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MOLECULAR DYNAMICS SIMULATION AND MEASUREMENT OF CONTACT ANGLE OF WATER DROPLET ON A PLATINUM SURFACE

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ABSTRACT

A water liquid droplet in contact with a platinum surface was simulated by the molecular dynamics method. Water molecules were modeled by SPC/E and one layer of harmonic molecules represented the platinum surface with the constant temperature heat bath model using the phantom molecules. Here, the water-platinum pair potential developed by Spohr (1989) based on extended Hückel calculations was employed. In the spreading process of the liquid droplet on the platinum surface, the area of contact region between water and platinum expanded just in proportional to the one-third power of time. This spreading rate was clearly in contrast to the case of Lennard-Jones droplet.

The contact angles of water on a platinum surface under saturated conditions are measured. The measurements are made in a vacuum container using de-ionized and degassed water on a clean platinum surface. The equilibrium static, advancing and receding contact angles are measured by changing the orientation of the platinum surface. The droplets of different masses are placed on the horizontal platinum surface. The surface is the inclined to 20, 30 and 40 degrees. The advancing and receding contact angles under these conditions are measured.

NOMENCLATURE

A	Area of water-platinum interface, (nm^2)
D	Initial droplet diameter, (mm)
m	Mass of droplet, (kg)
R	Nominal radius of first layer, (nm)
r	Inter-atomic distance, (Å)
t	Time, (ps)
T	Surface temperature, (°C)

Greek Symbols

α	Surface inclination angle, (degrees)
θ	Contact angle, (degrees)
ρ	Length of projection of distance vector onto surface plane, (Å)
ϕ	Potential, (10^{-19} J)

Subscripts

H2O-Pt	Between water and platinum surface
H-Pt	Between hydrogen atom and platinum surface
O-Pt	Between oxygen atom and platinum surface

INTRODUCTION

Molecular level understanding of dynamics of liquid and solid interface is important for phase change heat transfer such as evaporation and condensation. The authors have presented studies on equilibrium liquid droplet [1], vapor bubble nucleation [2], and liquid droplet nucleation [3] for the simple Lennard-Jones fluid system. By changing the potential parameter between fluid and solid molecules, considerable information is obtained about the wetting of surface. However, water is one of the most important molecules in engineering and in theoretical framework. Here, a molecular dynamics simulation of water droplet on platinum surface is performed. The spreading phenomenon of water on the surface was considered. The experimental measurements are also conducted for contact angles as a function of droplet sizes and surface orientation.

MOLECULAR DYNAMICS SIMULATION

The calculation system is shown in Fig. 1. Platinum surface was located at the bottom and mirror boundary condition at the top and periodic boundary conditions in 4 sides were employed. Water molecule was modeled with the well-known SPC/E model [4] and the platinum surface was represented by just one layer of <111> surface with 2900 harmonic molecules. The phantom molecules [2,3,5] were used beneath the layer of platinum surface in order to mimic the constant temperature heat bath. Harmonic potential parameters for platinum-platinum atoms were set as 46.8 N/m (spring constant) and r_0 = 0.277 nm (nearest neighbor distance). As the potential function between water and platinum surface, we employed the model developed by Spohr [6]. This potential model was derived from the extended Hückel calculations between a water molecule and a platinum cluster. The potential function is described as follows.

$$\phi_{H_2O-Pt} = \phi_{O-Pt}(r_{O-Pt}, \rho_{O-Pt}) + \phi_{H-Pt}(r_{H_1-Pt}) + \phi_{H-Pt}(r_{H_2-Pt}) \quad (1)$$

$$\phi_{O-Pt} = \{1894.2\exp(-1.1004r) - 1886.3\exp(-1.0966r)\}f(\rho) + 10^6\exp(-5.3568r)\{1 - f(\rho)\} \quad (2)$$

$$\phi_{H-Pt} = 1.7142\exp(-1.2777r) \quad (3)$$

$$f(\rho) = \exp(-0.5208\rho^2) \quad (4)$$

Here, r is inter-atomic distance, ρ is the length of the projection of the distance vector onto the surface plane. In these equations, the unit of potential energy is in 10^{-19} J, and is Å for r and ρ. This potential has the minimum value when a water molecule sits on top of a platinum atom with the dipole moment directing upward. This configuration of a water molecule is in good agreement with experimental result of single water molecule on platinum surface. Fig. 2 shows configurations of small cluster of water on the surface. Because of the hydrogen bonding of water molecules, each water molecules has different orientation from the single water case.

The famous Ewald method is usually used for the long-range correction of Coulomb potential. However, we used the cut-off method proposed by Wolf et al [7] in order to increase the computational efficiency. We employed the large cut-off length of 25 Å between water and water molecules and 15 Å between water and platinum atoms. The leap-frog method is used for the numerical integration of the equation of motion with the time step of 0.5 fs.

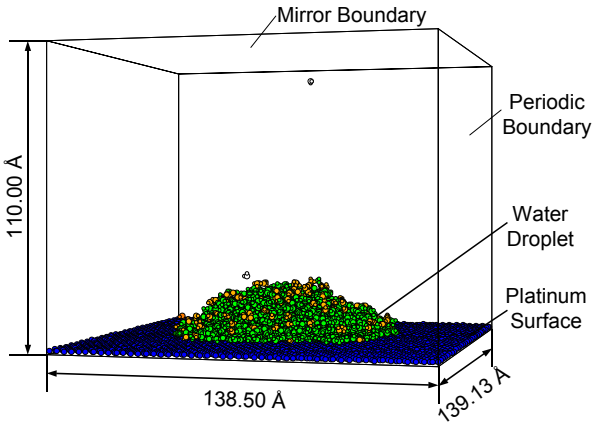


Figure 1: System Configuration.

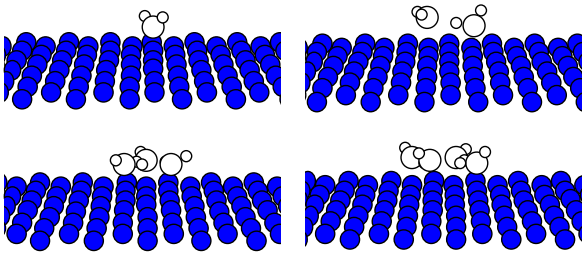


Figure 2: Small water clusters on platinum surface.

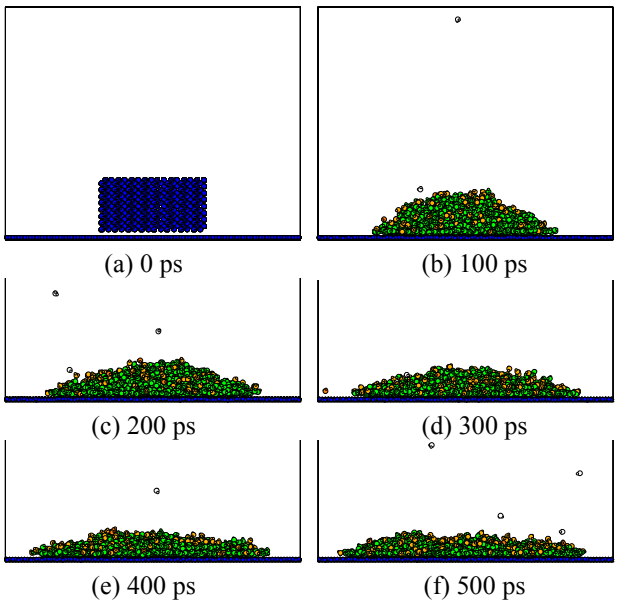


Figure 3: Snapshots of water droplet on platinum surface.

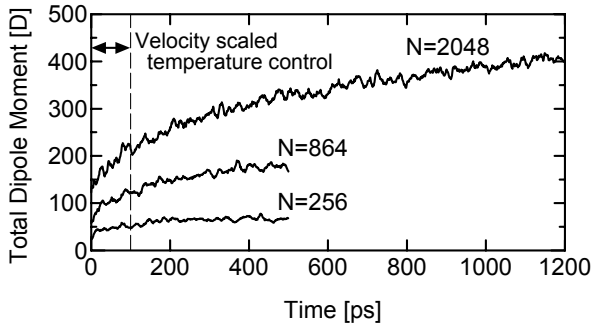
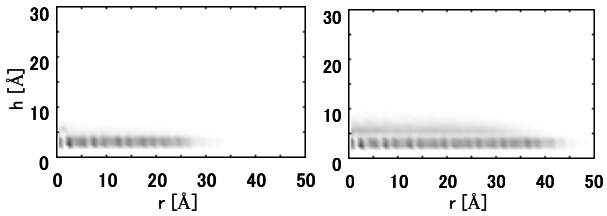


Figure 4: Variations of total dipole moment.



(a) N=256 (b) N=864

Figure 5: Two dimensional density profiles of small water droplet.

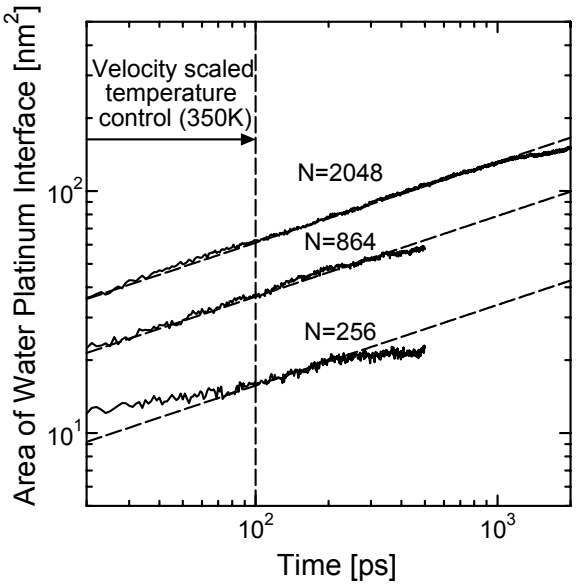


Figure 6: Expansion of water-platinum contact area.

As the initial condition, a water droplet with 256 to 2048 molecules with the density of bulk water at 350 K was placed on the center of the platinum surface of 138.50×139.13 Å. For the initial 100 ps, velocity scaling was used for the temperature control. After this initial rough control, only the phantom heat bath was used as the temperature control at 350K.

Figure 3 shows the snapshots of the water droplet with 2048 molecules. During the velocity scaling temperature control in 100 ps, the liquid vapor interface was already in spherical cap shape. Then, the gradual spreading of the water droplet was observed. Figure 4 shows the change in total dipole moment of the system. The increase of the total dipole moment is the good measure of the average orientation of water molecules. Since the contribution to the total dipole moment from a relatively free water molecule is large, the increase in the dipole moment shows the spreading. The smallest system with 256 water molecules reached the equilibrium at about 200 ps with the almost constant total dipole moment. The system with 856 molecules reached the equilibrium at about 400 ps. For the largest 2048 system, the equilibrium was not obtained even after 2000 ps.

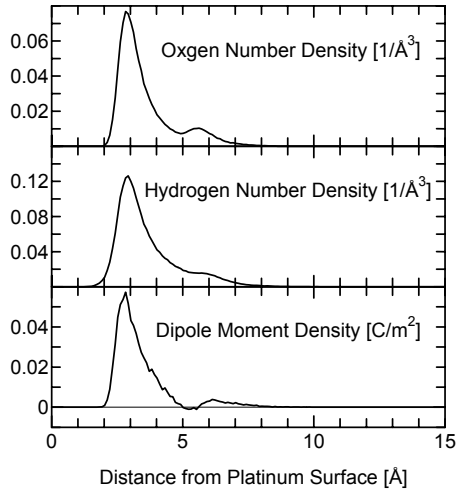


Figure 7: Oxygen, hydrogen and dipole moment density profile.

Figure 5 shows the two-dimensional density distribution of the water droplets in the equilibrium condition. It is clearly seen that only a monolayer of water is dominant for the 256 water system. Only a few molecules stayed on the monolayer. For the 856 water system, a minor second water layer was formed.

The spreading of water droplet is measured in Fig. 6 as the area of water-platinum interface. Except for the initial 100 ps when the velocity-scaling temperature control was done, this change of the interface area was proportional to the one-third power of time. Here, the deviation from the straight line is observed at the end of simulation when the equilibrium with constant area is approached. The broken lines are fit lines with $A \propto t^{1/3}$, or $R \propto t^{1/6}$ with the nominal radius of the first layer. Inspired by the direct ellipsometric measurements of monolayer and terraced liquid film [8], spreading of liquid on completely wet surface has been studied extensively in this decade. Even though the experimentally assigned spreading rate was $R \propto t^{1/2}$ [8], initial molecular dynamics simulations using Lennard-Jones potential resulted in contradictory $R \propto \log(t)$ [9] or $R \propto t$ [10] depending on the volatility or the surface conditions. More recent large-scale molecular dynamics simulations could predict the correct spreading rate; $R \propto t^{1/2}$ and extensive efforts of the modeling were being performed [11 and references therein]. The much slower spreading rate of water on the platinum surface compared with the case of simple molecules is probably because of the large friction of contact line movement due to the commensuration of water layer to the platinum crystal.

Figure 7 shows the number density distributions of oxygen and hydrogen and dipole moment distribution averaged from 1800 ps through 2000 ps for the system with 2048 water molecules. All distributions show that only the 2nd layer of water is formed in such a relatively large system. Here, the first peaks of oxygen number distribution and hydrogen number

distribution are almost at the same distance from the wall. Since single water molecule orients such that hydrogen atoms directing upward from the surface, this coincidence in the first peak positions indicates the strong hydrogen bonding within the first layer. The dipole moment distribution has the strong peak at the first layer and the distribution is much smaller at the second layer. The negative value of the dipole moment means that average orientation of water molecules in the second layer is opposite to the first layer probably because of the hydrogen bonding.

EXPERIMENTAL EVALUATION OF CONTACT ANGLE

To complement the theoretical work presented in the preceding sections, the contact angle for a water-platinum combination was determined experimentally. The objective was to obtain advancing and receding contact angles on a clean, polished platinum surface in the atmosphere of water vapor.

The procedure followed was similar to that reported by Kandlikar and Steinke [12]. The system was modified to include an evacuated vapor chamber.

EXPERIMENTAL SET-UP

The experimental apparatus was designed to provide an environment consisting of water and water vapor. The apparatus consisted of a stainless steel cylindrical vessel with viewing windows, a droplet delivery system, a leveling stage, a heated surface, and a cartridge heater. Figure 8 shows the schematic of the experimental apparatus.

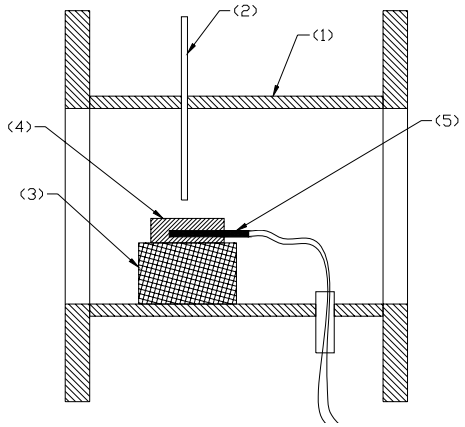


Figure 8: Experimental Apparatus. 1) Evacuated Cylindrical Stainless Steel Vessel, 2) Droplet Delivery System, 3) Leveling Stage, 4) Heated Copper Surface, 5) Cartridge Heater.

The vacuum chamber was constructed using stainless steel material. It consisted of a pipe and sealing flanges. The vacuum penetrations were also constructed of stainless steel material. The viewing windows were constructed of ½" thick Lexan polycarbonate. Lexan was selected for its very low outgassing properties, 0.10% Total Mass Loss (TML) and 0% Collected Volatile Condensable Material (CVCM). A vacuum sealing epoxy was used to seal any additional penetrations. The heated surface was made of electrolytic tough pitch copper C110 (99.9% copper, 0.04% oxygen).

EXPERIMENTAL PROCEDURE

The following procedure was used to prepare the test chamber and the platinum surface. First, the platinum surface was polished using a 0.5 μm alumina slurry and a polishing wheel. This process results in a surface roughness, Ra, value of 0.02 μm (average of five readings at different locations). The surface is then rigorously rinsed in 18 MΩ de-ionized water. The de-ionized bath is repeated for five times. Next, the surface is placed on the heated copper stage in the vacuum chamber to dry. Next, the surface underwent a cleaning bath. A modified RCA clean process is used to clean the surface of any organic material. The bath consists of 1 part NH_4OH, 3 parts H_2O_2, and 15 parts H_2O. The solution is prepared and heated to 70°C. The platinum surface is placed in this bath for 15 minutes. Next, the surface is rinsed for 5 minutes in a de-ionized water bath to remove any organic material from the platinum surface.

The chamber preparation is as follows. First, the chamber was evacuated to a pressure of 19.6 torrs. Next, degassed, de-ionized water is introduced into the droplet delivery system. The chamber is then filled with water vapor. The droplet delivery system is used to gently place a single droplet on the platinum surface.

Figure 9: One Droplet on Level Platinum Surface. m = 1.15 x10^{-6} kg, α = 0º, T = 22°C, and θ = 22.05º.

Figure 10: Two Droplets on Level Platinum Surface. m = 2.3 x10^{-6} kg, α = 0º, T = 22°C, and θ = 40.81º.

EXPERIMENTAL RESULTS

The camera system and platinum stage are calibrated to ensure an accurately measured contact angle. The platinum has a surface temperature of 22°C for all of the experiments. The contact angle is measured on both sides of the droplet. Several independent experiments were performed and the

measurements are averaged over that range. For example, the measurements for the one droplet with a 0 degree inclination (horizontal surface) were; 23.9, 23.6, 21.4, 20.7, 22.8, and 20.1. All contact angle values reported are the averaged values. All measured values recorded are within ±10% of the reported average. The angles are reported with an accuracy of ± 0.5 degrees as observed through repeated measurements using a CAD program.

A single droplet is placed on the level surface. The platinum surface was oriented at a 0º inclination angle. The droplet has a diameter of 2.8 ± 0.1mm. The droplet mass is 1.15 x10^{-6} kg. Figure 9 shows 1 droplet on a level surface. The contact angle was found to be 22.1º.

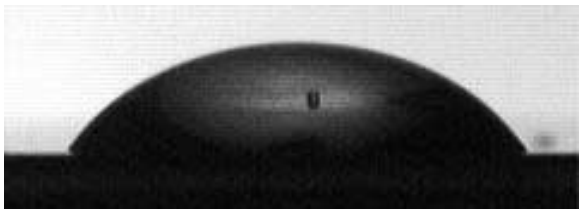


Figure 11: Three Droplets on Level Platinum Surface. m = 3.45 x10^{-6} kg, α = 0º, T = 22°C, and θ = 50.71º.

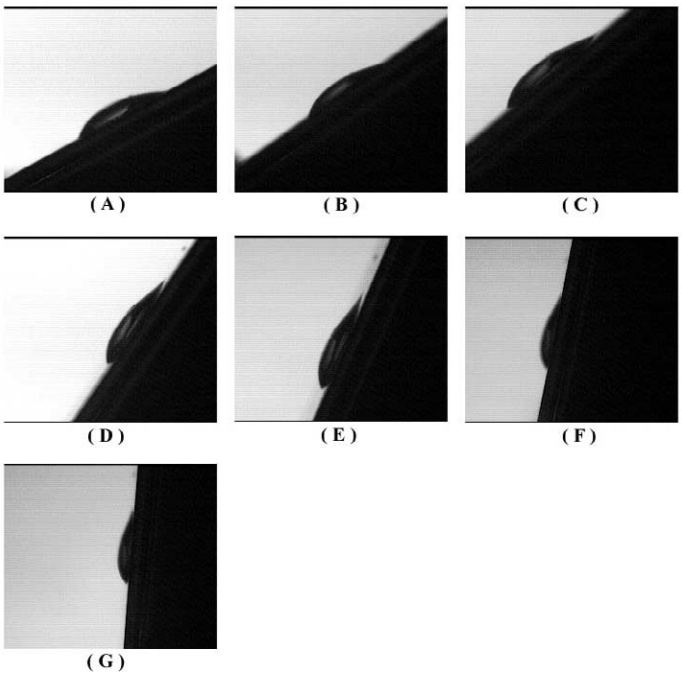


Figure 12: Single Droplet on an Inclined Platinum Surface. m = 1.15x10^{-6} kg, T = 22°C, Ts = 22°C; A) α = 28º, B) α = 36º, C) α = 40º, D) α = 56º, E) α = 67º, F) α = 79º, G) α = 86º.

Two droplets are placed on the level surface. The platinum surface was oriented at a 0 degree inclination angle. Figure 10 shows two droplets on a level surface. The contact angle was found to be 40.8º.

Three droplets are placed on the level surface. The platinum surface was oriented at a 0 degree inclination angle. Figure 11 shows two droplets on a level surface. The contact angle was found to be 50.71 degrees.

Figures 9 though 11 show the hysteresis effect. As the mass of the droplet increases, the equilibrium contact angle changes from static receding to static advancing contact angle.

The static advancing and receding contact angles can be found by inclining the platinum surface. Figure 12 shows a single droplet with a mass of 1.15x10^{-6} kg as it is tilted though a variety of angles. The surface is inclined at seven different angles as shown in Fig. 12.

The advancing and receding contact angles are reported from only the side views of the droplet. Figure 13 shows the effect of surface inclination upon the advancing and receding contact angles.

As expected, the advancing and receding contact angles vary between the limiting values. Since the droplet did not slide off at either ends, even for almost 90º inclination (vertical surface), the values reported here may not be these limiting values.

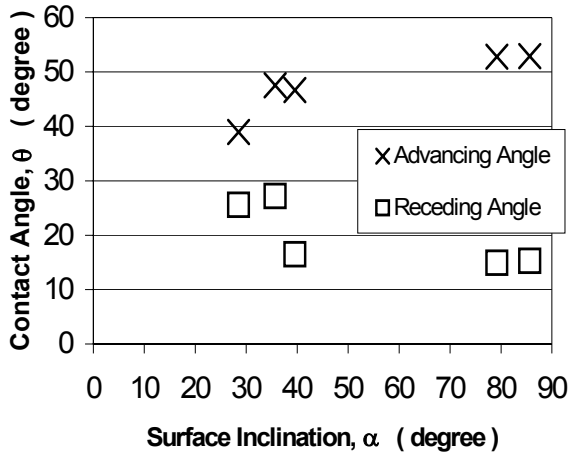


Figure 13 : Contact Angles verse Surface Inclination Angle.

Figure 14 shows a top view (camera approximately at 20º angle to the platinum surface) of the single droplet on a surface inclined at an angle of 86º. The receding edge is seen to form a tail leading into the meniscus region. In such cases, it became impossible to detect the thin region from the side view due to the resolution limits of the camera and the optical system.

Another interesting observation was made regarding the effect of surface cleanliness on the contact angle. The platinum surface was cleaned using acetone, DI water and bottled compressed air stream. The measurement of contact angle with this system using a single droplet yielded a contact angle of 61º. The effect of surface cleaning technique is therefore seen to have a significant influence on the contact angle behavior.

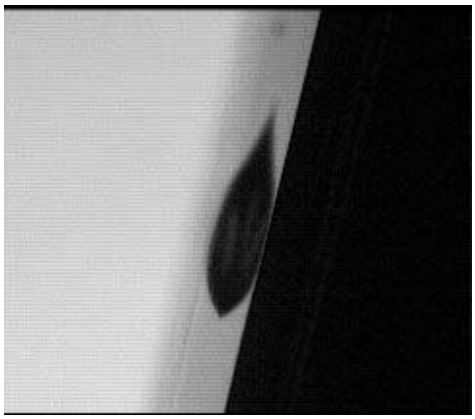


Figure 14 : Single Droplet on an Inclined Surface. m = 1.15 10^{-10} kg, α = 86 degrees, T = 22°C.

CONCLUSIONS

A molecular dynamics simulation is performed on clusters of 256 and 864 water molecules on platinum surface. The molecules spread forming a single monolayer in case of 256 molecules. In case of the 854 molecule cluster, the molecules form a thin secondary layer. From this information, it is not possible to derive the contact angle information as these layers of water molecules clearly lie in the adhesion region.

However, the following special characteristics of the spreading rate were observed: area of contact region between water and platinum expanded just in proportional to the one-third power of time. Since the same characteristic was observed for three different size droplets in the experiments, this dynamic feature may be further extended to compare with the macroscopic dynamics of the leading edge of the 3-phase contact line.

The experimental study performed on a clean platinum surface in water vapor environment at a temperature of 22ºC indicates that the limiting values of the advancing and receding contact angles were not reached even for a vertical surface with a single droplet of water. In order to gain more accurate information regarding the contact line processes, it is necessary to conduct these experiments with larger droplet sizes, which will cause droplet roll-off. The present optical system is being upgraded with high-resolution optics to obtain better pictures in the contact line region.

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