International Journal of Heat and Mass Transfer 124 (2018) 279–287

Contents lists available at ScienceDirect

International Journal of Heat and Mass Transfer

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

Evaporation-induced receding contact lines in partial-wetting regime on a heated substrate

Abbasali Abouei Mehrizi, Hao Wang *

Laboratory of Heat and Mass Transport at Micro-Nano Scale, College of Engineering, Peking University, Beijing 100871, China

ARTICLE INFO

Article history:
Received 23 December 2017
Received in revised form 19 March 2018
Accepted 20 March 2018

Keywords:
Volatile liquid
Evaporation
Contact line
Thin film
Atomic force microscope
Receding
Advancing

ABSTRACT

The moving contact line is a nanoscale joint providing critical boundary conditions for the liquid interface in a wetting system. Our understanding about the partial-wetting contact line is highly limited which is especially true when the situation is complicated by phase change that is ubiquitous in nature and technologies. In this work we explored evaporation-induced receding contact lines in partial wetting regime by means of two modes of atomic force microscopy scanning. By means of tapping mode scanning, the intrinsic meniscus profile was found to be linear down to the apparent contact line without bending in profile, which greatly facilitates the modeling about the intrinsic meniscus. The local angle on the contact line systematically varied with the moving speed, which fact is against the widely used constant assumption in hydrodynamic models. Using the tapping mode scanning and also force curve method with either soft or stiff probes, a layer of nano thin film was detected on the substrate beyond the contact line. The nano film thickness slightly decreased with the distance away from the contact line, and finally reached a constant that was the adsorbed i.e. non-evaporating film thickness if the tests were in a vapor chamber. We further investigated advancing contact lines in open air, and still detected the nano thin film in front of the contact line as a precursor. The nano thin film can provide extra evaporation area, which could rationalize the abnormal ultrahigh evaporation flux observed in recent experiments on nanoscale menisci. Guidance is provided for the calculation of partial-wetting contact line evaporation.

1. Introduction

Wetting of a solid surface with a liquid is a multi-scale process operating from macroscopic to molecular scale, complicated by many aspects including the liquid and surface characteristics [1], liquid-solid interactions, bulk motion and phase change [2], *etc.* For complete wetting the contact angle is near zero and a precursor film exists which facilitate the modeling [3]. The concept of disjoining pressure could be appropriate since the films are rather flat [4]. In contrast, for partial wetting regime our understanding about the contact line is highly limited and debates have persisted for years [5]. Significant progresses have been made on non-volatile liquids in recent years. Kuchin et al. [6] calculated the thin film profile for a nonvolatile liquid in a capillary tube. They found a convex bending in profile around 60 nm far from the surface. Taking the advantage of atomic force microscopy (AFM), Yu et al. [7] found that the contact angle extracted at about 100 nm thickness near the contact line of a macro droplet was equal to the macroscopic angle obtained by an optical method with a resolution of microns. Chen et al. [8] experimentally clarified the nanoscopic morphology using an AFM. A convex nanobending in film profile existed near the advancing contact line. The microscopic contact angle at the contact line, θ_m, was varying with the advancing speed. After that a large-scale molecular dynamic simulation explained that the main cause of θ_m variation was the microscopic force acting at the contact line region [9]. For receding non-volatile liquids, Deng et al. [10] have shown that the film profile was linear down to the contact line, meanwhile a nano residual thin film usually remained after the contact line receding. Liu et al. [11] further studied the criteria for the residual film to form and to maintain stable on the substrate.

For volatile liquids the contact lines are much more complicated due to evaporation-induced factors such as the evaporative cooling, Marangoni, and vapor recoil [12,13]. It was also speculated that the evaporation has direct effects on the movement of the contact line by allowing more liquid molecules to jump to the solid substrate [14]. Until now, however, the experimental evidences are extremely lacking. Morphology measurement of contact line region is challenging since traditional optical methods barely have nanoscale resolutions. Electron microscopy family [15] including the environmental scanning electron microscopy, transmission

---

* Corresponding author.
E-mail address: hwang@coe.pku.edu.cn (H. Wang).

https://doi.org/10.1016/j.ijheatmasstransfer.2018.03.066
0017-9310/

electron microscopy, and wet scanning transition electron microscopy have been popular in wetting studies, but most of the studies were about droplets during condensation, and the focus was the overall shape of the droplets rather than the contact line thin film [15]. The electron beam as a driving force could deform the droplet shape [16]. Optical methods have also been extensively used for thin film measurement, but limited to uniform films. Hu and Adamson [17] used an ellipsometry in a chamber to measure the thickness of adsorbed film of different vapor e.g. water, n-hexane, propanol onto different substrate surfaces such as carbon, linear polyethylene and smooth copper. They always found an adsorbed film on the surface for both hydrophilic and hydrophobic surfaces. Ellipsometry in addition of interferometry [18,19] was applied to detect the precursor film in front of the spreading droplet in complete wetting regime. Kavehpour et al. [19] combined a reflecting light microscope with an electro-optically phase-shifting laser feedback interferometer and found that the precursor length decreased with increasing the contact line velocity. Recently, Hanchak et al. [20] utilized a microscope-based reflectometry to measure thin film profile of complete-wetting n-octane on silicon wafer. They also used the Shack–Hartmann sensor to achieve higher speed and larger observable area [21].

The profile measurement in partial wetting regime is much more difficult than complete wetting because of the sharp thickness change at the contact line. Wiegand et al. [22] used reflection interference contrast microscopy and the lateral resolution was about 200 nm which was applicable only for low contact angle droplets. Gokhale et al. [23] improved data analysis technique to analyze the interferometry images of condensing droplets in a vapor chamber. They successfully obtained the meniscus film profile as well as the adsorbed film thickness. Gokhale et al. [24] also used the same experimental setup for evaporating droplets and found that the contact angle decreases by increasing the receding interface characteristic velocity due to higher evaporation. Recently tapping-mode atomic force microscope (TM-AFM) has shown the potential. After a series of work on non-volatile droplets [7,8,10], for volatile liquids Deng et al. [25] have depicted the nanoscopic film morphology of an equilibrium water contact line. Most recently Mehrizi and Wang [26] measured evaporating films, however the evaporation was driven by an environmental vapor heating instead of substrate heating. Partially due to the lacking of experimental information, the available models for partial wetting evaporation are basically following those for non-volatile liquids. As summarized in Table 1, in practical heat-transfer models the microscopic contact angle was either a variable or constant and mostly assumed constant. Usually a small truncation with an arbitrary thickness was used to avoid hydrodynamic also heat transfer singularity at the contact line. In more comprehensive models complex intermolecular forces in the form of the disjoining pressure have been considered and bending profiles at nanoscale were predicted [12]. Recently Li et al. [27] and Radha et al. [28] reported ultrahigh evaporation fluxes for nano menisci in nanochannels. The heat fluxes based on their modeling were breaking the limits predicted by the classical Hertz-Knudsen-Schrage equation.

The present study was to provide urgently needed nanoscale information about the partial-wetting evaporating contact line. Macro droplets with diameters of more than hundreds of microns were heated on silicon wafers to have the evaporating contact lines. Complete-wetting films as well as non-volatile films were also measured for comparison. Advancing contact lines were also studied.

2. Experimental setup

A state-of-the-art tapping-mode atomic force microscopy (MFP-3D-BIO, Asylum Research) has been used, based on its outstanding performance for soft matters like liquids and cells [7,36]. A schematic diagram of the experimental setup and a snapshot of the test section are presented in Fig. 1. Water, water-glycerol mixture and formamide (HO–C–NH$_2$) droplets were tested. The droplet evaporation was occurring either in a closed vapor chamber or in open still air where the temperature is 20 °C. A humidity sensing cell (AR) has been used to develop the chamber. The chamber was made of PEEK and the cover sealing was made of FKM to prevent contamination on the sample. There were ports on the chamber's walls that allowed to use heater and sensors to control and measure the temperature. The components of the chamber refer to the exploded view shown in Fig. 1(a). For the tests in the vapor, water droplets were put in the chamber. When saturation state was reached under room temperature 20 °C, the droplets stopped evaporation and we turned on the heater below the substrate and increased the substrate temperature by 1–3 °C to make contact lines evaporate and recede slowly. For the tests in open air, formamide and water-glycerol mixture droplets were used and the room humidity was around 25%. We didn't measure water evapo-

Table 1
Modeling studies in the literatures on evaporating contact line in partial wetting regime.

Authors	Object	Factors and equations	Boundary conditions and profile structure
Hu and Larson [29]	Water droplet in still open air without substrate heating; Millimeter-sized droplet	Vapor diffusion in air	Contact line pinned; Thin film profile assumed following the bulk i.e. part of a spherical cap; Fining mesh at the contact line
Janecek and Nikolayev [12,30]	Water wedge in pure vapor on heated substrate; Millimeter-sized droplet	Evaporation; Lubrication approximation; Marangoni; Disjoining pressure	Moving contact line with constant θ_m; θ_D dependent on U; bending within 2 nm thickness
Semenov et al. [31]	Water droplet in still air on copper with and without substrate heating	Diffusion and evaporation; Navier–Stokes equation in liquid; Conduction inside the substrate	Contact line pinned; Spherical cap; Fining mesh at the contact line
Ajaev [32]	Water and *n*-decane in vapor with uniform substrate heating; Millimeter-sized droplet	Evaporation; Lubrication approximation; Marangoni; Disjoining pressure	Quasi-steady; Assuming adsorbed layer in front of the droplet to resolve singularity; $\theta_m = 0$
Ajaev et al. [33]	Water on the inclined heated substrate; Micron film	Frumkin–Derjaguin theory for equilibrium contact angle; one-sided model of evaporation. Marangoni flow	Singularity relaxed by the extended meniscus; Apparent contact angle changes by contact line velocity; No bending observed
Semenov et al. [34]	Water in air on copper with substrate heating; Sub-micron droplets	Evaporation; Marangoni; Stefan flow	Contact line pinned; Spherical-cap; apparent contact angle $\theta_{ap} = 90^\circ$ to remove the heat flux singularity
Akkus et al. [35]	In saturated vapor with substrate heating; Micron droplets	Kucherov-Rikenglaz equation for evaporation; Navier–Stokes equation; Bi-directional SEM modeling	Singularity relaxed by the extended meniscus; Apparent contact angle assumed constant