

Non-locality of the contact line in dynamic wetting phenomena.

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Introduction

In 1805, Thomas Young proposed an equation

E-mail: a.lukyanov@reading.ac.uk to predict the value of the equilibrium contact angle

of a liquid

on a solid surface

Abstract

In a large category of wetting phenomena, the contact line was always regarded as a compact, one-dimensional object with only microscopic length scales involved. This prevailing opinion had a certain impact and repercussions on the developing theories, interpretation of experimental results and the subsequent modeling methodologies. In this report, we will demonstrate, on the basis of first principles of molecular dynamic simulations, that this is not always the case. In particular, this is not true in the complete wetting case, when the advancing contact line motion is often accompanied by a running ahead precursor film. We study the onset of the dynamic wetting regime with the precursor film present and its main characteristic properties, such as dimensions. We show how the contact line becomes wide and practically macroscopic, and how the presence of the precursor film is in principle captured by a localized approach.

Keywords: wetting, nano-scale, meso-scale, contact line, molecular dynamics simulations.

line. In equilibrium, at zero contact line velocity, the friction force $F = 0$ vanishes and the contact angle should attain the equilibrium value θ_0 in the absence of the hysteresis effects.

In both static and dynamic scenarios recreated in molecular dynamics simulations (MDS), the local character of the contact line was directly established. It was found that the contact line region, including the domain where the contact line friction force F was generated, was on the microscopic length scale of a few or so atomic distances, that is basically around one or two nanometers in dimensional units.^{7,8} In fact, the analysis and simulations performed in⁸ have confirmed the longstanding hypothesis postulated in the molecular kinetic theory^{9,10} about the existence of a friction force of non-hydrodynamic, that is of microscopic origin acting directly on the contact line and leading to the modified Young's law (2).

As one can see, the locality of the contact line region has important repercussions for the modelling of the dynamic wetting phenomena. In the current study, we consider a situation, when the local character of the contact line region is completely broken.

In general, non-locality in dynamic wetting is often associated with the presence of surface tension gradients (Marangoni effect) created by gradients of temperature or relative concentrations of surface phase components.¹¹ In this case, hydrodynamic motion can influence surface tension gradients on macroscopic length scales and therefore affect the local contact angle. The contact angle can be influenced directly if the system size is on the length scale comparable to the size of the contact line region, basically in the nano flow conditions.¹² In simple liquids at constant temperature, the interfaces areb in)-amitn)-amrium

To mimic the forced wetting regime, the solid wall particles were moving with velocity U in the z -direction ($[1,0,0]$ crystallographic direction), where the reflective wall was acting as a piston at rest. After initial equilibration during $t_{eq} = 10000 \tau_0$ with the time integration step $t_s = 0.01 \tau_0$

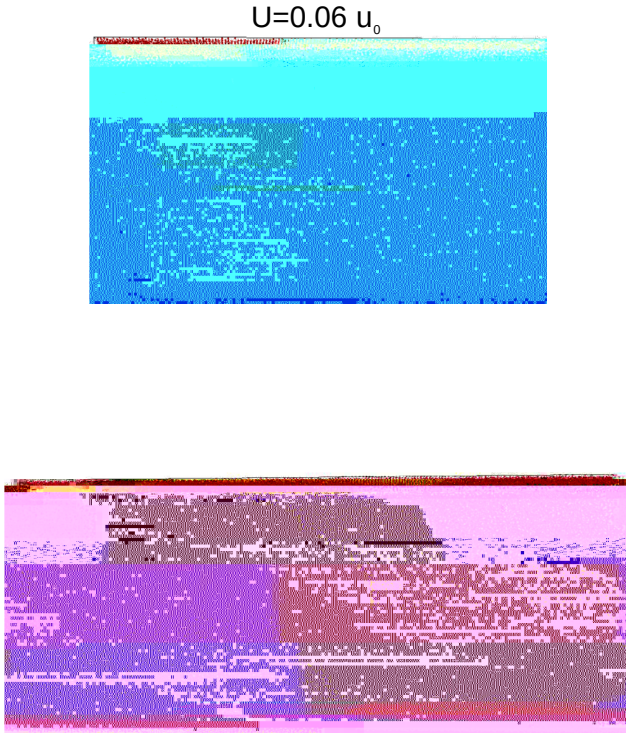


Figure 1: Snapshots of the cylindrical droplets in a steady state in MDS set-up at $H = 57$ and two dynamic contact angles: $\theta_c = 122.7^\circ$ at $U = 0.06 u_0$ and $\theta_c = 68.7^\circ$ at $U = 0.009 u_0$. The set-up is periodic in the x -direction with the total number of liquid particles in the simulations varied between 90,000 to 140,000. The solid wall was moving along the z -direction aligned in the $[1,0,0]$ crystallographic direction of the fcc lattice comprising the solid substrate. The steady state was reached following an equilibration period of 10000 τ_0 .

agates according to the diffusion law,

$$L_p = \sqrt{D_s t} \quad (3)$$

similar to the well-known in the capillary science Lucas-Washburn propagation dynamics. Here L_p is the length of the precursor film counted from the foot of the macroscopic liquid region and D_s is effective coefficient of surface diffusion. As one can readily observe, the velocity of the moving film front

$$\frac{dz_f}{dt} = \frac{1}{2} \sqrt{\frac{D_s}{t}} = \frac{D_s}{2L_p} \quad (4)$$

vanishes with time as the film length increases. This in turn implies that in a moving contact line problem, when, for example, a droplet is moving with macroscopic velocity U and the tip of the precursor film is propagating independently at the rate dz_f/dt in the same direction, the length of the precursor film is expected to attain a constant value defined by the droplet velocity and the coefficient of the surface diffusion

$$L_p = \frac{D_s}{2U} \quad (5)$$

when

$$\frac{dz_f}{dt} - U = \frac{dL_p}{dt} = 0: \quad (6)$$

In our MDS, the precursor film is only observed in the complete wetting cases ($\theta_0 = 0$), when the droplet velocity is below some critical value $U < U_T$, Tables 1 and 2. The steady state of the precursor film is indeed observed and is illustrated in Fig. 2. As one can see from the averaged density profiles at the foot of the wetting volume, the thickness of the film is about one atomic diameter. This is the typical morphology of the precursor films observed in our MDS in the liquids consisting of both short chain ($N_B = 5$) and long chain ($N_B = 50$) molecules. Consider now the obtained steady state in detail.

Results and discussion

Consider first how do our MDS results correspond to the predictions of the diffusion theory

represented by equation (3).

Figure 3: Illustration of the precursor film dynamics while the system was reaching the steady state in MDS set-up. Precursor film length L_p as a function of time t at different contact line velocities U and molecular length N_B at $T = 1 = k_B$. The solid lines are the fit given by equation (8).

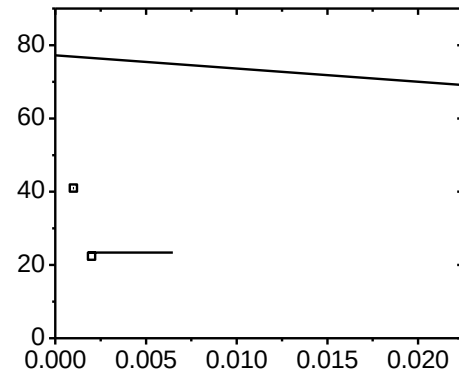


Figure 4: Precursor film length L_p as a function of the droplet velocity U in a steady state at different system parameters T , N_B and θ_{wf} . The solid lines are the fit $L_p = D_s/2U$.

Evolution of the precursor film

Integrating the evolution equation

$$\frac{dL_p}{dt} = \frac{D_s}{2L_p} - U \quad (7)$$

Table 1: Parameters of the MDS systems and dynamic wetting regimes: N_B

of the Im . Note, in the fitting procedure, only one parameter D_s in (8) has been allowed to vary.

with characteristic dimensions $z = 1$ and $y = 3$, and by averaging over the time interval $t = 10000 \tau_0$ and over the droplet depth in the x -direction. The distribution as a function of the tangential coordinate z has two characteristic regions, Fig. 6 (a). The first part of the distribution has a characteristic bell-shaped form and begins at the tip of the density distribution at the substrate. Further along the substrate, the bell-shaped region goes into a tail. We note that the characteristic length scale of the friction force variations is definitely microscopic.

The tail of the friction force distribution in our simulations is due to the small, finite size of the system H and corresponds well to the shear stress developed in the rectilinear flow between the solid substrates. Indeed, in the example shown in Fig. 6 (a), the shear stress in the tail region at $z > 20$ at the solid substrate was found to be $\tau_{yz} = 0.082 \pm 0.006 f_0$, while the value of $\tau_{yz} = \frac{6U}{H_e} = 0.073 f_0$ is expected assuming the Hagen-Poiseuille flow between the planes, where $H_e = H - 2s_{52}$ is the effective gap between the plates taking into account the size of the solid substrate $s_{52} = 2.75$.

As the system size increases, the value of the friction force in the tail region is observed to decrease at a given substrate velocity, as is expected in the rectilinear Hagen-Poiseuille flow conditions, and to eventually disappear in the macroscopic limit $H \rightarrow 1$.⁸ At the same time, the bell-shaped region in this limiting procedure is shown to be qualitatively invariant (subject

changes, though the concept itself is still useful. In a nutshell, the usually microscopic object, the contact line becomes geometrically macroscopic due to the developing precursor film. As a result, the processes usually taking place on the scale of a nanometer, are now occurring over much larger, tens of nanometers length scales. In terms of the macroscopic observables, the contact angle velocity dependence attains a

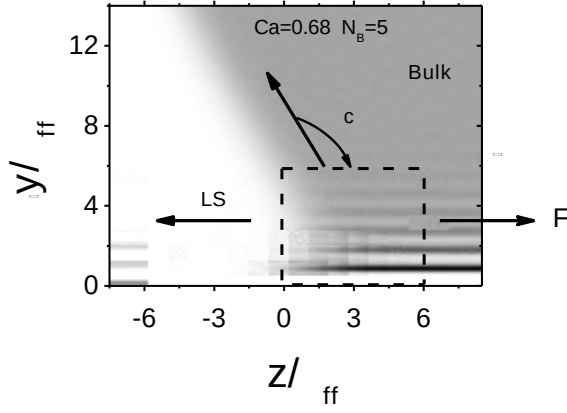


Figure 7: MDS in the complete wetting case, set (c) in Table 1, at the substrate velocity $U = 0.06 u_0$ and the dynamic contact angle $\theta_c = 123^\circ$. Force balance and the density distribution at the contact line region. The dashed box designates the contact line region. Distance y is measured from the equimolar surface of the solid wall particles, while distance z is measured from the centre of the simulation box.

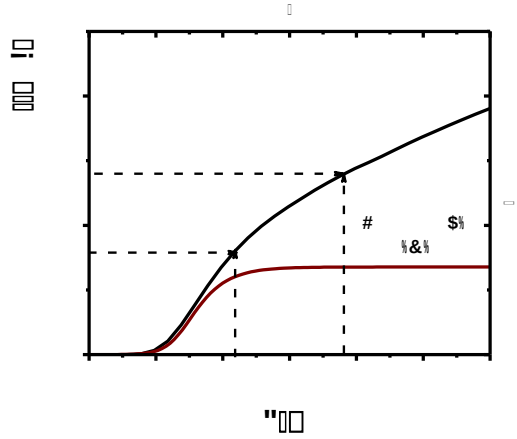


Figure 8: MDS in the complete wetting case, set (c) in Table 1, at the substrate velocity $U = 0.06 u_0$ and the dynamic contact angle $\theta_c = 123^\circ$. The upper solid line (black) is for the integrated friction force $F_D = \int_{z_0}^z F dz$ as a function of z at $z_0 = 5$. The second, lower solid line (brown) is the integrated force in the macroscopic limit at the same system parameters. The dashed lines designate the contact line region as the interface crossover shown in Fig. 7 by the dashed box and the integration region to achieve the force balance $F_D + F_{LS} + \cos \theta_c = 0$.

Figure 9: MDS in the complete wetting case, set (c) in Table 1, at the substrate velocity $U = 0.06 u_0$ and the dynamic contact angle $\theta_c = 123^\circ$. The force F_S per unit length (in the x -direction) acting on the surface of the variable side size y oriented perpendicularly to the z -axis and located at the right end of the dashed box in Fig. 7. The dashed line is the linear fit $F_S = A + B(y - y_0)$ at $A = 2.3 \pm 0.1 u_0$, $y_0 = 0.44 \pm 0.1$ and $B = 0.78 \pm 0.02 f_0$.

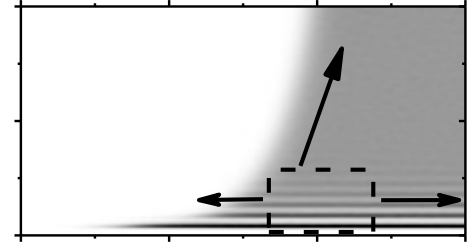


Figure 10: MDS in the complete wetting case, set (c) in Table 1, at the substrate velocity $U = 0.009 u_0$ and the dynamic contact angle $\theta_c = 68.7^\circ$. Force balance and the density distribution at the contact line region. The dashed box designates the contact line region. Distance y is measured from the equimolar surface of the solid wall particles, while distance z is measured from the centre of the simulation box.

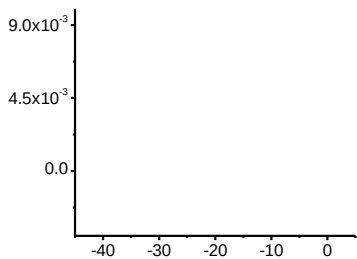


Figure 11: MDS in the complete wetting case, set (c) in Table 1, at the substrate velocity $U = 0.009 u_0$ and the dynamic contact angle $\theta_c = 68.7^\circ$. (a) Tangential component of the friction force F , (b) surface density ρ_s and (c) surface velocity v_s as functions of z . The dashed box designates the contact line region, with similar dimensions as in Fig. 7. The surface variables have been obtained in the boundary layer $y = 1:5$ at the solid wall.

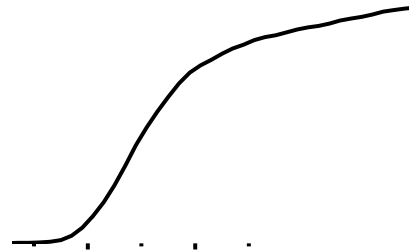


Figure 12: MDS in the complete wetting case, set (c) in Table 1, at the substrate velocity $U = 0.009 u_0$ and the dynamic contact angle $\theta_c = 68.7^\circ$. The integral of the tangential component of the friction force $\int_{z_0}^z F dz$ as a function of z .

that m_f , ℓ , ϵ and $\tau_0 = \frac{q}{\mu_f}$ provide basic scales for mass, length, energy and time respectively. At the same time, $\rho_0 = \frac{\mu_f}{\ell^3}$, $u_0 = \frac{\ell}{m_f} \frac{1}{\tau_0}$, $f_0 = \frac{\mu_f}{\ell^3}$, $\rho_0 = \frac{\mu_f}{\ell^2}$ and $\rho_0 = \frac{\mu_f}{\ell^2}$ provide necessary scales for particle density, velocity, pressure, $\rho_0 = 13.186 \frac{1}{6.939} \frac{1}{T d} [(p)] TJ \quad ET \quad q \quad 1 \quad 0 \quad t72$

means of harmonic potential $\phi_a = \frac{1}{2} k_a x^2$, with the strength $k_a = 800 \frac{\text{eV}}{\text{\AA}^2}$ chosen such that the root-mean-square displacement of the wall atoms $\sqrt{\langle r^2 \rangle}$ was small enough to satisfy the Lindemann criterion for melting $\sqrt{\langle r^2 \rangle} < 0.15 a_{\text{ww}}$. The strength of the harmonic potential was sufficient to guarantee rigidity of the solid wall, so that elasto-capillarity effects can be neglected, that is $(\gamma / \sigma)^{1/2} \ll 1$, where γ is equilibrium liquid-gas surface tension.²³ The anchor points in the layer of the solid wall facing the liquid molecules have been slightly randomized in the vertical y direction, with the amplitude $\sqrt{\langle y^2 \rangle} = 0.3 \text{ \AA}$. This small roughness allowed to avoid undesirably large slip lengths observed in MDS²¹ and any bias towards ideal substrates in this study. The substrate density ρ_s was set to $\rho_s = 1.41 \text{ g cm}^{-3}$ with the liquid-solid interaction length scale $\sigma_{\text{wf}} = 3.4 \text{ \AA}$ and the solid-solid interaction length scale $\sigma_{\text{ww}} = 3.4 \text{ \AA}$. Two parameters of the model, temperature T and strength of the liquid-solid interactions ϵ_{wf} have been varied in the simulations to obtain liquids with different viscosities and to emulate various wetting conditions (partial, $\theta_0 > 0$, or full wetting, $\theta_0 = 0$).

in the case of a free surface, and by

$$\gamma_{LS} = \int_0^Z \frac{\rho_L}{2} \frac{d\phi_s}{dy} dy \quad (14)$$

for a solid-liquid interface, where ϕ_s is the potential of the solid wall forces acting on the liquid particles and ρ_L is the particle density.^{25,26} The liquid-solid surface tension is calculated in the assumption of undeformable solid substrate, so that γ_{LS} is in fact the surface tension of the liquid.

The value of the zero shear rate viscosity in the liquid in the bulk conditions is evaluated by considering the correlation function

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle \sigma(t) \sigma(0) \rangle dt$$

at $\dot{\gamma} = 0$, details can be found in.²⁷

The methodology of the surface tension evaluation in MDS has been verified either by comparison with the Laplace law (by independently evaluating surface tension and the pressure in a large, levitating liquid drop)²⁸ or by comparison with the Young-Dupre equation in equilibrium $\cos \theta_0 = \gamma_{LS} / \gamma_{GS}$.²⁹ The Young-Dupre equation was probed by evaluating independently surface tensions and by directly measuring the equilibrium contact angle θ_0 from the shape of the free-surface profiles of cylindrical droplets.^{29,30} The difference between two static contact angles (measured geometrically and calculated via the Young-Dupre equation) was found not to exceed the accuracy of the contact angle evaluations.

Evaluation of the contact angles in MDS

The contact angle in our study has been inferred from the free-surface profiles defined as the locus of equimolar points and averaged over the x-direction, Fig. 1 and during the time period of $t = 10000 \tau_0$. The profiles were developed by means of a circular fit

$$(y - y_0)^2$$

has been applied to a part of the free-surface profile of length 20σ excluding h_s layer adjacent to the substrate corresponding to the liquid-solid interface, similar to the methodology developed in.³⁰ The accuracy of this approach is illustrated in Figs. 14 and 15. One may notice that the interface shape is very well described by the fit even at $Ca > 1$. The value of the cut-off distance h_s was varied in between $4\sigma \leq h_s \leq 8\sigma$ to exclude the area strongly affected by the solid wall potential with density variations on the scale of one atomic distance.

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Figure 15: Illustration of the free surface profiles (equimolar surfaces approximated by the fit (15), shown by the dashed line) developed from the particle density distributions obtained in MDS in a steady state in the case of complete wetting ($\theta_0 = 0$ at $N_B = 50$, $T_0 = 1" = k_B$ and $\epsilon_{wf} = 1.3$). Here, (a) $\theta_c = 90^\circ$, $U = 0.01 u_0$, $Ca = 0.67$ and (b) $\theta_c = 128.3^\circ$, $U = 0.1 u_0$, $Ca = 6.7$. In both cases $h_s = 8\sigma$ and the distance y is measured from the equimolar surface of the substrate particles of the bottom plate, while the distance z is calculated from the centre of the simulation box, as in Fig. 1.

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