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Dynamics of nanodroplets on wettability gradient surfaces

A Moosavi and A Mohammadi

School of Mechanical Engineering, Sharif University of Technology, Azadi Avenue,
PO Box 11365-9567 Tehran, Iran

E-mail: moosavi@sharif.edu

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Abstract

A lubrication model is used to study the dynamics of nanoscale droplets on wettability gradient surfaces. The effects of the gradient size, size of the nanodroplets and the slip on the dynamics have been studied. Our results indicate that the position of the center of mass of the droplets can be well described in terms of a third-order polynomial function of the time of the motion for all the cases considered. By increasing the size of the droplets the dynamics increases. It is also shown that the slip can considerably enhance the dynamics. The results have been compared with the results obtained using theoretical models and molecular dynamics simulations.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

A droplet residing on the boundary of two adjacent parts of a substrate with different wettabilities will move to the more wettable part. This is a well-known phenomenon [1–3] that has been extensively studied because of its importance in a variety of processes and applications ranging from biological systems [4, 5] and ink jet printing to the commercial lab-on-a-chip [6, 7]. The difference between the equilibrium contact angles of the droplet on the two parts gives rise to an interfacial driving force [2, 3] which displaces the droplet. The ensuing motion is confronted by viscous forces which balance the driving force and dissipate the energy [3]. Such a motion is not continuous as, by moving the droplet to the more wettable surface, the driving force diminishes and consequently the droplet stops. A non-stop motion can be achieved by providing a continuous wettability gradient [2, 3, 8]. There exist various experimental techniques which allow one to construct a chemically patterned surface including surface coating [9] and irradiating with a beam [10].

Despite much research performed to understand the dynamics of the droplets on wettability gradient surfaces [1–3, 8, 11–14] only recently have investigations at the nanoscale been given any attention [15]. It is obvious that understanding basic fluidic issues occurring at those scales is a prerequisite for optimal design of nanofluidic devices. Very recent theoretical studies on nanodroplets near and on top of a chemical step have revealed novel features for these systems.

Nanodroplets at some distances from the boundary of the two parts of a chemical heterogeneity can exhibit dynamics [16]. A size-dependent motion of nanodroplets on top of a chemical step has also been reported [17]. In [15] the dynamics of the nanodroplets on wetting gradient surfaces has been studied using molecular dynamics (MD) simulations. It has been found that the position of the droplets can be represented by a power law function of time of the motion. The maximum and minimum contact angles considered in [15] are roughly 90° and 20°, respectively, and the average gradient size is around 3.2° nm⁻¹. It is not immediately clear what would be the situation if different maximum and minimum contact angles (for example, small contact angles) were considered, namely whether the positions of the droplets can still be represented by a power law function of time or not. Also, an investigation is required to study the effect of the gradient size, the slip and the type of material (solid–liquid–gas) on the dynamics.

In the present study we focus on the dynamics of nanodroplets which span chemical gradient heterogeneities in the limit of small contact angles. As illustrated in figure 1 we consider a partially wetting, nonvolatile and incompressible liquid film composed of a nanodroplet on top of a precursor wetting layer on a impermeable solid substrate with a wettability gradient and study the dynamics of the nanodroplets. The presence of the precursor wetting layer is justified by the entropy gained by the system [18]. The system is supposed to be translationally invariant along the *z* direction. For numerical reasons, we restrict our

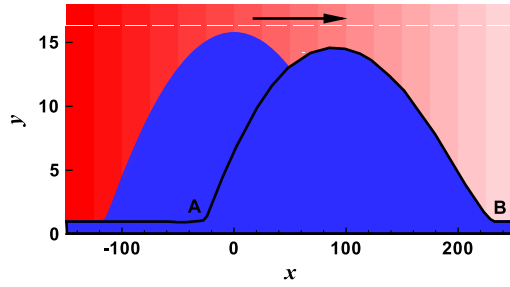


Figure 1. Motion of a nanodroplet with the height from the wetting film $a = 15$ on a solid substrate towards the more wettable parts. The total length of the system is equal to 400 ($-150 \leq x \leq 250$) and the droplet is initially positioned at $x = 0$. The substrate is designed such that the equilibrium contact angle decreases linearly from left to right as $\theta_{eq}(x) = (-0.04x + 15)^\circ$. The lengths are scaled by b (see the main text for definitions).

analysis to two-dimensional (2D) droplets, corresponding to three-dimensional (3D) liquid ridges (or rivulets) which are translationally invariant in the direction parallel to the step. Such liquid ridges have been experimentally studied, for example, in [19]. We first study the dynamics of the nanodroplets as a function of time for no-slip cases to check whether the results are in agreement with theoretical and MD results. The effect of the gradient size and the size of the droplets will be studied in this part. Then we develop the results to the cases with slip. We also extend the previous theoretical models to include the slip effect and compare the lubrication results with the theoretical outcomes.

2. Governing equations and the boundary conditions

At the small Reynolds numbers limit, where viscous forces are much larger than inertial forces the behavior of a Newtonian and incompressible liquid can be simply described by the following equations:

$$\nabla \cdot \mathbf{U} = 0 \quad (1)$$

$$\mu \nabla^2 \mathbf{U} = \nabla P \quad (2)$$

where $\mathbf{U}(u, v)$ represents the velocity vector and μ denotes the dynamic viscosity of the liquid. Considering a unidirectional flow [20] and assuming slip at the substrate and no shear at the fluid–gas interface h , i.e.

$$y = 0 \rightarrow u = \beta \frac{\partial u}{\partial y} \quad (3)$$

$$y = h \rightarrow \frac{\partial u}{\partial y} = 0 \quad (4)$$

where β stands for the slip length, one obtains

$$u = -\frac{\partial P}{\partial x} \frac{1}{2\mu} [2h(\beta + y) - y^2] \quad (5)$$

$$P = -\sigma \kappa - \Pi \quad (6)$$

where σ is the surface tension and κ represents the curvature:

$$\kappa = \frac{\frac{\partial^2 h}{\partial x^2}}{[1 + (\frac{\partial h}{\partial x})^2]^{2/3}} \quad (7)$$

which can be approximated for small contact angles by $\kappa \approx \partial^2 h / \partial x^2 = \Delta h$, where Δ is the Laplace operator. (Note that curvature is considered negative if the center of curvature is directed towards the droplet.) Π expresses the disjoining pressure (DJP) $\Pi = -\partial \Phi / \partial y$, where the effective interface potential Φ is the cost of free energy to maintain a homogeneous wetting film of prescribed thickness y [16, 17]. For the flow rate one has

$$Q(x, t) = \int_0^{h(x, t)} u(x, t) dy = -\left(\frac{\partial P}{\partial x}\right) \frac{1}{3\mu} [3\beta h^2 + h^3] \quad (8)$$

with t being time. Considering that $\partial h / \partial t = -\partial Q / \partial x$ one can finally obtain

$$\frac{\partial h}{\partial t} = -\nabla[m(h)\nabla(\sigma\kappa + \Pi)] \quad (9)$$

where the mobility factor $m(h)$ is given by

$$m(h) = \frac{1}{3\mu} (h^3 + 3\beta h^2). \quad (10)$$

For the no-slip case ($\beta = 0$) the mobility becomes $m(h) = h^3 / (3\mu)$ and for the slip-dominated case [21, 22], namely very large values of β , the mobility will be $m(h) = \beta h^2 / (\mu)$. The problem may be converted into non-dimensional form by scaling lengths with b , which is the equilibrium wetting film thickness on a homogeneous flat substrate, velocity with $\tilde{A}b / \mu$, where $\tilde{A}$ is an intermolecular parameter derived from the material parameters representing pair potentials (see [16, 17]), and pressure with σ / b . As a result the governing equations can be reformulated as

$$\frac{\partial h^*}{\partial t^*} = -\nabla[m^*(h^*)\nabla(\kappa^* + \Pi^*)] \quad (11)$$

where the mobility factor $m(h)$ is given by

$$m^*(h^*) = \frac{1}{3\tilde{C}} (h^{*3} + 3\beta h^{*2}) \quad (12)$$

with $\tilde{C} = \tilde{A}b / \sigma$. In this study, $\tilde{C}$ has been considered to be 1. Also, in order to simplify the presentation in the following, we drop the asterisks. For the DJP we consider a profile of the type suggested in [16, 17]. In dimensionless form the DJP may be represented as

$$\Pi(x, y) = C(x) \left(\frac{1}{y^9} \mp \frac{1}{y^3} + \frac{B(x)}{y^4} \right) \quad (13)$$

where C and B determine the strength and shape of the DJP, respectively. The sign of the second term can be negative or positive. We refer to these two cases as the minus (−) and the plus (+) cases. The profiles of the disjoining pressure are shown in figure 2. The admissible value ranges of C and B which provide partial wetting are also given in figure 3.

3. Force calculation

Before performing any simulation, the force calculation [16, 17] may provide a useful insight into the dynamics

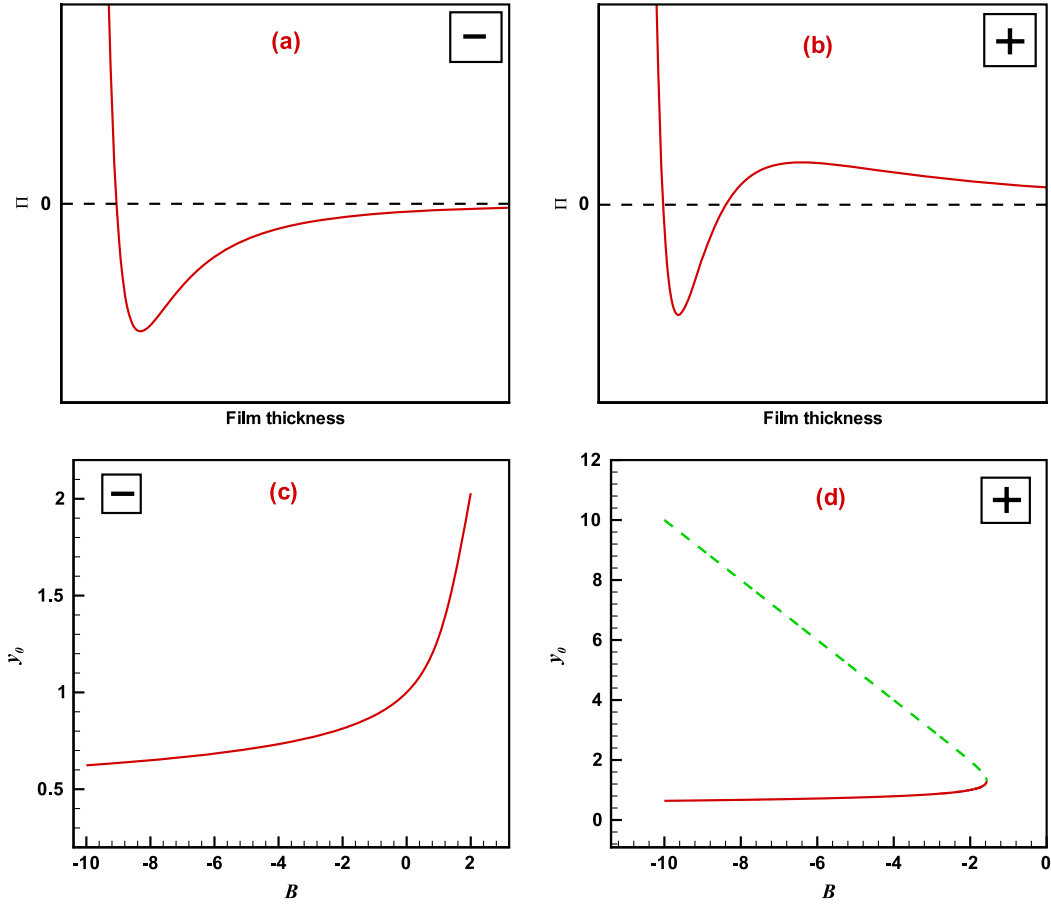


Figure 2. The typical profile of the DJP for the minus (a) and the plus (b) case and the corresponding zeros for cases (c) and (d). As is evident from part (d) there are two zeros (shown by a solid red line and green dashed line) for the plus case for a given value of B .

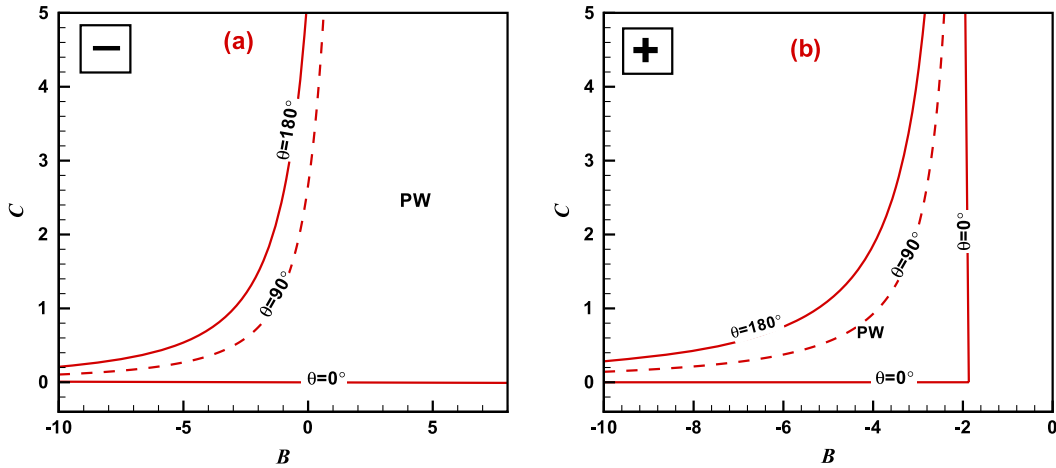


Figure 3. The value ranges of B and C for which the system exhibits a partial wetting (PW) situation, i.e. $0^\circ < \theta < 180^\circ$ for the minus (a) and the plus (b) case.

of the system. This can considerably decrease the number of test calculations for thoroughly studying the dynamics of the system. Such a method consists of placing the droplet with an equilibrium contact angle equal to that of the droplet center position at different positions along the substrate and calculating the lateral DJP-induced force on the droplet. The

force is calculated from the following relation:

$$f = \int_{\partial S} \Pi(x, y) \mathbf{n} ds \quad (14)$$

where ∂S is the droplet liquid–gas interface and $\mathbf{n}$ represents the outward-pointing unit normal vector. By assuming the

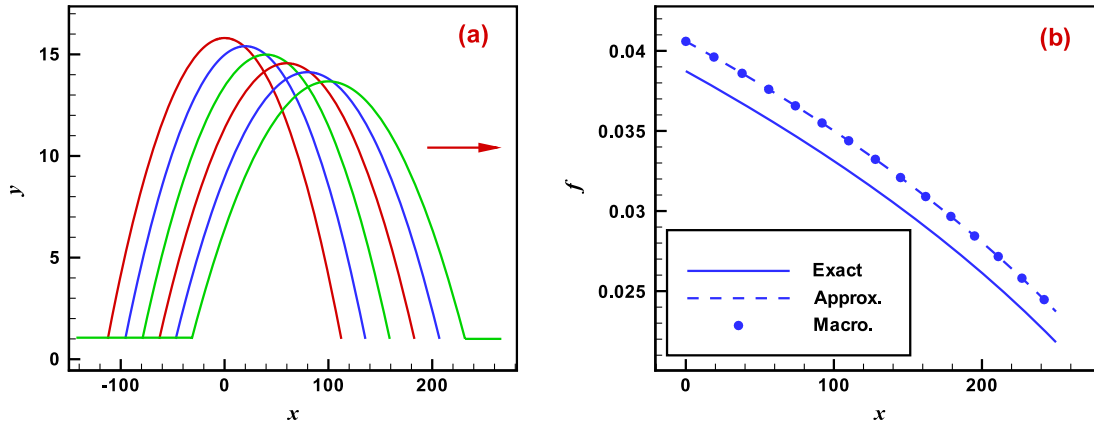


Figure 4. (a) The considered profile for the droplet for calculating the DJP-induced force on the droplets along the substrate. (b) The DJP-induced force on a droplet with $a = 15$ calculated by the exact method (equation (14)), the approximate method (equation (15)) and the macroscopic model (equation (16)). The contact angle changes linearly as $\theta_{eq}(x) = (-0.04x + 15)^\circ$ and the calculations have been done for the minus case with $m = 0$. f is measured in units of σ .

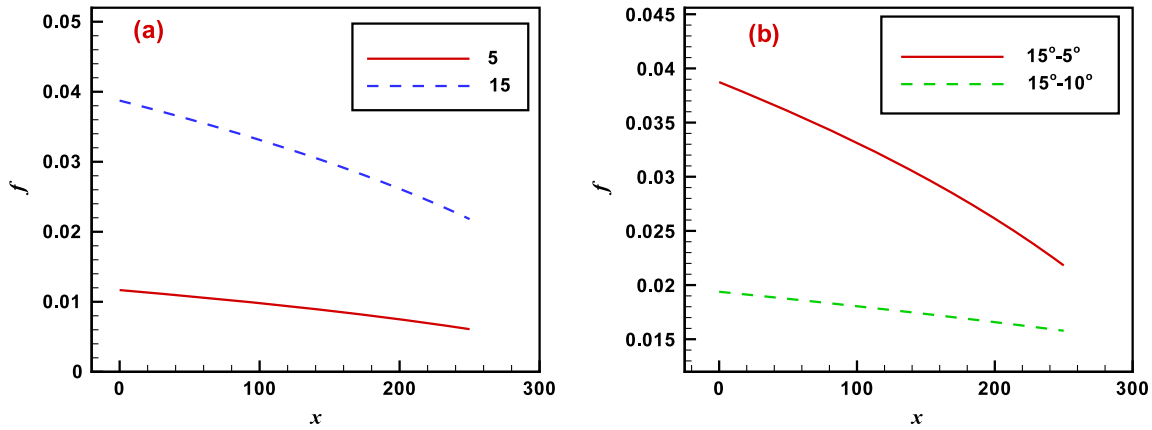


Figure 5. (a) The effect of the droplet size a on the calculated force. (b) The effect of the wettability gradient size on the force on a droplet with $a = 15$. The contact angle changes linearly as $\theta_{eq}(x) = (-0.04x + 15)^\circ$ and the calculations have been done for the minus case with $m = 0$. f is measured in units of σ .

droplet profile to be a rectangle the above force calculation can be approximated as

$$f \approx \int_{h_0}^{a+h_0} \Pi(x, y) dy|_B - \int_{h_0}^{a+h_0} \Pi(x, y) dy|_A \quad (15)$$

where h_0 represents the thickness of the wetting film, A and B are the receding and advancing contact positions of the droplet and the wetting film, respectively, (see figure 1) and a is the height of the droplet from the wetting film. Also, based on the macroscopic models the force on the droplet is given as

$$f = \cos \theta_{B_{eq}} - \cos \theta_{A_{eq}}. \quad (16)$$

Figure 4 compares the calculated DJP forces and the forces determined by the approximate and macroscopic models for droplets with height $a = 15$ on a substrate with wettability gradient of the form $\theta_{eq}(x) = (-0.04x + 15)^\circ$. The total length of the system is equal to 400 ($-150 \leq x \leq 250$). For all the cases the forces decrease along the substrate. The effect of the droplet size and the size of the gradient on the calculated

force are shown in figure 5. By decreasing the droplet size the height and base width of the droplet decrease and, as a result, the calculated force decreases. The effect of the DJP profile on the calculated force is shown in figure 6. Even though the droplets have the same size the lateral forces on the droplets are not equal. This may create different dynamics, as will be verified by numerical simulations.

4. Numerical algorithm

A standard central difference was used for the space derivatives and the time derivative was approximated by a forward difference. The equations were solved using a fourth-order Runge-Kutta method [23]. The size of the time step (Δt) and the number of points were checked to ensure that results are not dependent on the time step size and number of node points. A total number of 200–300 points were considered in the simulations and Δt was 5×10^{-5} to 10^{-3} based on the cases chosen.

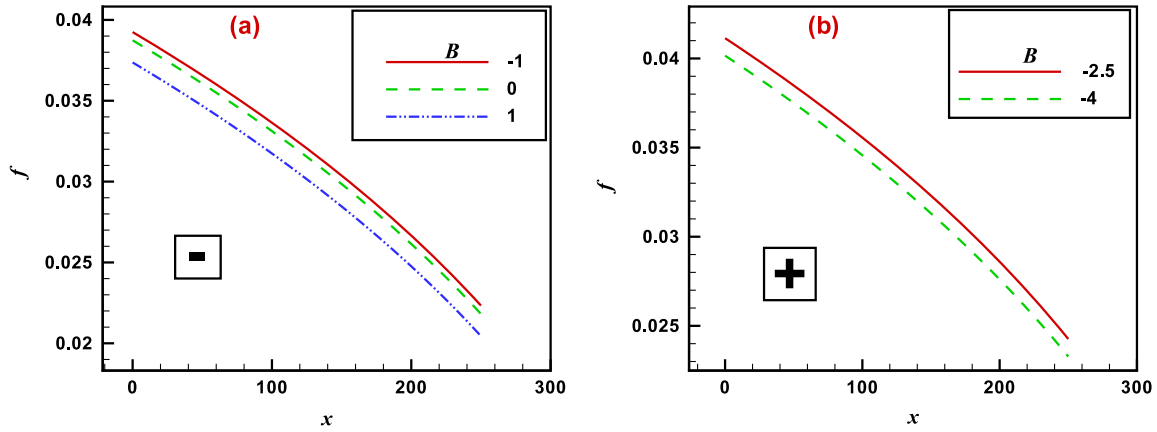


Figure 6. The effect of B on the lateral DJP force exerted on a droplet with $a = 15$ for the minus (a) and the plus (b) case.

For the initial droplet profile, a parabola [24, 25] was considered. However, since a simple parabola has a sharp corner at the base and this may introduce some difficulty in the numerical procedure for initial time steps, the profile at the contact line, where the core of the droplet and the wetting layer are matched slightly, was smoothed. The smoothed profile is described by

$$h(x) = h_0 + a \left[1 - \left(\frac{x - x_b}{a / \tan(\theta_{\text{eq}}/2)} \right)^2 \right]^{(1-x-x_0)^n + 1} \quad (17)$$

where a gives the centerline height of the droplet, x_0 represents the x component of the base center position and θ_{eq} is the equilibrium contact angle at x_0 . n is considered to be 10 in this study but the results of the study are independent of this value as the center of the droplets was placed at $x = 0$ and the droplets were allowed to relax and reach their equilibrium profile. In this step, the profile of the DJP is that of a simple homogeneous substrate. Any asymmetry may induce a lateral motion; the geometry and the arrangement of the nodes must be symmetric with respect to the z axis. After the relaxation step the geometry of the system was extended in the direction of motion and the DJP of the chemical gradient was applied such that a linear change in the equilibrium contact angle over the substrate as $\theta_{\text{eq}}(x) = (-0.04x + 15)^\circ$ was provided. This can be achieved in different ways using equation (13), namely either by changing the parameter C and considering B constant, or changing the parameter B and considering C constant, or finally changing both C and B . We only consider the cases with one parameter as a constant. Between these two cases the first one, i.e. B constant, is much simpler as the film thickness h_0 does not depend on C and its value can be calculated from equation (13) by considering $\Pi(x, y) = 0$, i.e.

$$\frac{1}{y_0^9} \mp \frac{1}{y_0^3} + \frac{B(x)}{y_0^4} = 0. \quad (18)$$

The results are given in figure 2. The relaxation step in this case can be simply modeled by considering C as

$$C = \frac{\cos \theta_{\text{eq}}(0) - 1}{\int_{h_0}^{\infty} \Pi(0, y) dy}. \quad (19)$$

However, in the second case the film thickness changes with B (see figure 2) and to find its value one should solve the following equation for the minus and the plus case:

$$3y_0^3(x) \frac{\cos \theta_{\text{eq}}(x) - 1}{C} \pm \frac{y_0(x)}{2} + \frac{5}{8y_0^5(x)} = 0. \quad (20)$$

The results are depicted in figure 7(a). From the value of y_0 and the contact angle one can calculate B from the following equation for the minus and the plus case:

$$B(x) = y_0^3(x) \left[\frac{\cos \theta_{\text{eq}}(x) - 1}{C} - \frac{1}{8y_0^8(x)} \pm \frac{1}{2y_0^2(x)} \right]. \quad (21)$$

The values of B are also given in figure 7(b). To provide the equilibrium shape before starting the simulation the value of C was calculated for any point such that the contact angle remains the same for all the points over the substrate. With known values of B and y_0 and the contact angle the strength factor C is calculated for the minus and the plus case using the following equation:

$$C(x) = \frac{\cos \theta_{\text{eq}}(x) - 1}{\frac{1}{8y_0(x)^8} \mp \frac{1}{2y_0(x)^2} + \frac{B(x)}{3y_0(x)^3}}. \quad (22)$$

The calculated values of C are shown in figure 8.

To study the dynamics of the droplets the position of the center of mass of the droplets ($\bar{x}_d, \bar{y}_d$) was calculated during the simulation as

$$\bar{x}_d(t) = \frac{\int_{\Omega_d} x(t) dV}{\int_{\Omega_d} dV} \quad \bar{y}_d(t) = \frac{\int_{\Omega_d} y(t) dV}{\int_{\Omega_d} dV}. \quad (23)$$

5. Results

In order to check the accuracy and reliability of the method, the results were compared with those of the accurate biharmonic boundary integral method (BBIM) [16, 17]. Figure 9 compares the results of these methods for a droplet with $a = 15$ on a surface with a gradient of the form $\theta_{\text{eq}}(x) = (-0.04x + 15)^\circ$. As can be seen the results of the lubrication model are in very close agreement with those of BBIM.

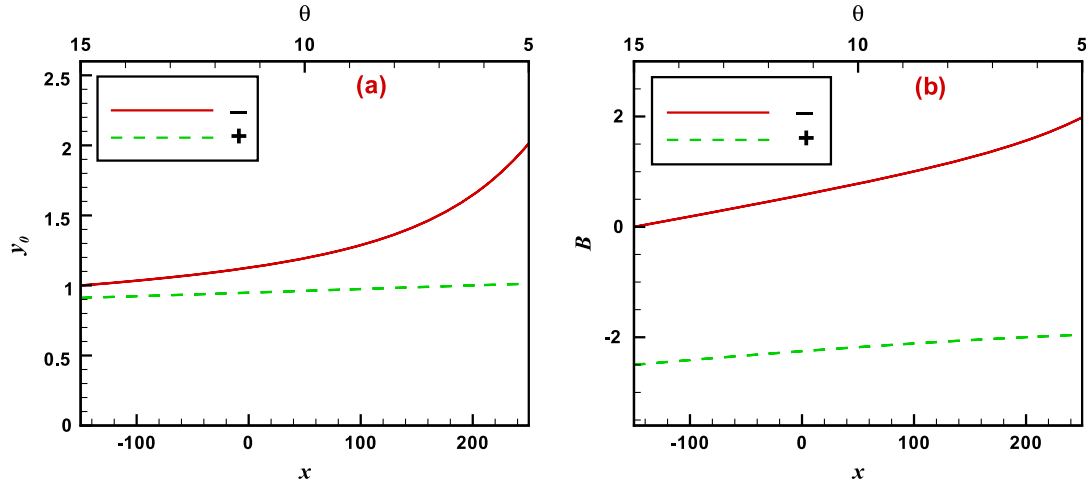


Figure 7. The thickness of the wetting layer along the substrate (a) and the values of B for the case with only C constant for the minus (–) and the plus (+) case. The equilibrium contact angle changes linearly as $\theta_{eq}(x) = (-0.04x + 15)^\circ$.

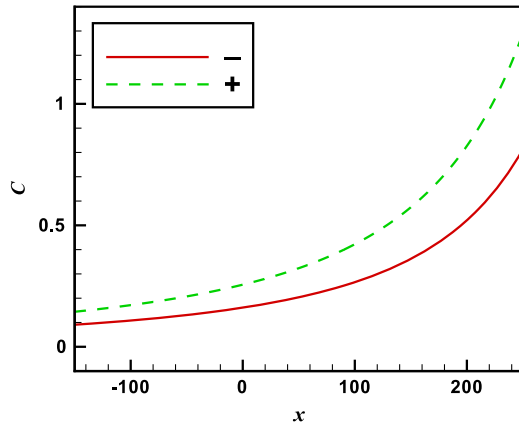


Figure 8. The values of C such that with B values the equilibrium contact angle would be equal to 15° for the minus (–) and the plus (+) case.

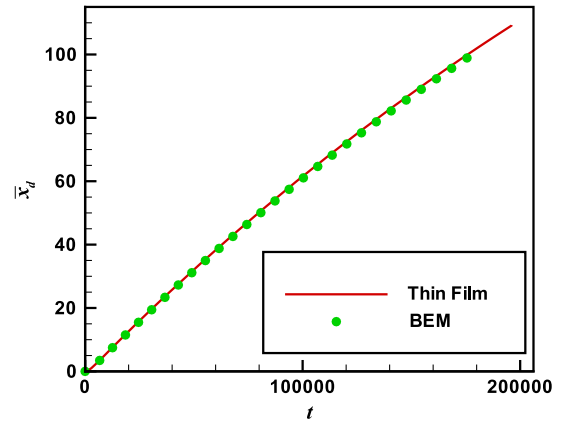


Figure 9. A comparison between the results of the biharmonic boundary integral method (BEM) [16, 17] and the lubrication model. The droplet size is $a = 15$ and the simulation has been done for the minus case ($m = 0$). The contact angle changes linearly as $\theta_{eq}(x) = (-0.04x + 15)^\circ$.

Figure 10 shows the results of the simulation for various size droplets on a substrate with a gradient of type $\theta_{eq}(x) = (-0.04x + 15)^\circ$ for the minus case ($m = 0$). The lateral position of the droplets during the motion $\bar{x}_d(t)$ is also depicted in figure 11. Increasing the droplet size strengthens the driving force (see figure 5) and this enhances the dynamics. For large contact angles, i.e. beyond the lubrication approximation, MD simulation [15] has shown that the lateral motion of the droplets can be represented in terms of a power law of time of the motion. However, the results of this study suggest that for small contact angles a third-order polynomial can better describe the lateral motion. This is in agreement with the results of Brochard [3] based on a theoretical model for small contact angles. Although the results can be roughly approximated by a power law, the exponent is $n \approx 0.9$ which is obviously different from $n \approx 0.45$ obtained using MD simulation [15]. For different size droplets the coefficients of the polynomial are given in table 1.

The effect of slip on the dynamics is depicted in figure 12. The slip can substantially enhance the dynamics. For different

Table 1. The coefficients of the third-order polynomial $\alpha_1 t + \alpha_2 t^2 + \alpha_3 t^3$ used to fit the data $\bar{x}_d(t)$ for different size droplets and values of slip.

a	β	α_1	α_2	α_3
5	0	4.0795×10^{-4}	-2.2057×10^{-10}	5.315×10^{-17}
10	0	5.4246×10^{-4}	-3.4213×10^{-10}	-3.1628×10^{-17}
15	0	6.0795×10^{-4}	2.2847×10^{-10}	-2.4670×10^{-15}
15	0.5	8.5203×10^{-4}	-1.1603×10^{-9}	8.1484×10^{-16}
15	1.0	9.8603×10^{-4}	-1.5353×10^{-9}	1.2873×10^{-15}
15	2.5	1.3547×10^{-3}	-2.7848×10^{-9}	3.1497×10^{-15}
15	5.0	1.9352×10^{-3}	-5.4151×10^{-9}	8.0700×10^{-15}
15	10	3.005×10^{-3}	-1.2857×10^{-8}	2.6343×10^{-14}
15	100	2.31×10^{-2}	-6.65×10^{-7}	7.6475×10^{-12}
15	1000	2.2310×10^{-1}	-6.0785×10^{-5}	5.9632×10^{-9}

values of β the coefficients of the polynomial are also given in table 1.

The effect of the wettability gradient size on the dynamics is shown in figure 13 for a droplet with $a = 15$ for the minus

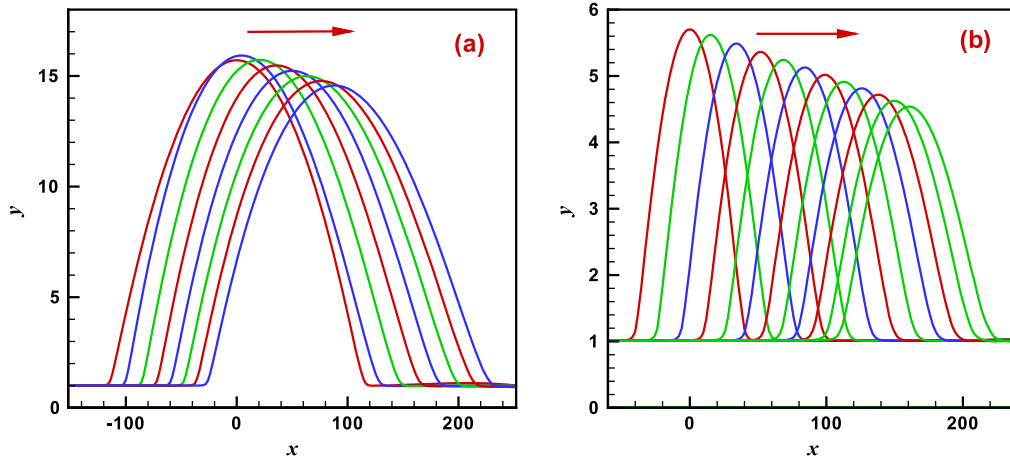


Figure 10. Time evolution of the profile of the droplets during the motion towards the more wettable parts for a droplet with $a = 15$ (a) and $a = 5$ (b). The gradient considered is equal to $\theta_{eq}(x) = (-0.04x + 15)^\circ$ and the simulations have been performed for the minus case ($m = 0$).

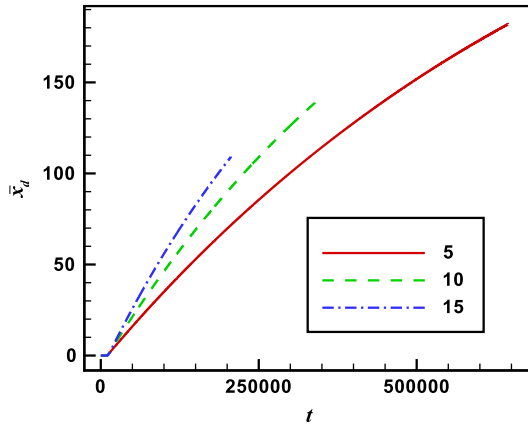


Figure 11. The lateral position of the center of mass for various size droplets $\bar{x}_d(t)$ as a function of time. The wettability gradient is equal to $\theta_{eq}(x) = (-0.04x + 15)^\circ$ and the simulations have been performed for the minus case ($m = 0$).

case. Decreasing the gradient size reduces the DJP-induced force (see figure 5) and this slows down the motion of the droplets.

The effect of the profile of the disjoining pressure is shown in figure 14 for a droplet with $a = 15$ for two different types of the DJP, namely $m = 0$ for the minus case and $m = -2.5$ for the plus case. For the plus case the droplet exhibits stronger dynamics. The difference increases for a smaller droplet $a = 5$. This can be explained by inspecting the calculated force on the droplets shown in figure 6. The lateral induced DJP force for the plus case is larger in spite of the fact that the equilibrium contact angles are equal. The tail of the DJP profile is positive for the plus case while for the minus case this part is negative. This means that

$$\int_{h_0^+}^{\infty} [-\Pi^+(x, y)] dy = \int_{h_0^-}^{\infty} [-\Pi^-(x, y)] dy$$

$$\Rightarrow \int_{h_0^+}^{a+h_0^+} [-\Pi^+(x, y)] dy > \int_{h_0^-}^{a+h_0^-} [-\Pi^-(x, y)] dy. \quad (24)$$

Figure 15(a) compares the lateral motion of a droplet with $a = 15$ for two cases of constant B and varying B . The gradients are equal to $\theta_{eq}(x) = (-0.04x + 15)^\circ$ for both cases but, similar to the previous case, the velocities are not equal. The reason can again be explained in terms of the force exerted on the droplets as depicted in figure 15(b).

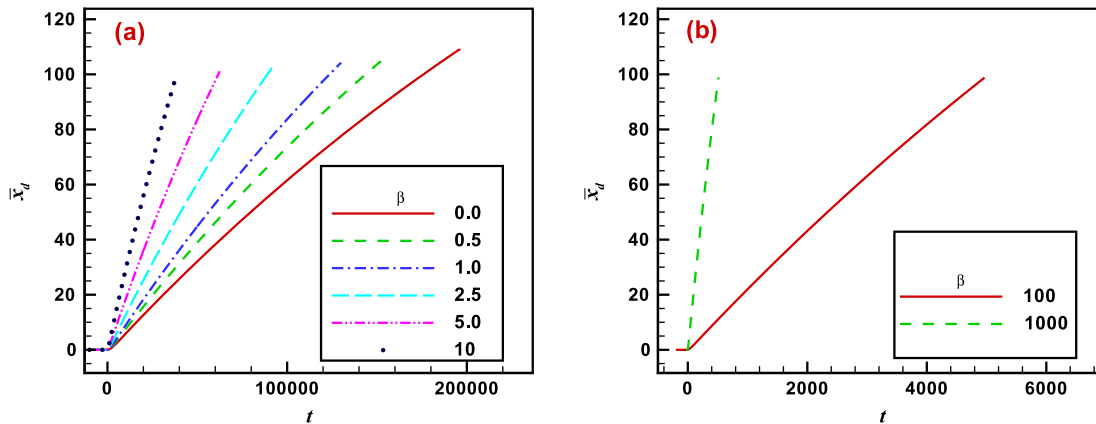


Figure 12. ((a) and (b)) The effect of slip on the lateral position of a droplet with $a = 15$ as a function of time. By increasing the slip coefficient the dynamics is enhanced. The gradient considered is equal to $\theta_{eq}(x) = (-0.04x + 15)^\circ$.

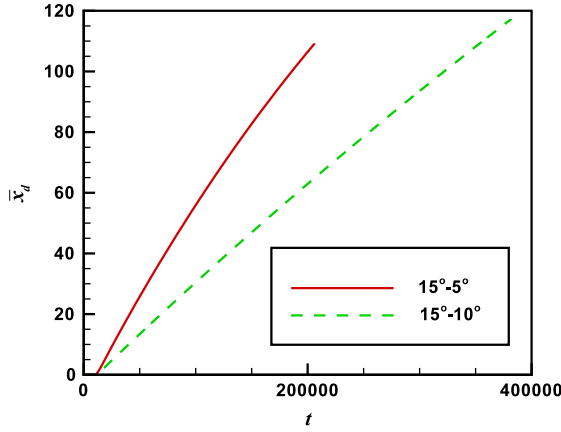


Figure 13. The effect of the wettability gradient size on the dynamics of the nanodroplets. The solid line corresponds to a wettability gradient of the form $\theta_{eq}(x) = (-0.04x + 15)^\circ$ and the dashed line corresponds to a wettability gradient of the form $\theta_{eq}(x) = (-0.02x + 15)^\circ$.

6. The energy calculation

The total free energy of the system, E_t , is determined by summing the work done on the system via intermolecular (E_Π) and surface tension (E_σ) forces which in dimensionless form can be give as [25]

$$E_t = E_\Pi + E_\sigma = \int \left[U(x, h) + \sqrt{1 + \left(\frac{dh}{dx} \right)^2} \right] dx \quad (25)$$

with $\Pi = -dU/dy$. Figure 16 shows the profiles of the energy for a droplet with $a = 15$ for the minus case ($m = 0$) during the relaxation step and the motion towards the more wettable part. In the relaxation step, E_σ decreases because of flattening the droplet and consequent reduction in the surface area. In contrast, the surface of the droplet experiences larger disjoining pressure and, as a result, E_Π increases. The reduction in E_σ is larger than the increase in E_Π and, as a result, the total energy of the system reduces. During the lateral motion the droplet experiences a secondary relaxation and, similar to the first step,

E_σ decreases. However, since the droplet moves to the parts with weaker DJP, in contrast to the first step, E_Π decreases. As a result the total energy of the system decreases.

7. Comparison with macroscopic analysis

Extending a method proposed in [3] (see the appendix) it can be shown that the velocity of the slipping droplets on wettability gradient surfaces can be given by

$$V = \frac{\ell \theta_{Oeq}^2 (1 + \beta)}{3\mu \ln(\ell/x_{min})} \frac{d\theta_{eq}}{dx} \quad (26)$$

where ℓ represents one-half the base length of the droplet and x_{min} is a molecular size. The velocity can be scaled by $\tilde{A}b/\mu$ and in dimensionless form one has

$$V = \frac{\ell \theta_{Oeq}^2 (1 + \beta)}{3C \ln(x_O/x_{min})} \frac{d\theta_{eq}}{dx}. \quad (27)$$

Figure 17 compares the velocity of the nanodroplets for the minus case ($m = 0$) with those predicted by macroscopic theory. ℓ has been chosen to be 250 and 120 for droplets with $a = 15$ and $a = 5$, respectively. Although the rate of the velocity change is approximately the same, the macroscopic theory underestimates the velocity of the droplets. Figure 18 shows the advancing and the receding contact line positions of the droplets along the substrate. Contrasting macroscopic theory, the profile of the droplet is not symmetric and the advancing contact line moves faster than the receding one.

8. Conclusion

The dynamics of nanodroplets on wetting gradient surfaces was studied within the lubrication approximation, namely for small contact angles. Parameters such as the droplet size, gradient size and slip effect were investigated. It was found that for all the wetting gradient surfaces for the no-slip cases the position of the center of mass of the droplets is a third-order polynomial function of time of the motion. The coefficients for various cases were calculated and reported. These results

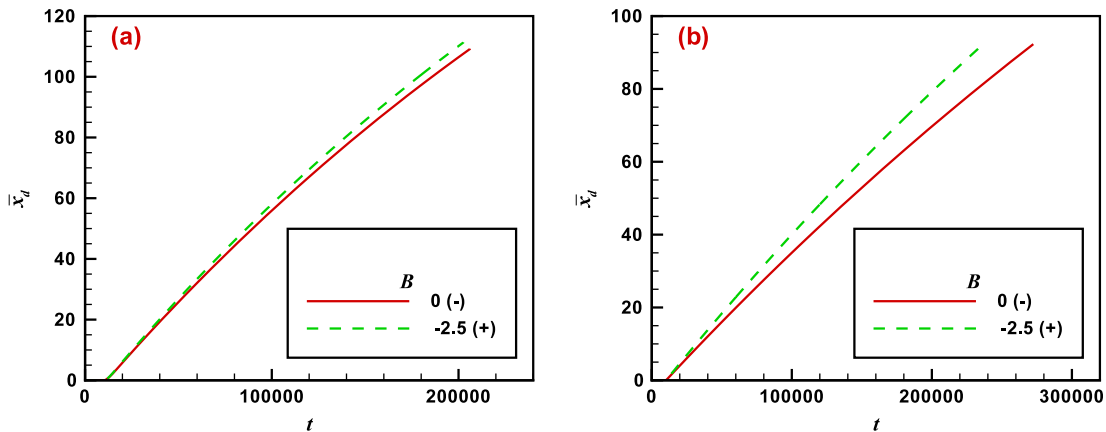


Figure 14. The effect of the profile of the DJP (the minus and the plus case) on the dynamics of the droplets for a droplet with $a = 15$ (a) and $a = 5$ (b). For the minus case $m = 0$ and for the plus case $m = -2.5$. The gradient considered is $\theta_{eq}(x) = (-0.04x + 15)^\circ$.

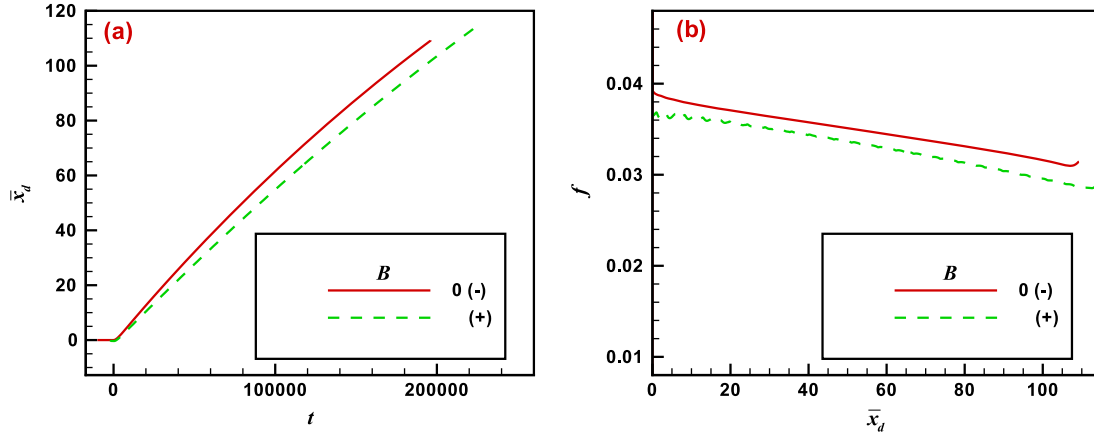


Figure 15. (a) The effect of the profile of the DJP on the dynamics of the droplets for a droplet with $a = 15$. For the minus case ($m = 0$) $B = 0$ is constant and the contact angle changes as $\theta_{eq}(x) = (-0.04x + 15)^\circ$. For the plus case B varies along the substrate such that the contact angle changes, similar to the minus case, as $\theta_{eq}(x) = (-0.04x + 15)^\circ$. (b) The corresponding calculated DJP-induced forces on the droplets. f is measured in units of σ .

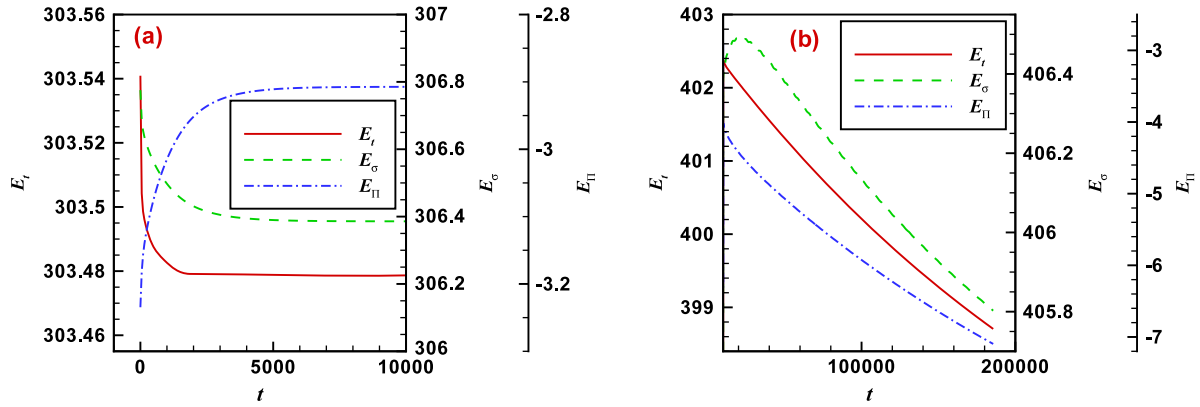


Figure 16. The energy changes of the system of figure 1 during the relaxation step (a) and motion towards the more wettable parts (b). The calculations have been done for the minus case ($m = 0$) for a droplet with $a = 15$. The total length of the system is equal to 400 and the wettability gradient changes according to $\theta_{eq}(x) = (-0.04x + 15)^\circ$.

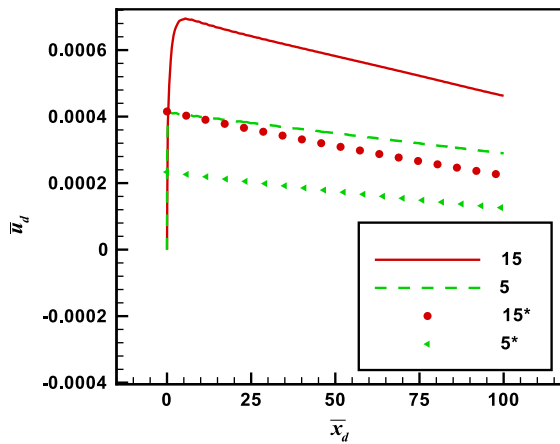


Figure 17. The velocity of the nanodroplets as a function of their position along the substrate for different size droplets. The results of the numerical simulation have been compared with those obtained using the theoretical model (*). The wettability changes according to $\theta_{eq}(x) = (-0.04x + 15)^\circ$ and the considered DJP profile belongs to the minus case with $m = 0$.

are in agreement with theoretical results already reported for macroscopic droplets [3]. Taking 1 nm and 0.05 N m^{-1} as typical values of b and σ , respectively, for the parameters used in figure 9, one obtains as the time scale $\mu/\text{\AA}$ values of the order of $10\text{--}8\mu \text{ Pa}^{-1}$ and the total distance traveled of about 100 nm . For μ between 1000 and 10000 Pa s (polystyrene at different temperatures), the droplet velocities in our simulations range roughly from 100 to 10 nm s^{-1} . Our study revealed that the velocity of the droplets increases with the size of the droplets. This is also in agreement with the theoretical and experimental results of [13, 14]. Our investigation showed that the dynamics of the nanodroplets may deviate from those predicted by equilibrium contact angle analysis. Differences between the profile of the DJP on two substrates with the same gradient of equilibrium contact angle may create different dynamics for the nanodroplets. This is a feature first reported in [17] for chemical steps and its effects on the dynamics of nanodroplets for chemical gradient cases were explained in the present study. It was also found that the slip can substantially modify the dynamics. The position

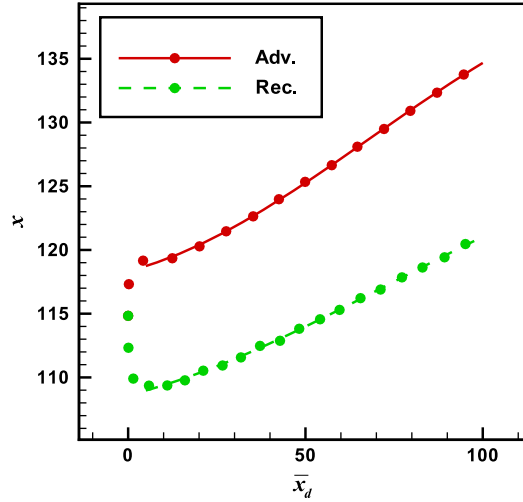


Figure 18. The advancing and receding contact line positions of the droplet with the wetting layer as a function of the droplet position ($\bar{x}_d(t)$) during the motion for a droplet with $a = 15$ for the minus case ($m = 0$). The substrate wettability changes as $\theta(x) = (-0.04x + 15)^\circ$.

of the center of the droplets can still be well represented in terms of a third degree polynomial. The previous theoretical model for dynamics of the droplets for small contact angles [3] was extended to include the slip effect. It was shown that the numerical results for the slip cases are in agreement with the theoretical results. Recent MD simulations [15] for large contact angles, namely beyond the lubrication limit considered in this study, have shown that the positions of the center of mass of the droplets can be described by a power law of the time of the motion. A comparison between our results and MD results of [15] suggests that different regimes may exist based on the maximum and minimum contact angles considered in this study. To further clarify the situation a thorough investigation for large contact angles is necessary and is suggested.

Appendix

The velocity of droplets on a surface with uniform gradient of the spreading coefficient has been derived in [3]. Here we simply extend the procedure to include the slip effect. The force acting at the receding contact line A (see figure 1) is given by the following [3]:

$$F_A = \sigma_{sl} + \sigma \cos \theta_{Ad} - \sigma_{sg} = \sigma (\cos \theta_{Ad} - \cos \theta_{Aeq}) \quad (A.1)$$

where the subscript d stands for the dynamic contact angle. By considering the velocity profile inside the droplet as equation (5) one can derive

$$u(y) = 3V \frac{-y^2 + 2h(y + \beta)}{2h^2(1 + \beta)} \quad (A.2)$$

where the mean velocity V is defined as $V = \int_0^h u(y) dy / h$. The viscous dissipation forces can also be derived by

integrating the viscous stresses $\zeta(x)$ over the droplet base interface which yields

$$\zeta(x) = \mu \frac{\partial u}{\partial y} \Big|_{y=0} = \frac{3\mu V}{h(1 + \beta)} \quad (A.3)$$

$$F_{VA} = \int_A^O \zeta(x) dx = \frac{3\mu V}{1 + \beta} \int_A^O \frac{dx}{h} \quad (A.4)$$

where O is the center of the droplet. Considering $h = (x - x_A)\theta_{Ad}$ one has

$$F_{VA} = \frac{3\mu V}{1 + \beta} \int_{x_{min}}^{x_O} \frac{dx}{(x - x_A)\theta_{Ad}} \quad (A.5)$$

where x_{min} is a molecular size and is considered here to remove the singularity at the contact line. After calculating the integral we obtain

$$F_{VA} = 3\mu \frac{V_A}{(1 + \beta)\theta_{Ad}} \ln \frac{x_O}{x_{min}}. \quad (A.6)$$

For the advancing contact line (B) a similar procedure yields

$$F_B = \sigma (\cos \theta_{Beq} - \cos \theta_{Bd}) \quad (A.7)$$

$$F_{VB} = \int_{x_B}^{x_O} 3\mu \frac{V}{(x - x_B)\theta_{Bd}} dx = 3\mu \frac{V_B}{(1 + \beta)\theta_{Bd}} \ln \frac{x_O}{x_{min}}. \quad (A.8)$$

Assuming $V_A = V_B = V$ and $\theta_{Ad} = \theta_{Bd} = \theta_d$ we can get

$$F_{VA} + F_{VB} = 6\mu \frac{V}{(1 + \beta)\theta_d} \ln \frac{x_O}{x_{min}}. \quad (A.9)$$

Also considering the balance of the driving and the viscous forces, i.e. $F_A = F_{VA}$ and $F_B = F_{VB}$ one has $\cos \theta_d = \frac{1}{2}(\cos \theta_{Aeq} + \cos \theta_{Beq})$. Using a Taylor series of $\cos \theta$ for small contact angles ($\cos \theta = 1 - \theta^2/2$) we have

$$\theta_d^2 = \frac{1}{2}(\theta_{Aeq}^2 + \theta_{Beq}^2) \simeq \theta_{Oeq}^2. \quad (A.10)$$

We also have

$$F_A + F_B = \sigma (\cos \theta_{Beq} - \cos \theta_{Aeq}) = \frac{\sigma}{2}(\theta_{Aeq}^2 - \theta_{Beq}^2). \quad (A.11)$$

Writing $F_A + F_B = F_{VA} + F_{VB}$, the procedure gives the velocity as

$$V = \frac{\theta_{Oeq}(1 + \beta)}{12\mu \ln} (\theta_{Aeq} + \theta_{Beq})(\theta_{Aeq} - \theta_{Beq}). \quad (A.12)$$

Since $\theta_{Aeq} - \theta_{Beq} = 2\ell d\theta_{eq}/dx$, where ℓ represents one-half the base length of the droplet and $\theta_{Aeq} + \theta_{Beq} \simeq 2\theta_{Oeq}$, we finally obtain

$$V = \frac{\ell \theta_{Oeq}^2 (1 + \beta)}{3\mu \ln(\ell/x_{min})} \frac{d\theta_{eq}}{dx}. \quad (A.13)$$

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