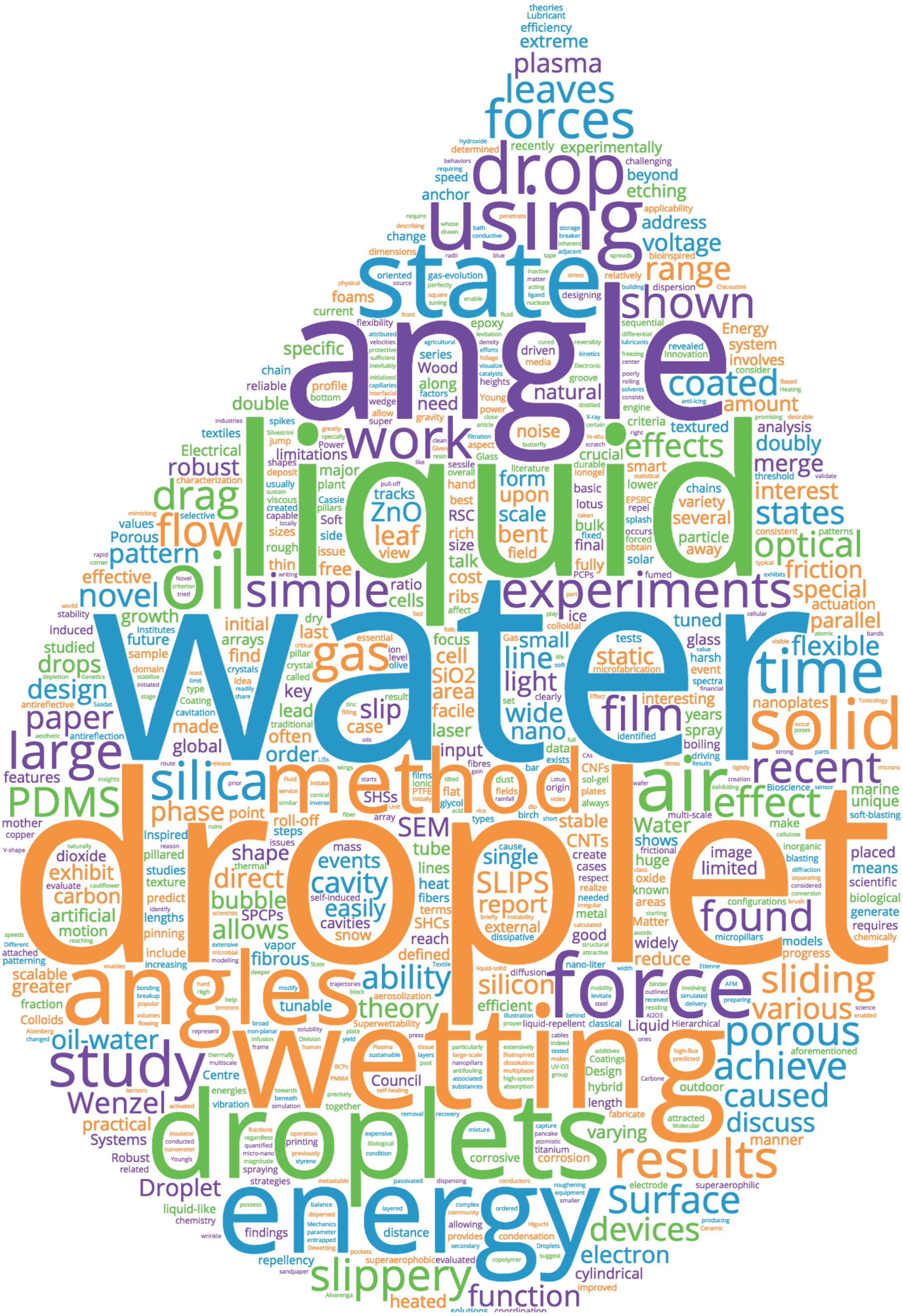
Book of Abstracts

Superhydrophobicity and Wetting Symposium

May 16-17, 2018

Aalto University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Content

Oral presentation abstracts

Plenary session 1

Wednesday 16th

08:40 - 09:40

Smart Interfacial Materials from Super-Wettability to Binary Cooperative Complementary Systems

Lei Jiang
Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China
School of Chemistry and Environment, Beihang University, Beijing 100191, China
*E-mail: jianglei@iccas.ac.cn

Learning from nature and based on lotus leaves and fish scale, we developed super-wettability system: superhydrophobic, superoleophobic, superhydrophilic, superoleophilic surfaces in air and superoleophobic, superareophobic, superoleophilic, superareophilic surfaces under water[1]. Further, we fabricated artificial materials with smart switchable super-wettability [2], i.e., nature-inspired binary cooperative complementary nanomaterials (BCCNMs) that consisting of two components with entirely opposite physiochemical properties at the nanoscale, are presented as a novel concept for the building of promising materials[3,4].

The smart super-wettability system has great applications in various fields, such as self-cleaning glasses, water/oil separation, anti-biofouling interfaces, and water collection system[5].

The concept of BCCNMs was further extended into 1D system. Energy conversion systems that based on artificial ion channels have been fabricated[6]. Also, we discovered the spider silk's and cactus's amazing water collection and transportation capability[7], and based on these nature systems, artificial water collection fibers and oil/water separation system have been designed successfully[8].

Learning from nature, the constructed smart multiscale interfacial materials system not only has new applications, but also presents new knowledge: Super wettability based chemistry including basic chemical reactions, crystallization, nanofabrication arrays such as small molecule, polymer, nanoparticles, and so on[9].

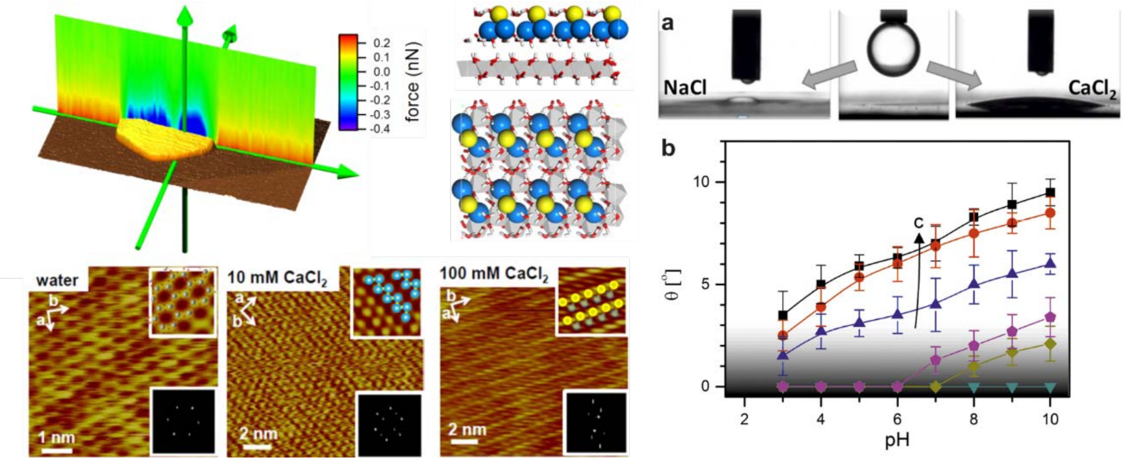
[1] (a) Adv. Mater. 2014, 26, 6872-6897.. (b) J. Am. Chem. Soc. 2016, 138, 1727-1748.
[2] Adv. Mater. 2008, 20 (15), 2842-2858.
[3] Pure Appl. Chem. 2000, 72 (1-2), 73-81.
[4] Small. 2015, 11, 1071-1096.
[5] Adv. Mater. 2011, 23 (6), 719-734.
[6] (a)Chem. Soc. Rev. 2011, 40 (5), 2385-2401; (b) Acc. Chem. Res. 2013, 46 (12), 2834-2846; (c) Adv. Mater. 2010, 22 (9), 1021-1024. (d) ACS Nano 2009, 3 (11), 3339-3342; (e) Angew. Chem. Int. Ed. 2012, 51 (22), 5296-5307;
[7] (a) Nature 2010, 463 (7281), 640-643; (b) Nat Commun 2012, 3, 1247.
[8] (a) Nat Commun 2013, 4, 2276; (b) Adv. Mater. 2010, 22 (48), 5521-5525.
[9] (a) Chem. Soc. Rev. 2012, 41 (23), 7832-7856; (b) Nat. Commun. 2015, 6, 6737. (c) Adv. Funct. Mater. 2011, 21 (17), 3297-3307; (d) Adv. Mater. 2012, 24 (4), 559-564; (e) Nano Research 2011, 4 (3), 266-273; (f) Soft Matter 2011, 7 (11), 5144-5149; (g Soft Matter 2012, 8 (3), 631-635; (h) Adv. Mater. 2012, 24 (20), 2780-2785; (i) Adv. Mater. 2013, 25 (29), 3968-3972; (j) J. Mater. Chem. A 2013, 1 (30), 8581-8586; (k) Adv. Mater. 2013, 25 (45), 6526-6533

Ion adsorption at mineral-electrolyte interfaces: from atomic scale AFM imaging to macroscopic wetting alteration

Frieder Mugele

University of Twente, Physics of Complex Fluids, PO Box 217, 7500AE Enschede,
(The Netherlands)

The distribution of ions and charge at solid-water interfaces plays an essential role in a wide range of processes in nature, science, and technology, including amongst many others the recovery of crude oil from geological reservoirs. While theoretical models of the solid-electrolyte interface date back to the early 20th century, experimental techniques largely rely on macroscopic averaging and therefore lack the spatial resolution to test key predictions. Making use of recent advances in high-resolution Atomic Force Microscopy (AFM) we show with atomic level precision how cations common in natural environments adsorb to heterogeneous mineral-electrolyte interfaces and thereby alter the electrostatic and chemical properties of the surface. In combination with density functional theory calculations, the experiments reveal a detailed picture of the formation of surface phases by templated adsorption of ions under the influence of electrostatic and hydration forces. These changes of the microscopic surface chemistry have dramatic consequences for the affinity of organic solutes and amongst others for the macroscopic wettability of the surfaces: mica surfaces immersed in ambient decane, display a transition from complete water wetting to partial wetting depending on the affinity of preferentially multivalent cations to the solid-electrolyte interface. This phenomenon is believed to play a major role for the success of modern technologies of enhanced oil recovery, in particular so-called Low Salinity Water Flooding.



Left: Ca-adsorption onto gibbsite nanoparticles on silica in ambient aqueous electrolyte. (adapted from: Siretanu et al. *Scientific Reports* 2014.) Right: salt-induced wetting transition in a water-oil-mineral system: contact angle vs. pH for variable Ca^{2+} concentration. (adapted from Mugele et al. *Scientific Reports* 2015.)

Contributed session 1A

Wednesday 16th

10:00 - 12:00

Polyurethane Based Robust Superhydrophobic Surface Coatings

Miray Cinar, H. Yildirim Erbil

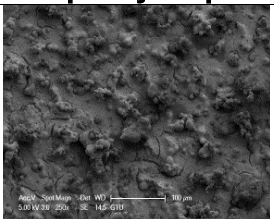
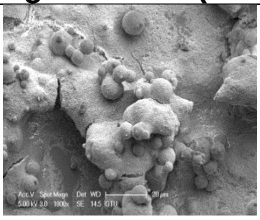
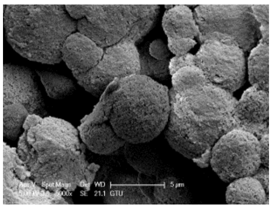
Gebze Technical University, Department of Chemical Engineering,
Gebze, 41400 Kocaeli, Turkey.

Polymeric superhydrophobic surfaces containing inorganic fillers have attracted much attention due to their water repellent properties in the last decade. These surfaces are applied in areas such as self-cleaning, corrosion protection, drag reduction and so on.[1-4]

In this work, robust polyurethane superhydrophobic coatings were synthesized with the addition of mixtures of hydrophobized fumed silica microparticles. Unmodified aliphatic polymeric hexamethylene diisocyanate and acrylate polyols were used as polyurethane components. Glass, aluminum, polyethylene and paper substrates were coated by these superhdrophobic coatings in single or multiple layers by both spraying and dip coating methods. Advancing and receding water contact angles on the coatings were measured and their surface morphologies were investigated by scanning electron microscopy (SEM). Three types of fumed silica additives having different hydrophobizations and particle sizes were tested.

Hierarchical micro/nano structured superhydrophobic PU surfaces were formed and it was determined that the addition of specific combinations of hydrophobized fumed silica for an optimum amount of 25 % by wt. increased both the surface roughness and water contact angles. Very robust superhydrophobic surfaces having ~165-172° advancing contact angles, ~10-16° contact angle hysteresis and 7H pencil hardness resistance were obtained in this work.

[1] H. Y. Erbil, A. L. Demirel, Y. Avci, O. Mert, Science, 299, 1377-1379 (2003).
[2] K. Liu K., X. Yao X., L. Jiang, Chem. Soc. Rev., 39, 3240–3255 (2010).
[3] Y. Li, S. Chen, M. Wu, J. Sun, Adv. Mater. 26, 3344-3348 (2014).
[4] I. Hejazia, G. M. M. Sadeghia, J. Seyfib, S. H. Jafaric, H. A. Khonakdar, App. Surf. Sci., 368, 216–223 (2015).

PU Superhydrophobic Coating on Glass (SEM)	
 **250 x**	 **1000 x**
 **5000 x**	**Water Contact Angles** **θ_A: 168˚** **θ_R:158˚** **CAH:10˚**

Efficiently preparation of remarkable anchor structures to enhance the robustness of SHCs

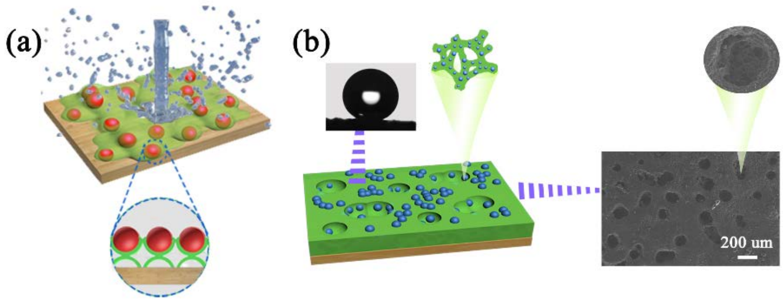
Shanshan Jia[1], Yan Qing[1], Yiqiang Wu[2]

[1]College of Materials Science and Engineering, Central South University of Forestry and Technology

Superhydrophobic coatings (SHCs) are highly desirable as protective layers in diverse materials, but their commercial applications still face huge challenges due to the complex surface roughening and poor mechanical durability. “ Paint+adhesive” method has been considered as one of the most promising approach to enhanced mechanical robustness. Because of the strong bonding strength from adhesive, SHCs could be tightly anchored on substrates.

It is a great challenge to generate sufficient roughness because the adhesive readily covers the nanoparticles (NPs), especially when massive adhesive was used. Although several strategies to rough the composite coating such as plasma/corrosive liquid etching, however, the need for pre/post treatment and special equipment make them less impressive for large-scale application. Moreover, the corrosive constituents and harsh etching treatment inevitably destroy the intrinsic performance of substrates.

In this work, we demonstrated a remarkable anchor structures starting from adhesive via an efficient, simple method, aiming to simplify the preparation routine to robust SHCs. The special structure (namely, NPs embedded in hierarchical adhesive) (figure b) was prepared by an efficient and scalable thermally driven method based on a solution consisting of epoxy, SiO_2 NPs, perfluorooctyltrimethoxysilane (F13-TMS), and ethanol. This one-step thermally driven method that we developed includes two stages, solution immersion and evaporation. The initial solution immersion process allows the ethanol to penetrate into the substrate where the epoxy layer is deposited beneath the NPs under different settling velocity effect. Micropores are created in the epoxy layer by the impact force from the release of gaseous ethanol during the following evaporation. These processes contribute to the hierarchical structure of the adhesive layer, and sufficient bonding strength between functionalized nanoparticles and substrates. To the best of our knowledge, this work is the first to report on the design of such a special anchor structure to efficiently enhance robustness without the need for post-treatments like etching and hydrophobization. Such this as-obtained SHCs exhibited excellent durability when subjected to mechanical abrasion, chemical corrosion, and harsh environmental conditions. Interesting, the different anchor structure could be obtained by tuning the preparation condition (figure a).



Demonstration of two anchor structures starting from adhesive

A novel method for fabricating super-hydrophobic self-cleaning surfaces

Yanan Li[1], Jianqiang Gu[1], Junwei Wang[1], Xin Xu[1],
Louis Winnubst[1,2], Chusheng Chen[1]

[1]CAS Key Laboratory of Advanced Materials for Energy Conversion and Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, PR China
[2]Inorganic Membranes, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

In nature many super-hydrophobic surfaces are found, such as lotus leaves, butterfly wings and rice leaves. These surfaces show water contact angles (CAs) of more than 150° and sliding angles as low as 10°. The key factors for super-hydrophobic surfaces include chemical composition and nano-hierarchical texture to achieve low surface energy and high surface roughness. An interesting needle-like nano-Al_2O_3 layer on a flat porous α-alumina substrate was obtained via a simple hydrothermal synthetic method. Subsequently a polydimethylsiloxane (PDMS) film was applied on this system. After silanization of this film in a non-oxidizing atmosphere (H_2:N_2 = 5:95), the material showed super-hydrophobic behavior with a water contact angle of 170° and a sliding angle of 5°. The material exhibits excellent chemical stability when immersing in acidic (pH=2) or alkali (pH =12) environment and hot water of 70 ^{o}C for 48 h. In addition, the super-hydrophobic surface shows excellent abrasion resistance. After an intense treatment with sandpaper, it still remained super-hydrophobic. This super-hydrophobic alumina wafer shows self-cleaning properties in air, as tested by putting ”artificial dust” (MnO_2 powder), which could be washed away from the surface with flowing water. After imersion in oil (hexadecane) a water droplet remained as sphere at the interface without any wetting of the hydrophobic surface.

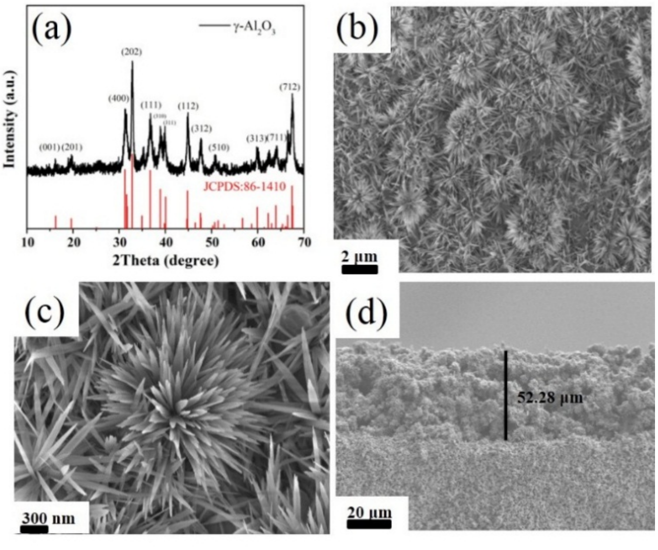


Figure 1 (a) XRD pattern of the as-synthesized γ-Al_2O_3 layer, as applied on a porous α-alumina support, (b) surface of needle-shaped nano-Al_2O_3 coated on a α-alumina support, (c) high-magnification image of a single ”flower-like” structure of the nano-Al_2O_3, (d) cross-section image of the α-alumina support, coated with nano Al_2O_3 and modified with silinated PDMS.

Towards transparent superhydrophobic coating with hierarchical morphology

Norbert J. Janowicz[1], Tanmoy Maitra[1], Ioannis Papakonstantinou[2], Ivan Parkin[3], Claire Carmalt[3], Manish K. Tiwari[1]

[1]Nanoengineered Systems Laboratory, UCL Mechanical Engineering, University College London
[2]Department of Electronic and Electrical Engineering, University College London
[3]Department of Chemistry, University College London

The ability to precisely control roughness of textured superhydrophobic surfaces/coatings down to submicro- and nanometer scales is beneficial in many phase change processes, for example, freezing, condensation, boiling etc. Particularly, nano scale roughness features minimize visible light scattering events, and helps to attain optical transparency, which is otherwise challenging. Therefore, different micro/nano-fabrication techniques have been established over the past few decades to control surfaces roughness at sub-micrometer and nanometer level. However, precise nanoscale control down to ~10 nm, is a formidable challenge.

In this project, we aim to address aforementioned issue by introducing new class of silica/ poly(dimethylsiloxane) (PDMS) nanocomposites. For a hierarchical roughness control we synthesized mesoporous silica nanoparticles of varying sizes (~25nm, ~50nm and ~100 nm, with pore sizes of ~2.5-5 nm) via modified sol-gel synthesis.[1,2] Additionally, we etched the silica nanoparticles surface with sodium borohydride solution for controlled roughness. Through in situ surface functionalisation, the silica nanoparticles were made compatible with PDMS and were dispersed in a hexane solution of PDMS. The stabilised PDMS/mesoporous silica dispersion was sprayed on clean glass substrates using an airbrush with a nozzle diameter of 1 mm, and subsequently cured at ~100°C resulting in superhydrophobic coating. A variety of concentrations of silica particles were used to study their effect on the hydrophobicity and transparency of PDMS. The effect of roughened mesoporous nanoparticles was compared against unetched mesoporous silica and unmodified PDMS.

Topologies of roughened mesoporous silica particles and hierarchical nanoporous superhydrophobic coatings are characterized by atomic force microscopy (AFM) and scanning electron microscopy (SEM). A wide variety of analytical tools, such as Raman spectroscopy, Brunauer–Emmett–Teller (BET) surface area, X-Ray Powder Diffraction spectroscopy (XRD), solid state ^{29}Si Nuclear Magnetic Resonance (NMR) and Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy were used to characterize the mesoporous silica particles. Wettability of the coating was characterized by performing advancing and receding contact angle measurements, and anultra-violet (UV) spectrometer was used to characterize the optical transparency.

[1] L. Han, Y. Zhou, T. He, G. Song, F. Wu, F. Jiang, J. Hu, J Mater Sci 48, 5718–5726 (2013).
[2] Y.-S. Lin, C. L. Haynes, J AM CHEM SOC 132, 4834–4842 (2010)

A novel approach to block copolymer lithography, for the fabrication of superhydrophobic surfaces

Sophia Laney[1], Tao Li[1], Manish K. Tiwari[2], Ivan Parkin[3] and Ioannis Papakonstantinou[1]

[1]Department of Electronic and Electrical Engineering, University College London
[2]Nanoengineered Systems Laboratory, UCL Mechanical Engineering, University College London
[3]Department of Chemistry, University College London

The control of surface/interface phenomena, such as water-condensation and ice-nucleation represents a key challenge spanning a diverse range of industries. Surfaces which exhibit superhydrophobicity have been extensively studied over the past few decades, with inspiration for the majority of such surfaces being drawn from examples in nature. Many natural superhydrophobic surfaces inherently possess re-entrant nanoscale structures, and mimicking this synthetically remains challenging, particularly for large scale fabrication.

Block copolymers (BCPs) are a powerful tool for nanofabrication, due to their ability to self-assemble into an array of different morphologies. Traditionally, their ability to self-organise into ordered nanoscale patterns with contrasting etch resistivities, has been the driving force behind their use, as this enables selective etching. However, this process often involves tedious and costly steps which include brush layer deposition and thermal or solvent-vapour annealing.

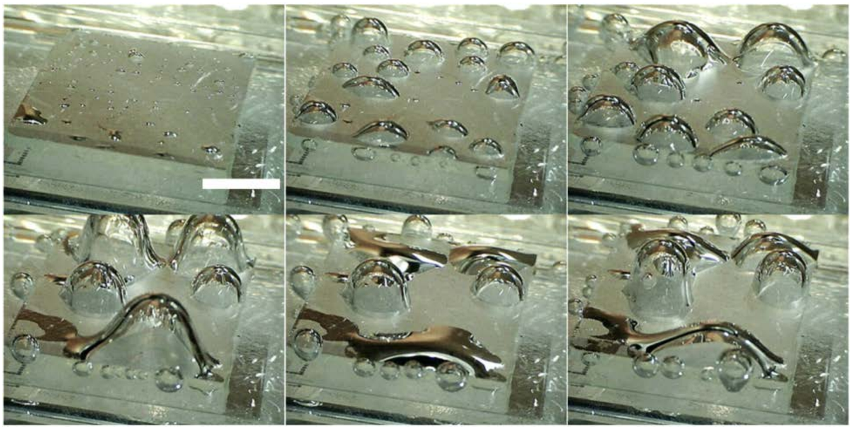
We demonstrate an alternative BCP lithographic process which negates the need for the aforementioned steps, by employing spherical micelles of poly(styrene-*block*-2-vinyl pyridine) (PS-*b*-P2VP) as a topographic contrast. The PS-*b*-P2VP BCPs are synthesised *via* living anionic polymerisation, allowing the domain sizes to be tuned. Subsequent dispersion in *m*-xylene promotes the formation of spherical micelles with a P2VP core. The micelles are directly spin-coated onto an SiO_2 layer followed by a series of dry etching steps into silicon to generate re-entrant, high aspect ratio and large area Si nanostructures, which can then be functionalised to obtain surfaces with tunable wettability. Extensive wettability characterisation tests are used to quantify the surface superhydrophobicity and wetting hysteresis.

Sustainable Thermoregeneration of Superhydrophobic Coatings

Tomer Simovich[1,2], Jaimys Arnott[1], Axel Rosenhahn[2], Robert N. Lamb[1,3]

[1]School of Chemistry, University of Melbourne, Parkville, Australia
[2]Analytical Chemistry – Biointerfaces, Ruhr- University Bochum, Bochum, Germany
[3]Canadian Light Source, Saskatoon, SK, Canada

A popular and desirable function of superhydrophobic coatings is their remarkable ability to retain an entrapped layer of air, called a plastron, when submerged underwater. The drawback is that the air layer is short lived due to solvation into the surrounding liquid. Liquid gas extraction has been explored for the purpose of respiration through oxygen filtering or generation via chemical reaction. Manipulating the solubility of gases using temperature is a possible approach but generally requires inefficiently heating large volumes of water. This paper introduces a novel method of extracting gas from water to replenish and stabilize the plastron on superhydrophobic surfaces for sustained antifouling, rust resistance and drag reduction abilities. This method involves locally heating the liquid surrounding a superhydrophobic coating, reducing gas solubility and causing the gas to nucleate at the liquid-air interface. The approach requires a relatively low energy input, due to the small volume of water that is locally heated combined with the small temperature difference required between substrate and liquid. With a constant supply of equilibrated water and minimal energy input, the plastron can survive indefinitely without the need for a mechanical delivery of air. The thermoregenerating superhydrophobic samples were shown to exhibit excellent anti-fouling behavior and inhibited diatom attachment over a period of 5 days.



Plastron growth on superhydrophobic surface submerged in an open system containing distilled water at 40 hour intervals illustrating the coalescence of bubbles into a continuous plastron (scale bar = 10 mm).

Multidroplets rolling and merging in a flexible bent superhydrophobic tube

Sasha Hoshian[1*], Sami Franssila[1], Ville Jokinen[1]

[1]Aalto University, Department of Chemistry and Materials Science

We introduced a fabrication process for superhydrophobic PDMS/titania flexible tubes[1]. Here we demonstrate controlled merging of two or three droplets sliding in a V-shape bent tube. The merge time can be controlled by droplet size and bent angle. Our flexible superhydrophobic tube with the length “L” was bent into a V-shape. The two ends of the tube were fixed with a metal wire to center to center distance “D” in entire of the experiments. In this configuration the bent angle “θ” is a function of “D” ($\cos\theta = \frac{D}{L}$). Water or blood droplets were applied into the tube one after another and a camera was used to film the experiment. The merge time was calculated from the video captured during the experiments.

Figure 1a-e shows the schematic of a merge experiment. When the first droplet (blue in the schematic) is applied, it oscillates for a while and settles to the gravity minimum (Figure 1a-b). When a second droplet (red in the schematic) is applied, it pushes the first droplet until after few oscillations a shared gravity minimum is achieved (Figure 1c-d). The merge time measurement started from the moment that the droplets start to move toward each other. From this point onward, the pressure between the droplets balances the gravity. The air then slowly escapes through the plastrons driven by the pressure differential, until the droplets merge (Figure 1e).

Figure 1f shows the dependency of the merge time on the steepness of the slope of the bent tube. The merge time can be tuned by one order of magnitude from 1 s to 10 s by changing the angle from 65° to 30°. The merge time is also dependent of the volume of the liquid droplet (Figure 1g).

[1] S. Hoshian et al, Scientific Reports volume 7, Article number: 16019 (2017)

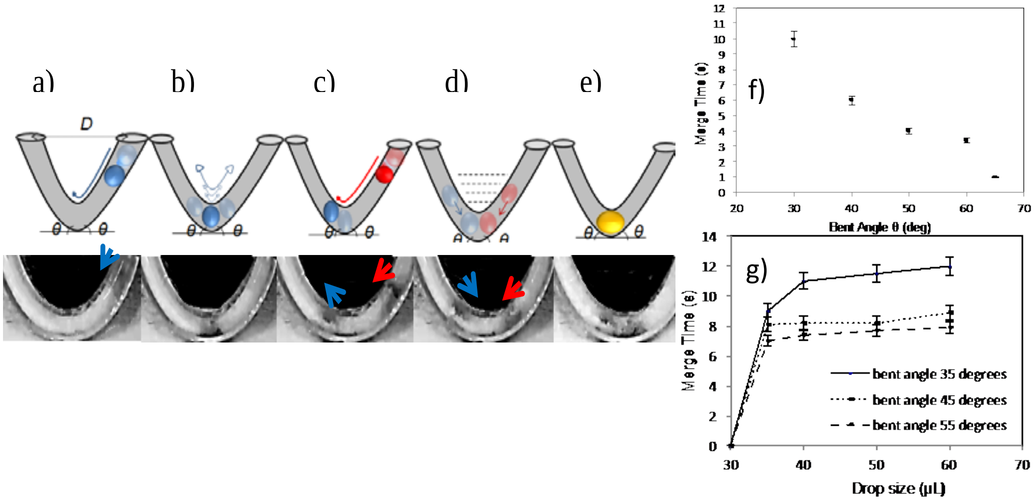


Figure1, a-e) Droplet merging experiment schematic with corresponding snapshots, Merge time f) as a function of bent angle, g) as a function of the drop size with bent angle as a parameter (error bars represent s.d. from average time values).

Bioinspired surfaces for fast droplet shedding

Yahua Liu[1], Zuankai Wang[2]

[1]Dalian University of Technology, Key Laboratory for Precision and Non-traditional Machining Technology of Ministry of Education
[2]City University of Hong Kong, Department of Mechanical and Biomedical Engineering

Many biological systems in nature orchestrate a high level of functionalities and adaptability to their environments enabled by an intricate control of solid-liquid-vapor interfaces, for example, self-cleaning lotus leaves and insect-capturing pitcher plant. One central question in the emerging field of bio-inspired surfaces for multifunctional applications is the maximization of water repellency or the minimization of the contact time of a droplet with solid surface. Until now it was generally believed that drop impacting on solid surfaces could always be separated into two phases: spreading and retraction. However, there exists a theoretical contact time limit when it comes to how long it takes for an impinging droplet to bounce off the surfaces.[1]

In this talk, I will briefly discuss our recent efforts and exciting progress to this classical and important problem. Two droplet bouncing mechanisms - pancake bouncing[2] and asymmetric bouncing[3] - were put forward to reduce the contact between impinging droplets and the underlying solid surfaces and several textured superhydrophobic surfaces have been fabricated to realize this goal. We believe that the discovery of pancake bouncing and asymmetric bouncing which can achieve significantly shortened contact time will stimulate new applications. For example, the complete and fast rebound of droplets, especially impinging supercooled droplets, from the underlying solid surface may considerably suppress the ice nucleation to achieve an overall anti-icing performance.

[1] D. Richard, C. Clanet, & D. Quéré, Nature 417, 811 (2002).
[2] Y. Liu, et al, Nat. Phys. 10, 515–519 (2014).
[3] Y. Liu, et al, Nat. Commun. 6, 10034 (2015).

Contributed session 1B

Wednesday 16th

10:00 - 12:00

Superwetting electrodes for Gas-involving Electrocatalysis

Nana Han[1], Wenwen Xu[1], Xiaoming Sun[1]

[1]State Key Laboratory of Chemical Resource Engineering, College of energy, and
Beijing Advanced Innovation Centre for Soft Matter Science and Engineering,
Beijing University of Chemical Technology, Beijing, 100029, China;

Electrochemical gas-involved reactions, including gas-evolution reaction and gas-consumption reaction, are essential parts in current energy conversion processes and industries. Although the exploration of the highly active catalysts has been very mature, less attention was paid on the gas management during the gas-involved reactions. Inspired from bio-inspired materials, scientists find that bio-mimicked electrodes ***with superwetting property*** will influence the gas transportation process during the electrochemical reactions. Our group fortunately found that the interface behavior of electrode could be tuned by surface architecture construction, for example, transferring from aerophobic to superaerophobic by engineering a series of superwetting micro-/nanostructured electrodes, e.g. MoS_2, Cu, WC nanoarray and Pt pine-like films[1-5]; transferring from aerophilic to superaerophilic by poly(tetrafluoroethylene) (PTFE) modifying, e.g. CoNCNT@CFP.[6] For gas-evolution reaction, constructing nanostructured superaerophobic electrodes is effective to improve the performance by enlarging the bubble contact angle and reducing the bubble adhesion force with the surface of the electrode, thus insuring smooth leaving of the gas products[7-8]. As to the gas consumption reactions, the superaerophilic electrodes are able to improve the performance by providing an unblocked gas diffusion pathway and a smooth electron transport. ***Therefore, construction of superwetting surface*** (superaerophobic for gas evolution reaction and superaerophilic for gas consumption reaction) ***can boost the performances of the electrodes by managing the surface bubbles.***

[1] Z. Lu, W. Zhu, X. Yu, H. Zhang, Y. Li, X. Sun, L. Jiang, Adv. Mater. 26(17), 2683-2687(2014).
[2] Y. Li, H. Zhang, T. Xu, Z. Lu, X. Wu, P. Wan, X. Sun, L. Jiang, Adv. Funct. Mater. 25(11), 1737-1744 (2015).
[3] Z. Lu, M. Sun, T. Xu, W. Xu, Y. Li, Z. Chang, X. Sun, L. Jiang, Adv. Mater. 27(14), 2361-2366 (2015).
[4] Y. Kuang, G. Feng, P. Li, Y. Bi, Y. Li, X. Sun, Angew. Chem. Int. Ed. 55(2), 693-697 (2016).
[5] N. Han, K. R. Yang, Z. Lu, Y. Li, W. Xu, T. Gao, Z. Cai, Y. Zhang, V. S. Batista, W. Liu, X. Sun, Nat. Commun. 9, 924 (2018).
[6] Z. Lu, W. Xu, J. Ma, Y. Li, X. Sun, L. Jiang, Adv. Mater. 28(33), 7155-7161 (2016).
[7] W. Xu, Z. Lu, P. Wan, Y. Kuang, X. Sun, Small, 12(18), 2492-2498 (2016).
[8] Z. Lu, W. Xu, W. Zhu, Q. Yang, X. Lei, J. Liu, X. Duan, Chem. Commun. 50(49), 6479-6482(2014).

Superwettability of Colloidal Photonic Crystals

Jingxia Wang[1,2], Lei Jiang[1,2]

[1]Key Laboratory of Bio-inspired Materials and Interfaces Sciences, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, China
[2]School of Future Technology, University of Chinese Academy of Sciences, Beijing, China
E-mail: jingxiawang@mail.ipc.ac.cn

Photonic crystals (PCs) demonstrate important applications in new optical devices owing to special property of light regulation[1]. This paper presents a series of functional PCs based on its special wettability. As-prepared metal-organic ($Pb(NO_3)$-COOH) PCs can achieve irreversible changes in color/morphology during the electrowetting process, developing a novel and simple water-lithography approach for the creation of the PC pattern[2]. The close-cell carbon dots inverse opals, which prepared from organosilane-polymerized carbon dots and low temperature process, show unique lyophilic but nonwettable wettability[3]. In addition, the special optical properties of the carbon dots endow the sample with tricolor-fluorescence, fluorescence enhancement and modulated optical limiting performance, making it well used in anti-fake pattern[4]. A novel humidity-induced actuator is prepared by the gradient wettability of polyionic liquid inverse opals[5]. Futhermore, Janus PC films can be obtained by asymmetric filling. The directional actuation and thermal shape memory function of PVDF PCs have been realized[6]. A colloidal microarray with optical waveguide behavior is obtained by using a superwettability assembly of fluorescent dye particles[7]. These works are of great significance for the preparation of multi-functional PC materials and new optical devices.

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Bio-Inspired Nanochannels with Superwettability

Ye Tian, Lei Jiang

Institute of Chemistry, Chinese Academy of Sciences, No. 2 Beiyijie, Zhongguancun,
Beijing 100190

tianyely@iccas.ac.cn

Biological nanochannels play very important roles in many functions by controlling ions transport, so mimicking the ion or transport properties are very important for both material science and nanodevices. We first prepare artificial ion pumps and adaptive gating states ion channel by integrating of different functional molecules and single nanochannels; after that, by modifying different molecules with different surface energy in nanochannels, we defined a new wetting threshold of different liquids, and further achieved separation of different organic liquids; by controlling the intermolecular forces between nanochannels and liquid molecules, continuous separation of different liquids can be achieved; by building two dimensional nanochannels with different wettability in silicon wafer, we prepared a superamphiphilic surface, on which uniform functional films can be prepared easily.

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Bioinspired smart wetting surfaces prepared by a femtosecond laser

Feng Chen*, Qing Yang, Jiale Yong, Xun Hou

State Key Laboratory for Manufacturing System Engineering & Key Laboratory of Photonics Technology for Information of Shaanxi Province, Xi’an Jiaotong University, Xi’an, 710049, P. R. China
E-mail address: *chenfeng@mail.xjtu.edu.cn.

Biological micro/nano-structures all comprise the goals for the next-generation smart artificial materials and devices. This presentation summarizes the recent progress in the development of bioinspired smart wetting surfaces via femtosecond laser microfabrication, with a focus on controllable, biomimetic, and switchable wetting surfaces, as well as their applications in biology, microfluidic, industry and environment protection et al., all of which demonstrate the ability of laser microfabrication in producing various multiscale structures and its adaptation in a great variety of materials[1-21]. In particular, Femtosecond laser microfabrication can realize special modulation, allowing much more freedom to achieve complex multiple-wettability integration. The current challenges and future research prospects of this rapidly developing field are also being discussed.

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Effects of slip and temperature jump on droplet impingement on heated superhydrophobic surfaces

Julie Crockett[1], Jonathan Burnett[1], Chunfang Guo[1,2], Daniel Maynes

[1]Brigham Young University, Department of Mechanical Engineering
[2]Dalian University of Technology, School of Mechanical Engineering

The dynamics of single droplet impingement on micro-textured superhydrophobic surfaces with isotropic slip and temperature jump are investigated both analytically and experimentally. For the analytical solution, a cylindrical droplet with a linear velocity profile is assumed. A prior analytical model, based on the energy equation, describes characteristics of this type of droplet impingement on superhydrophobic surfaces with a slip velocity boundary condition. This model, which includes the droplet velocity and spreading profile, has been incorporated into the heat diffusion equation which also allows an apparent temperature jump at the boundary. Using these equations, heat transfer to the droplet can be estimated during the impingement event. Experiments were performed with droplets of distilled water impinging on post micro-structured silicon surfaces with a Teflon coating, rendering them superhydrophobic. Thermal imaging allows an estimate of the average droplet temperature before and after the impingement event. An evaluation of the heat transfer and cooling effectiveness are made in both the model and experiments for droplets with initial Weber numbers ranging from 10-80. The surface slip velocity is varied (varying cavity fraction in the experiments) and surface temperatures from 60°C to 100°C are explored. Results show heat transfer to droplets is decreased for superhydrophobic surfaces as compared to smooth surfaces and cooling effectiveness decreases with increasing slip (or cavity fraction). Agreement between the experimental results and the model is very good.

Direct observations of cavitation and capillaries during force measurements

Mimmi Eriksson[1], Per Claesson[1,2], Mikko Tuominen[1], Mikael Järn[1], Viveca Wallqvist[1], Patrick Gane[3,4], Joachim Schoelkopf[3], Doris Vollmer[5], Michael Kappl[5], Hannu Teisala[5] and Agne Swerin[1,2]

[1]RISE Research Institutes of Sweden, Division of Bioscience and Materials, Sweden
[2]KTH Royal Institute of Technology, Division of Surface and Corrosion Science, Sweden
[3]Omya International AG, Switzerland
[4]Aalto University, School of Chemical Engineering, Department of Bioproducts and Biosystems, Finland
[5]Max Planck Institute for Polymer Research, Germany

The long-range attractive forces between hydrophobic surfaces in aqueous solution have intrigued scientists for over 30 years and are revisited in view of extreme liquid repellency, such as superhydrophobicity and superamphiphobicity. Cavitation or the formation of bridging bubbles has become the most widely accepted mechanism behind the long-range attraction, and it is clear that it explains many of the results reported in the literature. Still, there are only a few examples of force measurements and even less direct visual evidence of such cavitation to be found, and, to the best of our knowledge, no imaging of the proposed cavities have yet been documented.

Forces acting between rough hydrophobic and superhydrophobic surfaces have been reported to display attractive interactions at even longer range than observed between smooth surfaces. The shape of the force curves as a function of distance in such cases is often found to be inconsistent with the presence of a cavity with constant volume on separation. These extremely long-range interactions were instead suggested to be due to an increase in the cavity volume during separation caused by an influx of air from air pockets trapped in the surface features of the rough surface.

In the present study we use a combination of atomic force microscopy (AFM) and laser scanning confocal microscopy (LSCM) to image the formation and growth of cavities during measurements of forces between a superhydrophobic surface and a hydrophobic colloidal probe immersed in water. This configuration allows determination of the de-wetted surface area as well as the shape and volume of the cavity, together with direct calculation of the Young-Laplace capillary pressure. We also provide evidence for the presence of an air layer at the superhydrophobic surface, and growth of the capillary due to transport of air into the cavity. Thus, we now visualize the events that previously have been inferred to occur.

High-throughput nano-liter deposition using hydrophilic-superhydrophobic patterned surfaces

Bo Chang[1,2], Oskari Kivinen[2], Anna A. Popova[3], Pavel Levkin[3], Robin Ras[2], Quan Zhou[4]

[1]Shaanxi University of Science and Technology, College of Mechanical and Electrical Engineering
[2]Aalto University, Department of Applied Physics
[3]Karlsruher Institute of Technology, Institute of Toxicology and Genetics
[4]Aalto University, Department of Electrical Engineering and Automation

Micro and nanoscale droplet deposition is essential in many biomedical, chemical and microfluidic applications. All the existed droplet deposition methods, such as contact dispensing, non-contact dispensing and dip-pen nanolithography, are based on direct deposition of liquid on substrate. We report a new method for rapid and high-throughput deposition of nano-liter sized droplets by moving a larger droplet on a hydrophilic-superhydrophobic patterned surface. As the larger mother droplet detaches from a pattern, a small daughter droplet is left on the hydrophilic pattern. Star-shaped hydrophilic patterns with distinct number of spikes were fabricated and investigated. Experiments were carried out to study the influence of different process parameters including the volume of mother droplet, the moving velocity and the number of spikes to the deposition process. The results concluded that creating microarrays by moving large droplets on hydrophilic-superhydrophobic patterned surfaces yield a reliable, cost-efficient, high-accuracy and easily scalable deposition. The volume of the daughter droplet grows linearly with the velocity of the mother droplet and the number of spikes in a pattern, and decreases with the volume of the mother droplet. Furthermore, we reported a gravity-induced sliding droplets method and demonstrated that the method can be used for parallel nano-liter deposition using different liquids[1]. The proposed method is simple to apply and scalable, where the system only involves droplets and hydrophilic-superhydrophobic patterned surfaces. We believe the method has great potential in many applications e.g. cell microarrays, combinatorial materials study and lap-on-a-chip devices.

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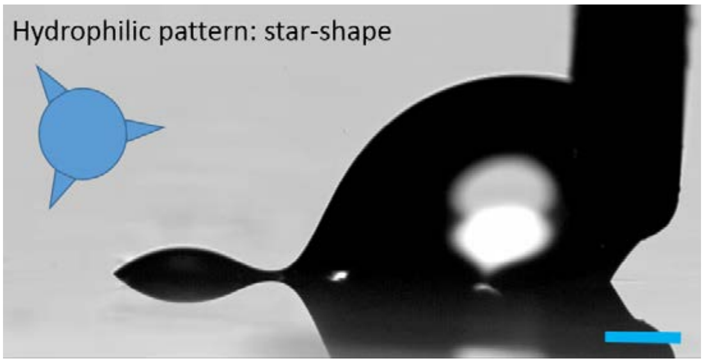

A daughter droplet is deposited on a star-shaped hydrophilic pattern by moving a larger droplet on the patterned superhydrophobic surface. Scale bar length 250 µm.

Mapping microscale wetting variations on biological and synthetic water repellent surfaces

Ville Liimatainen[1], Maja Vuckovac[2], Ville Jokinen[3], Veikko Sariola[1,4], Matti Hokkanen[1,2], Quan Zhou[1], Robin H.A. Ras[2]

[1]Aalto University School of Electrical Engineering, Department of Electrical Engineering and Automation
[2]Aalto University School of Science, Department of Applied Physics, Puumiehenkuja 2
[3]Aalto University School of Chemical Technology, Department of Materials Science and Engineering
[4]Tampere University of Technology, Faculty of Biomedical Sciences and Engineering

Droplets slip and bounce on superhydrophobic surfaces, enabling remarkable functions in biology and technology. These surfaces often contain microscopic irregularities in surface texture and chemical composition, which may affect or even govern macroscopic wetting phenomena. However, effective ways to quantify and map microscopic variations of wettability are still missing, because existing contact angle and force-based methods lack sensitivity and spatial resolution. Here we introduce wetting maps that visualize local variations in wetting through droplet adhesion forces, which correlate with wettability. We develop scanning droplet adhesion microscopy, a technique to obtain wetting maps with spatial resolution down to 10 µm and three orders of magnitude better force sensitivity than current tensiometers. The microscope allows characterization of challenging non-flat surfaces, like the butterfly wing, previously difficult to characterize by contact angle method due to obscured view. Furthermore, the technique reveals wetting heterogeneity of micropillared model surfaces previously assumed to be uniform.

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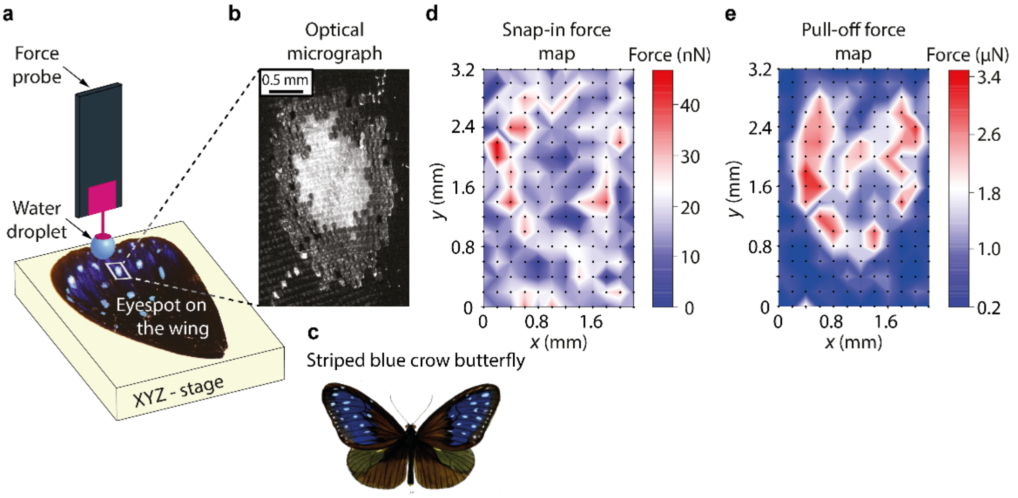


Concept of scanning droplet adhesion microscopy to construct wetting maps. **a** Schematic diagram of the microscope (not to scale). **b** Optical micrograph of scanned eyespot area on the wing of **c**, striped blue crow butterfly (typical wing span of adult specimen 80–90 mm; image by Frederic Moore, PD-1923); with corresponding **d** snap-in and **e** pull-off force maps.

Contributed session 2A

Wednesday 16th

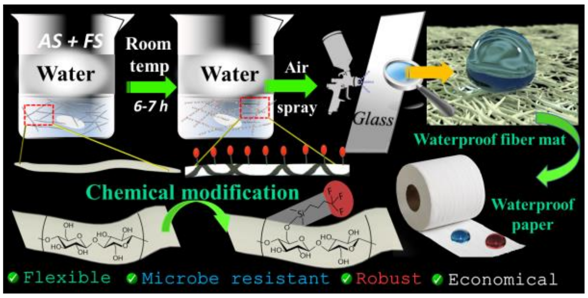
13:30 - 15:00

Organic Solvent-Free Fabrication of Durable and Multifunctional Superhydrophobic Paper from Waterborne Fluorinated Cellulose Nanofiber Building Blocks

Avijit Baidya[1,2,3], Mohd Azhardin Ganayee[1], Swathy Jakka Ravindran[1], Kam (Michael) Chiu Tam[4], Sarit Kumar Das[3], Robin H. A. Ras[2], Thalappil Pradeep[1,*]

[1]DST Unit of Nanoscience, Department of Chemistry, IIT Madras, Chennai, India
[2]Department of Applied Physics, Aalto University School of Science, Finland
[3]Department of Mechanical Engineering, IIT Madras, Chennai 600036, India
[4]Department of Chemical Engineering, Waterloo Institute for Nanotechnology, University of Waterloo, Waterloo, Canada

In the view of a great demand for paper-based technologies, non-wettable fibrous substrates with excellent durability have drawn much attention in recent years. In this context, the use of cellulose nanofibers (CNFs), the smallest unit of cellulosic substrates (5-20 nm wide and 500 nm to several microns in length), to design waterproof paper can be an economical and smart approach. In this study, an eco-friendly and facile methodology to develop a multifunctional waterproof paper *via* the fabrication of fluoroalkyl functionalized CNFs in the aqueous medium is presented. This strategy avoids the need for organic solvents, thereby minimising cost as well as reducing safety and environmental concerns. Besides, it widens the applicability of such materials as nanocellulose-based aqueous coatings on hard and soft substrates including paper, in large areas. Water droplets showed a contact angle of 160° (±2°) over these surfaces and rolled off easily. While native CNFs are extremely hydrophilic and can be dispersed in water easily, this waterborne fluorinated CNFs allow the fabrication of a superhydrophobic film that does not redisperse upon submersion in water. Incorporated chemical functionalities provide excellent durability towards mechano-chemical damages of relevance to daily use such as knife scratch, sand abrasion, spillage of organic solvents, *etc*. Mechanical flexibility of the chemically modified CNF composed paper remains intact despite its enhanced mechanical strength, without additives. Suprhydrophobicity induced excellent microbial resistance of the waterproof paper which expands its utility in various paper-based technologies. This includes waterproof electronics, currency, books, *etc*., where the integrity of the fibres, as demonstrated here, is a much-needed criterion.



Schematic representation of the overall work. For details please see this mentioned article.
ACS Nano (2017), 11(11), 11091-11099

Liquid-repellent surfaces for frictional drag reduction & noise attenuation

Federico Veronesi[1], Mariarosa Raimondo[1], Giulio Boveri[1], Elena Ciappi[2], Claudia Nicolai[2], Francesco La Gala[2]

[1]National Research Council – Institute of Science and Technology for Ceramics CNR-ISTEC

[2]National Research Council – Marine Technology Research Institute CNR-INSEAN

Skin-friction drag is a major source of energy dissipation in marine vehicles. In addition, self-induced noise generated by turbulent boundary layer can strongly limit the operation of on-board sensors. Therefore, designing surfaces with friction drag reduction and vibration control properties is a research topic of great interest for the marine transportation field, both in civil and military segments. Liquid-repellent surfaces have been identified as potential solutions for drag reduction and some papers have already proved their positive effects on drag[1,2], but also their inherent limits[3]. Moreover, no one has ever investigated the potential of liquid-repellent surfaces in terms of self-induced noise attenuation.

In our study, we first fabricated water-repellent surfaces following two well-known biomimetic approaches, namely the SuperHydrophobic Surface (SHS) approach and the Liquid-Infused Surface (LIS) one. Then, we performed experiments in a high speed water channel to evaluate frictional drag and vibration induced by the turbulent boundary layer ($Re \approx 10^6$). Drag experiments were performed on floating aluminum surfaces (48x28 cm^2) bearing a flexural load cell that measured the frictional force exerted by water flow. Meanwhile, in noise experiments a tray-shaped surface was fixed to a rigid frame while 8 piezoelectric accelerometers measured its vibrational response to water flow.

On one hand, SHSs showed quick air plastron depletion during the tests, leading to no drag reduction and higher vibration level compared to a reference uncoated panel. On the other hand, LISs showed remarkable drag reduction (up to 16%) in the 1.0÷3.5 m/s velocity range and reduction of the acceleration response spectra at medium and high frequencies, regardless of flow velocity.

These preliminary results suggest LISs as potentially relevant surfaces to reduce friction drag and self-induced noise, with perspective huge impact in marine transportation. Further experiments are needed to explain the observed noise attenuation and drag reduction effects, which indeed overcame expectations.

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Liquid super repellence – nanoscopic non-wetting forces and coatings on biobased materials

Agne Swerin[1,2]
[1]RISE Research Institutes of Sweden – Bioscience and Materials, Box 5607,
SE-114 86 Stockholm, Sweden
[2]KTH Royal Institute of Technology, School of Engineering Sciences, Biotechnology and Health, Department of Chemistry, Surface and Corrosion Science,
SE-100 44 Stockholm, Sweden

Extreme liquid repellence from surfaces is the focus of many important scientific and technical contributions in recent years. Superhydrophobicity and superamphiphobicity can be achieved on a large variety of substrates employing a large variety of different surface modification technique. It is shown by AFM-based wetting force measurements[1] that superhydrophobicity displays a set of specific events when compared with hydrophobicity and discuss the driving force for growth of the non-wetting cavity as the sum of change in free surface energy, caused by (i) the receding non-wetting liquid, (ii) the work spent on the formation of the liquid-vapor interface and (iii) the volume of the cavity.

A top-down overhang superamphiphobic coating on wood[2] showed extreme liquid repellence with contact angles >150 degrees and roll-off angles <10 degrees against water, ethylene glycol, diiodomethane and olive oil. The coating consisting of titania nanoparticles deposited by liquid flame spray and hydrophobized using plasma-polymerized perfluorohexane was applied to a birch hardwood. SEM imaging of coated areas revealed that capped structures were formed and this, together with the geometrically homogeneous wood structure, fulfilled criteria for overhang structures to occur.

A bottom-up pigment coating was developed to achieve superhydrophobicity in one step from a waterborne formulation containing NaOl-hydrophobized calcium carbonate and styrene-butadiene (SB) latex binder[3]. Coating formulation at higher solids content of 65 mass% improved scratch and water resistance. Water rinsing of the dried coatings further increased the water resistance due to reduced surfactant-assisted wetting from non-bonded NaOl and surfactant remaining in the latex. Capillary forces increase exponentially with increasing pigment volume fraction, suggested as prime reason leading to more efficient binder coverage during the important early stage of pigment coating consolidation. A recent reformulation[4] replaced the SB latex with more sustainable biobased AKD-wax hydrophobized cellulose nanofibrils as binder to achieve superhydrophobic properties.

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Plasma Micro-NanoTextured 3D Surfaces and Their Applications for Wetting and Antibacterial Control

K. Ellinas[1], D. Kefallinou[1], A. Tserepi[1], E. Gogolides[1]

[1]Institute of Nanoscience and Nanotechnology, NCSR Demokritos, Aghia Paraskevi, 15341, Greece.

We have developed a facile, mass production, amenable and rapid method to nanostructure and chemically modify surfaces using plasma processing, which we coin plasma micro-nanotexturing[1].

Our technology can be applied in a wide range of materials, such as: organic polymers (PMMA, COP, PEEK, PS etc.), silicon containing polymers (PDMS, Ormocer® etc.), polymer coated glass or other flat substrates. Structures in the form of cones, columns, or fibers random or quasi ordered are developed using plasma processing. Taking advantage of the topography created after the plasma treatment and its increased surface area, we have demonstrated that such roughened open surfaces are excellent substrates for the creation of superamphiphobic polymer surfaces[2,3]. On such surfaces water or other liquid drops (i.e. hexadecane) roll and have a large contact angle with a very small contact angle hysteresis (typically<10°). In addition, these surfaces exhibit pressure endurance exceeding 36 atm for phosphate buffer (i.e. more than 5 times higher than the state-of-the-art), and 7 atm for a low surface tension buffer/propanol mixture (36mNm^{-1}) (orders of magnitude higher than previously reported for oils[4].

Finally, the same surfaces reduce bacterial adhesion and if combined with an antibacterial agent (i.e. metal), they become very effective antibacterial surfaces for in vitro applications[5].

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Different liquid drops on various plasma micro-nanotextured polymeric substrates.

Robust and scalable superhydrophobic materials

Manish K Tiwari[1,2]

[1]University College London, UCL Mechanical engineering, Nanoengineered Systems Laboratory

[2]Wellcome/EPSRC Centre for Interventional and Surgical Sciences, London

Scalable manufacture and exploitation of bioinspired superhydrophobic surfaces have elicited tremendous interest from a broad palette of scientific community concerned with surface wettability. Features such as self-cleaning, precisely engineered phase change (condensation, freezing, boiling etc.), efficient oil-water separation, corrosion protection, drag reduction etc. are examples of the potential applications that have amplified this interest. However, a lack of robustness of superhydrophobic surfaces has limited their exploitation. Mechanical robustness (e.g. abrasion resistance and adhesion to substrates), ability to function under strong/turbulent flows, chemical stability, resistance to impalement by high-speed drops and jets, etc. are exemplar surface robustness criteria. Here I will share a number of new findings to address and assess this robustness challenge. Firstly, I will introduce a new approach to superhydrophobicity in the form of bulk components rather than 'surfaces/coatings.' Such bulk components are able to sustain continuous mechanical abrasion through a controlled, layer-by-layer material removal without compromising the superhydrophobic property. Next, I will present superhydrophobic sponges which are able to perform excellent oil-water separation even under strong turbulent flow conditions and in harsh chemical environments. Finally, I will introduce new all-organic nanocomposites with mechanical flexibility and exceptional chemical robustness, which can be used either as coatings or potentially be cast as bulk components. The coatings made from this formulation are able to sustain cyclic tape peels and Taber abrasion, maintain superhydrophobicity even when exposed to highly corrosive aqua-regia or basic solutions and, last but not the least, impact by high-speed drops and turbulent jets with speeds >30 m/s. I will discuss the physics and chemistry of such all-round robustness, highlight the key role played by the mechanical flexibility of the coatings, and share my perspectives on the future opportunities to enable fruitful exploitation of superhydrophobic materials in practical applications.

Ionogel-based omniphobic surfaces

Ramón Tena-Zaera, Eneko Azaceta, Jesús Palenzuela, Marta Fenero, Hans-Jurgen Grande

CIDETEC, Paseo Miramón 196, 20014 San Sebastian, Spain

Surfaces exhibiting omniphobicity, which may be defined as the ability of to repel liquids regardless their chemical nature and polarity, are attracting growing interest due to its extremely broad potential in different applications. In particular, good slippery surfaces may help significantly to repel liquids. Since the pioneering studies by Aizaneberg’s group,[1] Slippery Liquid-Infused Porous Surfaces (SLIPS), which is based on the retention of lubricating fluids on surfaces, are indeed a well-known approach to reach omniphobicity. However, their multiphase nature (i.e. solid + liquid) and relatively weak interaction of the lubricant with the surface may result in some practical drawbacks such as losses of the liquid lubricant and consequent loss of slippery performance over time (i.e. durability issues). In this talk, a new generation of omniphobic surfaces, based on a ionogel (i.e. single phase),[2] that overcome the SLIPS limitations will be presented. In particular, the deposition of ionogel-based coatings formed by a perfluorinated ionic liquid embedded in a crosslinked polymeric ionic liquid covalently bonded to a modified substrate surface will be described. The ionogel phase formation and its impact on different surface properties (e.g. surface free energy, contact and sliding angles to different liquids such as water and hexadecane) will be discussed. The key aspects to reach low tilting angles (i.e. < 5°) will be emphasized. The versatility of ionogel-based omniphobic coatings will be proven by showing examples on different substrates such as steel, paper, glass and polymeric materials. Furthermore, some laboratory tests simulating potential applications of the omniphobic gel-coated surfaces will be also shown, highlighting long lasting (i.e. > 18 months) of their properties in hot (100 °C) engine oil. A comparative overview of the ionogel-based coatings versus other approaches to develop omniphobic surface will be given.

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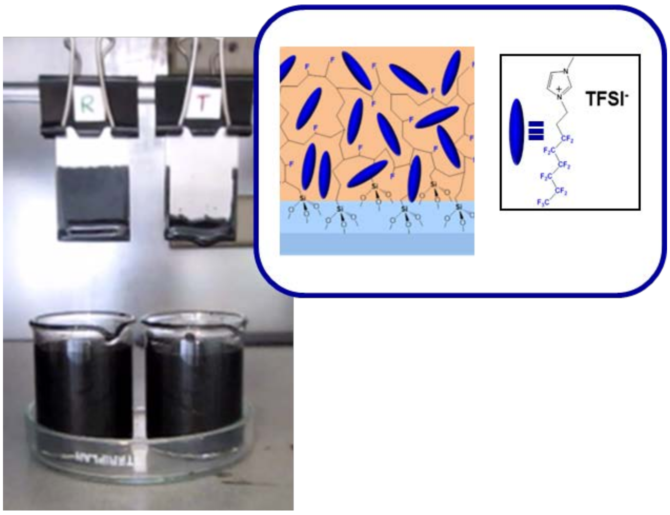


Steel samples (left: naked and right: omniphobic ionogel-coated) after being removed from used engine oil. A schematic view of the ionogel coating and perfluorinated ionic liquid is also shown in the inset.

Contributed session 2B

Wednesday 16th

13:30 - 15:00

Thermodynamics of a sliding drop

Lasse Makkonen[1]

[1]VTT Technical Research Centre of Finland

Theories of contact angles and wettability have been developed for over two centuries. Nevertheless, many basic phenomena, such as the pinning of a contact line and the contact angle hysteresis have been so poorly understood that even their origin has been controversial. The development in the field has been hampered by many widely-used concepts that are based on weak intuitions and dubious assumptions.

In this presentation, the problems encountered with the basic ingredients of the theory of wetting are outlined, and some recent attempts to direct future research on the right tracks are discussed. These include the following findings: 1) Young's equation[1] cannot be interpreted as a lateral balance of applied forces, because no such force exists on a dry solid surface[2], 2) The forces operating at the contact line do not determine the equilibrium contact angle, but the contact angle determines the force balance[3], 3) Sliding of a drop is thermodynamically irreversible[4], 4) Contact angles hysteresis is a fundamental phenomenon that exists already on an ideally smooth and homogenous surface[4], 5) Wettability, in terms of the contact angle hysteresis, can be modelled theoretically both on smooth and textured surfaces[4,5], and 6) Clear distinction between Young's equilibrium contact angle and the dynamic contact angles needs to be made when determining surface energies by contact angle measurements[5].

[1] T. Young, Phil. Trans. R. Soc. Lond. 95, 65-87 (1805).
[2] L. Makkonen, Scripta Mater. 66, 627-629 (2012).
[3] L. Makkonen., J. Phys.: Condens. Matter 28, 135001 (2016)
[4] L. Makkonen, J. Chem. Phys. 147, 064703 (2017)
[5] L. Makkonen, Int. J. Wettability Sci. Technol. 1 (2018), in press.

Icephobic Performance of Superhydrophobic Coatings: A Numerical Analysis

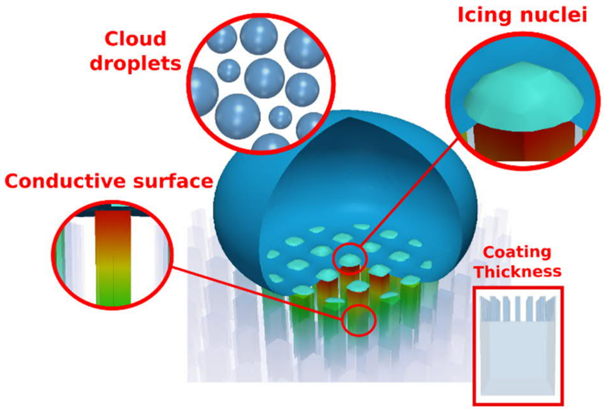
Reza Attarzadeh, Ali Dolatabadi

Concordia University, Department of Mechanical Industrial and Aerospace Engineering

Understanding the mechanism of cloud-sized droplet impact and freezing is crucial to find viable solutions to prevent ice accumulation on critical aerodynamic surfaces such as aircraft wing or nacelle. It has been reported that superhydrophobic surfaces (SHS) have promising anti-icing properties due to their excellent water-repellent characteristics. However, the anti-icing performance of such surfaces has not been fully understood. Due to the optical limitations to visualize inside a solidifying micron-size droplet upon impact, a systematic experimental investigation of this phenomenon is extremely challenging. We have employed a 3D computational fluid dynamics (CFD) analysis to provide more detailed information on droplet freezing under varied impact conditions on coatings with various textures, thermal conductivities, and thicknesses. This can be used as a design tool to engineer icephobic coatings under a given flight condition.

A multi-phase flow solver including free surface, phase change, and conjugate heat transfer at liquid-solid interface has been employed to model the icing of a micro-droplet as it impinges on a superhydrophobic substrate with a given thickness, texture, and material. The Navier-Stokes equation expressing the flow distribution of the liquid and the gas, coupled with the volume of fluid (VOF) method for tracking the liquid-gas interface, was solved numerically using the finite volume methodology. A dynamic contact angle model is applied as a boundary condition at liquid-solid contact lines. Heat transfer within the substrate was solved solely by conduction and the energy equations in both the liquid and solid portions of the droplet are solved using the Enthalpy method.

In order to replicate the in-flight condition, a droplet with a size of 20 µm is opted to simulate the impact of a cloud-sized droplet on a superhydrophobic surface. Modeling of the superhydrophobic surface topology is performed through series of micro-structured arrays with squared cross-sectional pillars. As such, thermal contact resistance is directly modeled by inclusion of air pockets underneath the micro-droplet. Consequently, direct effect of surface topology and thermal properties on droplet maximum spreading diameter, penetration to the surface asperities, contact time, and freezing time have been investigated. The results can be used to identify critical properties required by an icephobic coating to prevent the onset of ice formation under in-flight icing conditions.



The incipient of freezing upon impact of a micro-droplet on rough superhydrophobic surface

Modeling the adhesive forces of a liquid drop

Veikko Sariola[1]

[1]Tampere University of Technology, Faculty of Biomedical Sciences and Engineering

The super hydrophobicity of a surface can be quantified by touching the surface with a liquid drop attached to a force sensor, and measuring the forces during the contact.[1] Two important forces can be identified: the snap-in force – the force when the drop has just initiated contact with the surface – and the pull-off force – the peak force before the drop loses the contact with the surface.[2] These two forces can be related to the advancing and receding contact angles, respectively.

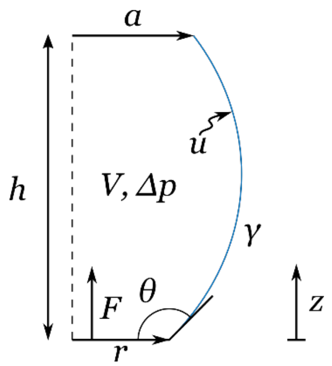
In this talk, I will discuss a computational model of the snap-in and pull-off forces. The model allows studying the relations between the forces, the contact angles, the contact radii and the volume of the drop. Relevant theory – Young-Laplace equation with boundary conditions – will be outlined. Two types of hysteresis are identified: contact angle hysteresis and the hysteresis resulting from the multiple stable configurations of the drop interface. The effects of surface topography will be discussed.

In the following part of the talk, I will interpret experimental results from a recent paper[1] using the model. In particular, I will use the model to show that the data is consistent with some of the surfaces having advancing contact angles beyond 179°. This poses an interesting dilemma that there are currently no other methods with comparable sensitivity to validate the results.

In the final part of the talk, I will discuss alternative approaches and further developments to the model and the theory, and some potentially interesting measurements for the experimentalists.

[1] V. Liimatainen et al., *Nat. Commun.*, 8, article number 1798 (2017). DOI: 10.1038/s41467-017-01510-7

[2] B. Samuel, H. Zhao & K.Y. Law, *J. Phys. Chem. C* 115, 14852–14861 (2011). DOI: 10.1021/jp2032466



In this talk, I will discuss a computational model that relates the adhesive forces of a liquid drop to contact angles and contact radii.

Modeling of Droplet Evaporation on Superhydrophobic Surfaces

Heitor C. M. Fernandes, Mendeli H. Vainstein, and Carolina Brito

Instituto de Física, Universidade Federal do Rio Grande do Sul, 91501-970 - Porto Alegre RS, Brazil

In this work, we consider two possible wetting states for a droplet when placed on a substrate: the Fakir configuration of a Cassie-Baxter (CB) state with a droplet residing on top of roughness grooves and the one characterized by the homogeneous wetting of the surface, referred as the Wenzel (W) state. A way to investigate the transition between these two states is by means of evaporation experiments, in which the droplet starts in a CB state and, as its volume decreases, penetrates the surface's grooves, reaching a W state. We present a theoretical model based on the global interfacial energies for CB and W states that allows us to predict the thermodynamic wetting state of the droplet for a given volume and surface texture. We first analyze the influence of the surface geometric parameters on the droplet's final wetting state with constant volume and show that it depends strongly on the surface texture. We then vary the volume of the droplet, keeping the geometric surface parameters fixed to mimic evaporation and show that the drop experiences a transition from the CB to the W state when its volume reduces, as observed in experiments. To investigate the dependency of the wetting state on the initial state of the droplet, we implement a cellular Potts model in three dimensions. Simulations show very good agreement with theory when the initial state is W, but it disagrees when the droplet is initialized in a CB state, in accordance with previous observations which show that the CB state is metastable in many cases[1]. Both simulations and the theoretical model can be modified to study other types of surfaces, as for example to investigate the wettability of reentrant surfaces[2].

[1] *Modeling of Droplet Evaporation on Superhydrophobic Surfaces,* Heitor C. M. Fernandes, Mendeli H. Vainstein, and Carolina Brito, **Langumuir,** v 31, 7652 (2015)

[2] *Wettability of reentrant surfaces: a global energy approach*, Marion Silvestrini and Carolina Brito, **Langmuir**, v 33, 12535 (2017)

Wetting of rough surface: dynamical effects along transition pathways

Sara Marchio[1], Simone Meloni[1], Alberto Giacomello[1], Carlo Massimo Casciola[1]

[1]Sapienza University of Rome, Dep. Mechanical and Aerospace Engineering, Rome, Italy

The robust design of surfaces able to stabilize gas/vapor phase within their asperities has a great technological importance, stemming from a set of remarkable properties which collectively define the superhydrophobic state. Superhydrophobicity is well suited for drag reduction applications, e.g., in microfluidic devices or marine vessels, and it is also involved in the control of heterogeneous cavitation and boiling. The destabilization and the consequent collapse of the liquid/vapor meniscus produce the breakdown of superhydrophobicity, i.e. the transition to the completely wetted Wenzel state. This is a quasi-irreversible phenomenon, in the sense that the recovery of the Cassie state has a huge energetic cost which makes the event very rare without external inputs. In this scenario a complete understanding of the mechanisms by which Cassie state collapses becomes crucial. The free energy profiles of vapor configurations between Cassie and Wenzel states have been evaluated by Giacomello et al.[1] in a simple square groove: at low vapor filling, i.e., close to the Wenzel state, the asymmetric state with the vapor bubble in one corner of the square groove has a lower free energy than the state corresponding to the symmetric shape of the bubble meniscus. Based on these quasi-static arguments, the asymmetric transition is thus expected to be energetically favored. However, in the experiments performed by Lv et al.[2] both the symmetric and asymmetric transition paths are found in the collapse of superhydrophobicity on a surface patterned with cylindrical nanopores. Asymmetric collapse is attributed to the presence of impurities at the pores bottom. In order to clarify this disagreement, we focus on the characterization of the kinetics of wetting and dewetting transitions via atomistic simulations, gaining qualitative and quantitative information on the preferred reaction mechanisms. To collect statistical data on the transition pathways, Molecular Dynamics implemented with a robust method to control pressure in multiphase systems[3], is combined to Forwards Flux Sampling (FFS)[4]. The implementation of the FFS algorithm generates an ensemble of reactive trajectories, which allows to go beyond the quasi-static picture common to the classical approaches and also to estimate of the transition rate. Varying the thermodynamical conditions, our simulations show when the symmetric mechanism of wetting/dewetting occurs with a significantly higher probability, even if the asymmetric one has the minimum free energy. Such behavior, which is ascribed to “inertial” effects that prevents the system to relax toward a minimum-free energy configuration, can be captured with FFS. The statistical analysis of the atomistic trajectories provides therefore a rigorous frame to interpret the prevalence of symmetric wetting observed in the experiments and provides a general framework to deal with the dynamics of the Cassie-Wenzel transition beyond quasi-static theories.

[1] A. Giacomello , et al. Langmuir 28.29, 10764-10772 (2012).
[2] P. Lv, et al. Langmuir 31.4, 1248-1254 (2015).
[3] S. Marchio, et al. Journal of Chemical Physics 148.6, 064706 (2018).
[4] R. J. Allen, et al. Journal of physics: Condensed matter 21.46, 463102 (2009).

Self-Recovery Superhydrophobic Surfaces

Alberto Giacomello[1], Emanuele Lisi[1], Simone Meloni[2], Carlo Massimo Casciola[1]

[1] Sapienza University of Rome, Department of Mechanical and Aerospace Engineering

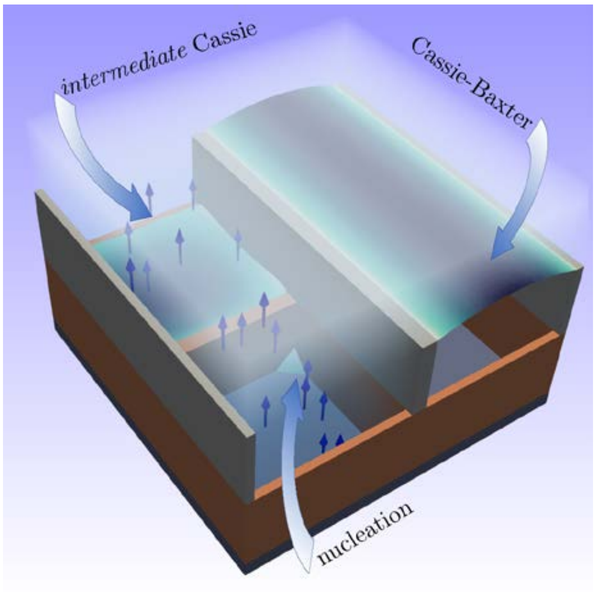
One of the crucial limitations to the technological applicability of superhydrophobicity is its fragility: once the suspended state experiences a transition to the fully wet Wenzel one, superhydrophobic properties are lost and recovering them typically requires a significant external energy input. However, it has been recently shown that nanostructured surfaces can overcome this limitation promoting completely passive (self-)recovery of superhydrophobicity thanks to a combination of extreme confinement and hydrophobic environment[1,2]. Self-recovery is based on the thermodynamic elimination of the Wenzel state over a range of pressures of engineering interest: once the pressure is decreased below a certain threshold the Wenzel state becomes unstable and superhydrophobicity is restored.

In this work we expand the original idea of self-recovery[1] in order to identify the surface characteristics which favour this mechanism[3]. Results show that nanoconfined cavities with extended hydrophobic surfaces and corners facilitate the destabilization of the Wenzel state. These features are however at odds with other functional properties which are required for a superhydrophobic surface: typically, low solid fractions both for slip and self-cleaning. The proposed solution is to realize modular surfaces which exploit the physical separation of the areas controlling recovery (cavity bottom) and superhydrophobicity (cavity mouth), in order to achieve self-recovery surfaces with enhanced functional properties[3].

[1] Giacomello, A., Schimmele, L., Dietrich, S., & Tasinkevych, M. (2016). Perpetual superhydrophobicity. *Soft matter*, *12*(43), 8927-8934.

[2] Li, Y., Quéré, D., Lv, C., & Zheng, Q. (2017). Monostable superrepellent materials. *Proc. Natl. Acad. Sci. USA*, 114(13), 3387-3392.

[3] Lisi, E., Amabili, M., Meloni, S., Giacomello, A., & Casciola, C. M. (2018). Self-Recovery Superhydrophobic Surfaces: Modular Design. *ACS nano, 12 (1), 359-367.*



Design of modular superhydrophobic surfaces combining self-recovery and low friction.

Contributed session 3A

Wednesday 16th

15:30 - 16:30

Manipulating Droplets on Lubricant Impregnated Surfaces

G. McHale[1], J.H. Guan[1], R. Ledesma-Aguilar[1], É. Ruiz-Gutiérrez[1], C. Semprebon[1],
G.G. Wells[1], D. Wood[1], B.B. Xu[1]
[1]Smart Materials & Surfaces Laboratory, Northumbria University,
Newcastle upon Tyne NE1 8ST, UK

Lubricant impregnated surfaces, also known as slippery liquid-infused porous surfaces (SLIPS), remove the contact line pinning normally associated with sessile droplets. Here we present studies on the mobility and motion of droplets on such surfaces. We show that diffusion-limited droplet evaporation on a SLIPS surface occurs in a constant apparent contact angle mode[1]. We then argue that small droplets confined between reconfigurable boundaries in a wedge geometry, can be continuously translated in an energy invariant manner with the dissipation dominated by the bulk contribution[2,3]. To control droplet position and motion on lubricated surfaces, we introduce the idea of a SLIPS Cheerios effect induced by structuring the underlying surface or by droplets in close proximity to each other. In particular, we show that a droplet on a SLIPS surface with a V-shaped groove has three equilibrium states and that droplet motion on the surface towards an equilibrium state occurs when the droplet-lubricant meniscus overlaps with the lubricant-surface meniscus caused by surface features[4].

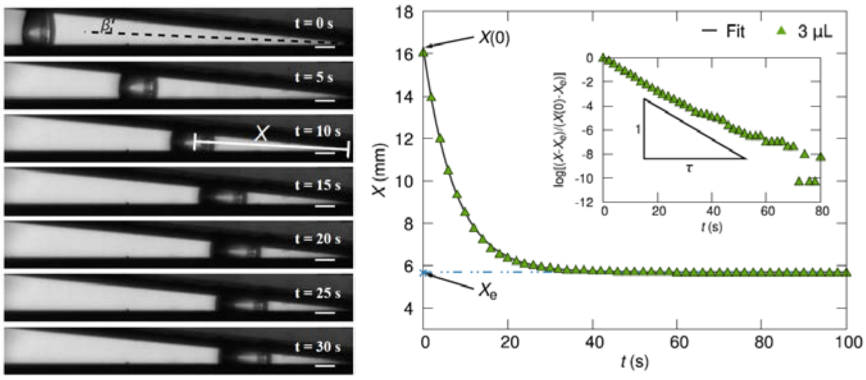
The financial support of the UK Engineering & Physical Sciences Research Council (EPSRC) and Reece Innovation Ltd is gratefully acknowledged.

[1] Guan, J.H. *et al.* Evaporation of sessile droplets on slippery liquid-infused porous surfaces (SLIPS)", *Langmuir* **31**, 11781-11789 (2015).

[2] Ruiz-Gutiérrez, É. *et al.* Energy invariance in capillary systems, *Physical Review Letters* **118**, 218003 (2017).

[3] Ruiz-Gutiérrez, É. et al. Statics and dynamics of liquid barrels in wedge geometries, *Journal of Fluid Mechanics* (2018).

[4] Guan, J.H. et al. Drop transport and positioning on lubricant-impregnated surfaces, Soft Matter 13, 3404-3410 (2017).



Relaxation to equilibrium of droplet in a wedge composed of slippery surfaces.

Wood surfaces protection based on silica and covalently attached liquid-like PDMS chains for water repellency, anti-fouling, anti-smudge and self-healing properties

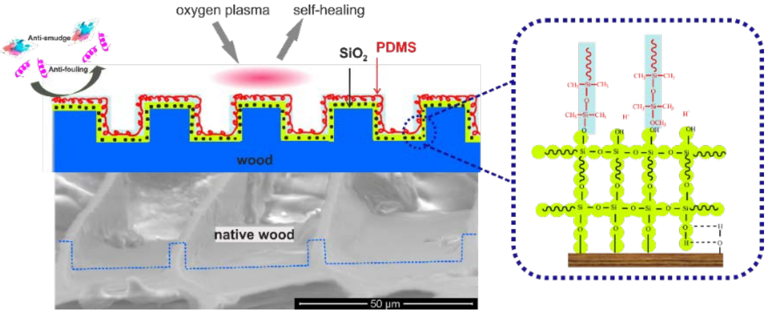
Yaru Wang[1,2], Wenqing Yan[3], Marion Frey[1,2], Marta Vidiella del Blanco[1,2], Mark Schubert[2], Etienne Cabane[1,2]

[1]Wood Materials Science, ETH Zürich, Stefano-Franscini-Platz 3, CH-8093 Zürich, Switzerland
[2]Applied Wood Materials, EMPA-Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland
[3]Laboratory for Surface Science and Technology Department of Materials ETH Zurich, Vladimir-Prelog-Weg 1-5/10, CH-8093 Zurich, Switzerland

Wood possesses many advantages: it is a lightweight mechanically robust material, with praised aesthetics and facile scale-up.[1] However, it is highly hygroscopic, leading to dimensional instability and to decay caused by cell wall degradation initiated by some microorganisms.[2] Thus, addressing the issue of water absorption is crucial to ensure the reliability of this biomaterial. Furthermore, combining self-healing, antifouling and water-repellency is of great interest for wood outdoor applications where both aesthetic appreciation and long service life are required.

To deal with the water absorption issue, we used the surface lubrication approach based on covalently bonded flexible liquid-like polymer chains.[3] The idea is to transform the solid wood surface to a liquid-like one. Compared to SLIPS (Slippery Liquid-Infused Porous Surface), this strategy does not require the structuration of the porous matrix "holder" and avoids potential depletion of the lubricant.[4] A smooth SiO_2 layer was first prepared in-situ on the wood surface followed by anchoring of flexible low-molecular-weight PDMS chains. Our modified wood showed improved sustained underwater water repellency with a constant contact angle (CA) around 91° over 19 days immersion in water, while the superhydrophobic control sample failed within 3 days. Due to the mobility of the PDMS chains, the modified wood can recover its CA after more than 5 cycles of plasma treatment. In addition, we observed a low adhesion between the PDMS-coated surface and wide range of other substances (e.g. protein, varnish, and paint). We expect this modification can increase the service life of wood with aesthetic appearance.

[1] Rowell, Roger M., and W. Bart Banks. Gen. Tech. Rep. FPL-50. Madison, WI: US Department of Agriculture, Forest Service, Forest Products Laboratory; 1985: 24, 50.
[2] Rowell, R. M. CRC press: 2012.
[3] Wang, L.; McCarthy, T. J. Angewandte Chemie 2016, 128 (1), 252-256.
[4] Wooh, S.; Vollmer, D. Angewandte Chemie International Edition 2016, 55 (24), 6822-6824.



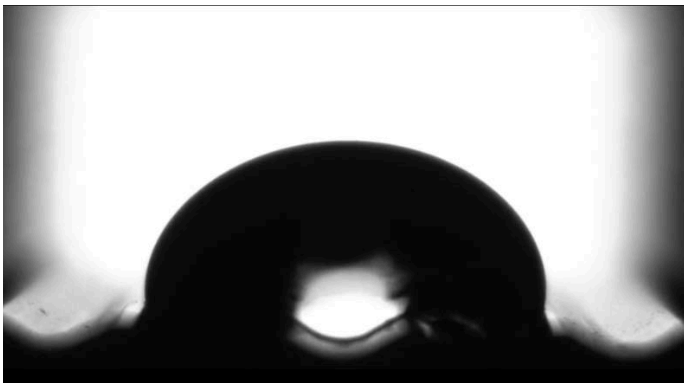
Scheme describing the wood surface modification approach using liquid-like PDMS chains.

Snap evaporation on smooth topographies

Gary G. Wells[1], Élfego Ruiz-Gutiérrez[1], Youen Le Lirzin[1,2] Anthony Nourry[1, 2], Bethany V. Orme[1], Marc Pradas[3] and Rodrigo Ledesma-Aguilar[1]

[1]Smart Materials & Surfaces Laboratory, Faculty of Engineering and Environment, Northumbria University, Newcastle upon Tyne, NE1 8ST, United Kingdom
[2]Institut Universitaire de Technologie de Lannion, Rue Edouard Branly, 22300 Lannion, France
[3]School of Mathematics and Statistics, The Open University, Milton Keynes, MK7 6AA, UK

Droplet evaporation on solid surfaces is important in many applications including printing, micro-patterning and cooling. While seemingly simple, the configuration of evaporating droplets on solids is difficult to predict and control. This is because evaporation typically proceeds as a “stick-slip” sequence—a combination of pinning and de-pinning events dominated by static friction, or “pinning”, caused by microscopic surface roughness. Here we show how smooth, pinning-free, solid surfaces of non-planar topography promote a different process called *snap evaporation*. During snap evaporation a droplet follows a reproducible sequence of configurations, consisting of a quasi-static phase-change controlled by mass diffusion interrupted by out-of-equilibrium snaps. Snaps are triggered by bifurcations of the equilibrium droplet shape mediated by the underlying non-planar solid. Because the evolution of droplets during snap evaporation is controlled by a smooth topography, and not by surface roughness, our ideas can inspire programmable surfaces that manage liquids in heat- and mass-transfer applications.



A water droplet on a lubricant-impregnated smooth wavy surface.

Oleoplaning droplets on lubricated surfaces

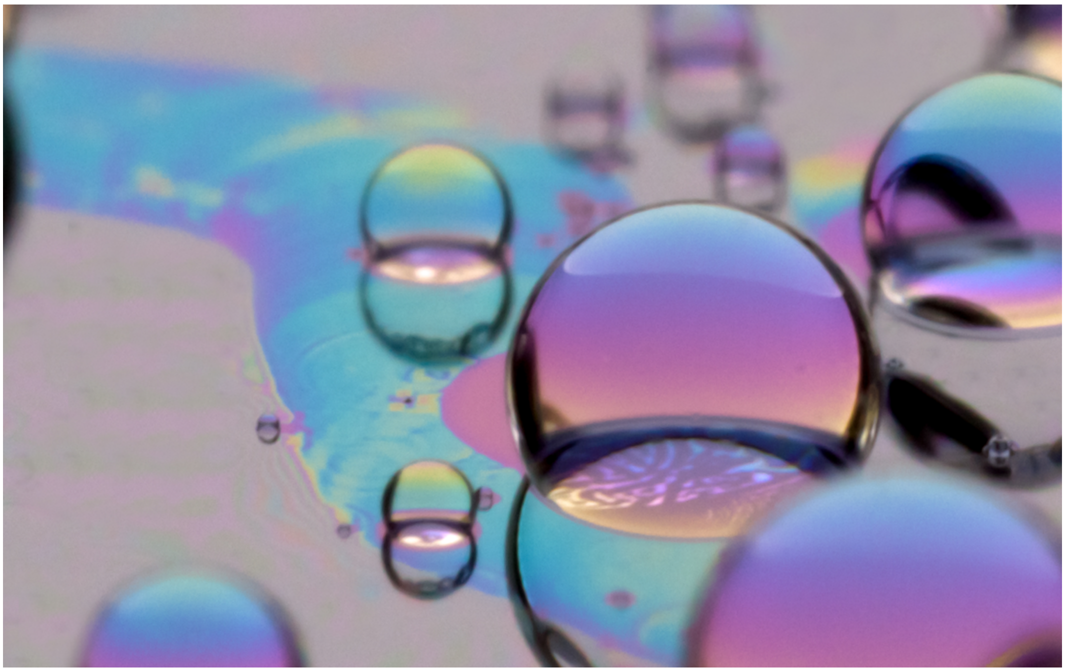
Dan Daniel[1+], Jaakko V. I. Timonen[1,2], Ruoping Li[3], Seneca J. Velling[3], Joanna Aizenberg[1,3,4*]

[1]John A. Paulson School of Engineering and Applied Sciences, Harvard University
[2]Department of Applied Physics, Aalto University School of Science
[3]Wyss Institute for Biologically Inspired Engineering, Harvard University
[4]Department of Chemistry and Chemical Biology, Harvard University

When infused with lubricant, surfaces can be highly liquid-repellent. The extent of their repellencies are typically quantified by static and dynamic contact angle measurements of a probe liquid droplet (typically water). Here, we show that such measurements (including contact angle hysteresis values) do not fully capture the dissipation process acting on droplet.[1] Instead, we measured the dissipative force for moving droplets using a custom-built force sensor with sub-μN accuracy and correlated it to the lubricant dynamics observed using optical interferometry. We find that on lubricated surfaces the dissipative force depends non-linearly on velocity, consistent with viscous dissipation in the lubricant layer. In contrast, on lotus-effect surfaces, the dissipative force is dominated by contact-line pinning and is independent on velocity. The techniques and insights presented here will inform future work on liquid-repellent surfaces and enable their rational design.

+Present address : Institute of Materials Research and Engineering, Singapore
*jaiz@seas.harvard.edu

[1] Daniel et al., Nature Physics **13**, 1020–1025 (2017)



On a lubricated surface, a moving droplet levitates over a thin lubricant film, resulting in bright iridescent colours—due to thin-film interference—beneath the droplet and along its trail.

Contributed session 3B

Wednesday 16th

15:30 - 16:30

Biomimetic Taro-like Structure for Super-Hydrophobicity

Soomin Son[1], Jaemin Park[1], Daihong Huh[1], Pil-Hoon Jung[1], Dongwoo Chae[1], Hee Chul Lee[2*] and Heon Lee[1*]

[1]Korea University, Department of Materials Science and Engineering
[2]Korea Polytechnic University (KPU), Department of Advanced Materials Engineering

A surface with hierarchical structure leads super-hydrophobicity which is extremely hard to wet. In particular, these hierarchical structures are usually found in natural plant leaves such as lotus, bamboo, rice and taro, and are currently applied in the fields of water resistance, mist condensation and pollution prevention.[1] In this research, super-hydrophobicity is reproduced by bio-mimic taro leaf surface, performed by direct imprint lithography, hydrothermal growth and self-assembly monolayer coating. The micro-structure was fabricated by direct imprint lithography using tungsten trioxide (WO_3) solution, and nano-structure was grown in the form of flakes using hydrothermal synthesis method to make artificial taro leaf surface. Finally, the self - assembled monolayer (SAM) coating was employed to modify the surface energy to reproduce the super-hydrophobic property.[2] Artificial surface morphology and crystal structure of artificial taro leaves were confirmed by scanning electron microscopy and X-ray diffraction. The changes of surface energy by SAM coating was investigated by X-ray photoelectron spectroscopy. The super-hydrophobicity according to each process was demonstrated by measuring the static contact angle. It was confirmed that bio-mimic taro leaves composed of WO_3 nano-in-micro hierarchical structure showed excellent self-cleaning ability.

[1] Z. Guo, F. Zhou, and J. Hao, W. Liu, J. Am. Chem. Soc. 127, 15670-15671 (2005)
[2] Choo, H.-J. Choi, H. Lee, Mater. Lett. 121, 170–173 (2014)

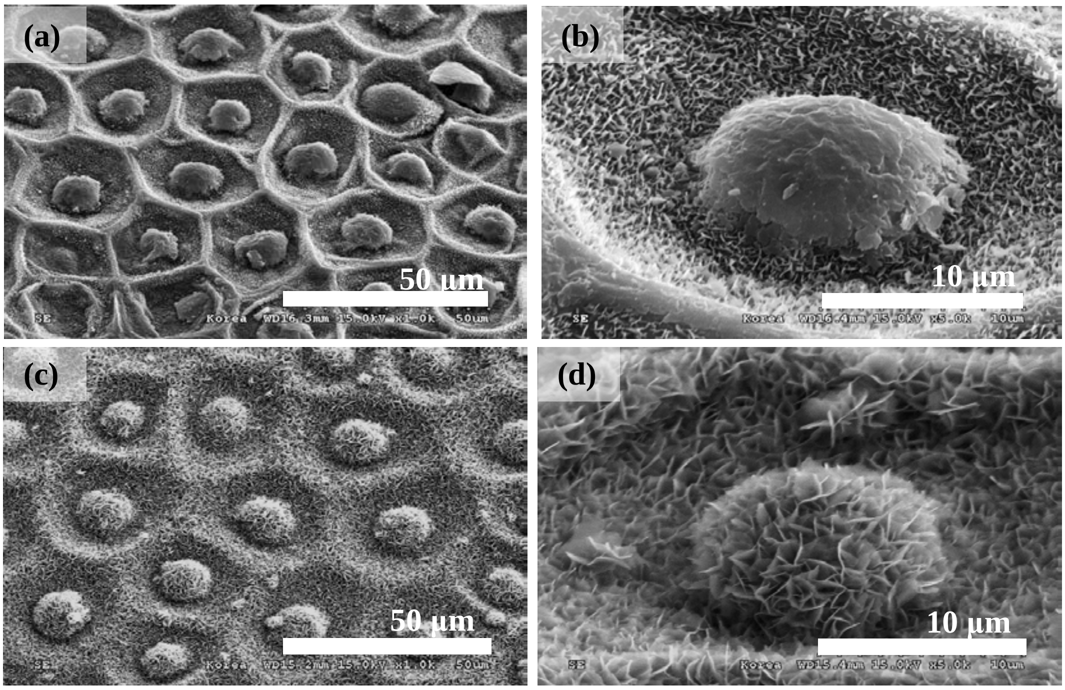


Figure. SEM Images of natural tar Leaf in (a), (b) and biomimetic taro leaf in (c), (d).

Underwater Superoleophobic Wood Cross Sections

Marta Vidiella del Blanco[1,2], Etienne Cabane[1,2]

[1]Wood Material Science, Institute for Building Materials (IfB), ETH Zürich, Zürich, Switzerland
[2]Applied Wood Materials, EMPA – Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland

Over the last years, the awareness over oil spill accidents in marine environment and aquatic ecosystems has increased leading to tighter regulations. Novel strategies to separate oil-water mixtures from industrial wastewaters, and polluted oceanic and river waters have become a global challenge. Given that traditional methods are limited with regard to their energy costs, low efficiency, and complexity of the separation, new functional materials that address these issues are highly needed. We have been working with wood, which is a renewable material, to develop membranes, which are capable of separating oil from water. The hierarchical porous structure of softwoods recalls the structure of the widely used separation membranes. Spruce, with a relatively narrow distribution of cell lumen size, is the perfect material for this application. By combination of the affinity of water to soak wood and the natural capillaries of spruce wood's structure, water is trapped in the wood's hierarchical structure forming a layer of water on the surface. Given the immiscibility of the two liquids (water and oil), the water film formed on the wood repels the oil resulting in an underwater superoleophobic wood surface (Figure 1). This underwater oleophobicity is shown for various oils (hexadecane, diesel, gasoline, motor oil, and olive oil) with high contact angles (144º to 155º) and low sliding angles (below 7º).[1] Moreover, the natural origin of wood together with the low processing required for this application makes this material both energy and cost efficient and highly competitive with other materials on the market.

Further studies will focus on producing an oleophobic wood membrane, which is capable of separating not only oil/water mixtures but also oil-in-water emulsions by the introduction of fluorinated polymers into the wood structure.

[1] M. Vidiella del Blanco, E. J. Fischer, E. Cabane, *Adv. Mater. Interfaces* **2017**, *4*, 1700584.

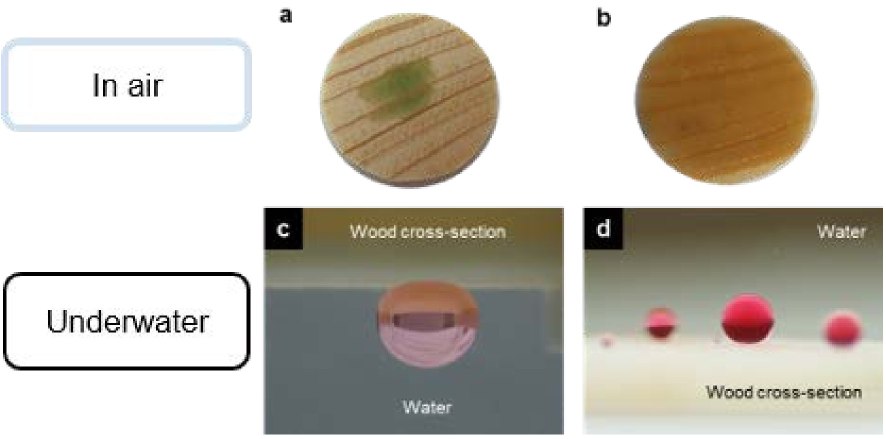


Figure 1: Wetting properties of wood cross sections. a,b) water and hexadecane droplet being absorbed by the wood in air and c,d) photographs of dyed light and heavy oils sitting on the water-immerged wood surface with high contact angles.

Bouncing, splashing and spreading on biological and biomimetic surfaces influenced by surface wettability and liquid tension

Kerstin Koch[1], Julia Koops[1], Axel Huth[1], Roland Grichnik[2]

[1]Rhine Waal University of Applied Sciences, Faculty of Life Sciences, Kleve, Germany
[2]Rhine Waal University of Applied Sciences, Faculty of Technology and Bionics, Kleve, Germany

In nature, surfaces with extreme wetting properties have developed. Well known samples are the superhydrophobic Lotus leaves with their self-cleaning property and superhydrophilic surfaces on which water spreads to a thin liquid film. Drops falling on surfaces, e.g. rain drops, either impact without any breakup, or cause a splash or splashing, in which the impacting drop releases smaller droplets flying away from the point of impact (Fig.). Splashing droplets (aerosolization of tiny water droplets) can carry and transfer human and plant pathogens over long distances[1]. Thus surface modification for suppression of splashing effects might be an appropriate solution to reduce microbial pathogen distribution caused by aerosolization. In our study we designed surfaces with superhydrophobic and superhydrophilic properties and characterized the droplet behavior of impacting water and water ethanol mixtures. Water droplet impacts and resulting dynamic wetting processes such as bouncing, splashing and spreading of water on biomimetic surfaces could be observed[2].

Comparison of structured and smooth, hydrophilic or hydrophobic coated surfaces showed reduced splashing in sequential drop impact events on micro-structured superhydrophilic surfaces. On these surfaces, water spreads by capillary forces away from the point of impact, whereas on smooth surfaces the water remained at the point of impact, leading to a corona splash with aerosolization of tiny water droplets (see figure) in sequential drop impact events. Significant changes in the dynamic wetting behavior of impacting droplets were found when surface tensions of the liquids were reduced.

[1] Jones R.M. & Brosseau L.M. J. Occup. Environ. Med. 57, 501–508, (2015)
[2] Koch, K. & Grichnik, R. Phil. Trans. R. Soc. A 2016 374 20160183 (2016)

Foto taken from a slow motion video, showing a corona splash created by impact of a water drop onto a wet surface[2]

Plenary session 2

Wednesday 16th

16:35 - 17:35

How to Control the Splat of an Impacting Droplet using Surperhydrophobic Patterns

H. Almohammadi and Alidad Amirfazli

Department of Mechanical Engineering, York University, Toronto, Canada

Drop impact onto a surface is seen in many natural and industrial processes from rain drops eroding soil, to printing electronics. In some cases drop impact causes splashing, but in many processes, e.g. printing, this is to be avoided. In fact in many precision and advanced manufacturing techniques involving droplets, the shape of the resulting splat after or during the impact needs to be controlled, e.g. to have a circular shape. Normally impact of a droplet on a simple flat surface results in a circular splat shape; but if the surface is inclined, moving, or has other topographical features, the ideal circular shape will not be seen. In this talk first the general conditions that give rise to deviation of splat shape from a circle will be discussed. We will show how surface texture or features, surface wettability, orientation or movement relative to the drop's trajectory can result in non-ideal (non-circular) splats, or spreading of an impacting droplet. Next we will discuss how using wettability patterns one can influence the spreading of an impacting drop, and ultimately the shape of the splat. Empirical results will be explained using theoretical reasoning based on dynamics of film retraction and contact angle hysteresis. Specific examples for drop impact onto an inclined surface or a moving surface, will be shown, as how simple superhydrophobic and hydrophobic patterns on a surface is used to manipulate the spreading of an impacting droplet and ultimately the splat shape.

Inherent physics inspiring design for supercooled water- and ice-shedding from surfaces

Dimos Poulikakos

Institute of Energy Technology, ETH Zurich, Switzerland

Spontaneous removal of discrete condensed matter from solids is of extreme importance in nature and in a broad range of technologies, e.g. self-cleaning, anti-icing, and condensation. Despite progress, the understanding of phenomena leading to such behavior, combined with rational surface design promoting their manifestation, remain a challenge. In this lecture I will show how water droplets resting on superhydrophobic surfaces in a low-pressure environment can self-remove through sudden spontaneous levitation and subsequent trampoline-like bouncing behavior despite surface rigidity seemingly violating the second law of thermodynamics. Trampoline bouncing results from the combined effect of droplet vaporization, vapor flow in the surface texture, and substrate adhesion leading to a forced, underdamped, mass-spring-damper system behavior. We show how sudden inctease in vaporization by recalescent freezing has a strong boosting effect and can spontaneously remove surface icing (by levitating or even launching away-generated icy drops) the moment they freeze. Finally, I will discuss how ice self-dislodging from rationally designed non-superhyprophobic surfaces can we realized.

Contributed session 4A

Thursday 17th

08:30 - 10:00

Leaf-structure patterning for antireflective and hydrophobic surfaces on solar cells

Zhongjia Huang[1,2], Xinying Shi[1], Taohai Li[3], Gang Wang[1,2], Marko Huttula[2], Wei Cao[2]

[1]Anhui Polytechnic University, School of Mechanical and Automotive Engineering
[2]University of Oulu, Nano and Molecular Systems Research Unit
[3]Xiangtan University, College of Chemistry

As the most abundant and cleanest source within human's disposal, solar energy can be converted and stored through light harvesting systems, either the manmade photovoltaics or the natural foliage. Despite huge efforts to study PV materials, the unwanted light reflection and ruins on surfaces lead to external quantum efficiency (EQE) loss, yet, deteriorating the overall PV performance. In contrast, the foliage is gifted with dedicated air-leaf interfaces countering reflections and ambient ruins after millions of year's evolution. Thus, engineering surface structures of manmade devices via bionic routes may be able to decrease the EQE loss.

Herein, we report on recent progresses of the ecological and bio-inspired coating strategy by replicating leaf structures onto Si-based solar cells. The key route can be generalized in Fig. 1 (a), where the surface structure of the master leaf is imprinted onto the Si cells for antireflection and hydrophobicity. The transparent photopolymer coatings with leaf surface morphologies are synthesized through a facile double transfer process. They can either be casted as free-standing foils or tightly cured on Si slabs. After bio-mimicked layer coverages, sunlight reflection drops substantially from more than 35% down to less than 20%. Consequentially, 10.9% gain of the maximum powers of the photovoltaic is obtained under the standard solar simulator conditions[1]. The strategy is more useful for low class PV cells or with smaller angle incident light. Under the nonparallel incident light, a maximum gain of 17% has been reached by placing the foil onto B-class PV cells[2]. Additionally, thanks to specific leaf morphologies, both the free-standing[3] and attached foils own special wettability for water repelling[1] as shown in Fig.1(b).

The physical mechanisms beyond antireflection and hydrophobicity are also explored. The finite differential time domain simulation shows that the nano- and micro-morphologies inherited from master leaves diffuse the light in the polymers[3], and guide lightwaves to reach the PV cells[1,2]. Hence, the optimized structure and morphology combinations will lead to a low refection down to 6% on the Si slab[4]. The hydrophobic surface and low rolling angle can be attributed to the "lotus" states[5], and kept stable under different corrosive ambiences. We also aim for future interdisciplinary applications by combining the present bioinspired media to the nano photocatalysts for water purification and hydrogen evolution.

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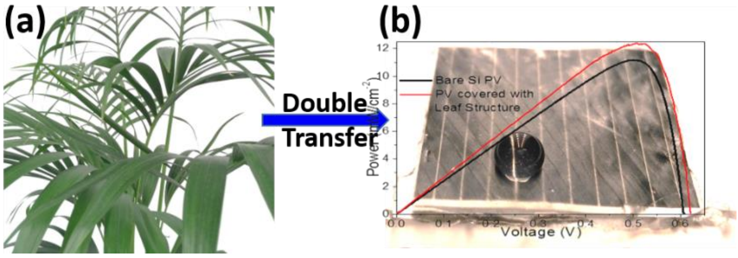

Fig.1 Double transfer process for antireflective and hydrophobic coating on a Si PV cell

Gas-perfused porous surfaces: Actuating droplets without levitating them

Nikolaos Vourdas[1,2], Vassilis Stathopoulos[2]

[1]NCSR Demokritos, Institute of Nanoscience and Nanotechnology
[2]Laboratory of Chemistry and Materials Technology, Technological Education Institute of Sterea Ellada

Porous surfaces are widely used for wetting phenomena control exploiting either the gas entrapped on the porous network, or their ability to be infused, or impregnated by lubricants[1]. Still gas entraps (pockets) tend to collapse after prolonged exposure to liquid environments, or at high liquid pressures, while lubricants tend to cloak the droplets and gradually dry out. In our study we combine the two aforementioned approaches and we use porous media and have them perfused with gas to dynamically actuate, and manipulate droplets on their surfaces. By adjusting the backpressure, i.e. the pressure from the rear side of the porous medium, the droplet may be actuated, and its downward velocity may be controlled without completely levitate it. This entails low values of backpressure, in the order of few mbar, depending on the porous network characteristics.

In this work we are going to present the basic principles of this approach[2,3], and demonstrate it in various applications including droplet impingement[2], valving in digital microfluidics[4], and droplet logic operations[5].

The mechanisms of actuation have been studied by means of simulations encompassing the momentum conservation and the continuity equations along with the Cahn−Hilliard phase-field equations in a 2D computational domain. The droplet actuation mechanism involves depinning of the receding contact line and movement by means of forward wave propagation reaching the front of the droplet, yielding to a forward skipping of the droplet[6].

New experimental results with highly viscous liquids and on non-symmetric surfaces will be shown.

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Pumpless, capillary force-driven transport of liquids on surfaces

Sherif Hamed[1], Tanmoy Maitra[1], Junfeng Lin[1], Manish K. Tiwari[1]

[1]Nanoengineered Systems Laboratory, UCL Mechanical Engineering, University College London, London WC1E 7JE

Surfaces with adjacent superhydrophobic and superhydrophilic regions, i.e. patterned wettability, are becoming increasingly popular in microfluidic systems. By strategically patterning wettable tracks onto non-wettable flat surfaces, capillary force-driven liquid flow can be achieved without the need for any external energy. This pumpless transport of liquids on open substrates offers a smart solution for low cost point-of-care (POC) devices and many lab-on-chip (LOC) applications.

In the present study, we employ a simple wettability patterning technique to create open hydrophilic tracks capable of transporting low surface tension liquids in a range of liquid volumes (typically ~1 – 500 µl depending on geometry). Our focus was on facile pumping and low-cost fabrication to make it suitable for applications in low-cost biomedical diagnostic devices. To achieve this, we synthesized a superomniphobic ZnO-PMC composite coating in a manner similar to that reported by Neelakantan et al.[1] to be spray coated onto a hydrophilic substrate. Commercial 3-D printer-based masks mirroring the desired geometries of the tracks were placed on the substrates prior to spray coating to achieve spatially-selective wettability conversion from superhydrophilic to superomniphobic. These specifically designed tracks with a diverging geometry were able to transport liquids, with no external actuation, with high meniscus speeds (~2 cm s^{-1}). By tuning the wettability contrast and the pattern geometries, both liquid flow-through systems as well as discrete droplet transport systems were achieved, allowing for a wide range of potential applications.

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Bio-inspired Controllable Liquid Transfer by Topological Asymmetric Fibers

Huan Liu,* Lei Jiang

School of Chemistry, Beihang University, Beijing, 100191, China.
E-mail: liuh@buaa.edu.cn

In nature, various biological fibrous systems exhibit unique dynamic wetting properties, which has shown many advantages in inhabiting local environments. However, controllable liquid transfer by an open fibrous system is still poorly understood and remains a challenge, because capillary coalescence is frequently encountered when fiber array interacted with a liquid. Here, we revealed the most fundamental of the Chinese brush for its capability in controllable liquid transfer: the unique anisotropic multi-scale structure of the freshly emergent hairs. Inspired by these findings, we developed model devices with flexible conical fibers that allows for direct writing functional microlines with 10 μm resolution and nanometer-thickness, with well-defined profile and uniform distribution on diverse substrates. To be noticed, the fibers-guided directional liquid transfer enables fine controlling the liquid/solid/gas three phase contact line (TCL) under multiple directional stresses. Taking advantages, highly oriented polymer thin film and aligned AgNWs film were fabricated in large scale, based on which high performance of polymer TFTs devices and the anisotropic flexible conductive electrode were developed, respectively. We envision that the controllable liquid transfer guided by the conical fibers will shed light on the novel template-free printing of functional photoelectric devices.

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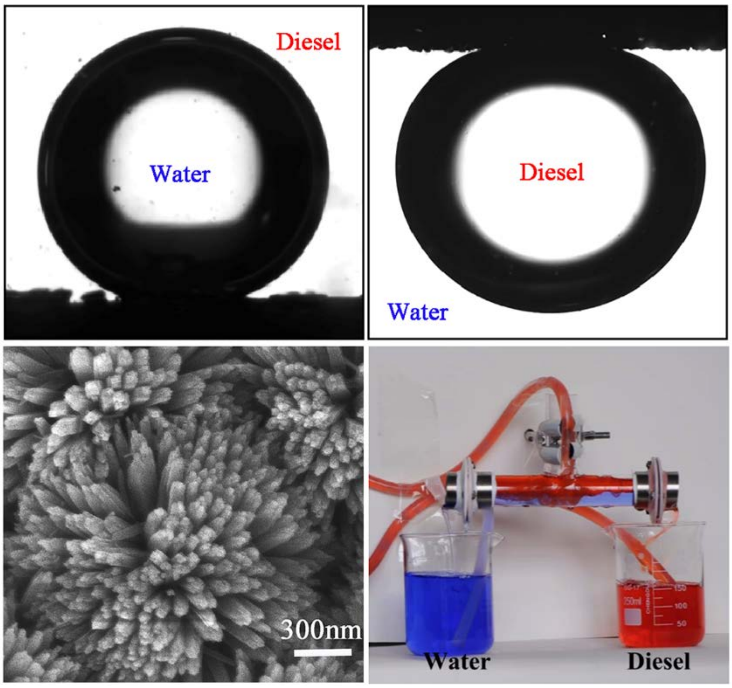
A dual superlyophobic copper foam with good durability and recyclability for high-flux, high-efficiency and continuous oil-water separation

Wenting Zhou[1], Song Li[1], Yan Liu[2], Zhengzheng Xu[1], Sufeng Wei[3], Guoyong Wang[1],
Jianshe Lian[1], Qing Jiang[1]

[1]Jilin University, Key Laboratory of Automobile Materials, Department of Materials Science and Engineering
[2]Jilin University, Key Laboratory of Bionic Engineering (Ministry of Education) and State Key Laboratory of Automotive Simulation and Control, Jilin University
[3]Changchun University of Technology, Key Laboratory of Advanced Structural Materials

Traditional oil-water separation materials have to own ultra-high or ultra-low surface energy. Thus they can only be wetted by one of oil and water. Our experiment here demonstrates that the wettability in oil-water mixtures can be tuned by oil and water initially. Hierarchical voids are built on commercial copper foams with the help of hydrothermally synthesized titanium dioxide nanorods. The foams can be easily wetted by both oil and water. The water prewetted foams are superhydrophilic and superoleophobic under oil-water mixtures, meanwhile the oil prewetted foams are superoleophilic and superhydrophobic. In this paper, many kinds of water-oil mixtures were separated by two foams, prewetted by corresponding oil or water respectively, combining a straight tee in a high-flux, high efficiency, continuous mode. This research indicates that oil-water mixtures can be separated more eco-friendly and lower-cost.



Contributed session 4B

Thursday 17th

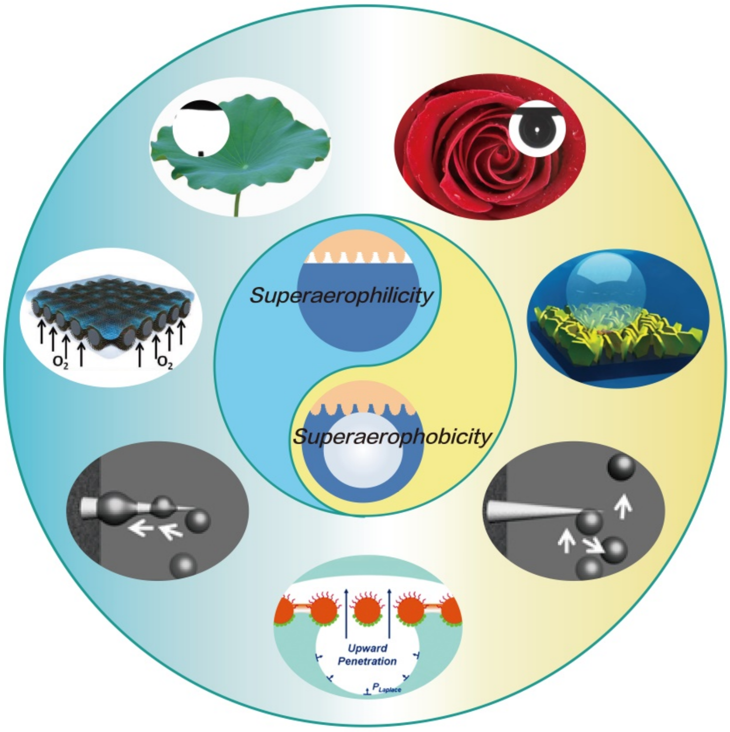
08:30 - 10:00

Superwettability of Gas Bubbles and Its Application: From Bioinspiration to Advanced Materials

Jingming Wang[1, 2], Peipei Zhang [1], Cunming Yu [1], Xiuzhan Xue[1]

[1]Key Laboratory of Bio-Inspired Smart Interfacial Science and Technology of Ministry of Education, School of Chemistry, Beihang University, Beijing 100191, P. R. China
[2]Beijing Advanced Innovation Center for Biomedical Engineering, Beihang University, Beijing 100191, P. R. China

The behaviors of gas bubbles on solid interfaces, including generation, growth, coalescence, release, transport, and collection, are crucial to gas-bubble-related applications, which are always determined by gas-bubble wettability on solid interfaces. Here, the recent progress regarding the study of interfaces with gas-bubble superwettability in aqueous media, i.e., superaerophilicity and superaerophobicity, is summarized. Some examples illustrate how to design microstructures and chemical compositions to achieve reliable and effective manipulation of gas-bubble wettability on artificial interfaces. These designed interfaces exhibit excellent performance in gas-evolution reactions, gas-adsorption reactions, and directional gas-bubble transportation. Moreover, some challenges are presented, such as the reliable manipulation of gas-bubble wettability and the establishment of mature theory for exactly and systematically explaining gas-bubble wetting phenomena.



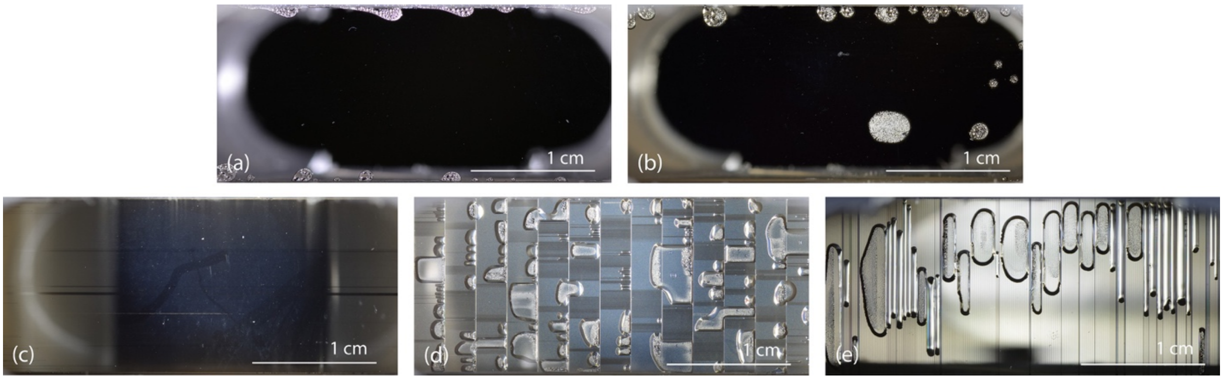
Gas bubble manipulations on the interfaces with designed microstructures and chemical compositions.

Bubble Nucleation in Superhydrophobic Microchannels due to Subcritical Heating

Adam Cowley[1], Daniel Maynes[1], Julie Crockett[1]

[1]Brigham Young University, Department of Mechanical Engineering

This work experimentally studies the effects of single wall heating on laminar flow in a high aspect ratio superhydrophobic microchannel. When water that is saturated with air is used as the working liquid, the non-wetted cavities on the superhydrophobic surfaces act as nucleation sites and allow air to effervesce out of the water and onto the surface when heated. The microchannel consists of a rib/cavity structured superhydrophobic surface and a glass surface separated by spacers. The microchannel is 60 mm long by 14 mm wide and two channel heights of nominally 183 and 366 microns are explored. The superhydrophobic side is in contact with a heated aluminum block and a camera is used to visualize the flow through the glass side. Thermocouples are embedded in the aluminum to record the temperature profile along the length of the channel. Temperatures are maintained below the boiling temperature of the working liquid. The friction factor-Reynolds product (*fRe*) is obtained via pressure drop and volumetric flow-rate measurements. Five surface types/configurations are investigated: smooth hydrophilic, smooth hydrophobic, superhydrophobic with ribs perpendicular to the flow, superhydrophobic with ribs parallel to the flow, and superhydrophobic with ribs parallel to the flow with several breaker ridges perpendicular to the flow. The surface type/configuration has a significant impact on the mass transport dynamics. For surfaces with closed cell micro-structures, large bubbles eventually form and adversely affect *fRe* and lead to higher temperatures along the channel. Once the bubbles grow large enough, they are expelled from the channel due to drag force caused by the flowing water. The channel size greatly effects the residence time of the nucleate bubbles and consequently *fRe* and the channel temperature. When degassed water is used no bubble nucleation is observed and the air initially trapped in the superhydrophobic cavities is quickly absorbed by the water.



Top view images showing bubble formation on five different test surfaces due to heating of the bottom channel wall to sub-critical surface temperatures. The surfaces are: a. smooth hydrophilic; b. smooth hydrophobic; c. superhydrophobic with rib structures parallel to the flow; d. superhydrophobic with ribs perpendicular to the flow; e. superhydrophobic with ribs parallel to the flow and sparse breaker ribs perpendicular to the flow.

Dynamics of superhydrophobic breakdown explored with in-situ ATR-FTIR

Nandi Vrancken[1,2], Stefanie Sergeant[2], Guy Vereecke[2], Frank Holsteyns[2], Herman Terryn[1], Stefan De Gendt[2,3], XiuMei Xu[2]

[1]Vrije Universiteit Brussel, Pleinlaan 2, 1050 Elsene, Belgium
[2]Imec, Kapeldreef 75, 3001 Leuven, Belgium
[3]KU Leuven, Celestijnenlaan 200, 3001 Leuven, Belgium

Wetting and superhydrophobicity are typical interfacial phenomena dictated by the liquid-solid-air interactions at the nanoscale. Proper understanding of the wetting behavior of structured surfaces is essential for the development of sustainable and reliable nanofluidic concepts, anti-fouling surfaces for medical applications and self-cleaning functional materials. Static analysis of nanoscale wetting states was recently demonstrated using a novel ATR-FTIR based method [1]. In the present work, this technique is extended to explore the dynamics of superhydrophobic breakdown on high aspect ratio functionalized silicon nanostructures.

ATR-crystals are prepared from wafers patterned with silicon nanopillars of different dimensions (height 78-265 nm, diameter 30-45 nm). The surface is rendered superhydrophobic through functionalization with a fluorinated silane (FDTS). Next, the crystals are mounted in a liquid cell and water is injected. The resulting FTIR spectra significantly differ for both wetting states (figure 1). Hydrophilic nanopillars yield similar spectra as acquired on plain silicon. In case of superhydrophobic structures, an air layer is present in between the pillars which attenuates the evanescent waves emerging from the crystal. IR-bands at low(er) wavenumbers can penetrate deeper into a sample and are therefore less sensitive to this attenuation than bands at high(er) wavenumbers. Consequently, the change in relative intensity ratio of the water bending (1640 cm^{-1}) and stretching (3380 cm^{-1}) bands can be regarded as a measure for the average wetting state on the crystal. This approach is explored to determine critical transition criteria for superhydrophobic breakdown as a function of surface geometry. Wetting systematically starts at lower contact angles than predicted by the classical wetting models, which emphasizes the importance of more accurate transition criteria. Further, a dynamic study of wetting kinetics near the critical transition criterion was conducted. Precise wetting actuation was demonstrated for the first time and wetting front velocities on the order of few µm/s are obtained. Careful design of partially functionalized ATR-crystals yields deeper insights into the wetting mechanism. This work is the first comprehensive study on nanostructures that includes a correlation of the wetting dynamics with the realtime driving force and can readily be extended to more advanced surface patterns.

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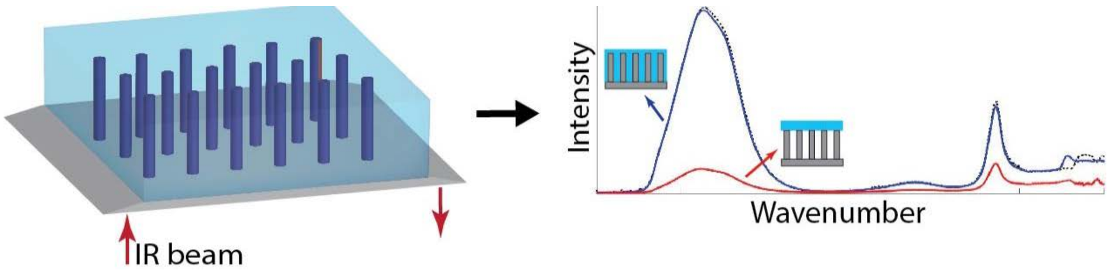

Simplified schematics of the experiments. FTIR-spectra are recorded after liquid injection on for fully wetted (blue) and superhydrophobic ATR-crystals (red).

The Effect of Surface Geometry and Chemical Composition on Wettability Properties

C. Elif CANSOY[1], Ugur CENGIZ[2]

[1]Piri Reis University, Faculty of Science and Letters
[2]Canakkale Onsekiz Mart University, Faculty of Engineering

Oil and water repellencies of surfaces are crucial properties of materials in many industrial applications such as anti-fouling, oil-water separation, anti-bacterial, anti-icing, anti-fogging, self-cleaning. Wettability of a solid surface can be defined indirectly by liquid contact angle measurements at the three phase boundary of a liquid, solid and vapor intersect. Both surface roughness and chemical heterogeneity affect the wettability of a solid surface. Wenzel and Cassie-Baxter theories were developed to identify the roughness and chemical heterogeneity effect on wettabilities of the surfaces. However, in the recent publications, it was experimentally determined that the applicability of both theories were wrong in case of super liquid repellent surfaces[1,2]. Perfluoroalkyl copolymers with varying surface energies[3], polymer-nano particle composites[4] and geometrically patterned[2] surfaces can be used to prepare liquid repellent surfaces.

When the effect of perfluoroalkyl content and hydrocarbon chain lengths on oleophobic properties of perfluoroethyl alkyl methacrylate-methyl methacrylate (Zonyl-TM-MMA) copolymers were investigated, it was found that the wettability of the films strongly depend on perfluoroalkyl chain lengths. Besides, increase in hydrocarbon chain lengths also caused an increase in contact angle results due to the stronger cohesion interactions of liquid molecules and thus weaker adhesion between the polymer film and the liquid drop[3].

Nano particles can also be used to improve the wettability properties of the surfaces. To investigate this affect, perfluoro-styrene copolymers with varying SiO_2 nano particle content were prepared. Water drop contact angles increased up to 170° and exhibited extremely superhydrophobic behavior at higher SiO_2 contents. However, an opposite behavior was observed with hexadecane drop; increase in both SiO_2 and perfluoro- contents have caused a decrease in hexadecane contact angles. While the surfaces that contain higher amounts of SiO_2 exhibited superhydrophobic behavior, their oleophobic behavior were reduced with the increase of nano particle content[4].

Geometrically patterned surfaces, such as cylindrical pillars, can also be used to prepare liquid repellent surfaces[2]. Cylindrical pillars with varying diameters between 10 μm to 100 μm, separation distances between 5 μm to 10 μm, constant heights of 40 μm ± 2 and solid area fractions [$f^{CB}s(geo)$] between 0.349 to 0.712 were prepared and coated with perfluoro styrene copolymer to improve their liquid repellencies. Oleophobic behaviors of the patterned surfaces were affected from the type of the hydrocarbon liquids used and with the increase of hydrocarbon liquid chain lengths cylindrical pillar surfaces exhibited more oleophobic behavior. Applicability of Cassie-Baxter equation on cylindrical pillar surfaces was also investigated and was found that CA values of both water and hydrocarbon liquids were not obeying Cassie-Baxter theory however in the case of hydrocarbon liquids deviations from the theory were much more larger.

Surfaces with liquid repellent properties that were prepared by using perfluoroalkyl copolymers, polymer-nano particle composites and micropatterns, as briefly summarized above, will be reviewed within this presentation.

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Wetting behavior of $Ge_2Sb_2Te_5$ nanoparticle decorated surfaces

Weiteng Guo, Bin Chen, Gert H. ten Brink, Bart J. Kooi and George Palasantzas

University of Groningen, Zernike Institute for Advanced Materials

The wettability of surfaces nanostructured with $Ge_2Sb_2Te_5$ (GST) nanoparticles has been extensively studied. A wettability switch composed of UV-O_3 treatment and hydrocarbon atmosphere has been revealed. Indeed, the static contact angle was 20° and the hysteresis was negligible after UV-O_3 treatment, while the static contact angle would increase up to 125° and the hysteresis would reach 115° after 1-day exposure to hydrocarbon atmosphere storage. Using high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) for specially designed GST nanoparticles decorated graphene substrates, we observed a network composed with hydrocarbon connected GST nanoparticles, which may be responsible for the hydrophilic-hydrophobic transition.

Furthermore, we discussed our results in terms of a new theoretical model to develop liquid repellant surfaces, where the van der Waals interactions with the deposited nanoparticles are taken into account. This is especially important for the systems involving low surface tension liquids that prohibit the formation of large-contact angle of liquid droplets on traditional materials, because of their lower surface tension as compared to that of the solid surfaces.

Plenary session 3

Thursday 17th

10:30 - 11:30

Drops on slippery surfaces

Doris Vollmer[a], Philipp Baumli[a], Hannu Teisala[a], Frank Schellenberger[a], Martin Tress[a], Stefan Karpitschka[b], Jacco Snoeijer[b] Hans-Jürgen Butt[a], Anke Kaltbeizel[a]

[a] Max Planck Institute for Polymer Research, 55128 Mainz, Germany

[b] Universiteit Twente, Physics of Fluids, 7522NB Enschede, The Netherlands

A few years ago Joanna Aizenberg, David Quéré, and Kripa Varanasi realized that textured substrates which are infiltrated by a lubricant form a new class of functional surfaces, called slippery surfaces. Slippery surfaces have several promising applications based on the fact that drops slide on these surfaces with almost zero friction.

We applied laser scanning confocal microscopy to visualize the shape of the different interfaces with micrometer resolution. Drop motion strongly depends on details of the underlying substrate. On micropillar arrays the contact angle of the "hidden" interface (lubricant/drop) at the front and rear of the drop can change by more than 20°. The advancing contact angle can reach its fundamental limit of 180°. Results are compared to solutions of the generalized Laplace equations describing the drop profile and the annular wetting ridge[2]. For all film thicknesses, experimental results agree quantitatively with the calculated drop and film shapes.

A critical drawback of slippery surfaces is that the lubricant is removed with foreign objects or shear flow. To improve the longevity of slippery surfaces, the problem of lubricant depletion needs to be solved. A flow of a oil-in-water emulsion is driven over a water-filled micropillar array in a flow cell. Confocal microscopy reveals that the oil drops attach to the pillar walls, grow larger, and finally coalesce and sink down to fill the structure. The replenishment can be realized with a broad range of lubricant/solid combinations.[3]

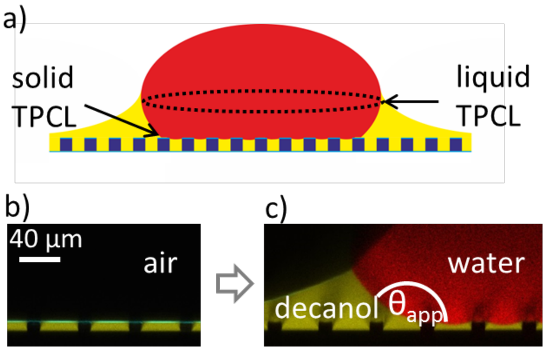

Figure. a) Sketch of a drop resting on a slippery lubricant-infused textured surface. The drop (red) resting on a micropillar array (blue) is surrounded by an annular wetting ridge (yellow) ending in a liquid three phase contact line. b) Confocal image of a micropillar array infiltrated with decanol (b) before and (c) after a water drop was deposited.

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Poster presentation abstracts

Dewetting of Liquid Films into Droplets

G. McHale[1], C.V. Brown[2],A.M. J. Edwards[2], R. Ledesma-Aguilar[1], M.I. Newton[2],

[1]Smart Materials & Surfaces Laboratory, Northumbria University,
Newcastle upon Tyne NE1 8ST, UK
[2]School of Science and Technology, Nottingham Trent University,
Nottingham NG11 8NS, UK

Recently, we have developed the concept of interface-localized liquid dielectrophoresis, which can induce and control droplet equilibrium shapes using a voltage (also called dielectrowetting)[1]. In the extreme case of an applied voltage beyond the threshold needed to initiate complete spreading of a droplet, we have shown it is possible to study the dynamics of surfactant-free superspreading from a droplet into a film[2]. Here we consider how this technique can be used to initiate a circular shaped liquid film on a non-wetting surface and then study the dynamics of dewetting as the film relaxes back to an equilibrium droplet shape once the voltage is removed[3]. We find the trajectory of shapes experimentally observed during axisymmetric dewetting of the film includes a constant speed rim with dimple phase followed by an exponential relaxation of a spherical cap shape, consistent with both analytical models and Lattice-Boltzmann simulations. We show how the dewetting process of a liquid film changes as the displaced second immiscible fluid phase is changed from air to a viscous liquid enabling control both of viscosity ratio and final equilibrium contact angle.

Acknowledgements. We would like to thank Dr Ian Sage for advice on TMPTGE and the financial support of the UK Engineering & Physical Sciences Research Council (EPSRC grants EP/K014803/1, EP/E063489/1 and EP/E063489/1).

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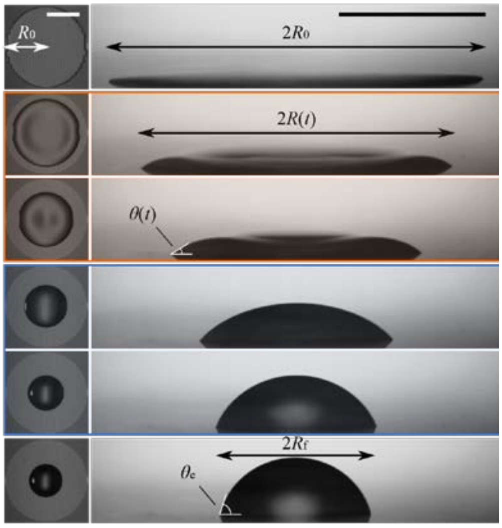
[2] McHale, G. *et al.* Voltage-induced spreading and superspreading of liquids. *Nature Communications* **4**, 1605 (2013).
[3] Edwards, A. M. J. *et al.* Not spreading in reverse: The dewetting of a liquid film into a single drop. *Sci. Adv*. **2**, e1600183–e1600183 (2016).



Dewetting of a liquid film in air.

Leidenfrost Transport Using Selective Heating

G. McHale[1], L.E. Dodd[1], N.R. Geraldi[1], J. Martin[1], M.I. Newton[2], G.G. Wells[1], D. Wood[1], B.B. Xu[1]

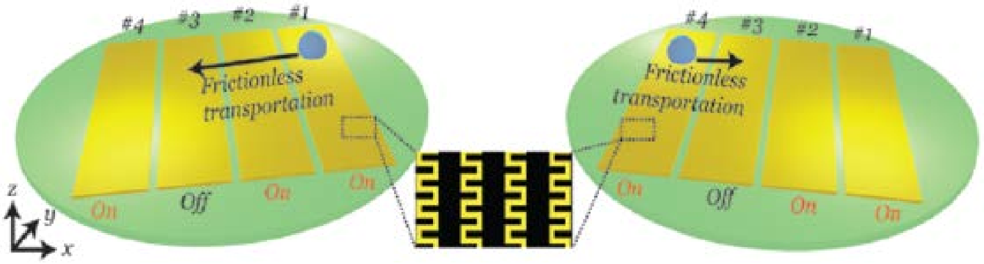
[1]Smart Materials & Surfaces Laboratory, Northumbria University,
Newcastle upon Tyne NE1 8ST, UK
[2]School of Science and Technology, Nottingham Trent University,
Nottingham NG11 8NS, UK

The Leidenfrost effect can be used to levitate and transport, or rotate droplets and disks of solid ices[1]. However, substrates are usually uniformly heated to a constant and high temperature requiring a significant input of energy. Here we report an approach to activating the Leidenfrost effect in both a spatially and temporally localized manner thereby significantly reducing the energy input required[2]. In our approach we selectively trigger Leidenfrost levitation of a droplet by the application of a voltage to micrometer-scaled serpentine shaped heating units, which have been microfabricated on the substrate in groups to create voltage addressable heating arrays. We demonstrate that the heating arrays are able to generate a Leidenfrost effect transition for droplets of isopropanol (γ_{LV}~20 mN/m), acetone (γ_{LV}~28 mN/m), and deionized water (γ_{LV}~72 mN/m). Experimental data for thermal distributions were compared with COMSOL simulation results for the phase diagrams describing metastable levitation of droplets as a function of device designs. To provide a proof-of-concept for low friction droplet transport and microfluidics, we conducted experiments on droplet transport down a tilted substrate with voltage addressable heating arrays. In these experiments, four heating arrays were used with typically three activated and one inactive. In each case, low friction high speed droplet transportation (~65 mm/s) across the activated heating arrays on a substrate tilted by ~7° was observed. Droplet motion ceased when the inactive electrothermal heating array was encountered.

Acknowledgements. The work was supported by the Engineering & Physical Sciences Research Council (EPSRC grants EP/L026899/1, EP/L026619/1, and EP/L026341/1). We also acknowledge funding from the EU-COST MP1106 network.

[1] Wells, G.G. *et al.* A sublimation heat engine. *Nature Communications* **6**, 6390 (2015).

[2] Dodd, L.E. *et al.* Low friction droplet transportation on a substrate with a selective Leidenfrost effect. *ACS Applied & Materials Interfaces* **8**, 22658–22663 (2016).



Droplet transport on voltage programmable microfabricated Leidenfrost elements.

Design and Fabrication of Superhydrophobic, Ice-/Snowphobic Coatings for High Voltage Power Lines Application

Giulio Boveri, Mariarosa Raimondo, Federico Veronesi

Institute of Science and Technology for Ceramics, ISTEC-CNR , Faenza (Italy)

The formation and accretion of ice and snow on high voltage (HV) power lines components represent a huge problem which can reduce the efficiency of current conduction and whose removal requires expensive and time-consuming treatments. Strong snowfalls can often involve severe drawbacks such as extended blackout and damages to the HV systems due to the accretion phenomena and the subsequent breakup of the lines.

Superhydrophobic surfaces (SHSs) - designed with a strict control of the surface chemical composition and morphology, e.g. coupling hierarchical micro-nanostructures with a very low surface energy - work in a stable Cassie-Baxter state preventing water drops from wetting the surface. SHSs have been widely investigated for many applications. Anyway, their potential use as icephobic and snowphobic materials have not been clearly highlighted yet, notwithstanding many recent papers on the subject[1,2].

In this work, 50 cm-long Anticorodal aluminum alloy (6082) conductors, commonly used in HV lines, were functionalized by dip coating into a ceramic oxide nanoparticles suspension, synthesized by sol-gel route, and chemically modified with fluoroalkylsilane (FAS) solution to obtain SHSs by the typical Lotus leaf approach. Some of them underwent an additional infusion step in a fluorinated oil (Krytox 100), according to the so-called SLIPS approach.

Both the design approaches provided materials with high dynamic performances (contact angle hysteresis < 10°), while the infused samples showed a static water contact angle of about 120°, much lower than the value of 170° reached by SHS samples. However, the presence of the fluorinated oil as outer layer involves a greater homogeneity of the coating with a decreasing of local defects.

To evaluate the influence of roughness on nucleation and accretion of the ice as well as on snow deposition, the functionalization was performed on smooth ($Ra = 0.3\ \mu m$) and sandblasted ($Ra = 3.6\ \mu m$) conductors, either by SHS and SLIPS approach.

The ice adhesion strength has been evaluated by shear stress analysis and the results exhibit a decrease of adhesion for both SHS and SLIPS samples with respect to the untreated ones.

During the last winter, coated samples were exposed outdoor at experimental facilities located in the west of Italian Alps, at an altitude of 959m asl.

Under the recorded snowfall events and conditions ($T = -2°C$, dry snow with low liquid water content (LWC) and spherical snowflakes), sandblasted SH cables showed a significant delay in snow deposition and snow/ice layer accretion, with a complete detachment of this layer before the end of the observed event. This behavior has to be underlined with respect to that of the other coated cables, whether smooth or sandblasted. However, in different conditions (i.e. $-2°C < T < 0°C$, wet snow with high LWC), sandblasted SHSs seem to lose the ability of delaying show and ice accretion.

[1] J. Liu, Z. A. Janjua, M. Roe, F. Xu, B. Turnbull, K. Choi and X. Hou; Nanomaterials, 2016, pp 232-241.

[2] P. Kim, T. Wong, J. Alvarenga, M. Kreder, W. Adorno-Martinez and J. Aizenberg; ACS nanoorg, 2012, 6569-6577.

Wettability of reentrant surfaces: a global energy approach

Marion Silvestrini[1], Carolina Brito[1]

[1]Instituto de Física, Universidade Federal do Rio Grande do Sul, 91501-970 – Porto Alegre, RS, Brazil

When a droplet is placed on a substrate it can reach different final states depending of different factors, which include surface chemistry, the type of liquid and its volume. Here, we consider two possible wetting states: the Wenzel (W) state, characterized by the homogeneous wetting on the surface and the Fakir configuration of a Cassie-Baxter (CB) state defined as a droplet residing on top of roughness grooves.

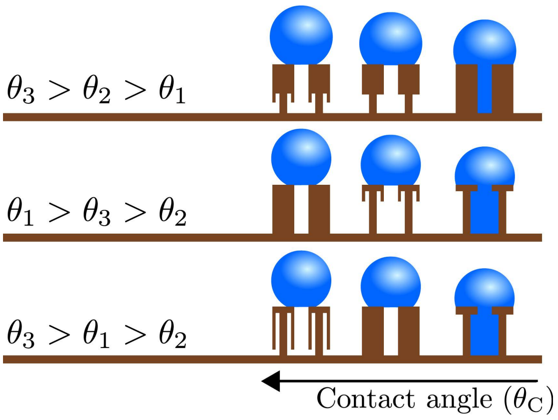
Using a theoretical model based on the global interfacial energies for both states CB and W, it is possible to study the wetting behavior of simple and double reentrant surfaces. From the equations of energy associated to each wetting state, we predict the thermodynamic wetting state of the droplet for a given surface texture and obtain its contact angle θ_C. We first use this model to find the geometries for pillared, simple and double reentrant surfaces that most enhances θ_C and conclude that the repellent behavior of these surfaces is governed by the relation between the height and width of the re-entrances.

We compare our results with recent experiments and discuss the limitations of this thermodynamic approach. To address one of these limitations, we implement Monte Carlo simulations of the cellular Potts Model in three dimensions, which allow us to investigate the dependency of the wetting state on the initial state of the droplet.

We find that when the droplet is initialized in a CB state, it gets trapped in a local minimum and stays in the repellent behavior irrespective of the theoretical prediction.

When the initial state is W, simulations show a good agreement with theory for pillared surfaces for all geometries, but for re-entrant surfaces the agreement only happens in few cases: for most simulated geometries the contact angle reached by the droplet in simulations is higher than θ_C predicted by the model. Moreover, we find that the contact angle of the simulated droplet is higher when placed on the re-entrant surfaces than for a pillared surfaces with the same height, width and pillar distance[1].

[1] Wettability of reentrant surfaces: a global energy approach, Marion Silvestrini and Carolina Brito, Langmuir, v 33, 12535 (2017).



The figure summarizes our theoretical findings. θ_1 denotes the thermodynamic contact angle of the droplet on the pillared surface, θ_2 on the reentrant and θ_3 on the double reentrant surface. We show that the contact angle of the droplet when placed on each of the surfaces depend on the geometrical parameters of such surfaces.

The interaction between the wetting line and arc-discharge carbon nanotube deposits

Markus Ahlskog[1], Matti J. Hokkanen[1,2]

[1]University of Jyväskylä, Department of Physics and Nanoscience Center
[2]Aalto University, Department of Applied Physics

Retention and detachment of colloidal particles from surfaces is often considered only in terms of spontaneous chemical dispersion when the surface is already fully submerged. Nevertheless, interfacial processes, where the particles are caught on a mobile liquid contact line by capillary effects are ubiquitous[1,3]. Theoretical description of such interfacial processes exist for spherical microcolloids, while for anisotropic shapes the literature is limited. Arc-discharge synthesized multiwalled carbon nanotube (MWNT) material contains besides the very anisotropic tubes also irregular amorphous carbon particles (ACP) that both are strongly hydrophobic[2]. As a water-air-solid contact line is swept over a deposition of MWNT material on a hydrophilic substrate, it causes selective detachment of the spherical ACPs over the one dimensional MWNTs. In this work we investigate the detachment process and the balance between the surface tension force and adhesive forces [3]. Our results show that on hydrophilic substrates the surface tension force of the liquid interface dominates over adhesion, sweeping away most of the material. However, clean MWNTs oriented perpendicular to the contact line are able to resist detachment. On the other hand, on hydrophobic surfaces adhesive forces dominate, possibly via the hydrophobic interaction. We discuss these results with conventional models of capillarity and adhesion, including the van der Waals force and the electrostatic double layer interaction. However, a fully satisfactory analysis will require e.g. computational modelling of the problem.

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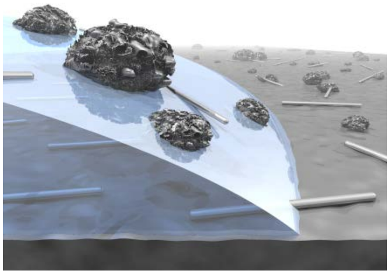
[2] M. Hokkanen, S. Lautala, D. Shao, T. Turpeinen, J. Koivistoinen, M. Ahlskog, *Applied Physics A*, **122**, 634 (2016)
[3] M. Hokkanen, S. Lautala E. Flahaut, M. Ahlskog, *Colloids and Surfaces A*, **533**, 109 (2017)



Schematic illustration of the water contact line sweeping over a raw arc-discharge MWNT deposit.

Effect of lubricant-infused layer on the adhesion force and contact angles of doubly reentrant micropillars

Zheqin Dong[1], Martin Schumann[2], Matti Hokkanen[3], Bo Chang[4], Quan Zhou[4], Robin Ras[3], Martin Wegener[2], Pavel Levkin[1]

[1]Karlsruhe Institute of Technology, Institute of Toxicology and Genetics
[2]Karlsruhe Institute of Technology, Institute of Nanotechnology
[3]Aalto University, Department of Applied Physics
[4]Aalto University, Department of Electrical Engineering and Automation

The ability to create superoleophobic surfaces with high contact angles (above 150°) for low surface tension liquids is important and has been recently demonstrated using reentrant or doubly reentrant microtopography. Both microstructures, however, lead to high contact angle hysteresis and high adhesive force due to the large liquid-solid contact area on top of the doubly reentrant microstructures [1,2]. By using direct laser writing technology, we show that the doubly reentrant topography can be combined with slippery liquid infused surface by infusing lubricants into its secondary nano roughness produced on top of the doubly reentrant micropillars. The slippery lubricant infused layer reduces the adhesive force and contact angle hysteresis of water on the doubly reentrant micropillars.

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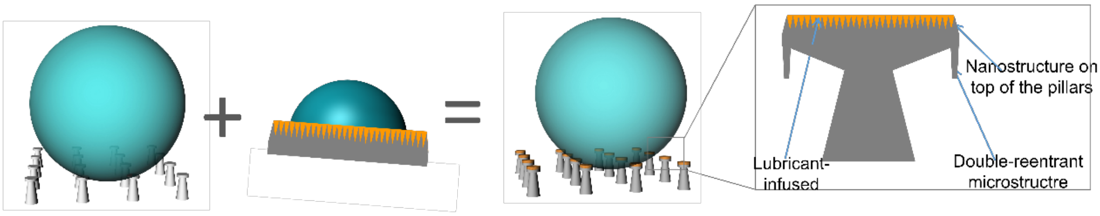
[2] T. Liu, C-J. Kim, Science. 28, 1096-1100 (2014).



Superoleophobic doubly-reentrant

Slippery lubricant-infused

Slippery superoleophobic doubly-reentrant

Concept of designing a slippery superoleophobic surface via combination of doubly reentrant structure and slippery infused porous surfaces.

Droplet impact dynamics on a slippery surface: A numerical analysis

Firoozeh Yeganehdoust[1], Ida Karimfazli[1], Ali Dolatabadi[1]

[1]Concordia University, Department of Mechanical, Industrial, and Aerospace Engineering, Montreal, Canada

Droplet impact on the liquid and solid surfaces is of great importance due to its wide range of scientific and industrial applications. For a moderate range of droplet impact velocities, it has been seen that droplet can spontaneously bounce off the surface. This spontaneous bouncing is caused by the air layer formation between the droplet and the surface. Lubricant Impregnated Surfaces that comprise a textured substrate with a low surface tension lubricant, have recently shown great promises in different applications that can overcome various challenges in superhydrophobic surfaces. Utilizing the slipperiness of LIS surfaces, the dynamic behavior of droplet impact on oil has been investigated by using the volume of fluid (VOF) methodology. Additionally, computational cells were considerably refined to capture the presence of the sub-micron layer of air trapped underneath the droplet during the impact. The air cushion formed beneath the droplet and its effect on droplet hydrodynamics was captured in this model. It was found that air layer would be stable irrespective of different range of lubricant viscosities. On the other hand, impact conditions and droplet properties had a significant role in droplet hydrodynamics. Moreover, entrapment of the air bubble has been observed in specific cases according to the formation of high pressure in the air layer region. The results is also assessed by the experimental data.

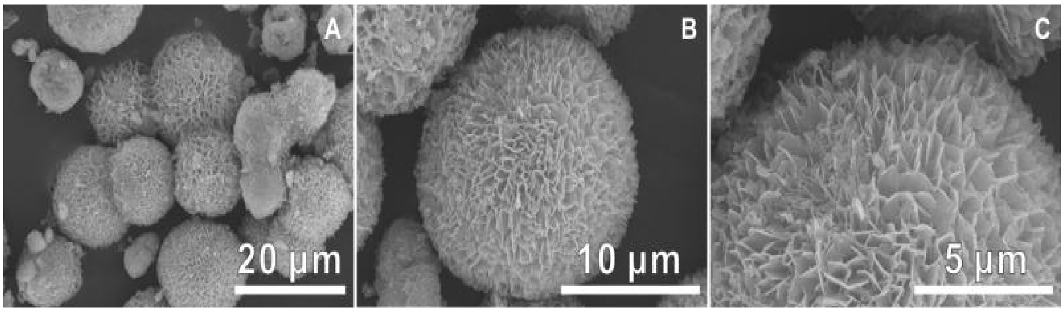
Fabrication of superhydrophobic zinc oxide-fluorocopolymer composite coating

PengFei Liu[1], Qiang Wang [1], Mengqiu Jia[1]

[1] Beijing University of Chemical Technology, College of Materials Science and Engineering

Superhydrophobic organic–inorganic hybrid composite coatings have received much more attention because of the simultaneous advantages of both inorganic and organic materials. It is now well-known that superhydrophobic surfaces result from the combination of a low surface energy and dual- or multiscale surface roughness. We prepared superhydrophobic ZnO–fluoropolymer hybrid particles, ZnO was formed by hydrolysis of zinc acetate dihydrate in diethylene glycol, mesoporous hierarchical ZnO were prepared by controlled etching of PVP protected oxide precursors with a low amount of inorganic acid[1]. The hybrid particles were obtained in two steps through the methacryloxypropyltrime-thoxysilane (MPS) treatment of ZnO and the radical polymerization of the MPS-treated particles with fluoroacrylate monomers, these nanoparticles create both microscale and nanoscale roughness, and fluoropolymer provides low surface energy. We used hybrid ZnO blended with epoxy resin, all the coatings were heated to cure, we also demonstrated the effects of varying the amount of fluoroacrylate monomers and concentration of the particles on the coating. The preparation of superhydrophobic coating has widely use in self-cleaning, metal corrosion and other fields.

[1] PAN J H. Langmuir, 2015, 31(15): 4566-72.



Hierarchical ZnO microspheres SEM image

Study of the influence of surface nanocorrugations on van der Waals interactions by ab-initio modeling and by characterization of optical properties and liquid / solid interactions

Anthony Hendrickx[1], Louis Dellieu[2], Olivier Deparis[1], Michaël Sarrazin[1,3]

[1]Namur University (BE), Department of Physics of Matter and Radiation
[2]AGC Glass Europe (BE), Technovation Centre
[3]Bourgogne-Franche-Comté University (FR), UTINAM Institut

Anti-reflective properties and superhydrophobicity have a major importance in the development of new technology, leading to numerous industrial applications. From a theoretical point of view, superhydrophobicity and antireflection are almost always studied separately. For instance, nanostructures are commonly used for developing superhydrophobic surfaces, and it is also known that nanostructurations have a great influence on optical properties such as reflectivity. However, available wetting theoretical models ignore the effect of nanostructurations on vacuum photon-mode and thus on van der Waals forces and hydrophobicity.

In 2014, a new model unifying these problems has been proposed, based on the Lifshitz-van der Waals interaction theory[1]. Taking origin from quantum vacuum fluctuations, these interactions are a major contribution to the interaction potential energy between macroscopic systems. They are shown to be tunable via antireflective nanostructured surfaces design. According to this, it is shown that superhydrophobicity of nanostructured surfaces is closely related to the optical properties of these surfaces.

As a case study, wetting contact angles of a water droplet above a nanostructured polyethylene surface have been obtained from the interaction potential energy calculated as a function of the droplet-surface separation distance. The current step is to experimentally validate this theory by measuring wetting contact angle on PET nanostructures, manufactured according to Checco's work[2], using a mask of PMMA+Al_2O_3 made with a combination of block-copolymer self-assembly in PS-b-PMMA and sequential infiltration synthesis of TMA in PMMA.

[1] L. Dellieu and al, Physical Review Letters 114, 024501 (2015)
[2] A. Checco and al, Physical Review Letters 112, 216101 (2014)

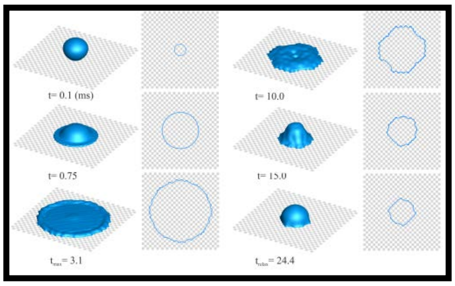
Equivalent contact angle for droplets impacting on checkboard-patterned surfaces

Ali Mazloomi Moqaddam[1], Dominique Derome[1], Jan Carmeliet[2]

[1]Laboratory for Multiscale Studies in Building Physics Empa, Swiss Federal Laboratories for Materials Science and Technology, 8600 Dübendorf, Switzerland
[2]Chair of Building Physics, Department of Mechanical and Process Engineering, ETH Zurich, 8092 Zurich, Switzerland

Drop impact on chemically heterogeneous flat surfaces consist of a regular checkboard pattern with alternate solid patches of different wettability characterized by two different Young's contact angles; hydrophilic and hydrophobic, is numerically studied using the entropic lattice Boltzmann method for two-phase flows[1]. The size of the heterogeneities to droplet radius is varied in a range at which the local contact angles along the contact line attain values varying between a minimum and maximum value, as impact evolves. It is found that the ratio of the patch size to droplet radius and the impact velocity of the droplet are two key parameters controlling the droplet distortion at the contact line and the resulting local contact angles of the impacting droplet on the checkboard surface. From our numerical observations during the entire process of drop impact on the surface, it is found that after impact first the cosines of the minimal and maximal local contact angles increase until maximum spreading reached and then they converge nearly to the cosines of the Young's contact angles of the hydrophilic and hydrophobic patches present on the surface and remain nearly constant until end of the impact when the drop attains its final deposit shape. It is also shown that the wetted area fraction on the hydrophilic regions is almost a constant value greater than 0.5 showing the tendency of the droplet to preferentially wet the hydrophilic patches as impact continues. Finally, the recently proposed notion "equivalent contact angle"[2] representing Cassie's apparent contact angle for a sessile droplet distorted on a checkboard-patterned surface is determined for droplets whose impact on such surfaces. It is demonstrated that the validity of the equivalent contact angle equation can be further expanded for impacting droplets on checkboard-patterned surfaces for which it can be used to represent the dynamics of the impacting droplets distorted on these surfaces by one single apparent contact angle. Our simulations exhibit that right after impact the equivalent contact angle value starts to increase until the maximum spreading reached. Then, it nearly converges to Cassie's contact angle and remains almost constant until the droplet reaches to a quasi-relaxation/equilibrium state.

[1] Mazloomi M., A.; Chikatamarla, S. S.; Karlin, I. V. ***Phys. Rev. Lett.*** 2015,114,174502.
[2] Carmeliet, J.; Chen, L.; Kang, Q.; Derome, D. ***Langmuir***, 33 (2017), 6192 6200.



Sequence snapshots together with the corresponding contact line profiles of a liquid droplet impacting on a checkboard patterned surface.