Droplets on Slippery Lubricant-Infused Porous Surfaces: A Macroscale to Nanoscale Perspective

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ABSTRACT: A recent design approach in creating super-repellent surfaces through slippery surface lubrication offers tremendous liquid-shedding capabilities. Previous investigations have provided significant insights into droplet–lubricant interfacial behaviors that govern antipenetration properties but have often studied using macroscale droplets. Despite drastically different governing characteristics of ultrasmall droplets on slippery lubricated surfaces, little is known about the effects at the micro- and nanoscale. In this investigation, we impregnate a three-dimensionally, well-ordered porous metal architecture with a lubricant to confirm durable slippery surfaces. We then reduce the droplet size to a nanoliter range and experimentally compare the droplet behaviors at different length scales. By experimentally varying the lubricant thickness levels, we also reveal that the effect of lubricant wetting around ultrasmall droplets is intensely magnified, which significantly affects the transient droplet dynamics. Molecular dynamics computations further examine the ultrasmall droplets with varying lubricant levels or pore cut levels at the nanoscale. The combined experimental and computational work provides insights into droplet interfacial phenomena on slippery surfaces from a macroscale to nanoscale perspective.

1. INTRODUCTION

Liquid repellency on metallic surfaces serves tremendous importance in maintaining instrument longevity for various commercial applications and industries, including biomedical devices,1 naval,2 and aviation.3–5 Traditional methods for creating super-repellent surfaces often rely on nanostructuring low-energy surfaces to create stable air pockets underneath the droplet for reduced solid–liquid contact,6 which is inspired by the strategies of the lotus leaves.7 Although such surfaces exhibit remarkable nonwetting behaviors, the robustness of functional surface depends on the stability of the air pockets. Structural damage and collapse of the trapped air, either through external wetting pressures8 or physical erosion, can easily lead to liquid flooding of the microcavities and thus liquid pinning.9

Inspired by the slick lip of a carnivorous Nepenthes pitcher plant10 that sends insect preys sliding down, a new paradigm for super-repellent surfaces suggests the combinational use of a slippery liquid (i.e., lubricant) and surface roughness.11,12 In contrast to the lotus-inspired approach that uses an air–liquid interface, slippery liquid-infused porous surfaces (SLIPS) create a fluid–fluid interface between a lubricant that is impregnated in the microporous solid and the immiscible liquid to be repelled. Stabilized by the capillary pressures of the porous media, the pockets of lubricant provide a slippery surface for the droplets to easily roll off. Prior investigations using the SLIPS have demonstrated superior repellence performance for all types of liquids and resistance to nonalkaline solutions12 using glass-, polymer-, and metal-based surfaces.13–21 In many industrial applications, metal-based SLIPS are needed to prolong and even prevent industrial surfaces from corrosion and fouling.

Although most of previous works regarding metal-based materials use randomly distributed pore structures that are stochastically prepared,18,22,23 the use of highly ordered porous media allows us to systematically relate detailed morphologies to their associated liquid repellency performances and durability. The robustness of slippery surfaces can then be strategically determined by physical characteristics of the porous medium, such as the structure porosity and thickness, which affect the space availability to store lubricant. For example, as thin porous medium receives sufficient surface damages, the lubricant film becomes unstabilized and is prone for easy removal. In addition, the pore network of a periodic porous medium can continuously excrete the reserved lubricant when needed to self-heal after surface damages,24 providing the durability of slippery surface.25 Thus, a three-dimensionally highly interconnected multilayered porous medium may serve as an ideal candidate for SLIPS.

Furthermore, while liquid repellency is effective with a sufficient lubricant level, the interfacial relationship between the lubricant and immiscible liquid changes as the lubricant
level recedes below the structure textures because of evaporation. Although lubricants with an appropriately high viscosity can delay the effects of evaporation for months, the surface slipperiness will eventually diminish leading to liquid adhesion with the solid textures without active lubricant replenishment.\(^ {27}\) Prior studies simulate the recession of the lubricant film by intentionally varying the lubricant thickness above or below the solid features to demonstrate drastic changes in the droplet–lubricant–solid interfacial characteristics, which consequently affects droplet mobility\(^ {28}–\)\(^ {30}\) and droplet evaporation.\(^ {31}\) These measurements are often conducted using droplet volumes on the scale of microliters, which possess characteristic size that is one hundred times larger than the lubricant thickness.\(^ {32}\) With such a relatively large droplet volume, gravity plays a major role in droplet mobility. The droplet mobility governed by the lubricant—liquid—vapor contact lines can be measured by an annular lubricant

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2. EXPERIMENTAL METHODS

2.1. Metal SLIPS Preparation. The multilayer porous architecture used in this study exhibits periodically interconnected spherical pores, known as inverse opal (IO).\(^ {39}–\)\(^ {41}\) As illustrated in Figure 1a–e,

Figure 1. Schematics on the preparation of lubricant-infused nickel IOs. (a) Monodispersed polystyrene spheres self-assemble into colloidal crystal packing on a gold-coated silicon wafer. (b) Nickel deposits into the void spacing between the spheres through galvanostatically electrodeposition. (c) Dissolving the polystyrene spheres reveals an IO structure composed of nickel. (d) Lubricant (Krytox GPL 100) permeates the voids throughout the three-dimensional porous structure that stabilizes the lubricant layer while creating a SLIPS. (e) Water droplet sheds at a low tilting angle. (f) Nickel IO morphology. Top and cross-sectional SEM images of nickel IOs with pore diameters of 300, 600, and 1000 nm. Structural thicknesses of ~3 and 9 μm are available for each set of pore diameter.

nickel IO fabrication starts with self-assembling monodispersed polystyrene spheres into a colloidal crystal template using capillary-assisted vertical deposition. A colloidal suspension [0.6% in deionized (DI) water] of the desired sphere size fills a well, and a base heating of ∼57 °C below the well provides gentle convective mixing of the spheres. A hydrophilic gold-coated silicon substrate (functionalized in an aqueous solution of 0.1 mM sodium 3-mercaptopropionate) is then placed in the well. The colloidal crystal forms as the suspension evaporates in the ambient environment. After annealing the opal template in an oven at ∼95 °C for 3 h, nickel galvanostatically electrodeposits into the empty spaces between the packed spheres with an effective current density of 1.5 mA/cm\(^2\), using a three-electrode setup in an aqueous solution of 0.6 M H\(_2\)SO\(_4\) + 0.2 M NiCl\(_2\) + 0.6 M H\(_3\)BO\(_3\). A bulk nickel plate, opal template-coated substrate, and Ag/AgCl serve as the counter, working, and reference electrodes, respectively. The duration of the electrodeposition process determines the structural thickness. Removing the opal template by immersing in tetrahydrofuran for a minimum of 12 h reveals an IO structure with interconnected
Figure 2. Liquid repellency of nickel IOs for varying states from the macroscale view. (a) Apparent contact angles from sessile drop measurements for dry IOs of various pore diameters and structural thicknesses and dry bare nickel plate. Insets feature representative camera captures of droplet profile. Scale bar is 200 nm. (b-d) Water droplet strongly pins to both (c) flat and (d) porous nickel even at 90° tilt, leading to a significantly high contact angle hysteresis. The purple and blue outlined pictures represent the camera captures for surface repellency for bare nickel and IO, respectively. When infused with lubricant, droplets become mobile at (e) an extremely low sliding angle with (f) a small contact angle hysteresis, as represented by the camera captures for lubricant infused (g) flat and (h) porous nickel. (i,j) After aggressively abrading the slippery surfaces, the minimum sliding angle of bare nickel dramatically increases, and the hysteresis resembles its dry state. The liquid repellency of porous IOs remains consistent, confirming the durable liquid repellency. Representative minimum sliding angles of lubricated and abraded (k) bare and (l) porous nickel are shown. The inset in (f) displays the lubricant infusion within the porous structure at an angled cross-section using environmental SEM. Scale bar is 5 μm. The insets in (i,j) display the top and angled cross-sectional SEM images of an abraded 600 and 1000 nm pore diameter IO, respectively. Scale bars are 1 μm.

2.2. Contact Angle Measurements. The contact angle measurements of DI water on samples are conducted at room temperature with 50% relative humidity, dispensing either 15 ± 4 nL or 10 ± 1 μL to study the effect of droplet volume on droplet mobility and evaporation at the macroscale or microscale, respectively. The larger deviation in the nanoliter droplet volume is caused by variation in injection pressure from the pneumatic dispensing system. The corresponding droplet diameter is measured before coming in contact with the surface and is estimated to be ~220 μm and ~2.5 mm for the nanoliter and microliter droplets, respectively. The apparent contact angles of nanoliter-sized droplets are measured using the sessile drop method with a goniometer (Kytowa Interface Science). A high-speed camera captures the droplet discharge at 1000 fps, and an embedded software (FAMAS) provided by the manufacturer fits the droplet profile using the half-angle method to determine the contact angle. More details regarding the half-angle approach for measuring contact angles of nanoliter droplet are provided in the Supporting Information. The evolution of the droplet height and radius over time is postprocessed from the camera capture that records in intervals of 10 ms. Microliter-sized droplets are dispensed through a micropipette, and a high-speed camera captures the discharge at 240 fps. The associated contact angles are postprocessed with the ImageJ software. We utilize sample tilting to apply a body force on the droplet. We determine the advancing and receding contact angles for both nanoliter- and microliter-sized droplets by measuring the front and back of the droplet before it begins to move. The minimum sliding angles of both nanoliter and microliter droplets are measured on a customized tilting stage, whereas a high-speed camera captures the droplet movement.

2.3. Structural Robustness. The rigidity of the lubricant-infused structure is examined by aggressively abrading with sandpaper (400 grit size) by hand. The abrasion is performed by applying slight pressure in a repeated unidirectional motion. After the abrasion
treatment, the surfaces are imaged by scanning electron microscopy (SEM).

2.4. Molecular Dynamics Computations. We perform molecular dynamics (MD) computations to understand how the level of lubricant exposures or pore cut impacts the droplet dynamics at the nanoscale. The computations are performed using the open-source code called Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS), and the results are visualized using Open Visualization Tool (OVITO). All the computations are conducted in a box with the size of 211.4 Å × 211.4 Å × 165.5 Å with periodic boundary conditions in the x, y, and z directions. The flat substrate consists of eight layers of nickel atoms, where the bottom two layers are kept fixed in order to avoid the migration and deformation of the solid wall. A water droplet containing 4000 molecules is placed on the surface with a density of 1.0 g/cm³. The atomic-level interactions between nickel atoms are modeled by the embedded-atom method.

The extended simple-point charge (SPC/E) water model is used for water because of its validity for dynamic droplet behaviors. Particle–Particle–Particle–Mesh (PPPM) is used to account for long-range Coulombic interactions, and the SHAKE algorithm is applied to keep the water molecules rigid. The water–nuclei interactions are described by the 12-6 Lennard-Jones potential with a cutoff of 12 Å, where ε_Ni-O is 2.85 Å, σ_Ni-O is 9.116 Å, ε_lubricant-O is 4.18 Å, and σ_lubricant-O is 4.1 Å. Then, a constant force of 2.97 × 10⁻⁵ eV/Å is applied to each water molecule in the z-direction in order to model dynamic droplet behaviors, resulting in the total force of 0.356 eV/Å to the system. The force is large enough to overcome the attraction forces between water molecules and the solid surface, such that the droplet slides in all the cases. We measure the dynamic contact angles by averaging the values of 15 frames from 0.6 to 0.9 ns.

3. RESULTS AND DISCUSSION

3.1. SLIPS’s Morphological Impacts on Durability Performance. The morphology of the prepared nickel IOs is confirmed using SEM through top and cross-sectional imaging, as shown in Figure 1f. By varying the sphere sizes in the colloidal template, IOs with pore diameters of 300, 600, and 1000 nm are created. Each set of pore diameter possesses two systematic structural thicknesses (∼3 and 9 µm, which hereafter will be denoted as thin and thick porous structure, respectively). Using a previously derived correlation between the pore diameter and the interconnected window, the structural porosity is calculated as ∼80% for all the cases.

We measure apparent and dynamic droplet physics for varying IOs’ pore diameter and thickness. The apparent contact angle measurements of both flat and porous nickel in their dry (as-fabricated) state show similar hydrophobic characteristics regardless of pore diameter and structural thickness (Figure 2a). Although nickel intrinsically possesses high surface energy, the rapid adsorption of hydrocarbon and contaminants from the ambient environment causes the flat and porous nickel surfaces to become nonwetting. Despite hydrophobicity, the droplet mobility is limited for the dry-state surfaces. The droplet remains pinned to the solid surface even when positioned vertically (90°), resulting in a high contact hysteresis of ∼50° and 70° for bare nickel and all nickel IOs, respectively (see Figure 2b–d). All values for advancing and receding contact angles during which droplet is mobile at the minimum sliding angle are reported in the Supporting Information. By infusing the flat and porous surfaces with a lubricant, liquid pinning is significantly reduced such that the droplet sheds at extremely low sliding angles (<5° for nickel IOs and <10° for bare nickel) and shows small hystereses (<7° for all lubricant-infused samples), as plotted and shown with representative camera captures in Figure 2e–h. However, the lubricant-coated bare nickel exhibits a slightly higher sliding angle, which suggests that a certain degree of underlying surface roughness is required for the installation of efficient repellency. Similar to the dry samples, the static contact angle of lubricant-infused nickel IO is independent of both pore diameter and structural thickness (see the Supporting Information). It is interesting to note that the hysteresis of lubricated bare nickel is similar to that of lubricated porous nickel despite not possessing microstructure surfaces. This can be attributed by the relatively thick lubricant coating that completely covers the surface textures such that the surface energy of the metal has limited effect on the droplet.

To understand the self-healing capabilities of IO-SLIPS under everyday operating conditions, the robustness of the lubricant-infused structure is examined by aggressively abrading with sandpaper. After such treatments, lubricant-infused bare nickel loses its ability to repel liquid, as demonstrated by the increase from ∼7° to ∼50° in the minimum sliding angle (see Figure 2i,k). In contrast, the IO-SLIPS demonstrate robustness water-shedding properties despite structural erosion with abrasion treatment, as shown through both low sliding angles and contact angle hystereses (Figure 2j,l). As the lubricant-infused microporous structures become damaged, the surface self-heals by passively wicking nearby lubricants to fill in the local surface defects. Although the lubricant may initially cover the microporous surfaces, the abrasion depletes the lubricant level to that of the exposed protruding microstructures. The locking of the lubricant films by the interconnected cavities also reduces further lubricant displacement during mechanical treatment, which otherwise can be easily removed to expose the underlying dry and nonlubricated areas, as observed with abraded bare nickel. Representative top and angled cross-section SEM images of the abraded IO-SLIPS (insets in Figure 2i,j, respectively) display the remaining intact micropores. Although the thickness of the IOs shows no difference in repellency behavior even with aggressive structural erosion, it should be noted that the thinner porous coating has eroded majority of its thickness, leaving a few remaining patches of rough and porous areas. The robustness of SLIPS can be theoretically maintained with a minimum surface roughness threshold that supports the thermodynamically metastable repellency state despite heavily damaged microstructures. This stability is evident with the remaining structural scaffolds of the thin abraded nickel IOs that contribute to the high surface roughness.

3.2. Lubricant Level’s Effect on SLIPS Performance. Despite leveraging novel lubricant-trapping porous architecture, the lubricant level will eventually deplete itself through extended operating conditions or surface damages. From the initial infusion of lubricant to its total evaporation, the lubricant level ranges from overfilling to underfilling and the solid textures can exhibit drastically different wetting or nonwetting performances. In this investigation, we mimic
the stages of lubricant evaporation in SLIPS by creating three general configurations: (1) the texture submerges underneath a semi-stable thick layer of lubricant (denoted as “flooded”); (2) stable thin lubricant film rests above the texture (“coated”); and (3) lubricant underfills between the protruding texture (“exposed”). See Figure 3a–c for a schematic representation of the configurations of various lubricant thickness levels.

Although the fundamental behaviors of microliter-sized droplets on SLIPS with varying lubricant thicknesses are well-studied, little is known regarding the properties of ultrasmall droplets on SLIPS. Corresponding to the varying lubricant thickness, we examine the associated significance of nanoliter-sized droplets through their three major characteristic differences. (1) The negligible gravitational effect on nanoliter-sized droplets causes the acting body forces on the droplet and the associated liquid shedding properties to be drastically different. (2) The relatively rapid evaporation of microscale droplets in comparison to macroscale droplets on SLIPS (i.e., minutes in comparison to hours) allows us to efficiently examine the droplet evaporation characteristics as a function of different lubricant thicknesses. (3) As the droplet size decreases down to microscales, the length scale between the microscale droplet and the lubricant thickness becomes comparable. Correspondingly, the changes in lubricant ridge characteristics may affect the droplet dynamics and evaporation, which is not as noticeable at the macroscale. Because the displaced droplet behaviors are independent of either pore diameter or structural thickness as shown earlier, the remaining study with lubricant thickness and droplet size is constantly conducted with a nickel IO with a pore diameter of 1000 nm and a thickness of 3 μm.

3.2.1. Microscopic Droplet Dynamics Using Nanoliter Droplets. We first compare the droplet dynamics between microliter and nanoliter droplets on SLIPS with varying lubricant levels to understand the droplet volume effects on the droplet mobility. As previously shown in Figure 2e, microliter droplets exhibit tremendous droplet sliding at a very low tilting angle. However, droplet mobility decreases with decreasing lubricant thickness, eventually leading to droplet pinning despite 90° in tilting angle (see Figure 3d). The exposure of the underlying solid texture and the underfilling lubricants creates a surface with heterogeneous energies. For the case of nanoliter droplets, we notice droplet sliding at an extremely low angle of <1° (see Figure 3e, insets for camera capture of droplet movement, and movie from the Supporting Information). The ease of nanoliter droplet mobility is similar for both the flooded and coated configurations, which may be because the lubricant level remains sufficiently thick in relation to the droplet size. By also assuming the negligible gravitational effect and dominant capillary forces of the nanoliter droplets, the droplet is expected to rest on top of the lubricant film rather than partially sink into the lubricant. The flat droplet–lubricant interfacial contact may allow the droplet to slide with minimal external forces, such as the tiny momentum from the pneumatic injection of the droplet displacement and air microconvection because the experiment is conducted open to the ambient environment. Unlike microliter droplets on the exposed configuration, nanoliter droplets still possess the ability to move with a minimum sliding angle of around 15°. Despite subjecting them to sufficient sample tilt, we sometimes observe that the nanoliter droplets progressively move upward against gravity (see Figure 3e inset and movie from the Supporting Information) which may be because of the combination of droplet’s negligible gravitational effect and gradient surface energies from the nonuniform lubricant coating and the exposed nickel surfaces.51 Other times, we observe that the droplets slide downward with gravity as expected.

The superior mobility of nanoliter droplets can also be attributed to the intrinsic lubricant–liquid–vapor interfaces of...
SLIPS at the microscale, often referred to as an annular "lubricant ridge" around the base of the droplet (see Figure 4a for schematic details).\textsuperscript{29,30} Although it has been theorized that the lubricant ridge acts as a viscous dissipation to the mobility of the droplet,\textsuperscript{29} the presence of a lubricant ridge indicates that a lubricant film is sufficiently available to form a slippery surface. The physical characteristics of the lubricant ridge in relation to the droplet determine the transient droplet dynamics, such as the evaporation rate that affects the transient contact angles, droplet diameter, and droplet height. Prior studies have investigated droplet behaviors on SLIPS using microliter-sized droplets, but the vast scale difference between the microliter-sized droplets and the lubricant coating makes the appearance of lubricant ridge almost unnoticeable (see inset illustrated in Figure 3d). For smaller droplets, the influence of such ridge becomes more significant and pronounced.

We identify how different lubricant coating thicknesses cause different ridge morphologies by examining the evolution of a nondimensionalized ratio between the ridge height $z$ and droplet height $h$ over time in Figure 4c. By using the half-angle method to trace the contour of the spherical droplet onto the base surface (visualized as the yellow dashed line in the Supporting Information Figure S12) and neglecting any initial lubricant cloaking of the droplet (further examined below), we can determine the prominent ridge height $z$ at the inflection point on the droplet profile where the three fluid interfaces meet and the stresses are balanced.\textsuperscript{4,52} $\gamma_{fl} + \gamma_{la} + \gamma_{ol} = 0$, where $\gamma_{fl}$, $\gamma_{la}$, and $\gamma_{ol}$ are surface tensions between the oil–liquid, oil–air, and liquid–air components, respectively. In flooded configuration, we observe that the initial ridge height $z$ is approximately over half of the displaced droplet height $h$. Within a few seconds, the ridge tail rises and cloaks the droplet (i.e., $z/h = 1$), as schematically and visually shown in Figure 4a,b (see movie from Supporting Information). Typical lubricant cloaking is dependent upon the interfacial energies between the lubricant and immiscible liquid,\textsuperscript{11} but we demonstrate here that significant droplet size reduction can also lead to cloaking behaviors. Contrarily, thinner lubricant coating produces smaller initial annular ridges (i.e., $z/h = 0.03$). As the droplet evaporates and reduces in height under the coated and exposed configuration, the lubricant ridge remains relatively the same size, causing the $z/h$ ratio to increase up to unity. As the droplet height sufficiently dwindles, the annular ridge begins to encapsulate more of the droplet. Representative camera captures of the droplet and the attached lubricant ridge at 38 s are displayed in Figure 4d–f for the flooded, coated, and exposed configuration.

The evolution of the transient contact angles and droplet height as a function of time provides insights into the effect of lubricant thickness on the droplet evaporation rate. The evaporation of a typical droplet is affected by the exposed liquid–vapor interface, but with the lubricant ridge encapsulates around the droplet, evaporation is limited to the remaining exposed droplet surface area. For example, a thicker lubricant-infused film (i.e., flooded configuration) induces a more prominent lubricant ridge around the droplet than a vapor diffusion barrier, resulting in slower decreases in transient contact angles and droplet height, as shown in Figure 5a,b. In comparison, the transient contact angles and droplet height of both the bare smooth nickel surface (purple solid line) and a nickel 10 (yellow dotted line) without lubricant impregnation are shown in Figure 5a. Without the presence of a lubricant film, the rate in contact angle decrease becomes drastically faster, further supporting the discernible evaporative inhibition with the lubricant film especially at the microscale. The evolution of droplet radius over time is presented in the Supporting Information.

We further examine the lubricant cloaking behaviors on the impinging droplets as a function of droplet size and lubricant thickness. The cloaking effect can be described using the spreading coefficient of the oil on the droplet, through\textsuperscript{53}

$$S_{dl} = \gamma_{fl} - \gamma_{la} - \gamma_{ol}$$

If $S_{dl} > 0$, the lubricant will cloak the oil. Otherwise ($S_{dl} < 0$), the lubricant will fail to cloak the droplet. Using the surface tension of DI water ($\gamma_{fl} = 72.4 \pm 0.1$ mN/m),\textsuperscript{41} Krytox GPL 100 ($\gamma_{la} = 17 \pm 1$ mN/m),\textsuperscript{54} and the interfacial tension between the two liquids ($\gamma_{ol} = 53$ mN/m),\textsuperscript{55} we determine the spreading coefficient $S_{dl} = 2.4$ mN/m, which suggests that the droplets are presumed to be encapsulated by the lubricant. However, the extensiveness of the cloaking significantly varies depending on both the lubricant layer thickness and droplet size.\textsuperscript{56} This is most evident when measuring the droplet evaporation rate with varying lubricant layer thicknesses for a
Figure 5. Effect of lubricant coating thickness on the droplet evaporation for nanoliter-sized droplets. The availability of the lubricant affects the lubricant coverage around the droplet such that the changes in evaporative behaviors can be observed through the temporal evolution of the (a) transient contact angle and (b) droplet height. The abundance of lubricant coating on the surface slows the rate of droplet evaporation.

Figure 6. Captures of liquid droplets on varying surfaces using molecular-level computations. A droplet containing 4000 water molecules is placed on a patterned nickel (navy)—lubricant (tan) surface with periodic boundary conditions. The varying exposed lubricant surfaces from 100 to 25% in (a–c) represent the varying lubricant coverage levels or pore cut levels.

given droplet size. The flooded configuration displays the most notable droplet cloaking effect with large lubricant ridges that quickly encapsulates the droplet (Figure 4). As the lubricant layer thins down, the droplet vaporizes at a faster rate, suggesting that the cloaking film thickness surrounding the droplet decreases to allow improved vapor diffusion (Figure 5). In addition to the cloaking-sized impact on droplet evaporation, sufficient lubricant cloaking can also improve droplet mobility on SLIPS. This is demonstrated when comparing the mobility of the nanoliter-sized droplets to that of the microliter-sized droplets (Figure 3). Because of the sufficient cloaking around the smaller droplets, they are able to slide with more ease even on the exposed configuration than the microliter-sized droplets (Figure 3).

3.2.2. Nanoscopic Droplet Dynamics Using Molecular-Level Calculations. To further support our observations of nanoliter droplet behaviors on nickel, lubricant-coated nickel, and heterogeneous lubricant-coated nickel surfaces from a nanoscale, we develop MD computation models. With the presence of lubricant on the nickel surface, the water droplet demonstrates relative hydrophobic characteristics with apparent contact angles of >90°. As the lubricant coverage changes from 100, 50 to 25% the apparent contact angle also decreases from 118°, 102°, and 96°, respectively. Such results suggest the importance of a uniform wetting of lubricant coating for super-repellent functionalities. The 100% lubricant coverage shown in Figure 6a represents both the flooded and coated configuration as the uniform interaction between the droplet and the lubricant-coated surface is predominantly governed by the interfacial surface energy between the droplet and the lubricant. Further thickening the lubricant coating provides negligible influences on the top lubricant layer in contact with the droplet. The patterned pockets of lubricants with 50 and 25% lubricant coverage (Figure 6b,c, respectively) represent the lubricant underfilling between the periodically exposed nickel IO structure. The varying spacing of exposed nickel surfaces between the lubricant mimics the different “cut level” of the tightly packed spherical pores, which consequently determines the characteristics of the nickel ligaments (i.e., the width of the nickel structure). Because of localized defects during the self-assembly of the opal template, a single cut through the IO may exhibit numerous domains of different planar cuts, impacting the droplet dynamics, in particular, for the exposed configuration. See the Supporting Information for further details.

We simulate the dynamic mobility of the droplet by perturbing it with a small body force. At the moment the droplet starts sliding, the advancing and receding contact angles are measured. With a uniform lubricant layer of 100% coverage, the moving droplet exhibits a small difference between advancing and receding contact angles with a hysteresis of 10°. For lubricant coverage of 50 and 25%, larger hysteresis values of 21° and 24° are recorded, respectively, suggesting that the heterogeneous surface energy contributes to temporary droplet adhesion with regions of “stick” and “slip.” With an increase in lubricant coverage over the nickel surface, the droplet slides faster because of the decrease in the water–solid interactions (see the Supporting Information for calculation details). It should be noted that the droplet size studied in the MD simulation is much smaller than the nanoliter droplet experiments to directly corroborate. Nevertheless, the MD simulation still accurately represents the apparent behavior of water-lubricant interaction at the nanoscale because of the dominant governing capillary forces. The presented molecular-level computation of the droplet mobility on both uniform and heterogeneous SLIPS provides significant insights into the dynamics of nanoscopic droplets that would otherwise be extremely difficult to perform empirically.

4. CONCLUSIONS

The lubricant-impregnated metallic porous architecture with three-dimensionally well-ordered pores provides remarkable repellency of water. With the presence of a lubricant layer, the liquid–liquid interface increases the mobility of the immiscible droplet even at extremely low sliding angles with low contact angle hystereses. The interconnectivity of the porous medium stabilizes the slippery surface from being displaced by locking in the lubricant film. Such interconnectivity also helps the structure self-heal by wicking lubricants to the local defect areas despite physical abrasion and scratches, which is an appealing property for common industrial and commercial
operating conditions. Although the independence of pore geometry on liquid repellency behavior is confirmed by leveraging the well-defined pore size, shape, order, and thickness of the periodic pore architecture, thicker porous structures can endure a greater extent of surface abuses and thus maintain their liquid shedding properties over a longer period of time. By acknowledging that even without surface damages, the majority of the lubricant coating in SLIPS will eventually deplete itself through passive evaporation. We assess the associated liquid shedding performance as a function of lubricant coating thickness by comparing microliter- and nanoliter-sized droplets in order to further understand the effect of droplet size on the mobility of the immiscible liquid from the macroscale to microscale view. As the lubricant level lowers to expose the underlying solid surface, liquid repellency of microliter droplets is diminished due to droplet pinning and lower contact angles. However, in the same case, nanoliter droplets are able to move at a decently low sliding angle, which may be attributed to the negligible gravitational forces that prevent the droplet from sinking into the available lubricant film and making sufficient contacts with the solid textures. Molecular-level computational modeling of nonuniform lubricant coating supports such observation of droplet mobility with minor perturbation forces. The new investigation into small-scale droplet interactive behaviors with lubricants reveals initial insights into slippery surfaces from nanoscale and microscale perspective views that support ongoing endeavors to improve evaporative heat transfer, vapor condensation, fog-harvesting, and antifogging applications. The lubricant-locking mechanism of a multilayer periodically interconnected pore architecture demonstrated here also represents a novel approach in making metallic surfaces capable of self-healing and self-cleaning.

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