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Interfacial Strategies for Smart Slippery Surfaces

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Abstract: The problem of contact line pinning on surfaces is pervasive and contributes to problems from ring stains to ice formation. Here we provide a single conceptual framework for interfacial strategies encompassing five strategies for modifying the solid-liquid interface to remove pinning and increase droplet mobility. Three biomimetic strategies are included, i) reducing the liquid-solid interfacial area inspired by the *Lotus* effect, ii) converting the liquid-solid contact to a solid-solid contact by the formation of a liquid marble inspired by how galling aphids remove honeydew, and iii) converting the liquid-solid interface to a liquid-lubricant contact by the use of an lubricant impregnated surface inspired by the *Nepenthes* Pitcher plant. Two further strategies are, iv) converting the liquid-solid contact to a liquid-vapor contact by using the Leidenfrost effect, and v) converting the contact to a liquid-liquid like contact using slippery omniphobic covalent attachment of a liquid-like coating (SOCAL). Using these approaches, we explain how surfaces can be designed to have smart functionality whilst retaining the mobility of contact lines and droplets. Furthermore, we show how droplets can evaporate at constant contact angle, be positioned using a Cheerios effect, transported by boundary reconfiguration in an energy invariant manner, and drive the rotation of solid components in a Leidenfrost heat engine. Our conceptual framework enables the rationale design of surfaces which are slippery to liquids and is relevant to a diverse range of applications.

Keywords: Superhydrophobicity, SLIPS, Liquid Marbles, Leidenfrost, SOCAL

1 Introduction

Over the last two decades there have been many studies on super-liquid repellent surfaces originating from the original work of Neinhuis & Bartlott^{1,2} inspired by the self-cleaning and water shedding properties of the *Lotus* leaf and by the original work of Onda *et al.*³ on fractal surfaces created using a paper-sizing agent. The ability of these surfaces to easily shed liquids rests on their combination of surface topography, at one or more length scales, and liquid repellent surface chemistry to ball-up droplets which then roll freely across their surface^{4,5,14–19,6–13}. Droplets on these surfaces are no longer pinned at their contact lines with the solid and in their motion across the surface pick-up and transport dust, debris and other particulates thereby cleaning the surface under the action of rain.

From a bio-inspiration perspective, the science of the self-cleaning properties of a *Lotus* leaf is the same as the natural waste disposal system used by gall-dwelling aphids^{20,21}. For these insects, their secretion of honeydew - the sticky liquid excrement they produce – risks turning the plant gall they live within into a trap in which they drown. The aphid's solution to this problem is to produce waxy powder which coats the liquid the moment it leaves their body and is the inspiration for the field of liquid marbles^{22,23,32,33,24–31}. This ability to transport a liquid by encapsulating it in a liquid marble rests on the tendency of the water-air interface to adhere hydrophobic particles - a counter-intuitive tendency for water-hating (“hydro”-“phobic”) particles to adhere to (“like”) the surface of water^{34–36}. An effect that has been used to create simple and three-dimensional complex geometric structures starting with membranes and planar structures using “*Capillary Origami*”^{37–42}.

A third natural system for inspiring liquid shedding surfaces is inspired by the carnivorous *Nepenthes* pitcher plant. Like the *Lotus* leaf, the surface of this plant is micro-textured, but unlike

the *Lotus* leaf it is entirely wetting – at least to a lubricant liquid. This enables the surface to lock in a lubricant liquid, which then repels the oils on the feet of insects, so they slide from the rim into the digestive juices at the bottom of the cavity formed by the plant’s cup shaped leaves^{43–46}. The ability of these slippery liquid-infused porous surfaces (SLIPS)⁴⁷, which are a type of lubricant-impregnated surface (LIS)^{48,49} and build upon concepts of hemi-wicking^{7,50–53}, to shed liquids rests on their combination of surface texture and the lubricant preferential wetting surface chemistry to remove pinning for other liquids so that droplets freely slide across their surface. Progress in understanding SLIPS and LIS and their applications is advancing rapidly^{54,55,64–66,56–63} and there is a need to understand the concepts underpinning these different bio-inspired approaches to creating slippery liquid-shedding surfaces being developed within the wider literature.

The above inspiration from nature for surfaces capable of shedding liquids appears diverse from minimizing contact with a liquid (i.e. *Lotus* leaf), to encapsulating a liquid with particles (i.e. galling aphids), and to covering their surface with a liquid (*Nepenthes* pitcher plan). However, each of these approaches use concepts of solid surface shape or texture and surface chemistry to fundamentally change the liquid droplet-solid interfacial interaction. In the remainder of this paper, we provide a conceptual framework encompassing these three, and two further, interfacial strategies to create surfaces which easily shed liquids. We focus on the physical concepts linking these strategies to show how their diversity is underpinned by common ideas. This enables the rationale design of surfaces which are slippery to liquids. In our concept of “slippery”, these are ones on which droplets are mobile and from which a droplet will be shed when the surface is tilted by a small angle. Whilst such a surface may have large static contact angle, it is not a necessary criterion from them to be slippery to a droplet. We then focus on how the “stick” can then be designed back into these surfaces and how droplet motion might be actuated, and droplets transported on such slippery surfaces.

2. Interfacial strategies for slippery surfaces

The variety of inspirations taken from nature provide common themes which come together to provide a set of strategies for creating surfaces slippery to liquids. Many of the successful strategies to create liquid shedding surfaces – one’s slippery to liquids – do not seek to create a smoother liquid-solid contact but seek to fundamentally alter the interaction by modifying the liquid-solid interface.

First consider, the idealized droplet-solid surface contact characterized by a Young’s law contact angle, θ_Y , given by

$$\cos\theta_Y = \frac{\gamma_{SV} - \gamma_{SD}}{\gamma_{DV}} \quad (1)$$

where the γ_{DV} , γ_{SD} and γ_{SV} , are the droplet liquid-vapor, solid-droplet liquid and solid-vapor interfacial tensions and θ_Y therefore depends on the surface chemistry^{67,68}. Equation (1) can be viewed as mechanical force balance at the three-phase contact line or, alternatively, as a condition for the minimum in the surface free energy local to the contact line. If a surface were perfectly smooth and homogeneous in its surface chemistry and equation (1) held at all points along the three-phase contact line, there would be no difference between the advancing contact angle, θ_A , and the receding contact angle, θ_R , since both would be equal to θ_Y ¹⁷. Since the force needed to create droplet motion is proportional to the product of the contact line length and the difference in capillary force per unit length of the contact line, $\gamma_{LV}(\cos\theta_R - \cos\theta_A)$ ⁶⁹, minimal force would be needed to cause a droplet to move across the surface irrespective of the value of θ_Y . Both hydrophobic and hydrophilic surfaces would be able to shed droplets and would therefore be slippery to liquids. It is not a fundamental requirement that a surface be hydrophobic (defined as a contact angle above 90°) for it to be slippery to a liquid. However, when contact between droplet and a solid surface is non-ideal and there is not simply a single Young’s law contact angle, the advancing and receding contact angles often differ significantly in value and contact line pinning occurs.

The first four interfacial strategies to overcome contact line pinning each modify the droplet contact with the solid (Fig. 1). The first strategy is to reduce the droplet-solid interfacial contact area through hydrophobic topography or texture and create a Cassie-Baxter suspended state^{52,70,71}. This gives a reduced droplet-solid contact area with high values for both the advancing and receding contact angles (Fig. 1b). In this case, the droplet balls up and has high mobility to roll across the surface thereby giving a liquid shedding surface. To now understand the second strategy, we recall that the liquid-vapor interfacial tension, γ_{LV} , has a vertical component to its force and that it is always energetically favorable to replace a liquid-vapor interface by a liquid-solid interface – even hydrophobic particles adhere to the water-air interface^{35,36}. Thus, if we imagine the droplet pulling up on the features of the superhydrophobic surface in Fig. 1b with such force they detach from the solid, we then create a liquid marble (Fig. 1c). In this case, the droplet balls up encapsulated in hydrophobic solid particles (with air between them) and rolls across the surface with ease thereby giving a liquid shedding surface. Effectively, the droplet-solid contact familiar from a droplet on a smooth solid surface (Fig. 1a) has been converted into a low adhesion solid-solid contact.

Returning now to the Cassie-Baxter concept, which replaces the droplet-solid contact surface by a composite surface with both droplet-solid and droplet-air contact, we find a route to the third and fourth strategies. By replacing the air within the solid surface texture in Fig. 1b with another fluid - an immiscible lubricant liquid - a composite surface with both droplet-solid and droplet-lubricant contact is created (Fig. 1d), pinning is reduced and droplets are easily shed^{48,53}. This third strategy of lubricant impregnation is most effective in creating a slippery surface for droplets when the lubricant has low surface energy and can completely coat the tops of all solid surface features⁴⁷. For this latter state, Wong *et al.*⁴⁷ gave three criteria (1) the lubricating liquid must wick into, wet and stably adhere within the substrate, (2) the solid must be preferentially wetted by the lubricating liquid rather than by the liquid one wants to repel, and (3) the lubricating and impinging test liquids must be immiscible. Effectively, the droplet-solid contact familiar from a droplet on a smooth solid surface (Fig. 1a) has been converted into a droplet-lubricant contact. If the lubricant liquid also wets the droplet in air, a full encapsulation of the droplet in lubricant occurs (Fig. 1e). The fourth strategy follows this idea of introducing a lubricant liquid but uses a vapor as the lubricant (Fig. 1f). Conceptually, reducing the Cassie solid surface fraction to zero to give perfect hydrophobicity and using a vapor surface area fraction of 100%, suspends the droplet on a lubricating vapor layer – the Leidenfrost effect^{72–74}. In this case, the droplet-solid contact is completely replaced by a droplet-vapor contact, the droplet moves easily on a virtually friction-free cushion of vapor and a liquid shedding surface is obtained.

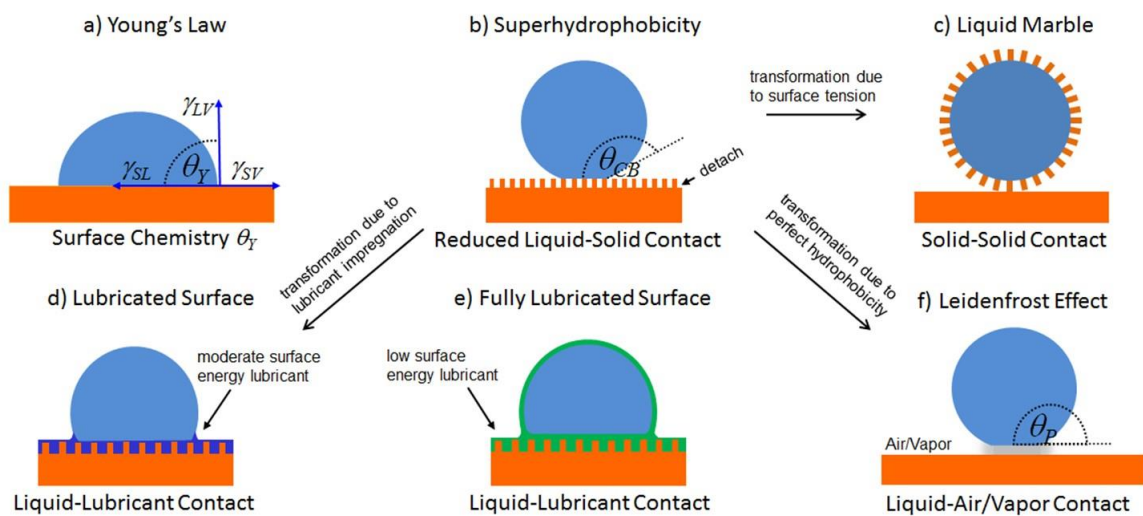


Fig.1 Interfacial strategies for creating surfaces slippery to a droplet of liquid.

Figures 1d,e are interesting because even though the droplet never contacts the solid (in this third strategy it rests on a continuous layer of lubricant liquid), a sessile droplet is still observed. For a

lubricant impregnated surface with a thin conformal liquid layer, a liquid version of Young's law (equation (1)) for an apparent contact angle, θ_{App} , can be derived⁷⁵. (see also references^{61,76})

$$\cos\theta_{App} = \frac{\gamma_{LV}-\gamma_{DL}}{\gamma_{eff}} \quad (2)$$

Here, the γ_{LV} and γ_{DL} are the droplet lubricant-vapor, droplet liquid-lubricant interfacial tensions and γ_{eff} is the effective interfacial tension of the droplet with the vapor, which is either $\gamma_{eff} = \gamma_{DV}$ (non-encapsulated by lubricant) or $\gamma_{eff} = \gamma_{DL} + \gamma_{LV}$ (encapsulated by lubricant) (see also ref.⁶¹). If we regard the vapor from the fourth strategy using the Leidenfrost effect (Fig. 1f) as a lubricant, equation (2) predicts $\theta_{App}=180^\circ$, which indicates a perfectly hydrophobic situation.

The slippery surface strategies in Fig. 1 now indicate a route to a fifth strategy developed from the idea of modifying a solid surface with a conformally thin lubricant layer. This fifth strategy replaces the droplet-solid contact by a droplet-lubricant contact but with lubricant attached to the surface whilst nonetheless providing a liquid-like quality to the surface. The implementation of this strategy uses short non-crosslinked, and therefore flexible, PDMS chains covalently attached to a smooth surface to completely remove contact angle hysteresis and create a solid Slippery Omniphobic Covalently Attached Liquid-like (SOCAL) surface⁷⁷. The advantage of this approach is the surface coating is stable, durable and does not minimize droplet-substrate surface contact area in the same manner as using a superhydrophobic/oleophobic strategy.

3. Example applications of slippery surface concepts

3.1 Droplet evaporation

The evaporation of sessile droplets differs from evaporation of an isolated suspended spherical droplet far from any surfaces even when the contact angle approaches 180° ^{78,79} (for a review see reference⁸⁰). This is because vapor cannot diffuse away from the droplet equally in all directions. Moreover, even when evaporation is slow, and it might be expected that the contact angle maintains a value consistent with Young's law (equation (1)), contact line pinning occurs. This pinning causes stick-slip motion and, for droplets containing solutes, ring-stain deposits⁸¹, which can impact negatively on applications such as quality of fluorescence in spotted microarrays⁸². It also means that the constant contact angle mode of evaporation, which requires a completely mobile contact line, is not usually observed.

We therefore created a silicone oil impregnated lithographically textured SU-8 layer and an octadecyltrichlorosilane (OTS) hydrophobic coating following the strategy in Fig. 1e to create a surface on which droplets of water slide at less than 1° of substrate tilt and apparent contact lines move without pinning⁸³. Small droplets of water on this surface appeared to be spherical cap shape in cross-section and displayed a wetting ridge due to the thickness of the lubricant layer (inset to Fig. 2). Data for evaporation of droplets on substrates with a wide range of Cassie solid surface fractions (10% to 81%) is shown in Fig. 2 indicating a linear change in the apparent contact area of a droplet with time. With a small correction for the presence of the lubricant skirt from the wetting ridge, the constant contact angle model of evaporation provided excellent estimates of the diffusion coefficient of the vapor⁸³.

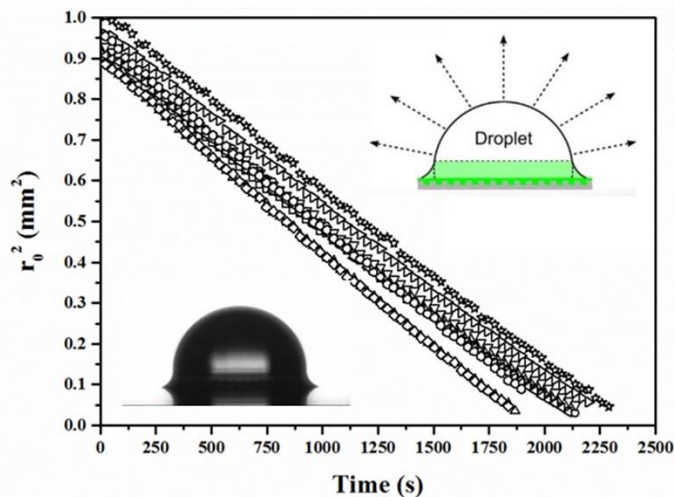


Fig. 2 Constant apparent contact angle droplet evaporation from a lubricant impregnated surface (see also Guan *et al.*⁸³). Change in apparent contact radius squared with time. Lower inset: Side view image of droplet with visible wetting ridge creating a lubricant skirt around the base of the droplet. Upper inset: Schematic of evaporation with restriction of evaporation near the base of the droplet due to the lubricant skirt.

Most recently, we implemented the SOCAL method on a glass substrate (the fifth slippery surface strategy) and reported the evaporation of water droplets over a wide range of relative humidity (10%-70%)⁸⁴. On these liquid-like surfaces droplets adopted perfect spherical cap shapes and contact lines were completely mobile with contact angle hysteresis of $\sim 1^\circ$. The evaporation of sessile droplets was described by the constant contact angle model of diffusion limited evaporation and provided excellent estimates of the diffusion coefficient⁸⁴.

3.2 Droplet positioning on lubricant impregnated surfaces

We next consider how a droplet can be positioned at a desired location on a slippery lubricant impregnated surface. The wetting ridge evident in the inset in Fig. 2 illustrates that on a lubricant surface a meniscus can be formed. This recognition of the existence of a meniscus provides a new concept for determining droplet position and motion through capillary interactions between a droplet and a topographic surface feature (Fig. 3a); it also suggests that adjacent droplets can also interact through the lubricant layer (Fig. 3b). Capillary interactions occur whenever there is an overlap of interfacial distortions, such as around floating particles, vertical plates/cylinders or particles confined in a liquid film⁸⁵. Interfacial distortions are controlled by the balance between a particle's weight and its wetting properties and may give rise to menisci of opposite sign just by changing the object's density⁸⁶. Over a wide range of distances, capillary forces obey a 2D version of Coulomb's law and so the concept of "capillary charge" is used in the literature. Interactions between deformations with meniscus slope angles of the same sign are attractive while opposite signs result in repulsion – the so-called "Cheerios effect"⁸⁶. Since the interfacial deformations caused by floating particles occur over the capillary length, this is also the range of the Cheerios effect. The aggregation of small objects can apply to solid objects (e.g. breakfast cereal in a bowl) or small living creatures, (e.g. nematodes in a thin liquid film⁸⁷). Moreover, water-walking insects can change their body posture to deform the water's surface and draw themselves up menisci at the water's edge⁸⁸. Control of menisci is therefore a powerful concept whenever capillary interactions dominate.

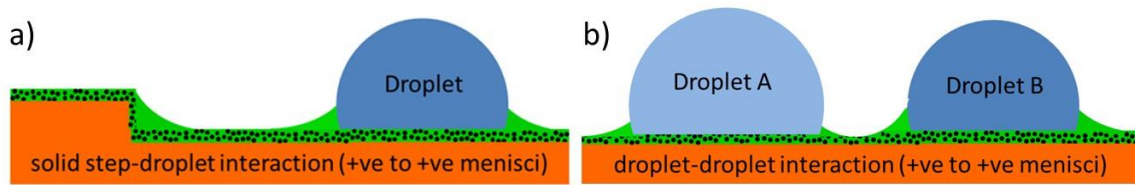


Fig. 3 Meniscus interactions and droplet-on-lubricant Cheerios effect concept illustrated using a lubricant retained on a surface by a hydrophobic nanoparticle coating. a) Droplet interaction with a step topographic feature, and b) Droplet-droplet interaction.

In our previous work we introduced the idea that a droplet on a lubricant impregnated surface (the third slippery surface strategy - Fig. 1d,e) gives rise to capillary forces and a completely new droplet analogue of the Cheerios effect, which can be used to control a droplet's position and motion on an otherwise completely friction free surface⁸⁹ (see also reference⁹⁰). To illustrate this principle, we lithographically fabricated a shallow constant depth groove, which viewed from above creates a tapered channel (Fig. 4). On this surface, the wetting ridge from a droplet on the channel either has no interaction with the lubricant menisci from the edges of the channel or overlaps with one edge or overlaps with both edges (Fig. 4 inset positions 1, 2 or 3). In the first state, the droplet can move freely in the 2-dimensional plane of the surface within the groove, but if it comes close to an edge of the groove it is attracted to that edge. In this second state, a droplet fixed to the edge can move freely along it in a 1-dimensional motion, but if it comes too close to the apex of the channel will interact with menisci from both edges. In this third state, the droplet is attracted to a stable position representing an absolute equilibrium.

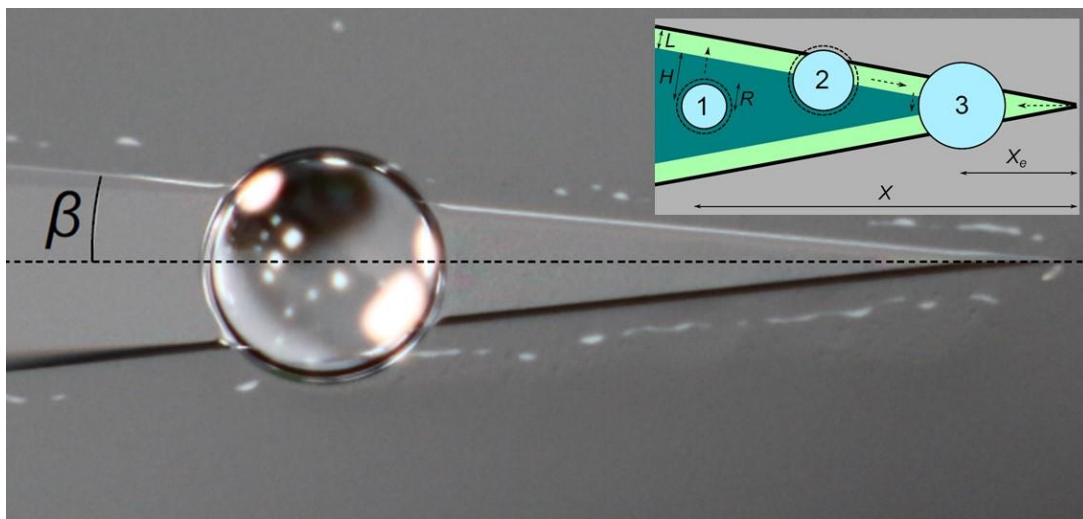


Fig. 4 Droplet on a constant depth triangular groove with a lubricant impregnated hydrophobic nanoparticle coating (viewed from above) (see also Guan *et al.*⁸⁹). Inset: Range of menisci interactions, L , due to the topography and three droplet positions with either 2D or 1D translational invariance or absolute stability (positions 1, 2 and 3 respectively).

The concept of topographic texturing of a lubricant impregnated surface provides control of droplet location and actuation of motion on a completely slippery surface. To illustrate the potential of this concept, and to relate it to evaporation and ring-stains discussed in the previous section, we can imagine creating an array of small dimples on a lubricant impregnated surface. This arrangement would fix the locations of droplets which nonetheless would evaporate with completely mobile contact lines. Since a droplet's contact line would be mobile and there would be no pinning of the contact line (although the drop would be fixed in position), a particle-laden droplet would be expected to evaporate without forming a ring stain. After evaporation, all particles within each droplet would be concentrated into a single deposit at the center of each dimple.

3.3 Energy invariant transportation by boundary reconfiguration

We now continue consideration of actuation of droplet motion on surfaces with vanishing levels of contact line pinning and highlight studies not previously possible. Consider a small sessile droplet on a completely slippery flat plate. The usual perspective is that the droplet adopts an equilibrium contact angle and because it is small has a spherical cap shape (Fig. 5a). An alternative perspective is that the sessile droplet is a sphere intersected by a planar surface which removes a spherical cap segment of a certain volume and leaves a droplet with the required contact angle (Fig. 5b). The importance of this alternative perspective is that the intersecting plane can be rotated around the spherical droplet and provided it retains the same volume in the spherical cap segment it removes, the interfacial areas of the droplet left on the surface will not change (Fig. 5c). Since the interfacial areas do not change, the surface free energy of the sessile droplet will be invariant to changes in orientation of the intersecting plane. This perspective can be applied to multiple planes intersecting the same spherical droplet at different angles. Thus, a droplet in a wedge (Fig. 5d) can be viewed as the consequence of a sphere with two intersecting planes removing two segments (Fig. 5e). Rotating these planes around the sphere whilst keeping constant the spherical cap segment volumes removed provides a set of equivalent surface free energy sessile droplets in a wedge (e.g. Fig. 5f). The only differences are that the position of the droplet in the wedge relative to the apex of the wedge and the opening angle of the wedge are different. Thus, provided the two solid surfaces of a wedge are completely slippery and the droplet is described by a portion of a sphere, altering the opening angle or separation of the two surfaces in the wedge should cause the droplet to move to regain its original surface free energy value, e.g. energy invariant translation between fig. 5e and fig. 5f^{91,92}.

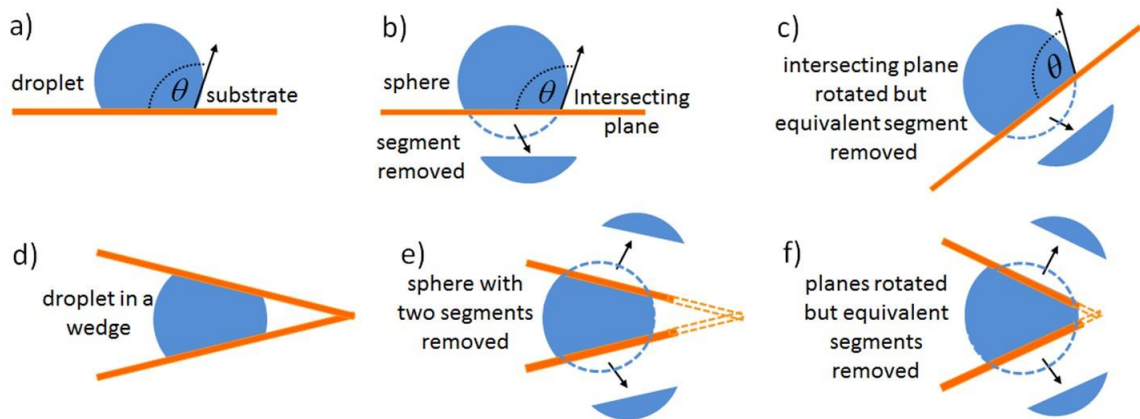


Fig.5 Droplet viewed either as a) a spherical cap on a planar substrate, or b) and c) as a portion of a sphere created by the intersection of a plane removing a spherical cap segment. d) Droplet in a wedge and e) and f) two energy invariant configurations from the viewpoint of the intersection of planes removing segments from a sphere.

The confirmation of energy invariant transport of droplets within a wedge has been given experimentally by Ruiz-Gutiérrez *et al* using two silicone oil impregnated surfaces^{91,92} (slippery surface strategy Fig. 1e). For the spherical droplet assumption to be valid in a wedge, the apparent contact must satisfy the condition $\theta_e > 90^\circ + \beta$, where 2β is the opening angle of the wedge. By adjusting the separation between the two surfaces, the apex of the wedge was moved relative to the droplet position and the droplet translated inwards or outwards to regain its equilibrium surface free energy with the same volume and apparent contact angle (Fig. 6). This ability to actuate motion in an energy invariant manner differs from actuation in a wedge by changing the contact angle⁹³.

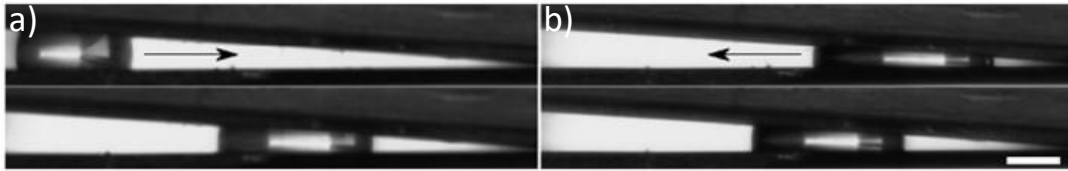


Fig. 6 Droplet in a slippery wedge translating (top image to bottom image) either (a) inwards towards the apex or (b) outwards away from the apex, when the wedge geometry is changed (see also Ruiz-Gutiérrez *et al.*⁹¹).

Whilst the example here has focused on actuating the motion of a droplet in a wedge at constant droplet volume, the principle of energy invariant actuation by boundary reconfiguration can be generalized to other situations. Moreover, since a droplet on a slippery surface will always maintain its apparent equilibrium contact angle and be in its equilibrium energy state, changes in volume on complex surfaces may also actuate motion. An example of this latter situation, termed “snap evaporation”, was recently given for the evaporation of a small droplet from a sinusoidally corrugated slippery surface⁹⁴.

3.4 Low friction rotors in a Leidenfrost engine

In our last example, we consider how the fourth slippery surface strategy (Fig. 1f) has enabled actuation of low friction rotational motion and a new type of heat and mechanical engine. When a droplet of water contacts a surface which is at a temperature well above 100°C a surface layer of the water instantaneously vaporizes and creates a thermally insulating layer on which the droplet is suspended – the Leidenfrost effect^{72–74}. If the object contacting a surface is a dry ice, a similar effect occurs, but rather than it arising from a liquid-to-vapor phase transition, it arises from the direct conversion of solid-to-vapor, i.e. sublimation. In both cases, vapor suspends an object (a droplet or the solid dry ice) and by using a ratchet shaped substrate a low friction directed motion of the vapor can be achieved which causes a propulsion and linear translation of the suspended droplet or dry ice^{95,96}. Thus, the Leidenfrost effect offers a strategy for achieving slippery surfaces for both liquids and solid although through the input of thermal energy.

Recently, we demonstrated that by creating a turbine-inspired shaped substrate rotation of droplets and sublimating droplets could be achieved⁹⁷. For the case of the sublimating solid, this enabled a Leidenfrost heat engine showing the first example of a thermal cycle using a solid-to-vapor transition analogous to the liquid-to-vapor Rankine cycle⁹⁷. This approach enables the harvesting of thermal energy using a phase change mechanism *via* the Leidenfrost effect and offers a virtually friction-free bearing provided by the vapor layer. This idea can be extended to driving the rotation of solid components, such as a glass plate, by using surface tension to couple the plate to a droplet and create a Leidenfrost rotor (Fig. 7)^{97,98}. Since levitation is energetically expensive, applications of this type of engine are likely to be in low or zero gravity environments, such as in space or on other planetary bodies, or microscale systems where the friction from high surface area-to-volume ratios is problematic. Effective use of this approach may also be enabled by replacing the machined turbine pattern of the substrate by a microfabricated electrode structure, such as recently shown for levitating droplets with a selective heating localized to droplet location⁹⁹.

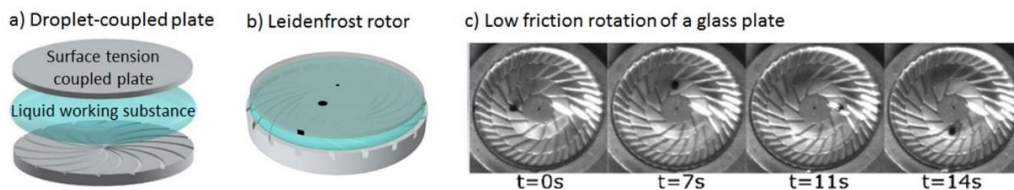


Fig.7 Droplet rotating a glass disk to create a rotor for a Leidenfrost engine (see also Agrawal *et al.*⁹⁸).

4. Conclusions

In this report we have interpreted what often appear to be separate experimental approaches within a single conceptual framework for interfacial strategies to create surfaces slippery to liquids. Three of these strategies have been inspired by how nature moves liquids and borrow the examples of the *Lotus* leaf, the *Nepenthes* pitcher plant and galling aphids. The engineering approaches motivated by these examples lead to super-liquid repellent surfaces, liquid/lubricant infused/impregnated surfaces and liquid marbles. These strategies involve modifying the droplet-solid contact using a fluid (air or a liquid lubricant) or particles (with air). In the case of a liquid/lubricant infused/impregnated surface, a complete layer of lubricant can be engineered to completely separate the droplet from the solid surface and this inspires a fourth strategy based on a continuous layer of vapor – using the Leidenfrost effect - as a lubricant. In the fifth and final strategy, we highlighted that a slippery surface could also be achieved by attaching short flexible PDMS chains to a solid surface as the lubricant using a superomniphobic covalently attached liquid-like layer (SOCAL). These approaches each provide freedom from significant contact line pinning and so enable the creation of surfaces slippery to liquids. We have exemplified how these strategies can be used for a range of novel studies including pinning free sessile droplet evaporation, droplet motion actuated by a droplet-on-lubricant Cheerios effect, energy invariant droplet transport by boundary reconfiguration and Leidenfrost rotors. These examples illustrate the wide applicability of our conceptual framework which can be applied to a wide variety of potential applications.

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