

Contact line dynamics in forced wetting

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Introduction

Recently some underlying principles of the dynamic process of colloidal drying (e.g. coatings, particle-assembly) have been published [1]. Ring/stain formation of drying colloidal suspensions is ruled by the contact line dynamics [2]. Receding contact lines are ubiquitous at evaporating drops but the time scale of these processes is extremely long. Instead, the first stages of drop evaporation can be experimentally emulated at shorter times.

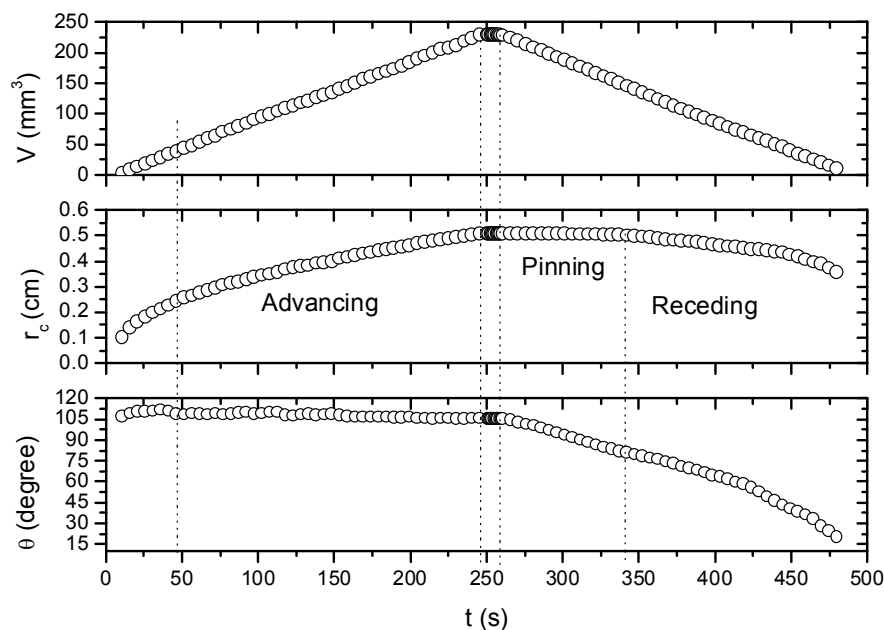


Figure 1. Low-rate dynamic contact angle measurements of water on PTFE, using the conventional method of volume variation. Volume and contact radius are also plotted.

During the evaporation of a sessile drop, before the backward movement of contact line, a receding contact angle is hold. Rigorously, receding mode corresponds to the *incipient* relative motion of three-phase contact lines on solid surfaces [3]. In practice, to measure meaningful values of receding contact angle is a no trivial task. Normally, the advancing contact angle approaches the minimum free energy state while the receding angle will be subject to vibrations and can attain one of many metastable

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states. This explains the relative reproducibility of the advancing contact angle as compared to the receding angle [3].

Forced wetting occurs when the wetted area of a solid surface is altered by a deliberate external action, dipping/rising the solid in/from the liquid, tilting the solid surface or changing the drop volume by direct liquid addition/removal. If the external action produces a slow relative movement between interfaces, then each dynamic state can be considered as a thermodynamic state.

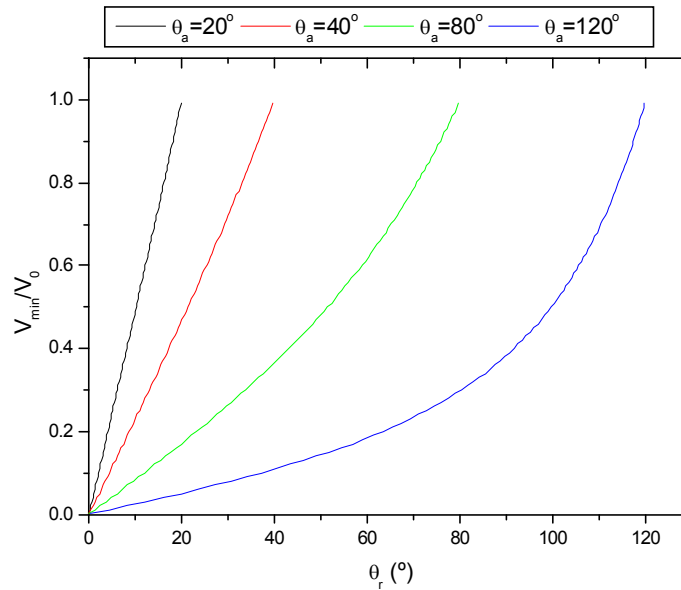


Figure 2. Dimensionless minimum volume of receding drops as function of the receding contact angle, for different values of initial contact angle.

Low-rate dynamic contact angle measurements [4] are based on forced wetting. In this technique, a small hole is drilled in the substrate sample and a tube is connected to this hole beneath the substrate. The volume of the drop is then changed by feeding/removing more liquid to the drop by means of this tube connected to a motorized micrometer syringe. The rate of advance or retreat of the symmetrical sessile drop on the substrate can be indirectly controlled to measure advancing and receding contact angles, respectively. However, there is a strong influence on the receding contact angle value from the rate of liquid removal from the drop.

An evaporating drop undergoes a minimum rate of liquid withdrawal. This scenario standardizes the impeding motion of the drop on the substrate, giving reliable receding contact angles [5]. But, a linear rate of change in drop volume does not correspond to a linear rate of motion of the contact line. We need a variable rate of withdrawal of the liquid during determination of receding angles under evaporation-like conditions, i.e. uniformly moving contact lines.

Method

Commonly, the low-rate dynamic contact angle measurements are achieved with a continuous linear variation of drop volume (see Figure 1). However, this way, the contact line is continuously

accelerated. This kinetic energy change can relax the system to other metastates different to the advancing and receding ones.

Instead, cubic variations of volume produce uniformly moving contact lines [6]. Due to the limitations of stepper-motor-driven syringe pumps, our strategy is based on the discontinuous variation of drop volume in time at increasing/decreasing motor speeds. We assured that the capillary number of the contact line was small enough ($\approx 10^{-6}$). Moreover, the time between each addition/removal of liquid was intentionally chosen greater than the interfacial relaxing time of drop (1–10 sec). Hence, the growing/shrinking drop was not altered by Hydrodynamics.

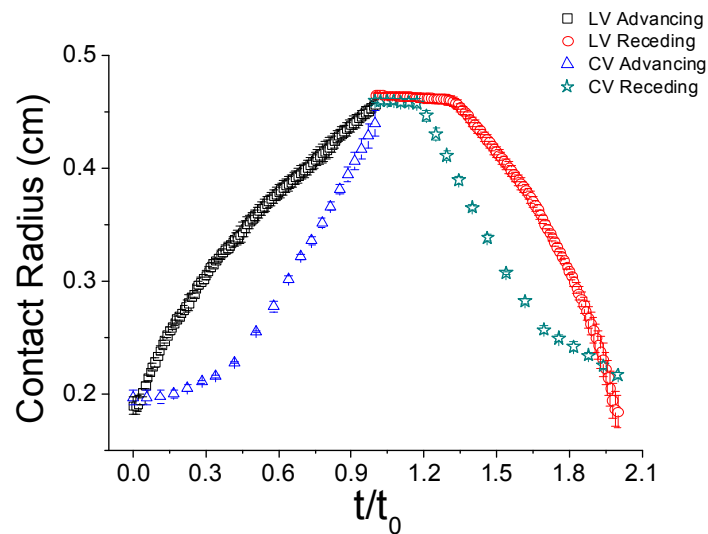


Figure 3 Contact radius as function of the dimensionless time in advancing and receding modes

A previously formed sessile drop on the substrate surface is contracted by applying a suction of the drop liquid through the tube. But, for a fixed receding angle, a sessile drop will recede provided that it had a minimum initial volume. This critical volume depends, at least, on the initial values of volume and contact angle. In Figure 2, the dimensionless critical volume for spherical receding drop is plotted for different values of initial contact angle. This was taken into account.

For the purpose of studying whether averaging of contact angles over time is allowed, correlation analysis was used [7].

We applied the technique Axisymmetric Drop Shape Analysis-Profile [7] using a microinjector Hamilton ML500.

Results

We measured the low-rate dynamic contact angles of distilled water (Millipore) at 22°C on smooth PMMA surfaces (4mm-thickness, GoodFellow), as provided by the supplier, using the linear variation (LV) and the cubic variation (CV) of volume variation.

The cubic variation produces the uniform motion of the contact line (Figure 3) over more surface area. Furthermore, the values of both advancing and receding contact angle were uncorrelated (Figure 4)

during the concerning contact line motion. Hence, the cubic variation provides statistically meaningful values of contact angle and more representative of the system (i.e. they are averaged over a greater area of the solid surface). The cubic variation forces the advancing metastate and stabilizes the receding one (see Figure 4).

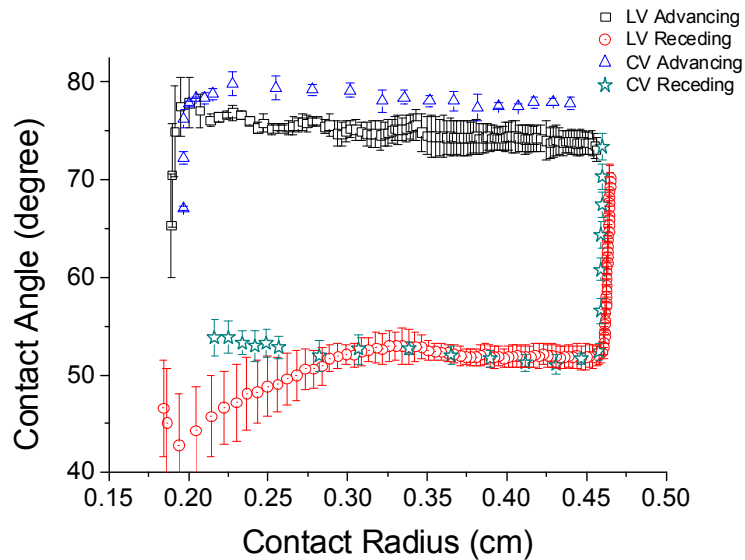


Figure 4 Contact angles as function of the contact radius in advancing and receding modes. It is worthy to highlight the minor error

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