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DESTRUCTION PROCESSES OF OIL FILMS OF EMULSION ENVIRONMENT

Introduction

Most of the methods aimed at studying the dynamics of growth of vapor bubbles which occur either in the liquid volume or on a superheated surface [1-3]. A peculiarity of emulsion media boiling is that the formation of a vapor phase occurs on the surface of liquid interface if one liquid (for example, oil) is a superficially active substance or in the emulsion there is a superficially active substance (in multicomponent emulsions), which is based on a decrease in the interfacial tension at the interface between the dispersive medium (water) and the dispersion phase (oil) [1, 3-6]. Experimental data [1, 3] indicate that the process of a new phase (vapor) formation is initiated by an internal thermal impact on the surface of the oil particles. Thus, for example, with a sudden pressure decay, the preheated emulsion will be in the supersaturation state of the thermolabile-water phase (the water is superheated against the saturation temperature at a given pressure), i.e. it will contain an excessive amount of heat [7-10]. This heat excess is expended on the work of vapor layer formation and further vaporization. The effect of oil films is ambiguous: on the one hand, when heated, they play the role of thermal resistance, thus, slowing down the heating process; on the other hand, they are the heat carriers which can be used for the formation and growth of the vapor phase and also they are superficially active substance, which contributes to achieving lower water supersaturation temperatures, i.e. early boiling [5]. The consideration of oil thermal effect plays an important role when regarding heat and mass transfer processes during the boiling of emulsion media.

Theoretical description and analysis of heat and mass exchange processes in emulsions, associated with the presence of oil and oil films, allows us to study more in detail the process itself, as well as to offer optimal parameters and characteristics for the processes of obtaining and processing a fine emulsion.

Research objective

The research objective is to consider a drop of emulsion (fig. 1), which consists of a drop of water covered with a layer of oil at the moment of emerged steam layer. At the initial time this system is under some pressure (for example, $p_0 > p_{atm}$) and at a temperature (for example, $T_0 = T_s(p_0)$). At some point of time the system is in the zone of low pressure p_4 ($p_4 < p_0$). Thus, the growth of steam volume and water evaporation will occur due to the fact that the water is superheated relative to the pressure p_4. The movement of the oil-vapor interface will occur under the influence of the pressure difference inside the vapor volume p_n and pressure on the surface of the oil layer p_4. In this case the whole system will be heated by air with the temperature T_{air}.
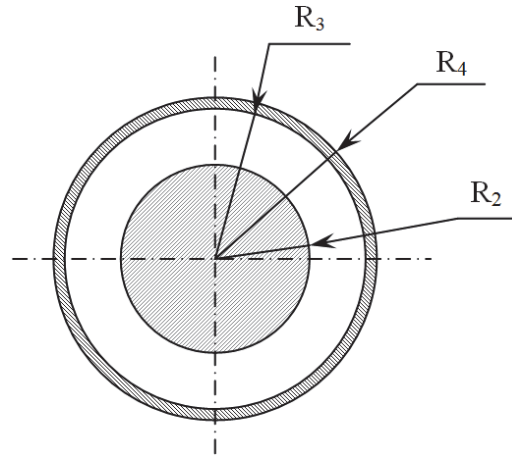
FIGURE 1. *The calculated model of vapor phase growth (R_2 is the radius of the water-vapor interface, R_3 is the radius of the oil-vapor interface, and R_4 is the radius of the oil-air interface)*

Most methods for calculating the radial motion of a liquid at the interface with a spherical enclosure use the Rayleigh equation [2, 4]. Considering the absence of any gas in the vapor volume, i.e. this volume consists only of vapor, taking into account the capillary forces and tangential stresses, the equation for the speed of the radial motion of the oil-vapor interface with the oil film of outer R_4 radius becomes:

$$\frac{dw_3}{d\tau} = \frac{p_3 - p_4 - 1.5\rho_{oil}w_3^2}{\rho_{oil}R_3} + \frac{w_3^2\left[1 + R_3/R_4 + \left(R_3/R_4\right)^2\right]}{2R_3} \tag{1}$$

$$p_3 = p_n - 2\sigma_3/R_3 - 4\mu_{oil}w_3/R_3$$

where:

w_3 – the speed of the oil-vapor interface (boundary), m/s,

τ – time, s,

p_3 – the pressure at the oil-vapor interface, Pa,

p_4 – the pressure at the oil-air interface, Pa,

ρ_{oil} – the oil density, kg /m³,

p_n – the pressure inside the vapor volume, Pa,

σ_3 – the surface tension at the boundary (interface) of the oil-steam, N/m,

μ_{oil} – the coefficient of the dynamic viscosity of the oil, Pa·s.

The equation (1) is the Rayleigh-Plesset equation for limited spherical volume.

Without phase transitions at the interface, we can write:

$$\frac{dR_3}{d\tau} = w_3 \tag{2}$$

To determine the temperature inside the vapor volume, we can use the first law of thermodynamics, which after differentiation takes the form:

$$\frac{dT_n}{d\tau} = \frac{1}{c_n m_n}\left[Q - c_n T_n \Delta m F_2 - p_n \frac{dV_n}{d\tau}\right] \tag{3}$$

where:

T_n – vapor temperature, K (Kelvin),

c_n – specific heat capacitance of vapor, J/(kg·K),

m_n – vapor mass, kg,

V_n – vapor volume, m³,

Q – the amount of heat, W,

F_2 – square meter, $F_2 = 4\pi R_2^2$, m².

We consider mass and heat transfer through the water-vapor interface in terms of the molecular-kinetic theory, which allows to estimate more accurately the kinetics of phase transitions on the liquid-gas surface [2]. We assume that the temperature of the vapor volume T_n is not equal to the temperature of the water-vapor interface T_2, i.e. the process will occur if there is a certain temperature jump at the interface. In this case the mass transfer intensity at the phase transition and heat-flux density between the vapor and the water-vapor interface [2, 4] are equal to:

$$\Delta m = 0.25\alpha_m\left[\rho_2 U_2(T_2) - \rho_n U_n(T_n)\right] \tag{4}$$

$$q = 0.25\rho_n c_n U_n(T_n)(T_2 - T_n) + \Delta m c_n T_2 \tag{5}$$

where:

$U(T)$ – arithmetic mean rate of thermal motion of vapor molecules at a temperature T, $U(T) = \sqrt{\dfrac{8BT}{\pi M_n}}$, m/s,

α_m – coefficient of evaporation,

B – absolute gas constant, J/(mole·K),

ρ_2 – water density, kg/m³,

Δm – mass-flux density, kg/(m²s).

Since the water cooling or its heating is caused by heat exchange with vapor and transfer of latent heat of vaporization, then taking into account the heat flux resulting from the temperature difference of the water drop center T_1 and the temperature of the water-vapor interface T_2 [2 , 7], we can write:

$$\frac{2\lambda_w}{R_2}(T_1 - T_2) = q + \Delta m L(T_2) \tag{6}$$

where:

λ_w – water thermal conductivity, W/(m·K),

$L(T)$ – heat of vaporization, J/kg.

The solution of this equation allows us to determine the unknown temperature T_2.

Equation (3) also includes unknown quantities: the vapor mass m_n, its specific heat capacitance c_n, pressure p_n and volume V_n, as well as the quantity of heat Q.

The vapor mass depends on the mass flow and is determined by:

$$\frac{dm_n}{d\tau} = \Delta m F_2 \tag{7}$$

The volume of the vapor layer is determined by the difference between the volume $\frac{4}{3}\pi R_3^3$ and water volume $\frac{4}{3}\pi R_2^3$:

$$V_n = \frac{4}{3}\pi\left[R_3^3(\tau) - R_2^3(\tau)\right] \tag{8}$$

The specific heat capacitance we consider a constant.

Heat Q consists of heat which comes from the liquid (water) or comes into it, as well as from the heat that comes from the oil film:

$$Q = qF_2 + \frac{4\pi\lambda_{oil}\left(T_4(\tau) - T_3(\tau)\right)}{\dfrac{1}{R_3(\tau)} - \dfrac{1}{R_4(\tau)}} \tag{9}$$

where λ_{oil} is oil heat conductivity, W/(m·K).

The vapor pressure depends on both its temperature T_n and density ρ_n.

For calculation we take the equation of Redlich-Kwong in Wilson's modification [11], which gives the smallest relative error in the definition $p_n = f(T_n, \rho_n)$. Then:

$$p_n = \frac{BT_n\rho_n}{M_n}\left[\frac{1}{1 - \dfrac{b\rho_n}{M_n}} - \frac{\delta_a}{\delta_b}\frac{b}{\dfrac{M_n}{\rho_n} + b}F\right] \tag{10}$$

$$F = 1 + (1.57 + 1.62\vartheta)\left(T_r^{-1} - 1\right)$$

$$\delta_a = 0.4274802327; \quad \delta_b = 0.08664035$$

$$b = \frac{\delta_b BT_{cr}}{p_{cr}}$$

where:

ϑ — azentricity factor,

M_n — molecular weight of vapor, kg/mole,

T_r — temperature reduction, $T_r = T/T_{cr}$,

T_{cr}, p_{cr} — thermal critical point and pressure.

Assuming homogeneity p_n and T_n in the vapor volume, as a consequence, the density of the vapor phase in the vapor volume ρ_n is homogeneous, i.e. $d\rho_n/dR_n = 0$, the function of changing of the vapor density in time can be represented in the following way:

$$\frac{d\rho_n}{d\tau} = \frac{1}{V_n}\left(\frac{dm_n}{d\tau} - \rho_n\frac{dV_n}{d\tau}\right) \tag{11}$$

Substituting the obtained values ρ_n from (11) and T_n from (3) into (10) we can determine the vapor pressure at any time.

The thermal side of the problem is to write the energy equations for oil and water, as well as boundary conditions. Equations of thermal conductivity for oil and water are:

$$\frac{\partial T(r,\tau)}{\partial \tau} = a_{oil}\left(\frac{\partial^2 T(r,\tau)}{\partial r^2} + \frac{2}{r}\cdot\frac{\partial T(r,\tau)}{\partial r}\right) - w_r\frac{\partial T(r,\tau)}{\partial \tau}$$

$$w_r = w_3\frac{R_3^2}{r^2}; \quad \tau > 0; \quad R_3 < r < R_4$$

(12)

$$\frac{\partial T(r,\tau)}{\partial \tau} = a_w\left(\frac{\partial^2 T(r,\tau)}{\partial r^2} + \frac{2}{r}\cdot\frac{\partial T(r,\tau)}{\partial r}\right); \quad \tau > 0; \quad 0 < r < R_2$$

(13)

where a_{oil}, a_w is temperature conductivity coefficient of oil and water, m/s².

Initial data:

$$T(r,0) = T_0; \quad 0 < r < R_4$$

(14)

Boundary condition with account of the equation (6):

$$-\lambda_{oil}\cdot\frac{\partial T}{\partial r}\bigg|_{r=R_4} = \alpha\left(T_{air} - T_4\right)$$

$$T_3(\tau) = T_n; \quad -\lambda_w\cdot\frac{\partial T}{\partial r}\bigg|_{r=0} = 0$$

(15)

where heat-exchange coefficient according to [5] is equal:

$$\alpha = \lambda_{air}/R_4$$

(16)

where λ_{air} is thermal conductivity of air, W/(m·K).

The speed of the water-vapor interface can be found from the equation:

$$w_2 = \frac{dR_2}{d\tau} = \frac{\Delta m}{\rho_w\left(T_2\right)}$$

(17)

The thickness of the vapor layer is:

$$\delta_n = R_3(\tau) - R_2(\tau)$$

(18)

The thickness of the oil film is determined by:

$$\delta_{oil} = R_4(\tau) - R_3(\tau)$$

(19)

The criterion for the final calculation is the critical thickness of the oil film at which it collapses [5]. Equations (1)-(19) must be supplemented by equations of the dependences of thermophysical parameters on temperature.

Calculation data

The calculations are performed for an emulsion drop which consists of a water drop of R_2 = 99 μm, a vapor layer of 1 μm thickness and an oil film of $\delta_{oil} = 15$ μm thickness. At the initial time this system has the same temperature equal to $t_0 = 180°C$, the vapor is saturated, i.e. is at atmospheric pressure of $p_0 \approx 10$ atm. At some point in time this system is in the zone of low pressure $p_4 = 1$ atm and at the same time it is heated by air at a temperature of $t_{air} = 300°C$.

The calculations were carried out using the method of finite differences with explicit selection of variables. The results are shown in figures 2-8.
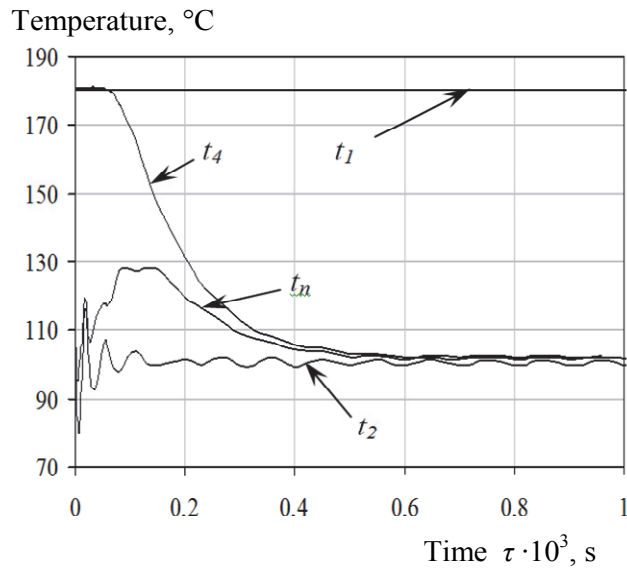
Temperature, °C
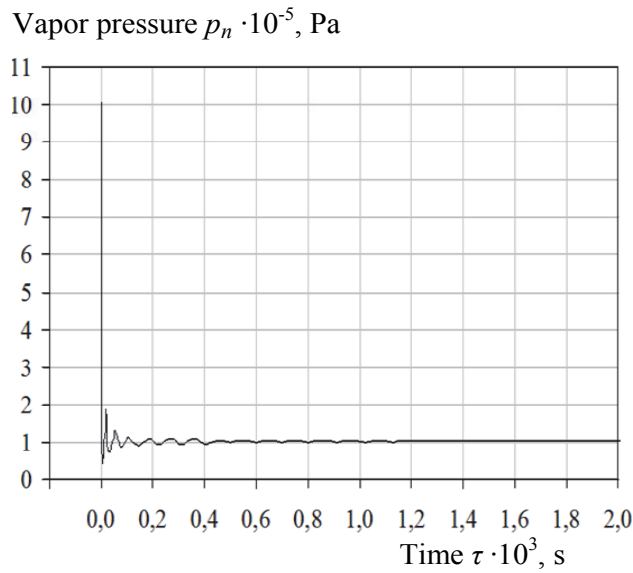

FIGURE 2. *Changes of interfaces temperatures and water center in time*

Vapor pressure $p_n \cdot 10^{-5}$, Pa

FIGURE 3. *Change of vapor pressure in time*
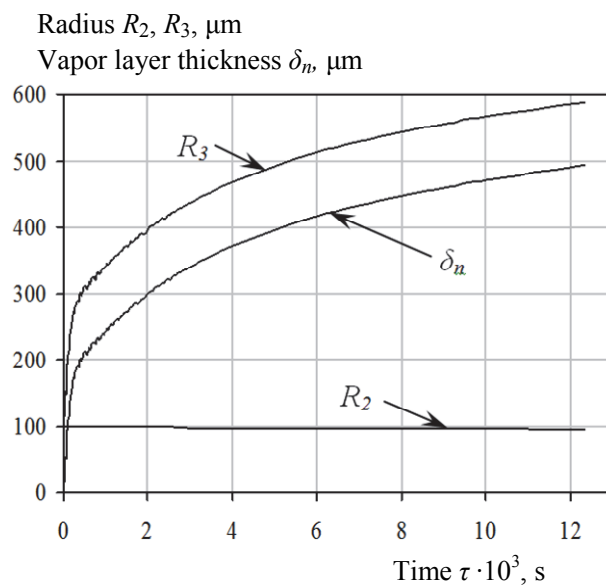
Radius R_2, R_3, μm
Vapor layer thickness δ_n, μm

FIGURE 4. *Change of radii of the interfaces between oil-vapor, water-vapor and the thickness of the vapor layer in time*
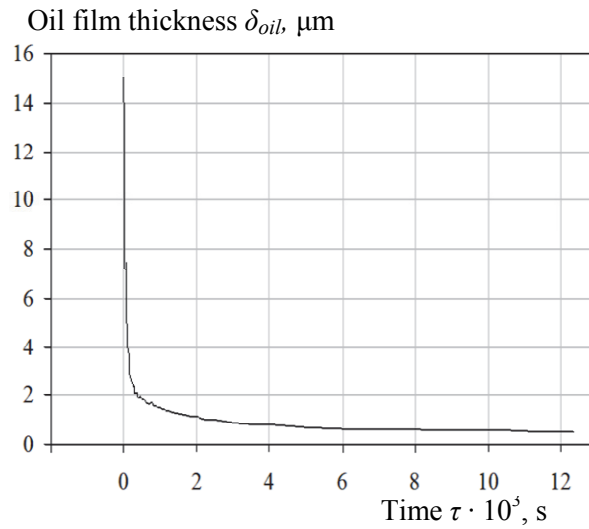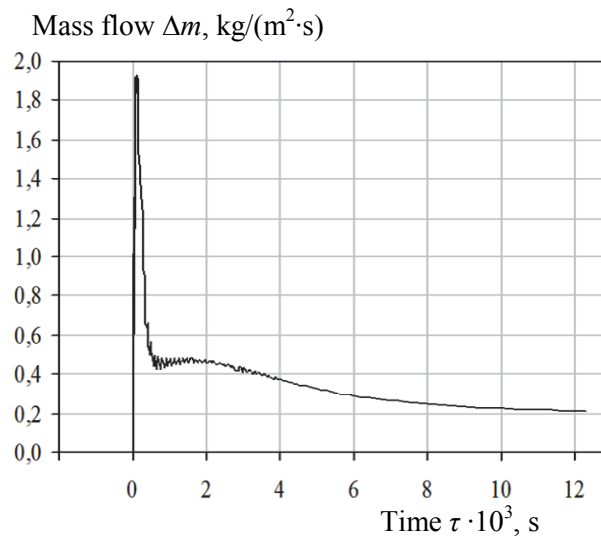
Oil film thickness δ_{oil}, μm

Time $\tau \cdot 10^5$, s

FIGURE 5. *Dependence of oil film thickness on time*

Mass flow Δm, kg/(m^2·s)

Time $\tau \cdot 10^3$, s

FIGURE 6. *Change in time of mass flow*

Motion speed $w_2 \cdot 10^4$, m/s

Time $\tau \cdot 10^3$,s
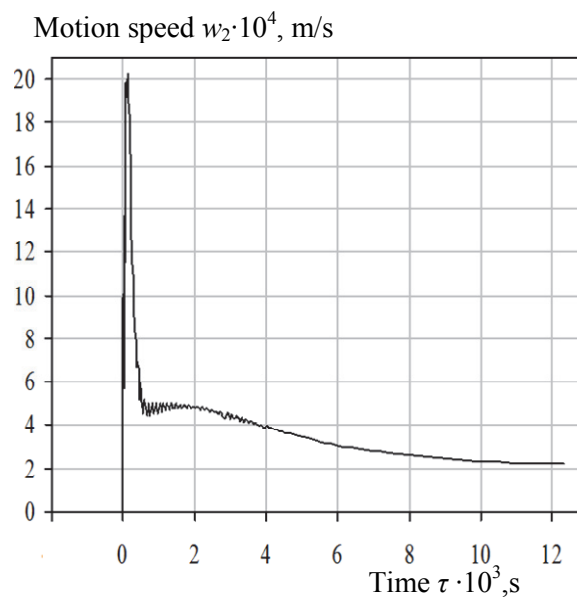
FIGURE 7. *Dependence of speed motion of the water-vapor interface on time*

Motion speed w_3, m/s
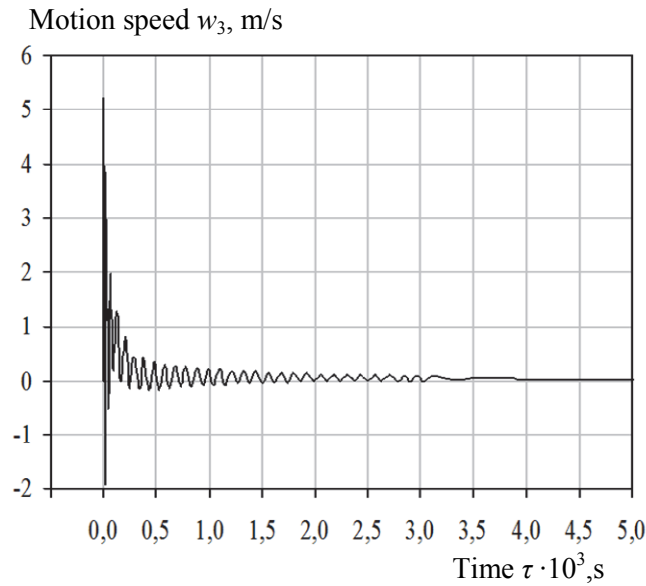

Time $\tau \cdot 10^3$,s

FIGURE 8. *Speed motion change of the oil-vapor interface in time*

It can be seen from figures 2-8 the radii oscillations of interfaces, temperatures, and vapor pressures, which corresponds to physics of the real process. The time up to the oil film destruction to is $\approx 1.23 \cdot 10^{-2}$ s. Figure 2 shows the time variation of interfaces temperatures of the water-vapor t_2, oil-air t_4, vapor t_n, and drop-water centers t_1. Obvious temperature oscillations are seen t_2, t_n, t_4 in the time interval $\tau < 3.7 \cdot 10^{-3}$ s, where the vapor temperature t_n is higher than the temperature of water-vapor interface which indicates its superheated state. This overheating is a consequence of the additional amount of heat coming from the oil film as a result of its heat exchange with the surrounding air. The highest superheat is observed during the time period $\tau \approx (0.05 \div 0.15) \cdot 10^{-3}$ s, which in its turn leads to the increase in the mass flux according to figure 6. In general, there is a consistency in the change of vapor and mass flow temperature, which indicates a significant role of the heat flux from superheated vapor to the water-vapor interface as a result of its heating from the oil film. The decrease t_n leads to the corresponding decrease of mass flow, which, starting at time $\tau > 4 \cdot 10^{-3}$ s, decreases steadily. As can be seen in figure 2, at the initial moment of vapor enclosure expansion the temperature t_4 increases insignificantly, after which its sharp decrease occurs practically to the temperature t_n. The first peak in vapor temperature rise $(\tau \approx 0.02 \cdot 10^{-3}$ s) is coherent with a sharp decrease in the radius of the oil-vapor interface (fig. 4) and, as a consequence, an increase in the oil film thickness (fig. 5). Accordingly, the vapor pressure increases figure 3. Oscillations of the temperature of the water-vapor interface are a consequence of the corresponding oscillations of the mass flow, the vapor temperature and its density. As shown in figures 2-8, the resulting oscillations of temperatures, pressures, interfaces radii, and motion speed of these interfaces are the decaying oscillations. So the temperatures t_2 and t_n tend to certain values, respectively, to $\approx 100°C$ and $\approx 102°C$, and after $\tau \approx 4 \cdot 10^{-3}$ s these fluctuations are not very noticeable. The vapor pressure reflects the combined effects of temperature and vapor density on the further development of the process, and, as can be seen from figure 3, at the beginning of vapor volume growth it is observed a significant reduction in pressure p_n to a pressure which is lower p_4, as a result of which the movement of the oil-vapor interface is carried out to the reduction of vapor volume (fig. 4), as shown in figure 8 by negative values of the motion speed w_3. This decrease in pressure p_n indicates that the mass flow with the heat flow from the oil to the vapor is not able to compensate for the dynamic effect of expansion of the vapor volume, which leads to a decrease in temperature and vapor density. The vapor pressure tends to a certain value, which is slightly higher than the environmental

pressure p_4. After the setting of this specific pressure (with small oscillations), it can be seen that the change of R_2 and R_3 radii, the oil film thickness δ_{oil} and the vapor layer δ_n (figs. 4 and 5) occurs steadily, and the speed of the oil-vapor interface (fig. 8) tends to some constant value.

The velocity of the water-vapor interface w_2 (fig. 7) has the same time behaviour with the mass flow (fig. 6), which indicates an insignificant role of changes in the water density with temperature on the process nature. The temperature of the center of the water drop t_1 (fig. 2) for ≈ 1 ms remains constant and equals to the initial temperature of the system (the inertial period), after which it decreases steadily, asymptotically approaching to t_2 temperature.

Conclusion

The consideration of dynamic forces plays a decisive role in the growth of the vapor layer and allows to study this process more accurately and in details. Using only the thermal side of the problem as for the growth of the vapor phase [5], one could only assume and initially set the temperature of the water-vapor interface, but using the molecular-kinetic theory and taking dynamic forces into account, it is possible to determine the temperature at each point of the calculation. The principal difference from the thermal problem, in which it was assumed that the vapor is always saturated and is at the same temperature throughout the growth interval of the vapor phase, is the change in the vapor density and its overheating. Therefore, we can conclude that it is necessary to solve both the dynamic and the thermal problems.

The most interesting point is the determination of the heat flux that comes into the system or is taken away from it, taking into account the change in Nusselt criterion and the dynamic effect from the medium, which can lead to the premature oil film destruction when the considered emulsion drop is in motion in the medium.

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