

Modelling and Investigation of the Dependence of Superhydrophobic Properties of Nanosurfaces on the Topology of Microchannels

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Abstract—In the Cassie-Baxter state anisotropic superhydrophobic surfaces have high lubricating properties. Such superhydrophobic surfaces are used in medical implants, aircraft industry, vortex bioreactors etc. In spite of the fact that quantitative understanding of fluid dynamics on anisotropic superhydrophobic surfaces has been broadened substantially for last several years, there still are some unsolved problems in this field. This work investigates dynamics of a liquid on unidirectional superhydrophobic surfaces in the Cassie-Baxter state, when surface texture is filled with gas and, consequently, the liquid virtually is located on some kind of an air cushion. Energy of the interphase boundary liquid-gas is much smaller than energy of the interphase boundary solid-liquid, that is why the contact angle at wetting such surfaces differs a lot from the Young contact angle and depends on contact area ratio of liquid-gas and liquid-solid in visible contact of liquid and surface. Considering difference in energy obtained if we slightly shift the three-phase contact line, expression for macroscopic equilibrium contact angle, which describes the Cassie-Baxter state, can be deduced. In the work the design formula for computing local-slip length profiles of liquid on the considered superhydrophobic surfaces is obtained.

Keywords—Cassie-Baxter state, local-slip length, mathematical modelling, superhydrophobic surface

I. INTRODUCTION

During last 25-30 years breakthrough progress in nano- and microtechnology, as well as aspiration to miniaturize physical, chemical, biological, pharmaceutical, electronic, bioengineering systems and processes with tight deterministic control at each stage of synthesis and functioning aroused heightened interest to micro-hydrodynamics and nano-hydrodynamics that are often called micro-fluidics and nano-fluidics, respectively (for instance, see [5]-[13] and relative references given there). In the framework of micro- and nano-hydrodynamics, the behaviour of small volumes (with order of micro- and nanoliter) and flows of fluid in

slender channels with diameter of micron scale, in which the laws of fluid flow differ significantly from the laws of classical hydrodynamics [14]: surface effects, which play a negligibly small role in classical hydrodynamics are crucial in micro-fluidics and nano-fluidics, and the skill of controlling these effects allows to optimize fluid flow in slender channels (see [15]-[21] and respective references given there). One of these controlled surface effects is slippage effect in pressure-driven fluid flow past superhydrophobic stripes (see [22]-[26] and respective references given there). Superhydrophobic surfaces combine natural hydrophobicity and roughness which results in almost complete nonwetting: on such surfaces, the contact angle is larger than 150° and, due to weak interaction forces

($\frac{W_{\text{adhesion}}}{W_{\text{cohesion}}} = 1$, where W_{adhesion} is the reversible

thermodynamic work of adhesion, W_{cohesion} is the work of cohesive forces) and high surface tension value, the so-called "lotus effect" occurs – a drop of liquid takes a spherical shape and reduces the contact area with a superhydrophobic surface, or the so-called "rose petal effect" – a drop of liquid is firmly held on a vertical surface and looks as if it were pinned to the surface (for instance, see [3], [4], [27]-[33] and respective references given there). While studying hydrodynamics of a fluid flowing past gas stripes of unidirectional superhydrophobic surfaces, an important task is to manage the process of stabilizing gas bubbles inside the cavities of such surfaces. The importance of this problem is due to the fact that superhydrophobic surfaces in the Cassie-Baxter state (sometimes also in the Wenzel state) can have exceptional lubricating properties [34]-[36] and generate secondary flows, transverse to the direction of the applied pressure gradient [37]-[39]. To achieve these lubricating properties, a controlled transition from superhydrophobic surfaces with a disordered texture to superhydrophobic surfaces with an ordered texture

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is required [40]. The wettability of the material, as well as its ability to repel water or hold a drop due to its strong adhesion to the solid surface, play a crucial role in such micro- and nanotechnologies and nanomaterials as vortex bioreactors, immersion lithography, dipping coating, inkjet printing, wear-resistant implant for human joint replacements, biological microelectromechanical systems, microscale thermalphysic devices, etc. [3]-[13], [41]. As shown in [42], if the liquid penetrates into the stripes of the nanostructured surface and fills them, then the Wenzel state occurs, which is characterized by

$$\text{hydrophilicity } \theta \in \left(0, \frac{\pi}{2}\right)$$

(with a probability of ≤ 0.7 [3], [4], [43]), or hydrophobicity

$$\theta \in \left(\frac{\pi}{2}, \frac{2 \cdot \pi}{3}\right]$$

(with a probability of ≤ 0.5), high hydrophobicity

$$\theta \in \left(\frac{2 \cdot \pi}{3}, \frac{5 \cdot \pi}{6}\right] \quad (\text{with a probability of } \leq 0.2),$$

$$\text{superhydrophobicity } \theta \in \left(\frac{5 \cdot \pi}{6}, \pi\right)$$

(with a probability of ≤ 0.1). As noted in [30], the “rose petal effect” is manifested when, despite the high hydrophobicity of the surface, only large-scale roughnesses of surface are completely filled with liquid, and small-scale roughnesses of surface are only partially filled and air always remains in them, i.e. the fluid is actually located on a gas cushion. With the maximum slope of the surface above which a drop of liquid begins to slide or roll down, the advancing wetting angle of a liquid drop is much larger than its receding wetting angle in the Wenzel state, and the difference between these angles, called wetting hysteresis $\Delta\theta$, is huge. If the surface property of superhydrophobicity is manifested not only for a

large wetting angle $\left(\theta \geq \frac{5 \cdot \pi}{6}\right)$, but also for small

wetting hysteresis $\Delta\theta \leq 10^\circ$, then this means that Cassi-Baxter state is present. According to [44], [45], a wetting hysteresis $\Delta\theta < 1^\circ$, and $\Delta\theta < 1^\circ$, respectively, is characteristic for the Cassie-Baxter state. In the state of Cassi-Baxter, liquid droplets are located both on the upper sections of the thin micron-scale slender channels and on the gas bubbles in their voids: the droplets are not able to force the bubbles out of these voids. Due to baseline adhesiveness of interaction of the contacting surfaces drops of liquid quickly slide or roll down from the surface already for the inclination angle $\alpha \approx 4^\circ$ and take with them pollution, which ensures self-cleaning of the surface with the “lotus effect” (the “lotus effect”) [46], i.e. there is a Cassie-Baxter sliding state [33] and, therefore, there is a mixed state – the Wenzel-Cassie-Baxter state [47]. In order to achieve the state of superhydrophobicity of nanostructured surfaces with the “lotus effect”, they are modified by additionally depositing water-repellent coatings on them in the form of ultra-fine layers of

compounds with low surface free energy [44], [46], [48]. In the work [40], the possibility of creating of high-hydrophobic nanostructured zinc oxide (ZnO) layers without any water-repellent coatings were experimentally demonstrated by means of pulsed electrodeposition from aqueous solutions: authors experimentally revealed the conditions for deposition of high-hydrophobic nanostructured zinc oxide layers characterized by the “rose petal effect” with specific morphology, optical properties, crystal structure and texture. Nevertheless, Cassie-Baxter state is, as a rule, unstable and prone to full or partial transformation to the Wenzel state under the external influences, for example, under the influence of pressure, heating, vibration or expulsion of drop [45].

In conclusion of this section, we emphasize that despite the impressive success achieved in the study of the mechanism of synthesis and control of superhydrophobicity of micro- and nanostructured surfaces (it is impossible not to note the stupendous theoretical and experimental achievements of Dr.Sc. Math.&Phys. O.I.Vinogradova (O.I.Vinogradova) and/or her numerous students from the Laboratory of Physical Chemistry of Modified Surfaces, A.N.Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences [18]-[20], [36]-[39], [49], [50], [67]; for more information, see [51]), problems of finding and synthesizing the best nanorelief of surfaces to maximize their superhydrophobic properties; the problem of the synthesis of coatings, possessing both superhydrophobic and superhydrophilic properties, as well as the problem of improving the adhesive and mechanical properties of such coatings and increasing their operational life; the problem of maintaining superhydrophobicity when exposed to the external environment; etc. problems are not yet fully resolved. The authors of this work believe that, along with the scientific reasons (mathematical, physical, chemical reasons), technological nature, etc., the reason for the insufficient learnedness of the above and other relevant problems is also the failure to use the powerful theory of inverse and ill-posed problems in studying these problems. As far as the authors know, at the moment the application of this apparatus in micro- and nano-fluidics, in particular, to the problem of determining dependence of nano-surfaces’ superhydrophobic properties on the topology of micro-channels, is just absent: one of options of application of theory of inverse and ill-posed problems is reducing the original direct problem (i.e. the problem of determining the superhydrophobic properties of a surface by given source data and by known controlled influences on this surface as well as on the corresponding processes taking place) to the parametrized inverse problem, in which according to the desired superhydrophobic surface properties (as if these properties are already achieved and, consequently, they are the given properties; obviously that these desired properties must firstly be mathematically formalized) it is required to find the feasible interval values of sought-for parameters (here we understand sought-for parameters as those controlled effects on the surface and on the processes taking place, owing to which the surface is superhydrophobic). This kind of reducing original direct problems to parameterized inverse problems (coefficient

inverse problems, boundary inverse problems, inverse identification problems, etc.) is a quite typical approach when solving wide classes of applied problems in the field of mathematical physics (for instance, see [52]-[54] and respective references given there); as shown in [55], [56], this approach can also be successfully applied in the field of mathematical economics, as well as in technical diagnostics [57]-[60].

II. DYNAMICS OF FLUID IN THE ATTRACTIVE FIELD ALONG THE SUPERHYDROPHOBIC SURFACE WITH A POINT SOURCE

As it is known [1], the influence of surface heterogeneity on the measured contact angle can be taken into account based on the relation

$$\cos(\theta) = \sum_{i=1}^3 s_i \cdot \cos(\theta_{i0}), \quad (1)$$

where s_i is portion of area of i -th type smooth sections on the surface of the considered material, characterized by a macroscopic contact angle θ_{i0} .

Here the type of surface area means the type of isotherm of disjoining pressure, which, in its turn, is determined by the nature of surface forces acting in a three-phase system solid-liquid-gas. If the smooth section of the surface of the material in question is of the first type, then the value of the integral in the equation

$$\cos(\theta_{10}) = 1 + \frac{(P(h) \cdot h) \Big|_{h=h_{e,d}}}{\sigma_{1,s,t}} + \frac{\int_{h \geq h_{e,d}} P(h) dh}{\sigma_{1,s,t}}, \quad (2)$$

will be positive, and then such an isotherm characterizes three-phase systems, in which complete wetting takes place. In (2) by $h_{e,d}$ we denote equilibrium depth of wetting thin film with disjoining pressure equal to capillary pressure in a drop; $P(h)$ is disjoining pressure; $\sigma_{1,s,t}$ is the surface tension of a liquid, dependence on the temperature T which is calculated by

the empirical formula
$$\sigma_{1,s,t} \approx \sigma_0 \cdot \left(1 - \frac{T}{T_{c,t}}\right)^{\frac{11}{9}},$$

which has shown itself working well for liquids with simple molecules, but it can also be used approximately for most of other liquids; if the fluid is water, it is recommended to use the interpolation formula

$$\sigma_{1,s,t} \approx 0.235 \cdot \left(1 - \frac{T}{T_{c,t}}\right)^{1.256} \cdot \left(1 - 0.625 \cdot \frac{T_{c,t} - T}{T_{c,t}}\right),$$

where $T_{c,t}$ critical temperature, σ_0 is determined on the basis of experiments with a fixed value of temperature [43],[61].

If the smooth section of the surface of the considered material is of the second type, then the integral value in equation (2) will always be negative: in three-phase systems with a second kind isotherm a "sitting" drop of liquid will be in equilibrium with a "dry" substrate free from liquid molecules. For three-phase systems with a third kind isotherm there is a balance between a drop of liquid and a substrate covered with a wetting film; if the value of the integral in equation (2) is positive, then

complete wetting can be established, if the value of this integral is negative, then incomplete wetting takes place. Large contact angles for liquid droplets on hydrophobic and superhydrophobic surfaces can be achieved in three-phase systems characterized by isotherms of the first and second kinds, and for this, a necessary condition is the presence in such three-phase systems significant forces of attraction, for example, structural forces.

Let us consider the isothermal dynamics of a thin film along a horizontal superhydrophobic surface with two orthogonal main directions of the sliding tensor in a field of gravity. Assuming that the linear scales of fluid flow far exceed the scale of micro- or nano-inhomogeneity of a surface, we can assume that the surface is a flat surface with a given slip condition. We will assume that the mass of the fluid continuously enters the surface microchannels from a localized linear source with negligibly small dimensions, and, it is assumed that the volume $V(t)$ of linear source power is set. Now let us introduce Cartesian coordinate system with origin in the source in such way that axis OX is directed along the underlying surface from the source, axis OY is directed perpendicular to axis OX , gravity force is directed down perpendicular to underlying surface. Then, within the framework of the assumptions made, the dynamics of slow fluid flows in microchannels of a superhydrophobic surface can be represented by the following model, which contains Navier-Stokes equations and continuity equation:

$$\begin{cases} \frac{\partial \mathcal{G}_x}{\partial t} = \nu \Delta \mathcal{G}_x + \nu \frac{\partial}{\partial x} \left(\frac{\mathcal{G}_x}{x} \right) - \frac{1}{\rho} \frac{\partial p}{\partial x} - \overset{\mathbf{r}}{\mathcal{G}} \nabla \mathcal{G}_x, \\ \frac{\partial \mathcal{G}_y}{\partial t} = \nu \Delta \mathcal{G}_y + \frac{\nu}{x} \frac{\partial \mathcal{G}_y}{\partial x} - \frac{1}{\rho} \frac{\partial p}{\partial y} - \overset{\mathbf{r}}{\mathcal{G}} \nabla \mathcal{G}_y - g, \\ \mathcal{G}_x + x \nabla \cdot \overset{\mathbf{r}}{\mathcal{G}} = 0, \end{cases} \quad (3)$$

where $\overset{\mathbf{r}}{\mathcal{G}} = \overset{\mathbf{r}}{\mathcal{G}}(\mathcal{G}_x(t, x, y), \mathcal{G}_y(t, x, y))$ is fluid velocity vector field; $p = p(x, y)$ is fluid pressure in the microchannel; $\rho = \rho(x, y)$ is fluid density; ν is kinematic viscosity of liquid; g is gravitational acceleration; t is time; operators Δ and ∇ are Laplacian and gradient, respectively;

vector operator $\nabla \cdot \overset{\mathbf{r}}{\mathcal{G}} = \frac{\partial \mathcal{G}_x}{\partial x} + \frac{\partial \mathcal{G}_y}{\partial y}$ is divergence.

Obviously, for the mathematical completeness of model (3), it is necessary to add the corresponding initial and boundary conditions: in the present paper we will neither discuss the methods of construction nor the concrete forms of these conditions.

If we introduce designation $\varepsilon = \frac{h}{l} = 1$ (ε is the relative thickness of the microchannel, by h we denote microchannel characteristic thickness, by l we denote characteristic longitudinal scale on which the dynamics of a thin film is considered) and make substitutions in (3) (for convenience, the symbols of new substitutions will remain the same)

$$x : hx; \quad y : hy; \quad t : \frac{l}{u} t; \quad \overset{\mathbf{r}}{\mathcal{G}} : u \overset{\mathbf{r}}{\mathcal{G}}; \quad p : \frac{ul \nu \rho}{h^2} p, \quad (4)$$

where u means the longitudinal local velocity of

component \mathcal{G}_x in a thin film (this value can be physically interpreted also as a measure of the displacement of the cross-sectional area of a thin film), then we obtain the following system:

$$\begin{cases} \varepsilon^3 \text{Re} \frac{\partial \mathcal{G}_x}{\partial t} = \varepsilon \Delta \mathcal{G}_x + \varepsilon \frac{\partial}{\partial x} \left(\frac{\mathcal{G}_x}{x} \right) - \frac{\partial p}{\partial x} \\ -\varepsilon^2 \text{Re} \mathcal{G} \nabla \mathcal{G}_x, \\ \varepsilon^3 \frac{\partial \mathcal{G}_y}{\partial t} = \Delta \mathcal{G}_y + \frac{\varepsilon}{x} \frac{\partial \mathcal{G}_y}{\partial x} - \frac{\partial p}{\partial y} \\ -\varepsilon^2 \text{Re} \mathcal{G} \nabla \mathcal{G}_y - \frac{\varepsilon^3 \text{Re}}{u^2} g, \\ \mathcal{G}_x + x \nabla \cdot \mathcal{G} = 0, \end{cases} \quad (5)$$

where $\text{Re} = \frac{ul}{\nu}$ is Reynolds number, which

does not have to be small, but the value $\varepsilon^2 \text{Re}$ is supposed to be small enough.

Depending on the order of smallness of neglected terms of equations, containing $\varepsilon = 1$, from the mathematical model (5), one can obtain various asymptotic models of the theory of Stokesian flows with point disturbances, which arise when studying various technological processes and objects (for instance, see [61], [62] and respective references given there). For example, if in (5) we neglect the terms of the equations containing the magnitude of the first and higher orders, then we find that the fluid pressure in the thin film does not change along the underlying surface from the source, nor does the microchannel depth.

Let us return to the substitutions (4), with the help of which the transition from model (3) to model (5) was made. Actually, longitudinal local velocity u of component \mathcal{G}_x in a thin film is not a priori known value and, moreover, is not a constant [24], since in real conditions the physical properties of the medium and processes are significantly different from the properties of an ideal model in which you can operate with assumptions like ‘‘unbounded medium’’, ‘‘incompressible fluid’’, etc. The desire to present a longitudinal local velocity by a constant is quite understandable: this simplifies and simplifies the simulated process and the constructed mathematical model, in which you can focus on quantitative and/or qualitative studies of other unknown parameters and functions that are considered by some reasons within the specific problem studied. In this work we omitting the course of derivation, offer the following nonlinear equation for finding longitudinal local velocity $u = u(t, x, y)$:

$$\frac{\partial^2 u}{\partial t^2} + \frac{\mu \rho}{2h} \left(\frac{\partial u}{\partial t} \right)^2 = a^2 \Delta u, \quad (6)$$

where $a = \sqrt{gh}$; μ is friction coefficient; nonlinear

term $\frac{\mu \rho}{2h} \left(\frac{\partial u}{\partial t} \right)^2$ of the equation characterizes total friction force per unit area.

It is easy to make sure that the value $-h \mathbf{e}^{\mathbf{r}} \nabla u \equiv \delta$, where $\mathbf{e}^{\mathbf{r}} = (1, 1)$, characterizing the increase in the level of liquid in the microchannel, satisfies

homogeneous linear wave equation $\frac{\partial^2 \delta}{\partial t^2} = a^2 \Delta \delta$. The

idea of solving a nonlinear equation (6) is set out below (perhaps there are more elegant ideas). Imagine the solution of (6) as $u(t, x, y) = f_1(\varphi_1) + f_2(\varphi_2)$, where

$$\varphi_1 = \frac{at+x}{at-x} \text{ and } \varphi_2 = \frac{at+y}{at-y}, \quad f_1(\cdot) \text{ and } f_2(\cdot)$$

are still unknown functions. It is not hard to make sure that

$$\frac{1}{a} \frac{\partial u}{\partial t} = \frac{1-\varphi_1}{at-x} f_1'(\varphi_1) + \left(\frac{1-\varphi_2}{at-y} \right)^2 f_2'(\varphi_2), \quad (7)$$

$$\begin{aligned} \frac{1}{a^2} \frac{\partial^2 u}{\partial t^2} &= \left(\frac{1-\varphi_1}{at-x} \right)^2 f_1''(\varphi_1) - \frac{2(1-\varphi_1)}{(at-x)^2} f_1'(\varphi_1) \\ &+ \left(\frac{1-\varphi_2}{at-y} \right)^2 f_1''(\varphi_2) - \frac{2(1-\varphi_2)}{(at-y)^2} f_2'(\varphi_2), \end{aligned} \quad (8)$$

$$\frac{\partial^2 u}{\partial x^2} = \left(\frac{1+\varphi_1}{at-x} \right)^2 f_1''(\varphi_1) + \frac{2(1+\varphi_1)}{(at-x)^2} f_1'(\varphi_1), \quad (9)$$

$$\frac{\partial^2 u}{\partial y^2} = \left(\frac{1+\varphi_2}{at-y} \right)^2 f_1''(\varphi_2) + \frac{2(1+\varphi_2)}{(at-y)^2} f_2'(\varphi_2). \quad (10)$$

Taking into account (7)-(10) in (6) allows us to obtain the following linear ordinary differential equation with

respect to $\frac{1}{f_j'(\varphi_j)}$, $j = 1, 2$:

$$\left(\frac{1}{f_j'(\varphi_j)} \right)' - \frac{1}{\varphi_j f_j'(\varphi_j)} + \frac{\mu \rho}{8h} \left(\varphi_j + \frac{1}{\varphi_j} - 2 \right) = 0. \quad (11)$$

Solving the linear equations (11), we get the formula

$$f_j(\varphi_j) = -\frac{8h}{\mu \rho} \int \frac{d\varphi_j}{\varphi_j^2 + \varphi_j - 2\varphi_j \ln \varphi_j - 1}, \quad j = 1, 2, \quad (12)$$

in which the integral, unfortunately, is not calculated analytically. By applying a numerical integration method to this integral, we can determine approximate expressions for the functions

$$f_1 \left(\frac{at+x}{at-x} \right) \text{ and } f_2 \left(\frac{at+y}{at-y} \right) \text{ and, consequently,}$$

to find the desired longitudinal local velocity of component \mathcal{G}_x of fluid velocity vector field in a thin film using the formula $u = f_1 + f_2$.

DYNAMICS OF FLUID IN NANOCANNEL OF STRUCTURED SUPERHYDROPHOBIC SURFACE AND SLIDING PHENOMENA

For the mathematical description of transport phenomena on a superhydrophobic surface with microrelief, in stripes of which the liquid, solid and gaseous phases occur, it is necessary to determine the physical mechanisms of sliding on the surface and formulate the corresponding boundary conditions (for instance, see [24], [25] and respective references given there). As mentioned in the introduction, sliding takes place if the value of the tangential component of the velocity vector at the interphase boundary is not zero. The simplest model of sliding phenomena suggests that tangential force acting per unit of surface area S , is proportional to the sliding velocity: $\mathcal{G}_{sl}|_S = \mu \tau|_S$, where \mathcal{G}_{sl} is this sliding velocity; τ stands for shear stress, μ stands for friction coefficient. This condition is called Navier sliding condition. For Newtonian fluid Navier sliding condition can be written in

the form $\mathcal{G}_{tan}|_S = L_{sl} \frac{\partial \mathcal{G}}{\partial y}|_S$, called Navier boundary

condition, where \mathcal{G}_{tan} is tangential velocity on the cavity wall; $L_{sl} = \eta \mu$ is the sliding length that characterizes the distance at which the velocity profile is extrapolated to zero, η stands for dynamic viscosity; $L_{sl} = 0$ corresponds to boundary condition of adhesion, at which the relative velocity of the liquid on the solid wall is zero; $L_{sl} \rightarrow \infty$ corresponds to the boundary condition of the absence of friction, at which plug-like flow takes place with zero speed gradient. Since fluid dynamics at the interface with a solid surface can be considered at different scales, as a rule (as a rule), three different types of sliding at the interphase boundary are distinguished: internal/molecular sliding; apparent sliding; effective sliding.

Internal sliding model suggests movement of molecules in the near-wall layer, and it cannot lead to large values of L_{sl} .

The apparent sliding model suggests formation of a gas cushion or a low viscosity liquid film near the solid wall. The seeming sliding is supported by a higher shear rate in the low viscosity layer compared to the shear volume rate. The apparent sliding length is defined as

$$L_{app.sl.} = \varepsilon \left(\frac{\eta}{\eta_\varepsilon} - 1 \right) \approx \frac{\langle h_{sulcus} \rangle \eta}{\eta_\varepsilon},$$

where η_ε is viscosity of interphase boundary (i.e. viscosity of the above mentioned gas cushion or liquid film); $\langle h_{sulcus} \rangle$ is averaged (in the sense of surface mean value) depth of the sulci. It should be emphasized that for all appearance simplicity, the apparent sliding model reflects the formation of rarefied gaseous layer near the hydrophobic wall and makes it possible to better understand the influence of the interface region structure on the phase transfer transport phenomena) [25].

The effective sliding model assumes the formation of a stable gas phase in the stripes of microrelief of the surface in the Cassie-Baxter state, and allows you to replace the actual non-uniform surface with a homogeneous smooth plane, showing the same hydrophobic properties as real surface. This approach allows, in addition to increasing the sliding length, also to find solutions to problems and analyze complex systems, without requiring time-consuming calculations of the local velocity field of the fluid to be performed. The effective sliding length is defined as the boundary condition.

$$\langle \mathcal{G}|_S \rangle = L_{eff} \cdot \left\langle \frac{\partial \mathcal{G}}{\partial y} \Big|_S \right\rangle,$$

where $\langle \cdot \rangle$ denotes mean value

for surface S and characterizes the sliding intensity of a fluid over a smooth surface with a sliding length L_{eff} . One of the first experimental studies of the effective sliding length of a Newtonian fluid was performed in Department of Mechanical and Industrial Engineering, University of Massachusetts [63], [64] using example of a flow in a microchannel with a rectangular cross section and a superhydrophobic coating on the bottom wall: surfaces with periodic sets of microbars or parallel sulci were used as a superhydrophobic coating with a surface portion of liquid-gas plots in the range 0.5÷0.9; the height of microchannels ranged in 76÷264 μm ; it was found that an increase in the surface fraction of the gas sections and the height of the microchannel leads to an increase in the sliding length, the maximum value of which was more than 20 μm with 0.9 surface fraction of the gas sections. The obtained experimental results are consistent with the results of theoretical studies in [65]-[67].

As mentioned in the introduction, with a high surface portion of the gas sections, the stability of the Cassie-Baxter state can be broken, resulting in liquid penetrating into the gaseous stripes [42]. Therefore, with the flow of fluid in the microchannel, in addition to the general thermodynamic stability criteria:

- stability criterion for a system with constant volume and entropy: only processes with a decrease in internal energy can spontaneously occur in the system, and consequently a stable state with a minimum of internal energy is stable;
- stability criterion for a system with constant pressure and entropy: only processes with a decrease in enthalpy can occur spontaneously in the system, and, therefore, the state with minimum enthalpy is stable;
- stability criterion for a system with constant volume and temperature: only processes with a decrease in free energy can spontaneously occur in the system. Therefore, only a state with a minimum of free energy

is stable;

- stability criterion for a system with constant temperature and pressure: only processes with a decrease in the thermodynamic potential can spontaneously occur in the system, and therefore the state with a minimum of the Gibbs thermodynamic potential is stable,

it is also necessary to take into account the balance of forces acting on the liquid-gas interface. The stability of the Cassie-Baxter state for an isotropic texture in the form of microbars set is ensured by the fulfillment of the inequality [68], [69]

$$2\sigma_{s.t.}\sqrt{\pi(1-r_{gas})}\cos(\theta)\leq r_{gas}T\Delta p, \quad (13)$$

where $\sigma_{s.t.}$ is the surface tension of a liquid (72 mN/m for water at 25°C); r_{gas} denotes surface portion of microchannel gas plots (i.e. the percentage of the surface that is perfect slip:

$$r_{gas} = \frac{h}{T}, \quad h \text{ is slip size); } \theta \text{ stands for contact angle; } T \text{ is period of microbars of the texture;}$$

$\Delta p = p_g - p_l$ is the pressure difference in gas and liquid (see Fig. 1, [68]). The stability of the Cassie-Baxter state for anisotropic texture in the form of parallel sulci is ensured by the fulfillment of inequality

$$2\sigma_{s.t.}\cos(\theta)\leq r_{gas}T\Delta p. \quad (14)$$

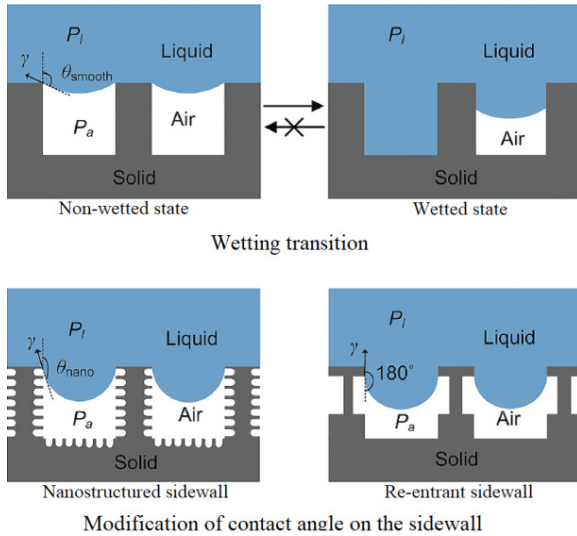


Fig. 1. Illustration of wetting transition on superhydrophobic surfaces.

As can be seen from (13) and (14), provided that Cassie-Baxter state remains stable, the maximum possible value of the surface portion r_{gas} of gas plots is inversely proportional to increment of values Δp and T , and, conversely, increases together with the value of contact angle. According to the results of [70], for $\theta = 120^\circ$ and for varying the pressure difference in gas and liquid Δp in the range 200÷300 Pa effective sliding length $L_{eff.}$ for an isotropic texture in the form of a microbars set with a period T in the range 50÷250 μm and with

surface portion $r_{gas} = 0.993$ of microchannel gas plots is equal to 94 μm ; and for anisotropic texture in the form of parallel grooves (parallel sulci) with a surface portion $r_{gas} = 0.976$ of gas plots the effective sliding length $L_{eff.}$ is equal to 185 μm (for the same range of Δp and T).

Now let us briefly describe the basis of the theoretical analysis of the effective sliding length: a theoretical analysis allows making the quantitative assessment of the influence of various factors on the effective sliding length, to explain the experimental results, find the optimal texture structure of a superhydrophobic surface with a stable Cassie-Baxter state. Consider a surface with an anisotropic texture in the form of parallel sulci and make the following assumptions: (1) there is a wide channel, $h \gg T$; (2) ideal liquid sliding conditions are fulfilled on the liquid-gas interphase surfaces; (3) liquid-gas interfaces are flat. Then the following relations hold [65], [66], [69]:

$$L_{eff.}^P = \frac{RT}{\pi} \ln \left(\sec \left(\frac{\pi r_{gas}}{2} \right) \right), \quad \forall r_{gas} > 0, \quad \forall T < 2\pi, \quad (15)$$

where $L_{eff.}^P$ is an effective sliding length for a longitudinal fluid flow along the furrow of the surface texture; R is size of the microsystem (R is radius (or average radius) if the sulcus is of cylindrical shape);

$$L_{eff.}^\perp : \frac{RT}{2\pi} \ln \left(\sec \left(\frac{\pi r_{gas}}{2} \right) \right) \text{ as } T \rightarrow 0, \quad r_{gas} \text{ fixed}, \quad (16)$$

where $L_{eff.}^\perp$ is an effective sliding length for a transverse fluid flow along the furrow of the surface texture;

$$L_{eff.}^\perp : \frac{r_{gas}}{4(1-r_{gas})} \text{ as } T \rightarrow +\infty, \quad r_{gas} \text{ fixed};$$

$$L_{eff.}^\perp : \frac{Rr_{gas}}{4} \text{ as } r_{gas} \rightarrow 0, \quad T \text{ fixed};$$

$$L_{eff.}^\perp : \frac{1}{4(1-r_{gas})} \text{ as } r_{gas} \rightarrow 1, \quad T \text{ fixed};$$

$$L_{eff.}^P : \frac{RT\pi r_{gas}^2}{4} \text{ as } r_{gas} \rightarrow 0;$$

$$L_{eff.}^P : \frac{RT}{\pi} \ln(1-r_{gas}) \text{ as } r_{gas} \rightarrow 1.$$

From (15) and (16) it follows that under certain conditions it can be said that the asymptotic values of $L_{eff.}^P$ and $L_{eff.}^\perp$ differ approximately twice: $L_{eff.}^P \approx 2L_{eff.}^\perp$ when $T \rightarrow 0$, and $r_{gas} \in (0, 2\pi)$ is fixed.

If the fluid flows at an arbitrary angle to the texture axis, then it is necessary to consider the effective sliding length as a tensor value $\hat{L}_{eff.} = \{L_{j,k}^{eff.}\}$, and to note that Navier sliding condition has the following form:

$$\left\langle \hat{g}_i \Big|_S \right\rangle = \sum_{j,k} L_{j,k}^{eff} \mathbf{r}_{j,k} \left\langle \frac{\partial \hat{g}_j}{\partial y_k} \Big|_S \right\rangle,$$

where $\left\langle \hat{g}_i \Big|_S \right\rangle$ is i -th component of the average sliding speed on a superhydrophobic surface with a texture in the form of parallel sulci; \mathbf{r}_k denotes k -th components of the outer normal \mathbf{n} to surface S .

In this case, instead of the effective sliding length, we can talk about the tensor of the effective sliding length, which can be represented as a symmetric positive definite matrix:

$$\hat{L}_{eff} = \begin{pmatrix} L_{11}^{eff} & L_{12}^{eff} \\ L_{21}^{eff} & L_{22}^{eff} \end{pmatrix} \geq L_0 > 0, \quad L_{12}^{eff} = L_{21}^{eff}.$$

It is obvious that if $L_{11}^{eff} \neq L_{22}^{eff}$, then this matrix will be guaranteed diagonalized:

$$\hat{L}_{eff} = \begin{pmatrix} L_{eff}^P & 0 \\ 0 & L_{eff}^\perp \end{pmatrix},$$

that is more convenient to use: knowing L_{eff}^P and L_{eff}^\perp (the essence of which are the eigenvalue of the tensor \hat{L}_{eff}), it is easy to calculate the effective sliding length tensor when flowing at an arbitrary angle to the texture axis.

III. CONCLUSION

In the present work, the dynamics of a liquid on unidirectional superhydrophobic surfaces in the Cassie-Baxter state is studied, when surface texture is filled with gas and, consequently, the liquid virtually is located on some kind of an air cushion. The model describing the dynamics of slow fluid flows in microchannels of a superhydrophobic surface is formulated. Besides, in the paper, an approach (one of many possible approaches) for finding the sought-for longitudinal local velocity of one of the components of the fluid velocity vector field in a thin film: the nonlinear equation and the idea of its analytical solution are proposed. Finally, in the work, the design formula for computing local-slip length profiles of liquid on the considered superhydrophobic surface is obtained.

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