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Nucleate boiling of refrigerant–oil mixtures: bubble equilibrium and oil enrichment at the interface of a growing vapour bubble

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Abstract

Equilibrium conditions of a vapour bubble, embedded in an infinite refrigerant–oil mixture, and oil enrichment at the interface of a bubble, growing in such a mixture are the main subjects of this paper. On the assumption of an ideal mixture behaviour and a non-volatile oil, an expression is derived that connects the temperature, the oil concnetration and the size of the bubble in equilibrium with the mixture. Using this expression, it is shown that oil, added to a refrigerant, can facilitate the bubble formation and improve the heat transfer. For this to occur, the oil must contain some surface active components. It is further demonstrated that the quantity of oil, corresponding to oil enrichment in the liquid due to bubble growth—the oil excess—suffices to envelop the bubble as a closed film already at a relatively low oil concentration. The film thickness increases as the bubble grows amounting to several monomolecular layers, if the oil excess is assumed to remain at the bubble surface. For the same bubble size, the number of such layers, 'the coverage number', is shown to be larger at a higher boiling temperature. When oil diffusion in the liquid occurs, a minimum driving temperature difference is needed for the film to establish. At a temperature difference above this minimum value, the oil film enveloping the bubble influences its growth kinetics. The film acts as 'an interphase' that must be passed through by refrigerant molecules to evaporate. © 1998 Elsevier Science Ltd. All rights reserved.

Nomenclature

a	thermal diffusivity
A	area
c	specific heat capacity
d	diameter of oil molecule
D	diffusion coefficient of oil molecules
Δh	latent heat of evaporation of refrigerant
Ja	Jakob number
k	coverage number
M	molecular mass
m	mass
N	Loschmidt number
n	number of molecules
p	pressure
q	heat flux
R	gas constant of refrigerant
r	actual bubble radius, equilibrium radius
t	time
T	temperature
V	volume
w	mass fraction of oil
x	mole fraction of oil.

Greek letters

α	heat transfer coefficient
δ	thickness of oil-rich layer, also diffusion layer
η	dynamic viscosity
ρ	density
σ	surface tension
ϑ	temperature
$\Delta\vartheta$	temperature difference.

Indices

L	liquid
Oil	oil

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s saturation
r at radius r
V vapour (pure refrigerant)
0 pure refrigerant
1 monomolecular coverage.

1. Introduction

Although the nucleate boiling of refrigerant–oil mixtures has been the object of numerous studies, the mechanisms of boiling heat transfer of such mixtures are still poorly understood [1–10]. This is probably associated with the large number of parameters that govern the heat transfer and the complexity of their mutual interactions that prevent desired insights into the boiling events. In nucleate boiling of mixtures, as in pure liquids, nucleation, growth, and departure of vapour bubbles are the key processes. In the case of a mixture, further phenomena such as selective adsorption on the heated surface and mass transfer in the phases are important. Selective adsorption changes the mixture composition in an ultra-thin liquid layer adhering to the heating surface in comparison with the bulk composition, and affects the bubble nucleation. If, for instance, the less volatile component (oil) is adsorbed in preference to the more volatile one (refrigerant), vapour bubbles must generate in a mixture region enriched with the less volatile species. This could require a larger superheat for bubble formation and lower the bubble density compared with the pure refrigerant. The interrelations can materially change if the oil contains some surface active components. Papers dealing with boiling of mixtures do not consider this phenomenon.

Mass transfer in boiling mixtures is caused by phase transition. A vapour bubble growing in a mixture withdraws mainly the more volatile component from the surrounding liquid. In a refrigerant–oil mixture, oil is practically non-volatile in the usual temperature range; the vapour in a bubble growing in such a mixture contains almost only the pure refrigerant. Thus the phase change results in an oil-rich liquid layer enclosing the bubble and the initially homogeneous liquid phase become inhomogeneous. This nonequilibrium state originates processes of mass transfer, such as diffusion, which tend to homogenise the mixture. However, it is not yet clear how far these processes can reduce the interfacial oil excess.

Phenomena of adsorption and processes of mass transfer have not been included in a detailed modelling of nucleate boiling heat transfer of mixtures considered. Heat transfer correlations are still of empirical nature and they are mostly mixture-specific [1]. On the basis of numerous experimental data, Anikin et al. [2] tried to develop a more general correlation. They formed dimensionless quantities, that should govern the heat transfer, using a model which also involved steps of mass transfer in the liquid phase. The expression recommended for calculating the heat transfer coefficient does, however, not provide the desired accuracy. Jensen and Jackman [4] performed an analysis of heat transfer including the mass transfer in the liquid layer immediately enclosing a growing bubble. The heat transfer equation from this analysis was proven by the authors comparing the calculated values with those of two experimental studies. A satisfying agreement was demonstrated at lower, but not at higher oil concentrations. The nature of the deviations between calculations and experiments at higher oil concentrations could put in question some of the model assumptions.

The addition of oil to a pure refrigerant usually causes deterioration in the heat transfer. In some cases, however, an improvement of heat transfer compared with pure refrigerant boiling under the same conditions is observed in the range of low oil concentration, e.g. [1, 3, 5–10]. A lowering of surface tension by addition of oil is usually considered to be responsible for such a boiling behaviour of mixtures, but no theoretical background supporting this idea has been offered so far.

The aim of this paper is to present some model considerations that could contribute to a better understanding of heat transfer with nucleate boiling of refrigerant-oil mixtures. Firstly, the dependence of heat transfer coefficients on surface tension of a mixture is examined on the basis of bubble equilibrium. For this purpose, a simple equation for the radius of a vapour bubble in equilibrium with the mixture is derived, assuming the mixture to behave ideally and the oil to be non-volatile. Secondly, the enrichment of oil at the interface of a growing bubble is discussed. The knowledge of this oil enrichment implies understanding of boiling events, that govern both the bubble kinetics and heat transfer. Our considerations indicate that the quantity of oil, corresponding to the oil enrichment in the liquid due to bubble growth mostly suffices to envelope the bubble as a closed film. Assuming this film to be built up of regular monomolecular layers, an equation is derived to calculate the number of such layers. This equation provides a means for explaining some phenomena with nucleate boiling of refrigerants by addition of oil, and in particular the deterioration in heat transfer. Examinations of mass transfer show that ordinary diffusion is unable to suppress the oil enrichment at the bubble surface and a closed oil layer is expected to envelop the bubble growing at common liquid superheats.

2. Equilibrium bubble in a refrigerant–oil mixture

2.1. An equation for the equilibrium temperature

The following considerations should lead to a relationship between the temperature and the size of a vapour

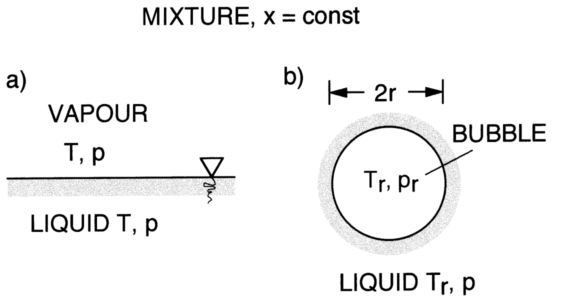

Fig. 1. Equilibrium of a vapour bubble in a refrigerant–oil mixture. Influence of curvature of the interface and mixture composition on the equilibrium temperature, (a) plane, (b) concave interface.

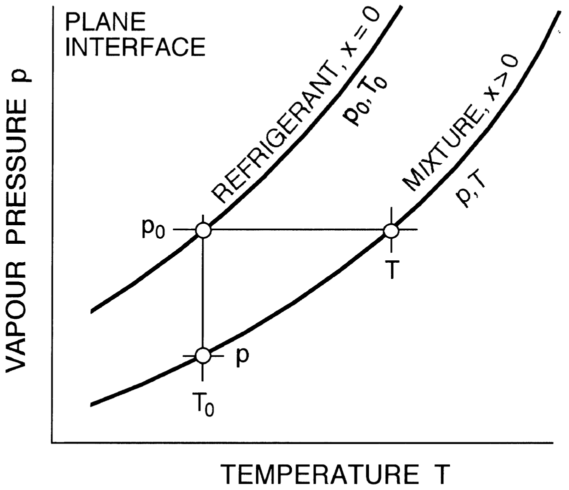

Fig. 2. Schematics of vapour pressure curves of pure refrigerant and refrigerant–oil mixture.

bubble in equilibrium with the mixture of given composition. The sketches in Fig. 1 should illustrate our task. They show two systems consisting of the same mixture; the vapour-liquid interface in Fig. 1a is plane, while it is concave in Fig. 1b. The pressure p in the liquid is the same in both cases and the corresponding equilibrium temperatures are T and T_r. The difference in these temperatures is to be determined.

According to our assumption, the mixtures should be homogeneous and ideal, the oil should be non-volatile. The vapour should consist of pure refrigerant only. The equilibrium temperature T of the system with the plane interface can then be approximated by

$$\frac{T-T_0}{T_0} = -\frac{RT}{\Delta h}\ln(1-x) \tag{1}$$

where T_0 and Δh denote the equilibrium temperature and the latent heat (enthalpy) of the refrigerant, R is its gas constant, and x is the mole fraction of the oil in the mixture, see, e.g. [11].

Equation (1) gives the isobaric rise of the boiling temperature of the mixture in comparison with the saturation temperature of the refrigerant. It is visualised in Fig. 2 for a constant value of x. The temperature of the mixture at a fixed pressure, say p_0, is larger than the corresponding one of the refrigerant. At a temperature T_0, the vapour pressure p of the mixture is less than p_0. The difference between them obeys the Raoult law,

$$p_0 - p = p_0 x. \tag{2}$$

Equations (1) and (2) are the basis of our examination of bubble equilibrium, which should be expressed in terms of the temperature. For this reason, we first relate the pressure p_r of the vapour in the bubble to the saturation pressure p_{rV} of the bubble surface thus gaining the Laplace–Thomson equation. A subsequent linearization of the Thomson equation then immediately results in the required temperature difference $T_r - T$.

The pressure p_r in the bubble is given by the well-known Laplace expression,

$$p_r = p + 2\frac{\sigma}{r} \tag{3}$$

where σ is the surface tension of the mixture and p the pressure in the liquid, Fig. 1. The saturation pressure p_{rV} may be obtained from the Thomson equation

$$p_{rV} = p - 2\frac{\sigma}{r}\frac{\rho_V}{\Delta\rho} \tag{4}$$

where p denotes the saturation pressure on the plane vapour–liquid interface of the mixture, ρ_V the vapour density, and $\Delta\rho = \rho_L - \rho_V$ the density difference[1].

Equations (3) and (4) may be combined to give the Laplace–Thomson equation,

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[1] Equation originally given by W. Thomson is valid for pure substances. Its use for binary mixtures has been discussed by Le Mer and Gruen [12]. It is worth mentioning—not only because of historical interest—that Thomson [13] already included binary systems into his considerations of equilibrium conditions at curved interfaces. Regarding the influence of an inert gas in the vapour phase on hydrostatic equilibrium, he noted: "Whether air be present above the free surface of the liquid in the several vessels or not, the condition of ultimate equilibrium is the same; but the processes of evaporation and condensation through which the equilibrium is approached will be very much retarded by the presence of air".

The Thomson reasoning is also applicable to liquid mixtures considered here. In this connection, a paper by Trimble [14] may be referred to.

$$\Delta p = p_r - p_{rV} = 2\frac{\sigma}{r}\frac{\rho_L}{\Delta\rho}. \tag{5}$$

The pressure difference Δp is illustrated in Fig. 3, showing that the actual pressure p_r in the bubble is larger by Δp than the saturation pressure p_{rV}. The vapour in the bubble at the equilibrium temperature of the plane interface is therefore condemned to condense and the bubble would disappear.

In order to prevent condensation, the temperature of the system with the bubble in Fig. 1b must be increased and, analogously to pure substances [15], the required temperature rise can easily be determined from equation (4). For this reason, the equation is derived with respect to T,

$$\frac{\mathrm{d}p_{rV}}{\mathrm{d}T} = \frac{\mathrm{d}p}{\mathrm{d}T} - \frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}T}\left(\sigma\frac{\rho_V}{\Delta\rho}\right) \tag{6}$$

and the derivative $\mathrm{d}p_{rV}/\mathrm{d}T$ replaced by the ratio $\Delta p/\Delta T$ of the differences, giving

$$\frac{\mathrm{d}p_{rV}}{\mathrm{d}T} \approx \frac{\Delta p}{\Delta T} = \frac{p_r - p_{rV}}{T_r - T} = \frac{2\frac{\sigma}{r}\frac{\rho_L}{\Delta\rho}}{T_r - T}. \tag{7}$$

Applying the same to the derivative $\mathrm{d}p/\mathrm{d}T$ of the vapour pressure on the plane surface of the mixture, Fig. 2, it follows that

$$\frac{\mathrm{d}p}{\mathrm{d}T} \approx \frac{p_0 - p}{T - T_0}. \tag{8}$$

Using equations (1) and (2), setting $p_0/(RT_0) = \rho_V$, equation (8) can be rearranged to give

$$\frac{\mathrm{d}p}{\mathrm{d}T} = -\frac{\Delta h \rho_V}{T_0}\frac{x}{\ln(1-x)}\left(1 + \frac{RT_0}{\Delta h}\ln(1-x)\right). \tag{9}$$

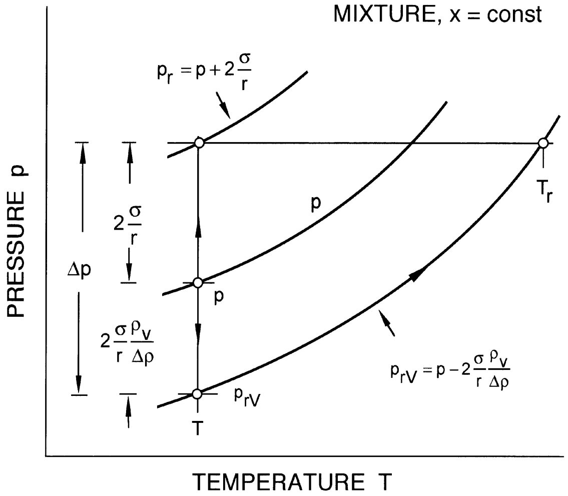

Fig. 3. Illustration showing mutual interaction between pressure and temperature in a vapour bubble. At a temperature T, the actual pressure in the bubble is larger by Δp than the saturation pressure. At the pressure p in the liquid, the required bubble equilibrium temperature is T_r.

Combining equations (6), (7), and (9), we obtain

$$\frac{2\frac{\sigma}{r}\frac{\rho_L}{\Delta\rho}}{T_r - T} = -\frac{\Delta h \rho_V}{T_0}\frac{x}{\ln(1-x)}\left(1 + \frac{RT_0}{\Delta h}\ln(1-x)\right) - \frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}T}\left(\sigma\frac{\rho_V}{\Delta\rho}\right). \tag{10}$$

The second term on the right-hand side of this expression may be omitted. The error introduced by this simplification can be neglected in most cases. Thus, with $\Delta\rho \approx \rho_L$, the equation becomes[2]

$$T_r = T - 2\frac{\sigma T_0}{r\Delta h\rho_V}\frac{\ln(1-x)}{x}\frac{1}{1 + \frac{RT_0}{\Delta h}\ln(1-x)}. \tag{11}$$

This equation expresses the equilibrium temperature T_r of the vapour bubble in Fig. 1 as a function of the bubble radius r and the oil fraction x in the mixture; T is the equilibrium temperature of the mixture, and T_0 the one of the pure refrigerant, both for plane interfaces.

At boiling temperatures common in refrigerating practice, the ratio $(RT_0)/\Delta h$ is considerably less than unity, $(RT_0)/\Delta h \approx 0.1$–$0.2$. For smaller values of x, say $x < 0.2$, equation (11) may therefore be simplified as

$$T_r = T - 2\frac{\sigma T_0}{r\Delta h\rho_V}\frac{\ln(1-x)}{x} \approx T + 2\frac{\sigma T_0}{r\Delta h\rho_V}(1 + 0.5x). \tag{12}$$

Supposing σ to be constant, this expression shows a larger difference between the temperature T_r and T at a smaller radius r and a larger oil fraction x.

For pure refrigerant ($x = 0$, $\sigma = \sigma_0$, $r = r_0$, $T = T_0$, $T_r = T_{r0}$), we have

$$T_{r0} = T_0 + 2\frac{\sigma_0 T_0}{r_0\Delta h\rho_V}. \tag{13}$$

Equations (12) and (13) are suitable for a comparison of equilibrium conditions of vapour bubbles in refrigerant–oil mixtures and in pure refrigerants. From the ratio $\Delta T/\Delta T_0$ of the temperature differences,

$$\frac{\Delta T}{\Delta T_0} = \frac{T_r - T}{T_{r0} - T_0} = -\frac{\sigma}{\sigma_0}\frac{r_0}{r}\frac{\ln(1-x)}{x} \approx \frac{\sigma}{\sigma_0}\frac{r_0}{r}(1 + 0.5x) \tag{14}$$

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[2] It should be noted that equation (11) deviates slightly from a corresponding equation given in [10] due to different approximations of the vapour equilibrium curve.

certain conclusions may be drawn. If the equilibrium bubbles in a pure refrigerant and in its mixture with an oil possess the same radii ($r = r_0$) and if an unchanged surface tension ($\sigma = \sigma_0$) is assumed, the difference of the saturation temperatures of the systems in Fig. 1 is larger for the mixture than for the pure refrigerant, $\Delta T > \Delta T_0$, $\Delta T/\Delta T_0 \approx 1+0.5x$. Conversely, at equal temperature differences, $\Delta T = \Delta T_0$, the equilibrium bubble is larger in the mixture than in the refrigerant, $r/r_0 \approx 1+0.5x$, at $\sigma = \sigma_0$.

The results obtained are also valid for other binary mixtures, which follow the same simplifications, that is, which behave ideally and possess only one volatile species. For considerations of bubble equilibrium in binary systems, consisting of both volatile components, the reader may be referred to literature, e.g. [16–18].

2.2. Consequences concerning heat transfer

When the same heated surface is used in boiling a refrigerant–oil mixture and its pure refrigerant, different boiling behaviours are observed at the same heat flux. This is partly caused by different conditions of bubble equilibrium in the two cases. For a rough estimation of the influence of these conditions on boiling, the differences ΔT and ΔT_0 of the equilibrium temperatures may be considered to be the superheats of the heated surface necessary for vapour bubbles just to exist in the mixture and in its pure refrigerant, respectively. Such conditions may be expected at low heat fluxes. From $q = q_0 = \alpha\Delta T = \alpha_0\Delta T_0$ and equation (14), we then get

$$\frac{\alpha}{\alpha_0} = -\frac{\sigma_0}{\sigma}\frac{r}{r_0}\frac{x}{\ln(1-x)} \tag{15}$$

where α and α_0 are the heat transfer coefficients of the mixture and the pure refrigerant at the same heat flux.

Equation (15) may be used to visualise the mutual interactions between heat transfer and surface tension σ. Since $x/\ln(1-x) \approx -1/(1-0.5x) \approx -1$, for small x, the equation tells us that the change of surface tension of refrigerant by addition of oil can cause an opposite change of heat transfer. In order to improve the heat transfer, the oil added must contain some surface active components to give $\sigma < \sigma_0$. With $\alpha/\alpha_0 > 1$, $\ln(1-x) \approx -x(1+0.5x)$ and $r = r_0$, equation (15) yields

$$x < 2\left(\frac{\sigma_0}{\sigma} - 1\right). \tag{16}$$

In this range of the mole fraction x, the nucleate boiling heat transfer of mixtures may improve in comparison with pure refrigerants.

Equations given so far are resting on the assumption of a single component oil. Actually, oils used in refrigerating techniques mostly consist of several components, some of which may be surface active. Viewed from the equilibrium conditions, which require the free energy of the system to be at minimum, the surface active components are expected to weaken not only the surface tension σ, but also the interactions between the refrigerant and the heating wall. The oil component, or components, adsorbed on the heated surface, could generate such a structure within the adsorbed layer that assists the nucleation process and rises the bubble density. It therefore seems most probable that both effects, namely, the reduction of bubble equilibrium temperature and increase in bubble density—caused by lowering of surface tension of mixtures—stimulate the phase change. They are likely to be the decisive steps within the chain of events responsible for the improvement of boiling heat transfer frequently observed at low oil concentrations.

The interrelation between the heat transfer and the surface tension expressed by equation (15) as well as the conclusion drawn are relying on several simplifications, such as ideal mixture behaviour and homogeneous oil distribution in the mixture; therefore the bubble kinetics is completely disregarded. In reality, however, the oil distribution in the liquid during the bubble growth is by no means homogeneous; the oil concentration increases at the bubble surface, and, moreover, in this region, the mixture hardly behaves ideally. The latter fact imposes a severe restriction on equation (15), which is certainly too simple to adequately describe the actual interrelations in broader parameter ranges. Particularly at higher oil concentrations, the positive effect of oil on heat transfer associated with change of surface tension is expected to become overshadowed by the processes of mass transfer that slow down the boiling kinetics.

3. Oil enrichment at the interface of a growing bubble

3.1. Coverage of bubble surface with oil and the coverage number

In boiling of a refrigerant–oil mixture, the bubble growth forces an enrichment of oil at the vapour–liquid interface. The oil concentration at the bubble surface is higher than in the bulk mixture and is governed by the processes of mass transfer. It reaches a maximum value when the oil transport relative to the bubble surface is precluded. The knowledge of the maximum interfacial oil concentration is important for several reasons. Therefore, the following questions should be asked:

Does the oil excess, caused by bubble growth, suffice to enclose the bubble as a continuous film?

Supposing such a film to be formed and to consist of regular monomolecular layers, what is then the number of these layers?

To answer these questions[3], we consider a spherical bubble, embedded and growing symmetrically in an infinite and initially homogeneous mixture, determine the oil excess caused by bubble growth, take it to cover an area monomolecularly and compare this area with the area of the bubble surface. We thereby specify the mixture composition by the mass fraction w, instead of the mole fraction x. The relation between them is

$$w = \frac{xM_{\mathrm{Oil}}}{xM_{\mathrm{Oil}} + (1-x)M_0} \tag{17}$$

where M_{Oil} and M_0 are the molecular masses of the oil and the refrigerant. The excess of oil in the liquid, arising from bubble growth, is easily determined by considering the vapour in the bubble to be the pure refrigerant. In such a case, we may think this vapour as withdrawn from a mass Δm of the mixture, consisting of a mass Δm_0 of the refrigerant and a mass Δm_{Oil} of the oil (Fig. 4). Since $\Delta m_{\mathrm{Oil}} = w\Delta m$, and $\Delta m_0 = (1-w)\Delta m$, we have

$$\Delta m_{\mathrm{Oil}} = \frac{w}{1-w}\Delta m_0. \tag{18}$$

If the bubble radius is $r(\Delta m_0 = 4r^3\pi\rho_{\mathrm{V}}/3)$, then

$$\Delta m_{\mathrm{Oil}} = \frac{4}{3}\frac{w}{1-w}r^3\pi\rho_{\mathrm{V}}. \tag{19}$$

Equation (19) expresses the oil excess in the liquid phase of the mixture due to bubble growth as a function of the actual bubble size, the vapour density ρ_{V}, and the initial oil fraction w.

On supposition of no oil removal from the bubble surface, the oil excess would be accumulated in a liquid layer of a thickness δ, as illustrated in Fig. 4. Such a layer would contain a further quantity $\Delta m_{\mathrm{Oil}w}$ of oil, corresponding to the initial oil fraction w. This oil quantity can be expressed using the volume V of the oil-rich layer ($\delta \ll r$),

$$V = 4r^2\pi\delta\left(1+\frac{\delta}{r}\right) \tag{20}$$

and the density ρ_{L} of the mixture,

$$\rho_{\mathrm{L}} = \frac{\rho_{\mathrm{L0}}}{1+\dfrac{\rho_{\mathrm{L0}}-\rho_{\mathrm{Oil}}}{\rho_{\mathrm{Oil}}}w} \tag{21}$$

as

$$\Delta m_{\mathrm{Oil}w} = V\rho_{\mathrm{L}}w = 4r^2\pi\delta\left(1+\frac{\delta}{r}\right)\frac{\rho_{\mathrm{L0}}}{1+\dfrac{\rho_{\mathrm{L0}}-\rho_{\mathrm{Oil}}}{\rho_{\mathrm{Oil}}}w}w. \tag{22}$$

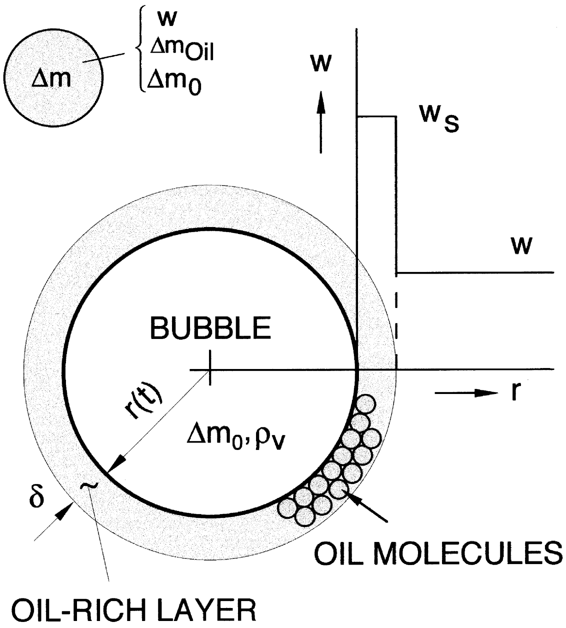

Fig. 4. Model illustrating the determination of the coverage number. The refrigerant withdrawn from the mixture leads to oil excess at the bubble surface. This oil usually suffices to create a film around the bubble that consists of several monomolecular layers.

The total mass of oil in the interfacial layer were thus $m_{\mathrm{Oil}\delta} = \Delta m_{\mathrm{Oil}} + \Delta m_{\mathrm{Oil}w}$, giving

$$m_{\mathrm{Oil}\delta} = \frac{4}{3}r^3\pi\rho_{\mathrm{V}}\left(\frac{w}{1-w} + \frac{3w}{1+\dfrac{\rho_{\mathrm{L0}}-\rho_{\mathrm{Oil}}}{\rho_{\mathrm{Oil}}}w}\frac{\rho_{\mathrm{L0}}}{\rho_{\mathrm{V}}}\frac{\delta}{r}\left(1+\frac{\delta}{r}\right)\right). \tag{23}$$

Rigorously viewed, equation (23) is incomplete. It does not account for any influence of the rapidity of bubble growth on the oil enrichment. This influence could basically become important in cases where the oil molecules possess a much larger inertia than the refrigerant ones and the bubble growth is very fast. When a bubble grows and accelerates the surrounding liquid—which consists of similar molecules, as in pure liquids—molecules, whose radial distance to the bubble surface is the same, possess the same (convective) velocity at all times. But in a mixture of different molecules, the molecules of larger inertia do not instantly assume the velocity of their surroundings. Hence, in refrigerant–oil mixtures, a slip of oil molecules in the refrigerant is expected to occur, resulting in a further enrichment of oil at the surface of a fast growing bubble. However, this effect is ignored in the present paper.

From equation (23), an average oil fraction w_{S} in the interfacial layer (Fig. 4) could be calculated as shown by Jensen and Jackman [4]. In the context of boiling kinetics,

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[3] It should be noted that Jensen and Jackman [4] in their analysis of mass transfer by diffusion in the liquid layer surrounding a vapour bubble assumed the oil fraction on the bubble interface to be $w = 1$. Starting from this assumption, they determined the thickness of, and an effective oil concentration within, the diffusion layer at the bubble interface at the moment of bubble break-off.

the coverage of bubble surface with oil, and particularly the question whether or not the oil mass $m_{\mathrm{Oil}\delta}$ is sufficient to create a closed film around the bubble, seems to be of a much greater importance. Because of this question, we obtain the number n of the oil molecules from

$$n = \frac{N}{M_{\mathrm{Oil}}} m_{\mathrm{Oil}\delta} \tag{24}$$

where $N = 6.025 \cdot 10^{26}\ \mathrm{kmol}^{-1}$ is the Loschmidt (Avogadro) number, and take these molecules to cover a plane surface monomolecularly at the densest packing. Assuming the oil molecules to be spheres, denoting their diameter by d, the area A, which can be covered with the oil, is

$$A = \frac{\sqrt{3}}{2} d^2 n. \tag{25}$$

This area may be expressed in terms of the actual area of the bubble surface, $A_r = 4r^2\pi$. Denoting the area ratio A/A_r by k, we get

$$4r^2\pi k = \frac{\sqrt{3}}{2} d^2 n. \tag{26}$$

Regarding equations (23) and (24), putting the thickness δ equal to the diameter of the oil molecules, $\delta = d$, equation (26) gives

$$k = \frac{\sqrt{3}}{6} d^2 r \frac{N\rho_{\mathrm{V}}}{M_{\mathrm{Oil}}} \left(\frac{w}{1-w} + \frac{3w}{1 + \dfrac{\rho_{\mathrm{L0}} - \rho_{\mathrm{Oil}}}{\rho_{\mathrm{Oil}}} w} \frac{\rho_{\mathrm{L0}}}{\rho_{\mathrm{V}}} \frac{d}{r} \left(1 + \frac{d}{r} \right) \right). \tag{27}$$

The definition of the quantity k and its numerical value obtained from this equation let us conclude that for $k \geqslant 1$ the bubble surface is completely covered with an oil film. The film is monomolecular for $k = 1$, bimolecular for $k = 2$, and so on. Since k represents the number of monomolecular oil layers, making up the film, this quantity should be called the coverage number in the following[4].

Equation (27) does not account for the increase of the reference area due to the oil layers already formed around the bubble. Because of this, the equation is not exact for $k > 1$, but the error is negligibly small as long as the thickness of the oil layer is much smaller than the bubble radius.

Equation (27) could principally be used for further discussions. But it is too cumbersome to illustrate some essential features of nucleate boiling of mixtures and should therefore be reduced a little more. In addition, it does not strictly respond to the question asked above. For these reasons, we will consider the diameter d of the oil molecules to be much smaller than the bubble radius allowing us to neglect the second term in the parenthesis, thus

$$k = \frac{\sqrt{3}}{6} d^2 r \frac{N\rho_{\mathrm{V}}}{M_{\mathrm{Oil}}} \frac{w}{1-w}. \tag{28}$$

This truncated equation gives practically the same results as equation (27) in late stages of bubble growth. It shows that the coverage number k is directly proportional to the bubble radius r; small bubbles are therefore not completely covered with oil. The radius $r = r_1$ of the bubble, covered with a closed monomolecular oil film, follows with $k = 1$ from equation (28) as

$$r_1 = \frac{6}{\sqrt{3}} \frac{1-w}{w} \frac{M_{\mathrm{Oil}}}{d^2 N \rho_{\mathrm{V}}}. \tag{29}$$

Given the mixture, which means, the quantities w, d, and M_{Oil}, the radius r_1 depends only on the vapour density ρ_{V}. In general, however, the densities of both mixture components (liquid refrigerant and oil) influence the radius r_1, as in equation (27). Like equation (28), equation (29) is valid for $r_1 \gg d$ only.

3.2. Importance of mass transfer at the bubble interface

3.2.1. Estimation of the coverage number

Equations (28) and (29) provide us with a means to visualise the states at the bubble surface and to follow the question of bubble coverage with oil. They are, moreover, suitable to emphasise the importance of mass transfer with nucleate boiling of mixtures in a simple way. Only the coverage number k is required for this. For $k > 1$, that is, for the radius r_1 less than the usual bubble departure radius, an oil film will envelop the bubble. The mass transfer is then expected to be significant during the further bubble growth.

To obtain a numerical value of the coverage number k, the diameter d of oil molecules and the molecular mass must be specified. We assume[5]: $d = 5 \times 10^{-10}$ m

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[4] The derivation of an equation for the coverage number could principally also have been started from an expression for the oil fraction w_{S} in the spherical layer enclosing the bubble (Fig. 4). The condition of the largest oil fraction ($w_{\mathrm{S}} = 1$) would have led to a layer thickness δ, and a comparison of this thickness with the diameter d of the oil molecules would then have given a coverage number. In this way, however, the existence of refrigerant molecules in this layer would be excluded, whereas equation (27) still allows the refrigerant molecules to occupy the empty places between the oil molecules.

[5] Some doubt may arise on the assumption that the molecules are spheres and on the magnitude of their diameter used for calculations. The oil molecules are probably elongated ellipsoids or possess a chain-like structure rather than being spheres adopted here. The equivalent diameter of the oil molecules, as determined by Rayleigh [19] from measurements of surface tension of water covered with a monomolecular oil film, is $d = 10 \times 10^{-10}$ m. This value might be too large because the thickness of the oil film was calculated from the weight of the oil droplet placed upon the clean water surface neglecting the amount of the oil absorbed by water. Data on density of molecules per unit of surface, as reported by Harkins and Roberts [20] for several liquids, give diameters d of molecules between 5×10^{-10} m and 8×10^{-10} m. The value $d = 5 \times 10^{-10}$ m used for calculations in this paper could indeed result in too low values of k.

Table 1
Coverage numbers and radii of monomolecularly covered bubbles for refrigerant R134a–oil mixtures depending on oil concentration

Oil mass fraction w	Departure radius experiments [3] r (mm)	Coverage number, equation (28) (k)	Bubble radius at monomolecular coverage, equation (29) r_1 (mm)
$\vartheta = 4.5°\text{C}$, $\rho_V \approx 16.7\ \text{kg m}^{-3}$			
0.000	0.220	—	—
0.005	0.170	1.24	0.136
0.020	0.080	2.37	0.034
0.050	0.065	4.97	0.013
0.100	0.060	9.68	0.006
$\vartheta = 31.8°\text{C}$, $\rho_V \approx 39.5\ \text{kg m}^{-3}$			
0.000	0.190	—	—
0.005	0.115	2.00	0.058
0.100	0.030	11.45	0.003

Bubble detachment radii were taken from experiments on refrigerant R134a–oil mixtures boiling on a horizontal cylinder (stainless steel, diameter 2.0 mm, heat flux $q = 18\ \text{kW m}^{-2}$, mineral oil Triton SE 55), Möller et al. [3]

and $M_{\text{Oil}} = 350\ \text{kg kmol}^{-1}$; we take the other properties, needed for calculations, from a paper by Möller et al. [3]. The results thus obtained are summarised in Table 1, which shows the experimental bubble departure radii, together with the corresponding coverage numbers, according to equation (28), and the bubble radii at the monomolecular ($k = 1$) coverage, calculated from equation (29).

As follows from Table 1, the coverage number, corresponding to bubble departure radius, is larger than one, $k > 1$. This means that the oil excess in the liquid due to bubble growth suffices in each particular case to create a closed film around the bubble consisting of several monomolecular layers. The coverage number k increases with the oil fraction w. The boiling temperature ϑ influences the bubble coverage not directly, but by vapour density. The increase in k with rising temperature is entirely due to the larger mass of refrigerant needed to generate a bubble of the same size, see equation (28).

The results of the above calculations illustrate the significance of mass transfer in nucleate boiling of mixtures. For example, at $\vartheta = 4.5°\text{C}$ and $w = 0.1$, the radius of the bubble, monomolecularly covered with oil, is $r_1 = 0.006$ mm, while the bubble departure radius is considerably larger, $r = 0.06$ mm. The bubble volume has thus risen by a factor of $(r/r_1)^3 = 1000$ under the influence of mass transfer. The radius r_1 may, therefore, be considered as a natural boundary between two periods with various kinetics of bubble growth. During the first growth period, that is, for $r(t) \leqslant r_1$, the mass transfer seems to play only a minor role; the bubble kinetics is then expected to be largely the same as with pure refrigerant. At approximately $r(t) = r_1$, the mechanisms and processes of mass transfer begin to act sensitively and involve themselves more and more into the bubble kinetics during the second growth period, $r(t) > r_1$. Some of these processes should briefly be discussed in the following, but no attempt is made to model them analytically here.

3.2.2. Mass transfer at the bubble surface

To explain the bubble growth in the second growth period, one would consider the processes of mass transfer to be able to prevent the bubble being covered with oil. These processes are the diffusion, the Marangoni flow, the natural, and the forced convection. The contributions of these processes to mass transfer are all different. Whereas the diffusion is always present, the others may be neglected under certain circumstances. Both the forced and the natural convection, expected to be less important, are disregarded within further considerations. The Marangoni flow is very complex; it lets only superficial insights into its origin, as shown below. The oil diffusion is viewed to be the decisive transport mechanism. It plays one of the central parts in the following examination of the conditions required for formation of a closed oil film around the bubble.

3.2.2.1. The ordinary diffusion. Ordinary diffusion at interfaces of fluid phases has been treated in a number of papers, e.g. by Ward and Tordai [21], in isothermal systems, by Scriven [22], in binary mixtures of both volatile components, and by Jensen and Jackman [4], at the interface of a vapour bubble growing in a refrigerant–oil mixture. Here, we wish to illustrate the mass transfer at the interface of a spherical vapour bubble growing symmetrically in an infinite mixture. In this case, the oil molecules are transported relative to the bubble surface only by diffusion. Our aim is to specify the condition for a closed oil film to form at the bubble surface. Beforehand, however, we should orientate ourselves about the nature of the processes occurring there and briefly state how these can be described by simple models.

Firstly, we should note again that the oil is non-volatile and the vapour in the bubble is the pure refrigerant. Because of this, the expanding interface of a growing bubble 'filters' the liquid phase, letting only the refrigerant molecules pass through into the vapour space (Fig. 5a). When evaporation continuously occurs and the interface expands, further oil molecules are steadily arriving at it. This is seen (by an observer moving with the interface) as a convective transport of oil molecules; it rises the coverage number in accordance with equation (28), as the bubble radius increases. The oil molecules, kept behind the interface, originate a diffusion process tending to transport the oil towards the liquid bulk. Thus there are two mechanisms that govern the interfacial mixture composition: the diffusion tends to lower, whereas the convection rises the oil concentration and, depending on the corresponding mass fluxes, the oil concentration at the interface increases, or even decreases, as time passes.

The actual process of mass transfer is too complex for an analytical treatment. The governing differential equations contain spatial and temporal changes of the quantities. The interface is moving. The initial and boundary conditions are not well definable. A closed analytical solution of this problem does not seem to exist yet. An analogous question, namely, the heat transfer to a vapour bubble, growing in a pure liquid, has been discussed by Forster [23]. The results he arrived at do not allow any explicit calculations. For this reason, and with sufficient accuracy for our present purpose, we should take another route in the analysis to follow and replace the actual physical picture by simple model processes. In the model, we consider the interface as a motionless, semipermeable membrane (permeable for refrigerant molecules) and allow the mixture to flow towards it; the internal region of the mixture, confined by the membrane, is supposed to be a volume sink (Fig. 5b).

Initially, the liquid is thought to be at rest. When the liquid flows radially towards the membrane concentration profiles form at the membrane thus starting the process of oil diffusion. The interplay between the diffusion and convection determines the interfacial mixture composition and the shape of these profiles. A rapid convection 'compresses' the profile of the oil concentration towards the membrane and the profile becomes steeper, while a quick diffusion 'stretches' it towards the bulk mixture.

In the following we will consider a specific situation, in which a liquid layer of a constant oil fraction w_S exists at the membrane. The thickness of such a layer is allowed to change with time so that its outer edge can move relative to the membrane. Outside this layer, the oil fraction w changes as sketched in Fig. 5b. The thickness $\delta(t)$ of the oil diffusion layer is equal to the penetration depth. We obtain this depth assuming the membrane to be plane and the liquid phase as semi-infinite. The penetration depth is then a function of the diffusion coefficient D only, and changes with the time t as $\delta(t) \sim (Dt)^{1/2}$, if D is

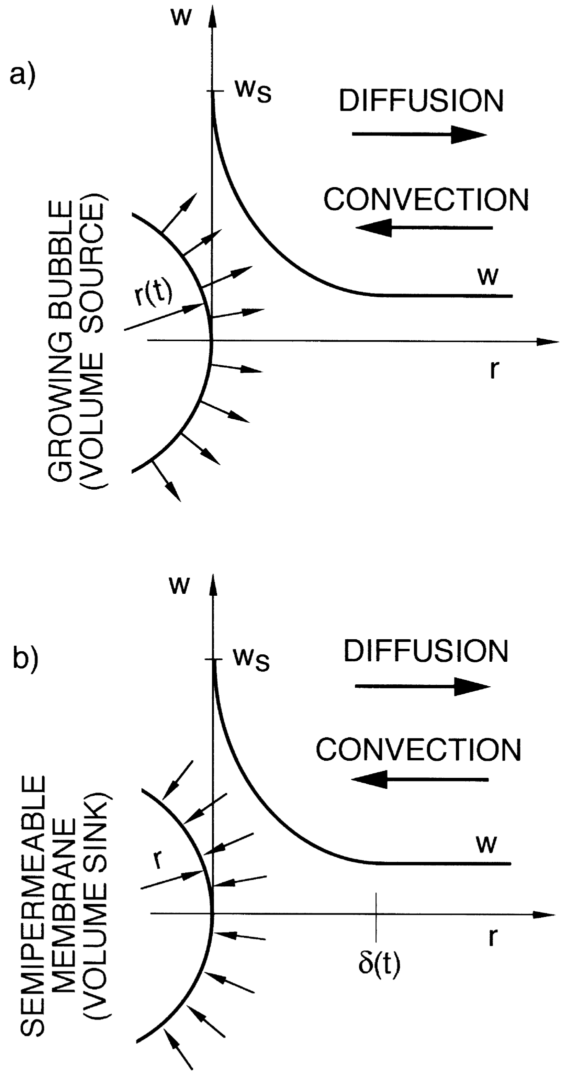

Fig. 5. Schematic illustration of mass transfer during the bubble growth in a refrigerant-oil mixture. (a) Expanding bubble surface (volume source) 'filters' the mixture resulting in an oil accumulation around the bubble. An observer moving with the interface realises the bubble growth as liquid convection. (b) Motionless semipermeable membrane representing the bubble surface; the liquid flows radially towards the membrane.

constant. Thus, the oil diffusion front penetrates the liquid at a velocity[6] $u_{\mathrm{Diff}} = \partial\delta/\partial t \sim (D/t)^{1/2}$.

The oil penetration is taking place not in a quiescent, but in flowing liquid. The liquid convection is acting against the oil diffusion. The velocity of this convention is not arbitrary in our model; it is dictated by the radial expansion of the bubble surface, for which a bubble growth relation may be adopted. Assuming the bubble growth to be thermally governed, we may use a relation of the form $r(t) \sim Ja(a_{\mathrm{L}}t)^{1/2}$ for the bubble radius r at the time t, where $Ja = (c_{\mathrm{pL}}\Delta\vartheta\Delta\rho)/(\rho_{\mathrm{V}}\Delta h)$ is the Jakob number and a_{L} the thermal diffusivity of the liquid. The radial velocity of the liquid at the stationary membrane is then $u_{\mathrm{L}} = (\rho_{\mathrm{V}}/\rho_{\mathrm{L}})\partial r/\partial t \sim Ja\rho_{\mathrm{V}}(a_{\mathrm{L}}/t)^{1/2}/\rho_{\mathrm{L}}$.

The velocities of the two movements, the diffusion and the convection, may be combined and used to visualise the state in the interfacial region. The velocity ratio,

$$\frac{u_{\mathrm{Diff}}}{u_{\mathrm{L}}} \sim \frac{1}{Ja}\frac{\rho_{\mathrm{L}}}{\rho_{\mathrm{V}}}\left(\frac{D}{a_{\mathrm{L}}}\right)^{1/2} \approx \frac{\Delta h}{c_{\mathrm{pL}}\Delta\vartheta}\left(\frac{D}{a_{\mathrm{L}}}\right)^{1/2} \qquad (30)$$

gives a suitable relation. It connects the physical properties with the driving temperature difference $\Delta\vartheta$. A variation of $\Delta\vartheta$ changes the velocity ratio of the two transport mechanisms; the temperature difference determines therefore the shapes of the concentration profiles and the mixture composition at the membrane.

In connection with bubble growth, it is of particular interest to obtain the temperature difference $\Delta\vartheta$, for which the two velocities become equal. The concentration profiles are then expected to move relative to the membrane, keeping unchanged their shapes. With $u_{\mathrm{Diff}} = u_{\mathrm{L}}$, we get from the expression (30) a criterion relationship

$$\Delta\vartheta = \vartheta_{\mathrm{L}} - \vartheta_{\mathrm{S}} \sim \frac{\Delta h}{c_{\mathrm{pL}}}\left(\frac{D}{a_{\mathrm{L}}}\right)^{1/2} \qquad (31)$$

where ϑ_{L} and ϑ_{S} are the liquid temperatures far from and on the bubble surface, respectively.

This result may be interpreted as follows:

At an actual temperature difference, which is larger than the theoretical one, given by equation (31), an enrichment of oil in the interfacial region of a growing bubble occurs such that at least a monomolecular film envelops the bubble. Below this temperature difference, the oil concentration at the interface is still larger than in the bulk mixture, but the oil diffusion is stronger than the convection and the formation of a closed oil film on the bubble surface is impossible.

This interpretation makes it desirable to obtain a numerical value of $\Delta\vartheta$, disregarding the uncertainties associated in the first place with the diffusion coefficient D of oil molecules. The diffusion coefficient depends on the state of the mixture and the nature of its components; it is expected to change in an unknown manner along the diffusion path, and seemingly only its order of magnitude can be estimated yet.

The diffusion coefficients in binary liquid mixtures usually lie in the range of about 10^{-9} m^2 s^{-1}. The thermal diffusivities of liquids range from nearly 10^{-6}–10^{-5} m^2 s^{-1}. Thus, with $a_{\mathrm{L}} = 5\times10^{-6}$ m^2 s^{-1}, $D = 10^{-9}$ m^2 s^{-1}, furthermore, with the properties of the refrigerant R134a at about 4°C, $\Delta h = 2\times10^5$ J kg^{-1} and $c_{\mathrm{pL}} = 1.3\times10^3$ J (kg K)$^{-1}$, the temperature difference $\Delta\vartheta$, obtained from equation (31), is nearly 2 K.

The theoretical value of $\Delta\vartheta$ lies quite close to the experimental ones. In this particular case, the model tells us that, for an actual driving temperature difference larger than 2 K, an oil layer will envelop the bubble. However, the obtained value of $\Delta\vartheta$ is incorrect, even within the model, which is due to the proportionality constants, all taken to be unity. The usual value of the proportionality constant is approximately 4 in the penetration depth $\delta(t)$, and $2/\sqrt{\pi}$ in the bubble radius expression $r(t)$. When considering these values, the proportionality constant in equation (31) is $2\sqrt{\pi}$, giving a temperature difference of $\Delta\vartheta \approx 4\sqrt{\pi} \approx 7$ K, instead of 2 K. If we use the constant $2\sqrt{3/\pi}$ in $r(t)$, as adopted in [4], the temperature difference becomes approximately 4 K. However, these values of $\Delta\vartheta$ are below those encountered in boiling practice, where the temperature difference in nucleate boiling region of mixtures mostly lies above 10 K.

Supposing the physical properties used for the exemplary calculations are representative for refrigerant–oil mixtures, we may, within the model restrictions, emphasise that the Fickian diffusion is unable to prevent the oil accumulation at the surface of a growing bubble[7]. The question whether or not the amount of oil liberated during the bubble growth suffices to envelop the bubble as a closed film, decisively depends on the initial oil fraction in the mixture. The lowest value of this fraction may be obtained from equation (29), requiring the actual bubble radius r to be larger than the radius at the monomolecular coverage r_1.

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[6] This velocity u_{Diff} obtained in this way is actually related to the outer edge of the layer having constant oil concentration. The penetration velocity relative to the membrane depends also on the thickness of this layer and the entire could be treated as Stefan's problem. However, for reasons of simplicity, we neglect the movement of the boundary. For the same reason, the liquid layer of constant composition at the interface is not indicated in Fig. 5.

[7] In connection with these results, it is interesting that much larger values of $\Delta\vartheta$ are required to prevent the thermal layer, enveloping a growing bubble, to penetrate the liquid. With $D \equiv a_{\mathrm{L}}$, equation (31) yields $\Delta\vartheta \sim \Delta h/c_{\mathrm{pL}}$.

3.2.2.2. Some critical remarks. Equation (31) contains two simplifications, associated with the velocities u_{Diff} and u_{L}, which we have not stated explicitly so far. The first one is concerned with the bubble growth expression that accounts for the thermal effects only. In the case of a mixture, the processes of mass transfer may dominate the bubble growth and the relation adopted for $r(t)$ might become questionable. The second simplification is concerned with the time t. The expression for u_{Diff} requires a liquid layer of a constant concentration at the bubble surface. Such a layer is formed when a monomolecular oil film envelopes the bubble. The time origin in this expression may therefore be considered to coincide with the instant of the formation of the first monomolecular oil layer at the bubble surface. Since the origin of the time in u_{L} is the beginning of bubble growth, the quantity time in the two velocities has not the same origin. We now wish to remark on these simplifications.

Regarding the influence of mass transfer on bubble growth, we may view the temperature difference in equation (31) as an effective quantity, which implicitly accounts for this influence. If written explicitly, the equation becomes

$$\Delta\vartheta \sim \frac{\Delta h}{c_{\mathrm{pL}}}\left(\frac{D}{a_{\mathrm{L}}}\right)^{1/2}\left(1-(y-x)\left(\frac{a_{\mathrm{L}}}{D}\right)^{1/2}\frac{c_{\mathrm{pL}}}{\Delta h}\left(\frac{\partial\vartheta}{\partial x}\right)_{\mathrm{p}}\right) \qquad (32)$$

where x and y are the mole fractions of one of the components in the liquid and vapour phase, $(\partial\vartheta/\partial x)_{\mathrm{p}}$ is the slope of the bubble-point-line of the mixture at constant pressure.

Equation (32) follows immediately from the model, if the bubble growth expression takes into account diffusion mass transfer in the liquid phase. At small values of $(\partial\vartheta/\partial x)_{\mathrm{p}}$ and $(y-x)$, the influence of mass transfer, represented by the second term in the parenthesis, can be neglected, resulting in equation (31). However, this term is positive so that equation (32) gives larger values for $\Delta\vartheta$ than does equation (31). Equation (32) is valid for a binary mixture of both volatile components; it is not unlimitedly applicable in our case. If an oil film at the bubble is formed, then, not the Fickian diffusion, but other mechanisms govern the mass transfer. This is discussed further below.

As mentioned above, the origin of the time in the expressions for the two velocities is not the same, because the diffusion (penetration) equation requires a liquid layer of a constant concentration to envelop the bubble. To get an idea about the span between the two time origins, we assume a monomolecular oil layer at the bubble surface. The time t_1, which elapses from the start of bubble growth to the formation of this layer, may be estimated from the expression $r(t) = (2/\sqrt{\pi})Ja(a_{\mathrm{L}}t)^{1/2}$ as

$$t_1 = \frac{\pi}{4}\frac{r_1^2}{a_{\mathrm{L}}Ja^2} \qquad (33)$$

where r_1 is the bubble radius at the monomolecular coverage. For example, at $r_1 = 120\times10^{-6}$ m (almost the largest value in Table 1, giving the largest time t_1), further, with $a_{\mathrm{L}} = 5\times10^{-6}\ \mathrm{m^2\ s^{-1}}$ (used above), and a Jakob number $Ja = 3$, we get from expression (33) $t_1 = (4\pi/5)\times10^{-4}$ s. The total growth period of bubbles, as may be deduced from the experiments by Möller et al. [3], is at least one order of magnitude larger.

In connection with bubble coverage, the interaction between oil molecules also needs to be mentioned. If at the interface of a growing vapour bubble a coherent oil film is formed, the oil molecules, making up its outer edge, must undergo a dissolution process prior to becoming individual particles capable of diffusion. The processes of dissolution[8] are analogous to those occurring in the interfacial region of two mutually soluble pure liquids that mix by inter-diffusion, and the experiments of May and Maher [24] with isobutiric acid and water may give some idea about their kinetics. The essence of their experiments, as far as our task is concerned, are the very small diffusion coefficients (measured values $10^{-18}\ \mathrm{m^2\ s^{-1}}$) in the interfacial region and very slow disappearance of the interface. The measurements were undertaken at states of the system not too far away from the critical point of the mixture (involving small differences in the chemical potentials), and the authors attributed these findings to the action of gravity. However, although gravity might play some role, the slow disappearance of the interface is seemingly dictated by the molecular processes of generation of single molecules.

The diffusion coefficients D of oil molecules in refrigerant-oil mixtures are expected to be smaller than the value taken above for the numerical illustration, particularly at low boiling temperatures T. This is indicated by the Sutherland–Einstein expression, $D\eta/T = \mathrm{const}$, where η is the dynamic viscosity of the mixture [25, 26]. Since the viscosity increases with rising oil fraction and reducing temperature, the expression gives smaller diffusion coefficients at lower temperatures and higher oil concentrations, i.e., in the mixture region near the bubble surface. The constant in this expression depends on the shape of diffusing species and takes the largest value for the spherical one. For oil molecules, probably having a complex structure, corresponding low values of the constant are expected to result in low diffusion coefficients, and, by equation (31) in small $\Delta\vartheta$.

Using the Sutherland–Einstein expression, equation (31) may be written as

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[8] These processes could be viewed as evaporation of oil molecules into the liquid refrigerant at a latent heat which were much less than in common evaporation, because the movement of the dissolved (evaporated) oil molecules is dictated by the molecular structure of the liquid refrigerant resulting in a low kinetic energy of the evaporated molecules in comparison to the true vapour state.

$$\Delta\vartheta = \mathrm{const}\cdot\frac{\Delta h}{c_{\mathrm{pL}}}\left(\frac{T}{a_{\mathrm{L}}\eta_{\mathrm{L}}}\right)^{1/2}. \tag{34}$$

The ratio $\Delta h/c_{\mathrm{pL}}$ decreases, while $T/(a_{\mathrm{L}}\,\eta_{\mathrm{L}})$ increases with rising temperature. The latter ratio seems to change much stronger with the temperature than the former one and a decrease in the temperature will result in a smaller $\Delta\vartheta$. It is interesting that $\Delta\vartheta$, expressed in equations (31) and (34), takes the nature of a physical property of the mixture at the given temperature.

3.2.2.3. The Marangoni convection. The results presented so far are confined to a spherical vapour bubble growing symmetrically in an infinite mixture. But in reality, the temperature in the liquid surrounding the bubble is inhomogeneous and the evaporation rate is not the same everywhere at the bubble surface (Fig. 6). The variation of the evaporation rate is accompanied by a variation of the oil concentration along the bubble surface which, like a temperature change, generates a gradient of surface tension. The latter tends to create a flow in the interfacial region. Therefore, the interfacial or the Marangoni convection could reduce the oil surplus at the bubble surface and should generally be considered under ordinary boiling conditions.

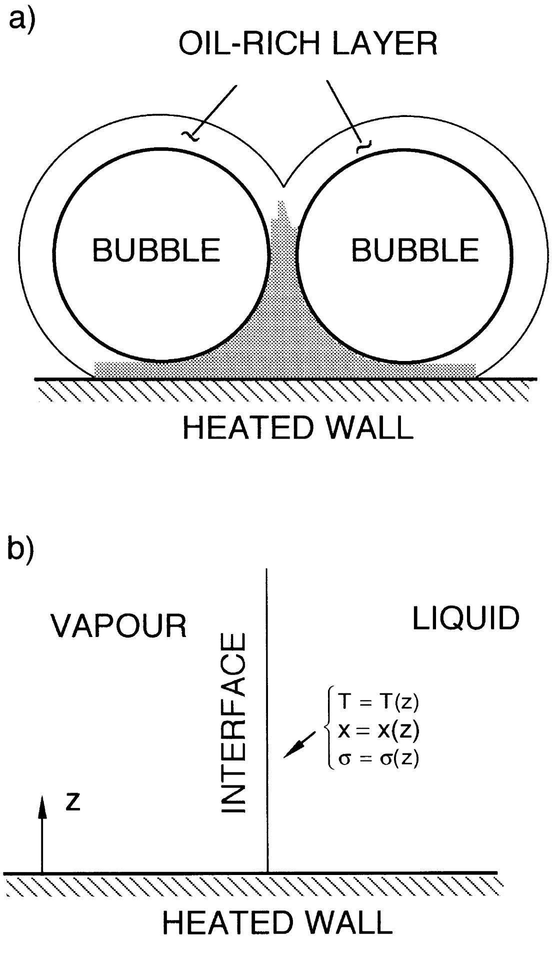

Fig. 6. Oil-rich layer at the interface of bubbles expected to form under real boiling conditions. (a) The shaded area indicates regions with a largely hindered mass transfer. (b) Along the vapour-liquid interface, the surface tension σ changes due to variation of both the temperature T and the oil fraction x.

In case of refrigerant–oil mixtures, however, it seems questionable if during the short period of time the vapour bubble adheres to the heated surface, such a flow originates at all[9]. In order to essentially influence the mass transfer at the bubble, this convection would have to develop simultaneously with the bubble, which appears less probable due to the rise of liquid viscosity in the interfacial region. Moreover, the change of oil concentration can oppose the effect arising from the temperature change. This follows from the expression

$$\frac{\mathrm{d}\sigma}{\mathrm{d}z} = \left(\frac{\partial\sigma}{\partial T}\right)_{\mathrm{x}}\frac{\mathrm{d}T}{\mathrm{d}z} + \left(\frac{\partial\sigma}{\partial x}\right)_{\mathrm{T}}\frac{\mathrm{d}x}{\mathrm{d}z} \tag{35}$$

that assumes the vapour–liquid interface to be orthogonal to the heated wall (Fig. 6b).

Usually, one expects the temperature T and the oil fraction x to decrease with z during the bubble growth; the sign of $\mathrm{d}\sigma/\mathrm{d}z$ is then determined by the signs of the partial derivatives $(\partial\sigma/\partial T)_{\mathrm{x}}$ and $(\partial\sigma/\partial x)_{\mathrm{T}}$. Whereas $(\partial\sigma/\partial T)_{\mathrm{x}}$ is negative, the derivative $(\partial\sigma/\partial x)_{\mathrm{T}}$ is positive, if there are no surface active components in the mixture. Thus depending on the values of these derivatives, the total change $\mathrm{d}\sigma/\mathrm{d}z$ can be positive or negative. At $\mathrm{d}\sigma/\mathrm{d}z = 0$, that is, for

$$\left(\frac{\partial\sigma}{\partial T}\right)_{\mathrm{x}}\left(\frac{\partial T}{\partial x}\right)_{\sigma}\left(\frac{\partial x}{\partial\sigma}\right)_{\mathrm{T}} = -1 \tag{36}$$

a stagnation line is established on the bubble surface. This line separates two areas from each other, and interfacial flows, if developed in these areas, will have opposite directions. For the case that equation (36) holds in a certain region of bubble surface, this region would behave as rigid regarding the Marangoni flow.

Taken together, if originated, the Marangoni convection could basically reduce the oil surplus at the bubble surface. But its development during the short period of bubble adherence to the heated surface seems unlikely under usual boiling conditions.

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[9] With respect to interfacial convection, it is of interest that, in the case of spreading of non-volatile oils on the surface of water, relatively high spreading velocities were observed. According to Marangoni's estimations [27], the spreading velocity is about 2 m s^{-1}. More accurate measurements by Landt and Volmer [28] gave values between 0.1 m s^{-1} and 0.6 m s^{-1}.

3.2.3. Channelling of refrigerant molecules—a new view of mass transfer at the bubble interface

Based on the foregoing considerations of mass transfer, we may state that the ordinary diffusion and Marangoni convection are not able to prevent the formation of an oil layer around the bubble in all cases. This raises the question of the actual mass transfer mechanism that governs the growth kinetics of a bubble covered with oil. A satisfactory answer to this question requires thorough investigation of transport processes in mixtures on molecular level and determination of the structure within the interfacial region. The question is too fundamental to allow a simple treatment. Nevertheless, some principal notions about the mass transfer seem possible.

The complex-shaped oil molecules (and/or much larger than the refrigerant ones) are likely to arrange themselves in the interfacial region such that a permeable oil layer builds up at the bubble surface thus creating a 'new' phase within the mixture, 'an interphase' (Fig. 7). The properties of this interphase are neither those of the bulk mixture nor of the pure oil. In order to let the bubble grow, the interphase must allow the refrigerant molecules to pass through; it therefore must be porous and its skeleton stretchable. On their way towards the vapour, the refrigerant molecules pass the interphase by a movement, which is similar to Knudsen's diffusion and which should be termed 'the channelling' process.

The channelling scenario can be pictured as the expansion of the interface, caused by the continuous bubble growth, leading from the macroscopic point of view to a permanent, but at the molecular level to a shock-like change in the structure of the interphase. This expansion does not allow the interphase to reach the equilibrium state. Even the statistical equilibrium of the oil molecules may be influenced by the expansion process, although the time needed for an attainment of this equilibrium is exceedingly short (order of magnitude 10^{-10} s, and less, or d^2/D, where d is the diameter of molecules and D their diffusion coefficient). While expanding, the interface opens itself for receiving further molecules, forcing the oil molecules to rearrange thus creating new channels within the interphase. The refrigerant molecules, being smaller than the oil molecules, 'take' any opportunity to slip through these channels from the liquid next to the interphase towards the vapour phase, as illustrated in Fig. 7.

The channelling of refrigerant molecules implies surmounting of an energy barrier offered by the interphase. An analytical description of this barrier and its action on phase change under dynamical conditions is by no means a simple task. As the author is aware, no attempts have been undertaken to model the mass transfer through an expanding interphase. However, basic notions of such a modelling could be received from studies dealing with evaporation through stationary, insoluble liquid films, e.g. [29]. In this connection also the experiments by Tang et al. [30] should be mentioned.

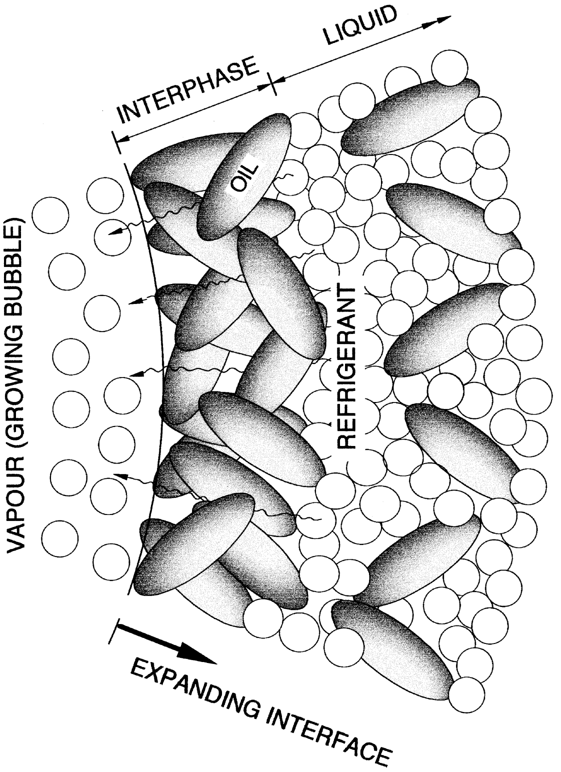

Fig. 7. A 'snapshot' of the state at bubble surface. Channelling of refrigerant molecules through 'the interphase'. The interphase is expected to form when the oil convection, caused by bubble growth, overcomes the oil diffusion. The expansion of the interface due to bubble growth permanently rearranges the oil molecules and creates new channels in the interphase through which the oil molecules slide from the liquid into the vapour phase. The shapes and sizes of the molecules should only illustrate their differences.

It is likely that the arrangement of oil molecules in and hence the permeability of the interphase depend on the evaporation rate. Higher evaporation rates, established at higher heat flux, lead to a faster expansion of the interface. This might result in a less ordered structure of the interphase, on average, which could raise its permeability and facilitate the boiling heat transfer. At fixed heat flux and oil concentration, the permeability of the interphase is a function of both the size and shape of the involved molecules. The channelling resistance to refrigerant molecules and therefore the heat transfer will depend on the refrigerant-oil pair.

4. Discussion of some boiling phenomena

4.1. Heat transfer reduction by addition of oil

Equation (28), for the coverage number, offers a possibility for a simple explanation of the influence of oil on heat transfer associated with bubble growth (transport of latent heat). As it shows, a larger oil fraction w corresponds to a larger coverage number k and to a thicker oil film at the bubble surface, see Table 1. This increases the resistance to the transport of refrigerant molecules through the interphase. The rise of the temperature difference, required to overcome this resistance, finally results in a deterioration of heat transfer in the mixture in comparison with the pure refrigerant. Note that experiments, without exception, show a considerable reduction of heat transfer at larger oil fraction. This conclusion in no way contradicts our reasoning about the improvement of heat transfer based on equation (15). The heat transfer improvement has its origin in a possible rise of bubble density and a reduction of bubble equilibrium temperature caused by lowering of surface and interfacial tensions. Regarding the heat transfer, these effects oppose oil enrichment at the bubble surface.

Furthermore, equation (28) shows the coverage number increasing with the vapour density, which means, that the interphase will become thicker and a stronger reduction of heat transfer by oil is expected at higher boiling temperatures. This is in agreement with experimental findings, e.g. [3, 10].

One might question, however, the use of equation (28) for explanation of experiments, because this equation involves the assumption of a uniform evaporation at the bubble surface, a notion which is hardly confirmed in reality. As pointed out in [31], during bubble adherence, the evaporation of pure liquids takes place mainly along the line, where all of the phases (liquid, solid, vapour) interact. In the case of a mixture, however, the evaporation along such a line, formed at the start of bubble growth, results in an increase in the oil concentration there, which is accompanied by a rise of boiling temperature and a corresponding reduction of evaporation rate (Fig. 6a). The place of the maximum evaporation rate may thus 'move' along the bubble surface further away from the heated wall, as the bubble grows. This effect could be accounted for by a somewhat modified consideration about bubble coverage with oil. Concerning the lowering of heat transfer, the results were largely the same, justifying at least partly, the use of equation (28) for explanations of boiling events under real conditions.

4.2. Formation of foam

The interphase enveloping the growing bubble (Fig. 7), facilitates the formation of foam, observed in boiling refrigerant–oil mixtures, particularly at higher heat fluxes. In the light of the present model, the foam may become generated, also in the absence of surface active components, when detached vapour bubbles, enclosed by the interphase, collide within the liquid phase or at its free surface. The film separating two associated bubbles is enriched with oil and is capable of stretching; it can withstand considerable stresses for a certain time. Before rupturing, the film must thin down to a few nanometers, mainly by liquid flow. This process is very slow because of the large film viscosity, small film thickness, and possible interfacial interactions. Further bubbles, arriving at the free mixture surface, associate with the 'older' ones thus leading to bubble clustering.

4.3. Bubble detachment size

Also a further 'mixture' effect, namely, the reduction of bubble detachment sizes in comparison with pure refrigerant, may be attributed to the interphase. As shown in Table 1, the bubble detachment radius r decreases by more than a factor of three as the oil fraction w increases from zero to ten percent. The effect is much stronger at a higher boiling temperature.

To explain this behaviour, we may consider the area formed between the vapour in a growing bubble and the heated wall to be largely covered with the interphase incapable of evaporation. Its thickness increases, the larger the oil concentration, and the creation of a pronounced contact line of the three phases is hindered. A distinct contact line in mixtures generally may be established under conditions of the so-called total evaporation[10] only, which is not possible in the case considered. If formed in the mixture, this line is much shorter than in the pure refrigerant under comparable conditions, and the adhesion force, exerted upon the bubble by the action of surface tension, is reduced. In this respect, the oil added to refrigerant facilitates the bubble detachment. At a higher boiling temperature, a thicker interphase and a shorter contact line are expected to be established resulting in a stronger oil effect on bubble departure size.

Further effects, that might also assist the bubble detachment, originate in requirements of equilibrium conditions. These effects are a possible re-condensation and surface movement of refrigerant molecules during bubble growth, both leading to a shorter contact line and therefore to a smaller bubble detachment size. The effects are not fully understood yet, but some speculations about them can be based on the time history of the temperature of bubble formation site. According to experiments with pure liquids, this temperature decreases as the bubble grows. Similar behaviour happens also with mixtures. At the very beginning of bubble growth, the parts of the vapour–liquid interface, which are practically in contact

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[10] With total evaporation, in analogy to total condensation, the phase change takes place without concentration gradients. For this to occur, the temperature of the heated surface must be above the dew point of the mixture at the liquid composition.

with the heated surface, are rich in oil because of the large wall superheat at the bubble start. As the superheat decreases with time, taking the pressure in the bubble as constant, the equilibrium conditions change, requiring a corresponding change of the composition, which means a reduction of oil or rise of refrigerant content. A change of the concentration in these regions (wall-parts of shaded area in Fig. 6a) is scarcely possible by channelling of the refrigerant molecules for the obvious reason. Also, an oil diffusion, that could re-establish the phase equilibrium, seems excluded. Other processes which could alter the mixture composition are a re-condensation of refrigerant from the bubble and a movement of refrigerant (or oil) molecules along the bubble surface.

The movement of refrigerant molecules along the bubble surface is basically possible by a series of jumps from site to site and by sliding. Each of them requires the interface to be covered at least with a monomolecular refrigerant layer. The existence of such a layer is indicated by the conditions of mechanical equilibrium, if the oil does not contain surface active components. Since the free (surface) energy of a system at equilibrium must be at minimum, the bubble interface will tend to cover itself with molecules of the component that has the lower surface tension. Assuming this component to be the refrigerant, a thin, probably monomolecular film of refrigerant could thus form on the vapour side of the interphase (Fig. 7). (In order to clearly illustrate the interphase, the refrigerant film is not shown in the figure.) A possible surface movement of the refrigerant molecules were confined to the refrigerant film only; it would be too weak to generate a flow within the interphase and must not be confused with the Marangoni convection.

5. Conclusions

The aim of this paper was to consider boiling phenomena of refrigerant–oil mixtures, but, in the first place, to describe the static conditions of bubble equilibrium and to examine the oil enrichment at the interface of a vapour bubble growing in such a mixture. Under the assumption of an ideal mixture behaviour, the bubble equilibrium follows an expression, connecting the temperature and the oil concentration with the bubble size. This expression was used to illustrate the influence of surface tension on boiling heat transfer, showing a higher heat transfer coefficient at a lower surface tension. An addition of oil to a refrigerant must not result in a deterioration in the heat transfer. If the surface tension of the refrigerant is lowered by surface active components, which may be present in the oil added, an improvement of heat transfer in mixture, compared with pure refrigerant, becomes possible. Surface active components are also expected to weaken the interactions between liquid and heated wall by changing the prenucleation structure of the adsorbed layer which may lead to an increase in bubble density. However, the improvement of heat transfer by oil is confined to low oil concentration. At higher oil concentrations, other effects predominate, resulting in a reduction of heat transfer.

The paper deals further with the mass transfer in the liquid surrounding a spherical bubble growing symmetrically in an infinite mixture. The mean results are as follows:

(1) A growing bubble withdraws refrigerant from its surroundings thus producing an oil excess in the liquid phase. The amount of oil corresponding to this excess mostly suffices to enclose the bubble as a continuous film.

(2) Supposing the oil to remain at the bubble surface, the first monomolecular oil layer envelopes the bubble relatively soon after the start of bubble growth. Depending on boiling temperature and initial oil concentration, bubbles monomolecularly covered with oil, are not larger than a few microns. The total number of monomolecular oil layers, 'the coverage number', is shown to depend mainly on the oil properties (size and mass of molecules), the initial mixture composition and on the boiling temperature. Larger oil molecules and both higher oil concentration and boiling temperature raise the coverage number. This reaches values considerably larger than unity prior to usual bubble detachment sizes (see Table 1).

These results underline the importance of mass transfer during bubble growth. A simple notion about the mass transfer gave an interesting relationship between some important parameters. The oil excess at the bubble surface is thought to be caused by the convection, generated by bubble growth, while the diffusion of oil molecules tends to reduce it. Depending on the rapidity of these processes, different situations are established. If the convection is stronger than the diffusion, the growing bubble may become covered with an oil layer, termed 'the interphase' (Fig. 7). For the given mixture, the driving temperature difference is the only parameter that decides whether the interphase forms or not; an equation is derived for calculating the temperature difference required for the interphase to generate. If this temperature difference is smaller than the actual one, the interphase is expected to form. In such a case, the oil diffusion is not the process that governs the mass transfer. The expansion of the interface, forced by bubble growth, is continuously rearranging the oil molecules and creating channels within the interphase through which the refrigerant molecules pass into the vapour phase. Instead of diffusion of oil molecules from the bubble surface towards the bulk liquid, a 'channelling' of refrigerant molecules through the interphase is then viewed as the key mechanism of mass transfer.

The kinetics of the channelling process depends upon the permeability of the interphase. This permeability is a function of the number of monomolecular oil layers, the size and shape of the molecules involved, and of the rapidity of bubble growth. The bubble growth determines the stretching rate of the interphase, thereby changing its structure and permeability. It is mainly this stretching, accompanied by a creation of channels in the interphase, that does not allow a simple model of mass transfer, in terms of, for example, the Fickian diffusion. The channelling of refrigerant molecules is, to some extent, comparable with Knudsen's diffusion.

With regard to the overall influence of oil on heat transfer of refrigerant with nucleate boiling, two decisive effects may be recognised: If surface active components are contained in the added oil, the oil facilitates both the bubble generation and bubble density, resulting in an improvement of heat transfer in comparison with pure refrigerant. On the contrary, the oil film formed at the surface of a growing bubble slows down the bubble kinetics and results in deterioration in heat transfer. The former effect is expected to predominate at a low oil concentration. In the light of this notion, an improvement of heat transfer appears to be impossible, if the oil does not reduce the surface and/or interfacial tensions.

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