

## ТЕПЛОЕНЕРГЕТИКА

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### MODELING OF PARTICLE MERGE OF DISPERSED PHASES OF EMULSION MEDIA

*The paper studies the processes of merging droplets of the dispersed phase of emulsion media using mathematical modelling to determine the final parameters of the resulting conglomerate based on the initial parameters of individual particles. The developed model of emulsion droplet merging allows one to obtain a general picture of the change in the parameters of emulsion droplets and, together with the models of fragmentation and movement, to describe the processes occurring during the boiling of the aqueous phase of the emulsion.*

**Keywords:** emulsion; drop; merge; boiling; water; oil; temperature.

*У статті досліджуються процеси злиття крапель дисперсної фази емульсійних середовищ за допомогою математичного моделювання для визначення кінцевих параметрів результуючого конгломерату на основі початкових параметрів окремих частинок. Розроблена модель злиття крапель емульсії дозволяє отримати загальну картину зміни параметрів крапель емульсії та разом з моделями фрагментації та руху описати процеси, що відбуваються під час кипіння водної фази емульсії.*

**Ключові слова:** емульсія; крапля; злиття; кипіння; вода; масло; температура.

### Problem's Formulation

Complex and diverse physicochemical phenomena that determine the stability of thin separating films of liquid and the structure of two-phase flows remain incompletely studied at present. This issue is considered quantitatively in the DLVO theory (Deryagin, Landau, Verwey, Overbeck) [1—3]. According to this theory, the stability of dispersed systems is determined by the action of electrostatic forces of repulsion of ionic charges in the electrolyte and Van der Waals forces of molecular attraction. The forces of attraction cause a destabilizing effect, which leads to the coagulation of particles. Coulomb repulsive forces provide a stabilizing effect in the region of relatively large values of inter-bubble distances. These forces have the greatest influence at inter-bubble distances of approximately  $10^{-9} \div 10^{-7}$  m, and it is important to know the potential of the surfactant [1]. As can be seen, the distances of action of these forces are quite small and these forces remain even more uncertain at different radii of the interacting particles since the whole theory is developed for two particles of the same size. All this shows that these forces for large distances can be ignored.

### Analysis of recent research and publications

A vapour layer is formed at the oil-water phase boundary in the process of boiling water-oil emulsions as a result of a sharp pressure drop [3—6]. An increase in the vapour volume (an increase in the radius of the oil-vapour interface) for droplets of different sizes occurs at the parameters inherent in each particle at a certain point in time. When droplets merge into a conglomerate, the parameters are averaged, and the consequence is the appearance of a larger drop with its velocities and growth accelerations [7, 8]. Therefore, consideration of these processes of combining boiling particles plays a fairly large role in determining the final size of the fragmented particles of the dispersed phase, and the process itself is an integral part of both boiling and movement and subsequent fragmentation of droplets [4, 7, 9].

### Formulation of the study purpose

The purpose of the article is to study the process of merging droplets of the dispersed phase of emulsion media by determining the final parameters of the resulting conglomerate based on the initial parameters of individual particles.

### Presenting main material

Let's consider two particles of different sizes that merge and determine the parameters of the resulting particle.

The total volume and mass of water after merging are

$$V_{w\Sigma} = \sum_{i=1}^2 \frac{4}{3} \pi R_{1i}^3, \quad m_{w\Sigma} = V_{w\Sigma} \rho_w, \quad i=1,2, \quad (1)$$

where  $R_1$  — is the radius of a water droplet.

To determine the temperature of the water of the formed particle, we determine the average temperatures by the cross-section of the water droplets of the initial particles. With a known number of calculated divisions of the cross-section of a water droplet and known temperatures in each layer of these divisions, the average temperature of the volume of water of each initial particle is determined by the expression

$$t_{sr_i} = \frac{\sum_{n=1}^{N_i} t_{n_i}}{N_i}, \quad (2)$$

where  $N_i$  — is the number of divisions of a given section of the volume of water of a particle. Then the average temperature of the resulting volume of water, assuming equality of heat capacities, is determined from the heat balance equation

$$t_{sr} = \frac{\sum_{i=1}^2 m_{w_i} t_{sr_i}}{m_{w\Sigma}}. \quad (3)$$

The total volume of water determines the radius of the resulting water droplet

$$R_1 = \left( \frac{3}{4\pi} V_{w\Sigma} \right)^{1/3}. \quad (4)$$

Equations (1)—(4) determine the resulting values of the radius of a water droplet and the temperature of a given volume. We assume that the temperature across the cross-section of a water droplet is equal to the average  $t_{sr}$  for further calculations. This assumption is based on the fact of complete mutual mixing of two volumes of water, as a result of which their temperature is determined by the value  $t_{sr}$ .

The mass of vapour in each particle can be determined using the model [3]. Then the total volume and mass of vapour are equal to

$$V_{st\Sigma} = \frac{4}{3} \pi \sum_{i=1}^2 (R_{2i}^3 - R_{1i}^3), \quad m_{st\Sigma} = \sum_{i=1}^2 m_{st_i}, \quad (5)$$

where  $R_2$  — is the radius of the oil-vapour interface.

The total volume of vapour, together with the known radius, determines the total radius of the resulting emulsion droplet.

$$R_2 = \left( \frac{3}{4\pi} V_{st\Sigma} + R_1^3 \right)^{1/3}. \quad (6)$$

The vapour density of the resulting drop is

$$\rho_{st} = m_{st\Sigma} / V_{st\Sigma}. \quad (7)$$

The temperature of the vapour of a new drop is determined from the heat balance equation under the assumption that the temperatures of the vapour of the original volumes are constant across their cross-section. Then

$$t_{st} = \frac{\sum_{i=1}^2 m_{st_i} t_{st_i}}{m_{st\Sigma}}. \quad (8)$$

Based on the known temperature and density of the vapour, the vapour pressure can be determined. Equations (5)—(8) determine the total radius of the new particle, as well as its thermodynamic state.

The amount of heat transferred from the oil to the vapour is determined from the heat balance with known initial values  $H$  [3] of each of the particles. Then

$$H = H_1 + H_2. \quad (9)$$

The obtained amount of heat allows us to determine the depth of penetration and the new value of the heat flow  $Q_{oil}$  coming from the oil to the vapour [3].

To determine the speed of the oil-vapour interface  $w_2$ , we add the kinetic energies of the motion of these boundaries of each of the original particles. The kinetic energy of each particle is determined by the expression [4]

$$E_{k_i} = \frac{1}{2} \rho_{oil} \int_{R_{2_i}}^{\infty} 4\pi w^2 r^2 dr = 2\pi \rho_{oil} w_{2_i}^2 R_{2_i}^3, \quad (10)$$

or in this case

$$E_{k_i} = 2\pi \rho_{oil} |w_{2_i}| w_{2_i} R_{2_i}^3, \quad i = 1, 2. \quad (11)$$

Then the speed  $w_2$  is equal to

$$w_2 = h \sqrt{\frac{\sum_{i=1}^2 E_{k_i}}{R_2^3}}, \quad h = \begin{cases} 1, & \sum E_{k_i} > 0; \\ -1, & \sum E_{k_i} < 0. \end{cases} \quad (12)$$

We will find the coordinates of the centre of the new drop from the ratio of forces without taking into account the acceleration of the drops

$$d(x, y)' = \frac{m_{w_2} + m_{st_2}}{(m_{w_1} + m_{st_1}) + (m_{w_2} + m_{st_2})} d(x, y), \quad (13)$$

where  $d(x, y)'$  — is the distance from the centre of drop 1 to the centre of the new drop;  $d(x, y)$  is the distance from the centre of drop 1 to the centre of drop 2.

Let us introduce the notation

$$M = \frac{m_{w_2} + m_{st_2}}{(m_{w_1} + m_{st_1}) + (m_{w_2} + m_{st_2})} = \frac{m_{p_2}}{\sum_{i=1}^2 m_{p_i}}. \quad (14)$$

Then, taking into account the consideration of the geometric similar triangles theorem, we will obtain the coordinates of the centre of the new drop

$$x = (x_2 - x_1)M + x_1, \quad y = (y_2 - y_1)M + y_1. \quad (15)$$

We will determine the projections of the speed vector of the formed droplet onto the axes using the impulse-momentum theorem

$$w_{kx} = \frac{\sum_{i=1}^2 m_{p_i} w_{k_i} \sin \gamma_i}{\sum_{i=1}^2 m_{p_i}}; w_{ky} = \frac{\sum_{i=1}^2 m_{p_i} w_{k_i} \cos \gamma_i}{\sum_{i=1}^2 m_{p_i}}, \quad (16)$$

where the angles are determined by the method described in [3]. Then the speed of the resulting drop is equal to

$$w_k = \sqrt{w_{kx}^2 + w_{ky}^2}. \quad (17)$$

Thus, equations (1)—(17) allow us to determine the parameters of the newly formed drop.

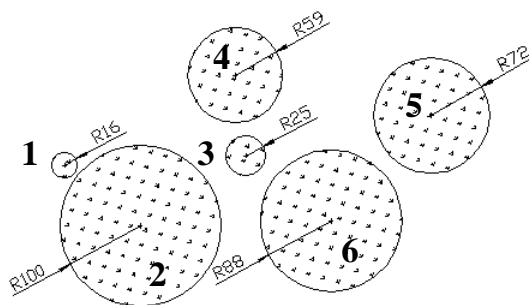


Fig. 1. To the calculation model of the merging droplets of the dispersed phase of the emulsion (characteristic dimensions in microns)

We perform calculations for the model shown in Fig. 1 according to the equations [3] at  $t_0 = 105^\circ\text{C}$ , taking into account the forces that can cause instability, the forces causing displacement, that is taking into account the displacement along the axes, and also taking into account the merging of drops. We assume that if a drop is fragmented or merged with another, then the numbering of the drops is reduced by one, starting with the number of the drop that is fragmented, or with the smallest of the numbers of the drops that merged. As calculations [3] showed, drop № 2 will be fragmented at the initial moment, therefore № 2 will become № 3, etc.

The results of the calculations are presented in Fig. 2—4.

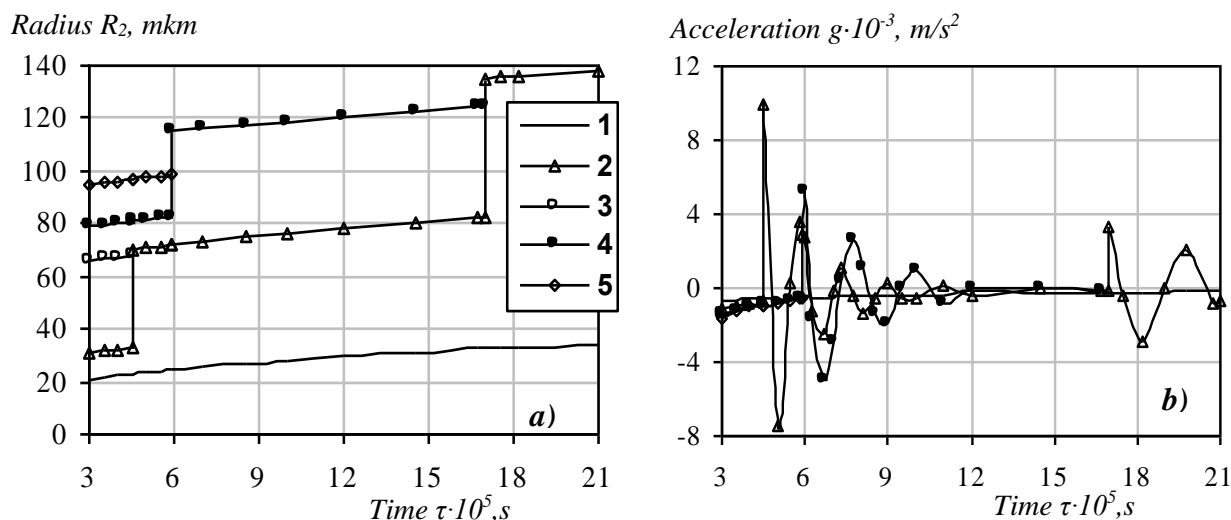


Fig. 2. Change in the radius of a droplet (a) and the acceleration of the oil-vapour interface (b) during the merging droplets over time as a result of the formation of a conglomerate

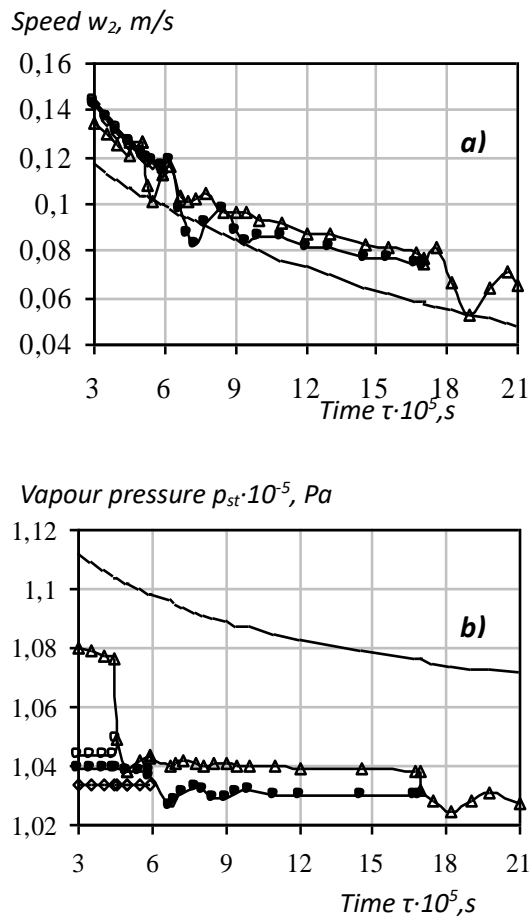


Fig. 3. Change in the oil-vapour interface speed (a) and vapour pressure (b) during droplet merging over time (the notations are from Fig. 2)

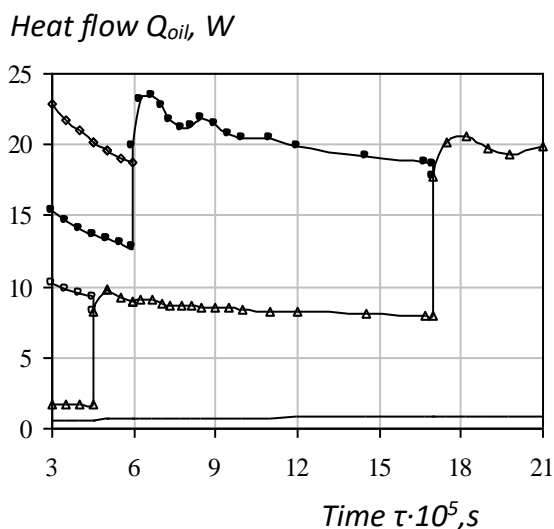


Fig. 4. Change in time of heat flow from oil to vapour during droplet merging (designations from Fig. 2)

These figures clearly show the moments of merging the drops: first [missing] 2 with № 3, then № 4 with 5, then № 2 with 4, etc. At the moment of merging two drops, after the formation of a new drop, the acceleration of the oil-vapour interface (Fig. 2b) increases abruptly, which is explained by a sharp decrease in the Laplace force, which is included in the Rayleigh-Plesset equation, due to a sharp increase in the radius of the interface. At the moment of merging, the main thermodynamic parameter (pressure) is determined by values between the two initially existing ones as can be seen from Fig. 3b.

The heat flow from oil to vapour can have a resulting value either between the two initial values or higher than the largest of the initial values (Fig. 4), which can be explained by the determining value of the radius of the formed particle. For example, during the merging of droplets  $\tau \approx 6 \cdot 10^{-5} s$  4 and 5, the relative increase in radius is greatest, and, as a consequence, the heat flow increases above the initial values.

The acceleration increase and its oscillations described above subsequently lead to corresponding speed oscillations  $w_2$  (Fig. 3a). These sharp changes in acceleration and speed values can also cause hydrodynamic instability of neighbouring droplets. However, in this case, the magnitudes of these forces caused by  $g$  and  $w$  are insufficient to break up nearby droplets as calculations have shown. Acceleration and speed oscillations have the character of damped and, as can be seen from Fig. 2, 3, the amplitude values of these parameters decrease with increasing time during further droplet merging, which is a consequence of both an increase in the size of the resulting droplet and a decrease in the total pressure in the system according to Fig. 3b. The corresponding sharp increase in speed leads to a decrease in values and vice versa. The heat flow changes inversely proportional to the vapour temperature.

### Conclusions

The developed model of emulsion droplet merging allows us to obtain a general picture of the change in the parameters of emulsion droplets and, together with the models of fragmentation and movement, to de-

scribe the processes occurring during the boiling of the aqueous phase of the emulsion. The assumption of the smallness of the electrostatic repulsion forces and the Van der Waals forces of attraction, as well as their exclusion from consideration at the last stages of droplet movement before they meet, is quite justified due to their complete uncertainty for droplets of different sizes. The merger time of two droplets of different sizes, calculated using the average radius and the technique [5], is equal to  $\Delta\tau \approx 10^{-7}$  s, which practically coincides with the calculation step. Another version of the boiling scheme is also possible, in which the droplets do not merge, but grow, interacting with each other, in the case where the stabilizing effect of the surfactant is large enough. But a combination of these schemes can also exist. In general, any scheme of consideration will lead to thermal equilibrium, both if we consider fusion and if we study thermal contact. Therefore, this method of calculating the boiling of emulsions is quite acceptable.

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### МОДЕЛЮВАННЯ ЗЛИТТЯ ЧАСТИНОК ДИСПЕРСНИХ ФАЗ ЕМУЛЬСІЙНИХ СЕРЕДОВИЩ

#### Реферат

Складні та різноманітні фізико-хімічні явища, що визначають стійкість тонких розділових плівок рідини та структуру двофазних потоків, наразі залишаються недостатньо вивченими. Шар пари утворюється на межі фаз вода-масло в процесі кипіння водно-масляних емульсій в результаті різкого перепаду тиску. Збільшення об'єму пари (збільшення радіуса межі розділу масло-пара) для крапель різних розмірів відбувається за параметрів, властивих кожній частинці в певний момент часу. При злитті крапель у конгломерат параметри усереднюються, наслідком чого стає поява більшої краплі з визначеними швидкостями та прискореннями росту межі поділу вода-масло. Тому врахування цих процесів об'єднання киплячих частинок відіграє досить велику роль у визначенні кінцевого розміру роздроблених часток дисперсної фази, а сам процес є невід'ємною частиною як кипіння, так і руху та подальшого дроблення крапель.

Розроблена модель злиття крапель емульсії дозволяє отримати загальну картину зміни параметрів крапель емульсії та разом з моделями дроблення та руху описати процеси, що відбуваються під час кипіння водної фази емульсії. Припущення про малість сил електростатичного відштовхування та сил Ван-дер-Ваальса, а також виключення їх з розгляду на останніх етапах руху крапель перед їх зустріччю, цілком виправдане через їх повну невизначеність для крапель різних розмірів. Звичайно, зроблене припущення про миттєве злиття крапель призводить до дещо некоректних результатів, але питання про час злиття двох крапель різних розмірів також залишається відкритим. Можливий також інший варіант схеми кипіння, при якому краплі не зливаються, а зростають, взаємодіючи одна з одною, у випадку, коли стабілізуючий вплив поверхнево-активної речовини достатньо великий. Тому цей метод розрахунку кипіння емульсій є цілком прийнятним.

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