temperature required to give temperature dependence of $\theta_y$ implied by Equation (3).
Figure 8: Comparison of contact angles for bubbles and droplets.
7 AUTHORS' CONTRIBUTIONS
K. H. Ardron - conceptualisation, methodology, formal analysis, investigation, writing.
G. Giustini - investigation, writing (visualisation, review and editing), funding acquisition.

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9 REFERENCES


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