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Numerical Analysis of Hertz-Knudsen Model of Condensation upon Small Droplets in Water Vapor

Notation

n_{inc} – number of molecules per unit area per second in the incident beam,
T – temperature,
t – time,
m – mass of molecule,
p – pressure,
k – Boltzmann constant,
α_c – condensation coefficient,
α_a – accommodation coefficient,
R – gas constant,
σ – surface tension,
r – radius of droplet,
ρ – density,
h – latent heat,
c – specific heat of liquid,
c_p – specific heat at constant pressure,
c_v – specific heat at constant volume,
λ – thermal conductivity,
l – mean free path,
κ – isentropic index,
η – viscosity.

The importance of predicting the size of droplets after they are born as nuclei of condensation has been stressed in many recent theoretical and experimental investigations on condensation phenomena. There is no doubt that the problem from physical point of view is very complicated and probably we will wait for a long time unless a satisfactory theory of kinetic type, including phase transition, is completed. Even then, the engineering type calculation could hardly be done because of very time-consuming character of a calculation based on statistics. What we certainly do expect from this type of theory is a better understanding of the phenomena in order to build up more reliable methods of calculation of the droplet size. The method must posses certain degree of simplicity as the common demand for engineering calculations.

Recently we have at hand the kinetic theory of gases which may help us to construct the idea what is going on at the liquid surface when evaporation and condensation occur [1]. This approach was introduced by H. Hertz and M. Knudsen [2, 3] when they used simple relations from the kinetic theory of gases in order to examine the condensation upon the mercury surface.

Following this idea it is possible to build up the equations for droplet growth which consist of the equation for the radius and the temperature of the droplet. In publications

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there exists a number of different models of condensation upon small droplets given by K. Oswatitsch [4], P. P. Wegener [5], P. G. Hill [6], G. G. Gyarmathy [7], R. Puzyrewski [8].

The main aim of the present work is to elucidate in what sense these different models are the simplification of more general equations based on Hertz and Knudsen idea, and what the numerical consequences of these simplifications are.

1. The main assumptions

The nuclei which arise as the result of fluctuations have the dimensions much smaller than mean free path of molecules of the surrounding vapor. Therefore it is justified to treat the mass, the impuls and the energy transport to and from the surface of the nucleus as being of a free-molecular type. The second important assumption concerns the surface of the nucleus which has been considered as a well determined surface. In fact a micro-region of the order of the amplitude of molecules vibration in the liquid spreads out between the liquid and the gas. This region is responsible for accommodation effect in the process of molecular exchange between the gas and the liquid. The commonly accepted model is of the droplet surface in the geometrical sense.

This surface is considered as being responsible for the surface tension, the mass accommodation and the thermal accommodation properties of liquid. A part of the molecules that strikes the surface from the gas side is captured into the liquid state another part is reflected.

If we assume that reflected molecules have the Maxwellian distribution, the temperature and the mass of the reflected gas will be determined by the condensation coefficient:

$$n_{\text{capt}} = \alpha_c n_{\text{inc}} \tag{1}$$

and thermal accommodation coefficient

$$T_{\text{ref}} = T_1 + \alpha_a (T_2 - T_1). \tag{2}$$

The growth of the nuclei treated as a small droplet and the change of the temperature of the droplet is possible to be described within the framework of the above mentioned assumptions.

2. The growth of droplet radius

The first attempt to describe the mechanism of condensation in the case of flat surface was undertaken by H. Hertz and M. Knudsen [2, 3].

The net condensation rate per a unit area when there are no reflected molecules has been given as

$$\frac{p}{\sqrt{2\pi m k T_1}} - \frac{p_s(T_2)}{\sqrt{2\pi m k T_2}}. \tag{3}$$

The structure of the above relation comes out from the following arguments. The expression

$p_1/\sqrt{2\pi mkT_1}$ represents the number of molecules passing the unit area per second in the gas with Maxwelian distribution. It was assumed by Hertz and Knudsen that this number of molecules reaches the surface of the liquid from the gas side. There must be molecules evaporated from the liquid. When the number of evaporated molecules and the number of condensed molecules are equal we have a stable situation – there is an equilibrium.

This fact expresses the relation (3) when

$$p = p_s(T_2), \qquad T_1 = T_2 .$$

For nonequilibrium the formula (3) is an extrapolation.

Furthermore the fact that the only part of the molecules is condensed and that the condensation causes the macroscopic flow of the gas towards the liquid surface, must be taken into account. The last phenomenon has been investigated by R. W. Charge [9].

According to these two contributions the net flow rate of condensed molecules on the flat surface may be rewritten in the form

$$\frac{2\alpha_c}{2-\alpha_c}\left(\frac{p}{\sqrt{2\pi mkT_1}} - \frac{p_s(T_2)}{\sqrt{2\pi mkT_2}}\right). \tag{4}$$

In the case of a droplet, the equilibrium pressure depends not only on the temperature but also on the radius and the surface tension of the droplet. For not a very high vapor pressure p_s, the equilibrium pressure for a given radius of a droplet r is

$$p_2 = p_s(T_2)\exp\left(\frac{2\sigma}{R\rho_2 T_2 r}\right). \tag{5}$$

Finally the equation for the growth of radius will have the form

$$\frac{dr}{dt} = \frac{2\alpha_c}{2-\alpha_c}\frac{m}{\rho_2\sqrt{2\pi mk}}\left[\frac{p}{\sqrt{T_1}} - \frac{p_s(T_2)}{\sqrt{T_2}}\,e^{\frac{2\sigma}{R\rho_2 T_2 r}}\right]. \tag{6}$$

The shape of this equation follows from the ideas given by H. Hertz and M. Knudsen. It matches the simplicity of consideration with uncertainty with respect to the numerical value of α_c. Nevertheless the main features of the condensation mechanism seems to be clarified by this approach. It is noteworthy that the terms in bracket are supposed to be equall for the conditions of metastable equilibrium because then for the nuclei treated as a critical droplet we have

$$r_* = \frac{2\sigma}{R\rho_2 T_1}\left[\ln\frac{p}{p_s(T_1)}\right]^{-1}, \tag{7}$$

$$T_2 = T_1 . \tag{8}$$

The value (7) has been used as the initial condition for the equation (6). At the very beginning of the growth the terms in the bracket in (6) are very close to each other. Therefore the solution of this equation is very sensitive on the initial disturbances which have either physical or numerical character. What is more important is the fact that different types of simplifications of the equation (6) lead to the completely different numerical value of the solution because of this sensitivity.

3. The temperature change of the droplet

The temperature of the small mass of the nuclei is under a strong influence of the incident beam of molecules. It makes the difference in comparison with the situation of a flat surface and the infinite mass. It is very important for the rate of condensation to evaluate the temperature of the surface of the liquid which may differ from the bulk temperature of the liquid. In the case of a small droplet it seems to be reasonable to assume that the temperature of the droplet is uniform. The energy balance can be established by means of the terms from the previous paragraph.

In order to do that we have to notice that the transport energy through the small area like the droplet surface differs from the macroscopic case. This is so called Knudsen effect of effusion which expresses the fact that instead of the full enthalpy we have to use for our case the relation like

$$e=\left(c_p-\frac{R}{2}\right)T \tag{9}$$

for the energy carried by the molecules beams.

The total change of the thermal energy of the droplets is due to the energy of captured molecules, reflected molecules and evaporated molecules.

The captured molecules have the energy

$$e_c=\left(c_p-\frac{R}{2}\right)T_1, \tag{10}$$

the reflected molecules

$$e_r=\left(c_p-\frac{R}{2}\right)[T_1+\alpha_a(T_2-T_1)], \tag{11}$$

and the evaporated molecules

$$e_e=\left(c_p-\frac{R}{2}\right)T_2. \tag{12}$$

These relations are valid if the Maxwelian distribution is assumed for all three beams. The relation for the mass of the captured molecules resulting from the mass balance has the form

$$m_c=4\pi r^2\frac{2\alpha_c}{2-\alpha_c}\,m\,\frac{p}{\sqrt{2\pi mkT_1}}, \tag{13}$$

for the reflected molecules

$$m_r=4\pi r^2\frac{2(1-\alpha_c)}{2-\alpha_c}\,m\,\frac{p}{\sqrt{2\pi mkT_1}}, \tag{14}$$

and for the evaporated molecules

$$m_e=4\pi r^2\frac{2\alpha_c}{2-\alpha_c}\,m\,\frac{p_s(T_2)}{\sqrt{2\pi mkT_2}}\,e^{\frac{2\sigma}{R\rho_2 T_2 r}}. \tag{15}$$

Thus we have the energy balance equation for the droplet

$$\frac{d}{dt}(\rho_2 \tfrac{4}{3}\pi r^3 i) = m_c e_c - m_r e_r - m_e e_e, \tag{16}$$

where

$$i = cT_2 + i_0. \tag{17}$$

Equation (16) can be rewritten into the form

$$\frac{dT_2}{dt} = \frac{3(h-\frac{1}{2}RT_2)}{rc}\frac{dr}{dt} - \frac{6m}{rc\rho_2}\frac{\alpha_c}{2-\alpha_c}\frac{p}{\sqrt{2\pi mkT_1}}\left(c_p - \frac{R}{2}\right)(T_2 - T_1) -$$

$$- \frac{6m}{rc\rho_2}\frac{(1-\alpha_c)\alpha_a}{2-\alpha_c}\frac{p}{\sqrt{2\pi mkT_1}}\left(c_p - \frac{R}{2}\right)(T_2 - T_1), \tag{18}$$

where the latent heat is introduced

$$h = c_p T_2 - cT_2 - i_0. \tag{19}$$

There is a simple interpretation of the temperature change of the droplet according to the equation (18). The first term on the right hand side describes the heat release of the condensed mass on the droplet. The second term comes from the fact that the condensed mass must be heated from the temperature T_1 to temperature T_2. This energy is taken from the droplet and it lowers the temperature of the droplet.

The third term is of a thermal conductivity character in a free molecular regime. The reflected beam of molecules carries the energy from the surface. This term vanishes in the cases when there is neither temperature difference $T_1 = T_2$, nor reflected molecules $\alpha_c = 1$, nor accommodation effect $\alpha_a = 0$; no one of these three cases seems to be an adequate model of reality. It should be pointed out that formally it is possible to combine the second and third term in the equation (18) because they are dependent on the temperature difference $T_2 - T_1$. Nevertheless they have quite different meaning in the physical sense.

4. The simplifications of basic equations

The equations (6) and (18) describe the history of the nuclei after it is born. Let us rewrite these equations in the more compact form

$$\frac{dr}{dt} = \frac{2\alpha_c}{2-\alpha_c}\frac{m}{\rho_2\sqrt{2\pi mk}}\left[\frac{p}{\sqrt{T_1}} - \frac{p_s(T_2)}{\sqrt{T_2}}\,e^{\frac{2\sigma}{R\rho_2 T_2 r}}\right], \tag{20}$$

$$\frac{dT_2}{dt} = \frac{3(h-\frac{1}{2}RT_2)}{rc}\frac{dr}{dt} - \frac{6m}{rc\rho_2}\frac{\alpha_c}{2-\alpha_c}\left[1 + \frac{(1-\alpha_c)\alpha_a}{\alpha_c}\right]\frac{p}{\sqrt{2\pi mkT_1}}\left(c_p - \frac{R}{2}\right)(T_2 - T_1). \tag{21}$$

The initial conditions are for $t = 0$

$$r = \frac{2\sigma}{R\rho_2 T_1}\left[\ln\frac{p}{p_s(T_1)}\right]^{-1}, \quad T_2 = T_1. \tag{22}$$

The set (20) and (21) is completed when the functions $p(t)$ and $T_1(t)$ are given.

Quite a few models of condensation can be found in the publications and almost all of them could be derived from these basic equations.

4.1. Oswatitsch formula for growth of small droplets [4]

Let us assume a priori that there is no significant temperature change of the droplet so that

$$\frac{dT_2}{dt} \approx 0 \tag{23}$$

and let us neglect the contribution from the Knudsen effect

$$h - \tfrac{1}{2}R_2 \approx h .$$

The equation (21) turns then into the equation for droplet growth

$$\frac{dr}{dt} = \frac{1}{h}\frac{2\alpha_c}{2-\alpha_c}\left[1+\frac{(1-\alpha_c)\alpha_a}{\alpha_c}\right]\frac{m}{\rho_2}\frac{p}{\sqrt{2\pi mkT_1}}\left(c_p-\frac{R}{2}\right)(T_2-T_1). \tag{24}$$

This equation can be rewritten in the form given by Oswatitsch

$$\frac{dr}{dt} = \frac{1}{h}\frac{Cp}{\rho_2}\sqrt{\frac{k}{mT_1}}(T_2-T_1), \tag{25}$$

where the constant C according to (25) should be

$$C = \frac{2\alpha_c}{2-\alpha_c}\left[1+\frac{(1-\alpha_c)\alpha_a}{\alpha_c}\right]\left(c_p-\frac{R}{2}\right)\frac{m}{k\sqrt{2\pi}}. \tag{26}$$

Taking into account only heat transfer effect in the equation (18) this constant may be simplified to the form

$$C = \frac{2(1-\alpha_c)\alpha_a}{2-\alpha_c}\frac{c_p-\dfrac{R}{2}}{k}\frac{m}{\sqrt{2\pi}}. \tag{27}$$

In this approach the equation (20) has been dropped and the growth of the nuclei is governed only by the part of energy balance.

4.2. Wegener's formula for growth of small droplets [5]

Another approach to the growth of small droplets has been proposed by P. P. Wegener. Dropping the second term in the bracket of equation (20) one can obtain

$$\frac{dr}{dt} = \frac{2\alpha_c}{2-\alpha_c}\frac{m}{\rho_2\sqrt{2\pi mk}}\frac{p}{\sqrt{T_1}}, \tag{28}$$

which is very similar to the Wegener's equation from [5]. This approach is based on the assumption that the mass transport towards the droplet is of a purely kinetic type and is not accompanied by the regression effect coupled with the temperature of the droplet. Therefore the energy balance equation has been dropped.

4.3. Hill's simplification of basic equations [6]

P. G. Hill has proposed [6] to drop the term dT_2/dt in the equation (21) and the simplification of the equation (20) neglecting the expotential term.

Thus one can get

$$\frac{dr}{dt}=\frac{2\alpha_c}{2-\alpha_c}\frac{m}{\rho_2\sqrt{2\pi mk}}\left[\frac{p}{\sqrt{T_1}}-\frac{p_s(T_2)}{\sqrt{T_2}}\right], \tag{29}$$

$$\frac{m}{\rho_2}\frac{2\alpha_c}{2-\alpha_c}\left[1+\frac{(1-\alpha_c)\alpha_a}{\alpha_c}\right]\frac{p}{\sqrt{2\pi mkT_1}}\left(c_p-\frac{R}{2}\right)(T_2-T_1)=(h-\tfrac{1}{2}RT_2)\frac{dr}{dt}\,. \tag{30}$$

In this approximation the drop growth rate is independent of the size and the equation (30) for the temperature of the droplet is in fact of an algebraic type. These simplifications are of a formal character and could hardly be explained in physical terms. The advantage which has been gained from these simplifications is the shortening of the computing time.

4.4. Gyarmathy's formula for droplet growth [7]

G. G. Gyarmathy [7] proposed after M. I. Mason [12] modified formula for the growth of the droplet in the macroscopic and free molecular region

$$\frac{dr}{dt}=\frac{\lambda RT^2}{\rho_2 h^2(r+1{,}59l)}\left(1-\frac{r_*}{r}\right)\ln\frac{p}{p_s(T_1)}\,. \tag{31}$$

If we assume that the radius of nuclei is small in comparison with the mean free path of molecules l the above formula may be rewritten in the form

$$\frac{dr}{dt}\cong\frac{5}{8}\frac{RT^2}{h^2}\frac{\lambda}{\rho_2 l}\left(1-\frac{r_*}{r}\right)\ln\frac{p}{p_s(T_1)}\,. \tag{32}$$

Let us try to obtain the above relation from our basic equations paying special attention to the assumptions which have to be done in the procedure of derivation of the equation (32).

If we assume that the temperature of a droplet and the ambient vapor are equal

$$T_2=T_1 \tag{33}$$

the equation (20) can be rewritten in the form

$$\frac{dr}{dt}=\frac{2\alpha_c}{2-\alpha_c}\frac{m}{\rho_2\sqrt{2\pi mk}}\frac{p_s(T_1)\,e^{\frac{2\sigma}{R\rho_2 T_1 r}}}{\sqrt{T_1}}\left(\frac{p}{p_s(T_1)\,e^{\frac{2\sigma}{R\rho_2 T_1 r}}}-1\right). \tag{34}$$

Assuming that the expression $p/p_s(T_1)e^{\frac{2\sigma}{R\rho_2 T_1 r}}$ does not exceed the unity significantly we can use the expanding formula

$$\frac{p}{p_s(T_1)e^{\frac{2\sigma}{R\rho_2 T_1 r}}}-1\cong\ln\frac{p}{p_s(T_1)}-\frac{2\sigma}{R\rho_2 T_1 r}=\left(1-\frac{2\sigma}{R\rho_2 T_1 r\ln\frac{p}{p_s(T_1)}}\right)\ln\frac{p}{p_s(T_1)}=$$

$$=\left(1-\frac{r_*}{r}\right)\ln\frac{p}{p_s(T_1)}. \tag{35}$$

Now instead of equation (34) we can get

$$\frac{dr}{dt}=\frac{2\alpha_c}{2-\alpha_c}\frac{m}{\rho_2\sqrt{2\pi mk}}\frac{p}{\sqrt{T_1}}\frac{p_s(T_1)e^{\frac{2\sigma}{R\rho_2 T_1 r}}}{p}\left(1-\frac{r_*}{r}\right)\ln\frac{p}{p_s(T_1)}. \tag{36}$$

Taking into account Clausius-Clapeyron equation after integrating we obtain

$$\frac{p_s(T_1)}{p}=e^{\frac{-h\Delta T}{RT^2}}, \tag{37}$$

where ΔT is supercooling, and can be expressed by the radius of nuclei when there is an equilibrium

$$\Delta T\approx\frac{2\sigma T}{\rho_2 hr}. \tag{38}$$

It is noteworthy that

$$\frac{p_s(T_1)e^{\frac{2\sigma}{R\rho_2 T_1 r}}}{p}\cong\left(1-\frac{h}{RT_1^2}\Delta T\right)\left(1+\frac{2\sigma}{R\rho_2 T_1 r}\right) \tag{39}$$

for a sufficiently small value of ΔT. It also means that the expression (39) is of the order of unity for large value of r. Thus we get from (36)

$$\frac{dr}{dt}\cong\frac{2\alpha_c}{2-\alpha_c}\frac{1}{\sqrt{2\pi}}\frac{1}{\rho_2}\sqrt{\frac{m}{k}}\frac{p}{\sqrt{T_1}}\left(1-\frac{r_*}{r}\right)\ln\frac{p}{p_s(T_1)}. \tag{40}$$

From the kinetic theory of gases we can take the expressions for the thermal conductivity [11]

$$\lambda=\frac{25}{32}c_v\frac{\sqrt{kmT}}{\sqrt{\pi}d^2} \tag{41}$$

and for the mean free path [11]

$$l=\frac{kT}{\sqrt{2}\pi pd^2}. \tag{42}$$

Although these formulae are valid for rigid sphere molecules they allow to estimate the expression

$$\sqrt{\frac{m}{k}}\frac{p}{\sqrt{T_1}}\cong\frac{32\alpha_c}{25\pi c_v(2-\alpha_c)}\frac{\lambda}{l} \tag{43}$$

and finally substituting (43) into (40) we get

$$\frac{dr}{dt}\cong\frac{32\alpha_c}{25\pi c_v(2-\alpha_c)}\frac{\lambda}{\rho_2 l}\left(1-\frac{r_*}{r}\right)\ln\frac{p}{p_s(T_1)} \tag{44}$$

which is very similar to the equation (32) with the only difference that the coefficient

$$\frac{5}{8}\frac{RT^2}{h^2} \tag{45}$$

is substituted by

$$\frac{32\alpha_c}{25\pi c_v(2-\alpha_c)}. \tag{46}$$

It is possible to get the same magnitudes of the expressions (45), (46) for a suitable value of α_c. For example for $T=360°\mathrm{K}$, $R=461\ \mathrm{m^2/(s^2\cdot °K)}$, $h=2.3\cdot10^6\ \mathrm{m^2/s^2}$, $c_v=1.4\cdot10^3\ \mathrm{m^2/(s^2\cdot °K)}$ these expressions became equal for $\alpha_c=0.05$.

4.5. Authors simplification of basic equations

In the previous work [8], [10] the author presented the simplified form of energy equation (18). The simplification concerned the second term on the right hand side

$$\frac{6m}{rc\rho_2}\frac{\alpha_c}{2-\alpha_c}\frac{p}{\sqrt{2\pi mkT_1}}\left(c_p-\frac{R}{2}\right)(T_2-T_1) \tag{47}$$

which has been dropped. For the small value of α_c the numerical results of integration were in good agreement with the solution of basic equations.

However, it has been shown that for the value of α_c close to unity there is a high discrepancy due to this simplification.

After the numerical analysis of the basic equations it has turned out that although some of the above simplifications look quite reasonable the solutions of equations (20) and (21) are very sensitive to the apparently slight change of the equations.

5. The linearized form of equations

The equations (20) and (21) are of nonlinear type and they are not typical for the analytical discussions. Therefore it is reasonable to start the discussion with the linearization of basic equations. Let us assume that there is no influence of condensing nuclei on the

vapor parameters. It may be true for the very beginning of nucleation zone. In such a case one can take the following formulae for isentropic expansion of ideal gas.

$$p = p_0 e^{\dot{p}t}, \tag{48}$$

$$T_1 = T_0 e^{\dot{p}\frac{\kappa-1}{\kappa}t}, \tag{49}$$

where the rate of expansion is given by

$$\dot{p} = \frac{1}{p}\frac{dp}{dt}. \tag{50}$$

For the sake of simplicity let us assume that $\dot{p}$ is constant. For the saturation temperature of liquid we shall use the integrated Clausius-Clapeyron equation

$$p_s(T_2) = p_s(T_0) e^{\frac{h}{R}\left(\frac{1}{T_0}-\frac{1}{T_2}\right)}. \tag{51}$$

Now the equation (20) and (21) may be rewritten into the form

$$\frac{dr}{dt} = \frac{2\alpha_c}{2-\alpha_c}\frac{m}{\rho_2\sqrt{2\pi mk}}\left[\frac{p_0}{\sqrt{T_0}} e^{\frac{1+\kappa}{2\kappa}\dot{p}t} - \frac{p_s(T_0)}{\sqrt{T_2}} e^{\frac{h}{R}\left(\frac{1}{T_0}-\frac{1}{T_2}\right)+\frac{2\sigma}{R\rho_2 T_2 r}}\right], \tag{52}$$

$$\frac{dT_2}{dt} = \frac{3\left(h-\frac{R}{2}T_2\right)}{rc}\frac{dr}{dt} - \frac{6m}{rc\rho_2}\frac{\alpha_c}{2-\alpha_c}\left[1+\frac{(1-\alpha_c)\alpha_a}{\alpha_c}\right]\times$$

$$\times \frac{c_p - \frac{R}{2}}{\sqrt{2\pi mk}}\frac{p_0}{\sqrt{T_0}} e^{\frac{1+\kappa}{2\kappa}\dot{p}t}\left(T_2 - T_0 e^{\frac{\kappa-1}{\kappa}\dot{p}t}\right). \tag{53}$$

Let us introduce the nondimensional temperature of a droplet

$$T = \frac{T_2}{T_0} \tag{54}$$

and the nondimensional radius of a droplet

$$\bar{r} = \frac{r}{r_*(p_0 T_0)}, \tag{55}$$

where

$$r_*(p_0 T_0) = \frac{2\sigma}{R\rho_2 T_0}\left[\ln\frac{p_0}{p_s(T_0)}\right]^{-1}. \tag{56}$$

For nondimensional radius and temperature we have the equations

$$\frac{d\bar{r}}{dt} = \frac{1}{\tau_r}\left[e^{\frac{1+\kappa}{2\kappa}\dot{p}t} - \frac{p_s(T_0)}{p_0} e^{\frac{h}{RT_0}}\frac{1}{\sqrt{T}} e^{\frac{2\sigma}{R\rho_2 T_0 r_* T}-\frac{h}{RT_0 T}}\right], \tag{57}$$

$$\frac{dT}{dt}=\frac{3\left(h-\frac{R}{2}T_0T\right)}{c\bar{r}T_0}\frac{d\bar{r}}{dt}-\frac{6m}{c\rho_2 r_*\bar{r}}\frac{\alpha_c}{2-\alpha_c}\left[1+\frac{(1-\alpha_c)\alpha_a}{\alpha_c}\right]\times$$

$$\times\frac{c_p-\frac{R}{2}}{\sqrt{2\pi mk}}\frac{p_0}{\sqrt{T_0}}e^{\frac{1+\kappa}{2\kappa}\dot{p}t}\left(T-e^{\frac{\kappa-1}{\kappa}\dot{p}t}\right), \tag{58}$$

where

$$\tau_r=\frac{\rho_2\sqrt{2\pi mkT_0}(2-\alpha_c)r_*}{2\alpha_c mp_0}. \tag{59}$$

For the small value of t we may expect small increments of $\bar{r}$ and T. Taking into account the linear expansion we may put

$$\bar{r}=1+\Delta r, \tag{60}$$

$$T=1+\Delta T. \tag{61}$$

The linearized equations which have been obtained from (57) and (58) are

$$\frac{d\Delta r}{dt}=at+a_1\Delta r+a_2\Delta T, \tag{62}$$

$$\frac{d\Delta T}{dt}=bt+b_1\Delta r+b_2\Delta T, \tag{63}$$

where

$$a=\frac{1+\kappa}{2\kappa}\frac{\dot{p}}{\tau_r}, \tag{64}$$

$$a_1=\frac{2\sigma}{R\rho_2T_0r_*\tau_r}, \tag{65}$$

$$a_2=\frac{1}{\tau_r}\left(\frac{1}{2}+\frac{2\sigma}{R\rho_2T_0r_0}-\frac{h}{RT_0}\right), \tag{66}$$

$$b=\frac{3}{\tau_r}\frac{\dot{p}}{c\kappa}\left[\frac{1+\kappa}{2}\left(\frac{h}{T_0}-\frac{1}{2}R\right)+(\kappa-1)\left(1+\frac{1-\alpha_c}{\alpha_c}\alpha_a\right)\right], \tag{67}$$

$$b_1=\frac{6}{c\tau_r}\left(\frac{h}{T_0}-\frac{1}{2}R\right)\frac{\sigma}{R\rho_2T_0r_0}, \tag{68}$$

$$b_2=\frac{3}{c\tau_r}\left[\left(\frac{h}{T_0}-\frac{1}{2}R\right)\left(\frac{1}{2}+\frac{2\sigma}{R\rho_2T_0r_0}-\frac{h}{RT_0}\right)-\left(1+\frac{1-\alpha_c}{\alpha_c}\alpha_a\right)\right]. \tag{69}$$

The general solution of the equations (62) and (63) has the form

$$\Delta r=A_1e^{\lambda_1t}+A_2e^{\lambda_2t}+At+A_0, \tag{70}$$

$$\Delta T=B_1e^{\lambda_1t}+B_2e^{\lambda_2t}+Bt+B_0, \tag{71}$$

where

$$\lambda_{1,2}=\tfrac{1}{2}[a_1+b_2\pm\sqrt{(a_1+b_2)^2-4(a_1b_2-a_2b_1)}], \tag{72}$$

$$\left.\begin{aligned} A&=\frac{a_2b-ab_2}{a_1b_2-a_2b_1}, \qquad B=\frac{ab_1-a_1b}{a_1b_2-a_2b_1},\\ A_0&=\frac{Ab_2-Ba_2}{a_1b_2-a_2b_1}, \qquad B_0=\frac{a_1B-b_1A}{a_1b_2-a_2b_1}, \end{aligned}\right\} \tag{73}$$

$$\left.\begin{aligned} A_1&=\frac{(a_1-\lambda_2)(\Delta r_0+A_0)+a_2(\Delta T_0-B_0)}{\lambda_2-\lambda_1},\\ A_2&=\Delta r_0-A_1-A_0,\\ B_1&=\frac{a_1-\lambda_1}{a_2}A_1, \qquad B_2=\frac{a_1-\lambda_2}{a_2}A_2, \end{aligned}\right\} \tag{74}$$

for the initial conditions at $t=0$

$$\Delta r=\Delta r_0, \tag{75}$$

$$\Delta T=\Delta T_0. \tag{76}$$

The numerical calculation has been done for the following set of parameters

$$T_0=354.6^\circ\,\mathrm{K}, \qquad p_0=1.0459\cdot10^5\,\mathrm{N/m^2},$$

$$R=461\,\mathrm{J/(kg^\circ K)}, \qquad c=4195\,\mathrm{J/(kg^\circ K)}, \qquad c_p=1983\,\mathrm{J/(kg^\circ K)},$$

$$k=1.38\cdot10^{-23}\,\mathrm{J/(kg^\circ K)}, \qquad h=2.308\cdot10^6\,\mathrm{J/kg},$$

$$\rho_2=10^3\,\mathrm{kg/m^3}, \qquad \sigma=6.26\cdot10^{-2}\,\mathrm{J/m^2},$$

$$\kappa=1.33, \qquad \alpha_c=0.15, \qquad \alpha_a=1.0.$$

The initial disturbance of the radius has been taken as either equal to one molecule or equal to zero. The results of the calculation according to (70) and (71) are shown in Fig. 1 and 2.

If there is no initial disturbance of radius the growth of nuclei is caused by the suitable change of parameters of the ambient vapor. The nuclei may also grow due to the initial change of critical radius.

The nuclei have the tendency to grow only in the case when they exceed the dimension of a critical radius with regard to parameters of vapor. For the listed parameters the critical droplet at the beginning was

$$r_*(p_0, T_0)=1.0437\cdot10^{-9}\,\mathrm{m}.$$

If the expansion takes place,

$$r_*(p_0, T_0)>r_*(p, T) \tag{77}$$

for $t>0$, there is an impulse for the growth of nuclei following the equation (20). A similar

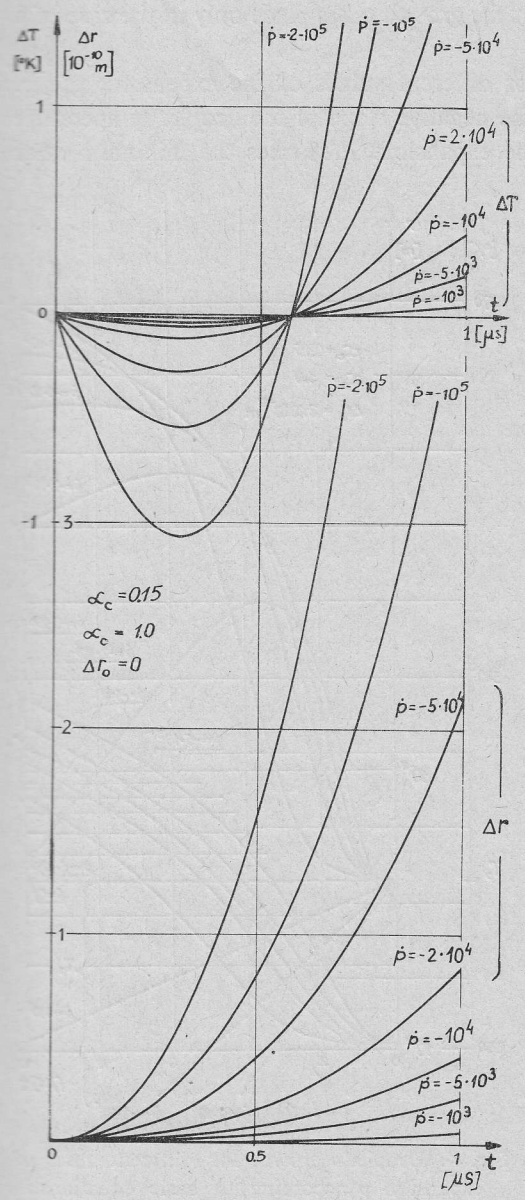

Fig. 1. Influence of the expansion rate $\dot{p}$ on the growth of nuclei for initial disturbance of radius equal to zero

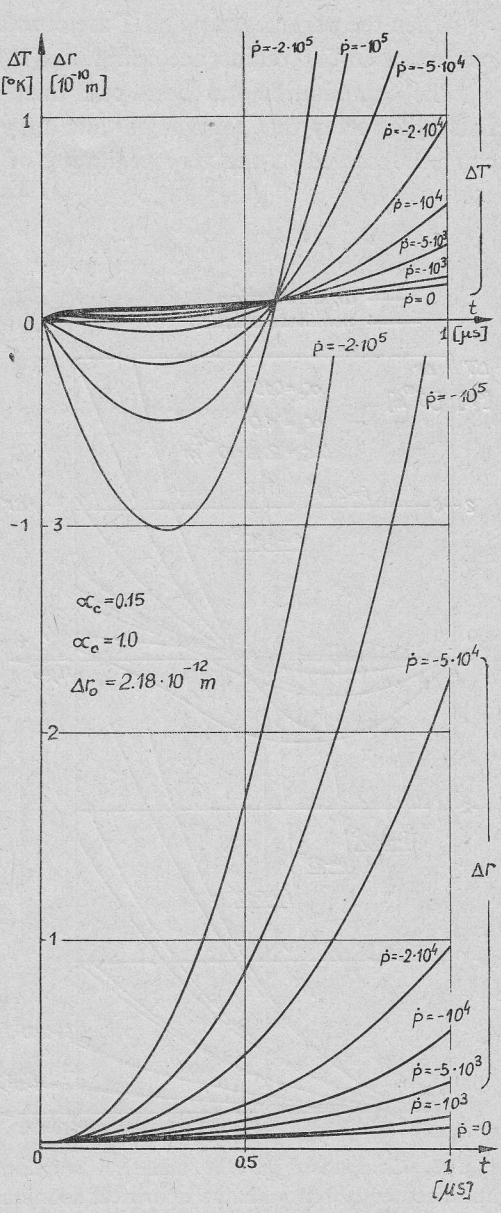

Fig. 2. Influence of the expansion rate $\dot{p}$ on the growth of nuclei for initial disturbance of radius equal to one molecule

situation may happen when at least one more molecule sticks to the critical droplet because we have again

$$r_*(p_0, T_0)+\Delta r_0 > r_*(p, T). \tag{78}$$

In our case $\Delta r_0 = 2.1844 \cdot 10^{-12}$ m.

When the parameters p and T are constant the growth takes place only in the case of a perturbed initial radius according to (78).

The computation has been performed for different values of the expension rate $\dot{p}$. It is noteworthy that for a high value of $\dot{p}$ the negative slope of the droplet temperature can be observed at the very beginning of the expansion. It reaches the minimum after

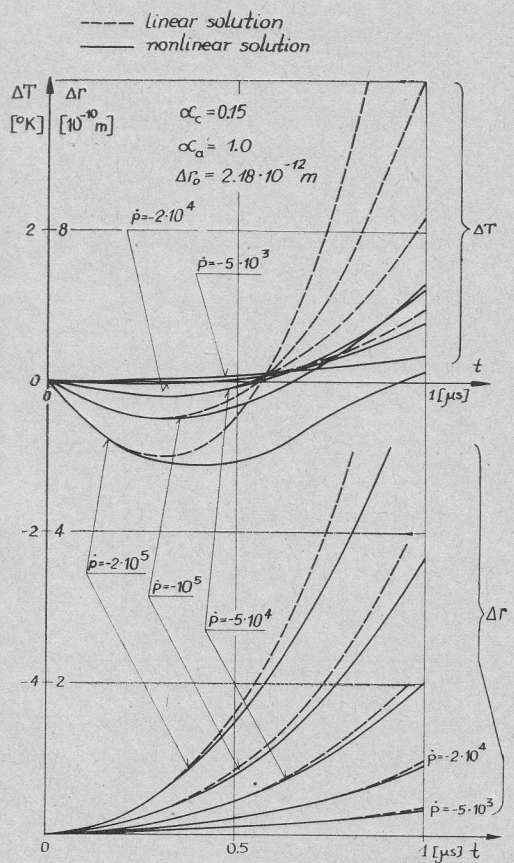

Fig. 3. Comparison of the analitical solution linearized equations with the numerical solution of basic equations

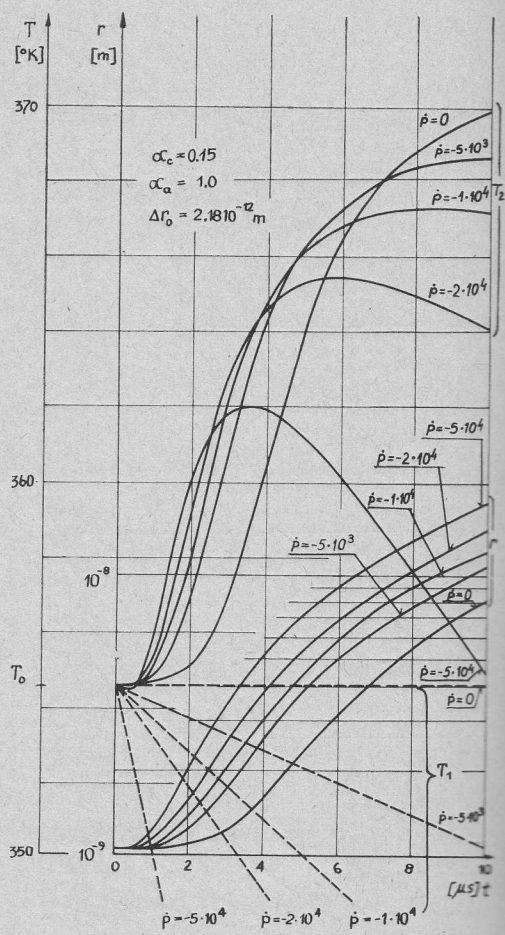

Fig. 4. Droplet's growth for different rates of expansion $\dot{p}$ according to basic equations

a short while and then rises because of the heating effect of condensed molecules. In this short period the mechanism of carrying off the heat from the droplet prevails the heating effect of the droplet. After this short time the situation changes and the temperature of the droplet rises due to the condensation.

In connection with the results presented in Fig. 1 and Fig. 2, there arises a question of validity of the linearization. This problem can be clarified by comparing these results with the results of the nonlinearized equations.

6. The numerical solution of nonlinearized equations

The Runge–Kutta method has been used to integrate the equation in its full form (57), (58). The results provide us with the information of the behaviour of solution in comparison to those of linearized equations.

As it can be noticed from Fig. 3 the validity of linearized solution is limited to a short period of time. The deviation from the linear solution rises very rapidly. The important fact is that at the very beginning the solutions of linearized and nonlinearized equations go very close to each other. In the authors' opinion it proves the applicability of the integrating method which has been used in these numerical experiments.

The influence of the rate of expansion and the value of α_c on the solution has been investigated. The behaviour of the solution for different values of $\dot{p}$ are shown in Fig. 4. At the starting point, for a small t, the growth of nuclei and the temperature according

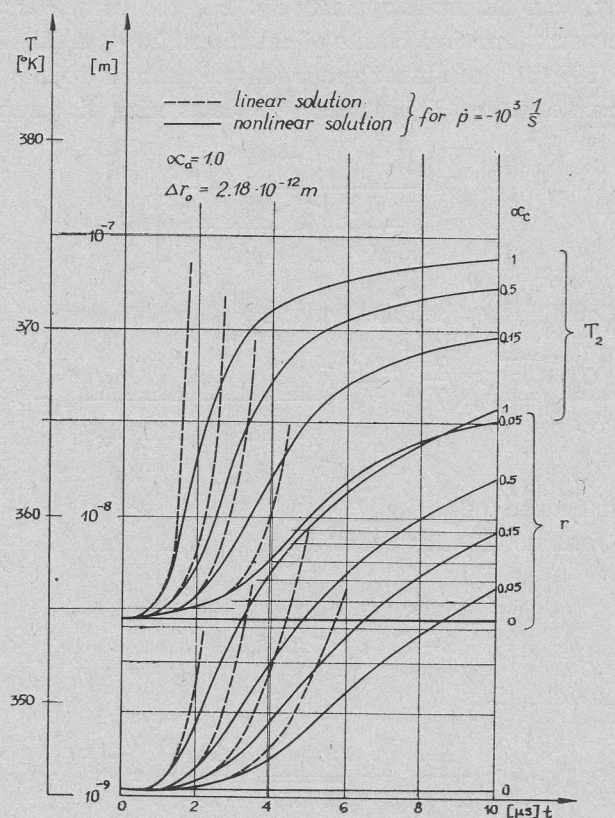

Fig. 5. Influence of α_c on the growth of nuclei according to basic equations

to the graphs in Fig. 5 are very similar to the linear solution. The differences can be noticed after a short time and they pronounce that the growth of the nuclei is smaller in the nonlinear region. The temperature of the droplet also behaves in a very peculiar way. After linear region when the temperature of the droplet begins to grow it reaches the point

when the differences between the temperature of the heated droplet and the gas is so high that in the equation (58) for the temperature change, the second term becomes predominant. Then we get the negative slope of the temperature line as it can be noticed in Fig. 4.

The radius of the droplet increases all the time although not so rapidly as the linear solution has predicted.

The influence of α_c is shown in Fig. 5. Changing the value of α_c from zero to unity we get a monotonic change of the curves. The important fact is that for $\alpha_c=1$ we get a limiting case of the radius growth. The highest possible value of the radius can be achieved within the framework of the discussed physical model for $\alpha_c=1$.

7. The comparison of different models of condensation

After the numerical solution is obtained it is possible to examine the different models which have already been discussed qualitatively. For the parameters listed previously the comparison between numerical results of equations (20) and (21) and the equations (26), (28), (29) and (30), (31) and author's equations taken from [10] has been done.

For the Oswatitsch equation, T_2 has been assumed as being the saturation temperature

$$T_2=\frac{T_0}{1-\dfrac{RT_0}{h}\left[\ln\dfrac{p_0}{p_s(T_0)}+\dot{p}t\right]} \tag{79}$$

and T_1 according to (49).

Thus the equation (25) has become

$$\frac{dr}{dt}=\frac{C}{h\rho_2}\sqrt{\frac{k}{m}}\,p_0\sqrt{T_0}\,e^{\dot{p}\frac{\kappa+1}{2\kappa}t}\left[\frac{1}{1-\dfrac{RT_0}{h}\left[\ln\dfrac{p_0}{p_s(T_0)}+\dot{p}t\right]}-e^{\dot{p}\frac{\kappa-1}{\kappa}t}\right] \tag{80}$$

and it has been integrated numerically.

The Wegener's formula (28) has been adopted into the form

$$\frac{dr}{dt}=\frac{2\alpha_c}{2-\alpha_c}\,\frac{mp_0}{\rho_2\sqrt{2\pi mkT_0}}\,e^{\dot{p}\frac{\kappa+1}{2\kappa}t} \tag{81}$$

which after integration gives

$$r=r_*(p_0, T_0)+\frac{2\alpha_c}{2-\alpha_c}\,\frac{mp_0}{\rho_2\sqrt{2\pi mkT_0}}\,\frac{2\kappa}{\dot{p}(\kappa+1)}\,(e^{\dot{p}\frac{\kappa+1}{2\kappa}t}-1). \tag{82}$$

For the calculation simplified expresions in their original form have been used

$$r=r_*(p_0\,T_0)+\frac{\alpha_c mp_0}{\rho_2\sqrt{2\pi mkT_0}}\,\frac{2\kappa}{\dot{p}(\kappa+1)}\,(e^{\dot{p}\frac{\kappa+1}{2\kappa}t}-1), \tag{83}$$

where the macroscopic flux of molecules towards the surface of liquid is neglected.

The equations (28) and (30) according to Hill's approximations may be, for the computation, rewritten into the form

$$\frac{dr}{dt}=\frac{2\alpha_c}{2-\alpha_c}\frac{m}{\rho_2\sqrt{2\pi mk}}\left[\frac{p_0}{\sqrt{T_0}}e^{\frac{1+\kappa}{2\kappa}\dot{p}t}-\frac{p_s(T_0)}{\sqrt{T_2}}e^{\frac{h}{R}\left(\frac{1}{T_0}-\frac{1}{T_2}\right)}\right], \tag{84}$$

$$T_2=T_0e^{\dot{p}\frac{\kappa-1}{\kappa}t}+\frac{h-\frac{1}{2}RT_2}{\left(c_p-\frac{R}{2}\right)\left[1+\frac{(1-\alpha_c)\alpha_a}{\alpha_c}\right]}\left[1-\sqrt{\frac{T_0}{T_2}}\frac{p_s(T_0)}{p_0}e^{\frac{h}{R}\left(\frac{1}{T_0}-\frac{1}{T_2}\right)-\dot{p}\frac{\kappa+1}{2\kappa}t}\right]. \tag{85}$$

The shape of the second equation is very convenient for the discussion and the calculation.

For Gyarmathy's formula the mean free path has been calculated from the relation

$$l=\frac{3}{2}\eta_0\sqrt{R}\frac{\sqrt{T_1}}{p_1}=\frac{3}{2}\eta_0\frac{\sqrt{RT_0}}{p_0}e^{-\dot{p}\frac{1+\kappa}{2\kappa}t}. \tag{86}$$

Taking into account the relations (48), (49) and (51) we get the following relation for the critical radius of nuclei

$$r_*=\frac{2\sigma}{R\rho_2T_1\ln\frac{p}{p_s(T)}}=\frac{2\sigma}{R\rho_2T_0e^{\dot{p}\frac{\kappa-1}{\kappa}t}\left[\ln\frac{p_0}{p_s(T_0)}+\dot{p}t-\frac{h}{RT_0}\left(1-e^{-\dot{p}\frac{\kappa-1}{\kappa}t}\right)\right]}. \tag{87}$$

Finally instead of (31) the following equation for the calculation has been used

$$\frac{dr}{dt}=\frac{\lambda T_0}{\rho_2h^2}\frac{R\,{}_0e^{\frac{\kappa-1}{\kappa}\dot{p}t}\left[\ln\frac{p_0}{p_s(T_0)}+\dot{p}t-\frac{h}{RT_0}\left(1-e^{-\frac{\kappa-1}{\kappa}\dot{p}t}\right)\right]-\frac{2\sigma}{r\rho_2}e^{\frac{\kappa-1}{\kappa}\dot{p}t}}{r+2.39\eta_0\sqrt{R}\frac{\sqrt{T_0}}{p_0}e^{-\dot{p}\frac{1+\kappa}{2\kappa}}}. \tag{88}$$

In addition to these formulae the simplified set of equations has been computed according to [10]

$$\frac{dr}{dt}=\frac{2\alpha_c}{2-\alpha_c}\frac{m}{\rho_2\sqrt{2\pi mk}}\left[\frac{p_0}{\sqrt{T_0}}e^{\frac{1+\kappa}{2\kappa}\dot{p}t}-\frac{p_s(T_0)}{\sqrt{T_0}}e^{\frac{h}{R}\left(\frac{1}{T_0}-\frac{1}{T_2}\right)+\frac{2\sigma}{R\rho_2T_2r}}\right], \tag{89}$$

$$\frac{dT_2}{dt}=\frac{3\left(h-\frac{R}{2}T_2\right)}{rc}\frac{dr}{dt}-\frac{6m}{rc\rho_2}\frac{(1-\alpha_c)\alpha_a}{2-\alpha_c}\frac{c_p-\frac{R}{2}}{\sqrt{2\pi mk}}\times$$

$$\times\frac{p_0}{\sqrt{T_0}}e^{\frac{1+\kappa}{2\kappa}\dot{p}t}\left(T_2-T_0e^{\frac{\kappa-1}{\kappa}\dot{p}t}\right). \tag{90}$$

In the original form of Oswatitsch equation [4] the constant is equal

$$c=\frac{3\sqrt{3}}{8}=0.65.$$

The value of 0.65 can be achieved from the relation (27) for $\alpha_a=1$, $\alpha_c=0.725$. Nevertheless, the results obtained from the equation (80) do not confirm the simplification of the basic equations. It can be seen from Fig. 6 that the behaviour of the solution for r differs considerably from the one resulting from the basic set of equations (57) and (58). The main

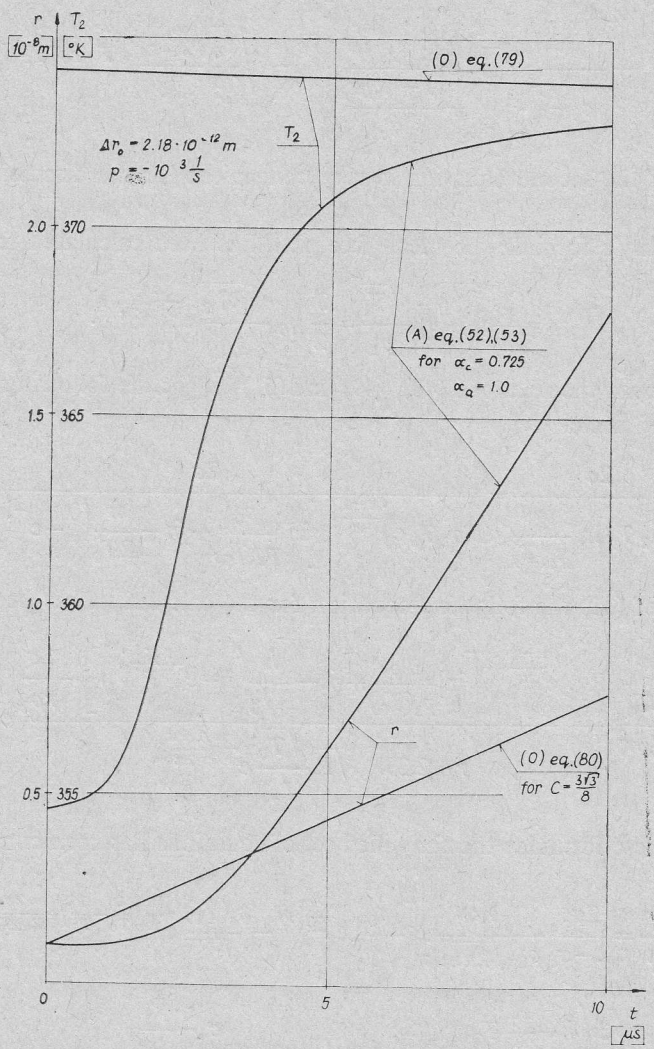

Fig. 6. Computed radius and temperature of droplet according to Oswatitsch equation (O) and nonsimplified equations (A) for $\dot{p}=-10^3\ \mathrm{s}^{-1}$

reason for the difference should be sought in the different behaviour of the temperature of the droplet in respect to the saturation temperature. The temperature of the droplet ought to be under the influence of condensation rate and this is not taken into account in the relation (80).

Against the numerical solution of (57) and (58) the results of Wegener's formula for the droplet growth is shown in Fig. 7. The discrepancy of these results is due to the fact that in the

Wegener's formula the evaporating process is not taken into account. The magnitude of these differences results from the physical meaning of the simplification.

The comparison to the solution obtained from Hill's approximation shows in Fig. 8 the difference in the temperature of the droplet in relation to the temperature resulting from

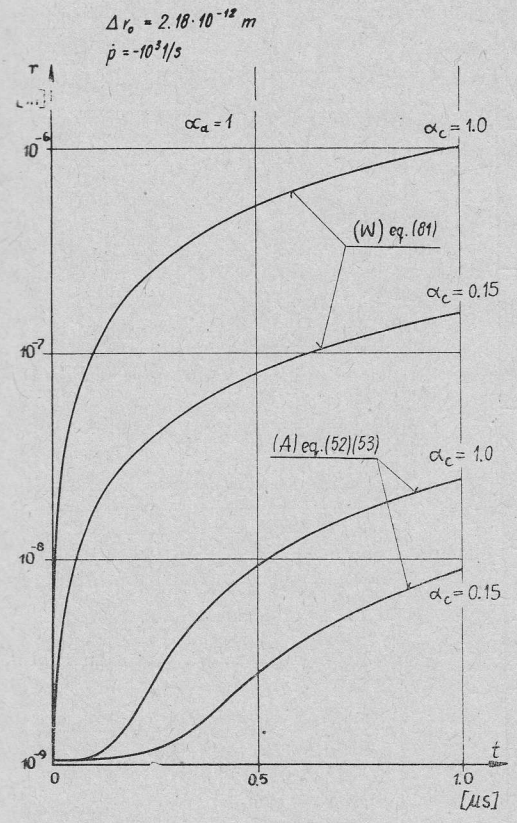

Fig. 7. Computed radius of droplet according to Wegener's equation (*W*) and nonsimplified equations (*A*) for $\dot{p} = -10^3\ s^{-1}$

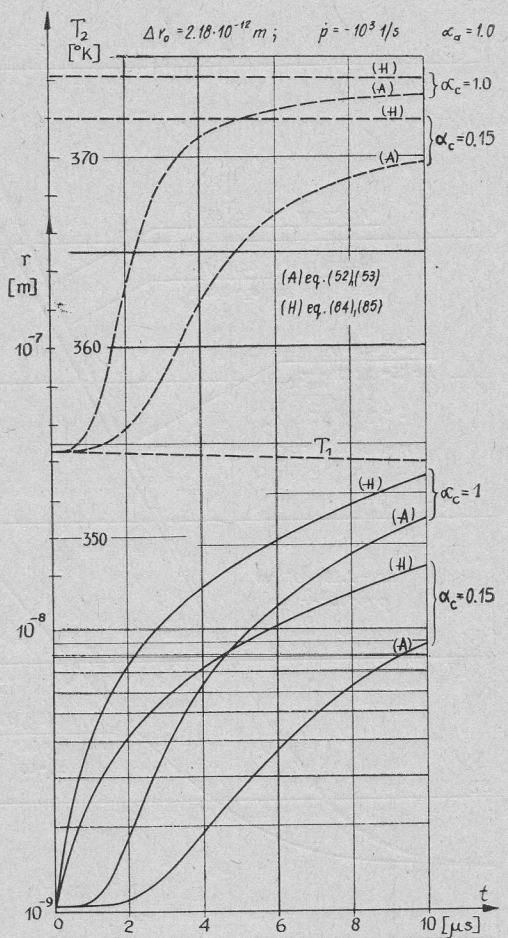

Fig. 8. Computed radius and temperature of droplet according to Hill's simplified equations (*H*) and nonsimplified equations (*A*) for $\dot{p} = -10^3\ s^{-1}$

the basic equation. The temperature of the droplet calculated from the equation (85) remains nearly constant and differs from the temperature T_1 already at the starting point. The negative sign ahead of the exponential term in the square brackets keeps off T_2 from the rapid rise. The behaviour of T_2 differs in this solution significantly from the solution of basic equation.

The solution obtained from Gyarmathy's formula is shown in Fig. 9. Although this

formulae can be justified by the Hertz and Knudsen model for the beginning of droplet growth it gives the noticeable departure from the curves (*A*).

The last Fig. 10 shows the comparison of the solution of the set (89) and (90) with the solution of the basic equations. The agreement is quite satisfactory for a small value of α_c but it fails for α_c close to unity. It is because the simplified set of equations does not take,

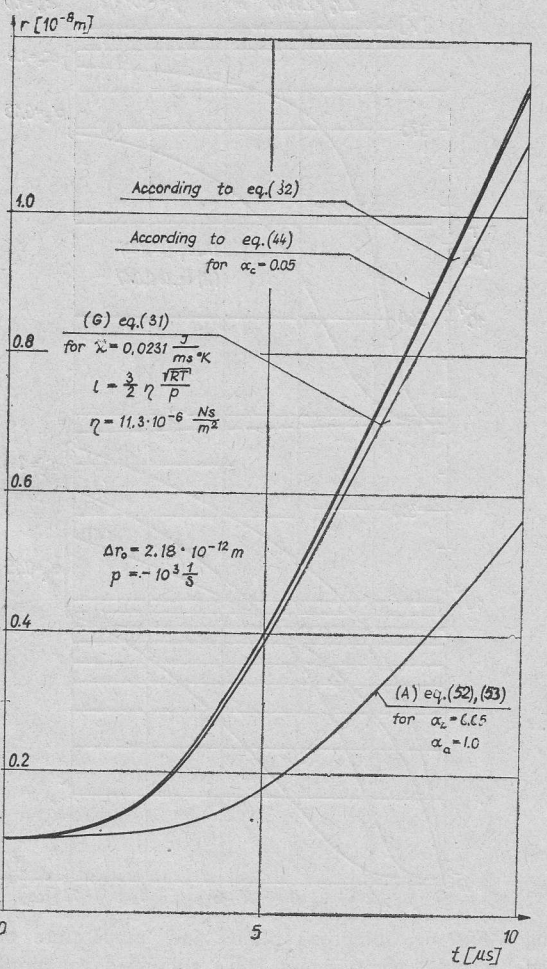

Fig. 9. Computed radius of droplet according to Gyarmathy's equation and nonsimplified equations for $\dot{p} = -10^3\ s^{-1}$

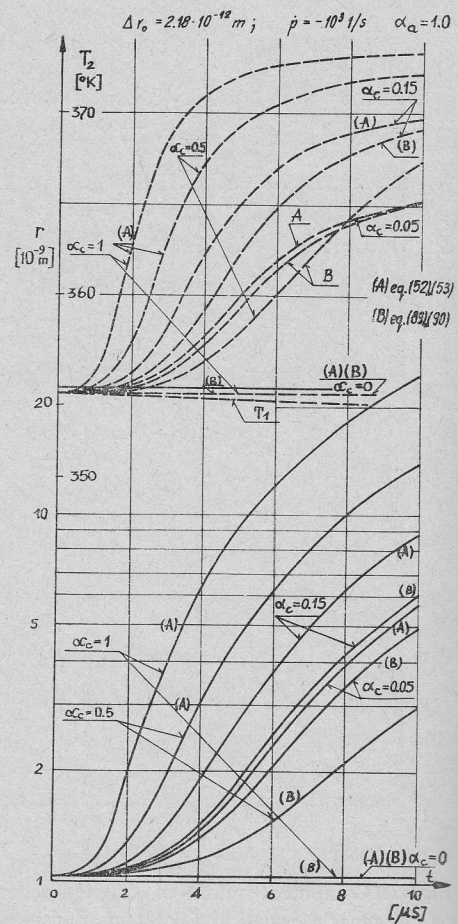

Fig. 10. Computed radius and temperature of droplet according to simplified (*B*) and nonsimplified (*A*) authors' equation for $\dot{p} = -10^3\ s^{-1}$

into account the amount of heat needed for heating the condensed mass from the ambient temperature T_1 to the temperature of the droplet T_2. It should be pointed out that even such an apparently slight simplification of the basic equations may cause huge differences in the solution.

8. Conclusions

The analysis presented clarified the problem of validity of different simplifications of the basic set of equations which take into account the concept of metastable equilibrium and the relations from the kinetic theory of gases.

The simplifications which are introduced into the basic equations are in fact equiponderant to the initial disturbance of nuclei at metastable conditions. This causes a different situation at the very beginning of the growth of nuclei as compared to the situation described by the basic equations. The disturbance of the droplet at metastable conditions innitiates a very high condensation rate which is contrary to the concept of equilibrium.

This disturbances are of a formal character and could hardly be justified in physical terms. The different values of a radius of growing nuclei after a short time of growth can be achieved from different models.

Table 1

After time growth $t=10\ \mu s$ at the expansion rate $\dot{p}=-10^3\ s^{-1}$ for the parameters listed in the paper the radius and the temperature of droplet according to different models

	Oswatitsch's formula (80)	Wegener's formula (82)	Hill's approximation (84), (85)
Controlling parameters	$C=\frac{3\sqrt{3}}{8}$	$\alpha_c=0.15$	$\alpha_c=0.15$ $\alpha_a=1.0$
r [m]	$7.68\cdot10^{-9}$	$1.57\cdot10^{-7}$	$1.54\cdot10^{-8}$
T_2 [°K]	373.8	–	371.7
r [m] from basic equations for equiponderant α_c and α_a	$1.77\cdot10^{-8}$	$8.96\cdot10^{-9}$	$8.96\cdot10^{-9}$
T_2 [°K] from basic equations for equiponderant α_c and α_a	372.8	369.7	369.7
from basic equations for equiponderant α_c and α_a	$\alpha_c=0.725$ $\alpha_a=1.00$	$\alpha_c=0.15$ $\alpha_a=1.0$	$\alpha_c=0.15$ $\alpha_a=1.0$
	Gyarmathy's formula (84)	Authors' approximation (89), (90)	
Controlling parameters	$\frac{\frac{5}{8}RT^2}{h^2}$	$\alpha_c=0.15$ $\alpha_a=1.0$	$\alpha_c=1.0$ $\alpha_a=1.0$
r [m]	$1.19\cdot10^{-8}$	$6.09\cdot10^{-9}$	$2.41\cdot10^{-8}$
T_2 [°K]	–	369.1	373.3
r [m] from basic equations for equiponderant α_c and α_a	$5.70\cdot10^{-9}$	$8.96\cdot10^{-9}$	$1.046\cdot10^{-9}$
T_2 [°K] from basic equations for equiponderant α_c and α_a	365.2	369.7	354.6
from basic equations for equiponderant α_c and α_a	$\alpha_c=0.05$ $\alpha_a=1.0$	$\alpha_c=0.15$ $\alpha_a=1.0$	$\alpha_c=1.0$ $\alpha_a=1.0$

Table 1 has been set down from computing curves for the time of growth of 10 μs. The discrepancy reaches the order of magnitude of the volume of droplets in comparison to the solution from unsimplified equations. When these relations are involved

in the set of conservation equations describing the gas dynamic of condensing vapor the gas parameters will depend on the chosen model of condensation upon nuclei.

The application of the numerical experiment, presented here, is limited to the region where there is no significant influence of condensation on the gas parameters. This is the region where the supercooling reaches its maximum and then begins to be diminished due to the condensation which consist of the nucleation phenomena and the growth of nuclei. Because of these two phenomena involved simultaneously it is difficult to split their influence on gasdynamics when the physical experiment with the nozzle is carried out. Therefore in the light of experimental results it is rather difficult to judge whether the presented model is adequate.

Nevertheless in the authors' opinion the approach following the idea of Hertz and Knudsen is consistent with the physical concepts and therefore the promising one.

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Analiza numeryczna modelu kondensacji Hertza-Knudsena na małych kroplach w parze wodnej

Streszczenie

Opierając się na modelu Hertza-Knudsena wyprowadzono równania opisujące zmianę promienia i temperatury kropli wody znajdującej się w ekspandującej przechłodzonej parze wodnej. Rozważania dotyczą kropli małych w porównaniu ze średnią swobodną drogą molekuł pary. Takie krople pojawiają się np. w strefie początku kondensacji w dyszach parowych.

W pracy pokazano jak z podstawowego układu równań wynikają uproszczone równania opisujące proces kondensacji, znane w literaturze, takie jak równania Oswatitsha, Wegenera, Hilla i Gyarmathiego.

Rozwiązanie podstawowego układu równań uzyskano za pomocą obliczeń numerycznych, a dla małych czasów wzrostu uzyskano również rozwiązanie analityczne.

W pracy pokazano wpływ współczynnika kondensacji i szybkości ekspansji na wyniki obliczeń numerycznych procesu wzrostu kropel. Z otrzymanych rezultatów wynika, iż dla pełnego układu równań istnieje maksymalna szybkość wzrostu promienia kropli dla wartości współczynnika kondensacji równej jedności, która jest jednak mniejsza od szybkości wzrostu wynikającej z modeli uproszczonych.

Obliczenia wykazują, że różne warianty uproszczeń prowadzą do zdecydowanie różnych wyników liczbowych. Wszelkie uproszczenia podstawowego układu równań są w istocie równoważne dodatkowemu zaburzeniu równowagi metastabilnej kropli, co jest przyczyną stwierdzonych rozbieżności.

Численный анализ Герц-Кнудсеновой модели конденсации на мелких каплях в водяном паре

Резюме

Основываясь на Герц-Кнудсеновой модели, выведены уравнения, описывающие изменение радиуса и температуры водяной капли, находящейся в расширяющемся переохлажденном паре. Рассуждения касаются капель мелких по сравнению со средней свободной дорогой молекул пара. Такие капли появляются, например, в зоне начала конденсации в паровых соплах.

В работе показывается, как из основной системы уравнений получаются упрощенные уравнения, описывающие процесс конденсации, известные в литературе, такие как уравнения Осватича, Вегенера, Хилла и Дьярмати.

Решения основной системы уравнений получены из численных расчетов, а для малых значений времени роста получены также аналитические решения. Из полученных результатов следует, что для комплектной системы уравнений существует максимальное значение скорости роста радиуса капель, когда коэффициент конденсации равняется единице. Эта скорость, однако, меньше скорости роста, получаемой из упрощенных моделей.

Расчеты показывают, что различные варианты упрощений приводят к сильно отличающимся численным результатам. Всякие упрощения основной системы уравнений по сути дела являются эквивалентными с добавочным возмущением метаустойчивого равновесия капель, что является причиной доказанных расхождений.