Studying the surfactant dynamics at non-isothermal liquid surface with thermography

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Abstract. The dynamics of liquid multiphase systems largely depends on the conditions on the interface. The behavior of a system with adsorbed surfactant layers at the interface boundaries may differ qualitatively from the behavior of a system with pure surface. The experimental study of such systems is difficult, since the presence of adsorbed layer can most often be judged only by indirect signs. Therefore, most of the research is carried out by numerical modeling. Unfortunately, the currently existing numerical studies of liquid multiphase systems with adsorbed surfactant layer are far from perfect due to numerous simplifications and approximations assumed in theoretical models. In this paper, we propose a new approach for visualization and studying the boundary between a clean surface and an adsorbed surfactant layer. It is based on the comparison of track images of the fluid motion in the volume and the registration of the temperature distribution at the interface boundary. This approach made it possible to unambiguously associate the characteristic regions on the temperature profile with the position of the so-called stagnation point. The proposed method for visualizing the stagnation point can be useful in a number of problems of interface hydrodynamics based on the thermocapillary effect.

1. Introduction

The use of thermography in hydrodynamic experiments is largely limited by the fact that almost all liquids are not transparent in the infrared range. Moreover, most materials that transmit visible light are also opaque in the infrared region of the spectrum. Therefore, the infrared images allow one to obtain the temperature distribution only at the surface of the liquid and only in the case of using special optical windows transparent in the IR in the design of the cuvettes. However, in hydrodynamic problems involving a non-isothermal free surface of a liquid, the thermal imager can be a powerful tool in experimental research. It is well known that the temperature distribution on the surface contains information about the structure of the flow in the near-surface layer, as, for example, in the case of the development of Rayleigh-Benard convection. The analysis of such characteristics as the spatial size of thermal inhomogeneities and their intensity also allows us to estimate some parameters of the volume flow [1, 2].

The use of a thermal imager is most effective in those tasks where the free surface of the liquid plays not a passive, but an active role, driving the liquid through the thermocapillary mechanism. In this case, the temperature distribution allows not only to visualize the convective structure, but also to calculate the magnitude of the tangential stresses of the thermocapillary nature. Of particular interest is the study of systems in which the development of thermocapillary flow is complicated by the presence of a surfactant layer on the interface. The processes of heat and mass transfer in such systems demonstrate a nonlinear character due to the presence of a feedback between the convective flow and the surfactant distribution on
the interface [3, 4]. Interest in such studies is due to their application for a variety of technological processes in various branches of chemistry, pharmaceutical industry, mining. The main problem during studying such systems is the lack of simple and cheap methods that allow one to obtain the information about the spatial distribution of the surfactant on the interface. In this paper, we propose a new experimental non-contact technique that allows us to simultaneously obtain data on both the flow structure and the parameters of the surfactant layer using thermal video imaging. For this purpose, the surface is heated by radiation distributed over the surface or localized in a small area.

2. Experimental setup
To create an inhomogeneous temperature distribution on the liquid surface, two types of radiation sources were used. The first made it possible to obtain local heating of the surface focusing the radiation of a halogen lamp in the form of a small spot. An infrared laser beam can also be used for this purpose. When using such a source, the size of the liquid surface should be significantly larger than the diameter of the spot that warms the surface. In this case, the spot diameter was 3 – 5 millimeters. When working with a local heating source, a glass Petri dish with a diameter of 10 cm was used as a cuvette (figure 1).

The second source allowed heating a narrow stripe of the water surface with a length $L$ limited by a plastic mask, which was placed in a Petri dish on the surface of the liquid. To do this, the radiation of the halogen lamp was focused on the surface of the liquid in a highly elongated spot using a system of spherical and cylindrical lenses. The special configuration of the lenses in the collimator makes it possible to obtain a distribution with a constant temperature gradient along the heat spot. The presence of a limiting mask allows you to heat the entire surface occupied by the surfactant layer. Varying the intensity of the radiation allows us to change the value of the temperature gradient.

The temperature distribution on the surface of the liquid was recorded using a thermal imager, the optical axis of the lens of which has a certain angle with a normal to the surface. This made it possible to avoid the influence of reflected radiation on the measurements carried out. To test the experimental technique, we visualized simultaneously the flow structure at the interface and in the volume. To do this, light-scattering particles were added to the liquid, to visualize the movement of which a light sheet formed by laser was used. The motion of the particles was recorded using a video camera. High-purity water was used as the working fluid.

After additional cleaning of the water surface, the required amount of oleic acid solution in hexane was applied to its surface. After the hexane has evaporated, a homogeneous surfactant layer with a given dimensionless surface concentration of $\Gamma_0 / \Gamma_e$ remains on the water surface.

![Figure 1. Sketch of the experimental setup, a – localized thermal source, b – distributed thermal source: 1 – cuvette, 2 – halogen lamp, 3 – lens system, 4 – plastic mask with a cutout in the shape of a narrow rectangle with length of $L$, 5 – thermal imager, 6 – laser sheet, 7 – video camera; $h$ – hot side and $c$ – cold side of water surface.](image)
The $I_c$ is a maximal concentration of close packed monolayer. Before each experiment, the surfactant content at the interface was monitored by measuring the surface pressure in the surfactant layer using a KSV Minimicro tensiometer. To do this, a Wilhelm plate was immersed in the liquid from the edge of the cuvette.

3. Results
The first series of experiments was performed using a localized heater. Initially the cuvette is filled with an isothermal liquid, on the free surface of which an insoluble surfactant is evenly distributed. Since on the surface $\text{grad}(I) = 0$ and $\text{grad}(T) = 0$, there are no tangential stresses of the capillary nature. Immediately after turning on the lamp, a temperature inhomogeneity appears on the surface in the form of a thermal spot, the temperature in the center of which increases rapidly until it reaches an equilibrium value. Under the influence of the temperature gradient around the spot a field of tangential stresses of a thermocapillary nature will arise. On a clean interfacial surface, this would immediately lead to the development of intense centrifugal convection with a characteristic surface velocity of about 10 cm/s.

In the case under consideration, the development of the thermocapillary flow leads to the transfer of surfactant molecules in the direction from the center of the thermal spot. The tangential stress caused by the soluto-capillary mechanism arising at the interface is directed towards the thermocapillary tangential stress. The structure of the resulting flow will be determined by the ratio of the contributions of each of the mechanisms. Quantitatively, this ratio can be described by the dimensionless parameter, called elasticity number, $E = \sigma'I_0 / \sigma'T$, which is the ratio of the soluto-capillary Marangoni number to the thermocapillary one. Here, $\Delta T$ is the temperature difference between the center of the thermal spot and the periphery of the cell, and $\sigma'I$ and $\sigma'T$ are the concentration and temperature coefficients of the dependence of the surface tension, respectively. At $E > 1$, the tangential stresses due to the inhomogeneous distribution of the surfactant concentration always balance the thermocapillary forces, and there is no movement on the surface.

The temperature profiles measured by the thermal imager on a free surface with an intense thermocapillary flow and on a motionless water surface containing a surfactant layer differ significantly. Figure 2 shows the temperature profiles on the surface and the flow structure in the volume for three cases. It should be noted that the radiation intensity in all the presented cases was the same. It can be seen that the temperature difference $\Delta T$ for the cases presented if figure 2(a) and figure 2(b) is very different. On the motionless surface covered with the surfactant, the temperature drop is maximum, the convective flow under the surface is slow and the streamlines are directed parallel to the interface. On a clean surface, the temperature drop is almost one order of magnitude less. In this case, the convective vortices are pressed against the free surface, which indicates an intense surface flow.

The most interesting case is shown in figure 2(c). In this case, $E < 1$, i.e., the thermocapillary forces in the center of the cell are greater than the concentration-capillary forces, as a result of which the liquid motion develops on the surface near the source, pushing the surfactant molecules to the periphery. The surface pressure in the surfactant layer increases as it is compressed, until a balance of two tangential stresses is established at the periphery. In this part of the surface, called the stagnant zone, fluid motion becomes impossible. The analysis of the images presented in figure 2(c) shows that an intense centrifugal flow at the interface is observed directly near the heat source. However, at some distance $X_c$ from the source, the streamlines dive under the surface, where the flow slows down. The surface outside the circular zone with radius $X_c$ is stationary. There is a break in the temperature profile at this point. At the boundary of the two zones, the fast-moving fluid is forced to dive under the stagnant zone, while changing the direction of the velocity vector. The difference of at least one order of magnitude between the temperature gradients inside and outside the circle with radius $X_c$ is caused by different heat transfer mechanisms along the liquid surface. Inside, it is mainly a convective mechanism, while outside, it is a conductive one. The most intense the thermocapillary convection, the greater the difference in the magnitude of the temperature gradients.
Important information about the properties of the surfactant layer can be obtained from the value of $\Delta T$ in the case of the temperature profile shown in figure 2(c). Comparison of this value with the surface pressure $\pi = \sigma_{\text{water}} - \sigma_{\text{surfactant}}$ showed that these values are directly proportional to each other. Surface pressure is one of the basic characteristics of surfactant layers, it determines how much the layer will resist compression. This can be compression by means of a solid moving boundary or compression distributed over the layer by viscous tangential stresses applied to it from the side of a liquid flow. In the second case, in the surfactant layer, these distributed stresses are summed over the entire area of the interface.

Localized heating of the surface in combination with thermal imaging allows us to detect the boundary of the layer and the surface free of surfactant, and therefore determine the surface area occupied by the surfactant. In the case of an insoluble surfactant, its amount on the surface remains unchanged. Knowing the surface area occupied by the layer before and after turning on the heating, you can easily calculate its new concentration. Moreover, the value of $\Delta T$ can be used to calculate the current surface pressure of the surfactant layer and to obtain the dependence $\pi = f(\Gamma)$, which is unique for each specific species. It is important to emphasize that the entire technique is non-contact, which allows us not to be afraid of surface contamination.

The use of the described above elongated thermal spot gives us some additional possibilities for manipulating the surfactant layer. The constant temperature gradient created by such a source along the surface leads to the fact that the slope of the temperature profile will be entirely determined only by the dominant mechanism of heat transfer on it. The boundary between the clean surface and the stagnant zone, as in the case of a localized source, manifests itself in the form of a sharp change in the slope at this point. But in contrast to the case discussed above, a distributed source allows us to influence the surface-active impurity on the entire surface, reducing its surface area several times in relation to the initial one. Figure 3 shows a series of temperature profiles obtained on a layer of surfactant with a fixed $\Gamma_0$, corresponding to different intensities of a halogen lamp. One can see how the $X_c$ coordinate on the profile shifts as the temperature difference $\Delta T$ increases. The area marked in gray corresponds to a surface free of surfactant.

The graph of the experimental dependence $X_c = f(\Delta T)$ for different values of $\Gamma_0$ is shown in figure 4. It is clearly seen that for small values of $\Gamma_0$, the graph first has a linear form, the larger the value of $\Gamma_0$, the smaller the length of the linear section. When $\Gamma_0 = 0.3$ the dependence $X_c = f(\Delta T)$ is initially nonlinear. The deviation from the linear dependence indicates a phase transition in the surfactant layer from the gas to the liquid-expanded phase state. More information about this can be found in the following paper [5].
4. Conclusion

This paper describes a non-contact technique for visualizing the boundary of a liquid surface area occupied by a surfactant layer and measuring the surface pressure in this layer. To do this, the surface of the liquid must be heated using infrared radiation. Two different heating configurations are proposed: localized and distributed heating. The first allows you to achieve large temperature differences on the surface, which is necessary for manipulating concentrated layers of surfactant. The second type of heating is more suitable for a detailed study of rarefied layers in the gas state, in particular, it allows you to fix the moment of the phase transition in the surface layer. The proposed method is suitable both for non-contact inspection of the interfacial surface in order to determine the amount of uncontrolled surfactant contamination, and for studies with pre-applied surfactant layers.

Another possible application of this technique is the experimental measurement of the distribution of viscous tangential stresses arising in a layer of surfactant located on top of a homogeneous isothermal fluid flow. For this purpose, the interfacial surface is proposed to be heated locally using a laser, until a characteristic temperature profile is obtained, as shown in figure 2(c). The value of $\Delta T$ allows you to calculate the surface pressure in the surfactant layer at the heating point. A sequential measurement at different points will make it possible to map the stationary distribution of viscous tangential stresses on such a surface. On the other hand, the observation of the time evolution of the temperature profile will allow us to obtain information about the time dynamics of the local viscous tangential stress at a point.

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References

[1] Saylor J R 2001 Rev. Scient. Instr. 72 4408–14
[2] Bower S M and Saylor J R 2011 Int. J. Heat and Mass Trans. 54 5348–58
[3] Wang T S and Shi W Y 2021 Int. J. Heat and Mass Trans. 171 121055
[4] Vinnichenko N A, Pushtaev A V, Plaksina Y Y, Rudenko Y K and Uvarov A V 2018 Int. J. Heat and Mass Trans. 126 400–10
[5] Shmyrov A V, Mizev A I, Demin V A, Petukhov M I and Bratsun D A 2019 J. Fluid Mech. 877 495–533