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CONTACT ANGLE HYSTERESIS ON ROUGH DOUBLY PERIODIC MICRO-TEXTURED SURFACES*

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The results of a numerical study of the wetting characteristics in Wenzel's regime of the static contact of a liquid meniscus with a homogenous but doubly-sinusoidal rough solid plate are presented. The system studied is that of a vertical plate with micrometer-level roughness, partially immersed in a liquid. The solutions for the meniscus shape are obtained numerically in the general case, using the full expression of the system free energy functional, and without further assumptions, limiting the validity of the solutions. The goal is to establish how the advancing and receding macroscopic contact angles depend on the magnitude of the surface roughness. The numerical results are compared with the known results of analytical methods, where the analytical expressions are obtained for small amplitude of the roughness. The numerical solutions are obtained in a broad interval of values of the ratio between the roughness amplitude and the roughness period and the limits of applicability of the asymptotic solutions in terms of that ratio are clearly determined.

1. Introduction. Wetting of a liquid on non-ideal solid surfaces is still an open problem of general interest [1]. The study of this problem is very important, since most of the real surfaces appearing in nature, in the laboratories, and in the different technological processes are not ideal, they are rough and heterogeneous. Roughness can affect the values of the apparent contact angles. Due to roughness, energy barriers appear which hinder the displacement of the liquid, which in turn leads to the appearance of multiple metastable equilibrium states of the meniscus. This is the reason why the macroscopic contact angle, as measured relative to the average plane of the surface, is not unique. Obtaining the bounds of the interval of possible equilibrium macroscopic angles is important for determining the wetting characteristics of the materials. Therefore, surface roughness is of key importance in determining wetting behavior, and much research has been devoted to modifying the surface, in order to obtain specific wetting properties. Surfaces with random roughness are difficult to treat theoretically, and cause problems in obtaining precise wetting characteristics. However, surfaces are fabricated with a controlled design, which are micro-patterned with posts or regular patches to form surface with given wetting characteristics. Thus the investigation of the wetting on single periodic (grooves) and doubly periodic rough surfaces, fabricated by regular arrangement of specific geometric structures (responsible for the surface roughness), is of high interest.

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The conditions of wetting are described as a function of the geometric parameters of the surface design of topographical patterning – periods, amplitude, etc. The effect of surface texture on wettability has been extensively investigated experimentally for the last few years. When the roughness is on microscopic scale, it is very important to establish a relation between the roughness parameters and the behavior of the observable macroscopic contact angle. Predicting the bounds of the interval of possible equilibrium macroscopic angles, called respectively receding and advancing contact angles, in three dimensions is much more complicated, because in this case the contact line can contort around the surface topographical features. We focus here on the prediction of the macroscopic receding and advancing contact angles in terms of the roughness parameters – period, amplitude of the defects etc., defined on a much smaller length scale, by performing numerical simulations in 3D space.

More precisely, we consider the simple basic case of surfaces with doubly periodic roughness pattern of the type $A \sin ax \sin ay$, and we study the contact between the fluid and the solid surface in Wenzel's regime, i.e., when the liquid completely penetrates into the indentations of the rough surface. Cox [2] has obtained asymptotic solution for the advancing and receding angles, assuming that the height of the roughness is sufficiently small. David and Neumann [3] have obtained numerical solution for these angles under the same assumption. There are only fragmented studies of the problem in the general case, without the above-mentioned assumption, for surfaces, determined by the functions $A \sin ax \sin ay$ [4], $A\,|\sin ax \sin ay|$ [5], and $A \sin ax$ (sinusoidal grooves) [6, 7]. Further continuation of these studies in the general case is very essential. Currently, it is of interest to obtain the hysteresis interval on the basis of the set of exact solutions for the meniscus position and shape, without any assumptions for small curvatures of the meniscus deformations, caused by the roughness of the plate, and for arbitrary roughness amplitude A, and that is the objective of the present study.

2. Problem formulation. We consider here vertical chemically homogenous but rough solid plate partially immersed in a tank of liquid and we focus on the meniscus, which the liquid forms with one side of the plate. The rough solid surface Σ_s is described by a horizontally and vertically periodic doubly-sinusoidal function

$$S(y, z) = A \sin(2\pi y/\lambda) \sin(2\pi z/\lambda + z_0), \tag{1}$$

where A is the amplitude and λ is the length of one period. The y-axis is horizontal and the z-axis is directed upwards. We assume that the meniscus with free surface Σ_{lg} wets the plate in Wenzel's regime [4]. We denote the contact line (CL), which the liquid meniscus forms with the solid surface with L, and the height of the CL with $h = h(y)$. The equilibrium liquid meniscus forms with the solid plate a contact angle (CA) θ_{eq}, which satisfies the equation

$$\cos \theta_{eq} = (\gamma_{sg} - \gamma_{sl})/\gamma_{lg}, \tag{2}$$

where γ_{sg}, γ_{sl} and γ_{lg} are the solid-gas, solid-liquid and liquid-gas surface tensions respectively.

We obtain an equilibrium meniscus state by finding a local minimum for the free energy of the system U [5]

$$U = \gamma_{lg} \int\limits_{\Sigma_{lg}} d\Sigma_{lg} + (\gamma_{sl} - \gamma_{sg}) \int\limits_{\Sigma_{sl}} d\Sigma_{sl} + \int\limits_{V} \rho g z \, dV \tag{3}$$

where, Σ_{sl} is solid-liquid surface, ρ is the liquid density, g is the gravitational acceleration, and V is the volume of liquid. In the differential formulation of the problem, instead of minimizing (3) one has to solve the Laplace equation to determine the surface Σ_{lg}:

$$\gamma_{lg}\left(k_1 + k_2\right) = \rho g z, \tag{4}$$

where k_1 and k_2 are the principal curvatures of the surface Σ_{lg}.

We consider the interesting case when the period $\lambda \ll l_c$, (l_c is the capillary length $l_c = \sqrt{\gamma_{lg}/\rho g}$). Under this condition the minimization problem has multiple solutions, i.e., the liquid meniscus has multiple metastable equilibrium states. We are interested in the value of the macroscopic contact angle θ_m, defined as the angle between the mean solid surface position and the liquid-air interface. For the considered problem [8] one has

$$\theta_m = \arcsin\left(1 - \langle h\rangle^2 \Big/ 2l_c^2\right). \tag{5}$$

Our main goal is to obtain the interval of macroscopic CAs, which form the set of equilibrium CAs, as a function of the ratio A/λ. The bounds of this interval, the advancing and receding contact angles, are denoted by θ_a and θ_r respectively. We obtain these angles as follows. Firstly, employing a minimization algorithm, we obtain an equilibrium meniscus state, starting from an initial flat horizontal surface Σ_{lg} of height $h_0 = l_c\sqrt{2\left(1 - \sin\theta_{eq}\right)}$, $z_0 = 0$. Using an iterative process of displacing the whole system by $\pm\Delta z$ ("+" for the receding and "–" for the advancing case) we find a sequence of metastable equilibrium states. This procedure imitates (models) the withdrawing and submerging of the plate into the liquid. Hence, we take the mean values of the CL heights $\langle h\rangle_i$ for each equilibrium state, corresponding to the respective translation i, and from (4) we obtain a sequence of macroscopic contact angles θ_m^i. We calculate θ_a and θ_r using θ_m^i, when the change of their values has reached periodic regime with the increase of i (as an extremum or average).

Since the roughness of the solid plate is periodic, we can take in consideration only one period along the y-axis and we search for a solution between the planes $\{y = 0\}$ and $\{y = \lambda\}$ with periodic boundary conditions, imposed at the boundaries of this area. Assuming that the dimensions of the tank are $\gg l_c$ (under this assumption far away from the heterogeneous wall the liquid meniscus is practically horizontal and equivalent to the plane $\{z = 0\}$), we apply the 3D numerical minimization process in an area, close to the vertical solid plate, and at the border of that area we apply a matching of our solution with the analytical 2D solution of the Laplace equation [8].

Here, we give only a very concise description of the numerical procedure, which here is further developed to take into account the roughness of the surface. It consists of parts, described in detail in [9]. For finding a numerical solution, the liquid free surface Σ_{lg} is approximated by a set of triangles with $N_i \times N_j$ nodes $\vec{r}_{ij}$. An example of the surface meshing for 900 nodes is displayed in Fig. 3. We obtain the metastable equilibrium states using minimization algorithm for the energy functional (3). The numerical method is based on the local variations approach [10] and is similar to the one, used in the public domain software "Evolver" [11]. With these two algorithms various equilibrium states of liquid in contact with non-ideal solid surfaces are obtained [4, 5, 7, 12–18]. The nodes $\vec{r}_{ij}$ of the triangles, approximating the meniscus shape, are shifted vertically and the nodes $\vec{r}_{i1}$ approximating the CL, are shifted tangentially to the solid surface with ∂r_{ij} each in the direction minimizing U. We check the precision of our numerical method by comparing the results for different values of the displacements ∂r_{ij} and for different number of nodes N_i, N_j (we check for $N_i = N_j = 30$, $N_i = N_j = 60$, $\partial r_{ij} = 3 \cdot 10^{-5} \div 2 \cdot 10^{-6} |\vec{r}_{i1} - \vec{r}_{i2}|$). For the studied here geometry a new re-mesh procedure is developed and after some number of displacements the mesh is resized, making it more uniform. Cross-check between Σ_{lg} and Σ_s is added in the numerical procedure. The correctness of the obtained solution is monitored by keeping track of the accuracy, with which the coordinates of the points of the Σ_{lg} surface satisfy the Laplace condition (4) and Young boundary condition (2). This procedure is described in details in [7]. Our investigations show, that the numerical results fit (2) (4) with high precision, and therefore we obtain equilibrium meniscus states and respectively CAs with high precision by the minimization method.

3. Results and discussion. We study and analyze the case, when $\theta_{eq} = 60°, \lambda = 0.01 l_c$. Equilibrium meniscus states are obtained for $A/\lambda = i/60$, $i = 1, 2, \ldots$ in order to obtain the advancing and receding CAs.

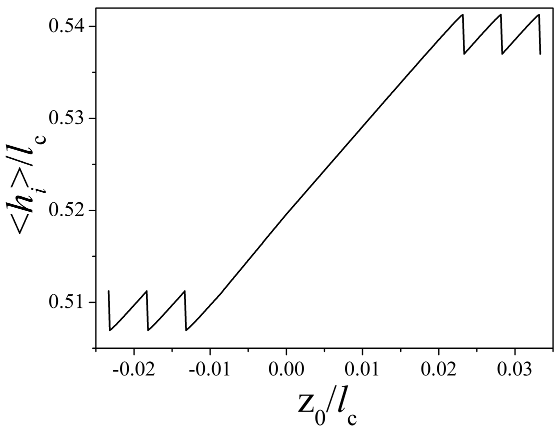

Fig. 1. Mean of the CL height as a function of the displacement of the plate for $A/\lambda = 1/30$ (in dimensionless units)

The computed results for the mean CL height are shown in Fig. 1, for a surface with $A/\lambda = 1/30$ (all the lengths are non-dimensionalized by the help of l_c). The abscissa shows the simulated displacement z_0 of the plate, relative to the pool of liquid. Each point represents the mean height of the CL after a step. The advancing and receding contact angles θ_a and θ_r are 60.51° (mean), 60.63° (extr.), and 58.72° (mean), 58.6° (extr.), respectively. One can see, that both methods (numerical and analytical) of obtaining the advancing and receding CAs lead to close results. This is so, since in the periodic changes regime (at the two ends of Fig. 1), the mean heights vary in an interval, sufficiently smaller than λ. The sudden changes in the mean CL height occur, when the CL jumps over the downward-facing or the upward-facing sides of the ridges, forming the rough surface. The obtained results for the advancing and receding CAs as a function of the ratio A/λ are shown in Fig. 2 with circles (advancing) and triangles (receding). The maximum value obtained for the receding CA is for $A/\lambda = 11/60$. The obtained equilibrium shape of the meniscus, close to the solid plate, for this case is shown in Fig. 3.

For larger values of the ratio A/λ it is not possible any longer to obtain solutions for the receding CA with the present model. Equilibrium meniscus states can be obtained up to average CL heights $1.1l_c$ with a macroscopic CA $\theta_m \approx 23^0$, however, for a further withdrawing of the plate, the minimization procedure starts to produce states, which are not physically feasible. The analytical solutions are shown with continuous lines in Fig. 2:

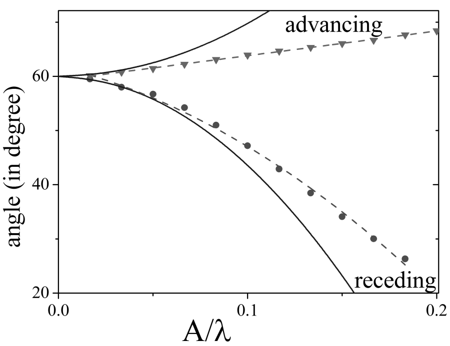

Fig. 2. Advancing and receding CAs as a function of the ratio A/λ

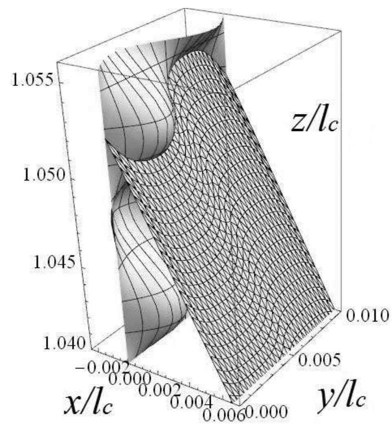

Fig. 3. Doubly-sinusoidal rough solid plate and equilibrium liquid meniscus shape in an area, close to the plate, for the receding CA (meniscus) when $A/\lambda = 11/60$

$$\theta_r = \theta_{eq} - 2.88\pi^2 (A/\lambda)^2 , \ \theta_a = \theta_{eq} + 1.71\pi^2 (A/\lambda)^2 \ \text{(in rad.)}, \tag{6}$$

for $\theta_{eq} = 60^\circ$, obtained asymptotically [2] under the assumption that $A/\lambda << 1$. With dashed lines are shown the quadratic fittings of the numerical results (note, the asymptotic solutions are also quadratic functions). The limits of applicability of the asymptotic solutions can be determined from Fig. 2 in terms of the ratio between the roughness amplitude and the roughness period. One can see from the numerical results in Fig. 2, that the asymptotic solution provides good results for $A/\lambda < 0.05$. In the general case, without the assumption for small deformations, the advancing and receding CAs are approximated well by quadratic functions of the ratio A/λ. Asymmetry of the deviation of the receding and advancing CAs from the equilibrium CA is observed. The analytical solutions (6) have the asymmetry like this as well.

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ИЗСЛЕДВАНЕ НА ХИСТЕРЕЗИСА НА КОНТАКТЕН ЪГЪЛ ВЪРХУ ГРАПАВА ДВОЙНО-ПЕРИОДИЧНА МИКРО-СТРУКТУРИРАНА ПОВЪРХНОСТ

Павел С. Илиев, Нина Х. Пешева, Станимир Д. Илиев

Представени са и са анализирани резултатите от числено изследване на мокрещите характеристики в режим на Венцел на статичния макроскопичен контактен ъгъл на течен менискус с химически хомогенна, но двойно-синусоидална грапава повърхност Изследваната система се състои от вертикална пластина (с грапавини на микро ниво), частично потопена в течност. Решенията за формата на мениската са получени числено в общия случай, използвайки пълния израз за свободната енергия на системата без допълнителни приближения и без ограничаващи валидността на решенията условия. Целта е да се установи как отстъпващият и напредващият макроскопични контактни ъгли зависят от големините на грапавостите. Получените резултати са сравнени с известни резултати от аналитични методи, където аналитичните изрази са изведени при предположение за малки големини на грапавостите. Числените резултати са получени в голям интервал от стойности на отношението на големината на грапавостта 08bи периода на грапавостта, давайки възможност ясно да се видят границите на приложимост на асимптотичните решения.