Droplet on a fiber: beyond the barrels and clam-shells, the spreading dynamics

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INTRODUCTION

A droplet on a fiber (of radius *r*) can adopt two completely different geometries. First, an axisymmetric form, known as the barrel shape (Figure 1, Top). This static configuration is well described by the Laplace equation, so that physical characteristics of the droplet, like the static contact angle θ^0 or droplet height h^0 can be predicted. When θ^0 remains high (how high is dependent on *r* and h^0), the droplet retains an asymmetric form, the clam-shell shape (Figure 1, Bottom). This time, the Laplace equation is not the relevant equation and, so far, no theoretical analysis of this conformation is known. The transition between the two geometries, the roll-up transition, is of particular industrial interests for the process of the detergency of oils from fabrics, and was therefore intensively investigated by Carroll [1], McHale et al [2], and Eral et al [3].

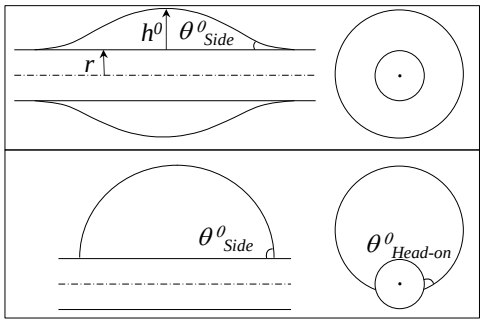

Figure 1: Barrel (Top) and clam-shell (Bottom) shapes of a droplet on a fiber at equilibirum. Side and Head-on views

However, to the best of our knowledge, the spreading dynamics, i.e. the dynamical process which leads to the two observed static configurations, has never been studied. This is the main goal of this ongoing study. As a first step toward a better understanding of the fundamental mechanisms that control the spreading of droplets on fibers, we are using large scale molecular dynamics to study the contact-line motion of a droplet of liquid *L* in contact with a fiber *F*

METHODOLOGY

$$U_{ij} = 4C_{A-B}\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

In our simulations, all potentials between atoms, fiber as well as liquid, are described by modified pair-wise Lennard-Jones 12-6 interactions U_{ij} with r_{ij} the distance between any pair of atoms *i* and *j*. The coupling parameters C_{A-B} enable us to control the relative affinities between the atoms. The subscript *A-B* stands for the various possible interactions pairs: *L-L*, *L-F*, and *F-F*. C_{A-B} is set to 1.0 for *L-L* and *F-F*, and to 0.9, 1.0, 1.05, 1.1 for L-F to tune the wettability of the fiber. The parameters ε_{ij} and σ_{ij} are related respectively, to the depth of the potential well and effective molecular diameter. For both fiber and liquid atoms, the Lennard-Jones parameters are ε_{ij} = 0.267 kJ/mol and σ_{ij} = 3.5 Å. In addition, we consider a confining potential between nearest neighbours to maintain a constant distance between any two adjacent atoms within a given liquid molecule (8 atoms in length) and an harmonic potential for the fiber atoms. This model is simplistic, but it contains all the basic ingredients to describe the details of wetting for flat surfaces [4] for example. A droplet with an initial radius of 8.5 nm (5000 molecules) and a fiber with a radius of 4 nm and a length of 59 nm were simulated. To describe the spreading dynamics, we need to know the droplet radius and the contact angle versus time. To achieve this, we record the position of the edge of the droplet via a density calculation throughout the simulation. We then approximate the drop shape by a spherical cap and fit it by a circle. We could thus extract from the successive configurations, the dynamic droplet height and contact angles (θ_{Side} and $\theta_{Head\text{-}on}$). To interpret these data, we focus on the molecular-kinetic theory (MKT) [5], which, in its simplified version, establishes the following relation between the velocity of the triple contact line (TCL) v and the driving force $\gamma(\cos\theta^0 - \cos\theta)$: $v = \gamma(\cos\theta^0 - \cos\theta)/\zeta^0$ with γ the surface tension of the liquid, θ the dynamic contact angle, and ζ^0 the contact line friction. Here, this single parameter characterizes the spreading dynamics. A step further is to assume that ζ^0 can be split into two parts, the first one originates from the viscosity of the liquid and the second from the liquid-solid interaction [5]. It yields the following expression $\zeta^0 \approx a\exp\left[b\gamma(1+\cos\theta^0)\right]$, with *a* and *b* constants for a given couple of liquid and solid. Thus the logarithm of ζ^0 is proportional to $\gamma(1+\cos\theta^0)$, i.e. to the work of adhesion between the liquid and the

fiber. Our main goal is to check if the spreading dynamics can be modelled by this theory.

RESULTS AND DISCUSSION

Figure 2 shows three successive snapshots of a droplet spreading on a fiber for $C_{L\text{-}F}$ = 0.9 (left side) and 1.1 (right side). These affinities leads respectively to a clam-shell and barrel shapes.

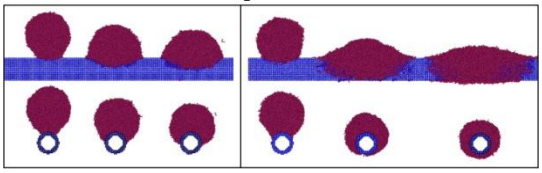

Figure 2: Snapshots of spreading droplet with $C_{L\text{-}F}$ = 0.9 (left side) and 1.1 (right side)

The dynamics of the contact angles associated to these simulations are presented in Figure 3. For $C_{L\text{-}F}$ = 0.9, both θ_{Side} and $\theta_{Head\text{-}on}$ remain larger than 0° which indicates partial spreading. After 5 ns, equilibrium is reached with θ^{0}_{Side} = 83.1° ± 4.5° and $\theta^{0}_{Head\text{-}on}$ =50.6° ± 6.0°. For $C_{L\text{-}F}$ = 1.1, $\theta_{Head\text{-}on}$ rapidly reaches a value of 0°, i.e. the droplet completely engulfs the fiber. Yet, the spreading dynamics is not over as θ^{0}_{Side} continues to slowly decrease. In this case, we can then consider that the spreading dynamics is a two-step process.

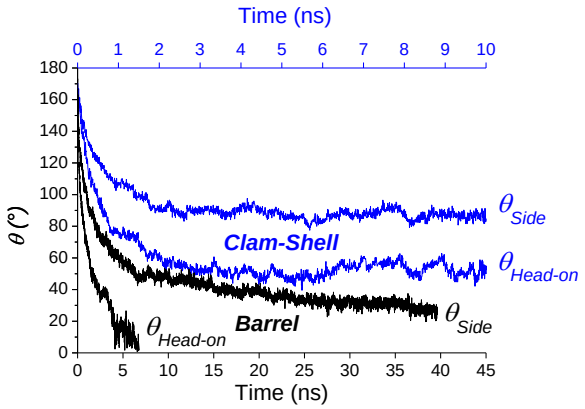

Figure 3: Dynamic contact angles, θ_{Side} and $\theta_{Head\text{-}on}$ for $C_{L\text{-}F}$ = 0.9 (blue lines) and 1.1 (black lines).

To determine the speed of the TCL, we use the G-Dyna software [6], which also yields ζ^{0} for the simplified version of the MKT. Figure 4 presents the data submitted to the G-Dyna software (gray symbols) and the best fits (black line), for coupling parameters equal to 0.9, 1.0, 1.05, and 1.1. The good agreement between the data and the fits reveals that the contact line friction could be a relevant parameter to describe the dynamics. Moreover, Figure 5 shows that a linear relation between the logarithm of ζ^{0} and the work of adhesion is plausible as predicted theoretically.

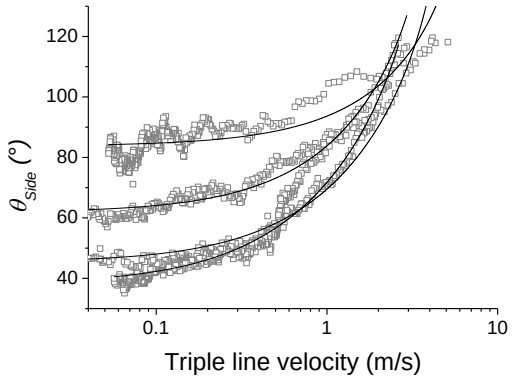

Figure 4: Contact angle dynamics and the MKT fits

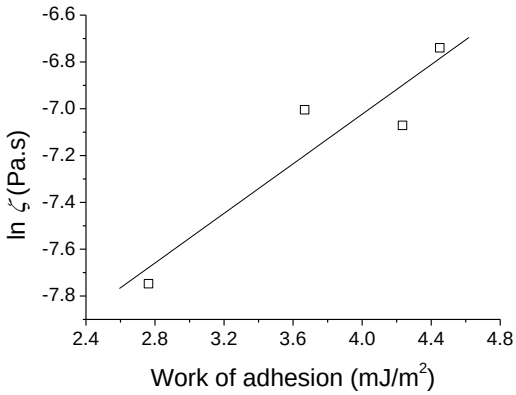

Figure 5: ln ζ^{0} versus the work of adhesion

CONCLUSION

We use large scale molecular dynamics simulation to model the spreading of droplets on fibers. We show that the dynamics can be modelled by the molecular-kinetic theory and that the contact line friction may be the relevant parameter to describe the dynamics. We believe that this is a first step towards a better understanding of droplet on fiber spreading dynamics. However, there is a particular need for more theoretical and experimental works. This is ongoing.

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