UDC 691-404.8

TRANSFORMATION OF A DISTURBED SITTING DROP

A.A. Ignatyev, V.M. Gotovtsev

Aleksey Aleksandrovich Ignatyev
E-mail: ignatyevaa@ystu.ru

Hydraulic and Road Engineering Department, Yaroslavl State Technical University, 40, Krivova St., Yaroslavl, 150048, Russia

Valeriy Mihailovich Gotovtsev
E-mail: gotovtsev_vm@mail.ru

Enterprise Management Department, Yaroslavl State Technical University, Yaroslavl State Technical University, 40, Krivova St., Yaroslavl, 150048, Russia

The paper presents the results of a study of equilibrium of a sitting drop from the standpoint of continuum mechanics. It is shown that the connection between internal forces and interfacial tensions is formed by gradients of internal pressures of a medium in interface layers that lead to forming body forces. It was found that the shape of a sitting drop with the contact angle equal $\theta_0 = \frac{\pi}{2}$ is the minimum surface energy state, in which the liquid - solid interface layer is not formed, and the surface energy of the drop takes the minimum value. It was also determined that the thickness of the interface layer varies depending on the values of the contact angle and reaches a maximum value at the complete wetting and complete non-wetting. Finally, the paper examines the impact of external and internal disturbances on the shape of a sitting drop.

Key words: *sitting drop, interphase layer, wetting angle*

For citation:
Ignatyev A.A., Gotovtsev V.M. Transformation of a disturbed sitting drop. Smart Composite in Construction. 2020. V. 1. N 1. P. 39-44 URL: http://comincon.ru/index.php/tor/V1N1_2020

DOI: *10.52957/27821919_2020_1_39*

INTRODUCTION

The history of surface phenomena research spans over more than two hundred years – almost all the important scientists of their time were involved in it. The first practical result was obtained by Young in 1805 when he was studying the liquid wetting of a solid surface. He derived an equation to determine the equilibrium value of a contact angle, which was named after him [1]. Almost at the same time as Young, Laplace also derived a formula linking the capillary pressure defined by the curvature of the free liquid surface with the surface tension and main radii of the curvature [2]. When studying the effects of liquid lifting and lowering in thin capillaries (capillary effects), Jurin obtained a formula determining the height of lifting (lowering) of the liquid column in the capillary tube [3].

The results are based on the equilibrium equations of the elements of the medium volume examined in combination with the Laplace formula, which connects the capillary pressure of the liquid-gas interface layer with the curvature of the free liquid surface. However, the recent publications [4-5] indicate inconsistencies and direct contradictions in the practical study of surface effects. Therefore, a question arises about the actual possibility of using a macroscopic approach to describe surface phenomena. Instead, it is proposed to switch to the micro level of surface effects, i.e. the level of intermolecular interactions [6]. This approach is based on the representation of molecules by separate objects, between which the body forces of attraction and repulsion act. It is assumed that the gravitational force acts at a distance, decreasing sharply with its increase. The range of attraction forces is several diameters of interacting molecules [5], the range of repulsive forces is assumed to be zero [7].

In the monograph [8], an alternative to the simulation of surface phenomena was proposed by not taking into account the body forces of the intermolecular interactions by replacing them with an equivalent stress tensor. This representation of the stress state of the medium makes it possible to establish a connection between the body forces of molecular interaction and surface forces, based on the general concepts of mechanics of continuous media. The forces of intermolecular gravity (van der Waals forces [9]) form the internal pressure of the medium, the value of which is immeasurably greater than the external manifestations of surface effects.

This discrepancy is determined by the small range of molecular gravity forces comparable to the size of molecules. In the equilibrium state of the medium, the molecular forces of attraction and repulsion balance each other in the absence of external manifestations of intermolecular interaction. However, when media with different internal properties come into contact with each other, a region needs to be formed, in which one internal state of the environment transitions to another, i.e. the interface layer is formed. The thickness of the interface layer depends on the range of the forces of gravity, the value of which is small, while the difference in the internal state of the contact media can be very significant. This leads to the fact that powerful gradients of internal pressure of the medium at the thickness of the interface layer are formed in the interface layers.

The presence of an internal pressure gradient in accordance with the principles of continuum mechanics results in a body force, the value of which is determined by the expression:

$$F_{\mathrm{V}} = \frac{1}{\rho}\frac{\mathrm{d}P}{\mathrm{d}z}, \qquad (1)$$

where F_{V} is the body force, P is the internal pressure of the medium, ρ is the density, z is linear coordinate flatwise to the surface of the interface layer. The body force is considered to be an external force in relation to the interface layer – this is the force that determines the external manifestations of surface effects. These include capillary pressure, surface tension, and other force factors to be measured experimentally. The value of the body force is determined by the ratio of the force acting on a small element of the medium caused by the pressure gradient to the mass of the element examined. The direction of the body force coincides with the direction of the pressure gradient vector, i.e. the body force is directed towards an increase in the internal pressure of the medium.

It follows from the above that the pressure gradient value in the interface layer can reach huge values, in the process of reduction the body force must be multiplied by the mass, the value of which is negligible if the thickness of the layer is taken into account. Accordingly, the integral effect of the body force on the macroscopic object will come in line with the external force factors acting on it. In the literature sources [5], the described mechanism is interpreted as the reason the liquid-gas interface layer can be formed. Internal pressures in the contacting vapor and liquid phases differ by several orders of magnitude, which leads to forming a powerful pressure gradient that creates the liquid-gas surface tension. However, the mechanism of its formation is rather complicated, it assumes that the compressibility of steam and phase transition is taken into account, and its examination is beyond the scope of this work.

MATERIALS AND METHODS

Fig. 1 shows the force factors acting on the sitting drop. The following notation is used here: P_{γ} is the capillary pressure of the liquid-gas interface layer; γ_{ls} is the liquid-solid surface tension; P_{N} is the solid surface reaction; F_{V} is the body force. These power factors are the external macroscopic load on the examined object. The right side of each figure shows the distribution of internal medium pressures over the thickness of the interface layers: P_{l} is the internal pressure in the liquid body phase; P_{ls} is the internal pressure of the medium in the interface layer; P_{s} is the internal pressure of the medium on a solid wall. These force factors are internal and therefore are not included in the equilibrium equations.

Internal pressure values can be found in the reference literature using the thermodynamic equation of the state of the medium [10] Note that the internal pressures are incomparably greater than the values of external force factors necessary to ensure the equilibrium of the drop. This is why the external force factors cannot change the internal pressures of the medium.

a *b*

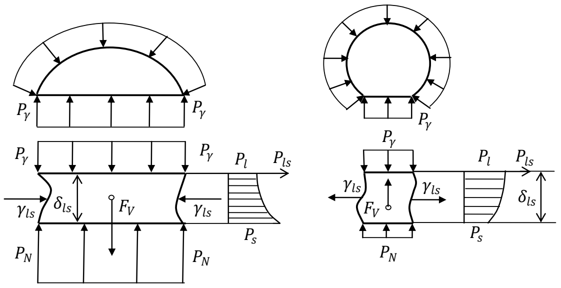

Fig. 1. Force factors in the liquid-solid interface layer: a – $\theta_0<\frac{\pi}{2}$; b –$\theta_0>\frac{\pi}{2}$

Fig. 1,a shows that when θ_0< 900 the body force F_V is directed to the solid surface and therefore creates additional pressure in the liquid-solid interface layer which tends to push the liquid out from the interface layer. However, the stresses created by the surface tension γ_{ls} lock the area of high pressure, preventing the liquid to be pushed out. When $\theta_0>\frac{\pi}{2}$, the reverse is observed, when a vacuum is created in the interface layer, and the stresses created by surface tension γ_{ls} prevent the inflow of liquid into the area of the interface layer. Thus the stress tensor in the liquid-solid interface layer is a pressure tensor. By definition, pressure determines the stress state in which the tensor contains three identical components.

RESULTS

Let us calculate the parameters of the sitting drop depending on the contact angle, modeling its shape by the ball segment on the known geometric ratios. Table presents the results of the calculation for a drop of constant volume equal to the volume of the ball with a radius of 1·10-3 m, which is V = 4.19·10-9m3. The table uses the following notation: θ_0– contact angle; R– curvature radius of the free spherical surface of a drop; S_{fs}– free surface area; S_{ca}– contact area; S_{full}– the total interfacial area; P_γ– capillary pressure; h– height of the ball segment.

The data given in the table shows that the minimum value of a full interface surface is reached when the contact angle θ_0 = 1800, and it corresponds to the complete non-wetting condition. At the same time, the capillary pressure in the drop reaches the maximum value and decreases with the decrease of the contact angle, taking the value P_γ = 0 when θ_0 = 00. The tendency of the liquid body to take the shape of a ball with a minimum surface energy is a universally recognized fact, but in the case of interaction of the liquid with a solid surface, the situation changes dramatically. In the academic literature, the fact of decrease in surface energy of a liquid in the course of wetting is mentioned, but during the simulation of the process this point is not taken into account.

When θ_0 = 900, the forces of adhesion and cohesion become equal, and it is no longer necessary to form an interface layer liquid-solid as a transition zone between contacting phases. Fig. 2,c shows the equilibrium of the liquid-gas interface layer under the capillary pressure P_γ and surface tension forces γ_{ls}. It is not difficult to verify the equation: $\gamma_{ls}\cdot 2\pi R = P_\gamma\cdot \pi R2$, which leads to the equilibrium of the examined object with no additional impact from the tension γ_{ls}. Accordingly, the contact area of a liquid with a solid surface will not be a part of the full area of an interface surface, which in this case is S_{full}= 9.97·10-6, m^2. It is clear that this value is less than the surface area of the ball, which is 12.56·10-6, m^2. Thus, when examining the interaction of a drop with a solid surface, the minimum surface energy of system is reached at θ_0 = 900, i.e. the drop tends to change to this state under any wetting conditions. For the sake of brevity, this state will be called equilibrium.

Table. Results of the calculation for a drop of constant volume to the volume of the ball

θ_0	180^0	150^0	90^0	30^0	0^0
$R\cdot10^{-3}$, m	1.000	1.004	1.26	4.26	∞
$S_{fs}\cdot 10^{-6}$, m^2	12.56	11.82	9.97	15.27	0
$S_{ca}\cdot 10^{-6}$, m^2	0	0.79	4.99	14.25	
$S_{full}\cdot 10^{-6}$, m^2	12.56	12.61	14.96	29.52	
$h\cdot10^{-3}$, m	2.000	1.866	1.000	0.134	0
P_γ, Pa	140.0	139.4	111.1	32.86	0

The result obtained is quite unexpected, and it does not fall within the scope of existing notions. To substantiate this, we will use the following assumptions. Fig. 1,b shows the direction of the interface tension γ_{ls} from the gas phase to the liquid phase, which corresponds to the accepted notions. The liquid-solid interface layer is in a stretched state and acts as a spring, preventing the system from reducing the contact angle and moving to a state close to equilibrium. When θ_0< 900, the interface layer is compressed, i.e. works as a "spacer" that prevents the contact angle from increasing and approaching the equilibrium state. Thus, in both cases, the system tends to transition to the equilibrium state, and the liquid-solid interface layer prevents it. The introduction of the concept of the equilibrium state of the sitting drop allows us to bring in line and unify the theoretical base not only for the known manifestations of surface effects, but also to explain the new, sometimes unexpected phenomena.

DISCUSSION

In recent years, due to the active development of outer space, the impact of gravity on many physical phenomena, including wetting, is being examined. As an example, there are some studies of various aspects of the spreading of drops on a solid substrate [11-13], in which it is noted that there is the process of wetting under conditions of changing gravity is not understood sufficiently. The work [14] shows the results of an experiment on studying the impact of gravity on the shape of a sitting drop. The experiment was conducted during parabolic flights of the European Space Agency, providing stable levels of gravity. It has been established that the change in gravity has a different effect on the shape of the drops depending on the contact angles.

Thus, when $\theta_0>\frac{\pi}{2}$, the increase in gravity causes the drop to flatten out and spread over the substrate at the same contact angle. When $\theta_0<\frac{\pi}{2}$, the drop does not spread, and the diameter of the wetted area remains constant with increasing gravity. The liquid at the edge of the drop "clings" to the substrate, and the contact *angle changes to adjust to different levels of gravity. Fig. 2 shows the drop profiles when changing the gravity level and contact angle. Fig. 2,a shows the transformation of a drop with the increase in gravity when $\theta_0 > \frac{\pi}{2}$. The disturbance, as it can be seen, has no effect on the contact angle, while the contact area increases. When the contact angle $\theta_0 < \frac{\pi}{2}$, its value increases with the increase of gravity, while the contact area stays the same, as shown in Fig. 2,b.*

Note that the increase in gravity causes the drop to flatten regardless of the type of wetting. The center of gravity of the drop moves lower, and the force of gravity, as an external force, performs a positive work in this process. According to the principles of thermodynamics, the internal energy in this process should decrease, and the disturbance caused by the increase in gravity should be accompanied by changes that bring the system closer to the equilibrium state. It is necessary to keep in mind that the type of wetting does not change with the change in gravity, i.e. the medium state parameters do not change as well as the character of their distribution over the layer thickness.

When $\theta_0 > \frac{\pi}{2}$, approaching the equilibrium state by the system is associated with a contact value decrease accompanied by an increase in the radius of the free surface of the drop R and a drop in capillary pressure. To analyze the transformation of a drop, the following equation of equilibrium of a liquid-solid interface layer will be used according to the diagram in Fig. 1,b:

$$P_N + F_V = P_Y. \qquad (2)$$

The equation above takes into account the force factors distributed over the contact area of the liquid and solid phases. When gravity increases, the values in the equation change: P_N increases, F_V remains unchanged for the reasons discussed above, P_γ decreases, reflecting the tendency of the system to equilibrium.

Two variants of the drop transformation are possible – when the contact angle decreases and when the contact angle is constant: θ_0 = const. Decrease of the contact angle is due to the change of wetting conditions, and that contradicts the accepted hypothesis F_V = const, and means that the external power factors have an impact on an internal state of medium. The second alternative θ_0 = const satisfies the requirement of constancy of body force taking into account the increase of the contact area of phases due to increase of radius R. The considered scheme is in full accordance with Fig. 2,a.

When $\theta_0 < \frac{\pi}{2}$, approaching the equilibrium state by the system is associated with the decrease of R and the increase of capillary pressure P_Y. The alternative associated with the increase of a contact angle is not examined for the reason noted above. The equation of equilibrium of the liquid-solid interface layer in accordance with Fig. 1,a is as follows:

$$P_N - F_V = P_Y. \qquad (3)$$

The increase in gravity should result in the flattening of the drop, the lowering of its center of gravity, and the increase in the value of the reaction of the solid surface P_N. The equilibrium equation above shows that, at F_V = const , the process should be accompanied by an increase of capillary pressure P_Y, which is possible due to the decrease of radius of the free surface of the drop R and the corresponding decrease of the phase contact area. As shown in Fig. 2,b the contact area of the disturbed drop remains the same as before the disturbance begins. However, the increase in gravity should increase the contact area during the spreading process, and its preservation at an undisturbed level should be considered as a reaction of the system to external disturbances. In accordance with the Le Chatelier principle, the system reacts to external influences in a way that minimizes them. Keeping the contact area constant prevents the drop's center of gravity from lowering, i.e. opposes external disturbance.

However, it leads to a new contradiction, which is associated with the increase of the contact angle, and that should not happen according to the foregoing principles. However, it is necessary to pay attention to the fact that all the stated principles were based on the hypothesis about the spherical shape of the free surface of the drop, therefore, the change in capillary pressure was possible only when the value of R changed. Another way of influencing the capillary pressure is used in this case: it is related to the increase of free surface curvature in the area of three-phase contact line. Hence, the apparent change of the contact angle in this abnormal situation cannot be seen as the change in the wetting conditions.

The study examines the change in gravity as a force factor of disturbance, i.e. the impact on the external force factor – the force of gravity. Let us examine a "simpler" task associated with the transformation of a sitting drop when the wetting conditions change, i.e. the internal force factors defined by the contact angle value. Let us assume that in the course of the experiment a material with a higher adhesive capacity was used as a substrate. In this case, the system is disturbed by influencing the internal pa-

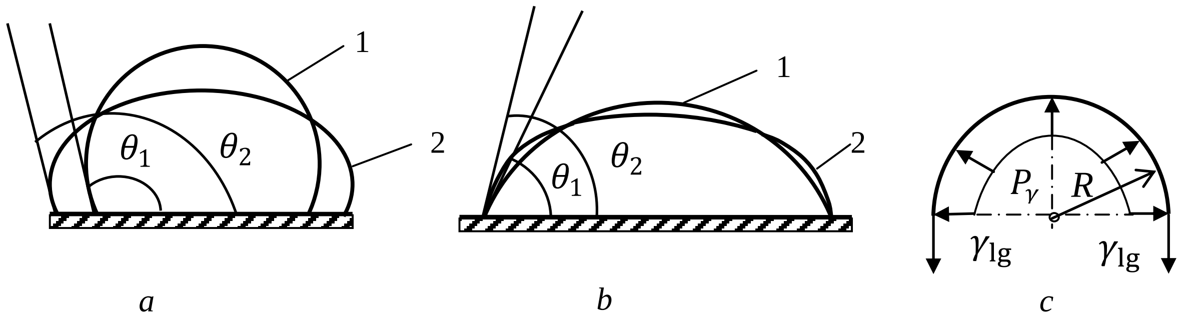

Fig. 2. Dependence of drop profile on gravity level and contact angle:
1 – gravity level is g (9,81 m/s²); 2 – gravity level is higher than g;
a-$\theta_0 < \frac{\pi}{2}$; b -$\theta_0 > \frac{\pi}{2}$; c - $\theta_0 = \frac{\pi}{2}$

rameter of the system, which leads to the increase of liquid attraction by a solid surface.

When the contact angle is $\theta_0 < \frac{\pi}{2}$, such disturbance will lead to the increase of P_s in distribution of internal pressure of the medium along the thickness of an interface layer according to Fig. 1,a. The law of pressure change caused by intermolecular interaction in the liquid phase will not change, but the thickness of the interface layer along with P_s will increase. Thus, taking into account the fixed position of solid phase molecules and the limited radius of action of molecular forces, the impact of the solid phase will be reduced to a change in the boundary condition. If the nature of distribution of internal pressure stays the same, it becomes possible only at the increase in a thickness of an interface layer while preserving the dependence of $P_{lg}(z)$ on initial thickness, where z is a linear coordinate flatwise to its surface.

The examined disturbance of the system is associated with the change of internal parameters of the system, i.e. the increase in its internal energy. That is why the system moves away from its equilibrium state under such influence. In the extreme case, when $\theta_0 \to 0$ and $R \to \infty$, all the drops of liquid are dispersed in the liquid-solid interface layer. However, this issue is related to the stability of thin liquid films on a solid surface and is not examined in this work.

Let us examine the behavior of a sitting drop when $\theta_0 > \frac{\pi}{2}$ with the strengthening of hydrophobic properties of a solid surface. The distribution of the internal medium pressure shown in Fig. 1,b will also change, which is necessary to increase the value of the volume force F_V. However, in this case, the force is directed from the solid surface into the liquid phase, contributing to the separation of the liquid from the separating plane. When $\theta_0 \to \pi$ $P_s \to 0$, the liquid-solid interface layer is transformed into a liquid-gas layer, and the drop takes the shape of a ball. Thus, the condition of complete non-wetting of the solid surface by the liquid is met.

It should be noted that measuring the contact angle is one of the most common ways to assess the adhesive properties of a liquid-solid body system. This raises the question of the effect of the drop volume on the contact angle. In terms of the ideas presented, the answer is negative for the following reason. As shown, the parameters of the liquid-solid interface layer are determined by the intermolecular interaction of liquid and solid phases, i.e. internal parameters of the system state, and the internal pressure of the liquid phase is the deciding factor. The impact of a solid surface is reduced to the boundary condition, i.e. to the pressure between the interface layer and the solid surface. Given that the internal pressure of the medium is incomparably greater than the external force factors discussed above, they cannot influence the interaction of the phases that determine the contact angle.

CONCLUSIONS

The following principles can be used to summarize the ideas discussed above.

The paper presents the force factors applied to a sitting drop in the equilibrium state. The factors applied were classified as external and internal. It is shown that the internal force factors such as the internal pressure of the medium is immeasurably greater that the external manifestations of surface effects. Accordingly, the interfacial tensions that define the shape of a sitting drop have no effect on the internal parameters of the state of the medium.

It is shown that the connection between internal forces and interfacial tensions is formed by gradients of internal pressures of a medium in interface layers that lead to forming body forces.

It was found that the shape of a sitting drop with the contact angle equal $\theta_0 = \frac{\pi}{2}$ is the minimum surface energy state, i.e. the equilibrium state. Under these conditions, the liquid-solid interface layer is not formed, and the surface energy of the drop is not included in the total internal energy of the sitting drop.

It is shown that under any wetting conditions, the system tends to take a form close to equilibrium, and the interface liquid-solid layer prevents it, providing the equilibrium of the object.

It was found that the thickness of the interface layer changes depending on the contact angle. It is zero in the equilibrium state and increases at any deviation of the angle from this value. When $\theta_0 = 0$, in case of complete wetting, all the liquid in the drop is spread in the solid-liquid interface layer. When $\theta_0 = \pi$, in case of complete non-wetting, the liquid-solid interface layer is transformed into a liquid-gas layer.

The work also reveals the mechanism of transformation of a drop with change in gravity, which was impossible within the scope of the previously established principles and views.

REFERENCES

1. ***Kikoin A.K., Kikoin I.K.*** *Molecular physics. M.: Nauka. 1976. 478 pp. (in Russian).*
2. ***Adamson A.*** *Physical Chemistry of Surfaces. Gast. A. New York: Wiley Interscience Publication. 1979. 784 p.*
3. ***Frenkel Y.*** *Kinetic theory of liquids. L.: Nauka. 1975. 301 pp. (in Russian).*
4. ***Roldugin V.I., Kharitonova T.V.*** *On the nonequilibrium thermodynamics of thermocrystallization motion of inclusions in solids. Colloid. J: Sci. Magaz. 2013. V. 75. N 2. P. 198-201 (in Russia).*
5. ***Rowlinson J.S., Widom B.*** *Molecular Theory of Capillarity. M.: Mir. 1986. 352 p.*
6. ***Rusanov A.I., Gudrich F.Ch.*** *Modern capillarity theory: to the 100th anniversary of Gibbs ' capillarity theory. L.: Khimiya. 1980. 344 p. (in Russia).*
7. ***Loitsyanskiy L.G.*** *Fluid and gas mechanics. M.: Nauka. 1950. 678 pp. (in Russia).*
8. ***Deryagin B.V., Churaev N.V., Muller V.M.*** *Surface forces. M.: Nauka. 1985. 398 p. (in Russia).*
9. ***Kaplan I.G.*** *Introduction to the theory of intermolecular interactions. M.: Nauka. 1982. 312 p. (in Russia).*
10. ***Vargaftik N.B.*** *Handbook of thermophysical properties of gases and liquids. M.: Nauka. 1972. 708 p. (in Russia).*
11. ***Ababneh A.. Amirfazli A., Elliott J.W.*** *Effect of Gravity on Macroscopic Advancing Contact Angle of Sessile Drops. Canad. J. Chem. Eng. 2006. V. 84. P. 39-43.*
12. ***Brutin D., Zhu Q., Rahli O.*** *Sessile drop in microgravity: creation, contact angle and interface. Microgravity Sci. Teecnol. 2009. V. 21. N 1. P. 67-76.*
13. ***Abel G., Ross G.G., Andrzejewski L.*** *Wetting of a liquid surface by another immiscible liquid in microgravity. Adv. Space Res. 2004. V. 33. N 8. P. 1431-1438.*

14. ***Kabov O.A. Zaitsev D.V.*** *The effect of wetting hysteresis on drop spreading under gravity. Dokl. Akad. Nauk. 2013. V. 451. N 1. P. 37-40.*

Received 11.09.2020
Accepted 12.10.2020