Dynamic Wettability Study at Nanoscale

Imaging in ESEM of Nanodroplet Nucleation and Growth

Quantitative wettability study at nanoscale was developed using transmitted electrons in the environmental scanning electron microscope. Water condensation was studied for the initial stages of nucleation and growth over nano-thick self supported water films. Irregularities at the water film boundaries constituted nucleation sites for filmwise and dropwise condensation. In situ imaging provided nanodroplet growth power law dependence and a dynamic study of coalescence events.

Background and Introduction

Wettability study of surfaces at nano-scale spatial resolution and high temporal resolution is an emerging field from both theoretical and practical aspects. Beyond its fundamental significance for nucleation and growth processes, wettability aspects are of large technological relevance for nanofluidic technology, soft lithography, lab on chip devices and other biotechnological and materials applications. Device miniaturization would require the understanding of the physical phenomena associated with the nanoscale, and in particular the role of boundary conditions. The development of innovative wettability experimental methods for the nanoscale and the in-situ dynamic characterization are the motivation for the current research.

The two main imaging methods for wettability study at high spatial resolution are the atomic force microscopy (AFM) and the environmental scanning electron microscopy (ESEM) [1]. The AFM method provides wettability study of nano-scale droplets over solid surfaces being limited to time resolution of a few minutes. Wettability study by ESEM is usually restricted to micron size droplets over bulk surfaces with 1 s time resolution. In-situ condensation and evaporation experiments in ESEM on smooth and textured bulk surfaces provides static contact angles as well as retarding and advancing angles by analysis of reflected secondary electrons due to electron-specimen interaction [2-3].

The innovated quantitative method for wettability study at nanoscale [4-6] is based on measuring transmitted electrons through nanodroplets using wet scanning
transmission electron microscope (wet-STEM) detector in the ESEM.

The quantitative information of the nanodroplet shape and contact angle was obtained by fitting Monte Carlo (MC) simulation results for transmitted electrons through spherical cap geometry with the experimental wet-STEM results using calibration polystyrene particles [4]. The characterization was demonstrated for the initial stages of nanodroplet condensation over self-supported nano-thick water films, which were produced in the holes of a holey carbon TEM grid.

The wet-STEM study of nanodroplet growth on self-supported thin films is typically of 10 nm spatial resolution and 1 s temporal resolution. It is conducted by controlling the humidity conditions of the sample, while increasing or reducing the ESEM chamber pressure at constant sample temperature for simultaneous condensation or evaporation around the dew point. Irregularities at the water film boundaries constituted nucleation sites for dropwise and filmwise condensation. The dynamic study provided the initial stage of nucleation (above the 10 nm resolution limit) and the growth power law dependence of single droplets under constant humidity conditions.

Experiments

Investigation was carried out using wet-STEM detector in the FEI Quanta 200 field emission gun (FEG) ESEM. The FEI wet-mode STEM detector is a solid-state two segment device attached underneath the sample grid holder assembly. The samples were holey carbon mesh copper grid being immersed in distilled water. Prior the ESEM pump down process, the samples were cooled down to 2°C by a Peltier cooling wet-STEM stage. The relative humidity (RH) in the specimen chamber was controlled by the pressure and temperature following the water-vapor phase diagram [7]. Condensation on these thin water films was obtained by elevating the chamber pressure in increments of 0.1 torr up to about 5.3 torr, while in situ wet-STEM imaging at constant sample temperature of 2°C. The dynamics was
successively recorded using bright-field (BF) STEM acquisition mode with 1 s intervals, determined by the solid-state detector response time. Relatively low scan magnifications (typically of 10 nm pixel resolution) were used for reducing the e-beam heating and contamination effects. The same order of magnifications and a similar e-beam dose were previously applied in ESEM for wettability study of solid interfaces [3], providing a clear distinction between hydrophobic and hydrophilic regions with corresponding contact angle measurement.

**Results and Discussion**

For the bright field STEM images (figs. 1-3), the grey scale levels are: bright for empty holes, dark for the carbon grid and grey for the thin water layers inside the holes. Droplets with typical lateral radius of 100 nm are shown on the carbon film and over the ultrathin water layers in the grid carbon empty holes (indicated by an arrow at fig. 1a). Figure 1b shows the calibrated measured intensity profile across the center of a nanodroplet and the calibration nanoparticle together with the MC simulation results. The droplet structure was fitted to the calibrated experimental results using a spherical cap geometry model and the contact angle was derived accordingly [4]. In addition to possible hydrocarbon contaminates, the droplet shape and contact angle are affected by pinning at the interface between the thin water layer and the holey carbon.

Complete and partial wetting phenomena (filmwise and dropwise growths correspondingly) are observed at figures 2-3 during *in situ* water vapor condensation over thin water films in vicinity of the carbon-water interface. Figure 2 shows the stages of the filmwise condensation process over the thin water films. The initial stage shows a thin film inside a carbon hole (arrow at fig. 2a). Upon increase of pressure from 5.3 torr (fig. 2a) to 5.5 torr (fig. 2b) at constant temperature of 2°C, a continuous film of water is formed from the outer film boundaries (at the carbon interface) towards the center (arrows at fig. 2b). As time proceeds, there is an increase in both the thickness and width of the layer (fig. 2c), and finally it breaks up into drops (fig. 2d) due to the capillary forces (for these scales the gravity is neglected).

Dropwise condensation was dynamically studied as shown in figures 3a-b for $t = 13$ s and $t = 27$ s following the initial nucleation at $t = 0$ s. The fitting droplet growth power law (signed here by $\mu$) for duration between $t = 14$ s and $t = 27$ s (at 94% constant RH) provided a value of $\mu = 0.55 \pm 0.02$ for the upper droplet (indicated as "1" at fig. 3a). Power law value of $\mu = 0.30 \pm 0.02$ was measured for several droplets, such as the one at the bottom of figure 3a (indicated as "2"). As elsewhere described [8], for small droplets, which have high perimeter to area ratios, the
growth is dominated by diffusion of water from the surrounding to the perimeter of the droplet, and is expected to obey power law dependence on time with $\mu = 0.5$. According to this description, for large droplets, the vapor nucleates at the droplet surface with power law dependence of $\mu = 1$. However, lower power law values of $\mu = 1/3$ have been reported [9] as well. The release of latent heat of condensation has to be evacuated through the substrate using a cooling device. In case that the heat of condensation cannot be released through the substrate, the temperature of the drop increases and the growth slows down and can even stop. Effective growth exponents of $\mu < 1/3$ were previously reported [10] for bulk samples under such conditions. Repeated experiments in current wet-STEM experimental set-up showed a distribution of power law values corresponding to $\mu = 0.5 \pm 0.2$, i.e., with variation beyond the error of the experiment.

Multi-droplet condensation and growth over self-supported thin liquid films provided imaging of nanodroplet at separation close to the resolution limit of 10 nm. Ref. 6 showed nanodroplets upon coalescence, which occurred within the 1 s time resolution over 30 nm droplet separation gap.

**Conclusions**

This work is unique in studying droplet growth at fluid self supported interface with 1 s temporal and 10 nm spatial resolutions. The kinetics of the nanodroplets supports previous power law growth description for the micron and sub-mm drops. However, the spread in power values for droplets within the same imaging area might indicate sensitivity of the dynamics at nano-scale to structural heterogeneties at the film boundaries, nucleus shape and possible thermal fluctuations. The nano-scale droplet growth is further affected by droplet-droplet interaction upon coalescence.

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**References**

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