**1. Introduction**

Evaporation of sessile droplets is a widely observed natural phenomenon and holds an important role in a variety of applications, including inkjet printing[1], DNA mapping[2], spray cooling[3], and microparticle detection[4], etc. Meanwhile, sessile droplet evaporation is a complex phenomenon with heat and mass transfer interaction between the gas, liquid and solid phase. It is a challenge to fully understand the mechanism of the sessile droplet evaporation since the evaporation process is controlled by several interdependent factors, such as the droplet contact angle and contact radius[5], contact line motion[6-8], substrate structure[9-14], temperature[15-20] and the surrounding environment[21-23].

In the seminal work of Picknett and Bexon in 1977[24], sessile droplet evaporation was systematically analyzed, and the concept of different evaporation modes was put forward, in which droplet evaporation was distinguished into evaporation modes: (1) constant contact radius (CCR) mode and (2) constant contact angle (CCA) mode. In CCR mode, contact line of the droplet is pinned which means the droplet contact radius remains constant and meanwhile droplet contact angle keeps decreasing. In CCA mode, droplet contact angle is unchanged, and the droplet contact line keeps receding. In today’s study of sessile droplet evaporation, another two evaporation modes are introduced: (1) the mixed mode in which both the contact radius and contact angle decrease during the evaporation, and (2) the stick-slip mode[25] in which droplet contact line is moved by the pinning and depinning force alternately.

It is a challenging task to determine the evaporation rate from the liquid surface in the sessile droplet problem. The analogy between the concentration field and the electrostatic field was suggested to solve the evaporation problem. The analytical solutions of this equivalent problem were first proposed by Lebedev[26]. In 2000, Deegan et al.[27] provided the framework of diffusion-driven model for solving the evaporation flux in their work of contact line deposition. Then, Hu and Larson[28] improved this method and provided a simple approximate expression for the evaporation rate of the sessile droplet with contact angle between 0 and . In 2007, Popov[29] provided the well-known analytical solution for the evaporation rate of sessile droplet and this evaporation rate expression is valid for arbitrary contact angle. This diffusion-driven model developed by Popov has been widely employed to predict the droplet evaporation dynamics due to the robustness of the model which only requires the pinning of the droplet contact line with the surface. Studies about sessile droplet evaporation with sliding contact line were also carried out and the diffusion-driven model was confirmed to be valid in these cases. Calculating results obtained by this diffusion-driven model shows great accuracy with the experiments data for droplet evaporation on hydrophilic surfaces[27, 29], hydrophobic surfaces with pinned[20] and sliding contact line[30] and superhydrophobic surfaces with pinned contact line[31] when the surfaces were not hot. Experiment of sessile droplet evaporation on superhydrophobic surfaces at room temperature with sliding contact line was carried out by Dash and Garimalla[32] and the diffusion-driven model was shown to overestimate the evaporation rate by approximately 20%. The same overestimation of evaporation rate for droplet evaporation on superhydrophobic surfaces with neglectable hysteresis was also observed by Aldhaleai et al.[33]. This derivation of the predicted evaporation rate is caused by the evaporative cooling of the droplet which causes a temperature decrease on the droplet surface. This nonuniform surface distribution contradicts the pivotal assumption in Popov’s diffusion-driven model that the temperature of the droplet surface is constant.

The effect of evaporative cooling for droplet evaporation at room temperature on hydrophilic and hydrophobic surface is not obvious because of the small evaporation rate. Moreover, droplet on hydrophilic and hydrophobic surface has a thinner shape compared with the droplet residing on superhydrophobic surface with the same volume, which results in smaller thermal resistance of the sessile droplet. The relatively small thermal resistance of the droplet makes the effect of evaporation cooling less obvious. Thus, it is reasonable to assume that the droplet surface temperature is the constant and is the same as the ambient temperature for droplet evaporation at room temperature, which also accounts for the wide validation of Popov’s diffusion-driven model for droplet evaporation on unheated surfaces. However, for droplet evaporation on heated superhydrophobic surfaces, the large thermal resistance and the increased evaporation rate of the liquid droplet can result in an obvious temperature mismatch between the droplet surface and the ambient or the substrate surface. Dash and Garimella[34] calculated the temperature distribution of water droplet evaporation on a heated superhydrophobic surfaces with a one-dimensional conduction heat transfer model. Large temperature differences between the droplet surface and the heated substrate were observed. Their calculating results showed that the maximum temperature difference between the droplet surface and the substrates at 40 °C, 50 °C and 60 °C were 13.3 °C, 19.05°C and 25.49 °C, respectively. These large surface temperature mismatch explained the significant overestimation of the evaporation rate by the diffusion-driven model for droplet evaporation on heated surfaces. Gleason and Putnam[35] modified Popov’s diffusion-driven model by considering the temperature distribution along the droplet cap surface. They provided an interpolated mapping function of the droplet surface temperature from numerical simulation results[34, 36] of sessile droplet evaporation. With this interpolated mapping function, they can obtain the surface temperature distribution of sessile droplet at arbitrary contact angle with just knowing the temperature of the substrate surface. The modified diffusion-driven model exhibited fair accuracy: the errors of evaporation rate between the experiments and the modified model were 1.84% and 2.83% for droplet evaporation on heated substrates at 50 °C and 60 °C. Popov’s diffusion-driven model with considering the liquid-vapor surface temperature distribution can accurately calculate the evaporation rate from the droplet cap surface and is an effective method to predict the evaporation dynamics of droplet evaporation on smooth heated substrates.

Droplets dwelling on substrate demonstrate different characteristics during the evaporation corresponding to the distinct properties of the substrate[37-39]. During the past two decades, inspired by natural structures such as the lotus leaf[40], various artificial surfaces with micro/nanoscale roughness been developed to exhibit large hydrophobicity or superhydrophobicity[41-44]. Generally, there are two kinds of wettings states for a liquid droplet on the micro-structured substrates: (1) Cassie state[45]: the droplet touches only the top surface of the microstructures and leaves air cavities underneath the droplet; and (2) Wenzel state[46]: droplet completely penetrates the cavities between micropillars. It has been found that the distinct pinning/depinning mechanisms and wetting/nonwetting contacts in these two wetting states would lead to completely different heat and mass transfer dynamics during the sessile droplet evaporation on micro-structured surfaces.

For the evaporation of liquid droplets in the Wenzel state on micro-structured surfaces, all the heat and mass transfer between the droplet and the ambient air occur at the liquid-vapor interface of the droplet cap surface and no evaporation happens at the droplet base because of the impenetrability of the solid substrate. The evaporation dynamic of droplet in Wenzel state is the same as that of the evaporation on smooth surfaces. However, due to the existence of the air/vapor cavities between the droplet base and the structured substrate, heat and mass transfer between a Cassie state droplet and the ambient air can be divided into two different components, i.e., (1) the evaporation from the droplet cap surface and (2) the evaporation from the droplet base surface as shown in Fig. (n). For Cassie state droplet evaporation at room temperature, the component of the evaporation from the droplet base surface is always neglected because of the relatively small liquid-vapor interface area and high relative humidity in the air/vapor cavities. Evaporation dynamics of Cassie state droplet evaporation on micro-structured superhydrophobic surfaces at room temperature can be predicted by the diffusion-driven model[47, 48]. In the cases of droplet evaporation on hot micro-structured substrates, the temperature increase of the substrate surface will result in the temperature increase of the droplet base surface which is in direct contact with the substrate. This temperature increase of the droplet base surface will improve the evaporation at the droplet base liquid-vapor interface. The component of evaporation from the droplet base becomes significant and cannot be neglected anymore[16, 49, 50]. The diffusion-driven model is always used to calculate the evaporation rate of the droplet cap surface and it doesn’t consider the evaporation from the droplet base surface. As a result, it is not practicable to predict the evaporation rate of Cassie state droplet on hot micro-structured substrates with the diffusion driven model even with considering the correction of droplet surface temperature distribution. The evaporation from the droplet base surface adds a new degree of freedom to the sessile droplet evaporation system and makes the Cassie state droplet evaporation on hot substrate much more complicated. Nevertheless, the effect of large evaporation contribution from the droplet base surface on the evaporation in the Cassie state has received very limited attention.

In this paper, the evaporation of solitary water droplet on hot micro-structured superhydrophobic substrates is experimentally and theoretically investigated. A water droplet is placed on the superhydrophobic substrate for evaporation and the substrate is heated by a hot plate from 40 °C to 80 °C. Variation of the geometry information and surface temperature of the droplet are recorded and three different evaporation modes (CCR, CCA and mixed mode) of the droplet are observed. The droplet is in Cassie state during most the evaporation process and transfers into Wenzel state at the very end of the evaporation. Based on a comprehensive thermal resistance analysis, a thermal circuit model has been developed to predict the droplet cap surface temperature and to calculate the evaporation rate from the droplet cap surface and the droplet base surface. An evaporation ratio 𝜑 defined as the ratio of evaporation rate from the droplet base surface and the total evaporation rate is analyzed in CCR mode and CCA mode respectively. Then the substrate is further heated from 80 °C to 120 °C until which a small rise of the substrate temperature will lead to the boiling of the droplet. Derivation between the experimental tested droplet surface temperature and the predicted surface temperature is observed for droplet evaporation at such high temperature substrates because of the internal fluid motion of the water droplet. An effective thermal conductivity is employed as a correction factor for the thermal circuit model to consider the effect of convection heat transfer in the water droplet. The average temperature of the droplet base surface is calculated to explain the delay of the onset of boiling of water droplet on the thin substrate with base temperature higher than 100 °C. This experimental and theoretical study of water droplet evaporation on hot micro-structured superhydrophobic substrates could improve our understanding about the heat and mass transfer process in the sessile droplet evaporation and provide a potential way to enhance sessile droplet evaporation.

[1]. P. Calvert, Inkjet Printing for Materials and Devices, Chem. Mater., 13 (10) (2001) 3299-3305.

[2]. A. Wu, L. Yu, Z. Li, H. Yang, and E. Wang, Atomic force microscope investigation of large-circle DNA molecules, Anal Biochem, 325 (2) (2004) 293-300.

[3]. W. Jia and H.H. Qiu, Experimental investigation of droplet dynamics and heat transfer in spray cooling, Exp. Therm. Fluid Sci., 27 (7) (2003) 829-838.

[4]. J. Song, W. Cheng, M. Nie, X. He, W. Nam, J. Cheng, and W. Zhou, Partial Leidenfrost Evaporation-Assisted Ultrasensitive Surface-Enhanced Raman Spectroscopy in a Janus Water Droplet on Hierarchical Plasmonic Micro-/Nanostructures, ACS Nano, 14 (8) (2020) 9521-9531.

[5]. S.A. Putnam, A.M. Briones, L.W. Byrd, J.S. Ervin, M.S. Hanchak, A. White, and J.G. Jones, Microdroplet evaporation on superheated surfaces, International Journal of Heat and Mass Transfer, 55 (21) (2012) 5793-5807.

[6]. P. Tsai, R.G. Lammertink, M. Wessling, and D. Lohse, Evaporation-triggered wetting transition for water droplets upon hydrophobic microstructures, Physical review letters, 104 (11) (2010) 116102.

[7]. L. Zhao and J. Cheng, The mechanism and universal scaling law of the contact line friction for the Cassie-state droplets on nanostructured ultrahydrophobic surfaces, Nanoscale, 10 (14) (2018) 6426-6436.

[8]. L. Zhao and J. Cheng, Analyzing the Molecular Kinetics of Water Spreading on Hydrophobic Surfaces via Molecular Dynamics Simulation, Scientific Reports, 7 (1) (2017) 10880.

[9]. X. He, J. Cheng, C. Patrick Collier, B.R. Srijanto, and D.P. Briggs, Evaporation of squeezed water droplets between two parallel hydrophobic/superhydrophobic surfaces, J. Colloid Interface Sci., 576 (2020) 127-138.

[10]. L.S. Lam, M. Hodes, and R. Enright, Analysis of Galinstan-Based Microgap Cooling Enhancement Using Structured Surfaces, Journal of Heat Transfer, 137 (9) (2015)

[11]. A. Al-Sharafi, B.S. Yilbas, and H. Ali, Droplet Heat Transfer on Micropost Arrays With Hydrophobic and Hydrophilic Characteristics, Journal of Heat Transfer, 140 (7) (2018)

[12]. C.-C. Hsu, Y.-A. Lee, C.-H. Wu, and C.S.S. Kumar, Self-propelled sessile droplets on a superheated and heterogeneous wetting surface, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 612 (2021)

[13]. F.G.H. Schofield, S.K. Wilson, D. Pritchard, and K. Sefiane, The lifetimes of evaporating sessile droplets are significantly extended by strong thermal effects, Journal of Fluid Mechanics, 851 (2018) 231-244.

[14]. B. Sobac and D. Brutin, Thermal effects of the substrate on water droplet evaporation, Phys Rev E Stat Nonlin Soft Matter Phys, 86 (2 Pt 1) (2012) 021602.

[15]. K. Gleason, H. Voota, and S.A. Putnam, Steady-state droplet evaporation: Contact angle influence on the evaporation efficiency, International Journal of Heat and Mass Transfer, 101 (2016) 418-426.

[16]. S. Adera, R. Raj, R. Enright, and E.N. Wang, Non-wetting droplets on hot superhydrophilic surfaces, Nat. Commun., 4 (2013) 2518.

[17]. R. Hays, D. Maynes, and J. Crockett, Thermal transport to droplets on heated superhydrophobic substrates, Int. J. Heat Mass Transfer, 98 (2016) 70-80.

[18]. M.S. Hanchak, A.M. Briones, J.S. Ervin, and L.W. Byrd, One-dimensional models of nanoliter droplet evaporation from a hot surface in the transition regime, International Journal of Heat and Mass Transfer, 57 (2) (2013) 473-483.

[19]. S.Y. Misyura, Contact angle and droplet heat transfer during evaporation on structured and smooth surfaces of heated wall, Applied Surface Science, 414 (2017) 188-196.

[20]. M.A. Kadhim, N. Kapur, J.L. Summers, and H. Thompson, Experimental and Theoretical Investigation of Droplet Evaporation on Heated Hydrophilic and Hydrophobic Surfaces, Langmuir, 35 (19) (2019) 6256-6266.

[21]. L. Liu, X. Liang, X. Wang, S. Kong, K. Zhang, and M. Mi, Evaporation of a sessile water droplet during depressurization, International Journal of Thermal Sciences, 159 (2021) 106587.

[22]. L. Bansal, S. Chakraborty, and S. Basu, Confinement-induced alterations in the evaporation dynamics of sessile droplets, Soft Matter, 13 (5) (2017) 969-977.

[23]. S. Semenov, F. Carle, M. Medale, and D. Brutin, Boundary conditions for a one-sided numerical model of evaporative instabilities in sessile drops of ethanol on heated substrates, Phys Rev E, 96 (6-1) (2017) 063113.

[24]. R.G. Picknett and R. Bexon, The evaporation of sessile or pendant drops in still air, Journal of Colloid and Interface Science, 61 (2) (1977) 336-350.

[25]. M.E.R. Shanahan, Simple Theory of "Stick-Slip" Wetting Hysteresis, Langmuir, 11 (3) (1995) 1041-1043.

[26]. N.N. Lebedev, Special Functions and Their Applications. Prentice-Hall. Englewood Cliffs, NJ, USA. 1965.

[27]. O.B. Robert D. Deegan, Todd F. Dupont, Greg Huber, Sidney R. Nagel, and Thomas A. Witten, Contact line deposits in an evaporating drop, Phys Rev E, 62 (2000)

[28]. R.G.L. Hua Hu, Evaporation of a Sessile droplet on a substrate, J Phys Chem B, 106 (2002) 1334-1344.

[29]. Y.O. Popov, Evaporative deposition patterns: spatial dimensions of the deposit, Phys. Rev. E 71 (3) (2005) 1-17.

[30]. T.A.H. Nguyen, A.V. Nguyen, M.A. Hampton, Z.P. Xu, L. Huang, and V. Rudolph, Theoretical and experimental analysis of droplet evaporation on solid surfaces, Chemical Engineering Science, 69 (1) (2012) 522-529.

[31]. H. Gelderblom, Á.G. Marín, H. Nair, A. van Houselt, L. Lefferts, J.H. Snoeijer, and D. Lohse, How water droplets evaporate on a superhydrophobic substrate, Physical Review E, 83 (2) (2011) 026306.

[32]. S. Dash and S.V. Garimella, Droplet evaporation dynamics on a superhydrophobic surface with negligible hysteresis, Langmuir, 29 (34) (2013) 10785-95.

[33]. A. Aldhaleai, F. Khan, T. Thundat, and P.A. Tsai, Evaporation dynamics of water droplets on superhydrophobic nanograss surfaces, International Journal of Heat and Mass Transfer, 160 (2020)

[34]. S. Dash and S.V. Garimella, Droplet evaporation on heated hydrophobic and superhydrophobic surfaces, Phys. Rev. E, 89 (4) (2014) 042402.

[35]. K. Gleason and S.A. Putnam, Microdroplet evaporation with a forced pinned contact line, Langmuir, 30 (34) (2014) 10548-55.

[36]. A.M. Briones, J.S. Ervin, L.W. Byrd, S.A. Putnam, A. White, and J.G. Jones, Evaporation Characteristics of Pinned Water Microdroplets, Journal of Thermophysics and Heat Transfer, 26 (3) (2012) 480-493.

[37]. J.T. Cheng and C.L. Chen, Active thermal management of on-chip hot spots using EWOD-driven droplet microfluidics, Exp. Fluids. , 49 (6) (2010) 1349-1357.

[38]. J.T. Cheng and C.L. Chen, Adaptive Chip Cooling Using Electrowetting on Coplanar Control Electrodes, Nanoscale Microscale Thermophys. Eng. , 14 (2) (2010) 63-74.

[39]. X. He, L. Zhao, and J. Cheng, Coalescence-Induced Swift Jumping of Nanodroplets on Curved Surfaces, Langmuir, 35 (30) (2019) 9979-9987.

[40]. L. Feng, S. Li, Y. Li, H. Li, L. Zhang, J. Zhai, Y. Song, B. Liu, L. Jiang, and D. Zhu, Super-Hydrophobic Surfaces: From Natural to Artificial, Advanced Materials, 14 (24) (2002) 1857-1860.

[41]. Z. Xue, S. Wang, L. Lin, L. Chen, M. Liu, L. Feng, and L. Jiang, A Novel Superhydrophilic and Underwater Superoleophobic Hydrogel-Coated Mesh for Oil/Water Separation, Advanced Materials, 23 (37) (2011) 4270-4273.

[42]. L. Feng, Y. Zhang, J. Xi, Y. Zhu, N. Wang, F. Xia, and L. Jiang, Petal Effect:  A Superhydrophobic State with High Adhesive Force, Langmuir, 24 (8) (2008) 4114-4119.

[43]. X.J. Feng and L. Jiang, Design and Creation of Superwetting/Antiwetting Surfaces, Advanced Materials, 18 (23) (2006) 3063-3078.

[44]. A. Lafuma and D. Quéré, Superhydrophobic states, Nature Materials, 2 (7) (2003) 457-460.

[45]. S.B. B. D. Cassie, Wettability of porous surfaces, Trans. Faraday Soc., 40 (1944) 546-551.

[46]. R.N. Wenzel, Resistance of Solid Surfaces to Wetting by Water, Industrial & Engineering Chemistry, 28 (8) (1936) 988-994.

[47]. G.M.S.A.N.J.S.M.I.N.a.H.Y. Erbil, Analysis of droplet evaporation on a superhydrophobic surface, Langmuir, 21 (2005) 11053-11060.

[48]. J.M. Stauber, S.K. Wilson, B.R. Duffy, and K. Sefiane, Evaporation of droplets on strongly hydrophobic substrates, Langmuir, 31 (12) (2015) 3653-60.

[49]. M. Wei, Y. Song, Y. Zhu, D.J. Preston, C.S. Tan, and E.N. Wang, Heat transfer suppression by suspended droplets on microstructured surfaces, Applied Physics Letters, 116 (23) (2020)

[50]. S.H. Kim, H. Seon Ahn, J. Kim, M. Kaviany, and M. Hwan Kim, Dynamics of water droplet on a heated nanotubes surface, Applied Physics Letters, 102 (23) (2013)