Theoretical background for simulation of the interfacial layer "liquid-gas"

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Abstract. The study shows that macroscopic approach to the description of surface phenomena used to simulate the interfacial layer as a membrane using Laplace equation allows to calculate the shape of liquid meniscus regardless of the determination of height of liquid elevation in a capillary. The use of van der Waals statements to describe the state of the medium in the interfacial layer makes it possible to estimate the distribution of molecular pressure along the layer thickness. The tensor of interfacial stresses, represented by a set of ball and deviator parts, is determined based on continuous medium equilibrium conditions. The stresses that form the surface tension of the fluid are deviator components of the tensor. As a result, the study provides the expression linking the parameters of interfacial layer thickness and surface tension of liquid.

1. Introduction
The differential equation determining the dimensional dependence of surface tension is presented in [1-2]. The analysis of mechanical equilibrium equations shows the surface tension of a liquid as a free surface attribute that is to be recorded when there is curvature. The "liquid-gas" interfacial layer is simulated as a zero-thickness membrane with tensile stresses that lead to a jump in pressure between contacting phases. Traditionally, the capillary pressure defined by Laplace formula is treated as hydrostatic pressure, while Laplace employed the molecular pressure in deriving the formula [3]. However, the values of these pressures are drastically different.

In [4], when considering the liquid meniscus equilibrium, it is stated that the pressure in the liquid is lower than the pressure in the gas phase. This assumption is in contradiction with the Laplace formula. The molecular pressure in the gas phase cannot be higher than the molecular pressure in the liquid. On the other hand, the standard explanation of liquid raise in thin capillary is: under concave interfacial surface, gas pressure is reduced, so the liquid rises up [5]. However, the convexity of the wall separating the media is always directed towards the medium with the lower pressure. Therefore, the question about the why the liquid column appears and remains in the capillary is still open.

In [6], Deryagin argues that surface phenomena are simulated by not taking into account the body forces and 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.

The purpose of this study is to solve analytically the problem of the liquid meniscus shape based on the equilibrium conditions of only one system, namely "liquid-gas". The problem is solved based on general concepts of mechanics about equilibrium. The impact of the interfacial layer on the liquid is
reduced to the capillary pressure. This pressure is caused by the curvature of the meniscus surface and is an external force with respect to the object in question. The pressure of the gas phase on free meniscus surface within the considered problem does not differ from the pressure on unperturbed liquid surface.

Forming the equilibrium equations leads to a question about the direction of capillary pressure applied to the free surface of the liquid meniscus. In [7-8], the cause of liquid rise in capillaries is considered as gas phase rarefaction above concave surface of meniscus, holding liquid column. In this case, the capillary pressure must be directed toward the center of surface curvature. There is also an opposing view. According to it, the convexity of the membrane between two media with different pressures is directed towards the medium with lower pressure [4], i.e., in conditions of considered problem, the capillary pressure should be directed towards liquid phase.

Figure 1, a shows a cross-section of a liquid meniscus formed on a flat solid wall. The hatching shows the liquid layer bounded on one side by the free surface and on the other side by the solid surface. The equilibrium object of an infinitesimal fluid volume ($dy, dz \rightarrow 0$) is reflected in figure 1, b. The element is affected by external factors: hydrostatic pressure of liquid $P$, gravity $G$, and capillary pressure $P_\gamma$.

\[
\begin{align*}
- P_\gamma \frac{dz}{\sin \theta} \sin \theta + Pdz - G &= 0; \\
G &= \frac{1}{2} \rho g dydz. 
\end{align*}
\]  

(1)

The weight of the selected element is represented as a product of two infinitesimal quantities, which allows it to be excluded from the equation. The result is:

\[
P_\gamma = \rho g y.  
\]  

(2)

Note that because the liquid mass in the meniscus has to be taken into account, according to [4], it is impossible to obtain an exact analytical solution of the problem.

Let's use Laplace formula for capillary pressure $P_\gamma = \frac{\gamma \rho g}{\bar{R}}$, where $\gamma_{lg}$ is the surface tension "liquid - gas", and $\bar{R}$ is the main curvature radius of free surface in considered point. The radius of curvature is:
\( \hat{R} = \frac{[1 + (y')^2]^{3/2}}{y''} \); \( y' = \frac{dy}{dz}; y'' = \frac{d^2y}{dz^2} \).  

(3)

Let us expand the created expressions, taking into account figure. 1, a:

\[ y' = \frac{dy}{dz} = \cot \theta; \quad y'' = \frac{d}{d\theta} (\cot \theta) \frac{d\theta}{dz} = - (1 + \cot^2 \theta) \frac{d\theta}{dz} \]

(4)

After some simple transformations, we get:

\[ P_y = - \gamma g \cos \theta \frac{d\theta}{dy} \]  

(5)

Substituting the expression \( P_y \) from equation (2), we obtain the differential equation:

\[ y dy = - \gamma g \cos \theta d\theta, \]

(6)

Integrating it while taking into account the boundary condition \( y = 0 \) at \( \theta = \frac{\pi}{2} \), we obtain:

\[ y = \sqrt{\frac{2\gamma g}{\rho g}} \left(1 - \sin \theta\right). \]

(7)

The maximum height of meniscus rise above the undisturbed liquid level \( h \) is reached at the angle \( \theta = \theta_0 \).

Equation (7), taking into account the above geometrical relations, can be solved with respect to the variable \( z \). Leaving out the intermediate transformations and using the boundary condition (at \( z = 0 \) \( \theta = \theta_0 \)) to determine the integration constant, the result is:

\[ z = \frac{\gamma g}{2 \rho g} \left[ \sqrt{2} \left( \sqrt{\frac{1 + \sin \theta}{2}} - \arctan h \sqrt{\frac{1 + \sin \theta}{2}} \right) - 2 (\sqrt{1 + \sin \theta} - \sqrt{1 + \sin \theta_0}) \right]. \]

(8)

arctan \( h \) denotes the argument of the hyperbolic tangent. The liquid meniscus length \( l = z_{\text{max}} \) can be found when \( \theta = \frac{\pi}{2} \). Setting \( \theta \) from the interval \( \frac{\pi}{2} \geq \theta \geq \theta_0 \), we can find coordinates \( y \) and \( z \) using expressions (7) and (8), i.e., construct the required dependence \( y(z) \) that determines the meniscus shape.

2. Results

Table 1 presents the results of calculations using equations (7) and (8).

| \( \theta \) | 0° | 15° | 30° | 45° | 60° | 75° | 85° | 88° | 90° |
|-------------|----|-----|-----|-----|-----|-----|-----|-----|-----|
| \( \theta_0 \) | 7 \times 10^3, m | 0 | 0.069 | 0.316 | 0.801 | 1.661 | 3.293 | 6.152 | 7.994 | 10.12 |
| y \times 10^3, m | 3.742 | 3.222 | 2.646 | 2.026 | 1.370 | 0.690 | 0.231 | 0.092 | 0 |

The calculations were performed for water with tension \( \gamma_{lg} = 0.07 \) N/m and density \( \rho = 1 - 10^3, \text{kg/m}^3 \).

The effect of solid surface on meniscus formation is determined by the value of the contact angle \( \theta_0 \) that characterizes the degree of wetting of solid surface by liquid. The contact angle \( \theta_0 \) is included in equations (7) and (8) from the boundary conditions of the problem and has no effect on the character of dependence \( y(z) \). Dependencies \( y(\theta) \) and \( z(\theta) \) are universal for liquid with given density \( \rho \) and surface tension \( \gamma_{lg} \). The value of the contact angle determines the reading on the \( y(z) \) curve plotted in the interval \( \frac{\pi}{2} \geq \theta \geq 0 \). Note that equations (7) and (8) contain the same liquid determinants as in the Jurin's law that determines the height of liquid rise \( h \) in a capillary of radius \( r \):

\[ h = \frac{2\gamma_{lg} \cos \theta_0}{\rho g r}. \]  

(9)
However, capillary pressure, keeping in mind its direction, is not the cause of liquid column retention in the capillary, but acts as a factor compensating liquid rarefaction in the area of meniscus rise. Solutions of the Laplace equation can describe the meniscus shape, but not the height of the liquid rise in the capillary. [9] shows that even for flat meniscus shape, the height of liquid rise in the capillary does not change. This demonstrates the independence of column height from meniscus shape and capillary pressure. Evidently, the reason of liquid rise in the capillary is interaction determined by the structure of interfacial layer. Accordingly, the rise of liquid in the capillary cannot be determined from the known meniscus free surface equilibrium. One should not assume that Laplace capillary pressure serves as a factor holding the liquid column in the capillary.

As shown, the capillary pressure over the concave meniscus is directed towards the liquid. This balances out the rarefaction caused by the meniscus rise. At contact angles $\theta_0 > \frac{\pi}{2}$, the meniscus surface will lower with respect to the unperturbed liquid level. The hydrostatic pressure of the fluid in the meniscus area increases. At a constant gas pressure above the free surface, the hydrostatic equilibrium of the liquid is achieved when the capillary pressure is directed towards the liquid phase. Thus, regardless of the meniscus shape, convex or concave, capillary pressure of liquid-gas interfacial layer is directed towards liquid.

The mentioned contradictions of the classical approach to consideration of the capillary phenomena testify to a lack of possibilities of macroscopic description of the capillary phenomena. It is necessary to go deeper into the micro description of intermolecular interactions.

2.1. Liquid-gas interfacial layer simulation

In spite of the fact that molecular forces are derivatives of electromagnetic forces, the total effect of their action must satisfy the conditions of mechanical equilibrium. This study proposes a way to describe surface phenomena from a mechanics perspective, which provides results for use in the field of nanotechnology.

From the point of view of continuum mechanics, an increase in the attraction of the molecules of the medium leads to an increase in its density. Accordingly, density can be used as an integral index of intermolecular interaction. In the "liquid-gas" interfacial layer, it changes by three orders of magnitude along the layer thickness, which manifests itself in the form of phase transitions.

In this regard, there is a need to use the equation of state of the medium, linking the thermodynamic parameters with the mechanical parameters of state. According to the van der Waals theory, the pressure of the medium $p$ on the solid wall can be calculated as [10]:

$$ p = \frac{RT}{V-b} - Ap, \quad Ap = \frac{a}{V^2}, \quad (10) $$

where $R$ is gas constant, $T$ is temperature, $V$ is volume of medium, $a$ and $b$ are constants. The additive $Ap$ in the right part of the equation is due to the action of intermolecular attraction forces. The parameter values of the equation from [11] allow us to estimate the internal pressure in liquid phase as $\approx 10^9$ Pa, while the external capillary effects are measured in millimeters of water column (1mm of water column = 10 Pa). External and internal force factors in surface phenomena are fundamentally different, which suggests that they should be distinguished. However, this requirement is not always met. Thus, the surface tension according to Bakker's formula:

$$ \gamma = \int_{\frac{\delta}{2}}^{\frac{\delta}{2}} (P_N - P_T) \, dz, \quad (11) $$

where $\delta$ is the thickness of the interface layer; $P_N$ and $P_T$ are the normal and tangential components of the pressure tensor; $z$ is the coordinate normal to the surface of the interface layer. The meaning of the components of the stress tensor in the integrand remains unclear.

The bulk force in continuum mechanics is defined by:

$$ F_V = \frac{1}{\rho} \frac{dP}{dx}, \quad (12) $$
where $\rho$ is the density of the medium; $P$ is pressure; $x$ is a linear coordinate.

Given the difference of densities of liquid and gas phases, there is powerful gradient of internal pressure on small thickness of interphase layer directed towards liquid phase. There is a variable field of internal pressures $P_{lg}$ with values $P_l \geq P_{lg} \geq P_g$, where $P_l$ and $P_g$ are internal pressures of liquid and gas phases.

Let us define a volume around the molecule in the form of a sphere with the radius equal to the radius of gravitational force $R$. Then attraction forces act upon the molecule in the center of the ball only from the side of the molecules confined inside the volume. Figure 2 shows the force factors acting on the spherical volume of medium $LG$ in the interfacial layer between liquid ($L$) and gas ($G$) phases. The center of the ball is located at point $C$ at a distance $z$ from the boundary with the liquid. Point $O$ is the zero of linear coordinates; $OY$ is the axis in the plane tangent to the interfacial area. Part of the volume is located in the liquid phase and the other part is located in the interfacial layer.

![Figure 2. External force factors in the liquid-gas interfacial layer.](image)

In figure 2, $a$, the effect of the liquid phase on the element is reduced to the internal liquid pressure $P_l$ at the boundary with the interfacial layer. The volume force $F_v$ manifests itself due to a larger number of molecules acting on the center of the ball from the liquid phase than from the gas phase. Each density value in the medium corresponds to a value of internal pressure:

$$\Delta p = P_{lg} - \frac{a}{V^2}, \quad (13)$$

where $P_{lg}$ is the internal pressure of the medium in the interfacial layer. Thus, along the thickness of the interfacial layer, the internal pressure varies from liquid pressure $P_l$ to saturated vapor pressure $P_g$ (by several digits). The condition is also taken into account: internal pressure in the interfacial layer is equal to the pressure in the contacting bulk phase; the internal pressure gradient at the boundary with the bulk phase is zero. The second boundary condition: the interfacial layer is an object in which properties and thermodynamic functions differ from those in the volume. The graph shown in figure 2 is constructed with regard to whether the internal pressure in the gas phase is several digits less than the pressure in the liquid. Therefore, the pressure $P_g$ is assumed zero. The thickness of the interfacial layer is equal to two radii of the attractive forces: $\delta_{lg} = 2R$. The condition of equilibrium of medium in interfacial layer is $\frac{d\sigma_{zz}}{dz} = 0$, where $\sigma_{zz}$ is normal to the surface of interfacial layer component of the interfacial stress tensor. Therefore, $\sigma_{zz} = \text{const}$. The value of the constant must be equal to the internal pressure in the liquid phase $P_l$. It is necessary to ensure compression of the medium to the liquid density at all points of the layer, except for those bordering the liquid. Thus, the interfacial stress tensor cannot
be a pressure tensor, and compression of the medium along the Z axis must be accompanied by tension along the other two axes.

Let us represent the interfacial stress tensor as a sum of the spherical and deviator parts. The spherical part of the tensor determines the internal pressure of the medium, according to figure 2, b, and the stress deviator allows the equilibrium condition \( \sigma_{zz} = P_l \). Tensor components:

\[
\sigma_{xx} = P_l g + \sigma'_{xx} ; \quad \sigma_{yy} = P_l g + \sigma'_{yy} ; \quad \sigma_{zz} = P_l g + \sigma'_{zz},
\]

where \( P_l g \) is the internal pressure at the considered point of the interfacial layer in accordance with equation (13), and the terms with dashed lines are the components of stress deviator.

Let us transform the recorded expressions with regard to the properties of the stress deviator:

\[
\sigma'_{xx} + \sigma'_{yy} + \sigma'_{zz} = 0. \tag{15}
\]

As a result, \( \sigma'_{zz} = P_l - P_l g \); \( \sigma'_{xx} = \frac{\sigma_{zz}}{2} = \frac{P_l - P_l g}{2} \).

The minus sign in the expression for the tensor components \( \sigma'_{xx} \) and \( \sigma'_{yy} \) indicates that the direction of the components is opposite to the pressure direction.

Figure 2, c shows the components of the stress tensor acting on the areas of the cubic volume of the medium in the interfacial layer. As can be seen, the tensor component \( \sigma_{zz} \) compresses the interfacial layer, while the components \( \sigma_{xx} \) and \( \sigma_{yy} \) stretch it. Stress tensor in the interfacial layer:

\[
A = \begin{bmatrix}
\sigma_{xx} & 0 & 0 \\
0 & \sigma_{yy} & 0 \\
0 & 0 & \sigma_{zz}
\end{bmatrix} = \begin{bmatrix}
P_l g & 0 & 0 \\
0 & P_l g & 0 \\
0 & 0 & P_l g
\end{bmatrix} + \begin{bmatrix}
\sigma'_{xx} & 0 & 0 \\
0 & \sigma'_{yy} & 0 \\
0 & 0 & \sigma'_{zz}
\end{bmatrix}. \tag{17}
\]

The deviator components of the stress tensor \( \sigma'_{xx} \) and \( \sigma'_{yy} \) act in the interfacial plane and form the liquid surface tension. Accordingly, the integrand in Bakker formula (11) can be applied as such: \( \sigma'_{xx} = \sigma'_{yy} = (P_N - P_T) \). It leads to:

\[
\gamma = \int_0^\delta \sigma'_{xx} dz \quad \text{or} \quad \gamma = \int_0^\delta \sigma'_{yy} dz. \tag{18}
\]

Summarized representation of spherical and deviator parts of interfacial stress tensor allows to determine the physical meaning of tensions forming surface tension of liquid.

3. Conclusion

We have developed the model of interfacial layer "liquid - gas" based on the notions of continuum mechanics. Within the research, we have obtained the distribution of stresses along the thickness of interfacial layer and determined the physical meaning of the stresses that form the surface tension of liquid.

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