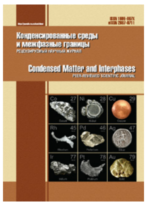

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The equilibrium shape of rolled out meniscus

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Abstract

The paper considers the issue of the equilibrium shape of the rolled out capillary meniscus in a homogeneous gravitational field. The approach used in this work differs from the earlier ones, as it takes into account the size dependence of the surface tension. With the help of such models, it will be possible to understand better the behaviour of small capillary bodies and to reveal the effects caused by the size dependence of physical parameters. For the purpose of the study, we propose to use an analogue of the well-known Tolman formula expressing the size dependence of the surface tension for the case of an interface with an arbitrary geometry. Taking into account the size dependence of the surface tension gives us equations which are predictably more complicated than the classical ones. Because of their complex nonlinearity, they cannot be solved by elementary functions, hence numerical methods are applied. The mathematical model of the meniscus is presented in a form that is better suited for numerical modelling of the profiles. We carried out computational experiments to determine the degree and nature of the effect of the parameter responsible for the size dependence of the surface tension on the equilibrium shape of the meniscus. We analysed the special cases when the exact solution of the Laplace equation and the exact relations between the meniscus profile coordinates can be obtained.

Keywords: Capillary meniscus, Surface tension, Size dependence, Capillary surface, Laplace equation, Capillary phenomena, Interfaces

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1. Introduction

Rolled out menisci, along with sessile/pendant drops and liquid bridges, are among the main types of axisymmetric capillary menisci. They can usually be observed when a cylindrical rod or spherical body is partially submerged in a liquid. Due to wetting, the surface of the liquid curves and takes a certain shape. The small volume of liquid that is now above the zero level is the rolled out meniscus. In English-language studies, these capillary systems are referred to by various names such as holms, rod menisci, etc. In Russian-language sources, the term "neck" can be used. We use the terminology adopted in the monograph [1]. A distinctive feature of this type of meniscus is its surface that asymptotically transitions to a horizontal plane as it moves away from the wetting line.

The study of the physical problems associated with rolled out menisci is of great theoretical and practical importance [2–6]. These configurations are observed, for example, in experiments to determine surface and linear tension, in studies of wetting and spreading phenomena, in technologies for growing single crystals from melts (Czochralski and Stepanov techniques), in studies of heat and mass transfer and electrical conductivity in nanosystems, flotation, probe microscopy and lithography, and in nanofluidics.

In the vast majority of cases where the rolled out meniscus is used as a model object, the problem of its equilibrium shape has to be considered. The main point of the problem is to determine the shape the meniscus takes in an external force field. Based on its solution, it is possible to draw qualitative and quantitative conclusions about the patterns of some processes occurring at the interface between immiscible media. The equilibrium shape problem in its general formulation does not have an exact solution. Therefore, it is crucially important to develop numerical methods which, in certain situations, make it possible to calculate the profiles of rolled out menisci with a good accuracy. Among the publications devoted to this issue, we should mention [7–13]. In general, the studies pay much less attention to rolled out menisci than to drops and bridges.

In this study, we considered the equilibrium shape problem of the rolled out meniscus in a homogeneous gravitational field. The novelty of the approach is that the model takes into account the size dependence of the surface tension, which is described by the generalised Tolman formula.

2. Size dependence of surface tension

The surface tension σ is the most important thermodynamic characteristic of the interface; it is the cause of almost all capillary phenomena [1]. It is well known that the value of surface tension, provided that all other conditions are equal, depends on the curvature of the interface [14–18]. This relationship is commonly referred to as the size dependence. Physically, the dependence is due to a change in the interatomic or intermolecular interactions near the interface. For example, the energies required to evaporate atoms or molecules from flat and curved surfaces can be ten times different from each other. If the surface is concave, the evaporation energy is higher than in the case of a flat interface. For a convex surface, the evaporation energy is lower (see Fig. 1).

The effect of the size dependence of the surface tension is most pronounced in low-dimensional thermodynamic systems, so studying it is especially relevant for the development of modern nanotechnology. At this point, the theory of size effects is certainly an independent (not exhaustively developed) direction in the physics of interfacial phenomena, which is considered to be an underlying principle of the type II capillary phenomena (according to L. M. Scherbakov's terminology).

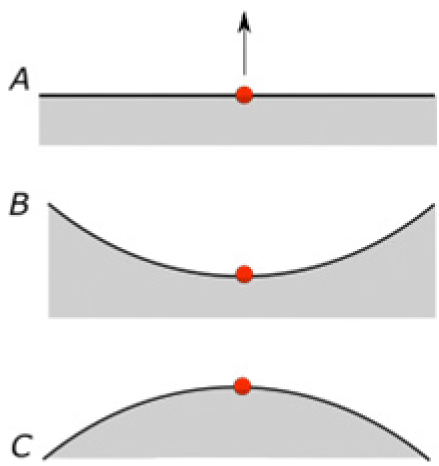

Fig. 1. Particle at the interface

The dependence of the surface tension for a small spherical drop is determined by the well-known Tolman formula [14, 15]:

$$\sigma = \frac{\sigma^{(\infty)}}{1+\frac{2\delta}{R}}, \tag{1}$$

Where $\sigma^{(\infty)}$ is the surface tension of a flat interface, R is the drop radius, and δ is a non-negative parameter that describes the thickness of the interface (the Tolman length). For interfaces with arbitrary geometry, we generalised formula (1) [19]:

$$\sigma = \frac{\sigma^{(\infty)}}{1+\delta\left(\frac{1}{R_1}+\frac{1}{R_2}\right)}, \tag{2}$$

where R_1 and R_2 are the radii of curvature of the interface in main directions. As can be seen from (2), $\sigma \to \sigma^{(\infty)}$ at $\delta \to 0$.

3. Theoretical model

Before proceeding to the equations, let us note the following. It is common to consider the size dependence of the surface tension when the volume of the condensed phase is rather small. On the contrary, the influence of gravity on the meniscus shape is significant at larger sizes. So, where the size dependence of the surface tension is taken into account, the effect of gravity can be ignored, and vice versa. However, the thickness of the interface layer δ increases with increasing temperature. Therefore, the dependence of the surface tension on the surface curvature, apparently, should also appear in macroscopic systems, for example, near a critical point. Second, in the considerations below, the gravitational field can be easily replaced by an artificial homogeneous gravitational field of higher strength. In this case, it only affects the numerical value of just one parameter. Anyway, it is important to derive the most general equations which take into account both the size dependence of surface tension and the gravitational field.

Let us consider a rolled out meniscus formed by the contact of a vertically placed cylinder with free surface of liquid. There are no restrictions on the radius of the cylinder in this problem. However, it should not be so small that a macroscopic description of the meniscus is no longer applicable.

The coordinate system associated with the meniscus profile and the designations are shown in Fig. 2: s is the arc length of the profile measured from the tangential point, φ is the slope angle of the tangent to the meniscus profile with the horizontal axis x, and (x, z) are the coordinates of an arbitrary point of the profile. In the gravitational field, the condition of mechanical equilibrium of the meniscus is defined by Laplace formula for excess pressure [1]:

$$\sigma\left(\frac{1}{R_1}+\frac{1}{R_2}\right) = -\left|\rho_l-\rho_v\right| gz, \tag{3}$$

where ρ_l, ρ_v are the densities of the liquid and gas phases respectively, g is the gravitational acceleration. We should further keep in mind that the value of the surface tension σ is not constant as previously thought. It depends on the mean curvature of the surface by formula (2). After inserting formula (2) in (3), we get:

$$\frac{1}{R_1}+\frac{1}{R_2} = -\frac{\beta z}{1+\delta\beta z}, \tag{4}$$

where $\beta = \left|\rho_l-\rho_v\right| g/\sigma^{(\infty)}$ is the capillary constant. If the surface has rotational symmetry, its principal curvatures are defined by the meridian section $z(x)$:

$$\frac{1}{R_1} = \pm\frac{d^2z/dx^2}{\left[1+(dz/dx)^2\right]^{3/2}},$$

$$\frac{1}{R_2} = \pm\frac{dz/dx}{x\left[1+(dz/dx)^2\right]^{1/2}}.$$

Then, after determining the sign, (4) transforms to the equation:

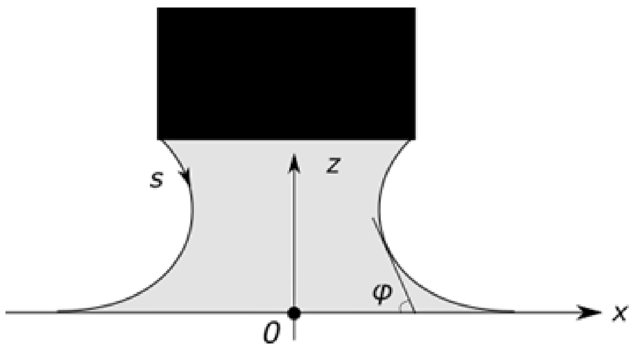

Fig. 2. Meniscus profile

$$\frac{d^2z/dx^2}{\left[1+\left(dz/dx\right)^2\right]^{3/2}}+\frac{dz/dx}{x\left[1+\left(dz/dx\right)^2\right]^{1/2}}=\frac{\beta z}{1+\delta\beta z}. \tag{5}$$

Usually, the equation for the rolled out meniscus profile is extended with the boundary conditions of the form:

$$\left.\frac{dz}{dx}\right|_{x=x_0}=\tan\left(\pi-\varphi_0\right),\left.\frac{dz}{dx}\right|_{x\to+\infty}=0, \tag{6}$$

where x_0 is the radius of the contact area, i.e., the cylinder, and φ_0 is the slope angle of the tangent at the point $x=x_0$. The first condition (6) is due to wetting of the cylinder by liquid, the second condition is caused by asymptotic degeneration of the meniscus surface into a plane as it extends away from the contact line.

The principal curvatures of the rotation surface can be expressed in another way:

$$\frac{1}{R_1}=\frac{d\varphi}{ds},\frac{1}{R_2}=\frac{\sin\varphi}{x}. \tag{7}$$

Based on (7), the basic equation (4) was rewritten as follows:

$$\frac{d\varphi}{ds}=-\frac{\beta z}{1+\delta\beta z}-\frac{\sin\varphi}{x}. \tag{8}$$

On the other hand, the expressions for a smooth flat curve are:

$$\frac{dx}{ds}=\cos\varphi,\frac{dz}{ds}=-\sin\varphi. \tag{9}$$

Combining (8) and (9), we finally obtained a system of equations:

$$\frac{dx}{d\varphi}=-\frac{\left(1+\delta\beta z\right)x\cos\varphi}{\beta xz+\left(1+\delta\beta z\right)\sin\varphi}, \tag{10a}$$

$$\frac{dz}{d\varphi}=\frac{\left(1+\delta\beta z\right)x\sin\varphi}{\beta xz+\left(1+\delta\beta z\right)\sin\varphi}. \tag{10b}$$

Thus, equilibrium profiles of the rolled out meniscus in the gravitational field, taking into account the size dependence of the surface tension, are described by solutions of equations (5) or (10). It is easy to check that in the absence of size effects, when the value of δ is zero, these equations transfer to the equations known from publications [1, 10]. Note that only axisymmetric configurations are involved. In the absence of symmetry, the mathematical side of the issue gets very complicated. Instead of ordinary differential equations we obtain partial derivative equations.

It is impossible to analytically derive a general solution of equations (5) or (10), so we have to use numerical methods. The most convenient technique for the numerical simulation of rolled out meniscus profiles [10] is based on the linearisation of equation (5). For now, we assume that δ = 0. For large values of the variable *x*, the inequality $dz/dx\ll 1$ is satisfied. Therefore, if we neglect the infinitesimal quantities of higher order in the denominator, (5) transforms into the equation:

$$\frac{d^2z}{dx^2}+\frac{1}{x}\frac{dz}{dx}-\beta z=0. \tag{11}$$

The solution of equation (11), having a horizontal asymptote, is defined by the expression:

$$z(x)=C\,K_0\left(\sqrt{\beta}x\right), \tag{12}$$

where *C* is the constant of integration, K_0 (*y*) is the modified zero-order Bessel function of the second kind. Function (12) describes only the "tail" of the meniscus profile, and it is not particularly interesting: z ≈ 0. In order to determine the part of the profile belonging to the region of small values of *x*, it is first necessary to match an arbitrary, but sufficiently large value of $x=x^*$ with the corresponding $z=z^*$ and the angle $\varphi=\varphi^*$ at a fixed *C*, using representation (12).

$$\varphi^*=\tan^{-1}\left[\sqrt{\beta}\,C\,K_1\left(\sqrt{\beta}x\right)\right],$$

where $K_1(y)$ is the modified zero-order Bessel function of the second kind. Then the set of numbers φ^*, x^*, and z^* is used as the initial data of the Cauchy problem for system (10). The latter can be effectively solved, for instance, by the Runge-Kutta or Adams methods.

However, the above procedure is not suitable at $\delta>0$, since equation (5) cannot be linearised in the same way. In this case, we take system (10) as the basis and inserted $\psi=\pi-\varphi$ in it.

$$\frac{dx}{d\psi}=-\frac{\left(1+\delta\beta z\right)x\cos\psi}{\beta xz+\left(1+\delta\beta z\right)\sin\psi}, \tag{13a}$$

$$\frac{dz}{d\psi}=-\frac{\left(1+\delta\beta z\right)x\sin\psi}{\beta xz+\left(1+\delta\beta z\right)\sin\psi}. \tag{13b}$$

Due to the characteristic of the rolled out meniscus, $z \to 0$ when $x \to +\infty$. So, the conditions to (13) must be as follows:

$$x(\psi = \psi_0) = x_0 < +\infty, z(\psi = \pi) = 0. \tag{14}$$

Problem (13)–(14) is also a boundary value problem. But unlike (5)–(6), it is considered on the finite segment $\psi \in [\psi_0, \pi]$ and it is easy to solve numerically by the shooting method.

In order to transform system (13) to dimensionless coordinates, it is appropriate to choose capillary length as a characteristic value $1/\sqrt{\beta}$. Upon dividing both parts of each of equations (13) by $\sqrt{\beta}$, we obtained:

$$\frac{dX}{d\psi} = -\frac{(1+Z\Delta)X\cos\psi}{XZ+(1+Z\Delta)\sin\psi}, \tag{15a}$$

$$\frac{dZ}{d\psi} = -\frac{(1+Z\Delta)X\sin\psi}{XZ+(1+Z\Delta)\sin\psi}, \tag{15b}$$

$$X(\psi = \psi_0) = X_0, Z(\psi = \pi) = 0. \tag{16}$$

where $X = \sqrt{\beta}x$, $Z = \sqrt{\beta}z$, and $\Delta = \sqrt{\beta}\delta$. Fig. 3 illustrates typical solutions to problems (15)–(16). The results of 3D modelling of the rolled out meniscus surface are shown in Fig. 4.

As noted above, the problem of equilibrium shape of capillary surface cannot be solved analytically. This is due to the complicated nonlinearity of the Laplace equation. Sometimes, however, it is possible to simplify the nonlinearity and to derive different kinds of exact formulas or analytical approximations to the theoretical profile. For example, in the absence of external force fields, the capillary surface transforms to a surface with a constant mean curvature. A sessile (pendant) drop takes a spherical shape, the bridge surface takes a catenoidal shape. Similarly, if we neglect the contribution of gravity in equilibrium equation (5) for the

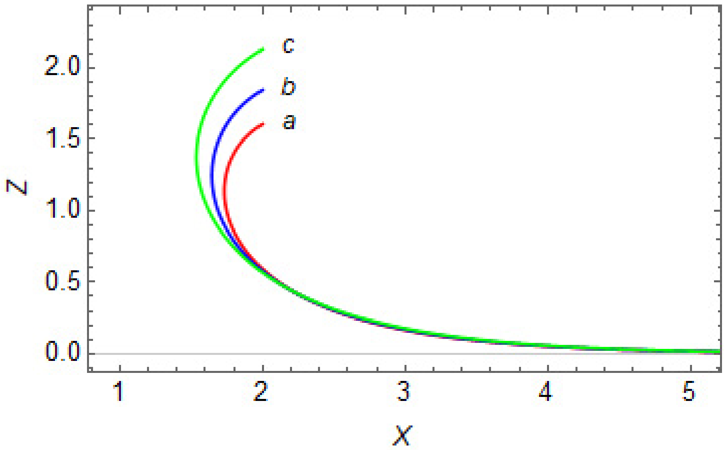

Fig. 3. Dimensionless profiles of the meniscus at $X_0 = 2$, $\psi_0 = 30°$ and different Δ: $a = 0$, $b = 0.4$, $c = 1$

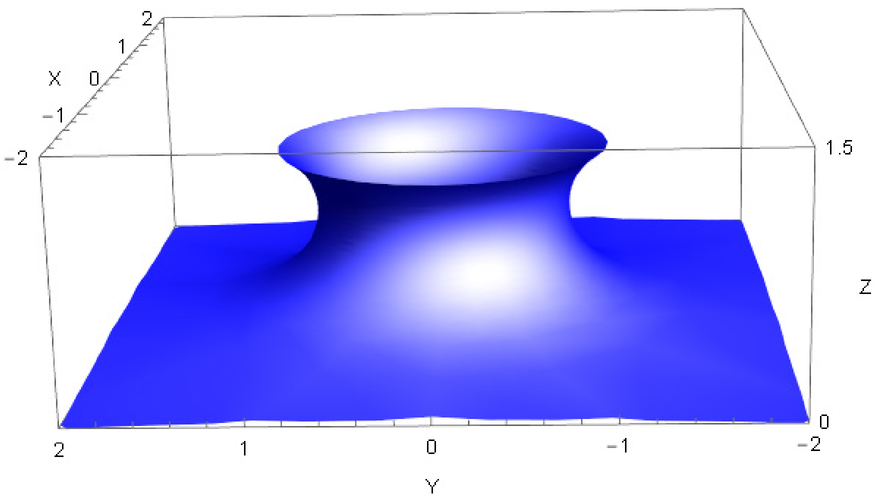

Fig. 4. 3D model of the meniscus

rolled out meniscus and assume $\beta = 0$, the exact solution is:

$$z(x) = C_1 \pm C_2 \ln\left(x + \sqrt{x^2 - C_2^2}\right), \tag{17}$$

where $C_{1,2}$ are the constants. In (17), however, the value of the constant C_2 must be zero, otherwise the function $z(x)$ is unbounded. As a result, the meniscus surface turns into the plane $z \equiv 0$. This trivial solution is obviously of no physical interest. In contrast to other basic types of menisci, the formation of a rolled out meniscus under gravity-free conditions is impossible. Without the action of the force field, the liquid of limited volume gathers into a ball, and the second boundary condition (6) cannot be satisfied.

A more important special case is the two-dimensional (cylindrical) meniscus, where the azimuthal curvature $1/R_2$ at each point is zero: $\sin\varphi / x \approx 0$. For the rolled out meniscus, this leads to the relationship between the coordinate z and the angle φ:

$$\frac{z}{\delta} - \frac{\ln(1 + \delta\beta z)}{\beta\delta^2} = 1 - \cos\varphi. \tag{18}$$

It is still not possible to derive z from it at positive values of δ using elementary functions. We have to solve the nonlinear equation, but it is already scalar, not differential. By tabulating the function $z(\varphi)$ with expression (18) over a certain range of the angle φ, the corresponding values of x can easily be deduced from the definition of the derivative.

If the parameter δ is decreased to zero, the left-hand side of (18) tends to $\beta z^2 / 2$. Then (10) and (18) provide the exact expressions for x and z known from earlier research [1]:

$$z = \frac{2}{\sqrt{\beta}} \sin\frac{\varphi}{2}, x = C - \frac{1}{\sqrt{\beta}}\left(\ln\tan\frac{\varphi}{4} + 2\cos\frac{\varphi}{2}\right), \tag{19}$$

where the constant C is defined by the condition $x(\varphi_0) = x_0$. As follows from (19), the maximum possible height z_0 of the rolled out meniscus is $2/\sqrt{\beta}$, irrespective of the value of x_0. For three-dimensional menisci, the maximum height generally increases as the radius of the contact line increases.

On the other hand, although z cannot be expressed analytically from expression (18), it allows one to analyse the nature of the dependence of the maximum height z_0 of the meniscus on the parameters β and δ. Then we inserted $\varphi = \pi$ in (18):

$$\frac{z_0}{\delta} - \frac{\ln(1 + \delta\beta z_0)}{\beta\delta^2} = 2. \tag{20}$$

Using the implicit function differentiability theorem, we obtained the following expression from implicit equation (20):

$$\frac{dz_0}{d\beta} < 0, \ \frac{dz_0}{d\delta} > 0,$$

i.e. the increase in δ is accompanied by an increase in z_0, and an increase in β is accompanied by a decrease in z_0. Note that even upon taking into account the size dependence of the surface tension, the maximal meniscus height z_0 does not depend on x_0. Moreover, the behaviour of δ upon changing of the capillary constant β does not depend on the Tolman length δ.

4. Conclusions

Equilibrium surface of the rolled out capillary meniscus in homogeneous gravitational field is described by solutions of nonlinear differential equations and their systems. The size dependence of the surface tension gives additional terms in the equations, further complicating the nature of nonlinearity. It is not possible to formulate their exact solutions in general terms. Therefore, numerical methods must be used to calculate the meniscus profiles. Due to the specific boundary conditions, the use of numerical techniques is also limited. The most practical method for numerical simulation of rolled out meniscus profiles, based on the linearisation of the Laplace equation, is not applicable in the presence of the parameter responsible for the size dependence. Thus, boundary value problems are the only option. However, with the proper choice of the variable parameters of the meniscus profile arc, the area where the solution is sought can be reduced to a finite segment instead of an infinite semi-axis. Then, well-known numerical methods, e.g. the shooting method can be applied.

In this study, we carried out computational experiments to determine the degree and nature of the effect of the parameters of the meniscus mathematical model on its equilibrium shape. From the analysis of the results, it follows, in particular, that the size dependence of the surface tension can cause a significant distortion of the meniscus shape.

Conflict of interests

The author declares that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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