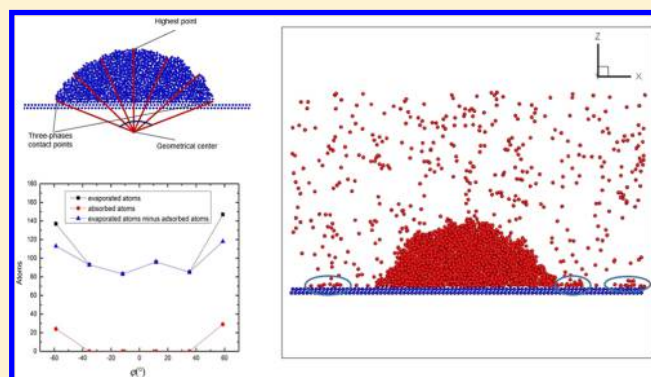


Evaporation Flux Distribution of Drops on a Hydrophilic or Hydrophobic Flat Surface by Molecular Simulations

Chiyu Xie,[†] Guangzhi Liu,[†] and Moran Wang^{*}

Department of Engineering Mechanics and CNMM, Tsinghua University, Beijing 100084, China

ABSTRACT: The evaporation flux distribution of sessile drops is investigated by molecular dynamic simulations. Three evaporating modes are classified, including the diffusion dominant mode, the substrate heating mode, and the environment heating mode. Both hydrophilic and hydrophobic drop-substrate interactions are considered. To count the evaporation flux distribution, which is position dependent, we proposed an azimuthal-angle-based division method under the assumption of spherical crown shape of drops. The modeling results show that the edge evaporation, i.e., near the contact line, is enhanced for hydrophilic drops in all the three modes. The surface diffusion of liquid molecular absorbed on solid substrate for hydrophilic cases plays an important role as well as the space diffusion on the enhanced evaporation rate at the edge. For hydrophobic drops, the edge evaporation flux is higher for the substrate heating mode, but lower than elsewhere of the drop for the diffusion dominant mode; however, a nearly uniform distribution is found for the environment heating mode. The evidence shows that the temperature distribution inside drops plays a key role in the position-dependent evaporation flux.



1. INTRODUCTION

Evaporation of a liquid drop on a solid substrate has a variety of applications including particle synthesis,¹ DNA/RNA arrangement,² medical diagnostics,³ and etc. All of these applications were inspired by a common phenomenon in everyday life, known as the “coffee-ring” effect, which was first depicted by Deegan et al.^{4–6} in detail. For a pure sessile droplet, the evaporation modes can be divided into three categories:^{7–9} constant contact angle mode, constant contact area (contact line pinning) mode, and both changing mode. In order to discover the mechanisms of the “coffee-ring” effect, Deegan et al.⁶ performed a contrary experiment of a droplet evaporating on a smooth Teflon. They proved that the contact line pinning mode and the evaporation enhancement at drop edge are two necessary conditions for the “coffee-ring” formation. Later, both numerical¹⁰ and experimental¹¹ results indicated that the inside flow pattern caused by the nonuniform evaporation rate along the drop interface directly controls this effect. As a consequence, the local evaporation flux distribution is of particular importance.

Since 1997, the local evaporation flux distribution of a sessile droplet has been of great interest and studied extensively. The diffusion based theory is one of the most popular and commonly accepted theories in this field, and the first pioneering work was done by Deegan and his co-workers.⁵ They indicated that the distribution of local flux $J(r,t)$ depends on the rate-limiting step: whether is the diffusive relaxation of the saturated vapor layer immediately above the drop or the transfer rate across the liquid–vapor interface. In the latter case, the flux is uniformly distributed; while in the former case, $J(r,t)$

has an exponent relation to the position, and the followed paper⁶ gave the detailed derivation. The authors restricted their study to the contact line pinning evaporation and diffusion dominant mode, with the assumption that temperature gradients and gravity can be ignored. Thence, it reduces to a diffusion problem, and the governing equation is expressed as

$$\Delta c = D^{-1} \frac{\partial c}{\partial t} \approx 0 \quad (1)$$

where t is the evaporating time, c the local liquid vapor concentration, D the vapor diffusivity, and the evaporation flux is described as $J(r,t) = -D \nabla c$. When applying appropriate boundary conditions, the approximation to the analytic solution of local flux distribution is obtained as

$$J(r, t) \propto (R - r)^{-\lambda} \quad (2)$$

with $\lambda = (\pi - 2\theta)/(2\pi - 2\theta)$, and the other related parameters are described in Figure 1.

As eq 2 only presents an approximation relation, Cachile et al.¹² derived an explicit expression of $J(r,t)$ for the droplets of extremely small contact angle. Further, by using the finite element method, Hu et al.¹³ got semiempirical correlations between $J(r,t)$ and contact angle ranging from 0° to 90° as

Received: May 25, 2016

Revised: July 19, 2016

Published: July 21, 2016

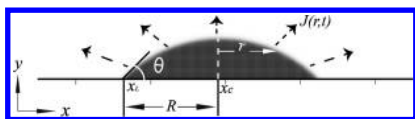


Figure 1. Physical model of a droplet evaporating on a horizontal substrate. R is the base radius, r is the distance to the drop axis, θ is the contact angle, x_c is the coordinate of droplet center, x_L is the left contact line position, and $J(r, t)$ is the local evaporation flux.

$$J(r, t) = \frac{D(c_s - c_\infty)}{R} (0.27\theta^2 + 1.30) \times (0.6381 - 0.2239(\theta - \pi/4)^2) \left(1 - \left(\frac{r}{R}\right)^2\right)^{-\lambda(\theta)} \quad (3)$$

where c_s and c_∞ are the vapor concentrations at the droplet surface and in the ambient air, respectively.

From eq 2 and eq 3, it is easily founded that $J(r, t)$ is strongly enhanced at the edge of the hydrophilic droplet and has a singular value at the perimeter. Deegan et al.⁶ proposed a “random walk” hypothesis to explain this phenomenon as a same random walk arranged at the edge allows the evaporating molecules to escape, but not the case for center. However, this explanation is somewhat suspicious, for other types of “random walk” (e.g., right side walk) may draw opposite conclusions. Unfortunately, no more better explanation is found so far.

Note that all the above studies are for the drops with a contact angle no larger than 90° . For hydrophobic drops, there are many contributions accounting for the total evaporation rate,^{14–16} but only Popov’s work¹⁷ is able to consider the local flux. Although his formula is valid for an arbitrary angle, it is too complex to operate analytically, and the author himself never gave any explicit results yet. Until recently, some results came out by using the commercial software, Wolfram Mathematica,¹⁸ which found that $J(r, t)$ drastically diminishes at the edge, conflicting with the hydrophilic cases. The results were explained by the smaller space for evaporation occurrence near the contact line; however, it also needs more validations. Nevertheless, this series of results based on the diffusion based theory have many applications such as predicting inside flow patterns,^{19–21} particle concentration mode controlling,^{22–25} and calculating the critical droplet size.²⁶ Simultaneously, many developments were made in countering thermal conduction at the base^{27,28} and removal of the spherical cap limitation.²⁹

Besides the diffusion based theory, there are also some other methods available, including the dynamic van der Waals theory, the statistical rate theory, molecular dynamics method, etc. The dynamic van der Waals theory is on the basis of entropy and energy functions containing the gradient contributions.³⁰ By introducing this theory into the energy equation, and combining with the continuity and momentum equations, Teshigawara et al.³¹ focused on the evaporation of a hydrophilic drop on an isothermal substrate. They counted the total evaporation rate and the evaporation rate in region as just about twice the interface width around the contact line. The results showed that the evaporation almost occurred at the contact line, especially in the late stage, which was qualitatively in accordance with the results from the diffusion based theory. However, the accuracy of this method needs more careful examination because the edge evaporation rate is surprisingly higher than the total evaporation for some cases.

The statistical rate theory (SRT), originally proposed by Ward³² in 1977, is a quantum thermodynamic based kinetic

approach and able to predict evaporation and condensation rate without any fitting parameters.³³ Unlike the diffusion based theory, SRT takes the temperature gradients into account and matches well with the experimental data.^{34,35} Duan et al.^{36,37} derived the expression of local evaporation flux by using this theory for hydrophilic cases. Combining with the experimental measurements, Duan et al. obtained a series of local flux distribution curves under different thermal conditions for a drop evaporating on a stainless steel funnel. Under most conditions, the local flux increases from the drop center to the periphery, which is the same as the diffusion-based predictions. The authors indicated that the temperature gradients at interface and the thermocapillary convection were necessary for the nonuniform flux distribution. However, there also emerged some different regularities, in which the maximum flux occurred in the region between the edge and center, but these “strange” behaviors have not been explained yet.

Since a complete understanding of drop evaporation and a usable evaporation flux distribution function are still vacant, a molecule-based method may provide a better way to discover the mechanisms. Sumardiono and Fischer³⁸ have studied a central drop evaporation heated by vapor. Wilhelmsen et al.³⁹ used square-gradient theory and nonequilibrium molecular dynamics to study the influence of curvature on the transfer coefficients for evaporation. Among those MD contributions, only one was found directly related to the issue of evaporation flux distribution,⁴⁰ which studied droplets evaporating on smooth heated substrates, with both hydrophilic and hydrophobic cases considered. This study divided the droplet into two spatial regions and counted the evaporation rate respectively: one region close to the substrate within a few molecular diameters height, and the other covering the rest drop surface. Based on this division, they concluded that the evaporation occurred preferentially in the vicinity of the contact line for the hydrophilic drops, which was consistent with the diffusion based analysis; while for the hydrophobic drops, there was no preferential location for the evaporation flux, which was different from the diffusion based analysis. Although the MD modeling gave reasonable results for hydrophilic drops, the division method is too rough to capture the evaporation flux distribution along the interface. Moreover, the results for hydrophobic drops are under doubt and they gave no explanation. Finally, they just considered one condition that the substrates were heated. As known, different conditions lead to different results, and therefore a more comprehensive MD modeling and a more systematic comparison with continuum theories are necessary for different conditions.

As is seen, the diffusion-based theory is limited to the diffusion assumption, while the results obtained by other methods are more suitable for temperature-controlled evaporation modes in general. In addition, it seems that there were some debates on the evaporation flux distribution regularities of hydrophobic drops. Therefore, this work aims to investigate the flux distribution of evaporating droplets under different conditions by MD simulations, and both hydrophilic and hydrophobic cases will be considered. Three evaporation conditions are compared: (a) the diffusion dominant mode, (b) the substrate heating mode, and (c) the environment heating mode. In order to count the flux distribution more accurately, an azimuthal angle-based division method will be proposed for careful comparisons.

The rest of this paper is organized as follows. In Section 2, the MD model used in our simulations is presented, and three

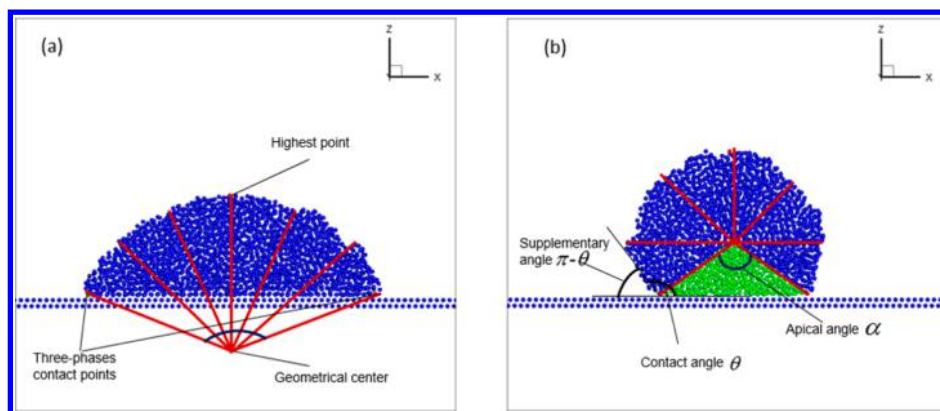


Figure 2. Angle-based division method. X - z plane of droplet on the substrate. Blue particles are liquid and solid ones, and green particles are liquid particles outside the sector. Red solid lines show the boundary of each divided region. (a) Hydrophilic case; (b) hydrophobic case.

kinds of evaporation conditions are implemented as well as the counting method for local flux calculation. In Section 3, the evaporation flux distribution results under different conditions are discussed and compared with previous works. Finally, the conclusions are drawn in Section 4.

2. NUMERICAL METHODS

In this work, as the major physics is concerned, only simple monatomic molecules are considered for both liquid and solid for simplification with a truncated Lennard-Jones potential for interaction:⁴¹

$$U(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (4)$$

where r_{ij} is the distance between two different atoms, σ and ϵ are the characteristic parameters of length and potential, respectively. In the following discussion, we will use reduced units made up of σ , ϵ , and m of a simple atom. The reduced unit of temperature is ϵ/k_B , and the reduced time unit is $\tau = (m\sigma^2/\epsilon)^{1/2}$.⁴²

2.1. Different Evaporation Conditions. Since our main focus is on the evaporation scheme, the realization of different evaporation modes and the statistics method for local evaporation flux are described as follows.

A. Diffusion-Dominant Mode. In the diffusion dominant mode, the concentration difference drives molecules to evaporate, and no temperature difference is considered in such a system. Liquid particles naturally diffuse from liquid-vapor interface to the surrounding phase by the concentration gradient. As long as the number of atoms diffusing in this direction is larger than the opposite direction, net evaporation flux appears. In order to realize this mode, we open the boundary of simulation box to vacuum when the equilibrium state is reached, and then just release the atoms that reach the boundary. We start to count up the evaporated atoms after releasing. Here, the equilibrium state means that the number of atoms reaches the box boundary keeps at a constant value with reasonable fluctuations. It is noted that, the boundary of simulation box is not that far away from the drop; therefore the situation here is a little different from the general case, as a drop evaporates to an infinite space.

B. Substrate Heating Mode. In the substrate heating mode, the evaporation is mainly caused by the hot substrate, which is commonly seen in industrial applications. In order to realize

this mode and be able to compare with previous work as mentioned in the introduction, we heat up the substrate through a thermostat after the system reaches an equilibrium state from the initial state. As a result, the atoms near the substrate would vibrate stronger and drive more molecules at the interface to escape the liquid, i.e., evaporate. In this mode, the simulation box is closed and the equilibrium state is defined as the state when the balance of evaporated molecules and condensed molecules is reached.

C. Environment Heating Mode. Because of numerous common existences in our daily life, we consider another evaporation mode, the environment heating mode, in this work. In this mode, the simulation box is closed as well, and the higher temperature of environment contributes most to the drop evaporation. In order to realize this mode, we suddenly rise up the temperature of vapor after the equilibrium state reaches. The evaporation occurs, and the system will get to a new equilibrium state.

2.2. Calculation of Evaporation Flux Distribution. As mentioned before, the two-region division⁴⁰ is too rough to capture the evaporation flux distribution along the interface. Therefore, we redivide the droplet into several finer regions as described in Figure 2. To exactly determine the interface position, here a cluster analysis method⁴⁰ is applied. We draw a bin around every atom, with the atom at the geometrical center of the bin. The number density of local position is obtained by summing up all the atoms in each bin. The bin size is set at $2 \times 2 \sigma^2$ in this work to ensure both the accuracy of local position and small enough fluctuation. If the number density is larger than a given value (e.g., half number density of liquid in this study), the atom type is judged as liquid, and otherwise it is treated as a vapor atom. When all the liquid phase is recognized, the contour of the drop is depicted. Three special points are marked in the contour: the two three-phases contact points and the highest point of the drop. Likewise, we assume the drop to be a spherical crown shape, which will be examined in Section 3.1. Thence we are able to get the geometrical center of the drop by judging whether the distances to the three special points are identical or not. With these two contact points and the center point, we can define an isosceles triangle. The two equal edges and the surface of the drop make up a sector. We divided the sector into six regions with uniform arc length. At every time step we count atoms crossing each arc from liquid to vapor as the absolute evaporation number, while atoms going opposite direction as the condensation number. Their difference is counted as the net evaporation flux number.

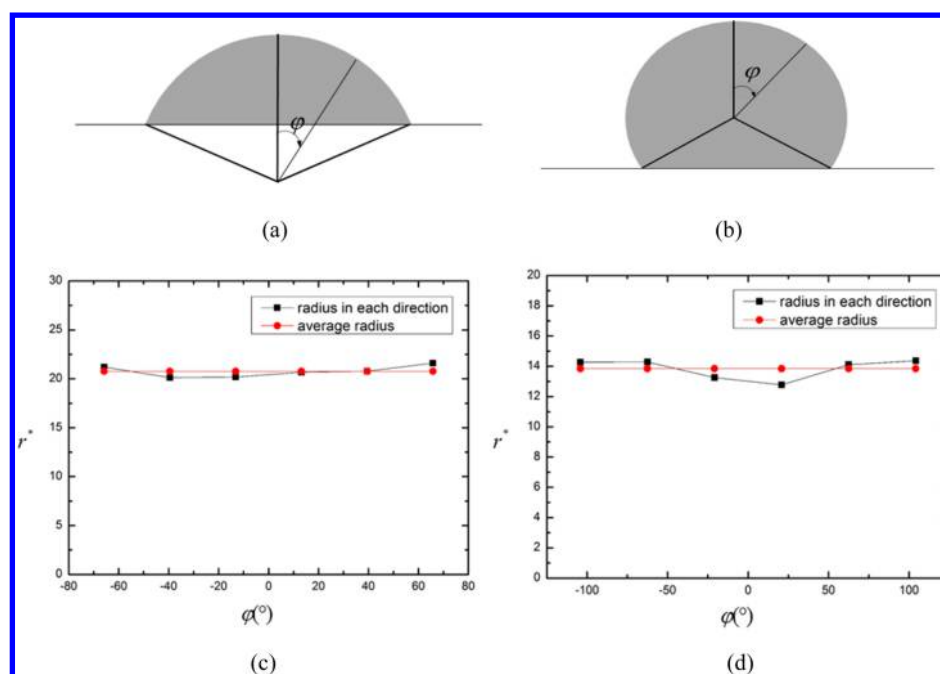


Figure 3. (a) Direction angle of the drop shown for hydrophilic case. (b) Direction angle of the drop shown for hydrophobic case. ϕ represents the direction angle. (c) Radius with respect to direction angle and their average value for hydrophilic case. (d) Radius with respect to direction angle and their average value for hydrophobic case. The radius is normalized by σ as $r^* = r/\sigma$.

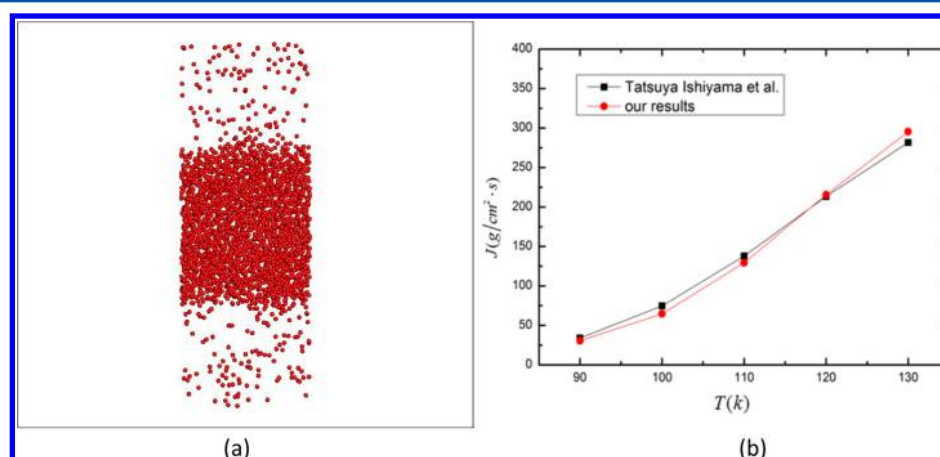


Figure 4. (a) Snapshot of a liquid film evaporation test. Red particles are liquid or vapor molecules; (b) Evaporation flux rate with respect to temperature. J is the evaporation flux rate, and T is the temperature.

Therefore, after a time averaging process in each fan-shaped region, we are able to calculate the evaporation flux distribution dependent on position.

3. RESULTS AND DISCUSSION

In this part, after the numerical framework is introduced, we give some numerical tests to validate our method. The evaporation flux distributions under three evaporation modes will be discussed.

3.1. Numerical Framework and Validations. The scale of our computation domain is set as $94.9 \times 4.8 \times 54.7 \sigma^3$, as shown in Figure 2. It is noted that we apply a periodic boundary condition to minimize the number of atoms in the y direction, and therefore two-dimensional drops are actually studied here. In other directions, reflection boundaries are applied to generate an enclosed space. There are 2424 liquid atoms in total placed tightly as a hemisphere in a FCC lattice

with a given liquid density, and no vapor atom at the beginning. It is worth mentioning that another drop with 3796 liquid atoms is simulated, but no difference of evaporation flux distribution is found. As a result, we use 2424 liquid atoms for all the following simulations. A cutoff radius of 2.2σ is used to calculate the interaction force between molecules. No far-field effect is considered, and the interaction force will not be counted in if the vapor molecules escape the domain. The interaction potentials between liquid–liquid, liquid–vapor, and vapor–vapor are all set as 1.5ϵ . The solid atoms set-ups are different corresponding to the evaporation mode: for the diffusion dominant mode and environment heating mode, two layers of solid atoms are fixed on their position in the lattice; while for the substrate heating mode, five layers of solid atoms vibrating in the vicinity of their equilibrium position under forces from liquid particles and an artificial spring are settled. The cross-interaction potential between the fluid and the solid

atoms is set as 0.65ϵ for the hydrophobic case, while 1.1ϵ for the hydrophilic one. The contact angles of equilibrium state at a temperature of $0.9\epsilon/k_B$ are about 70° and 131° , respectively. For all the interactions between different atoms, σ equals unity. In order to control the system temperature, we use a stochastic dynamics method as a thermostat.⁴³ The time step of simulation is 0.005τ . After the system relaxes to its equilibrium state, we start to change the temperature or the boundary condition according to different evaporation mode. To minimize the fluctuation of statistical results, each simulation case is run 24 times independently, and the results are averaged.

The assumption of spherical crown shape is examined primarily. By selecting atoms on the liquid–vapor surface and the mean distance of these atoms to the center in each region, we calculate and compare the mean radius of each region under the temperature of $0.9\epsilon/k_B$. To minimize the fluctuation, every radius is taken as its average value over a long period of time at equilibrium state. Figure 3 shows the comparison results for hydrophilic and hydrophobic cases as an example. Practices tell that the deviation decreases with an increasing total atoms number of drop. The deviations are found no higher than 4.0% for hydrophilic case and 7.7% for hydrophobic case when the liquid atoms number is higher than 1000. Therefore, the drop can be treated as of spherical crown shape as long as the number of liquid atoms is high enough.

To validate our evaporation scheme, a liquid film evaporating test is performed, as shown in Figure 4a. The computational domain is $14.6 \times 16.8 \times 41.3\sigma^3$, and it is initially filled with a liquid film with 2940 atoms in the middle. When a certain temperature is given, the vapor–liquid equilibrium state will be obtained. Subsequently we open the top and bottom boundary of the domain and the atoms start to evaporate to vacuum. Therefore, the evaporation flux is calculated at different temperature, and our results are compared with data from Ishiyama et al.,⁴⁴ as shown in Figure 4b. Good agreements are found to validate our codes and methods.

Since the previous studies claimed that the contact angle influenced the evaporation flux distribution significantly, we have to define the contact angle in our simulation. Geometrically, the apical angle (α) of the isosceles triangle we mentioned before is twice the contact angle (θ) for hydrophilic drop and twice its supplementary angle ($\pi - \theta$) for a hydrophobic drop, as shown in Figure 2b. Thence the apical angle of the isosceles triangle is used to calculate contact angle directly. Figure 5 shows that the contact angle of a hydrophilic droplet under temperature of $0.9\epsilon/k_B$, after an initial declining stage, will oscillate around its equilibrium value of about 68° . As this fluctuation is still large and hard to be diminished, we just use the reference contact angles (an average contact angle, for example the average value from 6000 to 10000 τ as shown in Figure 5) in the following discussions.

3.2. For Diffusion Dominant Mode. The diffusion dominant evaporation mode is first considered since this mode has been studied most in the previous studies based on the continuum theories. Both the hydrophilic and hydrophobic cases are investigated, and the results are shown in Figure 6, with reference contact angles being 70.5° and 131° , respectively. The temperature of system was set at $1.1\epsilon/k_B$. We also tried different temperature, such as $1.2\epsilon/k_B$, and the results illustrated that the temperature influenced only the evaporation rate but not the distribution rule. Therefore, the temperature $1.1\epsilon/k_B$ is used for all the following simulations.

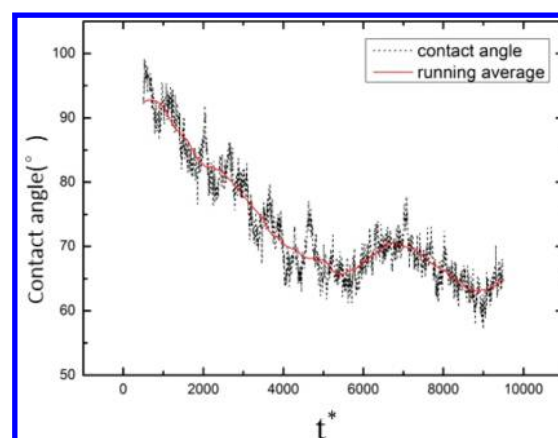


Figure 5. Contact angle of a hydrophilic drop as a function of time. Black dot line shows the fluctuation of contact angle and red solid line is its fitting curve. The time is normalized by τ as $t^* = t/\tau$.

Twenty-four independent simulations were performed for averaged evaporation flux rate in each divided region.

The hydrophilic results in Figure 6a show that the evaporation flux at the edge region is higher than other regions, which appears consistent with previous understanding based on diffusion theories. We also noticed that this edge enhancement was partially ascribed to the larger space angle for diffusion by the geometrical analysis.⁴⁵ Moreover, the molecular simulation in this work may provide more details of atoms distribution that may help us understand the mechanism beyond the continuum theory. For the hydrophilic interaction between liquid and solid, liquid atoms can be adsorbed on the solid substrate, as illustrated in Figure 7a, and diffuse from the drop edge on solid surface. This surface diffusion leads to a significant enhancement of evaporation near the drop edge. Most of these liquid atoms away from the drop by surface diffusion will also evaporate to vapor atoms finally. Therefore, higher evaporation flux at the edge is calculated. More quantitatively, we compare the atoms by surface diffusion with the directly evaporated ones, as shown in Figure 7b. The results show that the edge evaporation is obviously enhanced, and about half of the extra atoms are diffused on the solid substrate. This demonstrates the solid surface diffusion based on adsorption effect is also one of the main reasons for the edge evaporation enhancement.

For the hydrophobic drops, the results in Figure 6b indicate that edge evaporation flux is lower than other regions. As a result, on one hand, the geometrical space for diffusion is confined near the contact line for hydrophobic drops, and therefore weakens the edge evaporation. On the other hand, unlike the hydrophilic case, the adsorbed atoms are never found at the edge.

So far we only distinguish hydrophilic and hydrophobic cases. It should be an important issue to examine the contact angle effect that could continuously vary so that one could know the transition point between edge enhancement and edge weakening. However, this meets a huge challenge because of large fluctuations of contact angle by MD simulations. Therefore, we used two typical hydrophilic and hydrophobic cases, in Figures 6 and 7, with contact angles far away from the critical one. Furthermore, we implemented several cases with contact angles around 90° , and provided the results of two cases in Figure 8.

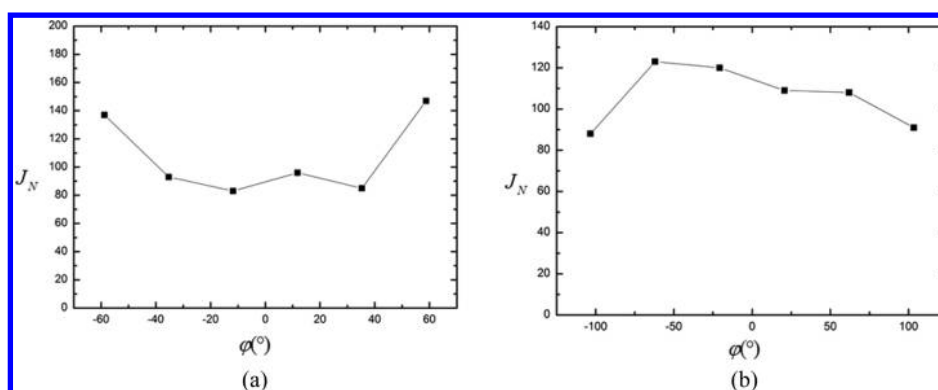


Figure 6. Evaporation flux distribution under diffusion dominant mode. φ is the direction angle, and J_N is the number of atoms that evaporate from different direction angle over the evaporation process. (a) Hydrophilic case; (b) hydrophobic case.

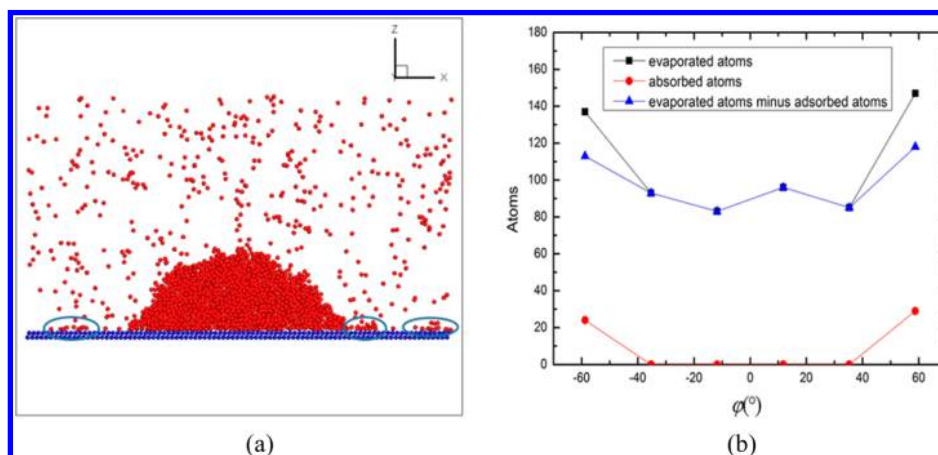


Figure 7. (a) Adsorption and surface diffusion on solid substrate for the hydrophilic case. Red particles are liquid and vapor atoms, blue particles are solid atoms. Blue ellipsoidal zones show atoms adsorbed on the substrate. (b) Liquid atoms by surface diffusion on substrate compared with the directly evaporated ones. Black squares show the number of evaporated atoms of a hydrophilic drop, red circles show number of atoms adsorbed on the solid substrate from different direction angle, and blue triangles are their differences. φ is the direction angle.

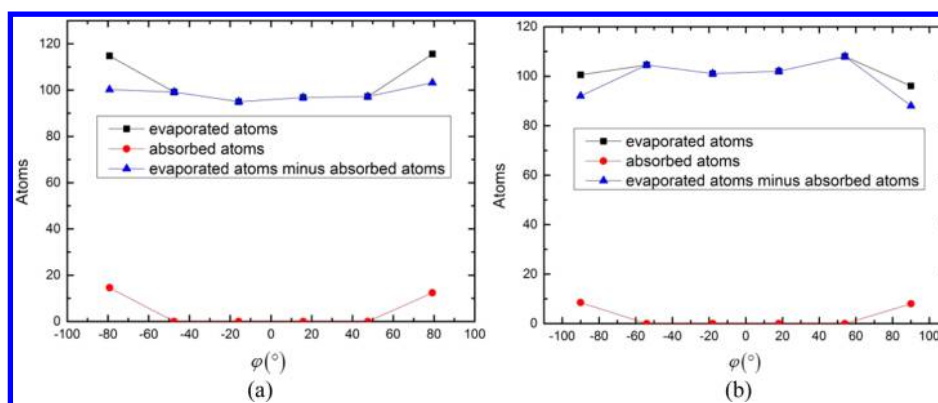


Figure 8. Evaporation flux distribution in diffusion-dominant mode with different contact angles. (a) Contact angle is about 95° ; (b) contact angle is about 108° .

Figure 8a shows that overall edge evaporation rate is enhanced when at a contact angle at about 95° . However, if we subtract the out-going atoms by surface diffusion from the overall evaporated atoms, the flux distribution seems close to uniform. In consideration of numerical fluctuation of contact angle, we believe it approaches agreement with diffusion theory, which states that evaporation flux distribution is uniform at a contact angle of 90° . However, the diffusion theory of continuum considers only “space angle effect,” but we have

found the escaped atoms by surface diffusion contribute to the edge enhancement at the same time. As a result of mixed effects from “space angle effect” and “surface diffusion effect”, the transition point ought to be somewhat larger than 90° , which is different from the classical diffusion theory. Figure 8b shows the evaporation flux distribution at a contact angle at around 108° , where the edge weakening appears. We can therefore draw a rough conclusion that the transition contact angle from edge enhancement to edge weakening is within 95° to 108° .

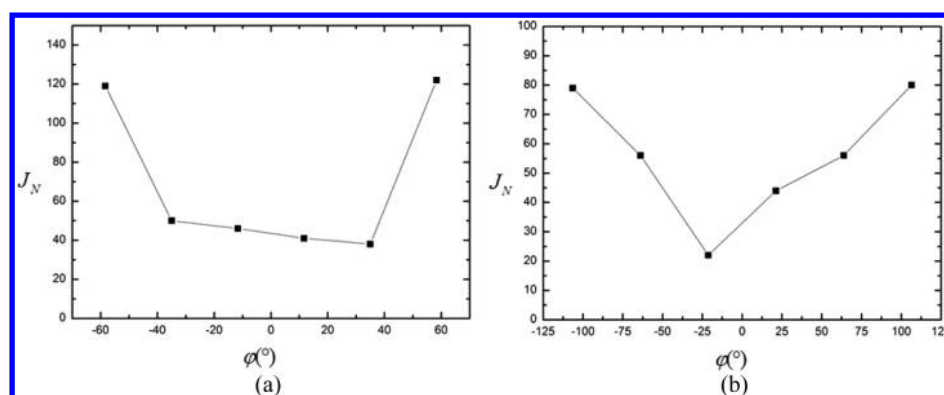


Figure 9. Evaporation flux distribution in substrate heating mode. ϕ is the direction angle and J_N is number of atoms which evaporate from different direction angle over the evaporation process. (a) Hydrophilic case; (b) hydrophobic case.

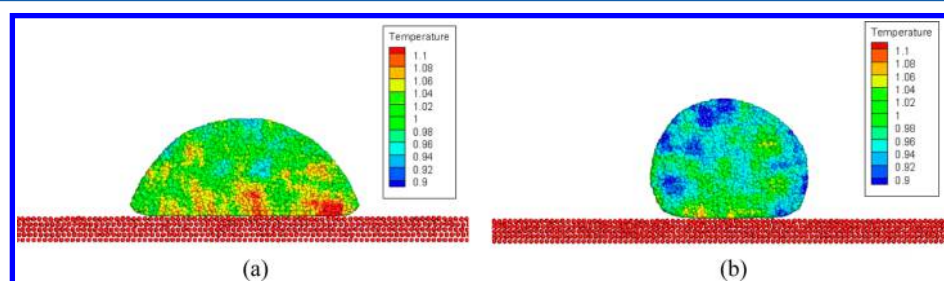


Figure 10. Temperature contour of the droplets under substrate heating mode. Temperature is normalized by ε/k_B . (a) Hydrophilic case; (b) hydrophobic case.

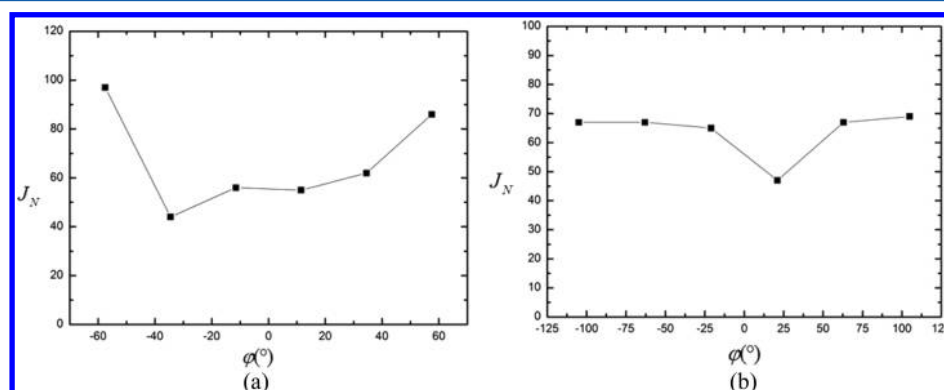


Figure 11. Evaporation flux distribution under environment heating modes. ϕ is the direction angle, and J_N is number of atoms which evaporate from different direction angles over the evaporation process. (a) Hydrophilic case; (b) hydrophobic case.

3.3. For Substrate Heating Mode. The evaporation in the substrate heating mode has many applications in industry and daily life. To realize this mode, we suddenly increase the substrate temperature from its original equilibrium state of $T_0 = 0.9\varepsilon/k_B$ to $T_1 = 1.1\varepsilon/k_B$. Then we start to calculate the evaporation flux before a new equilibrium state is reached. Over 24 independent threads are performed to minimize the fluctuation. Results for both hydrophilic and hydrophobic drops are shown in Figure 9, with reference contact angles being 72° and 126° , respectively.

Figure 9 shows significant differences of evaporation flux distribution between the diffusion-dominant mode and the substrate heating mode. First the evaporation fluxes at the edge are higher than elsewhere for hydrophobic drops in the substrate heating mode, in contrast to the lower ones at the edge in the diffusion dominant mode. For the hydrophilic cases, the evaporation flux located at other than the edges is

approximately uniform, represented by the “middle evaporation flux”, compared with the higher edge evaporation flux. If the “edge evaporation flux step” is defined as the difference between the edge evaporation flux and the middle evaporation flux, the edge evaporation flux step in the substrate heating mode is much higher than that in the diffusion dominant mode. The mechanism lies in the energy import through the hot substrate which changes the temperature distribution of drop surfaces. The nearer to the hot solid substrate, the lower is the thermal resistance of conduction, and therefore the higher of the temperature. The edge has the shorter distance to the substrate than elsewhere of drop, therefore is hotter. Since the evaporation flux is positively related to the temperature for a given condition, the edge evaporation flux is higher than elsewhere of drop surface. To make it more convincing, the temperature distribution of drops is drawn in Figure 10. It is clear that the temperature near the contact line is higher along

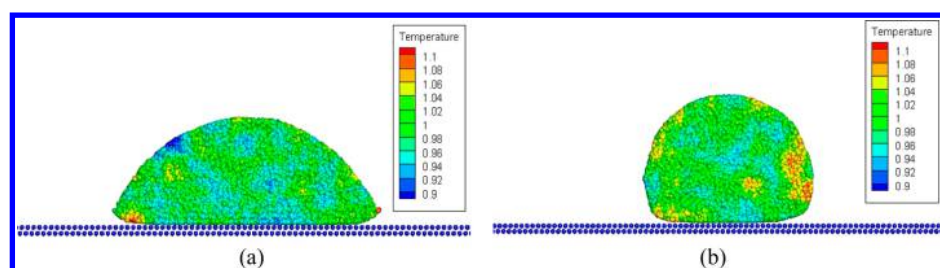


Figure 12. Temperature contour of the droplets under environment heating mode. Temperature is normalized by ε/k_B . (a) Hydrophilic case; (b) hydrophobic case.

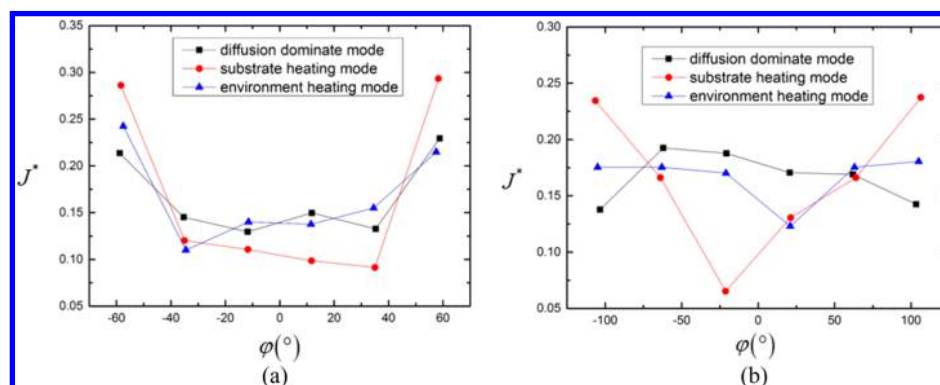


Figure 13. Comparison among the three evaporation modes. J^* is normalized evaporation flux, as $J^* = J_N/J_{\text{total}}$. J_N is number of atoms which evaporate from different direction angle and J_{total} is total evaporated atoms under each evaporation mode. (a) Hydrophilic case; (b) hydrophobic case.

the liquid–vapor interface for both hydrophilic and hydrophobic cases.

It is also noted that total evaporation flux is higher for hydrophilic than hydrophobic case. This is because the hydrophilic drop has a thinner shape and a larger contact area with the hot solid substrate in the same volume compared with the hydrophobic drop. These two factors lead to a much higher average temperature of hydrophilic drop than that of hydrophobic drop at the same time, as is illustrated in Figure 10, and thus a larger total evaporation flux is found for the hydrophilic drop.

3.4. For Environment Heating Mode. When the vapor pressure and the substrate temperature are given, the evaporation may change with the temperature of environment. This mode is often encountered in agricultural applications and our daily life. In this work, we suddenly increase the vapor temperature to $1.1 \varepsilon/k_B$ from its original equilibrium state of $0.9 \varepsilon/k_B$. We start to count the evaporation flux before a new equilibrium state reached. Here, over 72 independent simulations are adopted to minimize the fluctuation because fluctuation under environment heating mode is larger than other modes. Figure 11 shows the flux distribution for both hydrophilic and hydrophobic drop, with reference contact angles being 69° and 126° , respectively. Figure 12 describes the temperature distribution of the drops.

The results in Figure 11 show that the evaporation flux at the edge is enhanced for the hydrophilic case; however, an approximate uniform distribution is found for the hydrophobic case. Meanwhile for both cases, nearly uniform temperature distributions are found in Figure 12. Therefore, the edge enhancement of hydrophilic droplets is again caused by adsorbed atoms on solid substrate. While for hydrophobic drops, the absorption is weak, and thus a uniform evaporation

flux distribution follows its uniformly distributed temperature. It is noted that a lower point in Figure 11b may be caused by fluctuation, and remains the subject of further discussions. More work will be done to investigate the evaporation flux distribution under various temperature conditions in the future.

For further comparisons, the evaporation fluxes under three different evaporation modes are shown in Figure 13. For hydrophilic case (reference contact angle is about 70°), the edge evaporation is enhanced most heavily under substrate heating mode. Higher temperature at the edge of drop plays the key role. While the edge evaporation enhancement under the diffusion dominant mode and the environment heating mode is nearly in the same level. For hydrophobic case (reference contact angle is about 126°), the edge evaporation is enhanced under substrate heating mode and restricted under the diffusion dominant mode. The reasons are higher temperature of edge atoms near the substrate and the limit space restriction, respectively, as we have explained before. For both hydrophilic and hydrophobic case, we can conclude that substrate heating mode can enhance most to edge evaporation.

The total evaporation fluxes are compared under the three evaporation modes, as shown in Figure 14. The temperature increase for substrate heating and environment heating mode is from $0.9 \varepsilon/k_B$ to $1.1 \varepsilon/k_B$ and the constant temperature for diffusion dominant mode is $1.1 \varepsilon/k_B$. The total evaporation flux has a big difference between hydrophilic and hydrophobic cases under substrate heating mode, while being almost the same under the diffusion-dominant and the environment heating modes. The constant gradient of total evaporation flux with respect to simulation time under diffusion-dominant mode indicates that the system reaches a steady state, while the curves of the substrate heating and the environment heating modes converge to a constant because the system reaches equilibrium.

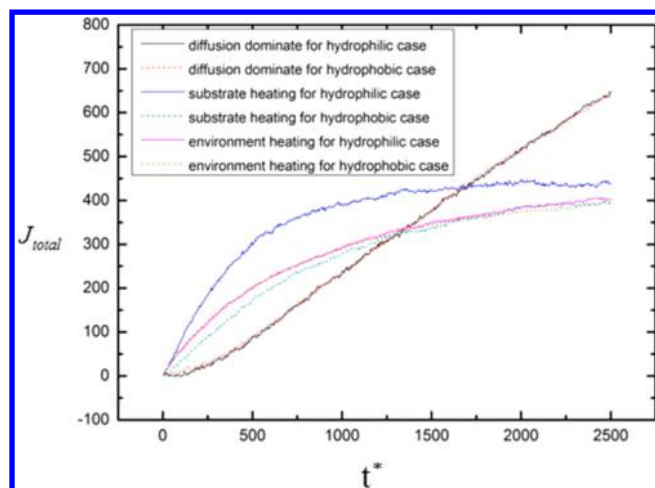


Figure 14. Total evaporation flux as a function of time under all three evaporation modes for both hydrophilic (solid line) and hydrophobic (dash line) cases. J_{total} is the total number of evaporated atoms over the evaporation process. The time is normalized by τ as $t^* = t/\tau$.

At the first stage of evaporation, before the evaporation rate slows down under the substrate heating and the environment heating modes, the drop evaporates fastest under the substrate heating mode for the hydrophilic case and under the environment heating mode for hydrophobic case. For both hydrophilic and hydrophobic cases, drops under diffusion-dominant mode evaporate at the slowest rate.

4. CONCLUSIONS

Molecular simulations were performed to investigate the flux distribution of evaporating drops under three different evaporation modes. An azimuthal angle-based division approach was proposed to capture the flux distribution. Our codes were validated well by a liquid film evaporation test.

The modeling results indicate that the evaporation flux distribution displays in different patterns. Under the diffusion dominant mode, we find that the edge evaporation flux is enhanced for hydrophilic drops, but weakened for hydrophobic ones. This is in accordance with the diffusion-based theory; moreover, the edge enhancement of hydrophilic drops is well explained by the mixed effects from both escaped atoms by surface diffusion on substrate and space angle effect of drop geometry. Because of the surface diffusion, the transition contact angle becomes larger than 90° , which is different with the conclusion from diffusion theory (right at 90°). Under the substrate heating mode, both the hydrophilic and hydrophobic cases show a higher evaporation flux at the edge of drop. The changed temperature by imported energy from substrate plays the key role in this mode. Under the environment heating mode, the evaporation flux distribution is also enhanced at the edge for hydrophilic drops, while it is uniformly distributed for the hydrophobic case. Furthermore, we conclude that substrate heating mode contributes the most to edge evaporation enhancement. Since the fluctuation of the contact angles were obtained by MD methods, we just considered two groups of cases falling into the hydrophilic and the hydrophobic range, respectively. More efforts will be made to establish a more precise correlation for the location-dependent evaporation flux distribution.

AUTHOR INFORMATION

Corresponding Author

*E-mail: mrwang@tsinghua.edu.cn; Tel: +86-10-627-87498.

Author Contributions

[†]The first two authors contribute equally to this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is financially supported by the Specialized Research Fund for the Doctoral Program of Higher Education of China (No. 20130002110077), the National Science and Technology Major Project on Oil and Gas (No. 2017ZX05013001), the PetroChina Innovation Foundation (2015D-5006-0201), and the Tsinghua University Initiative Scientific Research Program (No. 2014z22074).

REFERENCES

- (1) Malaquin, L.; Kraus, T.; Schmid, H.; Delamarche, E.; Wolf, H. Controlled Particle Placement through Convective and Capillary Assembly. *Langmuir* **2007**, *23*, 11513–11521.
- (2) Dugas, V.; Broutin, J.; Souteyrand, E. Droplet Evaporation Study Applied to DNA Chip Manufacturing. *Langmuir* **2005**, *21*, 9130–9136.
- (3) Wong, T.-S.; Chen, T.-H.; Shen, X.; Ho, C.-M. Nano-chromatography Driven by the Coffee Ring Effect. *Anal. Chem.* **2011**, *83*, 1871–1873.
- (4) Deegan, R. D. Pattern formation in drying drops. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **2000**, *61*, 475–485.
- (5) Deegan, R. D.; Bakajin, O.; Dupont, T. F.; Huber, G.; Nagel, S. R.; Witten, T. A. Capillary flow as the cause of ring stains from dried liquid drops. *Nature* **1997**, *389*, 827–829.
- (6) Deegan, R. D.; Bakajin, O.; Dupont, T. F.; Huber, G.; Nagel, S. R.; Witten, T. A. Contact line deposits in an evaporating drop. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **2000**, *62*, 756–765.
- (7) Picknett, R. G.; Bexon, R. The evaporation of sessile or pendant drops in still air. *J. Colloid Interface Sci.* **1977**, *61*, 336–350.
- (8) Kim, J.-H.; Ahn, S. I.; Kim, J. H.; Zin, W.-C. Evaporation of Water Droplets on Polymer Surfaces. *Langmuir* **2007**, *23*, 6163–6169.
- (9) Semenov, S.; Starov, V. M.; Velarde, M. G.; Rubio, R. G. Droplets evaporation: Problems and solutions. *Eur. Phys. J.: Spec. Top.* **2011**, *197*, 265–278.
- (10) Hu, H.; Larson, R. G. Marangoni Effect Reverses Coffee-Ring Depositions. *J. Phys. Chem. B* **2006**, *110*, 7090–7094.
- (11) Majumder, M.; Rendall, C. S.; Eukel, J. A.; Wang, J. Y. L.; Behabtu, N.; Pint, C. L.; Liu, T.-Y.; Orbaek, A. W.; Mirri, F.; Nam, J.; Barron, A. R.; Hauge, R. H.; Schmidt, H. K.; Pasquali, M. Overcoming the “Coffee-Stain” Effect by Compositional Marangoni-Flow-Assisted Drop-Drying. *J. Phys. Chem. B* **2012**, *116*, 6536–6542.
- (12) Cachile, M.; Bénichou, O.; Poulard, C.; Cazabat, A. M. Evaporating Droplets. *Langmuir* **2002**, *18*, 8070–8078.
- (13) Hu, H.; Larson, R. G. Evaporation of a Sessile Droplet on a Substrate. *J. Phys. Chem. B* **2002**, *106*, 1334–1344.
- (14) McHale, G.; Aqil, S.; Shirtcliffe, N. J.; Newton, M. I.; Erbil, H. Y. Analysis of Droplet Evaporation on a Superhydrophobic Surface. *Langmuir* **2005**, *21*, 11053–11060.
- (15) Dandan, M.; Erbil, H. Y. Evaporation Rate of Graphite Liquid Marbles: Comparison with Water Droplets. *Langmuir* **2009**, *25*, 8362–8367.
- (16) Sobac, B.; Brutin, D. Triple-Line Behavior and Wettability Controlled by Nanocoated Substrates: Influence on Sessile Drop Evaporation. *Langmuir* **2011**, *27*, 14999–15007.
- (17) Popov, Y. O. Evaporative deposition patterns: Spatial dimensions of the deposit. *Phys. Rev. E* **2005**, *71*, 036313.

- (18) Nguyen, T. A. H.; Nguyen, A. V.; Hampton, M. A.; Xu, Z. P.; Huang, L.; Rudolph, V. Theoretical and experimental analysis of droplet evaporation on solid surfaces. *Chem. Eng. Sci.* **2012**, *69*, 522–529.
- (19) Hu, H.; Larson, R. G. Analysis of the Microfluid Flow in an Evaporating Sessile Droplet. *Langmuir* **2005**, *21*, 3963–3971.
- (20) Kim, P. G.; Domingues, C.; Wan, J.; Stone, H. A.; Ristenpart, W. D. Influence of Substrate Conductivity on Circulation Reversal in Evaporating Drops. *Phys. Rev. Lett.* **2007**, *99*, 234502.
- (21) Berteloot, G.; Pham, C. T.; Daerr, A.; Lequeux, F. o.; Limat, L. Evaporation-induced flow near a contact line: Consequences on coating and contact angle. *EPL (Europhysics Letters)* **2008**, *83*, 14003.
- (22) Widjaja, E.; Harris, M. T. Particle deposition study during sessile drop evaporation. *AIChE J.* **2008**, *54*, 2250–2260.
- (23) Crivoi, A.; Duan, F. Elimination of the Coffee-Ring Effect by Promoting Particle Adsorption and Long-Range Interaction. *Langmuir* **2013**, *29*, 12067–12074.
- (24) Crivoi, A.; Duan, F. Evaporation-Induced Branched Structures from Sessile Nanofluid Droplets. *J. Phys. Chem. C* **2013**, *117*, 7835–7843.
- (25) Crivoi, A.; Duan, F. Three-dimensional Monte Carlo model of the coffee-ring effect in evaporating colloidal droplets. *Sci. Rep.* **2014**, *4*, 4310.
- (26) Xie, C.; Zhang, J.; Bertola, V.; Wang, M. Droplet Evaporation on a Horizontal Substrate under Gravity Field by Mesoscopic Modeling. *J. Colloid Interface Sci.* **2016**, *463*, 317.
- (27) Dunn, G. J.; Wilson, S. K.; Duffy, B. R.; David, S.; Sefiane, K. The strong influence of substrate conductivity on droplet evaporation. *J. Fluid Mech.* **2009**, *623*, 329–351.
- (28) Bigioni, T. P.; Vinokur, V. M.; Shchur, L. N.; Barash, L. Y. Evaporation and fluid dynamics of a sessile drop of capillary size. *Phys. Rev. E* **2009**, *79*, 046301.
- (29) Widjaja, E.; Harris, M. T. Numerical study of vapor phase-diffusion driven sessile drop evaporation. *Comput. Chem. Eng.* **2008**, *32*, 2169–2178.
- (30) Onuki, A. Dynamic van der Waals theory. *Phys. Rev. E* **2007**, *75*, 036304.
- (31) Teshigawara, R.; Onuki, A. Droplet evaporation in one-component fluids: Dynamic van der Waals theory. *EPL (Europhysics Letters)* **2008**, *84*, 36003.
- (32) Ward, C. A. The rate of gas absorption at a liquid interface. *J. Chem. Phys.* **1977**, *67*, 229–235.
- (33) Rahimi, P.; Ward, C. A. Kinetics of evaporation: statistical rate theory approach. *Int. J. of Thermodynamics* **2005**, *8*, 1–14.
- (34) Fang, G.; Ward, C. A. Expression for predicting liquid evaporation flux: Statistical rate theory approach. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **1999**, *59*, 429–440.
- (35) Ward, C. A.; Fang, G. Examination of the statistical rate theory expression for liquid evaporation rates. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **1999**, *59*, 441–453.
- (36) Duan, F. Local evaporation flux affected by thermocapillary convection transition at an evaporating droplet. *J. Phys. D: Appl. Phys.* **2009**, *42*, 102004.
- (37) Duan, F.; Ward, C. A. Investigation of Local Evaporation Flux and Vapor-Phase Pressure at an Evaporative Droplet Interface. *Langmuir* **2009**, *25*, 7424–7431.
- (38) Sumardiono, S.; Fischer, J. Molecular simulations of droplet evaporation by heat transfer. *Microfluid. Nanofluid.* **2007**, *3*, 127–140.
- (39) Wilhelmsen, O.; Trinh, T. T.; Kjelstrup, S.; Bedeaux, D. Influence of Curvature on the Transfer Coefficients for Evaporation and Condensation of Lennard-Jones Fluid from Square-Gradient Theory and Nonequilibrium Molecular Dynamics. *J. Phys. Chem. C* **2015**, *119*, 8160–8173.
- (40) Zhang, J.; Leroy, F.; Müller-Plathe, F. Evaporation of Nanodroplets on Heated Substrates: A Molecular Dynamics Simulation Study. *Langmuir* **2013**, *29*, 9770–9782.
- (41) Allen, M. P.; Tildesley, D. J. *Computer simulation of liquids*; Oxford University Press: Oxford, U.K., 1989.
- (42) Wang, M.; Liu, J.; Chen, S. Electric potential distribution in nanoscale electroosmosis: from molecules to continuum. *Mol. Simul.* **2008**, *34*, 509–514.
- (43) Hünenberger, P. H. Thermostat algorithms for molecular dynamics simulations. In *Advanced Computer Simulation*; Springer-Verlag: Berlin Heidelberg, 2005; pp 105–149.
- (44) Ishiyama, T.; Yano, T.; Fujikawa, S. Molecular dynamics study of kinetic boundary condition at an interface between argon vapor and its condensed phase. *Phys. Fluids* **2004**, *16*, 2899–2906.
- (45) Pan, Z.; Wang, H. Symmetry-to-asymmetry transition of Marangoni flow at a convex volatilizing meniscus. *Microfluid. Nanofluid.* **2010**, *9*, 657–669.