# THERMO-RESPONSIVE ENHANCED SHEDDING ON LUBRICANT INFUSED SURFACES

## Raza Gulfam[1], Daniel Orejon[2,3*], Chang-Hwan Choi[4], Peng Zhang[1*]

[1]Institute of Refrigeration and Cryogenics, Shanghai Jiao Tong University, Shanghai 200240, China
[2]Institute for Multiscale Thermofluids, School of Engineering, The University of Edinburgh, Edinburgh EH9 3FD, Scotland, United Kingdom
[3]International Institute for Carbon-Neutral Energy Research (WPI-ICNER), Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan
[4]Department of Mechanical Engineering, Stevens Institute of Technology, Castle Point on Hudson, Hoboken, New Jersey 07030, United States

## ABSTRACT

Slippery Lubricant Infused Porous Surfaces (SLIPSs) have received increasing attention in the past decade owing to their low adhesion minimising the interactions between liquids and such infused surfaces. The nature of the lubricant infused within the structures, mainly viscosity, has been extensively studied with greater droplet mobility velocities in the case of low viscosity liquid lubricants at ambient temperature. Other lubricants such as phase-change (PC) materials have been less considered. The impregnation of a phase-change material with a melting point near the ambient temperature allows for the manipulation and control of the phase of the lubricant infused in between the structures for temperature above and below the melting point. In turn, the different phases of the infused material shall provide different droplet-SLIPSs interactions, which are here further exploited during condensation phase-change. The different droplet size distributions and hence the different heat transfer performance when comparing the phase of the thermoresponsive SLIPSs studied is further demonstrated.

## 1.    INTRODUCTION

Slippery Lubricant Infused Porous Surfaces (SLIPSs) are of great importance for many applications where the adhesion between liquids and the surface are to be minimised such as self-cleaning, anti-icing, anti-fogging as well as in microfluidics applications [1]. The intimate control of the binary interactions between liquid droplets and advanced surfaces is of paramount importance for the effective design and optimisation for the specific applications. In this work we show the effective implementation of a SLIPS in the presence of a phase-change (PC) material, henceforth referred to as PC-SLIPS, able to shift between different states of the phase change material at moderate substrate temperatures. The thermoresponsive nature of the PC-SLIPS reported here in turn is exploited for the shift and control of the droplet size distribution during dropwise condensation phase change [2].

## 2.    EXPERIMENTAL SECTION

The PC-SLIPS was fabricated as in the work of Zhang et al. [3] although the infused liquid is in this case a common paraffin wax PC material with a melting temperature of ca. 60 °C, i.e., the infused PC material remains in the solid phase for lower temperatures while for higher temperatures it is in liquid state. Schematics showing the steps for PC material (paraffin P and xylene X) impregnation and annealing is included in Figure 1.

*Corresponding Author: zhangp@sjtu.edu.cn & d.orejon@ed.ac.uk
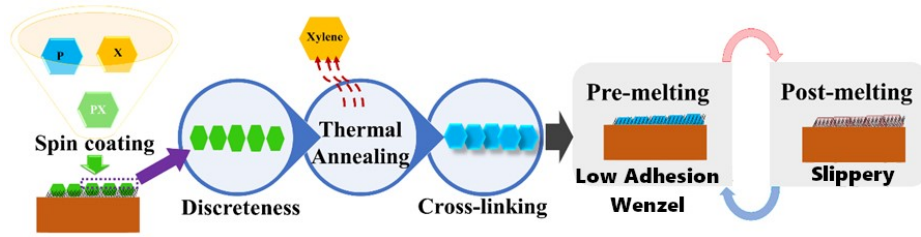
**Figure 1**: Schematics of the impregnation of paraffin P and xylene X including spin coating and thermal annealing. The thermosresponsiveness of the surfaces is then demonstrated by the pre-melting and post-melting cycles.

Paraffin and xylene mixture PX is spin coated on the surface and then subjected to thermal annealing to ensure full impregnation and the evaporation of xylene. During thermal annealing the xylene evaporates leaving a smoother surface with lower adhesion when compared to the not annealed PC-SLIPS. The characterisation of the prepared PC-SLIPSs before and after annealing in the solid phase as well as the PC material in the liquid phase was carried out via optical microscopy to address the different topography function of the phase of the PC material and melting behaviour, via contact angle goniometry to extract the apparent, sliding contact angle as well as the evaporative behaviour to address the wettability, while a condensation unit was custom-built to explore the different condensation behaviours function of the PC-SLIPS state.

## 3. RESULTS AND DISCUSSION

The characterisation of the PC-SLIPS in the solid phase, i.e., below the PC material melting temperature, before and after annealing in the different equilibrium contact angles along with the sliding angle for solid PC-SLIPS before and after annealing are presented in Figure 2(a-c) & (d-f) respectively. To note is the lower adhesion and smoother profile of the PC-SLIPS after annealing in the solid phase displayed when compared to solid PC-SLIPS before annealing as represented in Figure 2(d-f) & (a-c).
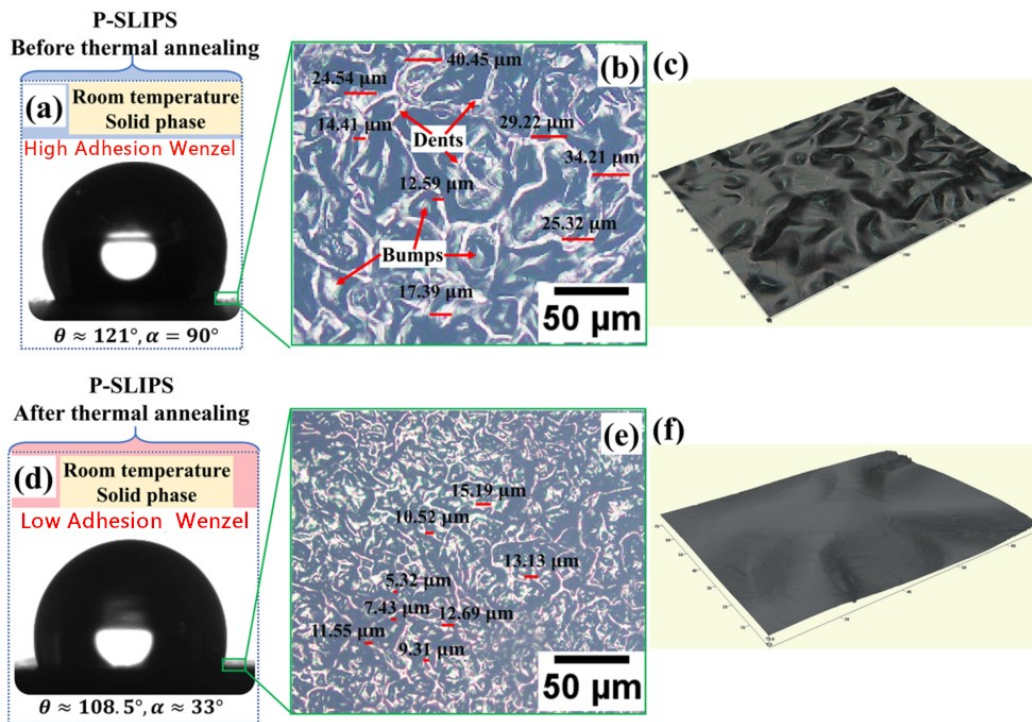


**Figure 2**: Characterisation of (a-c) PC-SLIPS in the solid phase before annealing and (d-f) PC-SLIPS in the solid phase after annealing, with (a & d) contact angle goniometry, (b & e) optical microscopy and (c & f) 3D surface profile via a noncontact optical profiler.

Further optical microscopy of the PC-SLIPS and contact angle goniometry looking at the sliding angle were applied to characterise the differences between the surface topography and the droplet-PC-SLIPS interactions depending on the phase of the PC material infused and whether the PC-SLIPS was annealed or not. Figure 3 introduces optical microscopy of the surface and sliding angle for (left) PC-SLIPS in solid phase before annealing, (middle) PC-SLIPS in solid phase after annealing and (right) PC-SLIPS in liquid phase after annealing.
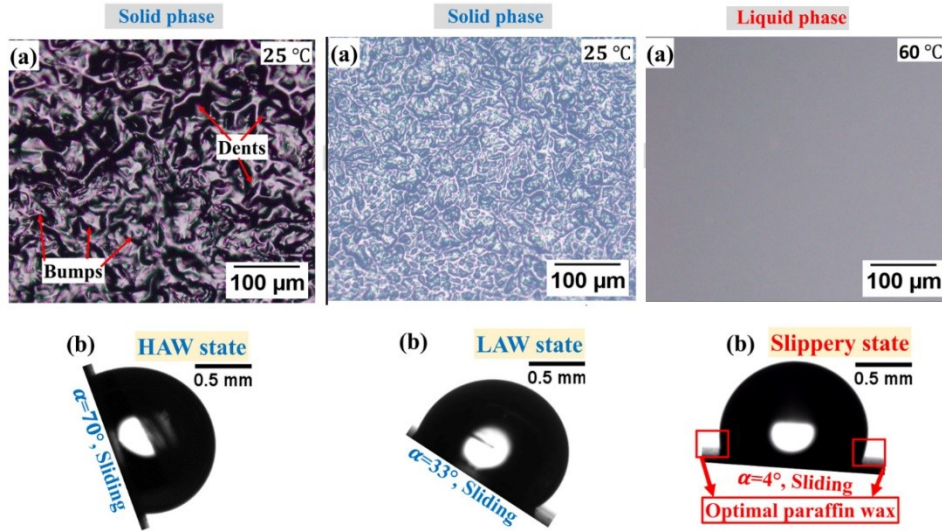


**Figure 3**: Characterisation of (a-top) surface topography via optical microscopy and (b-bottom) sliding angle on PC-SLIPS in (left) the solid phase before annealing, (middle) PC-SLIPS in the solid phase after annealing, and (right) PC-SLIPS in the liquid phase after annealing. Middle & right figures are from Reference 2 [2].

As a consequence of the different state of the PC material state depending on the surface temperature, i.e., liquid or solid, the wettability and more importantly the dynamics of the contact line differs greatly. To quantify the different adhesion depending on the phase of the PC-SLIPS, the depinnning force $F_d$ is estimated as estimated from droplet evaporation observations as $F_d = \sigma_w(\cos\theta_r - \cos\theta_e)$, where $\sigma_w$ is the water-air surface tension and $\theta_r$ and $\theta_e$ are the receding and equilibrium contact angles, respectively, as in the work of Orejon et al. [4] and Xu et al. [5], which is represented in Figure 4.
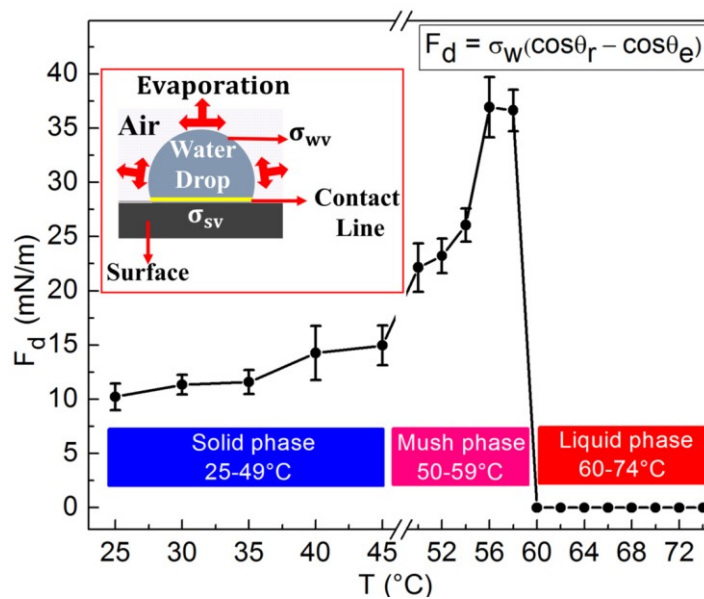


**Figure 4**: Depinning force, $F_d$ (mN/m), function of surface temperature, $T$ (°C) depending on the phase of the PC-SLIPS [2].

The liquid phase PC-SLIPS shows the lowest of the depinning forces implying that droplets evaporate in the Constant Contact Angle (CCA) regime with a continuous receding motion of the contact line, which is consistent with the characteristic behaviour of SLIPS. While on solid phase PC-SLIPS, the contact line is pinned during evaporation until the $F_d$ is overcome as a consequence of the free energy gained by the droplet and the contact line depins. The different pinning forces reported during droplet evaporation should in turn influence the different dynamics and performance of the condensate during dropwise condensation. Figure 5 presents experimental results on the droplet number distribution as the number of droplets versus droplet diameter on PC-SLIPS in both liquid and solid phases of the infused PC infused lubricant.
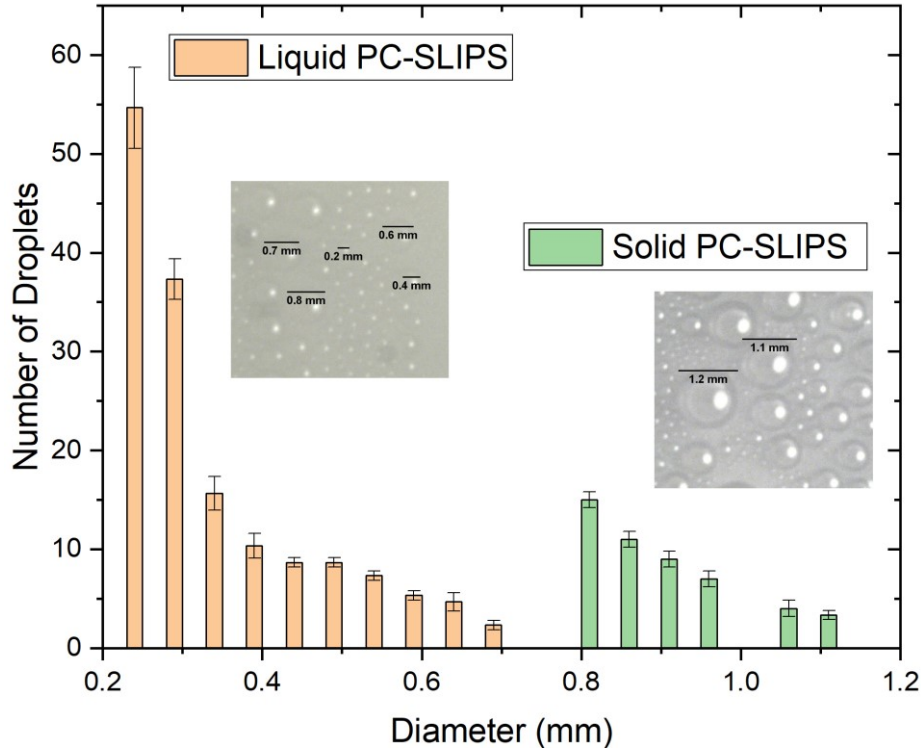


**Figure 5**: The number of droplets during dropwise condensation phase change showing different droplet sizes depending on the phase of the PC-SLIPS during steady-state condensation phase-change.

The different droplet size distribution function of the phase of the infused lubricant is evident from Figure 5, and support the different pinning forces introduced above in Figure 4. On solid PC-SLIPS, the majority of the condensing droplets are in the range of 800 to 1100 microns, while all the droplets observed on liquid PC-SLIPS are within the submillimetre range, i.e., diameters below 700 microns. The presence of smaller sized droplets is owing to the low adhesion, i.e., low depinning force $F_d$, of the condensate prompting the faster droplet re-nucleation, growth and coalescence, and shedding on liquid PC-SLIPS, which in turn allows for a greater number of condensing droplets. The droplet number density distribution is closely linked to the heat transfer performance when applying a heat transfer resistance based model through the condensing droplets [6, 7], which was adopted for nanostructured SLIPS by Weisensee et al. [8] and for hierarchical micro/nano-structured SLIPS by Maeda et al. [9]. The smaller the droplets is, the lower the heat transfer resistance is imposed, which can result in up to 80% of the overall heat flux for droplets with sizes below hundreds of microns. Hence the greater heat transfer performance expected on liquid-PC-SLIPS is demonstrated.

More recently, the condensation heat transfer performance on PC-SLIPS under different phases of the PC material infused was undertaken by Raza et al., [10] where PC-SLIPS in the liquid phase achieved up to 70% and 200% better condensation heat transfer performance than on solid and mush

phases respectively, and 40% better performance than filmwise condensation on the pristine copper plate at 1.5 °C subcooling conditions.

It is worth noting some of the traditional shortcomings of SLIPS such as stability of the lubricant and/or lubricant depletion as well as well-known structure mechanical stability and coating-surface adhesion [11, 12]. We then did look further on the plausible occurrence of lubricant depletion in the present case by subjecting the PC-SLIPS to up to 40 consecutive condensation experimental runs, i.e., 20 for liquid phase and 20 for solid phase for a total of 280 min. After condensation tests, the apparent angle on the PC-SLIPS was found to be 107±1° in both phases, which is within the standard deviation of the apparent contact angle determined before condensation tests (108±1°). This further characterisation indicates the great retention and the presence of paraffin wax on the examined surfaces after several condensation cycles. It is noted though that if there were to be a major mass loss of paraffin from the surfaces, the apparent angle should have been equal to that on the hydrophobized nanoporous copper substrate with which contact angles approximately is 153±1°. Further we also remind the reader on the excellent performance of a closed loop thermosiphon comprising a superhydrophilic evaporator and a SLIPS condenser where approximately 200 hours of operation were reported without the loose of heat transfer performance, i.e., without degradation of the slippery behaviour of the SLIPS condenser [3, 13].

## 4. CONCLUSIONS

The control of the droplet size distribution on PC-SLIPS during condensation phase-change via surface temperature has been demonstrated. The different phase states of the fabricated and characterised PC-SLIPS offer different wetting and dynamics of the contact line as well as condensation behaviours. A high-adhesion Wenzel mode is reported on solid-state PC-SLIPS while a low-adhesion slippery mode ensues on liquid-state PC-SLIPS. While dropwise condensation occurs on both surfaces, the low-adhesion slippery state enables the more frequent shedding of smaller droplets with the consequent expected greater heat transfer performance. The condensation heat transfer performance on the PC-SLIPS under different phases of the PC material enabled by the unique thermoresponsive properties of the surface was then further investigated. Up to 70% and 200% better condensation heat transfer performance is reported for PC-SLIPS in the liquid phase when compared to the PC-SLIPS in solid and mush phases respectively.

**REFERENCES**

[1] Wong, TS., Kang, S., Tang, S. et al. Bioinspired self-repairing slippery surfaces with pressure-stable omniphobicity. Nature 477, 443–447 (2011)

[2] R. Gulfam, D. Orejon, C.-H. Choi, P. Zhang, Phase-Change Slippery Liquid-Infused Porous Surfaces with Thermo-Responsive Wetting and Shedding States, *ACS Appl. Mater. Interfaces*, **12** (2020) 34306–34316

[3] P. Zhang, F.Y. Lv, A. Askounis, D. Orejon, B. Shen, Role of Impregnated Lubricant in Enhancing Thermosyphon Performance. *Int. J. Heat Mass Transfer*, **109** (2017) 1229−1238

[4] D. Orejon, K. Sefiane, M. E. R. Shanahan, Stick−Slip of Evaporating Droplets: Substrate Hydrophobicity and Nanoparticle Concentration. *Langmuir*, **27** (2011) 12834−12843

[5] W. Xu, C.-H., Choi, From Sticky to Slippery Droplets: Dynamics of Contact Line Depinning on Superhydrophobic Surfaces. *Phys. Rev. Lett.* **109** (2012) 024504

[6]  S. Kim, K. J. Kim, Dropwise Condensation Modeling Suitable for Superhydrophobic Surfaces. *J. Heat Transfer* **133**(8) (2011) 081502

[7]  S. Chavan, H. Cha, D. Orejon, K. Nawaz, N. Singla, Y.-F. Yeung, D. Park, D.-H. Kang, Y. Chang, Y. Takata, N. Miljkovic, Heat Transfer through a Condensate Droplet on Hydrophobic and Nanostructured Superhydrophobic Surfaces *Langmuir* **32** (31) (2016) 7774-7787

[8]  P. B. Weisensee, Y. Wang, H. Qian, D. Schultz, W. P. King, N. Miljkovic, Condensate droplet size distribution on lubricant-infused surfaces. *Int. J. Heat Mass Transfer* **109** (2017) 187-199

[9]  Y. Maeda, F. Lv, P. Zhang, Y. Takata, D. Orejon, Condensate Droplet Size Distribution and Heat Transfer on Hierarchical Slippery Lubricant Infused Porous Surfaces. *Appl. Therm. Eng.* **176** (2020) 115386

[10] R. Gulfam, T.-E. Huang, C. Lv, D. Orejon, P. Zhang, Condensation heat transfer on phase change slippery liquid-infused porous surfaces, **185** (2022) 122384

[11] F.Y., Lv, F. Zhao, D. Cheng, Z. Dong, H. Jia, X. Xiao, D. Orejon, Bioinspired functional SLIPSs and wettability gradient surfaces and their synergistic cooperation and opportunities for enhanced condensate and fluid transport. *Adv. Colloid Interface Sci.* **299** (2022) 102564

[12] S. Sett, X. Yan, G. Barac, L. W. Bolton, N. Miljkovic, Lubricant-Infused Surfaces for Low-Surface-Tension Fluids: Promise versus Reality, *ACS Appl. Mater. Interfaces* **9** (41) (2017) 36400–36408

[13] F. Y. Lv, P. Zhang, D. Orejon, A. Askounis, B. Shen, Heat transfer performance of a lubricant-infused thermosyphon at various filling ratios, *Int. J. Heat Mass Transfer*, **115** (2017) 725−736