## **Supporting Information:**

# Molecular Origin of Fast Evaporation at the Solid-water-vapor Line in a Sessile

## Droplet

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### 1. Methods and materials

An adsorption region is placed above the water droplet in the upper boundary of the simulation cell with a cutoff of 10 nm to attract molecules evaporating from the droplet. Before the evaporation, we simulate the system to equilibrium in three-dimensional periodic boundary for cohesive energy and contact diameter calculations. We collect 100 frames of the snapshots to calculate the cohesive energy distribution and the average value is used. The total simulation time is 9 ns (first 3 ns for the equilibrium stage and the subsequent 6 ns for the evaporation stage).

The droplet is placed on the substrate in the digital analytical balance (Sartorius) to record the real-time mass during the evaporation process. The camera is used in the same horizontal level of the droplet to photograph the side-view picture of the droplet. OCA20 (Dataphysics, Germany) and LSA100 surface analyzer (Lauda Scientific, Germany) are applied to detect the glass spheres on water droplet. The glass substrate is the slide, purchased from Sail Brand, China. The hollow glass spheres are provided by Sinosteel Maanshan New Material Technology Co., Ltd. The glass spheres are dispersed into deionized water at diverse concentrations

for evaporation test. We did not consider the effect of the surface charge in our experiments.

In our experiments, we use the pipette to get  $5.5-\mu$ L water droplet (containing the glass spheres) and place the droplet gently on the glass surface. The digital analytical balance records the real-time mass during the evaporation process of the water droplet.

## 2. Definition and calculation of the contact diameter in simulations

Contact diameter used in the paper is the average value of 100 contact diameters from 100 frames within time interval of 2 ps. In the first 2 ns, the contact diameter changes little, indicated by light grey span, and then decreases (dark grey region).



Figure S1 | Contact diameter remains almost the same during initial evaporation stage.

## 3. The L-J interaction equation

We get different contact diameters by changing the parameters in the L-J equation:

$$E = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right].$$

The  $\varepsilon$  and  $\sigma$  are well-depth and zero-energy distance respectively.

The parameters for different atoms are derived in the following form:

$$\varepsilon_{ij} = \sqrt{\varepsilon_i + \varepsilon_j},$$
$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j).$$

## 4. Calculation of the cohesive energy

We divide the droplet into small regions and calculate the average interaction on water molecules. Resolutions for height and radius are 0.25 nm and 0.8 nm. Other resolutions show the same results with difference in the value of cohesive energy  $(E_c)$ . The cut-off for  $E_c$  is 1 nm and a larger cut-off brings negligible change as shown below.



**Figure S2** | Delta value for  $E_c$  when the cutoff is 1 nm and 3 nm. The delta value is small compared to the  $E_c$ .

# 5. Evaporation at the contact line

We show the evaporated number of water molecules from different parts of the droplet. For different evaporation time, we find that largest number of molecules evaporates from the contact line.



**Figure S3** | Molecules evaporated ( $N_{eva}$ ) from surface at different heights within (a) 1 ns, (b) 2 ns and (4) 4 ns respectively. (d) The height (H) of the surface position as used in our manuscript Figure 2(c). Note that the zero-point is located at the bottom of the Si substrate as used in our manuscript.

## 6. Relationship of evaporation between contact diameter

We show the relationship between the evaporation rate and the contact diameter

on different substrates for different evaporating time in the following figure:



**Figure S4** | Relationship between evaporation and contact diameter for different evaporation time: (a) 3 ns; (b) 3.6 ns.

The evaporation rate derives from the number of molecules moving off the droplet and contact line is equal to contact diameter by multiplying with a constant  $\pi$ . We should point out that the contact diameter is the initial contact diameter rather than real-time diameter. The results indicate that the initial contact diameter determines the evaporation rate of the whole. Substrates affect the evaporation rate by changing the contact diameter.

## 7. Cohesive energy from the substrate

We calculate the effect of substrate on  $E_c$  as well. The interaction of substrate on the droplet is negative and thus it attracts the water molecules from the droplet, promoting the evaporation. The substrate works in the range of 1 nm below the dashed red line, out of which the interactions from substrate is zero.



Figure S5 | (a)  $E_c$  induced only by the substrate. The energy is negative, meaning the substrate attracts water molecules from the droplet and enhances the evaporation. (b)  $E_c$ -map without effects from the substrate.

### 8. Experimental part of glass sphere in increasing the evaporation rate

The glass spheres float on the water droplet. Although some spheres are submerged in the droplet, a few spheres float on the surface and increase the length of solid–water–vapor contact line. We notice that spheres rise up in the droplet and then float on the droplet and time is needed for the rising.



**Figure S6** | Distribution of glass spheres. (a) Partial of the droplet profile. Scale bar: 0.5 mm. The rifts in the red ellipses suggest that the glass spheres float on the surface, which is different from the continuous spherical water surface. (b) Side view of glass spheres on the glass box. Some spheres constitute the glass–water–vapor contact line.

In the experiments, we conduct two evaporation measurements listed in the following figure for droplet on glass slide with and without glass spheres. When glass spheres are added to the water droplet, the evaporation time (the time needed for a droplet to become dry with mass = 0) is decreased. The mass of the droplet with spheres decreases more sharply than that without spheres.



**Figure S7** | Mass change as a function of time for droplets with and without (w/o) glass spheres. The glass sphere concentration is 20 g/L.