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Equilibrium radii of small vapour bubbles and liquid droplets

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Abstract—Several equations are known for the calculation of the equilibrium radii of small vapour bubbles and liquid droplets. Differences in the results are mostly due to various simplifications in the derivation of such equations. The correct relationships can easily be obtained by means of two isothermal cycles. Thereupon it is also possible to decide which thermal state governs the thermal properties. As a by-product the Thomson equation for the vapour pressure at a curved surface can be found.

INTRODUCTION

In connection with the incipience or suppression of nucleate boiling, with subcooled boiling or with the appearance and vanishing of droplets the knowledge of the equilibrium radii of vapour bubbles and liquid droplets is of considerable interest.

In the literature several equations concerning the equilibrium radius of a vapour bubble and the necessary superheat of the liquid can be found. Normally, the starting point for the derivation was the Clausius–Clapeyron equation. Differences in the results are mostly caused by various simplifications. Often the influence of the vapour pressure change as a consequence of the interface curvature has not been considered.

SOME KNOWN RELATIONS

Rohsenow [1] uses the simplified Clausius–Clapeyron equation as the starting point. His derivation yields the following expression for the necessary liquid superheat

$$\Delta T = T_s - T_f = \frac{2\sigma T_s}{r\Delta h_s \rho''_{fs}} \frac{1}{1+\Delta T/T_{fs}}. \tag{1}$$

Davis and Anderson [2] started also from the simplified Clausius–Clapeyron equation. But they performed the integration in a somewhat different manner. The superheat, following from their calculation, is

$$\Delta T = \frac{2\sigma T_f}{r\Delta h_f \rho''_f}(1+\Delta T/T_f). \tag{2}$$

There are some differences between equations (1) and (2). If $1 \gg \Delta T/T_f$, it follows from equation (2) that

$$\Delta T = \frac{2\sigma T_f}{r\Delta h_f \rho''_f}. \tag{3}$$

Mitrović and Stephan [3] started from the complete Clausius–Clapeyron equation. Thereupon they found

$$\Delta T = \frac{2\sigma_f T_f}{r\Delta h_f \rho''_f}(1-\rho''_f/\rho'). \tag{4}$$

For values $\rho' \gg \rho''_f$ equation (4) passes over into equation (3).

Furthermore, Mitrović and Stephan [3] derived relations taking into account the influence of the interface curvature on the vapour pressure. The following equations result

$$\Delta T = \frac{2\sigma_f T_f}{r\Delta h_f \rho''_f}\left(1+\frac{\Delta T}{T_f}\cdot\omega\right) \tag{5}$$

with

$$\omega = \left(\frac{\Delta h_f}{RT_f}\frac{\rho'}{\rho'-\rho''_f}-1\right)\frac{\rho''_f}{\rho'-\rho''}. \tag{6}$$

Equation (5) also changes into equation (3) if $(\Delta T/T_f)\omega \ll 1$.

All the simplifications mentioned above result in moderate differences. It is, however, possible to obtain clear and doubtless results by applying an isothermal cycle as shown in the following.

THE ISOTHERMAL CYCLE

The scheme of the cycle is shown in Fig. 1. Vessel a contains a liquid with an even interface and a vapour in equilibrium with the liquid. At the interface the saturation pressure p_s exists.

Vessel b is filled with the same liquid at a pressure p_f. A capillary tube enters the vessel at the end of which a sphere shaped vapour bubble with radius r is formed. The pressure within the bubble is p_v. Machines c and d permit to convey vapour resp. liquid from one vessel to the other.

Assume that the pressures p_v and p_f are smaller than p_s. It will be proved later if this assumption is justified. Then it is presumed that all changes of state take place reversibly and isothermally at temperature t_s.

The cycle consists of the following steps. In vessel a

NOMENCLATURE

Δh	evaporation enthalpy
m	quantity
p	pressure
R	gas constant
r	radius
T	temperature
W	work.

Greek symbols

ρ'	liquid density at p_s, T_s
ρ''	vapour density at p_s, T_s
σ	surface tension
ω	correction factor.

Subscripts

c	subcooled
f	liquid at pressure p_f
m	mean
s	saturation
t	droplet
v	vapour.

the small quantity dm is vaporized, then expanded in engine c from pressure p_s to p_v and finally supplied into the vapour bubble in vessel b where it condenses at the interface. In the next step a quantity of liquid dm is taken from vessel b, compressed by machine d to p_s and transferred to vessel a in order to close the cycle.

It will be shown later that the vapour can be regarded as incompressible during the expansion. Engine c delivers the following work

$$\mathrm{d}W_1 = (p_s - p_v)\frac{\mathrm{d}m}{\rho''} \tag{7}$$

where ρ'' is the saturation density of the vapour at pressure p_s.

The isothermal compression of the liquid needs the work

$$\mathrm{d}W_2 = -(p_s - p_f)\frac{\mathrm{d}m}{\rho'} \tag{8}$$

where ρ' denotes the saturation density of the liquid at pressure p_s.

According to the second law the sum of the work dW_1 and dW_2 must vanish. If $|\mathrm{d}W_1| > |\mathrm{d}W_2|$, the cycle would produce work on account of heat taken from the surroundings which would violate the second law. Therefore, it follows from equations (7) and (8) that

$$(p_s - p_f)\rho'' = (p_s - p_v)\rho'. \tag{9}$$

Due to the surface tension σ_s the pressure p_v in the bubble is greater than that in the surrounding liquid. On account of the mechanical equilibrium the following is valid

$$(p_v - p_f)\pi r^2 = 2\sigma_s \pi r. \tag{10}$$

Equation (10) yields

$$\Delta p_1 = p_v - p_f = 2\sigma_s/r. \tag{11}$$

From equations (9) and (11) one obtains

$$\Delta p_2 = p_s - p_v = \frac{2\sigma_s}{r}\frac{\rho''}{\rho' - \rho''}. \tag{12}$$

This is the Thomson equation which gives the vapour pressure reduction over a concave curved liquid surface [4].

Finally one obtains

$$\Delta p = p_s - p_f = \Delta p_1 + \Delta p_2 = \frac{2\sigma_s}{r}\frac{\rho'}{\rho' - \rho''}. \tag{13}$$

These relations can be represented very clearly in a p,T-diagram. In Fig. 2 the course of the vapour pressure curve is shown. The equilibrium state at the even interface is given by pressure p_s and temperature T_s, point 1. In the vapour bubble the pressure p_v and the temperature T_s exist. According to point 2 the vapour is superheated. The state of the liquid surrounding the vapour bubble is given by pressure p_f and temperature T_s, point 3.

The saturation temperature of the liquid at pressure p_f is T_f, the temperature of the liquid in vessel b is T_s. Therefore, the liquid is superheated by $\Delta T = T_s - T_f$.

Finally the pressure differences Δp_1 and Δp_2 are

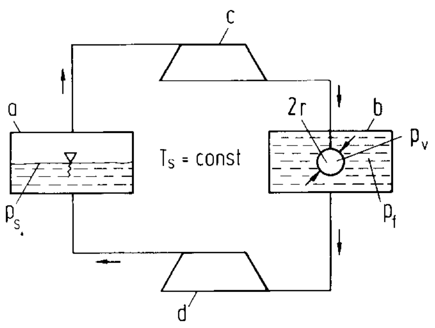

FIG. 1. Isothermal cycle: a, b, vessel; c, expansion engine; d, compressor.

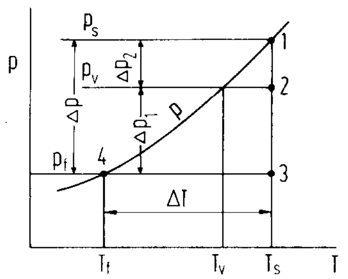

FIG. 2. Finding of liquid superheat.

indicated in Fig. 2. Δp_1 and Δp_2 can be calculated exactly by means of equations (11) and (12), hence the necessary superheat of a liquid in equilibrium with a vapour bubble with radius r can be taken from a steam table or a p,T-diagram. Of course, Δt can also be found by means of a vapour pressure equation.

The work $\mathrm{d}W_1$, equation (7), has been calculated assuming that the vapour can be regarded as incompressible during the expansion in engine c (Fig. 1). In the following it will be proved whether this assumption is admissible. It follows from equations (12) and (13) that

$$\Delta p_2/\Delta p = \rho''/\rho'. \tag{14}$$

If $\rho'' \ll \rho' : \Delta p_2 \ll \Delta p$. The vapour pressure difference Δp governing the liquid superheat ΔT is usually small. If, moreover, Δp_2 is essentially smaller than Δp, it is doubtless admissible to regard the vapour as incompressible during the isothermal expansion over the very small pressure difference Δp_2.

At the beginning it was presumed that $p_v < p_s$. Suppose $p_v > p_s$, then it would be necessary to compress the vapour in the cycle and thus to perform work. Likewise work would be necessary for conveying the liquid from vessel c back to vessel a. As reversibility of the cycle was presumed the working direction can be reversed. In this case both machines c and d would perform work and heat would be taken from the surroundings. This, however, would be a contradiction of the second law.

Summarizing it can be stated that it is possible to clear completely and in a simple manner the physical mechanisms governing the existence of a vapour bubble in a superheated liquid.

LIQUID SUPERHEAT AND BUBBLE RADIUS AT EQUILIBRIUM

Owing to the foregoing considerations it was possible to find out the necessary liquid superheat if the radius of the vapour bubble and saturation temperature T_s resp. saturation pressure p_s are known. Often the question is: which radius r has a vapour bubble at liquid pressure p_f in equilibrium with a liquid superheated by ΔT? This question will now be answered.

The following relation exists between the saturation temperatures T_s and T_f at pressures p_s and p_f (Fig. 2)

$$\Delta T = T_s - T_f. \tag{15}$$

From equation (13) it follows

$$r = \frac{2\sigma_s}{\Delta p}\frac{\rho'}{\rho'-\rho''} = \frac{2\sigma_s}{p_s - p_f}\frac{\rho'}{\rho'-\rho''}. \tag{16}$$

The pressure difference Δp belongs to the superheat ΔT according to equation (15) and can be calculated from a vapour pressure equation or taken from a vapour pressure–temperature diagram. As already mentioned the values of ρ', ρ'' and σ_s are saturation values for pressure $p_s = p_f + \Delta p$ (not p_f). Herewith it is possible to calculate the equilibrium radius for given values p_f and ΔT by means of equation (16).

If the bubble radius r and the liquid pressure p_f are given and the superheat ΔT is required, ΔT resp. the corresponding value Δp must be estimated in order to know the values ρ', ρ'' and σ_s belonging to pressure $p_s = p_f + \Delta p$. If these values do not satisfy equation (16) iteration is necessary.

If only small amounts of ΔT resp. Δp must be considered, it is possible to introduce the Clausius–Clapeyron equation

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta h \rho''}{T}\frac{\rho'}{\rho'-\rho''}. \tag{17}$$

With small values of ΔT and Δp it is admissible to use differences instead of differentials. Then, it is expedient to apply mean values T_m, Δh_m and ρ''_m belonging to

$$T_m = \frac{T_f + T_s}{2} = T_f + \Delta T/2. \tag{18}$$

One obtains

$$\frac{\Delta p}{\Delta T} = \frac{\Delta h_m \rho''_m}{T_m}\cdot\frac{\rho'}{\rho' - \rho''_m}. \tag{19}$$

From equations (16) and (19) it follows

$$r = \frac{2\sigma_s T_m}{\Delta h_m \Delta T \rho''_m}\frac{\rho' - \rho''_m}{\rho' - \rho''}. \tag{20}$$

Bubble radius r can be calculated from this equation if the liquid pressure p_f and superheat are given. ρ', ρ'' and σ_s must be taken at a temperature T_s, Δh_m and ρ''_m on the other hand at a temperature T_m.

The calculation of superheat ΔT at given values r and p_f by means of equation (20) is again only possible by iteration.

For values $\rho' \gg \rho''$ and $\rho' \gg \rho''_m$ it follows from equation (20) that

$$\Delta T = \frac{2\sigma_s T_m}{r \Delta h_m \rho''_m}. \tag{21}$$

A comparison with equation (3) shows that σ_s should be taken at a temperature T_s instead of T_f and the values of Δh_m and ρ''_m at a temperature T_m instead of T_f.

EQUILIBRIUM BETWEEN SUBCOOLED LIQUID DROPLETS AND THE SURROUNDING VAPOUR

The main relationships can very easily be clarified by means of an isothermal cycle. According to Fig. 3, vessel a contains a liquid with an even interface and vapour. Pressure p_s and temperature T_s prevail at the interface. A capillary tube enters vessel b from below. A spherical shaped droplet with radius r_t exists at the end of the tube. It is surrounded by vapour of pressure p_v. Because of the surface tension σ_s the pressure p_f within the droplet is higher than that in the vapour

$$\Delta p_1 = p_f - p_v = \frac{2\sigma_s}{r_t}. \tag{22}$$

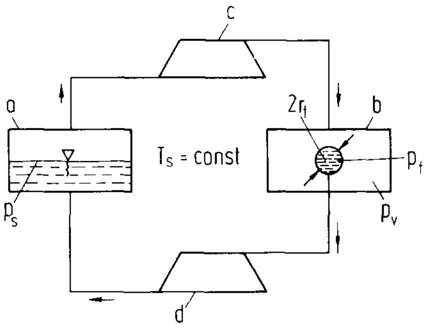

FIG. 3. Isothermal cycle: a, b, vessel; c, compressor; d, expansion engine.

Machines c and d make it again possible to convey vapour resp. liquid from one vessel to the other.

The procedure is now the same as before. It is presumed that all changes of state take place isothermally and reversibly.

The work dW_1 required for conveying the vapour quantity dm from vessel a to vessel b is given by

$$dW_1 = -(p_v - p_s)\frac{dm}{\rho''}. \tag{23}$$

Thereby it has been assumed that the vapour can be regarded as incompressible which is again admissible.

The vapour condenses at the interface of the droplet. The corresponding liquid quantity dm is removed from the droplet, expanded in machine d and given back to vessel a. During expansion the work is delivered

$$dW_2 = (p_f - p_s)\frac{dm}{\rho'}. \tag{24}$$

As the sum of all work must vanish it follows from equations (22) to (24) that

$$\Delta p_2 = p_v - p_s = \frac{2\sigma_s}{r_t}\cdot\frac{\rho''}{\rho' - \rho''}. \tag{25}$$

This is the Thomson equation for convex curved surfaces.

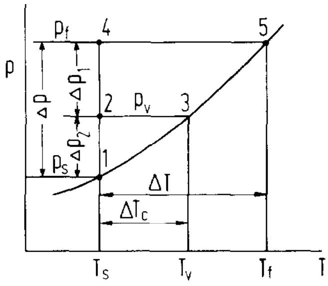

FIG. 4. Finding of vapour subcooling.

Finally equations (22) and (25) yield

$$\Delta p = p_f - p_s = \Delta p_1 + \Delta p_2 = \frac{2\sigma_s}{r_t}\cdot\frac{\rho'}{\rho' - \rho''}. \tag{26}$$

These connections are shown in the p,T-diagram (Fig. 4). The equilibrium state at the even interface is given by point 1. In vessel b the state of the vapour is marked by pressure p_v and temperature T_s corresponding to point 2. As saturation temperature T_v belongs to pressure p_v, the vapour is subcooled by $\Delta T_c = T_v - T_s$. While a vapour bubble can exist only in a superheated liquid, equilibrium between a droplet and the surrounding vapour is only possible if the vapour is subcooled.

The liquid in the droplet has a pressure p_f and a temperature T_s according to point 4. It is subcooled by $\Delta T = T_f - T_s$.

Subcooling ΔT_c of the vapour at given radius r_t can be found by means of equation (25), as ΔT_c belongs to the pressure difference Δp_2 along the vapour pressure curve.

However, if T_s and ΔT_c are known, r_t can be determined likewise by equation (25) if the pressure difference belonging to ΔT_c has been ascertained before.

From equations (25) and (26) it follows that

$$\Delta p_2/\Delta p = \rho''/\rho'. \tag{27}$$

The pressure difference Δp_2 is also in the droplet case very small. Therefore, it is especially advantageous to apply the Clausius–Clapeyron equation. Analogous to the earlier considerations the following equation can be found

$$r_t = \frac{2\sigma_s T_m}{\Delta h_m \Delta T_c \rho'}\,\frac{\rho''}{\rho''_m}\,\frac{\rho' - \rho''_m}{\rho' - \rho''}. \tag{28}$$

Because of the very small pressure difference Δp_2, mostly: $T_m \approx T_s$. Then: $\Delta h_m \approx \Delta h$ and $\rho''_m \approx \rho''$. With $\rho'' \ll \rho'$, it results

$$r_t = \frac{2\sigma_s T_s}{\Delta h \Delta T_c \rho'}. \tag{29}$$

This equation has already been given by Merte [5].

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RAYON D'EQUILIBRE DES PETITES BULLES DE VAPEUR ET DES GOUTTELETTES LIQUIDES

Résumé—Différentes équations sont connues pour le calcul des rayons d'équilibre des petites bulles de vapeur et des gouttelettes liquides. Des différences dans les solutions sont principalement dues aux simplifications apportées dans l'établissement de ces équations. Les résultats corrects peuvent être obtenus facilement au moyen de deux cycles isothermes. Il est aussi possible de décider quel état thermique gouverne les propriétés thermiques. On peut trouver incidemment l'équation de Thomson puis la pression de vapeur sur une surface courbe.

GLEICHGEWICHTSRADIEN KLEINER DAMPFBLASEN UND FLÜSSIGKEITSTROPFEN

Zusammenfassung—Zur Berechnung der Gleichgewichtsradien kleiner Dampfblasen und Flüssigkeitstropfen sind mehrere Berechnungsgleichungen bekannt. Unterschiede in den Ergebnissen sind meist durch unterschiedliche Vereinfachungen bei der Ableitung der Gleichungen verursacht. Die korrekten Beziehungen können sehr einfach mit Hilfe von zwei isothermen Kreisprozessen ermittelt werden. Daraufhin ist es auch möglich zu entscheiden, welcher thermische Zustand für die Wahl der Stoffwerte maßgebend ist. Als Nebenprodukt wird auch die bekannte Thomson-Gleichung für den Dampfdruck an gekrümmten Oberflächen gefunden.

РАВНОВЕСНЫЕ РАДИУСЫ НЕБОЛЬШИХ ПАРОВЫХ ПУЗЫРЬКОВ И КАПЕЛЬ ЖИДКОСТИ

Аннотация—Известен ряд уравнений для расчета равновесных радиусов небольших паровых пузырьков и капель жидкости. Несовпадение результатов расчета по этим уравнениям обязано в основном различным упрощениям, применяемым при выводе таких уравнений. Более точные соотношения легко выводятся из рассмотрения двух изотермических циклов, после чего можно решить, какое из тепловых состояний определяет тепловые характеристики. Кроме того, можно получить уравнение Томсона для определения давления пара на искривленной поверхности.