Theoretical background for simulation of physical processes in the interfacial layer "solid-liquid"

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Abstract. The paper considers the model of "solid-liquid" interfacial layer represented as a tensor of interfacial stresses by a tensor of molecular pressure. It assumes that the constant density of the medium within the interfacial layer taking into account the low compressibility of fluids. This made it possible to determine the distribution of pressure along the layer thickness. The research shows that if the wetting is adequate, the pressure on the solid wall is considerably higher than the pressure in the liquid volume phase. It has been established that to provide meniscus equilibrium conditions, it is necessary to change the thickness of the interfacial layer along the meniscus height. The research shows that the "solid-liquid" interfacial layer is considerably less thick than the "liquid-gas" layer. As a result, we have obtained theoretical equations to determine state parameters of the interfacial layer in question.

1. Introduction
In [1], the engineering approach to continuum mechanics is used to describe the mechanism of liquid-gas interfacial layer formation. Constant interfacial tension normal to the surface of the interfacial layer ensures the equilibrium of the interfacial layer. However, it is difficult to keep at small thickness of the interfacial layer and significant difference of densities and molecular pressures in the bordering volume phases. It becomes possible by using a set of globular and deviatoric components to represent the interfacial stress tensor. The spherical part of the tensor defines the pressure of the medium according to the density, while the deviator components ensure that the equilibrium conditions of the interfacial layer are fulfilled. It is the deviator components of the tensor (in the plane tangent to the layer surface) that form the surface tension of the liquid.

The existence of the surface tension of liquids has been repeatedly confirmed experimentally [2, 3]. The experts in the field believe that the surface tension of any interfacial layer can be formed only by stresses in the plane of the interfacial layer. This stereotype leads to contradictions in the theory of capillary phenomena. Roldugin [4] mentions that liquid rises in the capillary meniscus because solid molecules attract liquid molecules. The pressure in the "solid-liquid" interfacial layer grows, but there are no components of stress tensor with stresses tangent to the plane of interfacial layer and capable of holding a column of liquid. At the same time, it is clear that the additional pressure in the interfacial layer caused by molecular forces contains three tensor components, including tangential ones, capable of holding the liquid column.

Another example of "losing" one of the components of pressure tensor is the effect of swelling of wetted solids. A. Adamson in [5] criticizes the derivation of the Young's equation because it does not
consider the surface tension component normal to the interfacial area. At the same time, in the "liquid-gas" interfacial layer, the layer is formed by phase transition accompanied by a global change in the medium's density and its internal pressure. In turn, in the "solid-liquid" interfacial layer, keeping in mind that liquids are difficult to compress, the density and molecular pressures change differently, and the mechanism of creating surface tension should be different in this case.

2. Theory and discussion

We believe that in the interfacial layer "solid-liquid", the pressure to the boundary liquid phase builds up. The interfacial stresses represent a tensor containing three identical components. This makes it possible to detect "lost" components of the tensor — tangential and normal. Next, it is necessary to determine the nature of the impact of the solid phase on the liquid phase. The fixed position of solid molecules makes it impossible to form a bulk force field. The boundary condition in the liquid-solid contact region is observed: \( P_{ls} = P_s \), where \( P_{ls} \) is liquid pressure in the interfacial layer and \( P_s \) is liquid pressure at the interface of interfacial layer with solid phase [6].

At low compressibility of liquid, the molar volume \( V \) and density of medium within interfacial layer in question can be considered constant. Under conditions of good wettability of solid with liquid (\( \theta_0 < \frac{\pi}{2} \)), the liquid surface pressure \( P_s \) is greater than that in the bulk phase \( P_l \). Figure 1 shows the mechanism of solid-liquid interfacial layer formation.

![Figure 1. Mechanism of formation of solid-liquid interfacial layer.](image)

Similarly to [1], as an object of equilibrium, we consider a spherical volume with radius equal to radius of forces of molecular attraction of liquid. In contrast to the liquid-gas interfacial layer, only the liquid phase will form the bulk force field, and the solid impact is reduced to the boundary condition \( P_{ls} = P_s \) on the wall. The thickness of the solid-liquid interfacial layer will be equal to the radius of long-range action of molecular forces in the liquid phase, i.e. \( \delta_{ls} = R \) (in the liquid-gas interfacial layer \( \delta_{lg} = 2R \)). The equilibrium of the ball element in figure 1, a is provided by wall pressure \( P_s \), liquid volume phase pressure \( P_l \), and volume force \( F_v \) (if there is pressure gradient in the interfacial layer). Figure 1, c shows the components of the interfacial stress tensor, which is a pressure tensor containing three identical, equal components \( \sigma_{xx} = \sigma_{yy} = \sigma_{zz} = P_{ls} \).

Let us write down the boundary conditions for pressure distribution throughout the thickness of the solid-liquid interfacial layer (figure 1, b). At the interface of the interfacial layer with the liquid phase at \( z = \delta_{ls} = R \), the boundary conditions have the same form as in the liquid-gas interfacial layer [1]:

\[
P_{ls} = P_l, \quad \frac{dP_{ls}}{dz} = 0.
\]
These conditions are determined by the mobility of the interfacial layer molecules on the considered boundary surface. The boundary conditions on the solid wall at $z = 0$ require special consideration since pressure $P_s$ and pressure gradient $\frac{dP_{ls}}{dz}$ on the wall are unknown. In addition, there are gradients of the medium state parameters at the solid surface [6].

To determine the unknown distribution parameters, Young's equation is used:

$$\cos \theta_0 = \frac{\gamma_{sg} - \gamma_{ls}}{\gamma_{lg}},$$

(2)

where $\theta_0$ is the contact angle; $\gamma_{sg}, \gamma_{ls},$ and $\gamma_{lg}$ solid-gas, solid-liquid, and liquid-gas surface tensions, accordingly. Note that the values $\gamma_{sg}$ and $\gamma_{ls}$ cannot be measured experimentally, and the Young's equation is usually used to find the difference $(\gamma_{sg} - \gamma_{ls})$ based on the measured values $\theta_0$ and $\gamma_{lg}$ [7]. The surface tension $\gamma_{sg}$ is applied to the solid phase, while the line in question is formed by the liquid phase. Therefore, we propose a new variable $\gamma_{ls} = (\gamma_{sg} - \gamma_{ls})$ to introduce in Young's equation. Given that the separate definition of the summands in the bracket is not possible, let us use this proposed variable.

Here is a new equilibrium equation for the three-phase contact line: $\gamma_{ls} = \gamma_{lg} \cdot \cos \theta_0$, when projected on Y axis (Fig. 1, a). Under the absolute wetting of a solid by a liquid $\theta_0 = 0$, a $\gamma_{ls} = \gamma_{lg}$. The expression for liquid-gas surface tension is presented in [1]:

$$\gamma_{lg} = \frac{P_i \delta_{lg}}{16}.$$  

(3)

Given the equality of surface tension $\gamma_{ls} = \gamma_{lg}$, considering that $\delta_{lg} = 2R$, the result is:

$$\gamma_{ls} = \frac{P_i \rho}{8}.$$  

(4)

We approximate the dependence of pressure $\Delta P_s(z)$, which exceeds the pressure of the bulk liquid phase, by a power function with exponent $n$, to be further determined:

$$\Delta P_{ls} = (P_s - P_l)(1 - \frac{z}{R})^n.$$  

(5)

There are two unknown quantities in equation (5) — pressure on the solid wall $P_s$ and power $n$. We will use the scheme shown in figure 1, a to estimate them. Let us form the dependence $\Delta P_{ls}(z)$ based on the boundary conditions. The pressure gradient on the solid wall can be found by the value of the bulk force $F_v$ at $z = 0$. The bulk force in continuum mechanics is defined by the ratio of the force, which is applied to a small element of the medium, to the mass of the element [8]. When $\delta_{ls} = R$ and $z = 0$, the considered ball volume is affected by a force $P_s \pi R^2$ from a solid. The mass of the volume is half the mass of the ball, i.e. $\frac{2}{3} \rho \pi R^3$, where $\rho$ is the density of liquid. Thus,

$$F_v = \frac{P_s \pi R^2}{2\rho \pi R^3} = \frac{3P_s}{2\rho R} = \frac{1}{\rho} \frac{dP_{ls}}{dz}.$$  

(6)

This leads to:

$$\frac{dP_{ls}}{dz} = \frac{3P_s}{2R}.$$  

(7)

On the other hand, the pressure gradient can be obtained by differentiating equation (5) at $z = 0$:

$$\frac{d\Delta P_{ls}}{dz} = n(P_s - P_l) \frac{1}{R}.$$  

(8)

By equating (7) and (8), we obtain:

$$n = \frac{3}{2} \frac{P_s}{(P_s - P_l)}.$$  

(9)

Let us express the surface tension $\gamma_{ls}$, using Bakker formula [2]:
\[ y_{ls}^* = \int_0^R (P_s - P_l) \left( 1 - \frac{z^2}{R^2} \right) \, dz = \frac{R(P_s - P_l)}{n+1}. \]  

(10)

From the condition of equality of surface tensions \( y_{ls}^* = y_{lg} \) at \( \theta_0 = 0 \); when accounting for the expression (8), we obtain the quadratic equation to determine \( P_s \):

\[ y_{ls} = \frac{(P_s - P_l)}{\frac{2}{3}(P_s - P_l) + 1} = y_{lg} = \frac{P_lR}{8}; \quad 8(P_s - P_l)^2 = \frac{3}{2} \frac{(2P_s - P_l)}{2} P_l, \]

(11)

The solution to which is: \( P_s = 2.8 P_l \), and according to (5), \( n = 2.33 \).

The final result can be represented by dependencies:

\[ P_s = 2.8 P_l; \quad y_{ls}^* = y_{lg}; \quad \delta_{ls} = \frac{1}{2} \delta_{lg} = R; \quad \Delta P_{ls} = (P_s - P_l)(1 - \frac{z}{R})^{2.33}. \]

(12)

Under absolute wettability of a solid body, internal pressure of a liquid at the boundary with the wall increases by 200% compared to the pressure in the volume. Note that due to the intermolecular attraction forces, the internal pressure is one of the factors determining the strength of the medium's material. Thus, the pressure growth in the solid phase area can explain the nanoeffects associated with increased strength of the material.

2.1. Mutual influence of interfacial layers in liquid meniscus

The results of studying the solid-liquid interfacial layer (12) are obtained assuming the maximum possible solid-liquid influence during the absolute wetting of solid by liquid. When the boundary wetting angle \( \theta_0 \) is other than zero, all values in (12) should decrease. To take into account the influence of wetting conditions on the characteristics of the interfacial layer, we compose the equilibrium equation of the three-phase contact line of meniscus using the surface tensions in the interfacial layers along:

\[ y_{ls}^* = y_{lg} \cos \theta_0. \]

(13)

An increase in the contact angle \( \theta_0 \) indicates a decrease in the mutual attraction of the liquid and solid phases, resulting in a lower pressure on the solid wall \( P_s \). In this case, the essence of intermolecular interaction in the liquid phase, as shown in [1], does not change. This means that when the dependence \( y_{lg}(z) \) shown in Fig. 1, b keeps constant, the z-coordinate readout will shift to the right and lead to a decrease in pressure \( P_s \) with a decrease in the thickness of the interfacial layer. (12) and (13) can be used to determine the magnitude of this shift — to find the pressure on the wall for a contact angle other than zero. However, in our opinion, it does not make sense determining a strict dependence because there is no information on this issue in the known literature sources.

In spite of it, the provisions put forward can be confirmed by looking at the parameters of an interfacial layer at the contact angle \( \theta_0 = \frac{\pi}{2} \). Equation (13) brings us to \( y_{ls}^* = 0 \), and this means that there is no effect of solid phase on liquid. It follows that \( \Delta P_{ls} = 0 \) and \( P_s = P_l \), i.e. pressure on the wall is equal to the internal pressure of the liquid bordering it. In this case, the offset of the z-coordinate reference is \( R \), and \( \delta_{ls} = 0 \), i.e. no interfacial layer is formed. This is possible when the solid has the same effect on the liquid as the surrounding liquid, i.e. the adhesion forces are equal to the cohesion forces. This result is within the scope of the points put forward.

The results obtained above allow us to determine the characteristics of the solid-liquid interface in the liquid phase that is not perturbed by the meniscus. Within the meniscus area, the interfacial layer parameters should change to ensure the medium equilibrium. [1] shows that in each point of free surface of meniscus, there is capillary pressure due to surface curvature that satisfies the hydrostatic equilibrium conditions of liquid. Obviously, such mechanism cannot be realized in a flat solid-liquid interfacial layer. For hydrostatic equilibrium of liquid, it is necessary that in each section of meniscus located at a certain height, on the side of interfacial layer, the liquid is subjected to additional pressure equal to capillary pressure.

In a flat interfacial layer, the only way to create additional pressure may be to change the thickness. Suppose that the interaction between liquid and solid phases is constant in any meniscus cross-section.

\[ \gamma_{ls} = \int_0^R (P_s - P_l) \left( 1 - \frac{z^2}{R^2} \right) \, dz = \frac{R(P_s - P_l)}{n+1}. \]  

(10)
\( P_s = \text{const} \). As can be seen from figure 1, b, the pressure in the volume can be increased by shifting the interfacial layer border with the liquid to the left, which is equivalent to reducing the thickness of the solid-liquid interfacial layer. In the meniscus area, it is possible to create additional pressure on the liquid by reducing the thickness of the interfacial layer \( \delta_{ls} \) from a value in the liquid not perturbed by the meniscus to zero at the upper point of the meniscus. Figure 2 shows the scheme of interaction of interfacial layers of liquid meniscus. The main assumption is that the effect of the solid phase on the liquid is reduced to the boundary conditions without affecting the nature of the intermolecular interaction. The dependence \( P_{ls}(z) \) in the interval \( R \geq z \geq 0 \) in figure 2, a, defines the internal pressure in the liquid when it is exposed to a solid surface. In the absence of influence for \( \theta_0 = \frac{\pi}{2}, P_s = P_l \), the solid phase shifts to the position corresponding to D. At the maximum possible interaction of the phases, the pressure in the liquid becomes equal to the pressure \( P_s \) at point A. For the values of the boundary contact angle in the interval \( \frac{\pi}{2} > \theta_0 > 0 \), the origin of the z-coordinate will shift to the right, and the solid phase will take the position passing through point B. The pressure on the wall will decrease by \( \Delta P(\theta_0) \), and the thickness of the interfacial layer will decrease from \( R \) at \( \theta_0 = 0 \) to \( \delta(\theta_0) \). This mechanism links interfacial layer parameters with the contact angle.

![Figure 2](image.png)

**Figure 2.** Scheme of interaction of interfacial layers in the meniscus.

Figure 2, b shows the mechanism of additional pressure generation in the liquid volume phase for the meniscus section located at distance \( y \) from the undisturbed liquid level. In this case, the interfacial layer thickness decreases from \( \delta(\theta_0) \) at \( y = 0 \) to \( \delta(\theta_0,y) \) in figure 2, a. At the same time, the pressure of the interfacial layer on the liquid increases by \( \Delta P(y) \). At point K on the three-phase contact line, the interphase layers converge, and the capillary pressure value reaches its maximum. This leads to "locking" of "solid-liquid" interfacial layer, preventing the flow of liquid from the region of increased pressure to the region of rarefaction in the "liquid-gas" interfacial layer, ensuring the equilibrium on the three-phase contact line.

2.1.1. Discussion summary. The study using apparatus of continuum mechanics has shown that ensuring equilibrium laws is a necessary condition to forces of intermolecular interaction within the
microdescription of medium. The only microparameter in the obtained dependences (12) is the radius of long-range action of intermolecular attraction forces $R$.

The hypothesis that the tensor of interfacial stresses is a pressure tensor with three identical components has been used to simulate the solid-liquid interfacial layer. In traditional approach to consideration of three-phase contact line equilibrium for liquid drop on solid substrate at $\theta_0 < \frac{\pi}{2}$, the surface tension of "solid-liquid" interfacial layer [6] appears directed as in "liquid-gas" interfacial layer (towards liquid phase). However, this direction does not fit into the equilibrium conditions, which led to the introduction of a new "solid-gas" tension directed from the liquid to the gas phase. In our case, the components of the pressure tensor act to provide equilibrium, which allows us to exclude the "solid-gas" surface tension from the equilibrium equation of the three-phase contact line. It is considered in [9].

An alternative approach to the description of surface phenomena based on Gibbs theory [10] is based on the notion of a separating surface which position is undefined. In this case, the thickness of the interfacial layer is also unknown. [11] introduces the concept of disjoining pressure in thin films during interaction with a solid. The pressure distribution over the interfacial layer thickness can be studied on the basis of continuum mechanics.

3. Conclusion
At good wettability $\theta_0 < \frac{\pi}{2}$, the molecular pressure of liquid on solid surface is much higher than that in bulk phase, resulting in disjoining pressure.

It is shown that the interaction of interfacial layers in liquid meniscus is reduced to a change in the thickness of the "solid-liquid" interfacial layer along the meniscus height. This satisfies the hydrostatic equilibrium conditions of the fluid and provides geometric matching of the interfacial layers at the upper point of the meniscus.

It is shown that using the apparatus of continuum mechanics to study the surface effects is a suitable alternative to the thermodynamic method.

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