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Correction to the Paper "The Condition of Mechanical Equilibrium on the Surface of a Nonuniform Thin Film" [1]

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Abstract—The correction is introduced to the definition of the disjoining pressure of wedge-shaped film formulated in the authors' previous publication. In refined definition, the nondiagonal pattern of pressure tensor even in cylindrical coordinates is taken into account and the disjoining pressure is introduced by analogy with the case of the transition zone of wetting meniscus. The alternative procedure of the definition of the disjoining pressure through the diagonal pressure tensor in the middle of the wedge is also considered.

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Note at once that general relations derived in [1] remain valid. The correction that is introduced refers to the specific case of wedge-shaped film considered in [1] as one of the examples. As early as in [2, 3], we mentioned the statement, according to which the diagonalization of pressure tensor in heterogeneous systems occurs in the absence of external fields as a result of the metric of space filled with substance. In other words, pressure tensor becomes diagonalized in a curvilinear coordinate system that diagonalizes the metric tensor. This statement has not been proven by anyone and has an intuitive character; now, we can say that it is not always true. In particular, it is not correct as applied to wedge-shaped film capable of existing in wedge-shaped cavities of a solid. In order to be sure in this statement, it is sufficient to take a look at the figure (α is the film region; β and γ are the walls of wedge-shaped cavity, which can be of different natures). Assuming for simplicity that the cavity is hollow and the only source of pressure tensor are the molecular forces of attraction between its walls, we can see that pressure vector **p** on the lower wall cannot be directed along the normal to this wall, because the forces of attraction on the left-hand side of opposite wall (it is just closer) are stronger than those on the right-hand side. When the cylindrical coordinates r, φ, z are used, this means that, in addition to normal component $p_{\varphi\varphi}$, there is nondiagonal component $p_{r\varphi}$ of pressure tensor inside the film (it is evident that other nondiagonal components are equal to zero due to the symmetry of a problem). Both components are interrelated by the condition of mechanical equilibrium

$$\frac{1}{r}\frac{\partial p_{\varphi\varphi}}{\partial \varphi} + \frac{2p_{r\varphi}}{r} + \frac{\partial p_{r\varphi}}{\partial r} = 0, \quad (1)$$

which, in turn, implies that normal component $p_{\varphi\varphi}$ is, generally speaking, a variable dependent on both r and φ. However, it is easy to be assured that, upon the motion along the coordinate line φ, one can always find the point inside the wedge where condition

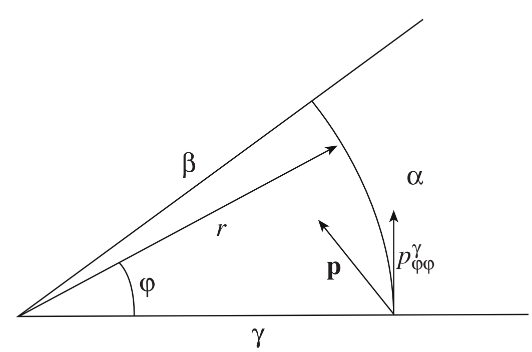
$$\frac{\partial p_{\varphi\varphi}}{\partial \varphi} = 0 \quad (2)$$

is fulfilled.

The matter is that the change in the dihedral angle by the separate rotation of β and γ walls leads to physically undistinguishable states. Thus, the work of $p^{\gamma}_{\varphi\varphi}$ (see figure) and $p^{\beta}_{\varphi\varphi}$ (analogous force from the wall β) forces is the same and forces themselves are identical

$$p^{\gamma}_{\varphi\varphi} = p^{\beta}_{\varphi\varphi}. \quad (3)$$

Condition (3) states that the $p_{\varphi\varphi}(\varphi)$ function is symmetric inside the wedge. However, it should then pass through the extreme value at which condition (2) is precisely valid. Thus, this condition is valid only in one point, but not throughout coordinate line φ inside the wedge, as was assumed in [1].



Cross cut of wedge-shaped film α between solids β and γ and the interpretation of pressure tensor in cylindrical coordinates r and φ.

Let us now consider the definition of the disjoining pressure of wedge-shaped film. In [1], it had the following form:

$$\Pi \equiv p_{\varphi\varphi} - p^{\alpha}, \tag{4}$$

where p^{α} is the pressure in the mother phase of a film at the same values of temperature and chemical potential as in the film (i.e., the pressure in real equilibrium bulk phase α in a wide part of wedge, if this is the case). Because it is $p_{\varphi\varphi}$, which is the normal pressure in cylindrical coordinates, definition (4) matches the classical approach to the theory of flat films and there is no reason to disregard this approach. However, it was stated in [1] that, since the $p_{\varphi\varphi}$ value is independent of φ, it is unimportant which φ value it is taken for. This statement is now replaced by the opposite statement, i.e., since $p_{\varphi\varphi}$ value is only dependent on φ, it is necessary to specify which coordinate φ the $p_{\varphi\varphi}$ value is taken for. It is evident that two variants are suggested, i.e., either the middle of the wedge when condition (2) is fulfilled or the wedge walls when condition (3) is valid. The most complete analogy with the case of flat film is found in the first variant because the pressure tensor becomes diagonalized. Denoting the mean coordinate by φ_m and the value of its normal pressure by $p_{\varphi\varphi}^{m} = p_{\varphi\varphi}(\varphi_m)$, we can write the definition of mean disjoining pressure Π_m of wedge-shaped film as

$$\Pi_m \equiv p_{\varphi\varphi}^{m} - p^{\alpha}. \tag{5}$$

In addition to mean pressure, we can also introduce boundary disjoining pressure Π_b of wedge-shaped film. For this purpose, using Eq. (3), we write

$$\Pi_b \equiv p_{\varphi\varphi}^{\beta} - p^{\alpha} = p_{\varphi\varphi}^{\gamma} - p^{\alpha}. \tag{6}$$

A similar approach, which was used by us upon the introduction of the disjoining pressure of the transition zone of wetting meniscus [1], can be applied to the flat part (where no capillary pressure can exist) of the boundary of any small fluid object. In view of the $p_{\varphi\varphi}(\varphi)$ function (it is set by the nature of molecular forces), the two aforementioned definitions of the disjoining pressure are not independent and, upon their selection, one can be guided by practical considerations. It will be evident at some future date which one of these definitions is more convenient.

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