Colloids and Surfaces A: Physicochem. Eng. Aspects 455 (2014) 19–27

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

# Experimental and computational study of triple line shape and evolution on heterogeneous surfaces

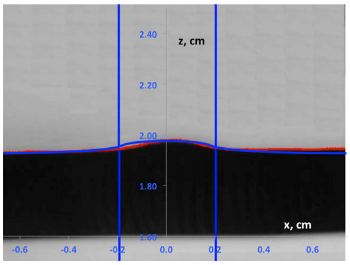
Neeharika Anantharaju[a], Mahesh V. Panchagnula[b,*]

[a] Department of Mechanical Engineering, Tennessee Tech University, Cookeville, TN 38505, USA
[b] Department of Applied Mechanics, Indian Institute of Technology Madras, Chennai 600036, India

## HIGHLIGHTS

- Current work studies the effect of macroscale chemical heterogeneities on triple line.
- Triple line shape and kinetics are studied, especially the nature of pinning.
- The triple line shape is shown to depend on the geometry of the chemical heterogeneity.
- The interfacial energy is shown to reach a maximum value in the pinned state.
- The system energy shows a gradient descent phase prior to the sudden jump due to de-pinning.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

*Article history:*
Received 27 March 2014
Received in revised form 13 April 2014
Accepted 18 April 2014
Available online 26 April 2014

*Keywords:*
Triple line
Kinetics of wetting
Contact angle hysteresis

## ABSTRACT

Wetting of smooth, chemically heterogeneous surfaces was studied experimentally and computationally during the advancing and receding processes. The motion of the triple line is known to play an important role in determining the macroscopic contact angle due to its ability to be pinned at various defect locations on real surfaces. This effect is known to cause contact angle hysteresis. The shape of the triple line during these pinning/de-pinning events on various chemically heterogeneous surfaces was captured using an experimental and a computational technique. The experimental study employed a Modified Wilhelmy Plate Technique. The novelty in the current experimental setup lies in its ability to capture the microscopic triple line shape and its evolution in addition to measuring the local contact angles, which were both studied. The triple line shape was observed to be very sensitive to minor imperfections of the substrate. In addition, Surface Evolver was used to study the triple line shape computationally. Evolver was used to solve the complete three-dimensional problem by minimization of the total energy taking into consideration, both gravity and contact angle hysteresis. The studies showed that the temporal evolution of the triple line was significantly different during the advancing and receding processes based on the nature of the chemical heterogeneity. The results from the current work could be used in the design and fabrication of chemically heterogeneous surfaces for desired wetting applications.

## 1. Introduction

Wetting of chemically heterogeneous surfaces, fabricated from two or more component materials with different wetting properties, has a wide range of practical applications [1]. For example,

---

* Corresponding author. Tel.: +91 44 2257 4056.
*E-mail address:* mvp@iitm.ac.in (M.V. Panchagnula).

http://dx.doi.org/10.1016/j.colsurfa.2014.04.052

such composite surfaces can be engineered with the objective of employing surface energy forces originating from the hydrophobic/hydrophilic interactions, to control the motion of the liquid [2]. In most instances, however, the component materials, themselves, are not entirely defect free and could therefore exhibit *intrinsic* contact angle hysteresis, apart from the hysteresis originating due to the heterogeneity.

A fundamental property that characterizes wettability of a material is the contact angle, $\theta$, which a sessile drop manifests on the solid substrate. However, this macroscopic contact angle measurement is observed to vastly vary with the triple line structure.[1] In fact, for a *real* surface, it is not possible to identify a unique contact angle for the sessile drop, as it varies locally around the triple line [3]. The triple line is subject to local energy minima in the wetting process, owing to which it is likely to be pinned at various chemical and/or topological defects on the real surface [4–7]. This phenomenon is believed to be one of the causes of contact angle hysteresis [8]. Thus, a study of the triple line shape and its temporal evolution is important to understand contact angle hysteresis on real surfaces as first pointed out by Shanahan [9]. For example, triple line pinning and de-pinning events in the case of evaporating sessile drops has been shown to affect the rate of evaporation [10,11].

The experimental studies of the wetting/de-wetting of liquid on a solid surface are broadly performed by either sessile drop spreading on a flat surface or by plunging/withdrawing a substrate into/from a liquid [12]. The studies using a sessile drop capture the two-dimensional shape of the drop and measure the contact angle therein [13]. The traditional Wilhelmy technique, on the other hand, is used to measure the forces acting on the plate, in order to calculate the contact angle exhibited by the liquid meniscus on the solid surface [14]. Both these approaches are consistent as far as the measurement of the macroscopic contact angles [15] are concerned but fail to capture the local triple line behavior. For instance, in the sessile drop method, the triple line is curved and is difficult to image. Most of the recent research in understanding the triple line motion was performed either numerically or computationally with very little validation against experiments [16–18]. The current effort involves the use of a novel experimental setup to experimentally capture the local triple line behavior and compare to the results from a computational study.

The current experimental apparatus uses the setup of the traditional Wilhelmy plate [19], with two major modifications. Firstly, the substrate is inserted/withdrawn into/from the liquid bath at an angle and secondly, it includes the capability to capture the triple line along the width of the surface. The triple line is captured both during the insertion and withdrawal of the surface from a water bath at very low speeds. This yields the shape of the triple line during both the advancing and receding states. In this process, it is ensured that the liquid meniscus is allowed to reach equilibrium at each time instant; therefore, the process is quasistatic. The average contact angle is measured using the height to which the free surface rises/drops above the liquid meniscus surface. Thus the current experimental technique, which is referred to as the *modified Wilhelmy plate technique* is able to capture the microscopic triple line shape in addition to the local and average contact angles during the same experimental run, thus providing a more complete picture of the wetting process useful for validating computational studies.

The computational study on wetting was performed by employing the Surface Evolver (SE) [20], an interactive program for the study of surfaces shaped by surface tension, and gravity. The user specifies an initial surface, the constraints that the surface should satisfy throughout the evolution, and an energy function that depends on the surface. SE then modifies the surface, subject to the given constraints, so as to minimize the energy. This minimization of energy is performed through a gradient descent method.

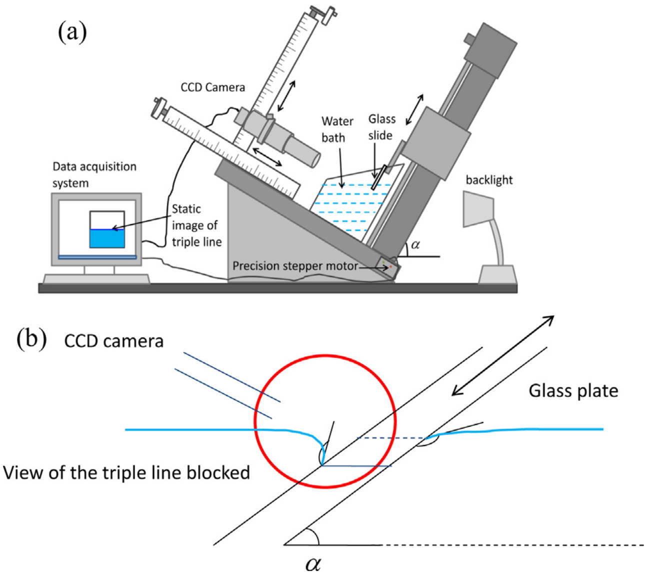


**Fig. 1.** (a) Schematic of a modified Wilhelmy plate apparatus. (b) Shape of the meniscus for a hydrophobic surface submerged in a water bath.

The strength of SE that makes it applicable to a breadth of problems lies in its capability to handle arbitrary topology, volume constraints, boundary constraints, boundary contact angles, prescribed mean curvature, crystalline integrands, gravity, and constraints expressed as surface integrals [21]. For this reason, SE proved to be a good tool for capturing the triple line shapes and their temporal evolution in the current computational study of chemically heterogeneous surfaces. However, being a gradient descent algorithm devised to operate on the energy landscape, there is no natural source of directional information. Directionality is important to handling contact angle hysteresis, as the advancing and receding angles are states, which are only accessible from specific directions. If this information can be coupled into SE, it is likely to become a tool with significantly expanded capabilities, especially in the realm of modeling wetting of real surfaces. Recently, Santos and White [22,23] and Prabhala et al. [24] have independently demonstrated a methodology by which the Dussan [25] and Hocking [26] model for contact angle hysteresis can be coupled into SE. This approach allows for the directional information to be incorporated into SE. The mathematical description is briefly presented in the *Computational method* section hereunder. The results from exercising this model on a wide range of model chemical heterogeneity surfaces are presented and discussed. We also present experimental measurements of the triple line shape and contact angles for the same cases. Finally, the experimental and computational results are compared and discussed. It must be mentioned that the surfaces under study are smooth but chemically heterogeneous. But the arguments presented herein could also be extended to triple line pinning due to topological heterogeneities.

## 2. Methods and materials

### 2.1. Experimental method

The experimental set up (see Fig. 1) consists of a substrate oriented at angle, $\alpha$ ($60^\circ$, in this case) with respect to the liquid interface. The specimen under study was cleaned thoroughly and

---

[1] The triple line in this context is the set of points where the solid, liquid and vapor phases meet.