Droplet Deformation under Conditions of Neutral Buoyancy

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Abstract. One of the classical problems of hydrodynamics is the problem of droplet deformation in the state of neutral buoyancy under the action of an external force. It is assumed that if the droplet size is initially equal to or less than the capillary diameter, it takes the shape of a regular sphere, regardless of the density gradient in the environment and the droplet, the degree of their mutual solubility, the possibility of Marangoni convection, and the time elapsed since the creation of the system of liquids. To elucidate the influence of these unaccounted factors as well as that of initial deformation of the droplet, we experimentally studied the evolution of the shape of large-diameter droplets in the solution with density stratification. The droplet behaviour was studied in the case when it took the form of a spheroid flattened vertically under the action of gravity. The interferometer was used to visualize the distribution of solution concentration near the drop. The dependence of the ratio of the vertical to horizontal diameter of the droplet on time and the average concentration gradient in the surrounding medium was determined.

1. Introduction

One of the best known problems of hydrodynamics is the problem of deformation of a droplet in the state of neutral buoyancy under the action of some external force. For the first time this approach was applied by Joseph Plato in 1840 while studying the shape of droplets in a rotating liquid [1].

Formally, to achieve neutral buoyancy, it suffices to ensure equal density of liquids. Typically a drop itself finds the position of equal density in case of a density-stratified solution [2-7]. It is considered that if the droplet initially has the size equal or less than the capillary diameter, then it takes the shape of a regular sphere regardless of the value of the density gradient in the environment and the droplet, the degree of their mutual solubility, possibility of the onset of the Marangoni convection, and time elapsed from the moment of liquid system creation. At the same time, the equality of the density of the surrounding liquid and droplet does not prevent the occurrence of gravitational convection inside the droplet due to diffusion of its components. In particular, the effect of “overturning” of a drop of two-component mixture floating in the density-stratified solution is explained exactly by the development of Rayleigh-Taylor instability due to diffusion [8].

As a rule, all the above mentioned factors are not taken into account in experiments on deformation of droplets under the action of external forces, although they can introduce a significant error in the results of measurements. To estimate the influence of these factors, we experimentally investigated the evolution of the shape of droplets with different diameters in a density-stratified solution.

2. Experimental procedure

In the experiments performed in this study, we used a Fizeau interferometer to measure the density gradient in the liquid near the drop and a digital photo camera to record images of the drop shape (Fig.1a). We also developed a glass cuvette 12 cm long, 5 cm wide and 9 cm high (Fig. 1b). The cuvette contains a two-layer liquid system 1-2, droplet 3 under study, an interference cell 4 for measuring the density gradient in diffusion zone and a ruler 6 for determining the droplet size. The interference cell is formed by plane-parallel glasses 1.0 cm wide and 3.8 cm high with a gap of 0.124 cm between them. The cell was adjusted to an interference band of infinite width. Due to its design, the cell had neither top
nor lateral solid walls and was easily filled with liquid as it was poured into the experimental cuvette. To determine the scale during video recording of interferograms, a reference plate of 1.00 cm length was glued to one of the cell glass walls. A thin dashed line was drawn along the wall of the cuvette for determining the drop position in the density gradient.

Tests were carried out on droplets consisting of aniline or a mixture of acetic acid (AA), chlorobenzene (CB) and benzene (B). Acetic acid is infinitely soluble in benzene and water, while benzene and chlorobenzene are poorly soluble in water (0.08% and 0.18% at 25°C), the same as water in them (0.05% and 0.1% [9]). Aniline is also poorly soluble in water (3.5%). As a base liquid, distilled water was used. To create a liquid substrate, the density of which is higher than that of the droplet, an aqueous solution of sodium chloride was employed. The interfacial tension $\sigma$ between the droplet and surrounding liquid decreases as the concentration of the diffusing component increases [10]. This dependence of $\sigma$ at constant value of the force of gravity makes it possible to significantly change the shape of the drop.

Table 1 presents a number of physicochemical parameters of the selected fluid systems and the capillary radius corresponding to their droplets

$$r_c^2 = \frac{2\sigma}{(g\Delta\rho)}$$

where $\Delta\rho = \rho_1 - \rho_2$ is the density difference between the droplet and the surrounding liquid. It is clearly seen that the liquids with lower interfacial tension have a smaller capillary radius. Using this ratio, the droplets with an initial diameter of more than two capillary radii were selected. Note that these droplets were initially deformed due to gravity.

Before the experiment, the two-layer system of liquids with a sufficiently wide diffusion zone was created in the cuvette. The magnitude of the density gradient in this zone was monitored using an interferometer. Then the drop was placed into the diffusion zone. The end of the droplet formation coincided with the beginning of video recording of the cuvette, which made it possible to simultaneously visualize the concentration distribution in the diffusion zone and to record images of the drop shape. This time was taken as the beginning of the experiment.

At the preparation stage, we investigated the structure and evolution of flows and concentration fields near and inside droplets placed in a thin vertical interference cuvette. In such a cuvette, the droplets changed their shape from spherical to cylindrical with flat ends. The visualization showed the presence of weak buoyancy convection in the droplets of all liquid systems under study. The development of capillary convection was observed only in the case when the acid diffused from the drop of a ternary mixture into distilled water. The preliminary dissolution of acid in water sharply reduced the intensity of both diffusion and Marangoni convection.
Table 1. The droplets, surrounding liquids and liquid substrates

| Composition of the droplet/surrounding liquid/liquid substrate                              | $\Delta \rho$, g/cm$^3$ | $\sigma$, dyne/cm | $r_c$, cm | $V_c$, cm$^3$ |
|------------------------------------------------------------------------------------------|-------------------------|------------------|-----------|--------------|
| Aniline/water/sodium chloride solution                                                   | 0.020                   | 5.8$^a$          | 0.77      | 1.9          |
| Aniline saturated with water/water saturated with aniline/sodium chloride saturated with aniline | 0.024                   | 4.5$^b$          | 0.62      | 1.0          |
| Benzene mixture (B-5%; CB-45%)+AA (50%)/water/aqueous sodium chloride solution          | 0.059                   | 33.2             | 1.07      | 5.1          |
| Benzene mixture (B-5%; CB-45%)+AA (50%)/aqueous solution of AA (62%)/aqueous solution of sodium chloride with AA (62%) | 0.008                   | 2.0$^c$          | 0.71      | 1.5          |

$^a$ at 20°C [9]

$^b$ Experiment + calculation according to Antonov's rule

$^c$ at 20°C [10]

3. Results of the experiment

The interferogram of the diffusive zone between the water and sodium chloride solution and the corresponding vertical distribution of NaCl concentration in this zone are presented in Figure 2.

![Interferogram of the diffusive zone between water and NaCl solution](image)

Figure 2. Vertical changes in the NaCl concentration in the zone of mixing of its solution with water.

- (a) interferogram at $t = 0$ s, the reference plate ($l = 1.00$ cm) is seen on the left;
- (b) concentration distribution for different times elapsed from the beginning of the experiment, $t, s: 1–0, 2–410$.

It is clearly seen that, at the periphery of the diffusion zone, the distribution of sodium chloride concentration significantly differs from the linear one used in theoretical studies.

Let us consider the factors influencing the shape of a droplet in a stratified liquid under conditions of neutral buoyancy. Figure 3 shows a series of photographs reflecting changes in the shape of aniline droplet in water with variation of the density gradient in the diffusion zone. It can be seen that the droplet has the shape of a spheroid compressed along the vertical axis. Moreover, the upper part of this spherical drop is asymmetric with respect to the lower part due to the nonlinear distribution of sodium chloride concentration.
Figure 3. Photographs of drops of aniline in water on a substrate of aqueous solution of NaCl with $C_a = 5\%$ at different vertical density gradients, $\partial C/\partial z$, cm$^{-1}$: (a) - 0.16; (b) - 0.22; (c) - 0.28; (d) - 0.31. Time elapsed since drop formation $t = 300$ s. Initial drop diameter $D_0 = 2.12$ cm.

Analysis of the above photographs shows that one of the main factors determining the droplet shape in the absence of external forces is the density gradient in the surrounding liquid. To analyze this dependence, we tested the drops of different liquids with equal initial volume ($V_0 = 5$ cm$^3$). This was motivated by the fact that the diffusion coefficients of most liquids are close and, accordingly, all drops are approximately at the same stage of the dissolution process.

The ratio of the vertical to the horizontal diameter of droplets vs the NaCl concentration gradient in the surrounding liquid is presented in Figure 4. Note that we considered the magnitude of the gradient determined by the vertical difference in sodium chloride concentration between the poles of the droplets and did not take into account the nonlinear structure of the concentration field.

Figure 4. Dependence of ratio of vertical to horizontal diameter of droplets of different liquids on the average concentration gradient $\nabla C$ of sodium chloride in the diffusion zone. Initial droplet diameter $V_0 = 5$ cm$^3$. Curves I and II (filled and unfilled symbols, respectively) - time elapsed from the beginning of the experiment $t = 0$ s and $t = 300$ s. Points 1 and 2 - aniline droplet in water with aniline, 3 and 4 - aniline droplet in distilled water; 5 and 6 - droplet of benzene-acid mixture in distilled water, 7 and 8 - droplet of benzene-acid mixture in the aqueous solution of acid.

As it follows from Table 1, the selected droplets had the volume which is 2 - 5 times greater than that of the droplets with the capillary radius (except for the case with the benzene-acid mixture). To compensate the increasing influence of the gravity effect on the drop shape, we introduced a normalization factor $D_0 / D$, where $D_0 = 2r_c$.

Curve I corresponds to the beginning of the experiment ($t = 0$ s), when the magnitude of the gradient in the surrounding liquid reaches its maximum value. Curve II corresponds to the instant of time ($t = 300$ s) at which mass transfer practically ceases to exist. In both cases the drop deformation monotonically decreases with decreasing concentration gradient in the surrounding liquid. Note that curve II is significantly higher than curve I at the same values of the salt concentration gradient in the environment.

A possible reason for the decrease in the deformation of the droplet is an increase in its interfacial tension due to the long-term diffusion of the soluble component (a surfactant), or the absorption of a surface inactive liquid.

The droplets of benzene-acid mixture in water were outside the region of the obtained dependencies, which was possibly due to equality of the initial drop diameter to the capillary diameter, because at such
coincidence the effect of the capillary forces completely compensates the gravitation effect, despite the development of a capillary motion at the initial stage after drop formation.

There are two more factors that affect the drop shape in the state of neutral buoyancy. The first is the change in the density gradient in the surrounding liquid over time. The effect of diffusion widens the mixing zone and reduces the density gradient. The second factor is the diffusion of soluble components from or into the droplet. This mass transfer process changes the density of the droplet itself. The total change in the density ratio sets the drop in motion so that it reaches a new equilibrium position and acquires a new shape (Fig. 5).

![Figure 5](image)

The obtained results demonstrate that the density stratification of the surrounding liquid causes the drop to deform significantly even in the absence of external forces. Moreover, the presence of mass transfer between the droplet and the medium, characteristic of most liquid systems, as well as the development of capillary convection, raise the question of the applicability of such criteria as the capillary radius.

Figure 6 shows the ratio of the vertical to horizontal diameter for droplets of different initial sizes at a fixed time $t = 15$ s. Curve 1 corresponds to the case of aniline droplets in water. In this liquid system, there is no Marangoni convection, and therefore the aniline droplets retain spherical shape even when their sizes are slightly larger compared to the capillary diameter. Curve 2 describes the behavior of the droplets of benzene-acid mixture in the aqueous solution of the same acid. In this case, there is an intensive capillary motion, and therefore the droplets of the three-component mixture lose their spherical shape prior to reaching the capillary diameter. After completion of Marangoni convection, the shape of these drops is again close to spherical.

![Figure 6](image)
4. Conclusions
The results of the experiments demonstrated the existence of a direct relationship between the degree of drop deformation in the state of neutral buoyancy and the density gradient in the surrounding liquid. It was found that this density gradient, which is a necessary attribute of the neutral buoyancy method, causes the droplet to deform even in the absence of external forces. The study of the dynamics of the ratio of the vertical to horizontal diameter of droplets lying on a liquid substrate indicates that a change in the drop shape occurs not only due to a change in the density gradient in the surrounding liquid, but also due to an increase in the interfacial tension induced by mass transfer between the drop and environment. A noticeable role is played by the decrease in the density gradient with time due to the diffusion process in the liquid surrounding the droplet. It is shown that the development of the capillary motion at the interface contributes to the drop deformation. Hence it can be concluded that all above mentioned factors are the causes of errors in the experiments with drops under the action of external forces, and therefore they must be taken into account in the studies performed using the method of neutral buoyancy.

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References
[1] Plateau J 1863 Experimental and Theoretical Researches on the Figures of Equilibrium of a Liquid Mass Withdrawn from the Actions of Gravity (Washington, DC: Ann. Rep. Board of Regents of the Smithsonian Institution) p. 270-285.
[2] Myshkis A, Babskii V, Kopachevskii N 1987 Low-Gravity Fluid Mechanics: Mathematical Theory of Capillary Phenomena (Springer-Verlag) p. 583.
[3] Morozov K, Lebedev A 2000 Bifurcations of the shape of a magnetic fluid drop in a rotating magnetic field JETP 118 pp 1188-1192.
[4] Kosvintsev S, Reshetnikov D 2001 Drop motion induced by diffusion of soluble surfactant the external medium: Experiment Colloid J 63 pp 350-358.
[5] Lebedev A, Morozov K, Engel A and Bauke H 2003 Ferrofluid drops in rotating magnetic fluids New J of PHYS 5 57.
[6] Brasaemle D, Wolins N 2006 Isolation of lipid droplets from cells by density gradient centrifugation Curr Protoc Cell Biol. chapter 3.
[7] Bei Z, Jones T, Harding D 2010 Electric field centering of double-emulsion droplets suspended in a density gradient Soft Matter 6.
[8] Kostarev K, Briskman V 2001 Dissolution of a drop with a content of a surface-active substance Doklady Physics 378 pp 187-189.
[9] Nikolsky B 1965 Guide-Book for Chemist vol 3 ed B Nikolsky (M.:Chemistry) 1008 p.
[10] Abranzon A., Bocharov V., et al. 1979 Surface-active substances: Handbook ed. Abranzon A, G Gaevoj (L: Chemistry) p 376.