

# How to create an efficient surface for nucleate boiling?

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## Abstract

From a brief historical overview of the ideas on bubble generation, some directives for developing of efficient structures with nucleate boiling are deduced in the first part of the paper. Then, starting from the survival conditions of a vapour bubble in a liquid with a temperature gradient, a criterion is obtained for the creation of such structures. The efficiency of a heater surface covered with a structure is considered ideal if the driving temperature difference does not change with the heat flux. Experiments show that constancy of the wall superheat can be realized on surfaces provided with an appropriate micro-structure. The required properties of the structure are: It must be generated from identical elements which are arranged in a mono-pattern on the heating surface, the structure elements (protrusions) must trap vapour after bubble detachment and generate a possibly long three-phase-line (TPL) formed by intersection of the vapour–liquid interface with the heating surface.

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## 1. Introduction

Nucleate boiling of liquids has been the subject matter of a number of studies, which cover questions ranging from formation of stable bubble nuclei in metastable liquids, via bubble growth and departure to boiling heat transfer under various conditions. The state of the art can be obtained from several review articles and monographs, e.g., by Westwater [1], Nesis [2], Carey [3] and Collier and Thome [4], to name only a few. The capillarity theory is mostly used to describe the bubble equilibrium in a superheated liquid. This theory requires a liquid–vapour interface of macroscopic properties to exist and is, therefore, not applicable to the very start of bubble formation. The processes preceding formation of a stable vapour bubble are still poorly understood; consequently, there is not a theory that could describe these processes successfully. The existence of the heating surface makes the system heterogeneous and the boiling physics much more complicated in comparison to homogeneous sys-

tems. Particularly the effect of surface structure of nano- and micro-sizes on formation of premature bubble embryos and bubble growth are still to be explored.

Despite these facts considerable effort has been undertaken in the last decades to develop efficient boiling surfaces. The guiding idea is to provide the surface with a structure that increases the heat flux in comparison to technical surfaces at the same surface superheat. The achievements in this direction are considerable, as may be taken, e.g., from Thome [5]. The boiling characteristics of such surfaces are qualitatively similar to the ones of technical surfaces showing a dependency of the heat flux on the surface superheat. This behaviour allows the conclusion that the potential for vapour generation on structured surface is still available.

In the present paper a relationship originally developed by Hsu and Graham [6] is used to deduce some directives on how to create an efficient heat transfer surface for nucleate pool boiling. This equation specifies the condition for bubble grow under the conditions of a temperature gradient and leads to a relationship for the surface structure (size of bubble cavity) in dependence of process parameters. As will be shown, a surface having an appropriate monostruc-

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### Nomenclature

|            |                           |                                    |  |
|------------|---------------------------|------------------------------------|--|
| $A$        | interface area            | $\delta$                           | distance to wall                         |
| $C$        | constant                  | $\lambda$                          | thermal conductivity                     |
| $d$        | pin diameter              | $\rho$                             | density                                  |
| $\Delta h$ | enthalpy of phase change  | $\kappa$                           | thermal diffusivity                      |
| $L$        | length                    | $\sigma$                           | surface tension                          |
| $m$        | mass                      | TPL                                | three-phase-line (solid, liquid, vapour) |
| $n$        | pin number density        | <i>Subscripts and superscripts</i> |  |
| $n_L$      | surface density of TPL    | $B$                                | bubble                                   |
| $q$        | heat flux                 | $C$                                | cavity                                   |
| $\dot{Q}$  | heat flow rate            | CR                                 | critical                                 |
| $R$        | thermal resistance        | $L$                                | liquid, length TPL                       |
| $r$        | radius                    | $I$                                | interface                                |
| $T$        | temperature               | $V$                                | vapour                                   |
| $\Delta T$ | temperature difference    | $W$                                | wall                                     |
| $t$        | time                      | $\infty$                           | far from wall                            |
| $u$        | velocity                  | —                                  | average                                  |
| $y$        | coordinate, wall distance |                                    |  |
| $\alpha$   | heat transfer coefficient |                                    |  |

ture results in a boiling characteristic that is different from the ones of technical surfaces. Namely, in a certain range of the process parameters, the heat flux is largely independent of the wall superheat.

The paper begins with a short historical overview mainly focussing on the evolution of the ideas and growth of the knowledge at the beginning of the research in the area of bubble formation.

## 2. Early studies on bubble generation

Like in many fields of science, also the beginning of boiling physics in written form cannot be stated very precisely, but the following text seems to shed some light on the issue [7]:

*“The well-known incident of the failure of the pump to suck water from a deep well occurred when Galileo Galilei (1564–1642) retired to his villa at Alcatraz and his life was drawing to a close. All the ingenuity of the Grand Duke’s artisans failed to make the water rise more than about 30ft in the suction pipe.<sup>1</sup> When asked for his advice, Galileo replied that it would be well to find out why the water rose at all, and to the suggestion that Nature abhorred a vacuum, he answered that it was apparently only a vacuum less than about 30ft that Nature was to averse to.”*

The above remark by Galilei probably stands at the very beginning of experiments with *liquids under tension*. Obvi-

ously, he had in mind the difference of the pressures acting on the free water surface (in the well) and in the suction pipe expressing his wondering about the water sustaining such a tension. This remarkable thought occurred at a time where the atmospheric pressure was still to be discovered.<sup>2</sup>

Some twenty years later, *Christiaan Huygens* (1629–1695) [8] made public the discovery of *tensile strength of water*. He observed that water can resist a considerable tension when filled in a tube that is arranged vertically and open at its lower end. In 1669 he also demonstrated before the Royal Society of London columns of air-free water to not subside in the tube. The studies by *Robert Hook* (1635–1703), who originated the idea of mechanical strength of materials, *Denis Papin* (1647–1712), who invented the digester (pressure cooler), and of many others, were guided by the desire to mainly understand the *Toricelli empty* [9]. Since then, the vapour nucleation in liquids has attracted the attention of physicists and engineers both as a natural phenomenon and from a practical point of view. In this context it is also interesting that already *Aristotele* [10] was aware of transition of phases and that *see-water can be rendered potable by distillation*. As it seems, *experiments on boiling and condensation* were first performed not with pure liquids but with *mixtures*, while making liquors [11].

<sup>1</sup> Grand Duke of Tuscany, Ferdinand the II<sup>nd</sup>.

<sup>2</sup> Evangelista Torricelli is supposed to have been present to this memorable occasion, and thus, being drawn to consider the question, he conceived the happy idea of making a vacuum in a tube by means of a liquid heavier than water [7].

### 2.1. Historical development of the ideas on bubble nucleation

Important in several respects, the question of bubble formation in liquids has been debated extensively in the past, but a satisfactory answer to the question does not seem to exist in the literature. In modern publications in this area of engineering science one usually takes a bubble as given, formed somehow. In the following, a brief historical development of the ideas is presented, aiming at keeping and supporting discussion on this important and interesting subject.

Edmé Mariotte (1620–1684), well known from the isothermal pressure–volume relationship of gases, supposed that *water contains air*, which escapes during boiling thus assisting in bubble formation. As boiling continues after the air has completely escaped, he assumed the existence of *another matter which appears only in connection with boiling*. In 1690, Edmund Halley (1656–1742) [12], the discoverer of a comet which bears his name, held

*“that warmth does separate the particles of Water and emit them with a greater and greater Velocity as the heat (temperature) is more and more intense.”*

At about the same time, Denis Papin and Gottfried Wilhelm Leibniz (1646–1716) argued that the effect of superheated water, *the fulmination*, is caused by the water itself. As it now appears, the vapour pressure was meant by this term. In addition, Leibniz ascribed the *boiling sound* to beating of fluid particles against the heating wall.

Some 70 years later, Henry Cavendish (1731–1810) [13], discriminated between *evaporation* (in presence of a gas) and *boiling with bubble formation*:

*“Water as soon as it is heated ever so little above that degree of heat which is acquired by the steam of water . . . , is immediately turned into steam, provided it is in contact with steam or air; this degree I shall call the boiling heat, or boiling point. It is evidently different according to the pressure acting on the water. If the water is not in contact with steam or air, it will bear a much greater heat without being changed into steam, namely that which De Luc calls the heat of ebullition.”*

Cavendish also gave an explanation of the chief phenomena of boiling:

*“When water is set on the fire and begins to boil, the lamina of water in contact with the bottom of the pot is heated till either small particles of air are detached from it, or till bubbles of steam are produced by ebullition. As these particles or bubbles ascend, the water in contact with them, if at all hotter than the boiling point is immediately turned into steam. . . though the coat of water immediately in contact with the bubbles during their passage is not hot-*

*ter than the boiling point, yet the rest of the water has not time to communicate much of its heat to that coat before the bubble is past. For this reason when the water boils with a vast number of small bubbles its heat ought in general to exceed the boiling heat less than when it boils with large bubbles succeeding one another slowly.”*

Regarding the heat of ebullition (*boiling inception*), Cavendish says:

*“The excess of the heat (temperature) of the water above the boiling point is influenced by a great variety of circumstances. The quantity of air in the water has a very great influence; for the more air it contains, the less heat will the water in contact with the bottom be capable of receiving, and the greater number of bubbles will be discharged. It is this which seems to be the reason of the difference between water beginning to boil and long boiled.”*

In addition, a Committee appointed by the Royal Society concerning the fixed points of thermometers that was chaired by Cavendish recommended [14]:

*“ . . . not to dip the thermometer into the water, but to expose it only to the steam, . . . ”*

in order to exclude the wall effect on boiling temperature.

Doubtlessly, the notions of Cavendish could fill lines of an actual publication.

De Luc (1727–1817) [15,16] stated that boiling is produced by *bubbles of the air which the heat disengages from the liquid*.<sup>3</sup> Deprived of air, water can boil only on the upper or free surface, he concluded.

By a number of experiments Achard (Franz Carl Achard 1753–1821) [19], much more known as the inventor of the Prussian Sugar and who was the first to built up a factory for making sugar from sugar-beet, arrived in 1785 at the conclusion that the *boiling point of water varies much more in metallic than in glass vessels*. He also noticed that a drachm of *iron-filings* or some other insoluble solids added to water *lowers its boiling point*, and that there were considerable differences in the lowering degree, depending on whether the *solid is in powder or in lump*.

In 1812 and 1817, Gay-Lussac (Joseph Louis, 1778–1850, well known from the isobaric temperature-volume relationship of gases) [20,21], supposed the boiling point to *vary in different vessels according to the nature of their surfaces and the materials*, the variation depending on both the *conducting power of the material* for heat and on the *polish of the surface*. According to Marcet [22] the lower boiling

<sup>3</sup> De Luc (Jean André De Luc, or John Andrew de Luc, frequently written DELUC) was a member of the above mentioned Cavendish’s committee. He was for many years Reader to Queen Charlotte, and was engaged in many field of science of the late eighteenth century [17]. For an account of De Luc’s achievements see Emeis [18].

temperature of water on metallic surfaces in comparison to glass surfaces is caused by a corresponding weaker *adhesion* of water particles to the wall. Bubble generation is expected when the *repulsive action of heat* overcomes the *cohesion of the liquid* along with the atmospheric pressure. He also noticed the dependence of the *bubble departure diameter* and the *bubble frequency* on the *strength of heat source* (heat flux).

It is interesting that some basic studies of boiling phenomena were originated from the development of thermometers and explosions of steam boilers. To the former group of works belong at least by part also the studies by Cavendish [14]. In a paper by Rudberg [23] there are considerations of liquid evaporation during bubble rise through the liquid and expansion of vapour making the bubble.

First precise experiments on a *negative pressure in liquids* were performed by Berthelot (1827–1907) [24] at constant volume, showing that liquids can sustain a considerable tension (water 50 bar, ether 150 bar, approximately). However, for the present purposes of much greater interest is the isobaric liquid superheat. Dufour [25] seems to be the first who investigated the superheat of *water droplets suspended in oil* thus avoiding a direct contact between the test liquid and the solid wall. By this method, he was able to obtain water superheats up to 70 K at atmospheric pressure. He termed the state of the superheated liquid *metastable*. Dufour's experiments aimed at clarifying the cause of explosion of steam boilers. At high superheats, he observed a vapour generation in the whole liquid mass. Krebs [26] reported on similar boiling behaviour, which he called *explosive boiling*. As it appears, both authors reached in their experiments nearly a *homogeneous vapour nucleation*.

Two further classical contributions to the understanding of bubble nucleation are worth mentioning. Tomlinson [27] stressed that formation of bubble nuclei depends not only on the *state of the surface* (clean, unclean) but also on its *porosity*. He gave a very interesting definition of a liquid near or at its boiling point:

*“A liquid at or near its boiling point is a supersaturated solution of its own vapour, constituted exactly like soda-water, champagne, and solution of some soluble gases.”*

Tomlinson's ideas have sharply been criticized by Aitken [28], remarking, we cannot imagine a porous body while under the same conditions both to absorb vapour from the water and give it out again in a constant, never-ceasing flow. Aitken continues to describe the boiling supposing a free surface to exist. The free surface is formed by adsorption of gases that were dissolved in the liquid. He says:

*“...bubbles have sprung from certain points where the water is not in contact with the vessel, but is separated from it by a small quantity of gas or vapour; into this gas or vapour the water vaporises till it grows to such a size that part of it breaks away and rises to the surface,*

*leaving part still attached to the vessel to form a centre from which another bubble grows, to be thrown off in turn, and while the bubbles rise in rapid succession the root remains fixed.”*

Aitken also discussed the *effect of roughness* and of *surface active substances* on bubble generation, but he assumed gas nuclei for formation of vapour bubbles, which was not a new idea.

From this short review of the literature we may draw the following conclusions concerning the state of the art in the area of nucleate boiling (bubble nucleation) at the end of 19th century:

- (1) Bubble generation is intimately connected with inert gases, either dissolved in the liquid or adsorbed on the surface of the wall.
- (2) The boiling temperature (liquid superheat) depends on the amount of the dissolved gases, the surface roughness/porosity and the interaction liquid–solid wall.
- (3) The state of a superheated liquid is instable and bubble formation in such a liquid can be initiated in various ways. At a strong superheat the boiling manifests itself explosively.

The papers referred to so far are scarcely mentioned in current literature. The notions about bubble formation described in these old and vastly forgotten publications are interesting not only from a historical point of view.

## 2.2. Theoretical speculations

The conclusions above are mainly based on experimental observations. Besides, there are also theoretical models in this area aiming at deeper insights into the boiling phenomena. The model connecting the separation of liquid particles by action of heat was originally proposed by Halley [12]. In Query 31, Isaac Newton (1642–1727) [29] has drawn the attention to particles, released from and beyond the attraction of a body, receding from it and from one another with great strength. The idea developed by Antoine Lavoisier (1743–1794) [30] unifies the notions of Halley and Newton. He assumed that the particles of all bodies are subjected to both *attractive and repulsive forces*. When removed beyond the limits of attraction, a change of state (phase) might be expected. This idea has already been developed by Desaguliers (1683–1744) [31] and Boskovic (1711–1787, Roger Josph Boskovich, or Rudjer Josip Bošković) [32]. Desaguliers postulated that in liquids there exists both a *repulsive* and an *attractive* force between the particles. The former would be augmented and suppress the attraction if the temperature is increased and elastic fluid formed. Boskovic [32] speaks in his Theoria (§462), appeared in 1763, of *evaporation* and *ebullition*. According to Boskovic, *a slow evaporation will take place when the repulsive force does not greatly exceed the attractive force*. An *ebullition* is expected when the mass

sandwiched between the limits of approach and recession arrives at the *outside of the attraction*.

The theoretical contributions of fundamental importance in this area by *William Thomson (Lord Kelvin, 1824–1907)* [33], *J.W. Gibbs (1839–1903)* [34], and *J.J. Thomson (1856–1940)* [35], resulting in analytical relationships, remained unrecognized for decades. This might be due to the complexity of the ideas, particularly by Gibbs, as may be deduced from the foreword to the German translation of Gibbs' studies by *W. Ostwald*<sup>4</sup> [36]:

*“Anmerkungen und Erläuterungen hinzuzufügen hat der Verfasser nicht die Zeit und der Übersetzer nicht den Mut gehabt.”*

On the basis of a thought experiments, *W. Thomson* [33] quantified the *effect of curvature* of the interface on *vapour pressure*, while *Gibbs* [34] introduced an *energy barrier* equal to the *work of bubble formation*. The other *Thomson, J.J.*, derived an equation for the *liquid superheat arising from the interface curvature* [35,37].

More recent works in the area of bubble formation and boiling heat transfer mostly deal with specific phenomena such as *fluctuation of state parameters* preceding bubble nucleation, an issue, which can be traced back to the time of *van der Waals* [38], and even of *Boskovic* [32]. The heat transfer to a growing bubble, adhering to a heater surface, occurs mainly in the region where all the phases involved (liquid, vapour, solid wall) are interacting and the heat flux may change its direction [39]. The detection of this phenomenon makes the boiling process by no means simpler, but contributes to understanding the boiling events occurring around a growing bubble. The issue becomes much more complicated if the heater surface is provided with a micro-structure that should enhance boiling kinetics, see, e.g., *Thome* [5] and *Webb* [40].

### 3. Efficient boiling surfaces

#### 3.1. Vapour trapping and ideal boiling surface

The above short overview of the literature shows that the effect of wall on boiling temperature has been recognized almost three centuries ago. First systematic investigations of the wall effect on nucleate boiling heat transfer were seemingly performed by *Jakob and Fritz* [41]. *Corty and Foust* [42] reported heat transfer data obtained with different liquids boiling on surfaces of various polish. Depending on the pair liquid–surface, *Corty and Foust* [42] observed the heat transfer coefficient to be almost independent of the wall

superheat. As they noticed, the micro roughness of the boiling surface was one of the fundamental factors governing the heat transfer:

*“It may be postulated that there exist cavities in the metallic surface and that in these cavities vapour is trapped after an earlier bubble has broken loosely. The trapped vapour then acts as the nucleus for the next bubble from the same spot.”*

*“A vapour-filled cavity may act as nucleus for bubble formation as long as the superheat in the surface is high enough to support the vapour phase inside the cavity against the constrictive effect of surface tension in the phase boundary.”*

These findings by *Corty and Foust* in 1955 (PhD dissertation of *C. Corty* 1951) concerning the *vapour rest* acting as a nucleus for the next bubble are perfectly in agreement with the ideas developed by *Aitken* [28] in 1878. *Corty and Foust* applied an expression for the equilibrium temperature of a concave interface to a bubble in a cavity. This seems to be for the first time to specify the *minimum wall superheat in nucleate boiling required by thermodynamics for a stable vapour bubble*. This idea has been extended by *Hsu and Graham* [6,43] to *non-isothermal systems* and refined in the mean time by many others. We will use the *Hsu and Graham* relationship in a slightly modified form further below to estimate the cavity size of an efficient surface for nucleate boiling. Prior to this, however, it seems appropriate to define an ideal surface regarding the boiling heat transfer:

*A heat transfer surface in nucleate boiling is considered to be ideal if the variation of the heat flux does not result in any change of the driving temperature difference.*

Fig. 1 illustrates typical shapes of boiling curves. As schematically shown in Fig. 1(c) and (d), the heat flux  $q$  is independent of the wall superheat  $\Delta T$ . This heat flux independency requires a change of the thermal resistance  $R$  to nucleate boiling according to the expression

$$q \cdot R = \Delta T = \text{const} \quad (1)$$

which means that any increase in the heat flux results in a decrease in the thermal resistance thus keeping the heat transfer potential unchanged. This relationship follows the general *Theorem of Moderation* (*Le Chatalier Principle*, as a particular case):

*Any system in a steady state undergoes, as a result of a variation in one of the factors governing this state, a compensating change in a direction such that, had this change occurred alone it would have produced a variation of the factors acting in the opposite direction.*

<sup>4</sup> “The author had no time and the translator no courage to provide comments and explanations”. *W. Ostwald* was one of the leading scientists in physical chemistry of his time.

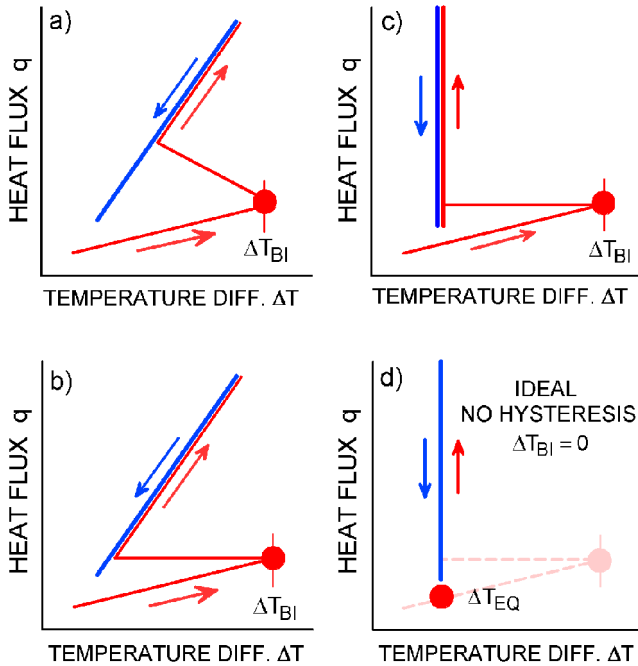


Fig. 1. Some shapes of boiling characteristics: (a) Partial activation of bubble sites after boiling inception; (b) Simultaneous activation of bubble sites after boiling inception; (c) Simultaneous activation of bubble sites followed by independency of wall superheat on heat flux; (d) Ideal boiling surface at zero inception superheat.

What could be the nature of these factors in case of nucleate boiling in accordance with Eq. (1)?

To answer this question requires an analysis of the mechanisms of boiling heat transfer. These mechanisms have been discussed in several publications dealing with the boiling on common, technical surfaces, and a recent paper by Yu and Cheng [44] should be mentioned in this context, instead of giving a literature review. According to the well-accepted figure of nucleate boiling, the bubble density increases with rising heat flux. Consequently, the *stirring effect* of growing and detaching bubbles should principally be included when discussing Eq. (1). However, considering that an improvement of the stirring effect requires a corresponding increase in bubble frequency and/or bubble density, the stirring effect does not represent a direct event in the chain of bubble events and the reduction of the thermal resistance with increasing heat flux according to Eq. (1) seems less probable by this effect. The same holds for other transfer mechanisms like *Marangoni convection* or *displacement of hot liquid* by growing bubbles. They all depend on the wall superheat so that an increase in the heat flux necessitates a rise of the wall temperature [44].

A direct heat transfer event in nucleate boiling would be evaporation at an existing vapour–liquid interface which interacts with the heating surface, if the molecules leaving the liquid phase receive the necessary energy jump (activation energy) immediately from the heating wall. This idea implies that the wall heat flux is completely consumed by vapour generation directly on the wall surface, as it occurs on

the three-phase-line (TPL, liquid, solid, wall). For the idea to be realistic, the bubble frequency and/or the activation of further bubble cavities must take place without any additional increase in the wall temperature. One possibility to accomplish this is to adopt the ideas of Aitken [28] and Corty and Foust [42] and to *postulate* a permanent existence of the vapour–liquid interface on the heating surface. Another one could be based on an appropriate surface structure interacting with the bubble–induced liquid flow in a way which assists in bubble generation. We will return to this question further below.

### 3.2. Criterion of bubble growth

From the above, we may draw the conclusion that a surface efficient in nucleate boiling should be able to generate vapour bubbles at (nearly) zero waiting time. This implies a vapour rest to remain in the surface cavity at the bubble detachment. The existence conditions of this vapour rest would then formulate a criterion for bubble growth. This criterion must not be confused with the condition of boiling inception.

Like Corty and Foust [42] also Griffith and Wallis [45] proposed a relationship between the cavity size and the wall superheat:

$$r_{CR} = 2 \frac{\sigma T_{\infty}}{\Delta h \rho_V (T_W - T_{\infty})} \quad (2)$$

Here  $r_{CR}$  denotes the radius of the cavity mouth,  $\sigma$  the surface tension,  $\Delta h$  the evaporation enthalpy,  $T$  the temperature, and  $\rho$  the mass density. The indices  $V$ ,  $W$  and  $\infty$  refer to vapour, wall and to liquid at a large distance from the wall, respectively.

The temperature difference  $T_W - T_{\infty}$  in Eq. (2) represents the minimum wall superheat required by the thermodynamic equilibrium conditions for a concave interface of the radius  $r_{CR}$ . Being derived by J.J. Thomson in 1886 for the first time, it would be safe to name this equation *Thomson's (J.J.) nucleation criterion*.

As noted above, the conditions of bubble existence in a system with temperature gradient was apparently first formulated by Hsu and Graham [6,43]. Their analysis starts from the (J.J. Thomson) equation for a bubble in a liquid of homogeneous temperature,

$$T_B = T_{\infty} + 2 \frac{\sigma T_{\infty}}{\Delta h \rho_V r_B} \quad (3)$$

which is identical to Eq. (2); the index  $B$  refers to the bubble.

The fate of a bubble in a liquid of an inhomogeneous temperature will depend both on its size and place with regard to the temperature distribution near the wall. As illustrated in Fig. 2 for a liquid of a linear temperature distribution, all bubbles of the temperature  $T_B$  and the radius  $r_B$  are thermodynamically stable in the layer  $\delta$  adhering to the wall. By contrast, bubbles above the line  $T_L$  (outside  $\delta$ ) were unstable and would condense [46]. Analogously, another bubble temperature  $T_B$  would require a corresponding bubble radius.

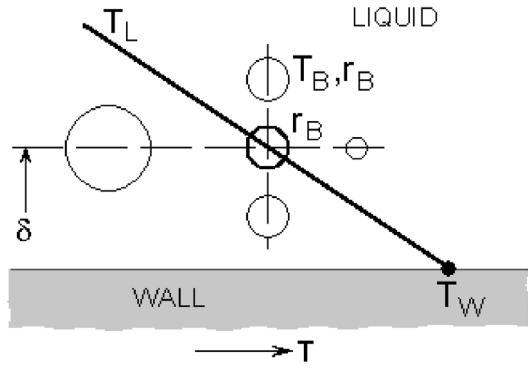


Fig. 2. Illustration of bubble survival conditions.

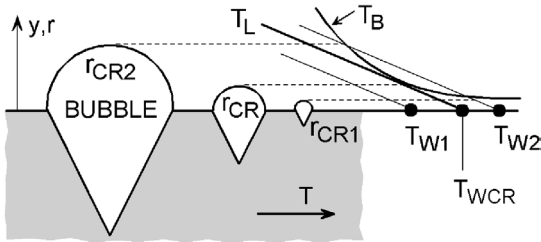


Fig. 3. Illustration of bubble growth criterion.

If the line  $T_L$  in Fig. 2 intersects the bubble interface, an evaporation–condensation process may be expected to occur, and the conditions of bubble growth would demand

$$\frac{dm_V}{dt} = - \int_A \rho_L (u_{LI} - u_I) dA \geq 0 \quad (4)$$

where  $m_V$  is the mass of the vapour,  $u_{LI}$  the radial velocity of the liquid at the interface moving at the velocity  $u_I$ , and  $A$  the interfacial surface area. This equation requires the evaporation to balance or overcome the condensation; the liquid temperature  $T_L$  at the distance  $\delta + r_B$  must at least be equal to the bubble temperature  $T_B$ , as stated by the nucleation criterion (3).

For a semi-spherical bubble attached to the mouth of a cavity of the radius  $r_C = r_B$ , the temperature  $T_B$  in Eq. (3) can be plotted as a function of the wall distance  $y = r_B$ , Fig. 3 [47]. A linear temperature distribution in the liquid near the wall,

$$\frac{dT_L}{dy} = - \frac{q}{\lambda_L} \quad (5)$$

and the requirement of tangency at  $y = r_{CR}$  give

$$\frac{dT_L}{dy} = \frac{T_B - T_{WCR}}{r_{CR}} = - \frac{q}{\lambda_L} = - \frac{\alpha(T_{WCR} - T_\infty)}{\lambda_L} \quad (6)$$

$$T_{WCR} - T_\infty = 2 \frac{\sigma T_\infty}{\Delta h \rho_V r_{CR}} \left/ \left( 1 - \frac{\alpha r_{CR}}{\lambda_L} \right) \right. \quad (7)$$

where  $\lambda_L$  denotes the liquid thermal conductivity,  $\alpha$  the heat transfer coefficient, and the index CR refers to the critical bubble (cavity) radius. The structure of this equation is identical to the one reported by Howell and Siegel [48].

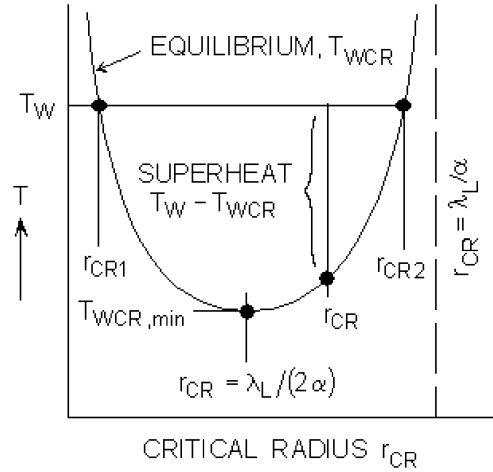


Fig. 4. Effect of wall temperature on critical bubble radius.

Because of  $T_{WCR} - T_\infty > 0$ , Eq. (7) requires

$$\alpha < \alpha_{\max} = \frac{\lambda_L}{r_{CR}} \quad (8)$$

and the critical radius  $r_{CR}$  according to Eq. (7) lies in the range  $0 < r_{CR} < \lambda_L/\alpha$ , Fig. 4. At the minimum of the curve,

$$r_{CR} = \frac{1}{2} \frac{\lambda_L}{\alpha} \quad (9)$$

we have

$$T_{WCR, \min} - T_\infty = 8 \frac{\sigma T_\infty \alpha}{\Delta h \rho_V \lambda_L} = 4 \frac{\sigma T_\infty}{\Delta h \rho_V r_{CR}} \quad (10)$$

For a wall temperature  $T_W > T_{WCR}$ , the spectrum of bubble radii able to grow falls between  $r_{CR1}$  and  $r_{CR2}$ . The existence of the two critical radii at the same wall temperature is associated with the thermodynamic equilibrium condition (region  $r < r_{CR1}$ ) and by condition of heat transfer (region  $r < r_{CR2}$ ) that can cause large bubbles to condense.

### 3.3. Creation of an efficient surface

For a given  $r_{CR}$  within the range  $r_{CR1} < r_{CR} < r_{CR2}$ , the temperature difference

$$T_W - T_{WCR} = T_W - T_\infty - 2 \frac{\sigma T_\infty}{\Delta h \rho_V r_{CR}} \frac{1}{1 - \frac{\alpha r_{CR}}{\lambda_L}} \quad (11)$$

represents the wall superheat above the thermodynamic minimum (equilibrium), and by this temperature difference the system (wall, liquid and bubble) is shifted from its equilibrium state. Taking the temperature as a system coordinate, the temperature difference  $T_W - T_{WCR}$  defines a force driving the system towards the thermal equilibrium.

The driving force is different for different bubble cavities. As follows from Fig. 4, it is zero for  $r_{CR} = r_{CR1}$  and  $r_{CR} = r_{CR2}$ , but maximum for  $r_{CR}$  given in Eq. (9),

$$T_W - T_{WCR, \min} = T_W - T_\infty - 4 \frac{\sigma T_\infty}{\Delta h \rho_V r_{CR}} \quad (12)$$

As is obvious from Fig. 4 and Eq. (11), any increase in the wall superheat above the thermodynamic minimum could result in an activation of surface cavities in the range  $r_{CR1} < r < r_{CR2}$ . Because the size of the cavities is a fractal quantity, any increase in the wall temperature would, at least theoretically, correspond to activation of certain *fraction of the cavity size*, and by this process also the heat flux could be fractioned. As discussed by Yu and Cheng [44], a relationship between the wall superheat (or heat flux) and the fractal dimension of cavities would result. Such a behaviour, however, would not be in accordance with the definition of the ideal boiling surface stated above, Eq. (1), because any activation of new cavities (other fractal level) would require surmounting the energy barrier as a measure of the thermal resistance.

The expression given in Eq. (11) shows us a way how to create an efficient boiling surface. Namely, in order to keep the temperature difference constant, *the cavity radius  $r_{CR}$  must be fixed, that is, all the cavities must have the same radii*. In this way we would exclude the existence of cavities of other sizes thus generate a *mono-cavity-pattern*. As a consequence, the thermodynamic wall superheat corresponding to this cavity pattern would be the same for the whole surface.

In the case of a mono-cavity-pattern all the cavities are expected to become activated simultaneously at the same superheat. An increase in the wall temperature beyond the one required by the thermodynamic equilibrium would result in faster vapour production on the heating surface, and not in activation of further bubble sites. As the vapour production mainly occurs at the TPL, the wall superheat would remain unchanged whereas the heat flux (evaporation rate) would rise. In other words, *a rise in the heat flux would be possible without increasing the wall temperature*.

This notion requires two further conditions to be fulfilled:

- (a) Bubble formation at (nearly) zero waiting time, which means a viable vapour rest in the cavity after the bubble detachment. A vapour rest able to grow immediately after the bubble break-off could be realised in an appropriately formed structure.
- (b) The mutual distance of the cavities must also be prescribed in a certain manner for the surface to be efficient. For this reason, the pattern of the cavities must be chosen so that (ideally) no heat is transferred from the heating surface to the liquid, but at the same time any single cavity be supplied sufficiently with the heat required for bubble growth.

The mutual distance of the cavities could be estimated from their thermal interaction through the wall. Distributed on the heating surface in a way that the surface area thermally occupied by one cavity just touches the ones of the neighbouring cavities, would largely prevent the heat transfer from the wall to the liquid and the heat would be consumed almost completely by vapour generation directly on the wall

surface. Because of vapour rest remaining in the cavity on bubble detachment, the energy barrier of bubble nucleation would be reduced considerably and the temperature of the wall surface would approximately remain constant. This would change the boiling characteristic substantially because the increase in the wall temperature with rising heat flux in nucleate boiling on common surface is associated with the nucleation barrier of cavities having different both size and shape. In this context the reader may be referred to the studies dealing with surface roughness, e.g., [48–53] and the review paper by Fujita [54].

#### 4. Experimental evidence

Corty and Foust [42] observed boiling characteristics with *n*-pentane and diethyl ether on polished copper surfaces with wall superheat largely independent of the heat flux, ascribing the micro roughness of the heater surface a fundamental role. Similar behaviour have been reported by You et al. [55] on particle-layered surface, see also Bar-Cohen [56]. More than two decades ago, the present author conducted boiling experiments with the Refrigerant R11 ( $\text{CF}_2\text{Cl}_3$ ) on a flat heater surface provided with artificial nucleation sites, Fig. 5. The surface cavities (diameter 180  $\mu\text{m}$ , depth 120  $\mu\text{m}$ , density 460  $\text{cm}^{-2}$ , approximately) were arranged hexagonally.<sup>5</sup> They were generated by photo-etching technique, first used by Messina and Park [57]. The experimental findings have been presented at a meeting in 1988 [58], but not published yet. As the results seem to be still interesting, Fig. 6 shows the boiling characteristics obtained with R11 at nearly atmospheric pressures. In the region of developed boiling, the experimental uncertainty of the heat flux was estimated to be less than 2% and of the temperature difference below 1.5%.

The constancy of the wall superheat is observed only at relatively high heat flux. In the case of increasing heat flux, the surface cavities were activated at nearly the same heat flux. The bubble detached almost simultaneously on the whole surface, resulting in a piston-like boiling oscillation. This boiling behaviour was observed only in the horizontal position of the heating surface.

Recently, Wei and Honda [59] published very interesting results on boiling FC-72 using chip surfaces provided with different micro-pin fins. The boiling characteristics were observed to depend on the liquid subcooling and fin geometry. Some surfaces show almost constant wall superheat in the range of the wall heat flux. At the same time, the hysteresis at boiling inception was practically zero.

*A novel microstructure.* As a further example, a paper by Mitrovic and Hartmann [60] dealing with nucleate pool boiling of the Refrigerant R141b should be mentioned. They

<sup>5</sup> It should be noted that the walls of the cavities were not smooth but covered with a fine structure that largely governed the wall superheat.



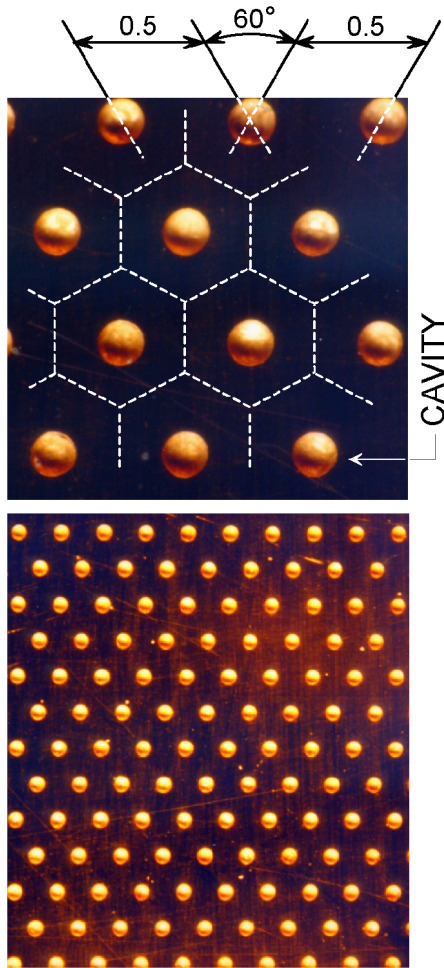


Fig. 5. Photograph showing the pattern of cavities on the heating plate used in the experiments with R11.

used a horizontal tube provided with a novel microstructure. Fig. 7 shows an example of the surface structures. Prior to presenting some experimental result obtained with R141b, the main steps of generating the structure are given next.

The microstructure shown in Fig. 7 is generated by electro-deposition in a galvanic process. The basic steps are illustrated in Fig. 8. A thin polycarbonate foil (thickness below 100 μm) is irradiated by heavy ions. This treatment creates ion-tracks in the foil which can be widened to micropores in an etching process. The density and the diameter of the pores can be altered by variation of ion density in the ion ray and the etching duration, respectively.

The treated foil is then affixed to the specimen and the ensemble subjected to a electrolytic process, in which the pores become filled by material deposition. In a further etching process, the foil is completely removed leaving behind pins metallurgically connected to the surface of the specimen. The height of the pins can be varied by the duration of the electro-deposition, but is limited by the foil thickness. Appropriate managing of the galvanic deposition may result in different shapes of the top of the elements. The whole process permits an almost continuous variation of the structure dimensions.

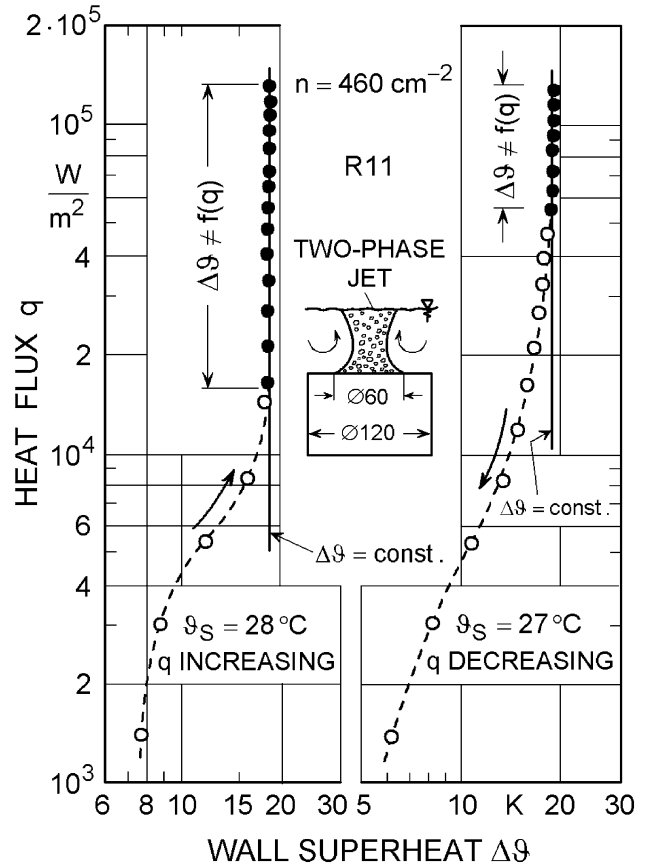


Fig. 6. Boiling characteristic of the surface shown on Fig. 5.

The height of the pin-shaped elements, having diameters between 1 μm and 25 μm, can be realized in the range from 10 μm to 100 μm, while the pin density can be varied from  $1 \times 10^4 \text{ cm}^{-2}$  to  $1 \times 10^7 \text{ cm}^{-2}$ . The structure can be created on cylindrical specimens like tubes in almost all electro-chemically depositable materials. For the purposes of the present investigations, both specimen (tube) and the structure are made of copper because of its high thermal conductivity and the advantages regarding the electro-deposition process.

Fig. 9 shows the boiling characteristic of the novel microstructure on a single horizontal tube (OD 18 mm, heated length 180 mm) with pool boiling. The heat flux  $q$  is taken to be independent of the circumferential position, but the wall temperature was obtained in the vertical and the horizontal planes of symmetry. The experimental uncertainty of the heat flux and the wall superheat  $\Delta T$  was less than 2% and 1.5%, respectively.

The different boiling characteristics observed at different circumferential positions of the tube are considered to be caused by free convection that affects the heat transfer particularly at the bottom of the tube. At the tube top, the wall superheat is practically independent of the heat flux, as required by Eq. (1). The slight reduction in  $\Delta T$  with rising  $q$  is not fully understood yet, but it could basically be caused by pins protruding the bubble surface.

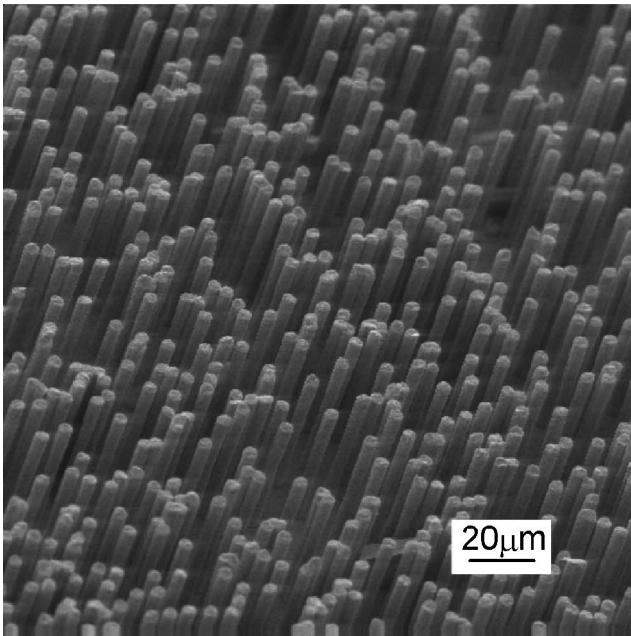
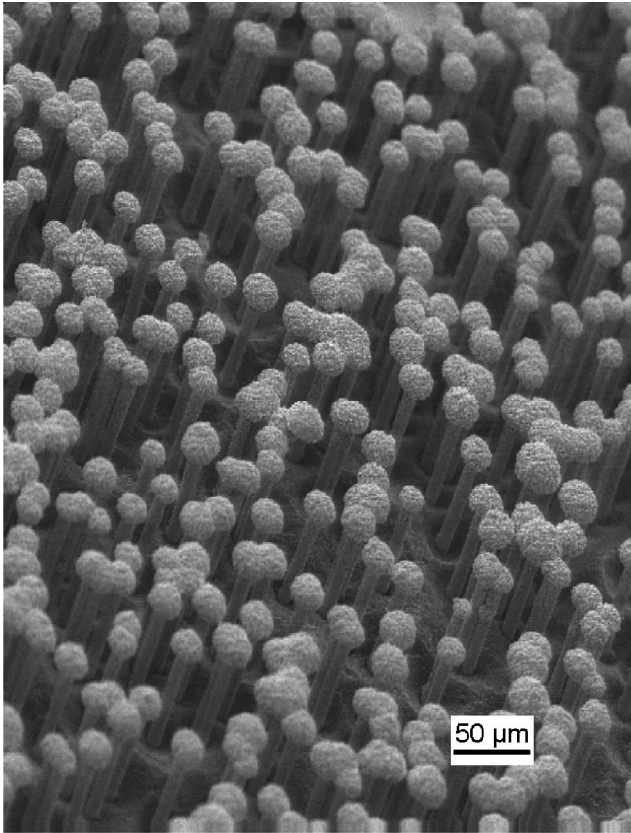


Fig. 7. Examples of surface structures consisting of micro pins.

Fig. 9(b) compares the novel structure with a plane tube, both investigated at the same apparatus. As is obvious from this Figure, the wall superheat increases with increasing heat flux for the plane tube. On the contrary, the wall superheat of the structured surface remains practically constant in the region of *fully developed* nucleate boiling.

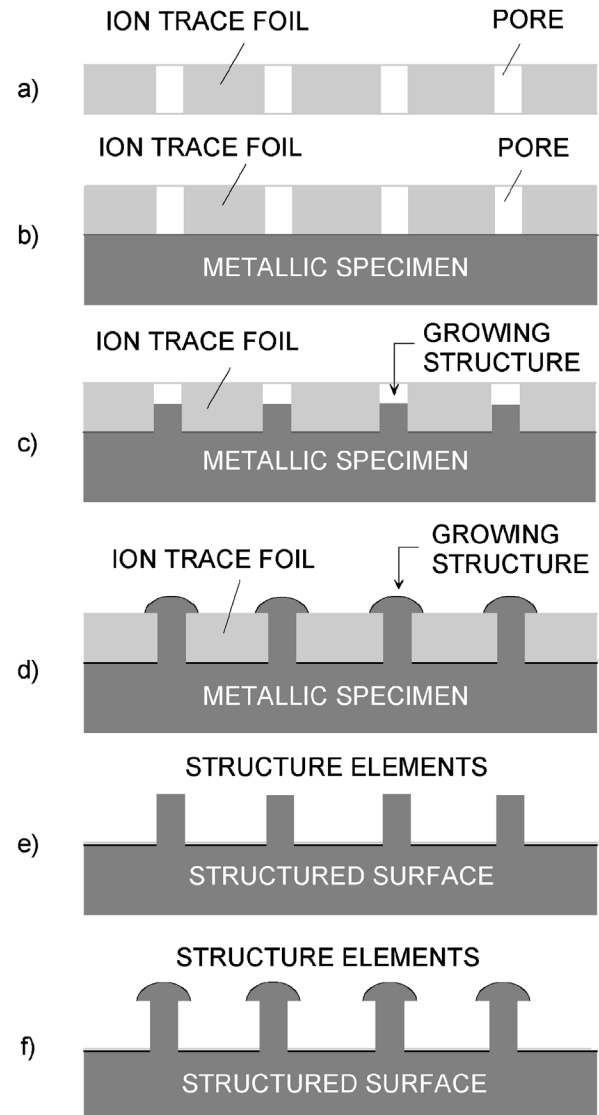


Fig. 8. Generation steps of a novel microstructure: (a) Ion-perforated poly-carbonate foil; (b) Foil affixed to specimen; (c) Electro-deposition process; (d) Structure elements with torospherical tops; (e) Structure after etching process; (f) Structure after etching process with torospherical tops.

*Isothermality of the boiling surface.* An explanation of the surface isothermality given in the following is based on a simple idea. As illustrated in Fig. 10, a growing vapour bubble interacts with several pins at a low system pressure, Fig. 10(a). The liquid layer underneath the bubble becomes thinner as the heat flux increases, Fig. 10(b). At a very high (near-critical) pressure, a growing bubble if sufficiently small interacts with only a few pins, Fig. 10(c). Depending on system pressure, that is, on the bubble size it may be expected that different number of pins pierce the interface if a liquid wedge is assumed sandwiched between the bubble and the wall, thus creating a TPL at any single pin with a strong evaporation, Fig. 11(a). In case of a motionless interface for a time period, the liquid evaporated at the TPL is replenished by a cross flow originating from the capillary action of the pins and by gravity, Fig. 11(b).

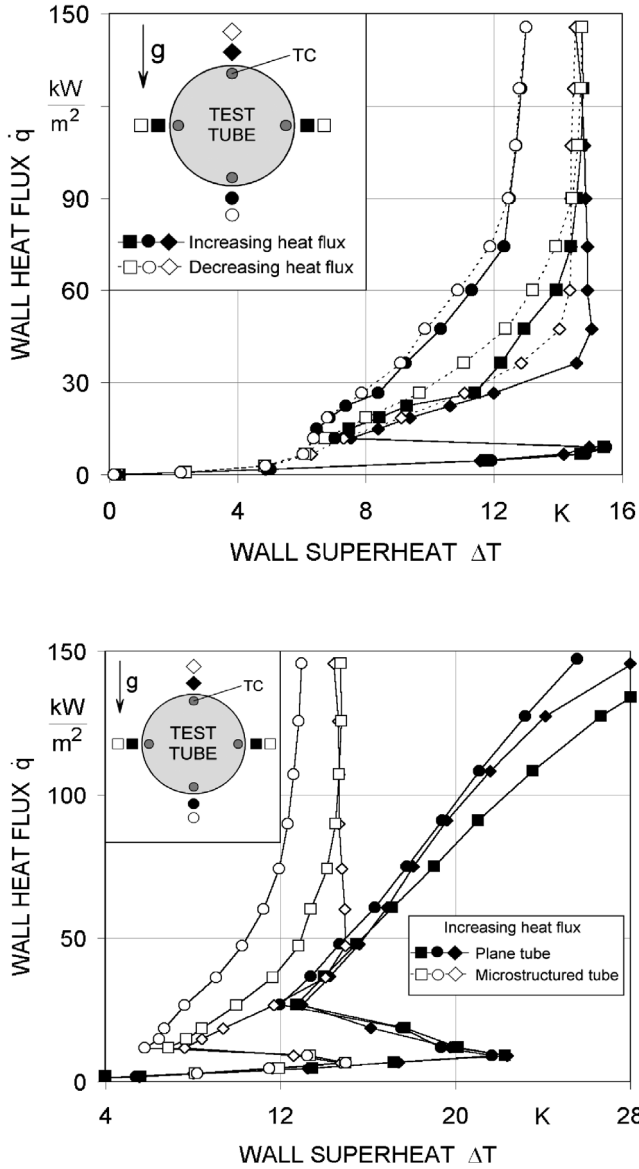


Fig. 9. Preliminary results of pool boiling of R141b on a tube surface provided with micro pins (a) and comparison with plain tube (b).

By this model, processes taking place at the TLP are essential for boiling kinetics. The TPL is the place of strong vapour production acting simultaneously as a heat sink. In a first approximation, the relationship

$$\bar{L}_{TPL} \sim \dot{Q} \quad (13)$$

is expected to hold, where  $\bar{L}_{TPL}$  denotes the length of the TPL and  $\dot{Q}$  the heat flow rate under common steady-state conditions; the bar refers to the averaged value.

The ratio  $\bar{L}_{TPL}/A$ , where  $A$  is the area of the heating surface, represents the surface density  $\bar{n}_L$  of the TPL,

$$\bar{n}_L = \frac{\bar{L}_{TPL}}{A} \quad (14)$$

thus

$$\bar{q} \sim \bar{n}_L \quad (15)$$

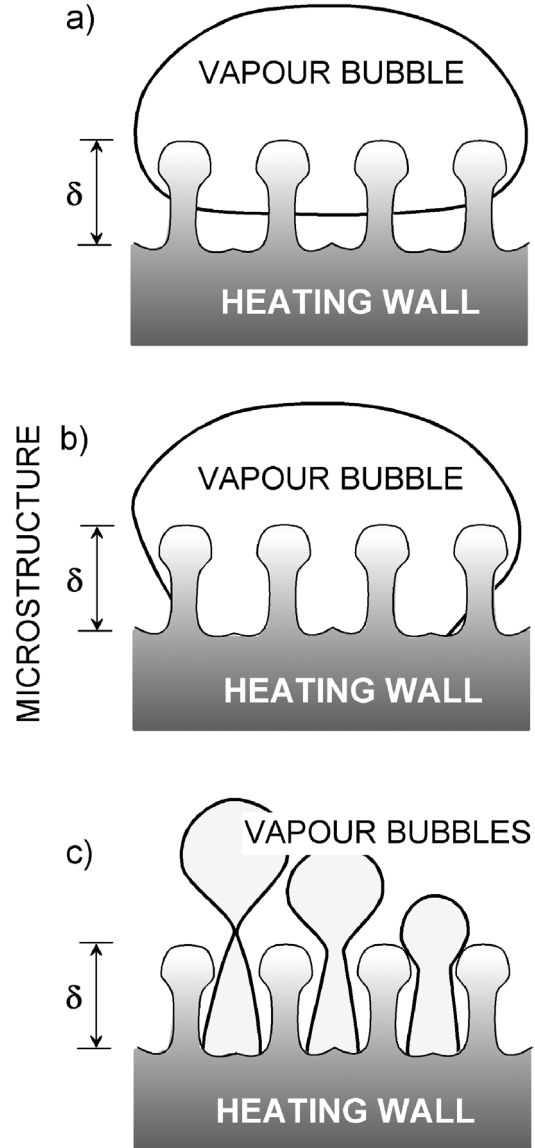


Fig. 10. Sketch of a vapour bubble growing on a surface with micro-pins: (a) Low pressure and/or low heat flux; (b) High heat flux; (c) High pressure.

with  $\bar{q} = \dot{Q}/A$  as the wall heat flux.

The length  $\bar{L}_{TPL}$  of the TPL depends on the surface structure, the number of growing bubbles, the size of each single bubble, and the angle the surface of the liquid wedge cuts the pins, Fig. 11(a). The quantity  $L_{TPL}$  of each single bubble is expected to change with time. Since its calculation for the whole surface is impossible, we will consider a representative vapour bubble.

Taking the bubble at the time  $t$  as semi-spherical of a radius  $r = r(t)$  without a dry-spot, Fig. 10(a), we obtain the length  $L_{TPL}$

$$L_{TPL} = \pi \cdot n \cdot d \cdot A = \pi^2 \cdot n \cdot d \cdot r^2 = f(t) \quad (16)$$

where  $n$  is the number density and  $d$  the diameter of the pins;  $A$  is the bubble surface area projected onto the heating surface,  $A = A(t) = \pi \cdot r^2(t)$ .

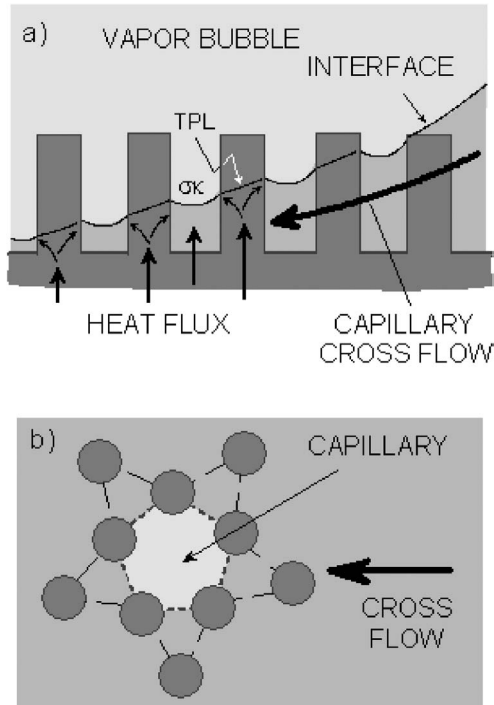


Fig. 11. Illustration of the effects of micro-pins on heat transfer: (a) Piercing the interface by pins results in a large TPL; (b) Cavity formed by neighbouring pins.

Furthermore, assuming the bubble growth to be governed by heat diffusion, we may expect a relationship<sup>6</sup>

$$r(t) = C(\kappa t)^{1/2} \quad (17)$$

where  $C$  is the growth constant and  $\kappa$  the thermal diffusivity, thus

$$L_{TPL} = (C\pi)^2 \kappa \cdot n \cdot d \cdot t \quad (18)$$

which gives a constant growth rate of the TPL,  $dL_{TPL}/dt = (C\pi)^2 \kappa \cdot n \cdot d$ , Fig. 12. The quantity  $L_{TPL, \min}$  corresponds to the vapour rest remaining in the structure after the bubble break-off.

This interesting result shows by the relation (13) that the heat flow  $\dot{Q}$  increases during the bubble growth at the same rate as the length of the TPL,

$$\dot{Q} \sim L_{TPL} = (C\pi)^2 \kappa \cdot n \cdot d \cdot t \quad (19)$$

Relating the length  $L_{TPL}$  to the projected bubble surface area,  $A = A(t) = \pi \cdot r^2(t)$ , we get the surface density  $n_L$  of the TPL and the heat flux  $q$  for a single bubble,

$$n_L = \pi n d \quad (20)$$

$$q \sim \pi n d \quad (21)$$

showing that the both quantities remain constant during the bubble growth time.

<sup>6</sup> This equation is usually derived by assuming the evaporation on the whole bubble surface. As can be shown, it is also valid for any part of the surface, thus also for the interline region.

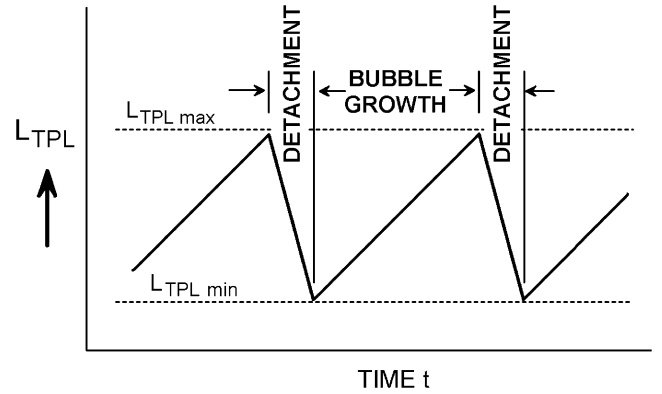


Fig. 12. Time history of TPL. After bubble detachment, the TPL does not disappear; its length  $L_{TPL, \min}$  corresponds to volume and shape of vapour rest for given structure.

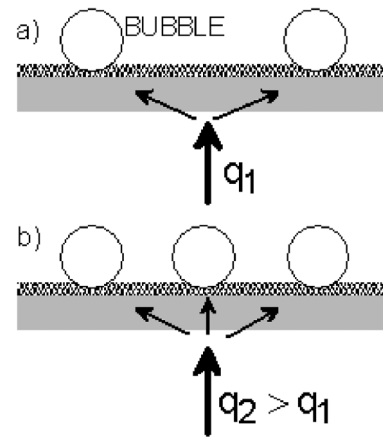


Fig. 13. Increase in bubble density at the same wall superheat.

To obtain an estimate of the quantity  $n_L$  we may set:  $n = 10^5 \text{ cm}^{-2}$ ,  $d = 20 \times 10^{-6} \text{ m}$ . Then,  $n_L = 2\pi = 6.28 \text{ m} \cdot \text{cm}^{-2}$ , which is surprisingly large; even for  $d = 1 \times 10^{-6} \text{ m}$ , we get  $n_L = (\pi/10) = 0.314 \text{ m} \cdot \text{cm}^{-2}$ .

Eq. (21) leads to the conclusion that the driving temperature difference  $\Delta T$  for any single bubble linearly depends on the thermal resistance  $R$ ,

$$\Delta T = q \cdot R \quad (22)$$

However, the growth of the TPL associated with bubble growth seems to act against the change in the thermal resistance  $R$  thus giving a constant wall superheat  $\Delta T$ . This interesting interplay does, however, not suffice to answer the question asked in connection with Eq. (1) regarding the compensation of the wall heat flux rise. With increasing heat flux both the frequency and the density of the bubbles increases. By Eq. (21), the heat flux is constant during a bubble cycle. The constancy of the wall superheat at various heat fluxes is decisively governed by the corresponding change in the bubble density, Fig. 13. As the activation of further bubbles in the structure is equally probable at any place of the surface, new bubbles become generated at the same surface superheat.

Despite its simplicity, this analysis provides an explanation of the independency of the wall superheat on the heat flux. Within the Theorem of Moderation, the *growth of the TPL*, associated with bubble density and bubble growth reduces the thermal resistance thus leading to a constant wall superheat.

The pins do not only act as generators of the TLP. They also tend to prevent (by capillary action) the formation of a dry spot beneath the bubble thereby improving the heat transfer. When a bubble detaches from the heater surface it is expected that the necking and break-off of the bubble occurs in the outer part of the capillary structure. The vapour rest remaining in a *capillary formed by neighbouring pins* acts as nucleus for the next bubble which drastically reduces both the waiting time and the energy barrier of bubble formation in comparison to a plane surface, Fig. 11(b).

Regarding the optimum distance of active bubble sites, the pin structure possesses some *self-regulating potential*. In contrast to artificial cavities that are fixed on the heating surface, the pin structure allows bubble formation at any place of the surface having a sufficient superheat. From this model it becomes obvious that the shape and number density of the pins will strongly affect the heat transfer. It is generally expected that, for pure liquids under optimal conditions, the number density of the pins must be increased with the pressure. This quantity could basically be connected with the bubble equilibrium [60], but its reliable determination would require precise experiments. In this way, we could tailor boiling structures in dependence of the system parameters that largely behaves according to Eq. (1).

This idea is basically not new. In 1963 J.W. Westwater [61] wrote in a very remarkable contribution entitled *Things We Don't Know About Boiling Heat Transfer*:

*“... in principle, it is possible to produce a tailor-made surface which will have a predetermined distribution of pore sizes and thus a predetermined boiling curve ...”*

Our guiding idea, however, contradicts somewhat to the Westwater statement regarding the distribution of pore sizes. We try to tailor a heating surface not with a distribution of pore sizes, but with a *mono-pin structure pattern formed by identical elements*. These elements communicate with each other through the liquid, which is not necessarily the case with cavities formed in the heating wall. In other words, an efficient surface should *not be provided with cavities but with protrusions of the same shape homogeneously distributed over the surface*.

The elements of the micro-structure can possess any shape. Fig. 14 illustrates an arbitrary shape of the elements arranged on the heating surface in a staggered pattern. The cross-section of each element should be the same, but there is not a specific requirement regarding its shape. However, as we are interested in a possibly long TLP, the border line of the cross-section of the element

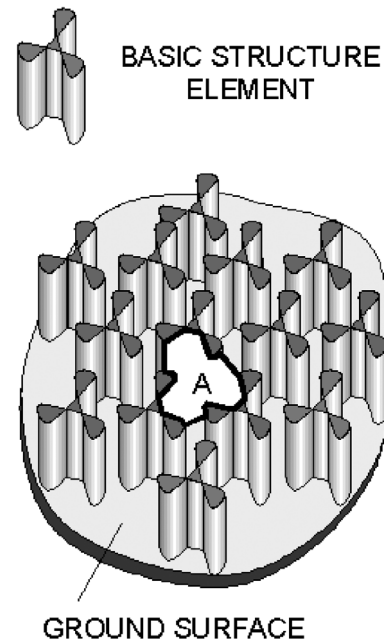


Fig. 14. Mono-element pattern of a surface structure; A represent a cavity formed by neighbouring surface elements.



Fig. 15. The von Koch fractal curve as border of the cross-sectional area of a structure element.

should not be smooth but composed of small pieces resulting in a zig-zag fashion of the envelope. In other words, this line should be a *fractal* like the coast line of an island [62]. Suitable for this purpose could be, for instance, the well-known von Koch curve giving islands of various shapes, Fig. 15.

The von Koch curve is one of the classical fractal objects. It is constructed from a line of length  $c$ . The central third of this line is replaced by two lines of the length  $c/3$  in a triangle form. This process is continued by replacing the central third of any line segment at each fractal step by two lines of the length  $c/3$ . The protrusion of the replacement is always on the same side of the curve. At each step the total length of the curve is increased tending to infinity as the number of steps goes to infinity, but the surface area  $A$  enveloped by the curve is finite,  $A = (2/5)c^2\sqrt{3}$ , if the basic line forms a triangle, Fig. 15.

The circumference of the structure element designed as the von Koch curve would provide a long TLP and, in addition, give rise to capillary action also along each element thus assisting in boiling kinetics.

## 5. Limits of the model

The above considerations rest on the assumption that an interface of a *concave* curvature already exists. However, depending on the cavity shape and the interaction liquid-wall, the vapour–liquid interface could principally be *convex* thus affecting both the equilibrium conditions and the driving temperature difference, Eq. (7). Also an attractive action of the wall on the liquid would alter the equilibrium conditions [37]. Furthermore, inert gases dissolved in the liquid or adsorbed on the heater surface could affect both the equilibrium state and the surface tension at the TPL. As discussed by Uhlig [63], the surface tension of liquids decreases with increasing fraction of gas dissolved in the liquid. In addition, the model gives no information about the wall superheat at the boiling incipience.

A further effect that should be mentioned in this context is the nonisothermality of the system. The model postulates the equilibrium at the vertex of the bubble of a constant interface curvature. Actually, micro-relief of the heater surface can affect the interface curvature in the region of the TPL. Furthermore, during the bubble generation the temperature of the interface is not constant so that a part of the free energy change of the system is bounded as latent heat required to keep the temperature of the interface constant when its area is increased, and the total interface energy  $\sigma - T(d\sigma/dT)$  would have to be considered when dealing with the equilibrium conditions and bubble growth.

## 6. Conclusions

The mechanisms of bubble generation in liquids have attracted the attention of many *natural philosophers* in 18th and 19th centuries. At the end of 19th century the knowledge in this area was at such a high level, that the ideas largely survived to the present time.

On the basis of these old ideas and a criterion by Hsu and Graham [6,43] the possibilities of creation of efficient surfaces regarding the nucleate boiling are discussed. It was found that surface structure must adjust itself when operating ideally. In other words the surface structure must have such properties that the heat transfer resistance decreases with rising heat flux. A structure consisting of appropriately arranged micro pins shows such a boiling behaviour in the region of fully developed nucleate boiling. The essential outcome of the considerations is that the boiling surface should be provided not with cavities (holes), as is usually recommended in the literature, but with identical protrusions.

## References

[1] J.W. Westwater, Boiling of liquids, *Advances in Chemical Engineering* 1 (1956) 1–76.

- [2] E.I. Nesis, Boiling of liquids, *Soviet Physics Uspekhi* 8 (1966) 883–907.
- [3] P.V. Carey, *Liquid–Vapour Phase-Change Phenomena*, Taylor and Francis, New York, 1992.
- [4] J.G. Collier, J.R. Thome, *Convective Boiling and Condensation*, Clarendon Press, Oxford, 1994.
- [5] J.R. Thome, *Enhanced Boiling Heat Transfer*, Hemisphere, Washington, DC, 1990.
- [6] Y.-Y. Hsu, R.W. Graham, *Transport Processes in Boiling and Two-Phase Systems*, Hemisphere, Washington, DC, 1976.
- [7] Anonymous, *Evangelista Torricelli*, *Engineering* 8 (1909) 136.
- [8] Th. Birch, *A History of the Royal Society of London*, Millar, London, 1756–1757.
- [9] G.S. Kell, Early observations of negative pressures in liquid, *Amer. J. Phys.* 51 (1983) 1038–1041.
- [10] Aristotele, *Meteorologica* (English translation by H.D.P. Lee), Harvard University Press, London, 1978.
- [11] T. Fairley, Notes on the history of distilled spirits, especially whisky and brandy, *The Analyst* 30 (1905) 293–306.
- [12] E. Halley, An Account of the Circulation of the watry vapours of the sea, and of cause of springs, *Philosophical Transactions of the Royal Society of London* 17 (1690/1691) 468–473.
- [13] H. Cavendish, in: E. Thorpe (Ed.), *The Scientific Papers*, Cambridge University Press, Cambridge, 1921 (particularly vol. II, Unpublished Papers, Theory of Boiling).
- [14] H. Cavendish, et al., The Report of the committee appointed by the Royal Society to consider of the best Method of adjusting the fixed Point of Thermometers; and the precautions necessary to be used in making Experiments with those Instruments, *Philosophical Transactions of the Royal Society of London* 67 (1777) 816–857.
- [15] J.A. De Luc, On evaporation, *Philosophical Transactions of the Royal Society of London* 82 (1792) 400–424.
- [16] J.A. De Luc, *Introduction a la Physique terrestre par les Fluids expansibles*, Nyow, Paris, 1803.
- [17] S.A. Dymont, Some eighteenth century ideas concerning aquaous vapour and evaporation, *Annals of Science* 2 (1937) 465–473.
- [18] S. Emeis, *Der Meteorologe und Geologe J.A. Deluc (1727–1817) und der Wandel naturwissenschaftlicher Sicht- und Denkweisen während seiner Schaffenszeit*, *Freiberger Forschungshefte (Montan- und Technikgeschichte)* D 207 (2002) 27–37.
- [19] F.C. Achard, *Nouveaux Mémoires de l'Académie Royale de Berlin* for 1784–1785.
- [20] J.L. Gay-Lussac, D'un Mémoire sur la déliquescence des corps, *Annales de Chemie* 82 (1812) 171–177.
- [21] J.L. Gay-Lussac, Note sur la Fixité du degré d'ébullition des liquides, *Annales de Chemie et de Physique* 7 (1817) 307–313.
- [22] F. Marcet, Untersuchungen über gewisse Umstände, welche auf die Temperatur des Siedepunktes der Flüssigkeit vom Einfluss sind, *Annalen der Physik und Chemie* 57 (1842) 218–241.
- [23] F. Rudberg, Über die Construction des Thermometers, *Annalen der Physik und Chemie* 116 (1837) 39–62.
- [24] M. Berthelot, Über einige Phänomene der gezwungenen Ausdehnung der Flüssigkeiten, *Annalen der Physik und Chemie* 158 (1851) 330–335; *Annales de Chemie et de Physique* 30 (1850) 232–237.
- [25] L. Dufour, Über das Sieden des Wassers und über eine wahrscheinliche Ursache des Explodierens der Dampfkessel, *Annalen der Physik und Chemie* 200 (1865) 295–328.
- [26] G. Krebs, Versuche über Siedeverzüge, *Annalen der Physik und Chemie* 133 (1868) 673–677; *Annalen der Physik und Chemie* 136 (1869) 144–151; *Annalen der Physik und Chemie* 138 (1896).
- [27] C. Tomlinson, On the action of solid nuclei in liberating vapour from boiling liquids, *Proceedings of the Royal Society* 17 (1869) 240–252.
- [28] J. Aitken, On boiling, condensing, freezing, and melting, *Transactions of the Royal Scottish Society of Arts Edinburgh* 9 (1878) 240–287.
- [29] I. Newton, *Opticks*, second ed., Innys, London, 1718.

- [30] A. Lavoisier, Elements of Chemistry, Translated by Kerr, Creech, Edinburgh, 1790.
- [31] J.T. Desaguliers, An attempt to solve the phenomenon of the rise of vapours, formation of clouds and descent of rain, Philosophical Transactions 36 (1729) 6–22.
- [32] R.J. Bosovich, Theoria Philosophiae Naturalis, Venetiis, 1763; English translation by J.M. Child: A Theory of Natural Philosophy, MIT Press, 1921.
- [33] W. Thomson (Lord Kelvin), On the equilibrium of vapour at a curved surface of liquid, The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science Series IV 42 (1871) 448–453.
- [34] J.W. Gibbs, On the equilibrium of heterogeneous substances, Transactions Connecticut Academy of Arts and Sciences 3 (1874–1878) 108–248.
- [35] J.J. Thomson, Applications of Dynamics to Physics and Chemistry, Macmillan, London, 1886.
- [36] J.W. Gibbs, Thermodynamische Studien (Deutsche Übersetzung von W. Ostwald), Engelmann, Leipzig, 1982.
- [37] J. Mitrovic, On the equilibrium conditions of curved interfaces, Internat. J. Heat Transfer 47 (2004) 809–818.
- [38] J.D. van der Waals, The thermodynamic theory of capillarity under the hypothesis of a continuous variation of density, J. Statist. Phys. 20 (1979) 197–224 (Translation by J.S. Rowlinson).
- [39] J. Mitrovic, On the profile of the liquid wedge underneath a growing vapour bubble and the reversal of the wall heat flux, Internat. J. Heat Mass Transfer 45 (2002) 409–415.
- [40] R.L. Webb, Principles of Enhanced Heat Transfer, Wiley–Interscience, New York, 1994.
- [41] M. Jakob, W. Fritz, Versuche über den Verdampfungsvorgang, Forschungsarbeiten auf den Gebiet des Ingenieurwesens 2 (1931) 435–447.
- [42] C. Corty, A.S. Foust, Surface variables in nucleate boiling, Chem. Engrg. Progress Sym. Ser. 51 (17) (1955) 1–12a.
- [43] Y.Y. Hsu, On the size range of active nucleation cavities on a heating surface, ASME J. Heat Transfer C 84 (1962) 207–216.
- [44] B. Yu, P. Cheng, A fractal model for nucleate pool boiling heat transfer, ASME J. Heat Transfer 124 (2002) 1117–1124.
- [45] P. Griffith, J.D. Wallis, The role of surface conditions in nucleate boiling, Chem. Engrg. Progress, Sym. Ser. 56 (30) (1960) 49–63.
- [46] J. Mitrovic, Survival conditions of a vapour bubble in saturated liquid flowing inside a micro-channel, Internat. J. Heat Mass Transfer 44 (2001) 2177–2181.
- [47] W.M. Rohsenow, Status of and problems in boiling and condensation heat transfer, Progr. Heat Mass Transfer 6 (1972) 1–44.
- [48] J.R. Howell, R. Siegel, Activation, growth, and detachment of boiling bubbles in water from artificial nucleation sites of known geometry and size, NASA TN-D 4101, 1967.
- [49] H.B. Clark, P.S. Streng, J.W. Westwater, Active sites for nucleate boiling, Chem. Engrg. Progress Sym. Ser. 55 (29) (1959) 103–110.
- [50] C.-Y. Han, P. Griffith, The mechanism of heat transfer in nucleate pool boiling, Internat. J. Heat Mass Transfer 8 (1956) 887–913.
- [51] A. Singh, B.B. Mikic, W.M. Rohsenow, Active sites in boiling, ASME J. Heat Transfer 99 (1976) 401–406.
- [52] K. Bier, D. Gorenflo, M. Salem, Y. Tanes, Effect of pressure and surface roughness on pool boiling of refrigerants, Internat. J. Refrig. 2 (1979) 211–219.
- [53] K. Cornwell, Naturally formed boiling site cavities, Lett. Heat Mass Transfer 4 (1977) 63–72.
- [54] Y. Fujita, The state of the art—nucleate boiling mechanism, in: Pool and External Flow Boiling, ASME, Santa Barbara, 1992, pp. 83–97.
- [55] S.M. You, T.W. Simon, A. Bar-Cohen, A technique for enhancing boiling heat transfer with application to cooling of electronic equipment, Proceedings IEEE/ASME ITherm 3 (1992) 66–73.
- [56] A. Bar-Cohen, Hysteresis phenomena at the onset of nucleate boiling, in: Pool and External Flow Boiling, ASME, Santa Barbara, 1992, pp. 1–14.
- [57] A.D. Messina, E.L. Park Jr, A new tool for nucleate boiling research, Chem. Engrg. Comm. 4 (1980) 69–76.
- [58] J. Mitrovic, Wärmeübergang bei der Verdampfung von R11 an einer ebenen Heizfläche mit künstlichen Vertiefungen, GVC – VDI Sitzung “Wärme- und Stoffübertragung” Bad Dürkheim 28/29 April 1988.
- [59] J.J. Wei, H. Honda, Effects of fin geometry on boiling heat transfer from silicon chips with micro-pin-fins immersed in FC-72, Internat. J. Heat Mass Transfer 46 (2003) 4059–4070.
- [60] J. Mitrovic, F. Hartmann, A new microstructure for pool boiling, Superlattices Microstruct. 35 (2004) 617–628.
- [61] J.W. Westwater, Things we don’t know about boiling heat transfer, in: J.A. Clark (Ed.), Theory and Fundamental Research in Heat Transfer, Pergamon Press, Oxford, 1963, pp. 61–73.
- [62] B.B. Mandelbrot, How long is the coast of Britain? Statistical self-similarity and fractal dimension, Science 155 (1967) 636–638.
- [63] H.H. Uhlig, The solubility of gases and surface tension, J. Phys. Chem. 41 (1937) 1215–1225.