The Mechanism of Action and Place of Application of Capillary Forces

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Abstract—The question of the mechanism of action and the place of application of capillary forces has been discussed. It has been shown that the conventional notions of the character of capillary forces are often contradictory. A molecular-kinetic approach has been employed to determine the places of application of capillary forces and the mechanism of their action.

INTRODUCTION

This article is a result of our attempts to present a simple physical explanation of well-known capillary effects. Formally, new relations will not be derived in this work. Only a nonstandard interpretation of the capillary effects will be given on the basis of molecular-kinetic concepts. This will enable us to solve a number of contradictions that arise when using the traditional approach to the description of capillary phenomena (the contradictions will be denoted when considering specific systems). However, as will be shown below, the absence of new relations does not exclude the possibility of finding new regularities of the processes relevant to the action of capillary forces.

Note that the molecular theory of capillarity has been rather well developed [1]. At the same time, in both monographs [1] and reviews [2, 3], capillary phenomena are interpreted within the framework of traditional ideas that have been considered in textbooks [4]. Molecular-kinetic models are only used to express the surface tension (and relevant values) via intermolecular interaction potentials. At the same time, there are some difficulties in the understanding of capillary phenomena (see, e.g., works [5, 6] and response [7] to them). In our opinion, these difficulties result namely from a wrong interpretation of the mechanism of action and understanding of the place of application of capillary forces. Many questions may be answered if a nontraditional description of the mechanism of action of capillary forces is used. Formally, the proposed molecular-kinetic consideration remains within the framework of the current ideas [1, 3] regarding the capillary effects; however, it represents a nontraditional approach to them.

In our analysis, we shall confine ourselves to a strongly simplified consideration of surface layers, which takes into account only their basic features. This, however, does not violate the general character of the described results, because they do not comprise secondary details that are of importance for the characterization of peculiarities of specific systems.

HOMOGENEOUS SURFACE AND THE YOUNG EQUATION

Contact Angle

Let us begin with the classical Young equation. Figure 1a schematically illustrates the standard approach to the determination of contact angle θ. The balance of forces applied to the three-phase contact line in horizontal directions is considered. This consideration yields the following well-known relation:

$$\cos\theta = \frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}}, \qquad (1)$$

where σ_{sv}, σ_{sl}, and σ_{lv} are the surface energies at the solid/gas, solid/liquid, and liquid/gas interfaces, respectively. Therewith, the solid surface is assumed to be smooth and unchangeable under the action of liquid molecules.

Let us note some uncertainty inherent in the standard approach (possibly, this uncertainty has previously been noted; however, it will be of importance for us in the subsequent consideration). The three-phase contact line is concerned. This notion has no physical embodiment. The force balance may be considered only as applied to real physical objects. It may be assumed that the role of the three-phase contact line is played by some group of liquid molecules located in a meniscus (a thin physical line with a thickness nearly equal to the thickness of a surface layer). Hereafter, the
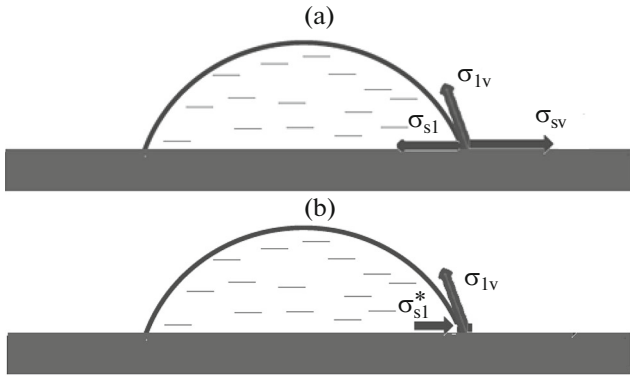
Fig. 1. Schematic representation of the forces applied to the three-phase contact line (a) in terms of the generally accepted approach and (b) in reality.

three-phase contact line will be understood precisely in this way.

In this case, the use of the force balance seems to acquire a specific meaning. Indeed, it is the liquid that is displaced over a solid surface when the force balance is disturbed; therefore, the consideration of the three-phase contact line as a portion of only liquid is quite justified. However, a problem is, in this case, encountered, which has, so far, been ignored. Namely, the tangential component of the force applied to liquid molecules from the side of a smooth solid surface is equal to zero. This follows from the fact that all the positions of a molecule moving along the surface are equivalent (we ignore the molecular structuring of the surface). That is, the tangential component of the interaction force the between liquid molecules and the solid body may be ignored. In this context, the component related to σ_{sv} should a priori be excluded from the consideration of the force balance. The possibility of ignorance of σ_{sv} may also be substantiated by the fact that surface tension σ_{sv} is, by definition, applied only to solid body molecules, while, when deriving Eq. (1), the force balance is considered as applied to liquid molecules.

Indeed, the possibility to ignore σ_{sv} is confirmed by the direct calculation of σ_{sl} performed in, e.g., work [3], in which it has been shown that

$$\sigma_{sl} = \sigma_{sv} + \sigma_{sl}^*, \qquad (2)$$

where σ_{sl}^* is the tension acting in the near-surface (with respect to a solid body) layer of a liquid, this tension being governed by the interaction between molecules and the normal component of the force of their interaction with the solid. That is, the following relation will be more correct than Eq. (1):

$$\cos\theta = \frac{\sigma_{sl}^*}{\sigma_{lv}}. \qquad (3)$$

Thus, the condition for the immobility of the meniscus is determined by the equality of the components of only two forces (Fig. 1b) resulting from the corresponding surface tensions. It is of fundamental importance that Eq. (3) concerns the surface tensions relevant only to the liquid. The surface tension of the solid body is excluded from the consideration at all. Of course, the solid body affects the value of σ_{sl}^*, but only in an indirect manner via the potential of attraction between molecules and its surface, i.e., via the normal-to-surface component of the effective force applied to liquid molecules.

Let us consider this effect in a simplified form within the framework of a quasi-thermodynamic approximation [1]. The condition for the mechanical equilibrium in the surface layer of a liquid, which we consider as an incompressible continuous medium with particle density n_0, is written as follows:

$$n_0 \frac{dU(x)}{dx} + \frac{dp}{dx} = 0, \qquad (4)$$

where $U(x)$ is the effective potential of molecules (mean force potential) in the surface layer and x is the coordinate normal to the solid surface (along the surface, the system properties are unchanged).

The integration of Eq. (4) yields

$$p(x) = p_0 - n_0 U(x), \qquad (5)$$

where p_0 is the liquid pressure far from the surface and we have assumed that, in the bulk liquid, the potential is equal to zero.

Thus, the tension in the boundary layer of the liquid may be easily found via the following well-known mechanical notion:

$$\sigma_{sl}^* = \int_0^\infty (p_{nn} - p_{\tau\tau})dx, \qquad (6)$$

where p_{nn} is the normal component of the stress tensor, this component coinciding with p_0, and $p_{\tau\tau}$ is the tangential component, which, under the considered approximation, coincides with the pressure, i.e., is preset by Eq. (5). We have assumed that coordinate $x = 0$ corresponds to the solid surface. From here, we arrive at

$$\sigma_{sl}^* = n_0 \int_0^\infty U(x)dx = \int_0^\infty (p_0 - p(x))dx. \qquad (7)$$

Note that, formally, expression (7) with effective potential $U(x)$ may be used for a liquid surface facing an arbitrary phase. Let us show the form of the effective potential.

Suppose that the intermolecular interaction potential may be represented as follows:

$$U_{ij} = -\frac{C_{ij}}{(X+a)^6}, \qquad (8)$$

where subscripts i and j denote the types of molecules, X is the intermolecular distance, C_{ij} is the intermolecular van der Waals interaction constant, and a is the potential cutoff parameter, which provides the potential with a finite value and is equal to several atomic sizes.

Now, we shall consider a liquid molecule located at distance x from an interface (Fig. 2). Let us isolate a layer $2x$ thick adjacent to the interface. Then, an isolated molecule is obviously subjected to the action of a zero force from the side of the molecules composing the layer with this thickness ($2x$); therefore, the contribution from this layer will be ignored. Thus, we encounter the necessity to calculate the force of the interaction between the molecule and the condensed phases located at distance x from the molecule. This interaction is easily calculated [8] to yield the following expressions for liquid molecule/liquid U_{ll} and liquid molecule/solid (to be more specific) U_{ls} potentials:

$$U_{ll} = \frac{\pi}{6}\frac{C_{ll}n_0}{(x+a)^3}, \quad U_{ls} = -\frac{\pi}{6}\frac{C_{ls}n_s}{(x+a)^3}, \qquad (9)$$

where n_s is the number concentration of solid molecules.

Effective potential $U(x)$ is, evidently, the following sum of the potentials (9):

$$U(x) = \frac{\pi}{6}\frac{1}{(x+a)^3}(C_{ll}n_0 - C_{ls}n_s). \qquad (10)$$

Parameters C_{ij} are related to Hamaker constants A_{Hij} via the relations [9]

$$A_{Hij} = \pi^2 C_{ij}n_i n_j, \qquad (11)$$

which, in turn, are related to surface tension [9] and can be determined experimentally.

For a liquid/gas interface, $C_{ls}n_s$ in Eq. (10) should be replaced by corresponding values for a gas or vapor. Since the number concentration of molecules in the gas is three orders of magnitude lower than that in the liquid, this term may, generally speaking, be ignored. Then, it follows from Eq. (7) that the surface tension of the liquid is related to the negative excess pressure in the boundary layer. After the integration of the pressure over the layer thickness, we arrive at a negative two-dimensional pressure or σ_{lv}. The interpretation of the surface tension as a negative two-dimensional pressure corresponds to the conventional opinion on it [8−10]. The excess pressure appears to be negative, because the molecular forces "pull" molecules into the bulk liquid; that is, as molecules move from the bulk liquid to the surface, their potential, as can be
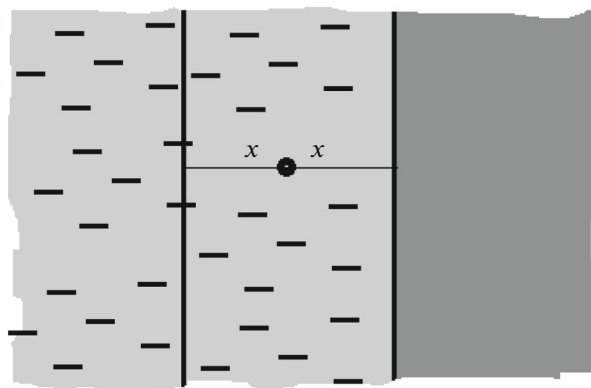

Fig. 2. Toward the calculation of the interaction potential between molecules and an interface.

seen from Eq. (10), increases, while the pressure, according to relation (5), decreases.

For the liquid/solid interface, the pressure in the boundary layer may have any sign. If the interaction of liquid molecules with a solid body appears to be stronger than with their own liquid phase, $C_{ll}n_0 < C_{ls}n_s$, molecules are attracted to the surface and the pressure in the boundary layer is increased. On the contrary, at a stronger interaction of liquid molecules with their own phase, the pressure in the boundary layer is decreased. In the case of an approximate parity of the interactions, the pressure is neither increased nor decreased. Three variants of the contact angle, i.e., acute, obtuse, and right (Fig. 3), correspond to the three considered variants of the relation between the interactions. That is, when the interaction of liquid phase molecules with the solid body prevails, the liquid wets the body. On the contrary, when the interaction of the liquid molecules with their own phase is stronger, it does not wet the solid body.

The following important circumstance must be noted. The matter concerns the liquid molecule/solid body interaction force component normal to the surface. The pressure value is determined (with no regard to the secondary factors) by the depth of the potential well for the effective molecule/surface interaction. The deeper the potential well, the higher the pressure and the smaller the contact angle (Fig. 3).

Thus, it can be seen that the surface tension of a smooth solid surface has no effect on the value of the contact angle. This value is governed by the tensions in the surface layers of the liquid phase at liquid/gas and liquid/solid interfaces. The surface tension in a liquid layer at the interface with a solid body is related only to the normal component of the effective force of the interaction of liquid molecules with it.

However, there is an implicit relation between the σ_{sl}^* value and the surface energy of the solid body. It is determined by the fact that parameter of the van der Waals interaction (attraction) of liquid molecules with
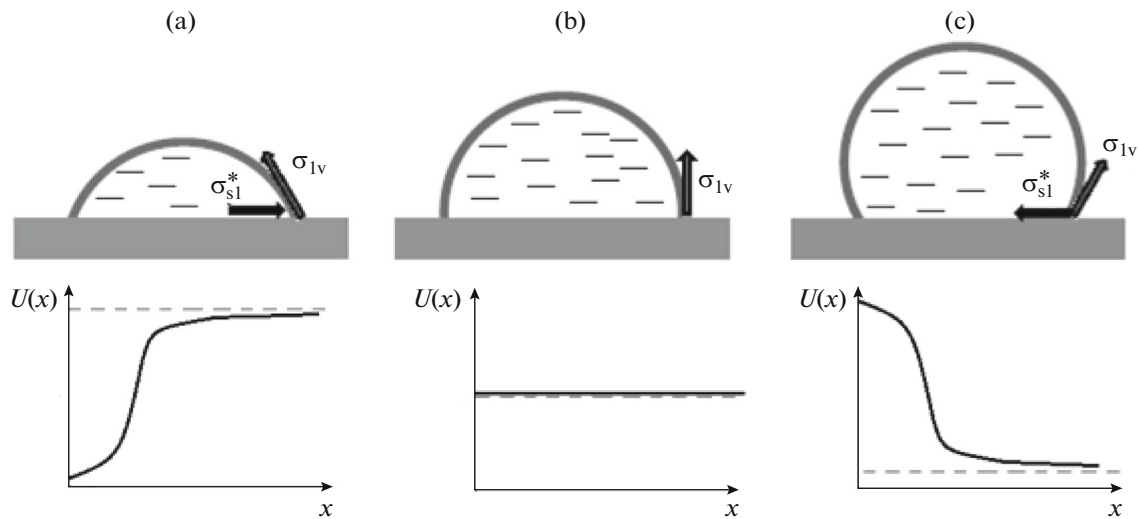
Fig. 3. The relation between the droplet shape (top) and the effective interaction potential between liquid molecules and a solid body surface (bottom) for the cases of (a) wetting, (b) indifferent equilibrium, and (c) nonwetting. The dashed line indicates the level of the potential of molecules in the bulk liquid.

the solid body C_{ls} may be approximately represented as $C_{ls} \approx \sqrt{C_{ll}C_{ss}}$. In turn, parameter C_{ss} of the intermolecular interaction in the solid body is related [9] to the surface energy (its dispersion component) as $C_{ss} \sim \sigma_{sv}$ (analogously, $C_{ll} \sim \sigma_{lv}$). Hence, tension σ_{sl}^*, as well as potential $U(x)$, depends on surface energy σ_{sv}. From the physical point of view, this is quite understandable. The stronger the intermolecular interaction in a solid body (and, accordingly, the higher its surface energy), the stronger the attraction of any molecules to this body (the higher the σ_{sl}^* value).

Mechanism of Liquid Spreading over a Solid Surface

All of the aforementioned causes us to revise the mechanism of liquid spreading over a solid surface. A liquid is not "stretched" by the surface tension of a solid body, because the tangential component of the force acting from the side of the solid body is equal to zero. Molecules are pulled into the boundary layer by
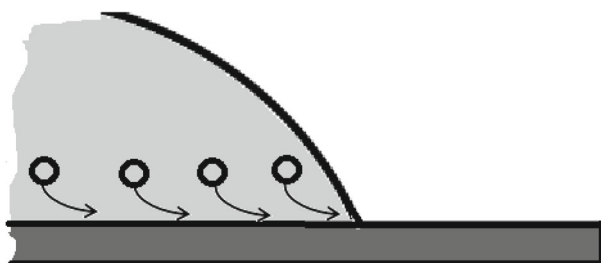

Fig. 4. The movement of molecules in a liquid spreading over a substrate.

forces normal to the surface and are "pushed aside" in it, thereby forcing the meniscus to move along the surface.

If contact angle θ is larger than the equilibrium one, the pressure in the boundary layer is lower than the equilibrium pressure (it is not completely "tightened" at the periphery); however, the pressure may provide a tangential force applied to the meniscus, this force being higher than the value of $\sigma_{lv}\cos\theta$, where θ is the current value of the contact angle. Before the equilibrium is reached, the force that pulls the molecules is not compensated by an excess pressure, and they are incorporated into the boundary layer. Therefore, the latter spreads in the tangential directions, as can be seen in Fig. 4. Note that the penetration of molecules into the boundary layer under the nonequilibrium conditions occurs throughout the area of the liquid/solid contact. In other words, liquid molecules are displaced not only in the meniscus region, but also throughout the boundary layer. It is the displacement of molecules in the boundary layer that induces the movement of the bulk liquid. This mechanism of spreading eliminates a problem that commonly accompanies the standard consideration of liquid spreading over a solid substrate, which entails a zero velocity at the boundary with a solid body. The introduced zero velocity leads to contradictions when considering the hydrodynamic behavior of a liquid in the meniscus. The new mechanism proposed for the spreading of a wetting liquid requires revision of the kinetics of the process. The kinetics will be considered in greater detail in a subsequent communication.

HETEROGENEOUS SURFACE

Movement of a Droplet

Now, let us consider the mechanism of the movement of a droplet over a heterogeneous surface. Imagine that a droplet is located on a boundary between the surfaces of two solid bodies characterized by different σ_{sv} values and, accordingly, contact angles. It is known that the droplet will be displaced toward a solid body with a higher surface energy and a smaller contact angle. Figure 5 illustrates the classical explanation of this fact: a higher tension acting from the side of body with the higher surface energy causes the droplet to move.

Two problems are encountered in this case. First, an equilibrium contact angle arises almost instantaneously, so that the force applied to the three-phase contact line is, on average, equal to zero. Were the force nonzero, the three-phase contact line would rapidly acquire a high velocity (because of its small mass as compared with the mass of the droplet). That is, there is an obvious discrepancy here. Second, as has been noted above, the force applied to liquid molecules from the side of a homogeneous solid substrate is equal to zero. That is, the scheme presented in Fig. 5a is unreal.

Indeed, the force from the side of the solid body is applied to the liquid at another site. This force acts in the transition zone between the surfaces of two different solid bodies. Figure 5b (bottom region) presents the profile of the potential well depth for liquid molecules near the solid body (we purposely speak of only the depth of the potential well: the potential has a similar profile at any distance from the surface). As has been mentioned above, the smaller the contact angle, the deeper the potential well. In other words, liquid molecules in the transition zone "go down" from a shallow potential well into a dipper one. A force proportional to the potential gradient is applied to the molecules. It is clear that this force (per unit length) is integrally (per the entire thickness of the boundary layer) equal to

$$F_1 = \sigma^*_{sl1} - \sigma^*_{sl2}, \qquad (12)$$

where σ^*_{sli} is the surface tension in the liquid adjacent to region i.

The solid-body surface energy per se is again of no significance. The situation is governed by the difference between the effective potentials of the interaction of liquid molecules with the surfaces of two solid bodies. This difference predetermines the appearance of the tangential component of the force in the transition zone. It is this force that displaces the molecules in the boundary layer, and these molecules entrain the bulk liquid. As in the case of spreading, the movement of molecules in the boundary layer plays the key role. Therewith, the droplet (to be more exact, its surface
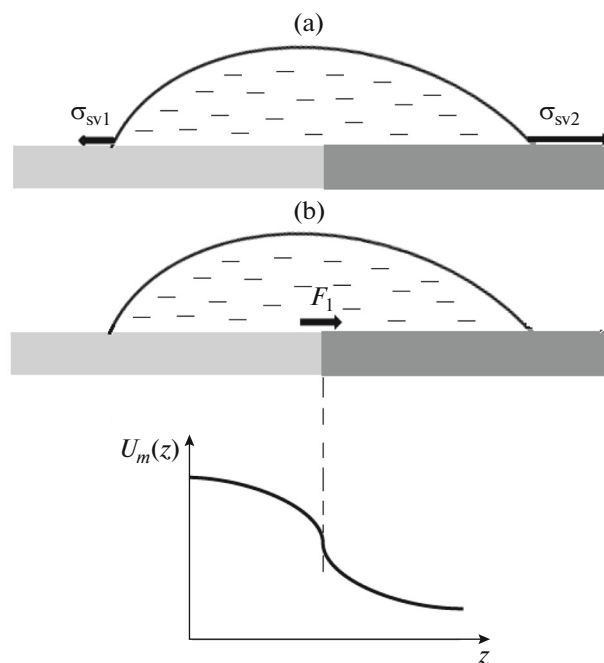

Fig. 5. Toward an explanation of the mechanism of droplet movement over a heterogeneous substrate.

layer) behaves as if it were descending into the deeper potential well.

Droplet on a Heterogeneity Spot

Let us consider a system the behavior of which can hardly be explained by the action of surface tensions on the three-phase contact line. Assume that there is a circular hydrophilic spot surrounded by a hydrophobic surface (to be more specific, we shall speak of hydrophilic and hydrophobic regions). Then, the contact angle of a sessile droplet on the hydrophilic region may take different values (Fig. 6), provided that they do not exceed the contact angle corresponding to the hydrophobic region. This fact is rather difficult to explain in terms of the surface tensions acting on the three-phase contact line, especially taking into account that the difference between the σ_{sv} values on the different regions of the free surface is compensated by the elastic forces in the solid body. In this case, we are, as it were, dealing with multiple equilibrium states.

This behavior is easy to explain within the framework of the concepts under consideration. The potential profile near the potential well minimum is depicted in Fig. 6d. The figure qualitatively shows the values of the forces applied to the boundary layer in the tangential direction within the transition zone (the arrow lengths correspond to the force values). A total (integral) force acts on the three-phase contact line. It is evident from the figure that, as the droplet size increases, the edge of the boundary region gradually
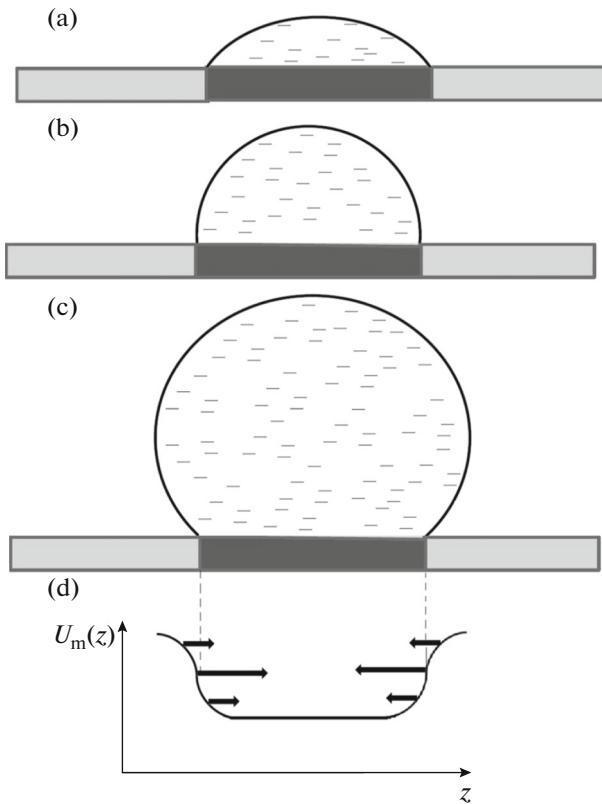
Fig. 6. Panels (a–c): possible states of a droplet on a spot of heterogeneity and panel (d): the profile of the minimum of the effective liquid molecule–solid substrate interaction potential.

shifts to the region of higher potentials, while the total magnitude of the tangential force increases. This also leads to an increase in the contact angle. After leaving the limits of the transition zone, the contact angle acquires a value corresponding to the hydrophobic region of the surface.

CAPILLARY RISE

Now, let us consider the well-known phenomenon of capillary rise (Fig. 7a). It is commonly explained [4] by the fact that the pressure is decreased under a concave interface; therefore, a liquid rises by a height of

$$h = \frac{2\sigma_{lv} \cos \theta}{\rho g R_c}, \tag{13}$$

where R_c is the radius of a capillary.

Here, questions arise as to the origin and the place of application of the force that retains the liquid column. The matter is that no forces are applied to the liquid in the meniscus region. Indeed, the capillary surface is smooth in this region, and there are no forces acting on the liquid in the vertical direction. A decrease in the pressure under the meniscus is due to the intermolecular interaction in the liquid. This is an internal interaction that cannot retain the liquid column. Thus, the aforementioned questions are quite consistent. Moreover, it has been shown [11] that, if a meniscus is "flattened" (e.g., by applying a wettable weightless piston onto it, Fig. 7b), the height of the liquid rise remains unchanged. This follows from the
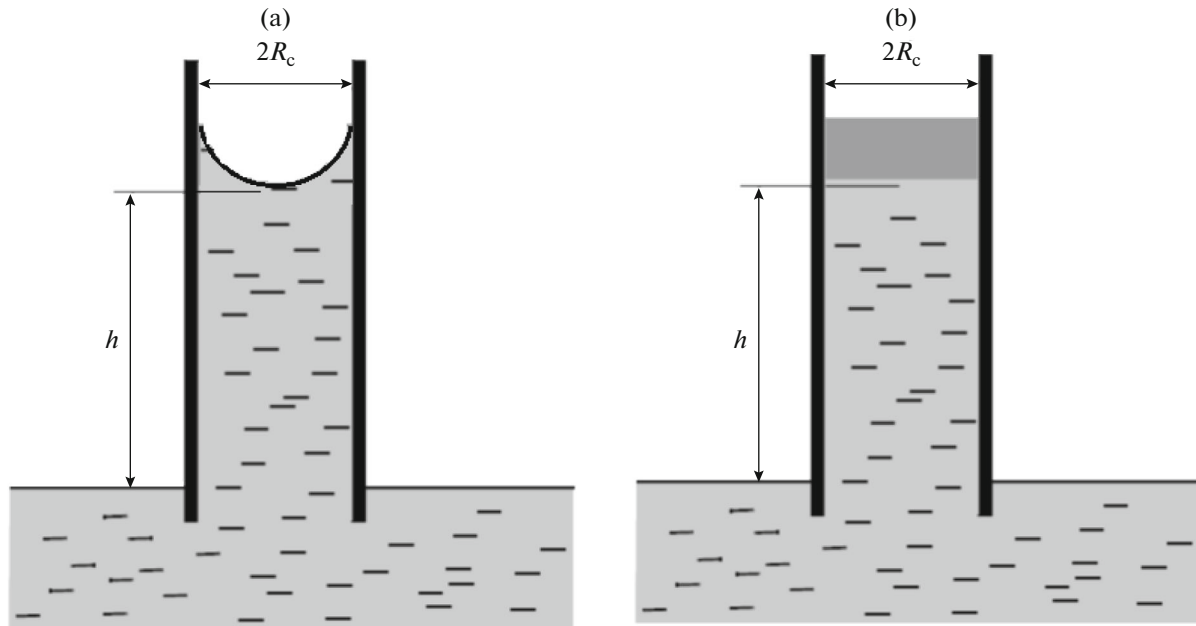

Fig. 7. The heights of the capillary rise for a liquid in the (a) presence and (b) absence of a spherical meniscus.
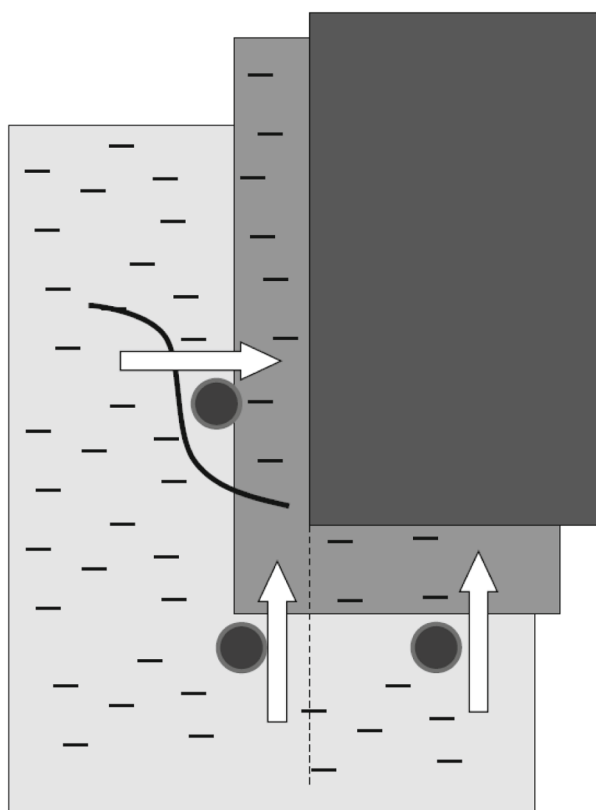
Fig. 8. Forces applied to liquid molecules at the lower edge of a wettable capillary. The intermediate gray color denotes the boundary layer of the liquid.

consideration of the condition for the minimum free energy of the system upon the meniscus displacement. This may also be shown on the basis of the aforementioned considerations. In the region of the boundary layer, the piston undergoes the action of a force related to the excess pressure in this layer (Eq. (5)):

$$F_p = 2\pi \int_0^{R_c} (p(r) - p_0)r\,dr$$

$$\approx -2\pi R_c \int_0^{R_c} n_0 U(r)\,dr = 2\pi R_c \sigma_{sl}^* = 2\pi R_c \sigma_{lv}\cos\theta. \quad (14)$$

Here, we have used the condition for the smallness of the boundary layer thickness as compared with the capillary radius. Since the liquid column weight is $\pi R_c^2 \rho g h$, Eq. (14) directly yields expression (13). Thus, the meniscus curvature is not the driving force of the liquid-column rise.
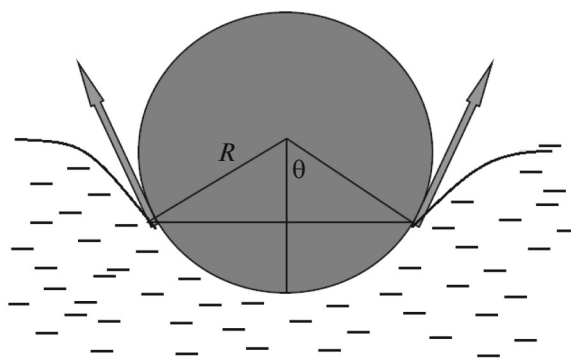

Fig. 9. Forces applied to a hydrophobic needle on a water surface in the standard interpretation.

It is clear that the force that retains the liquid column may act only in a "heterogeneous" zone of the capillary, i.e., at its lower edge immersed in the liquid. Indeed, at the lower edge of the capillary, surface forces arise (Fig. 8), which attract liquid molecules to the capillary and have a nonzero vertical component. This vertical component of the force retains (or, under nonequilibrium conditions, raises) the boundary layer, which, in turn, retains (or raises) the liquid column. The value of this force is obviously determined by Eq. (10). Thus, the rise of the liquid occurs due to the forces that act at the lower edge of the capillary rather than at the spherical meniscus. In the next section, it will be shown what forces occur when a nonwettable capillary is immersed in a liquid.

TWO MORE EXAMPLES

Floating Needle

Let us consider a well-known system—a hydrophobized metal needle on a water surface (Fig. 9). Having a density higher than that of water, the needle may, nevertheless, float on a water surface due to the action of the capillary forces. The standard explanation consists in the following [4]. The force at which the surface tension acts on the needle in the region of the three-phase contact line is equal to

$$F_N = 2\sigma\sin\theta. \quad (15)$$

This is one of the main forces providing the floating of the needle [4].

However, it is well known that a liquid may slip along a strongly hydrophobic surface. That is, there is no adhesion between a liquid and a solid body. So, how can the liquid support the needle?

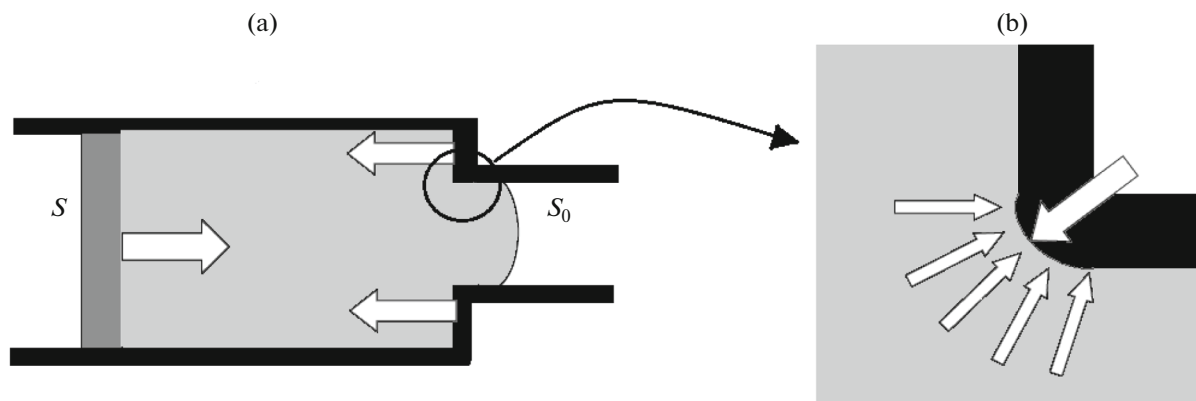The answer is as follows: force (15) is just an equivalent of forces having an absolutely different nature.

Fig. 10. Panel (a): the apparent distribution of forces upon pressing mercury into a narrow capillary and panel (b) the force arising at the capillary edge.

Namely, the surface of the liquid under the needle is curved, while the pressure is increased over a concave surface. The increase in the pressure is described by the Laplace equation (in the case of a cylindrical needle) as follows:

$$\Delta p = \frac{\sigma}{R_N}, \qquad (16)$$

where R_N is the needle radius. The integration of this increased pressure over the region of the water/needle contact yields the following:

$$F_N = \Delta p R_N \int_{-\theta}^{\theta} \cos\alpha \, d\alpha = 2\sigma \sin\theta. \qquad (17)$$

We have obtained the same result; however, the mechanism of the action of capillary forces becomes obviously different from the generally accepted one [4].

Problem Relevant to Mercury Porosimetry

Let us consider one more instructive example, which reflects the processes that occur, in particular, during mercury porosimetry or impregnation of hydrophobic porous bodies with water. Assume that we have a cylindrical tube, which narrows to form a capillary. The cross-sectional areas of the tube and the capillary are S and S_0, respectively. Suppose that mercury is pressed into the narrow capillary by excess pressure p_i. Let this pressure coincide with the Laplace pressure under a curved meniscus in the capillary. Then, the equilibrium state illustrated in Fig. 10a may take place in the system.

Let us consider the external forces applied to mercury. Force $p_i S$ is applied from the left-hand side (the side of the plunger), while force $p_i(S - S_0)$ (response

of the walls) acts from the right-hand side. The forces arising in the curved meniscus are of internal nature; therefore, they may be ignored in the total force balance. Thus, it seems that we encounter an imbalance of the forces. An additional force must take place equal to $p_i S_0$.

We shall find this force by considering the capillary edge. Indeed, as can be seen from Fig. 10b, near the edge, we have a curved mercury surface, under which an excess (Laplace) pressure is applied to the capillary edge. The response of the edge yields the aforementioned additional force $p_i S_0$.

CONCLUSIONS

It has been shown that, in many cases, the generally accepted ideas of the mechanism of action of surface forces appear to be erroneous. Nevertheless, the used relations remain valid. This is due to the fact that the relations are commonly derived using the conditions of mechanical equilibrium, which can be calculated on the basis of different approaches, including those ignoring the real action of capillary forces. However, it is, from our point of view, necessary to reveal their real mechanism and the place of application for clarifying the capillary effects in more complex situations, with nonequilibrium processes, in which the conditions of the mechanical equilibrium appear to be violated, being primarily among such situations.

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