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Morphological hysteresis of droplets wetting a series of triangular grooves

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Energetics and morphology of a microdroplet of varying volume settled on a surface covered with triangular grooves were investigated. The study was carried out by numerical computations performed with the Surface Evolver program. The obtained results showed that the droplet morphology underwent bifurcation into the filament-like one (F) and bulge one (B) when its volume had reached a certain value. This bifurcation point (BP) was affected by the number of grooves and the Young contact angle. At volumes smaller than that corresponding to BP, the droplet adopted the only stable morphology F, while the prediction of its morphology above the BP is a complex problem. As a result of the difference between BP and the volume of free energy equilibrium between F and B states, the droplet can assume various stable or metastable states. The actual state of the droplet was found to depend on the direction of volume changes and the possibility of overcoming a local energy barrier between the morphologies. As a result of fluctuation, the droplet can switch from one morphology to the other, hence the hysteresis of the dependence of linear droplet dimensions on its volume is observed. Morphology B was shown to be realized only if the canthotaxis condition was not exceeded otherwise, the droplet spread on the surface adjacent to the area with grooves. The appearance of the bifurcation effect depended on the number of grooves and the Young contact angle. The increase in these two parameters caused a decrease in differences between morphologies F and B, and finally the disappearance of bifurcation.

1. Introduction

The behavior of a droplet on inhomogeneities of solid surfaces has recently become a hot subject of interest mainly because changes in the droplet shape are of importance in designing micro- and nanofluidic systems of a wide range of applications, e.g. in biomedical devices, lab-on-a-chip, microreactors and sensors [1–3]. Although much knowledge has been gained, there is still much to be done in this area.

The solid inhomogeneities can be divided according to their character into energetic (chemical) and structural (topological) ones, and also according to their dimension into one- [4–12] and two-dimensional [13–18] ones. Of particular interest among them are the surfaces with one-dimensional structures (chemical and topological) [1]. The droplet settled on such surfaces wets them anisotropically because of the pinning of the three-phase triple line to linear inhomogeneities, undergoing spreading along the one-dimensional structures [19]. Pinning effect on the surface covered with a series of triangular grooves (see Fig. 1) takes place if the canthotaxis condition is met [20]

$$\theta_Y < \phi < \pi - \beta + \theta_Y \quad (1)$$

where θ_Y is the Young contact angle, ϕ is the pinning angle and β is the opening angle at the extreme edges of the grooves.

Gau et al. [21] have noted that the droplet deposited on a linear inhomogeneity with large length to with ratio can abruptly change its shape as a result of Rayleigh-Plateau instability. This discovery has started studies of this phenomenon. The hitherto literature reports have mainly concerned single inhomogeneities such as striped surface domain [5,6,21,22], triangular or rectangular groove [23–27], or the droplet behavior between two posts or parallel fibers [28–33]. Description of this phenomenon on more complex structures still remains a challenge.

The hydrophilic surface with a single triangular groove or a series of parallel triangular grooves seems to be a suitable object for the study of the effect of the surface geometry on the morphology of the droplet settled on it. The interesting point is that on the one

Abbreviations: SE, Surface Evolver; F, filament-like; B, bulge; EEP, equivalent energy point; BP, bifurcation point.

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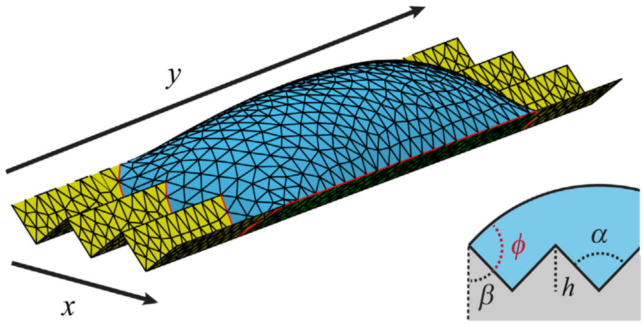

Fig. 1. The droplet equilibrated at pinning angle ϕ deposited on a series of triangular grooves of dihedral angle $\alpha = 90°$ and height $h = 0.1$ ($\tilde{V} = 400$, $\theta_Y = 75°$, $G = 3$). The opening angle β at the extreme edge is also shown.

hand a pattern of linear inhomogeneities on a surface increases the surface wettability along the axis parallel to the grooves (effective wettability angle is smaller than the Young angle as a result of the Concus-Finn effect [3]) but on the other hand, it decreases the wettability along the axis perpendicular to the grooves as a result of the droplet pinning to the groove edge. The droplet settled on such a surface must then assume anisotropic morphology and the change in parameters describing the system droplet – surface can lead to discontinuous changes in the droplet shape in a way similar to that described in [6].

The authors of [4] have proved that the shape of the droplet settled on a single triangular groove ($\alpha = 90°$, $\theta_Y = 75°$) depends in a complex way on its volume. At first (1) the droplet of relatively small volume assumes a shape of a part of sphere cut off by walls of the groove, then (2) with increasing volume the groove is filled and the droplet shape is deformed because of pinning to the external edges of the groove, the droplet starts to expand along the groove and its free surface (liquid-gas) assumes a filament-like (F) morphology until a certain critical volume V_C, (3) further increase in the droplet volume causes a discontinuous change in the droplet shape, it gets shortened and assumes a bulge (B) morphology, and with further increase in volume only the size of the cap increases. The discontinuous change in the droplet morphology has been found to resemble a phase transition because of a discontinuous change in the energetic parameters of the system.

A similar behavior has been observed for the droplets settled on more complex linear surface structures. In [34] an attempt was made to characterize the behavior of a droplet wetting a series of triangular grooves of dihedral angle $\alpha = 90°$, for different contact angles θ_Y. The increase in the droplet volume above the critical value V_C was shown to cause a change in its shape from F to B or to lead to irreversible wetting of the next groove if canthotaxis condition is met (Inequality 1). Moreover, with increasing number of grooves wetted by the droplet and with decreasing contact angles θ_Y, the effect of the discontinuous change in the droplet morphology disappears.

The method applied in [4,34] for investigation of the droplet morphology and energy relations involved minimization of the system energy in which the initial shape of the droplet was much different from the optimized shape. Analysis of the morphologies obtained indicated that their transformations are triggered by a stimulus which was the Laplace pressure difference between different morphologies. The difference between the critical value V_C and the volume at which the energies corresponding to the two morphologies are the same indicated that in the vicinity of the morphological transitions some metastable states can appear, similar to those observed by Ferraro et al. [5] for the droplet settled on rectangular posts and by Brinkmann and Lipowsky [6] for the droplet settled on a striped surface.

In the present study, an attempt was made to verify the hypothesis of occurrence of metastable states of a droplet settled on a surface with a series of triangular grooves. The aim of the study is determination of the behavior of the droplet in the vicinity of morphological transition, the ranges of volume in which stable and metastable droplet morphologies occur, their energetic characterization and the character (continuous or discontinuous) of the morphological transitions between filaments and bulges. The study was performed by means of numerical computations with the finite element method, using the public domain software Surface Evolver (SE) [35], by minimization of surface and interface energy of the droplet deposited on a series of triangular grooves.

The paper is organized as follows. First, we introduce the detailed assumptions needed to construct a realistic model and the applied methods of collection of system parameters (Section 2). Then we present an example of geometrical behavior of the droplet of varying volume consisting of the bifurcation of the droplet morphology trajectory into two branches at a certain volume (Section 3.1). In Section 3.2, the energetics and the Laplace pressure as stimuli of the droplet morphology transition are discussed in categories of the classification of states into stable or metastable, the possibility of continuous and discontinuous changes in the droplet shape and the hysteresis of the morphology trajectory. The analysis of the dependencies of the bifurcation volume and the volume at which the energies of both morphologies take the same value on some system parameters (the number of grooves, the contact angle) is presented is Section 3.3. Section 3.4 discusses model limitations specified by relations between boundary conditions of the series of grooves (namely the opening angle at extreme edges) and pinning angles. Finally, the conclusions drawn from the work are presented in Section 4.

2. Numerical computation method

In numerical computations performed with the SE, the free surface of the liquid droplet and grooves faces was represented by a mesh of small triangles spanning the lattice nodes. The system studied was a droplet of adjustable volume initially settled on the arbitrarily chosen number of adjacent grooves G and pinned to the assumed boundary edges along the y direction (see Fig. 1). The solid surface was represented by adjacent parallel grooves of a height h falling into the capillary range and dihedral angle $\alpha = 90°$ identical in all series of computations and the Young angles of values from the range 60–90° with a step of 2.5°. The h value was used as a normalizing constant of geometrical parameters of the system. The length of the grooves was unlimited. The study was performed for G ranging from 2 to 8. The strategy of model evolution applied in this study did not permit getting reliable results for $G = 1$ because of their poor convergence following from elongated shape of the droplet. Nevertheless, the results presented in [34] imply that a similar behavior of the droplet should be expected in the whole range of $G = 1$–8.

A single sequence of computation consisted in a series of the energy minimizations for different reduced dimensionless droplet volumes $\tilde{V}$ ($\tilde{V} = V/h^3$), changed step by step by the value $\Delta\tilde{V} = 20$. The range of $\tilde{V}$ studied depended on the initial parameters on the system and usually, it was 20–25,000. An exemplary morphology of a droplet settled on a surface with grooves, together with the notation of geometric quantities considered in the text is shown in Fig. 1. The opening angle at the extreme edge, β, defining the geometry of the surface outside the analyzed set of grooves is also depicted in Fig. 1. The angle β takes values from 0 to $(\pi + \alpha)/2$ for a flat surface.

The initial volumes of the droplets for each numerical computation were chosen to ensure a stable initial morphology (which