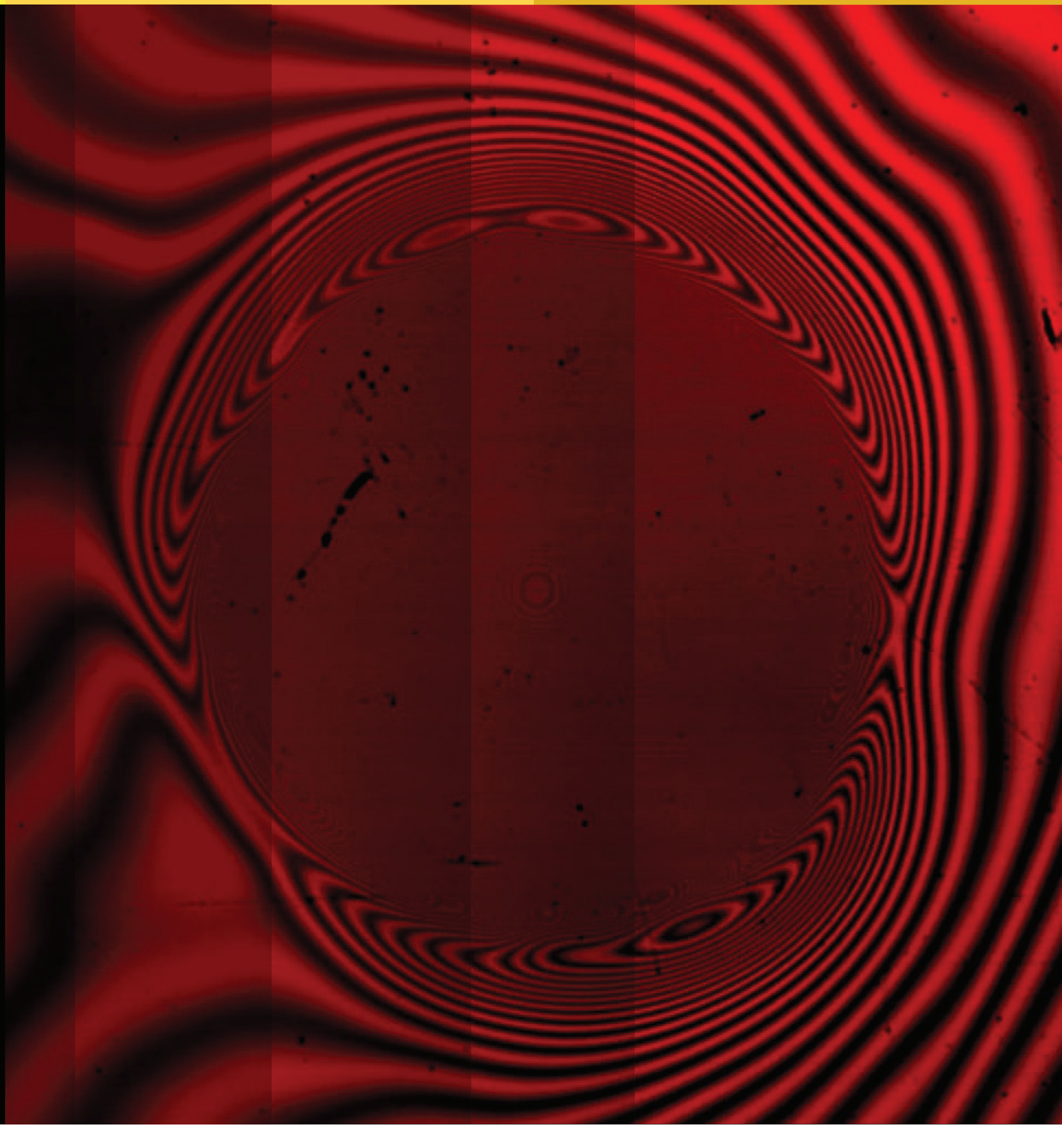
MAGIC AT INTERFACES

Sushanta K. Mitra

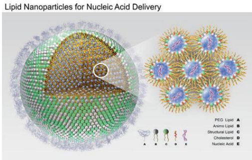
Micro & Nano-scale Transport Laboratory,
Waterloo Institute for Nanotechnology,
Department of Mechanical & Mechatronics Engineering,
University of Waterloo, Waterloo, N2L 3G1, Ontario, Canada

UNIVERSITY OF WATERLOO



APPLICATIONS OF ENCAPSULATION

Pharmaceuticals

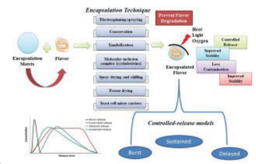


Samaridou, E., et al. *Adv. Drug Deliv. Rev.* **2020**, 154, 37-63.

Nutraceuticals

Source: pexels.com

Food and flavors

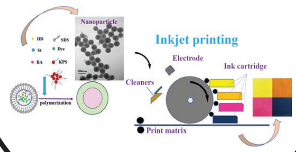


Premjit, Y., et al. *Food Res. Int.* **2022**, 110879.

Cosmetics and personal care

Source: Google

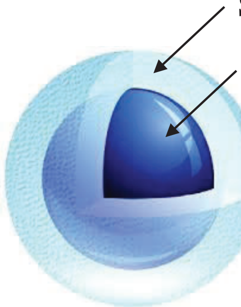
Inkjet printing



Li, J., *et al.*, *ACS Omega* **2018**, 3, 7, 7380-7387

But why a new encapsulation technique?

S. Misra

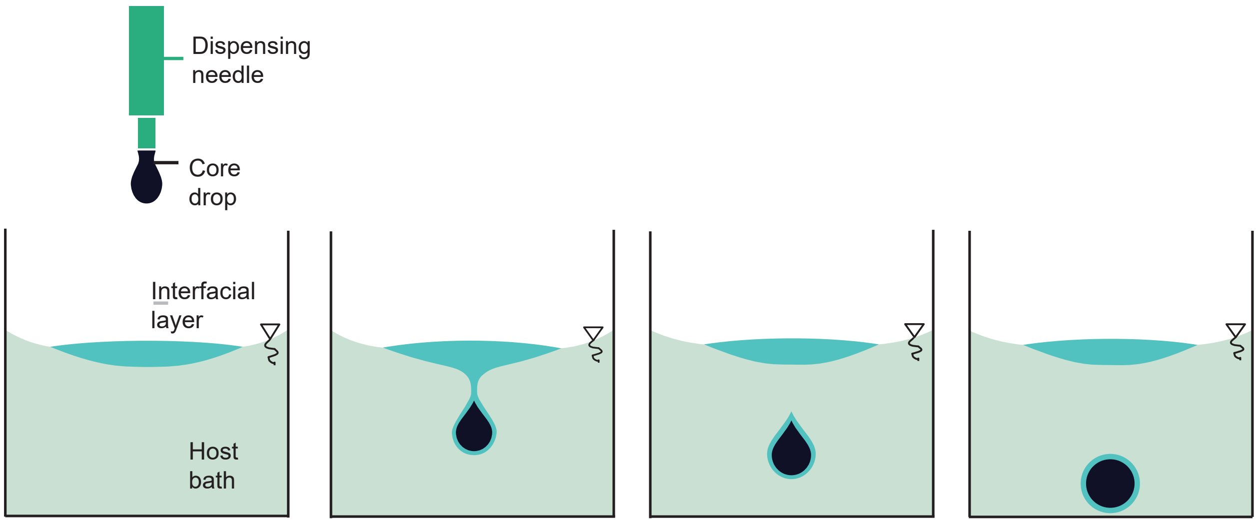


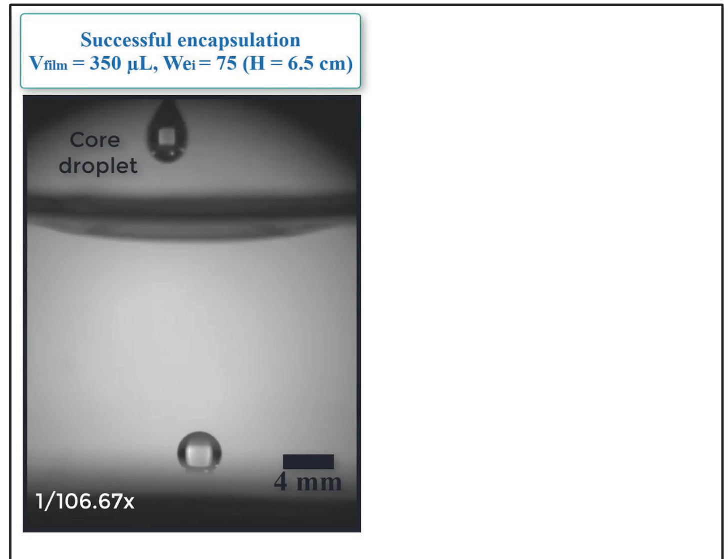
Existing encapsulation methods are either –

- Very case specific, with limited flexibility regarding material selection
- Restrictive in the range of applicability
- Involves intricate material processing or handling steps
- Requires complex and expensive infrastructure
- Simple methods offer limited control on dosage size

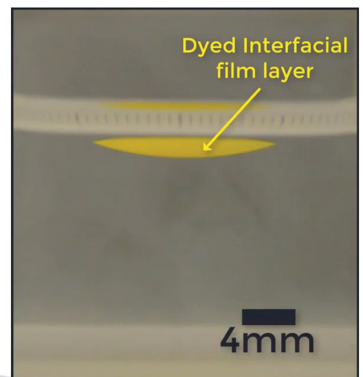
MNT Micro & Nano-Scale Transport Laboratory · WATERLOO INSTITUTE FOR nanotechnology · UNIVERSITY OF WATERLOO

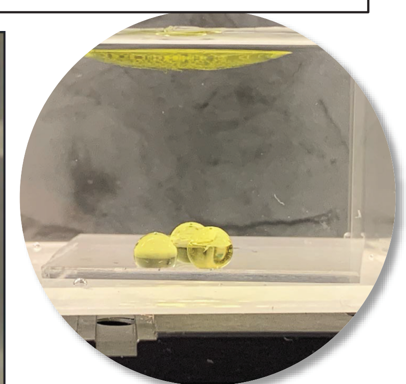
Encapsulation with an interfacial liquid layer: a novel liquid-based wrapping





- Ultrafast (~ 50 ms/encapsulation) and therefore scalable
- Surface tension driven wrapping – minimally restrictive on materials
- Controllably produces stable monodispersed encapsulated drops
- Allows multilayer encapsulation
- Allows precise shell thickness control (~500 nm – 2 mm) by shell volume control
- Simple, executable as a table-top experiment





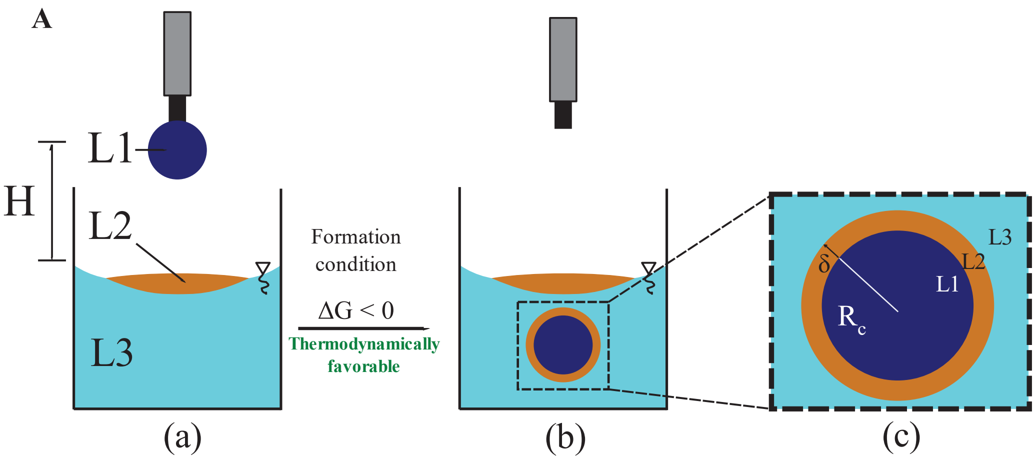
S. Misra *et al.*, *Journal of Colloid and Interface Science*, **2020**, 558, 334-344.
S. Mitra *et al.*, *U.S. Patent Application No. 17/432,848*, **2022**.

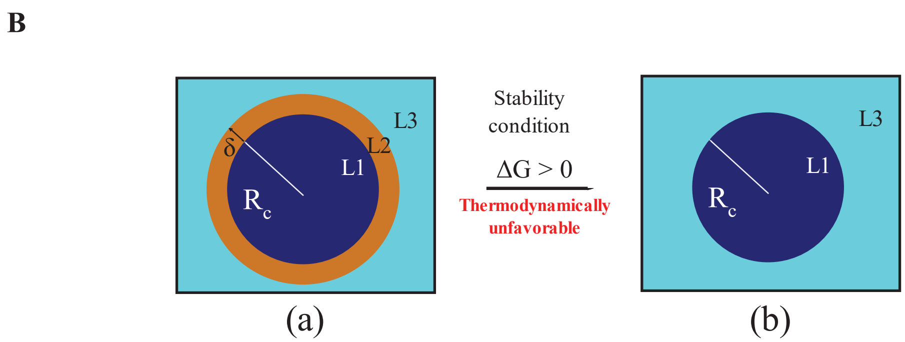
MNT Micro & Nano-Scale Transport Laboratory

Waterloo Institute for nanotechnology

UNIVERSITY OF WATERLOO

A thermodynamic understanding of the encapsulation process





Thermophysical requirements:

- $\rho_1 > \rho_3 > \rho_2$
- L2 and L3 are physico-chemically compatible (i.e., unreactive, immiscible).

❖ Condition for formation of encapsulated drop:

$$\Delta G_{\text{formation}} = G_{A(b)} - G_{A(a)} \approx 4\pi R_c^2(\gamma_{12} + \gamma_{23} - \gamma_1) - \frac{4}{3}\pi R_c^3 \rho_1 g H < 0$$

$$\rightarrow (\gamma_{12} + \gamma_{23} - \gamma_1) < 0 \quad [\because H \text{ is a positive variable}]$$

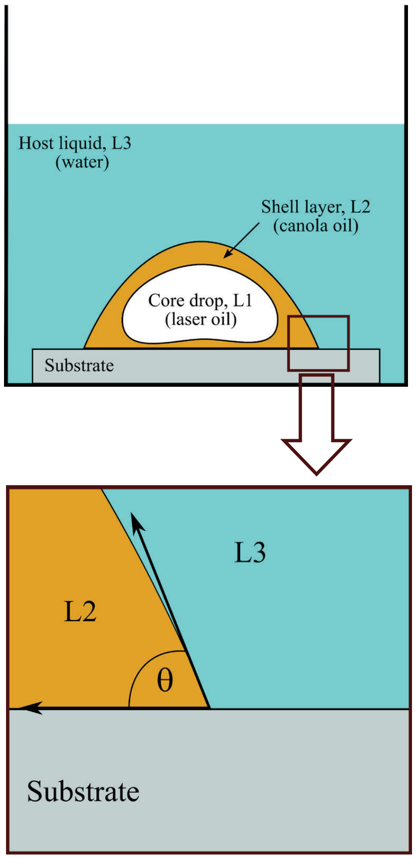
❖ Condition for stability of encapsulated drop:

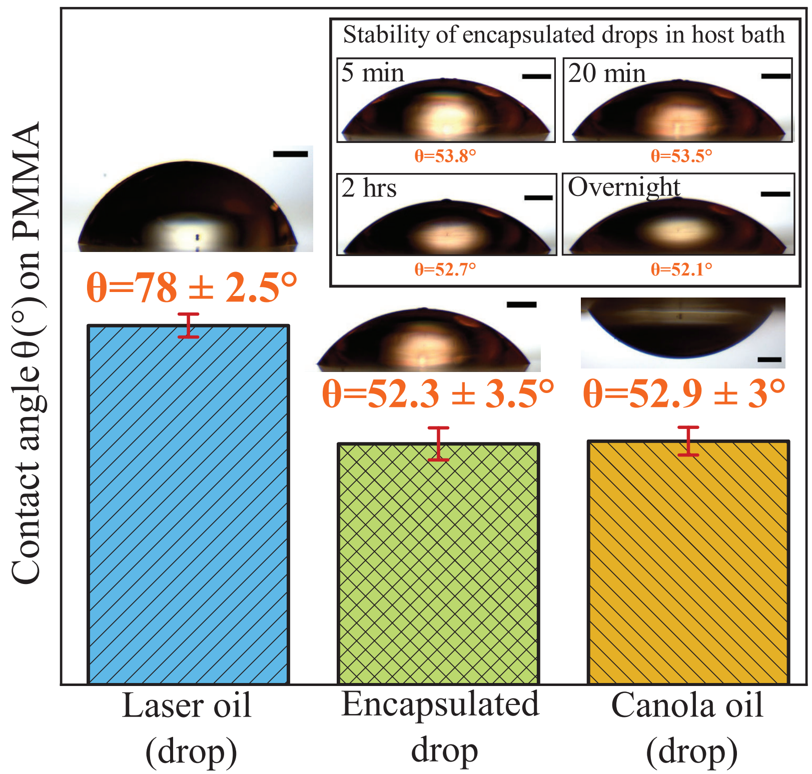
$$\Delta G_{\text{detachment}} = G_{B(b)} - G_{B(a)} \approx 4\pi R_c^2(\gamma_{13} - \gamma_{12} - \gamma_{23}) > 0$$

$$\rightarrow (\gamma_{13} - \gamma_{12} - \gamma_{23}) > 0$$

S. Misra *et al.*, *Journal of Colloid and Interface Science*, **2020**, 558, 334-344.
S. Mitra *et al.*, *U.S. Patent Application No. 17/432,848*, **2022**.

Wetting Signature





Resemblance in underwater wetting signature between encapsulated drop and shell liquid confirms integrity of wrapping

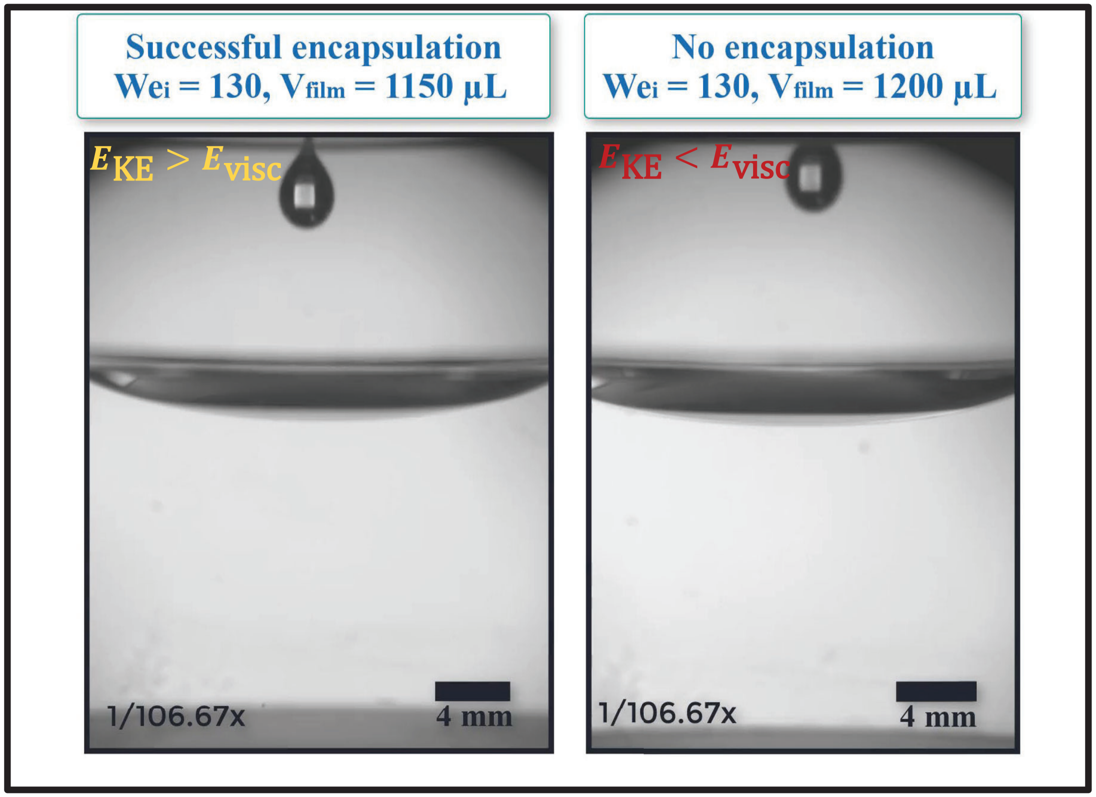
MNT Micro & Nano-Scale Transport Laboratory

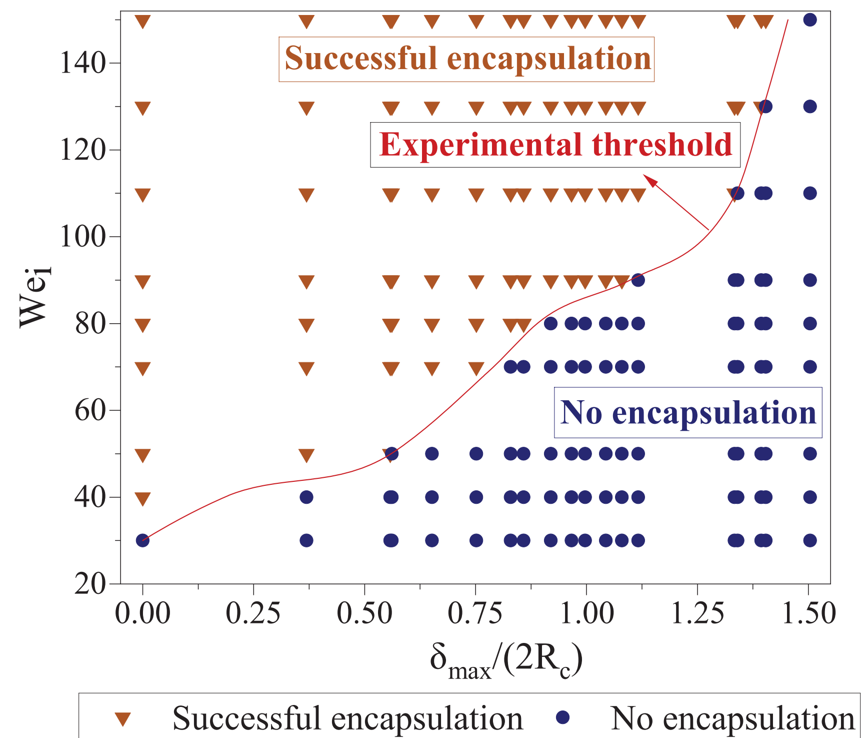
WATERLOO INSTITUTE FOR nanotechnology

UNIVERSITY OF WATERLOO

Role of viscous dissipation: deviation from ideal thermodynamic estimate

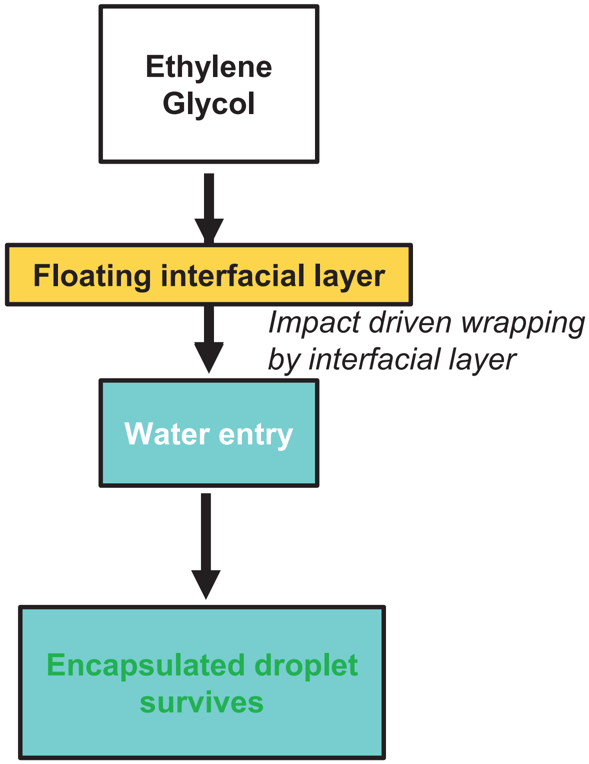
- ($\gamma_1 > \gamma_{12} + \gamma_{23}$) is not sufficient for encapsulation as viscous dissipation remains unaccounted in equilibrium thermodynamic analysis.
- Encapsulation is possible only if $E_{KE} > E_{visc}$.

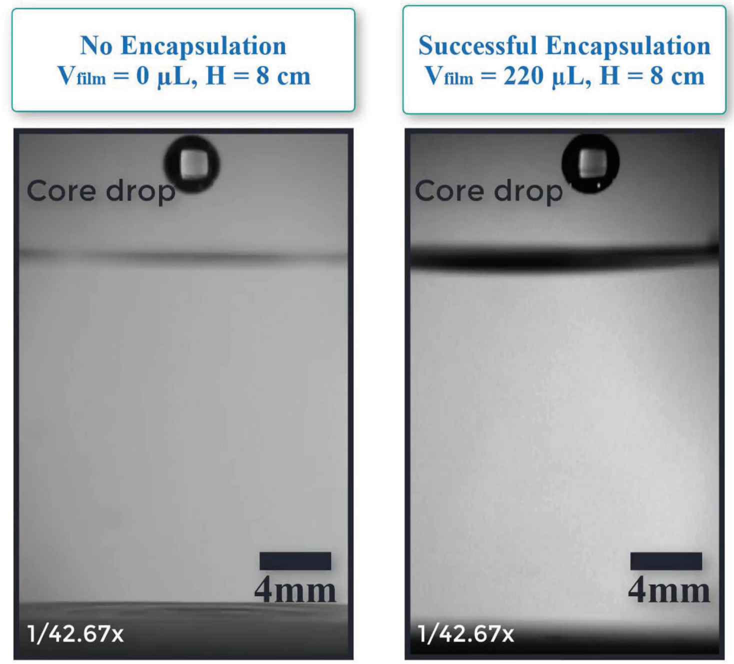




S. Misra *et al.*, *Journal of Colloid and Interface Science*, **2020**, 558, 334-344.
S. Mitra *et al.*, *U.S. Patent Application No. 17/432,848*, **2022**.

Applicability in providing protection from aggressive surrounding





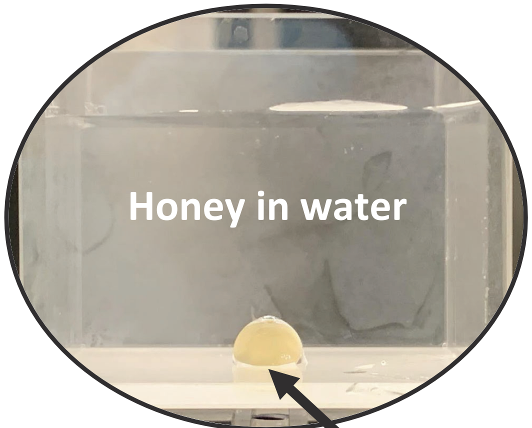
Miscible core (Ethylene Glycol) - surrounding (water) combination

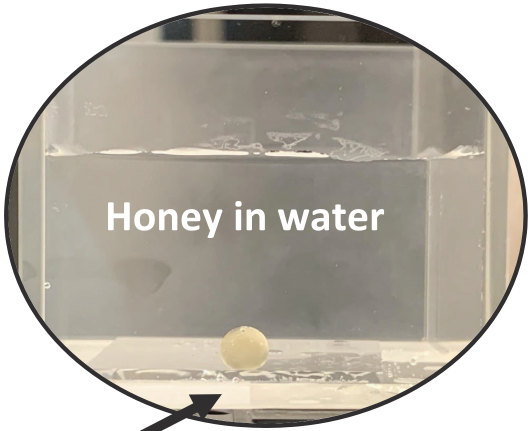
The wrapping layer provides effective protection to Ethylene glycol drop (water soluble) from surrounding water medium

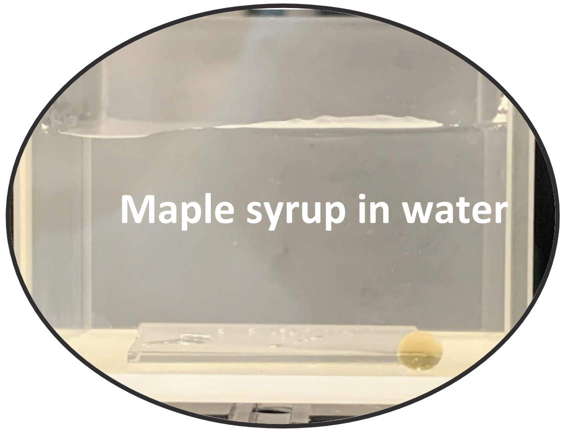
S. Misra *et al.*, *Journal of Colloid and Interface Science*, **2020**, 558, 334-344.
S. Mitra *et al.*, *U.S. Patent Application No. 17/432,848*, **2022**.

Demonstration of practical use cases – versatility

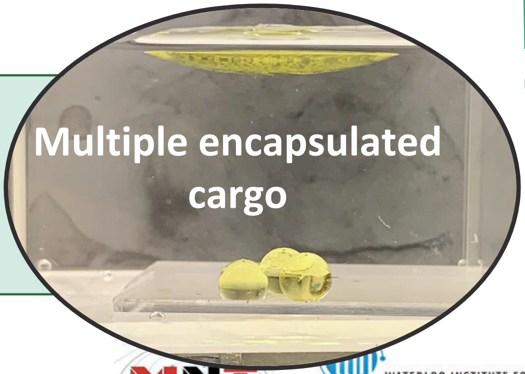
Encapsulated cargo inside liquid phase (e.g., flavoured beverages)



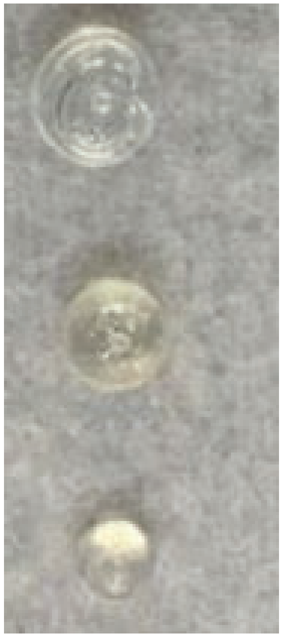




- Efficient Control on shape and size of encapsulated cargo
- Perfectly spherical capsules!
- Excellent protection despite miscibility!



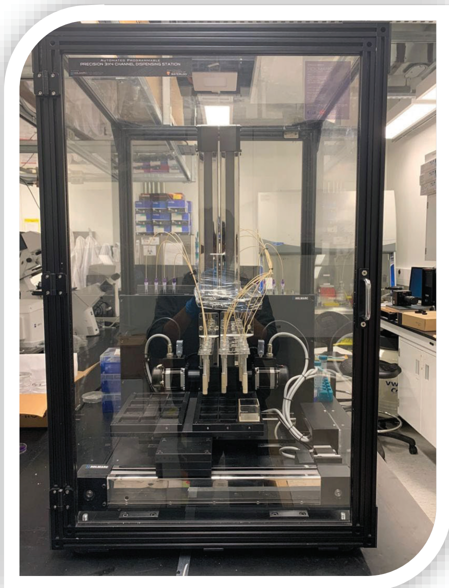
Individual extracted cargo



Shell-hardened (UV) capsules of varying sizes

Commercialization pathway

Fully functional High throughput commercial prototype



SLE ENTERPRISES

SLE Enterprises B.V.
High Tech Campus 27,
5656 AE Eindhoven, Netherlands
www.sle-enterprises.com
sushanta.mitra@sle-enterprises.com

HIGH TECH XL

BRAINPORT EINDHOVEN

SLE – *Revolutionizing encapsulation machines*

Nutraceutical

Food & beverages

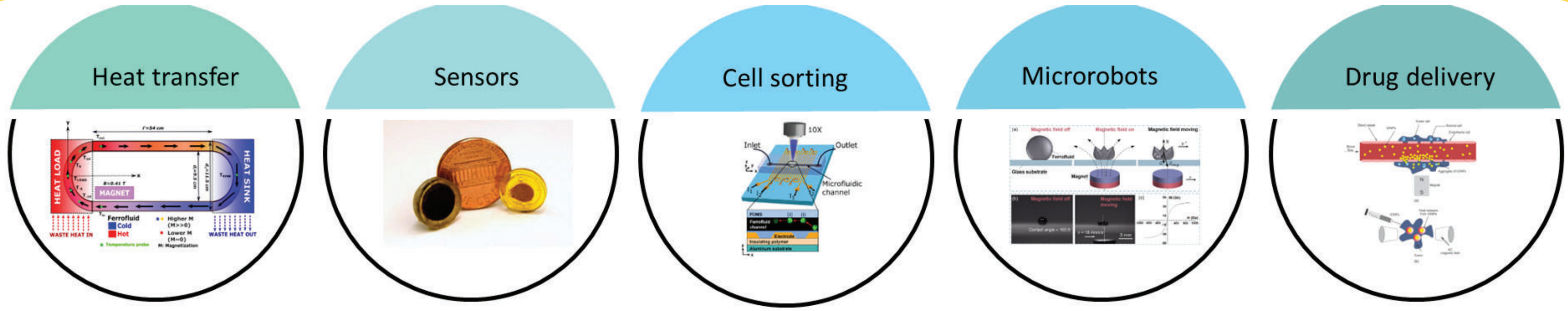
MNT Micro & Nano-Scale Transport Laboratory

WATERLOO INSTITUTE FOR nanotechnology

UNIVERSITY OF WATERLOO

APPLICATIONS OF FERROFLUID

- Ferrofluid is the colloidal solution made of magnetic nanoparticles (MNPs of size ~10 nm) coated with surfactants suspended in organic fluid/water/oil *which offers contact-less magnetic manipulation.*



Pattanaik, MS, *et al.*, *Sci Rep* **2021**, 11 (24167)　Chitnis, G., *et al.*, *JMM* **2013**, 23 (125031)　Kose A R., *et al.*, *PNAS* **2009**, 106 (21478-21483)　Chen D., *et al.*, *APL* **2021**, 118 (134101)　Asfer M., *et al.*, *JMMM* **2017**, 436 (47-56)

U. Banerjee

S. Misra

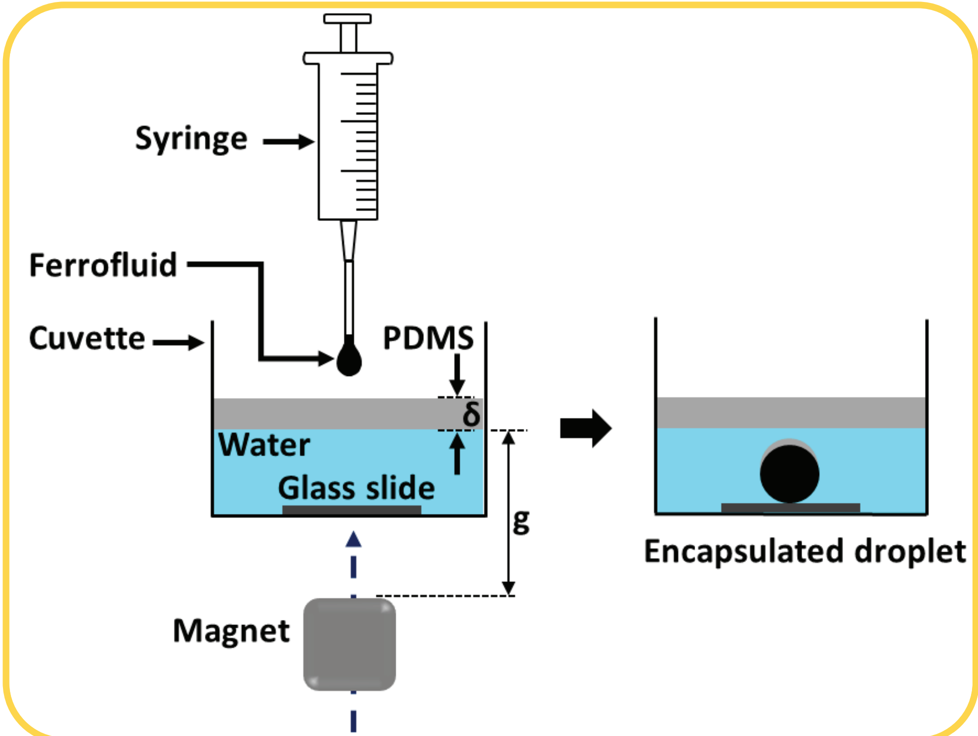
MNT Micro & Nano-Scale Transport Laboratory　WATERLOO INSTITUTE FOR nanotechnology　UNIVERSITY OF WATERLOO

Research Problem

Magnet-assisted encapsulation of ferrofluid inside a PDMS shell

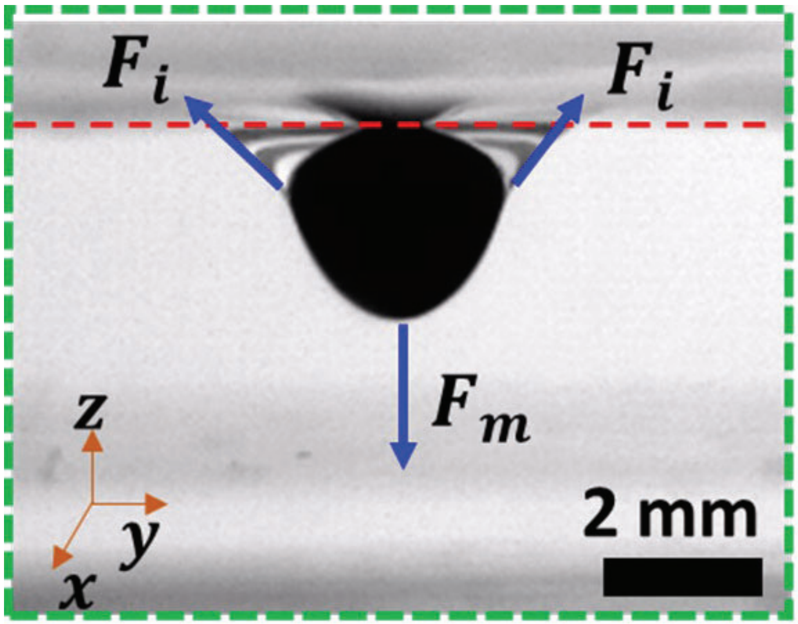
Research Questions

- How magnetic field can be tuned for successful encapsulation
- What is the criteria of successful encapsulation

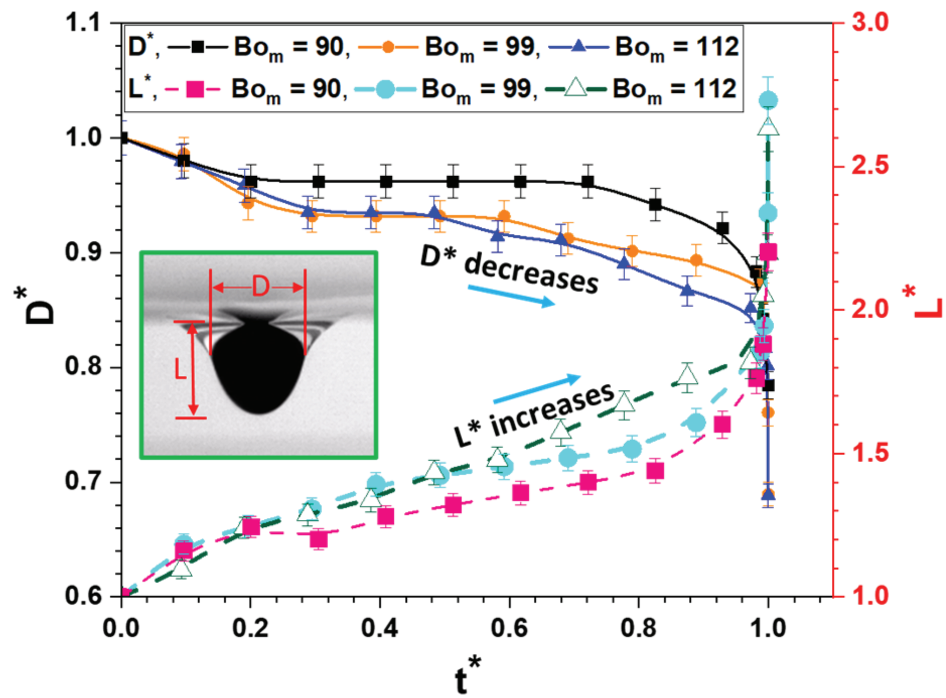


U. Banerjee*, S. Misra* & S.K. Mitra, *Adv. Mater. Interfaces* **2022**, 9, 21, 2200288

Shape evolution of the Ferrofluid-PDMS interface



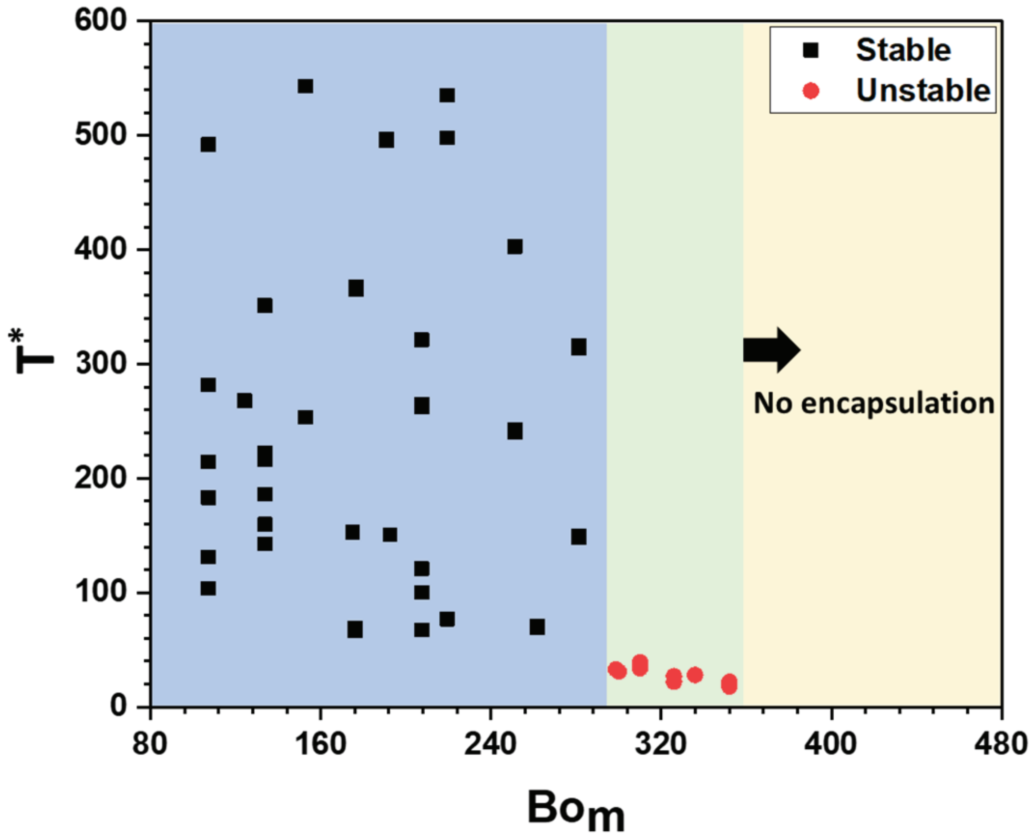
Interplay of forces



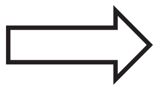
- $L^* = \frac{L}{L_0}$, $D^* = \frac{D}{D_0}$, $t^* = \frac{t}{T}$, $Bo_m = \frac{F_m}{F_i}$

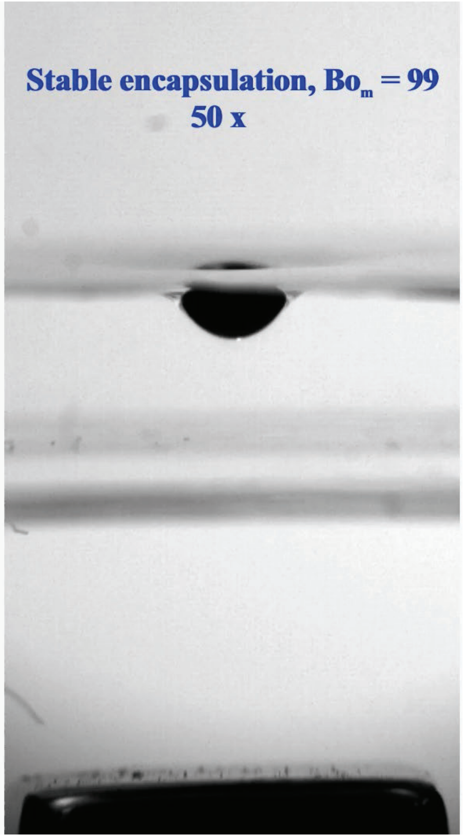
U. Banerjee*, S. Misra* & S.K. Mitra, *Adv. Mater. Interfaces* **2022**, 9, 21, 2200288

Regimes of encapsulation



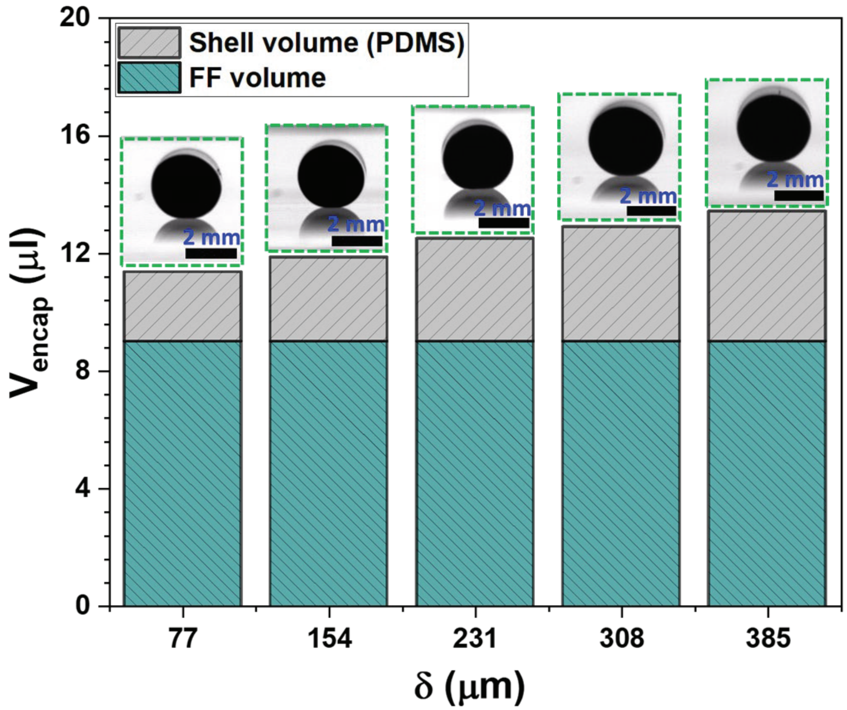
Regimes



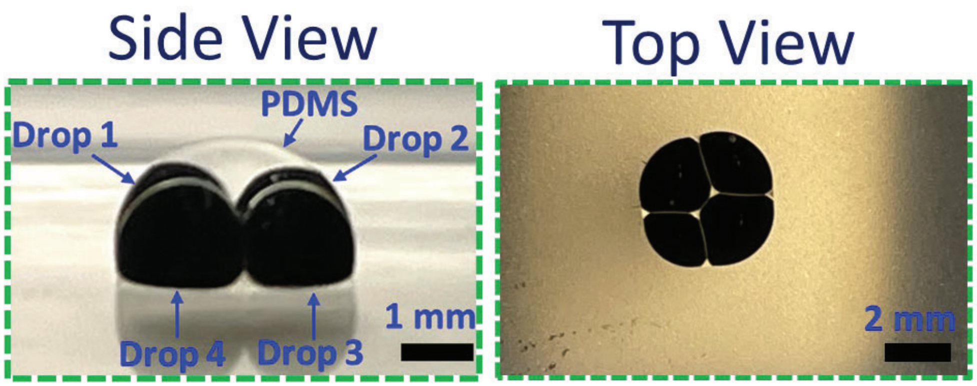


U. Banerjee*, S. Misra* & S.K. Mitra, *Adv. Mater. Interfaces* **2022**, 9, 21, 2200288

Shell layer control and multiple encapsulation



Variation of shell thickness

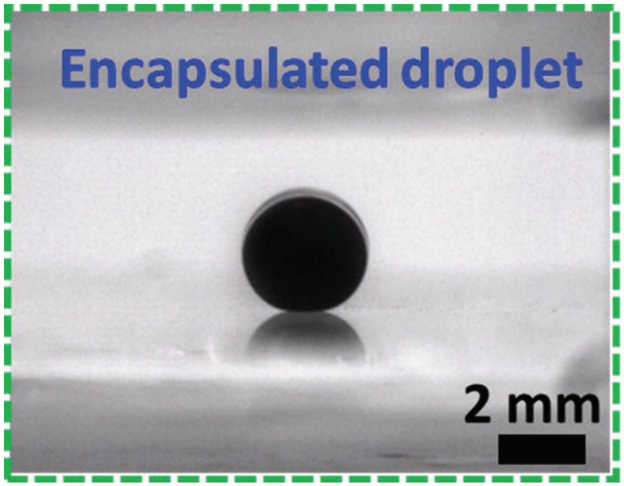


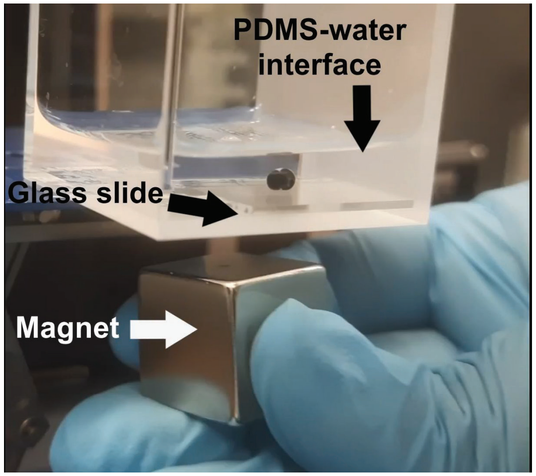
Encapsulated cargo containing four ferrofluid droplets inside the PDMS shell

U. Banerjee*, S. Misra* & S.K. Mitra, *Adv. Mater. Interfaces* **2022**, 9, 21, 2200288

SUMMARY

- Magnet-assisted technique for encapsulating single and multiple ferrofluid droplets inside a PDMS shell
- Stable shell layer which is ensured from the under-water magnetic manipulation of the encapsulated cargo

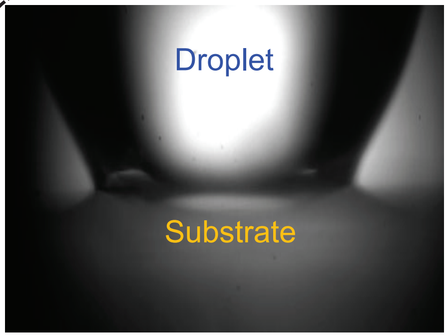




U. Banerjee*, S. Misra* & S.K. Mitra, *Adv. Mater. Interfaces* **2022**, 9, 21, 2200288

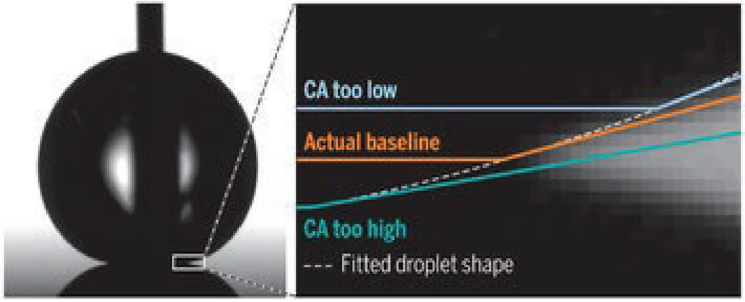
Why is direct adhesion measurement important?

Fundamental understanding



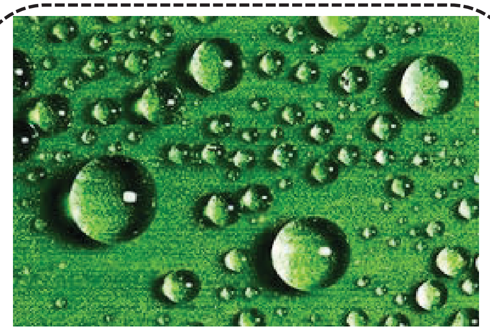
Source: MNT Lab

Uncertainties in Contact Angle Goniometry



Liu et. al, Science, 2019, ***363, 1147-1148,***

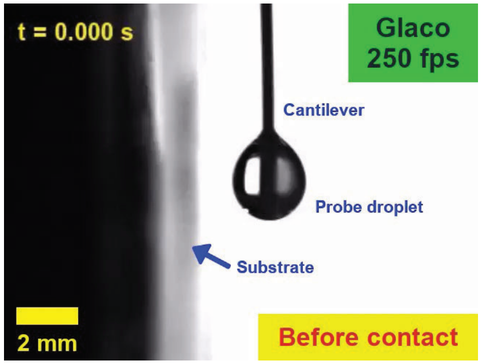
Development of coatings



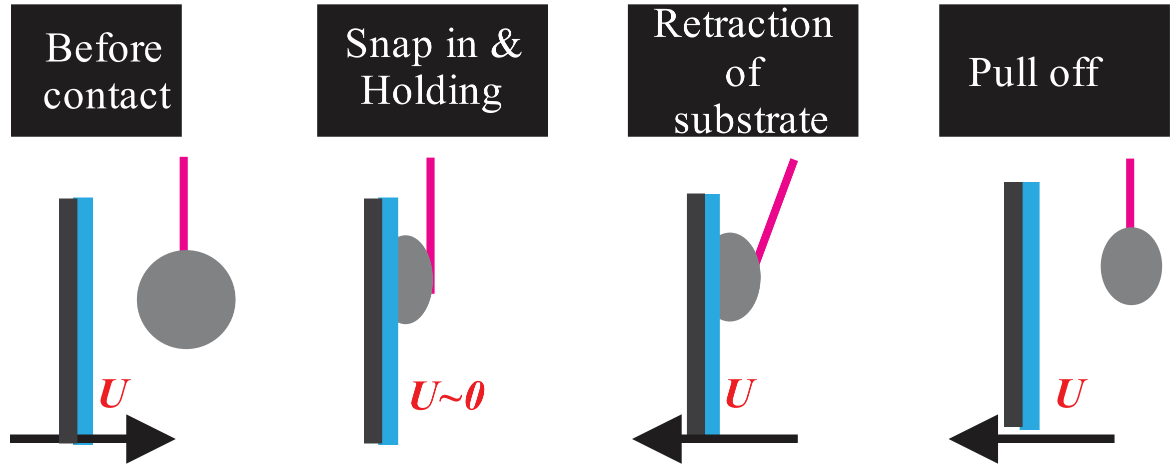
Source: https://blog.paryleneconformalcoating.com/is-parylene-hydrophobic/

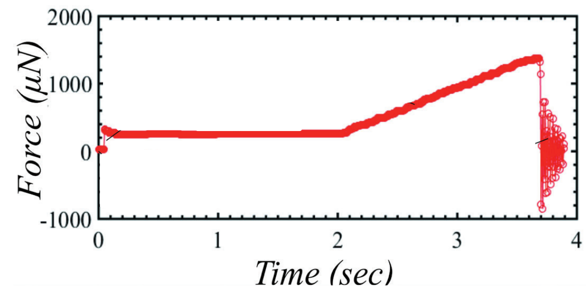
S. Shyam*, S.Misra*, S.K. Mitra, *Journal of Colloid And Interface Science* **2022**, 630, 322-333

Cantilever based direct adhesion measurement



Cantilever based direct adhesion measurement





A typical force-time graph

$Force(F) = kX$
K: *stiffness of the cantilever*
X: *displacement of the cantilever*

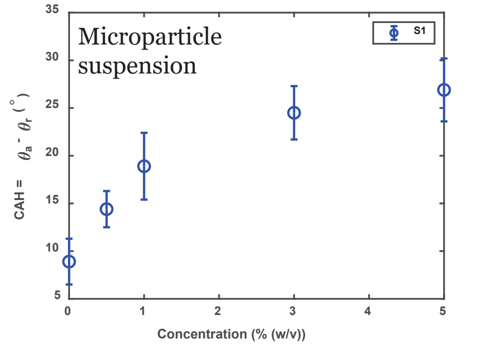
S. Shyam

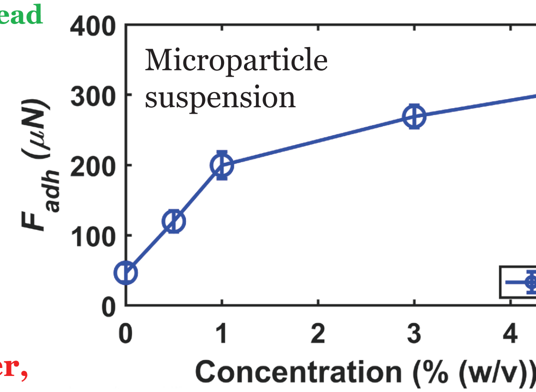
S. Misra

S. Shyam*, S. Misra*, S.K. Mitra, *Journal of Colloid And Interface Science* **2022**, 630, 322-333

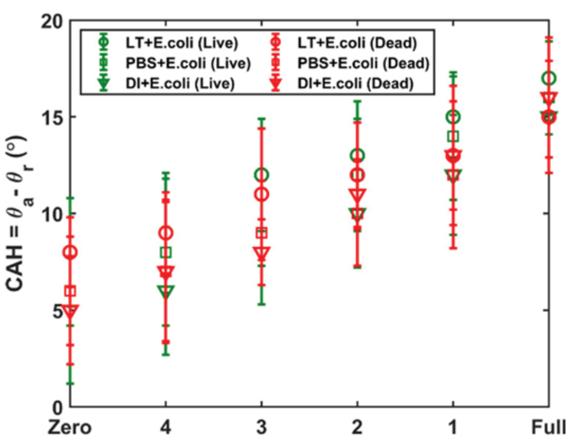
Bacterial Adhesion: a tricky affair

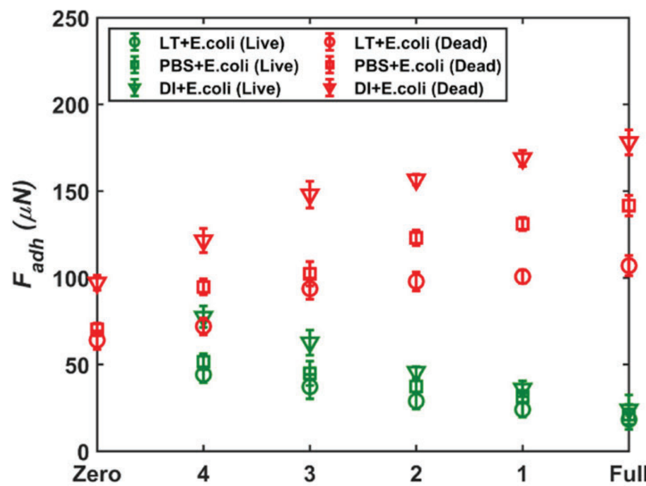
Increasing CAH with concentration increment for both live & dead





However,



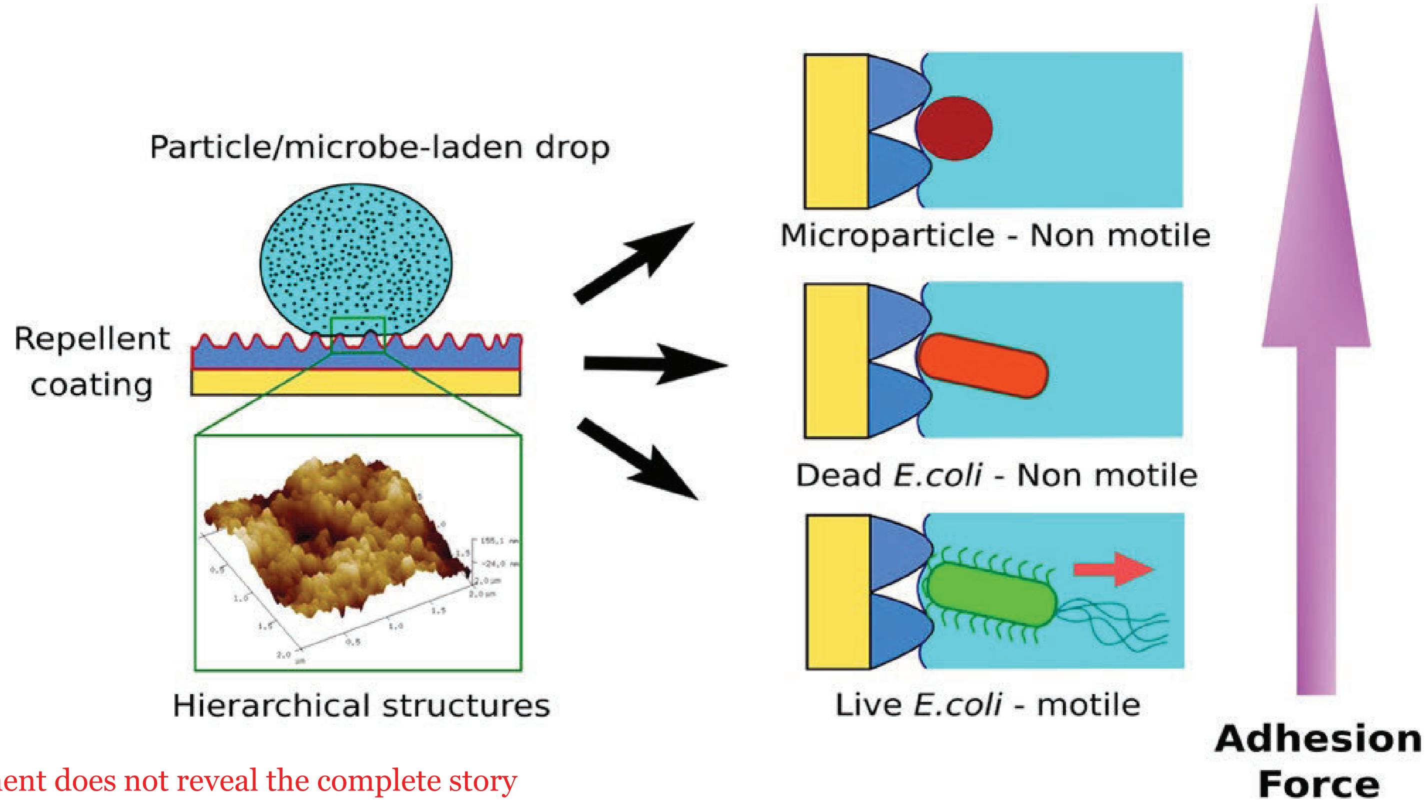


	Conc.	CAH	F_{adh}
Microparticle suspension	↑	↑	↑
Dead bacteria	↑	↑	↑
Live bacteria	↑	↑	↓

K. R. Melayil

K. R. Melayil, S. Misra, & **S.K. Mitra**, *Langmuir* **2021**, 37(4), 1588–1595.
K. R. Melayil, S. Misra, & **S.K. Mitra**, *Langmuir* **2020**, 36(45), 13689–13697

Makes us wonder: Are bacteria and microparticles comparable?

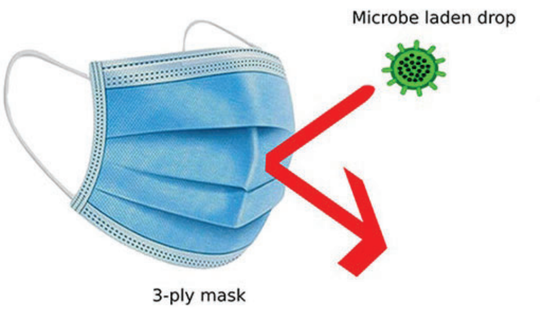


- ➢ CA measurement does not reveal the complete story
- ➢ Microparticles can not be used as a proxy for living bacteria – the mechanism of interaction is much intricate

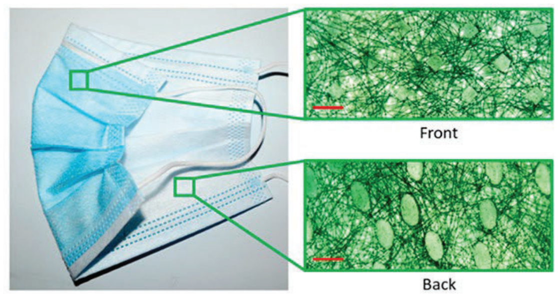
K. R. Melayil, S. Misra, & **S.K. Mitra,** *Langmuir* **2021**, 37(4), 1588–1595.
K. R. Melayil, S. Misra, & **S.K. Mitra,** *Langmuir* **2020**, 36(45), 13689–13697

And then we get a virus laden drop : Wetting, adhesion and COVID-19

The problem

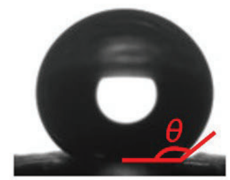


Possible solution avenues



(a)

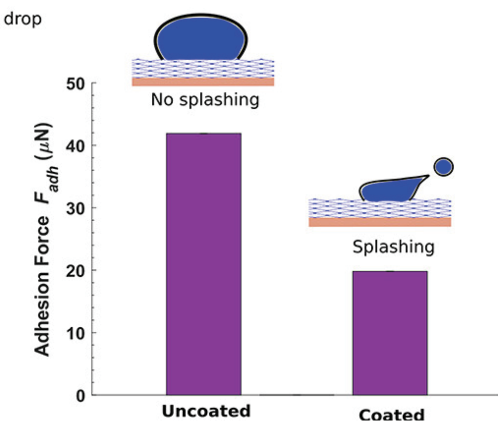
Goniometry



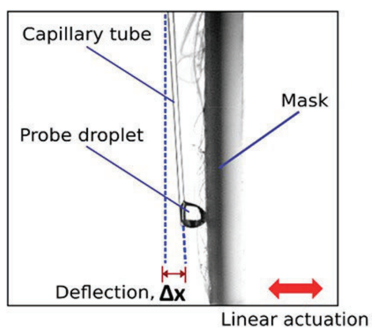
(b)

Understanding adhesion is key

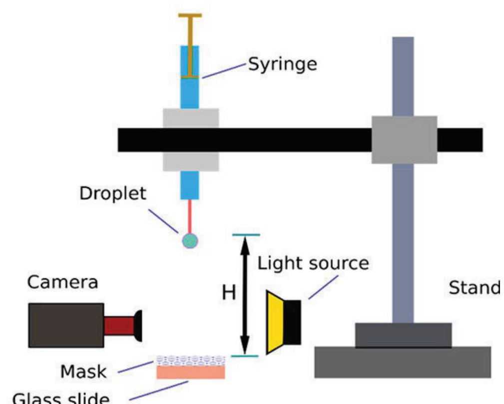
Droplet impact on mask



Adhesion measurements



(c)



(d)

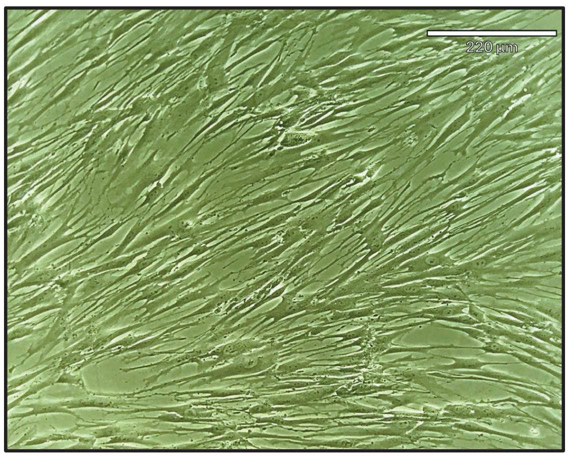
Impact experiments

Now virus....

Nanoparticles might not be a suitable proxy for viruses

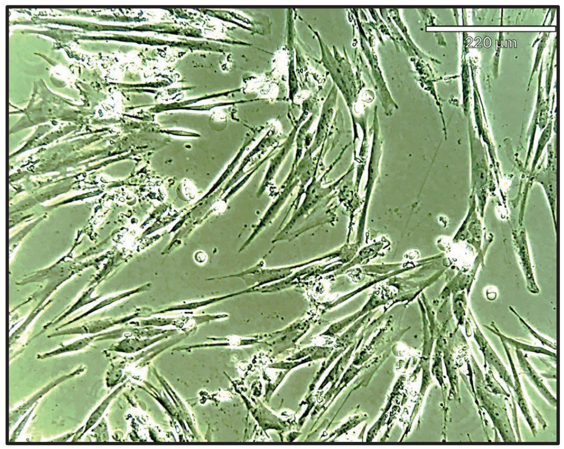
Establishment of a host cell line → Cell seeding and transfection of the viral load onto healthy cells → Onset of cell cytopathy and subsequent collection of viral stock → Interface science experimentation

Healthy lung epithelial cells

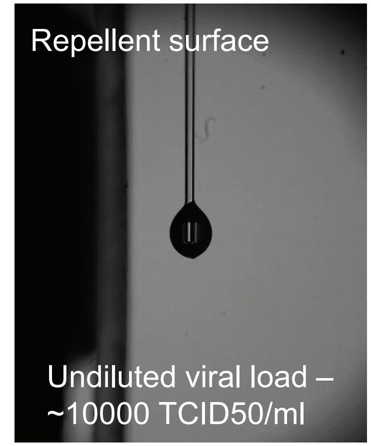


Viral transfection

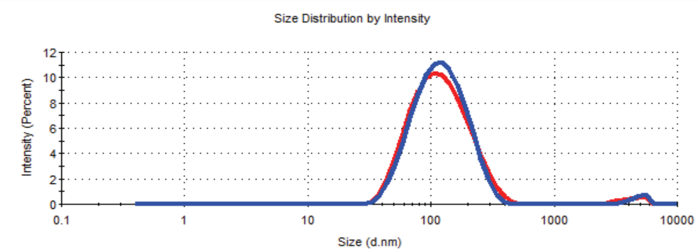
Cells with prominent viral cytopathy



Ongoing work



			Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm):	100.2	Peak 1:	129.8	98.1	61.88
PdI:	0.280	Peak 2:	4841	1.9	704.0
Intercept:	0.938	Peak 3:	0.000	0.0	0.000
Result quality :	Good				

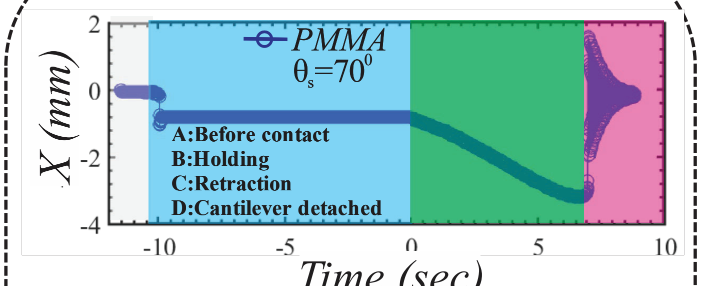


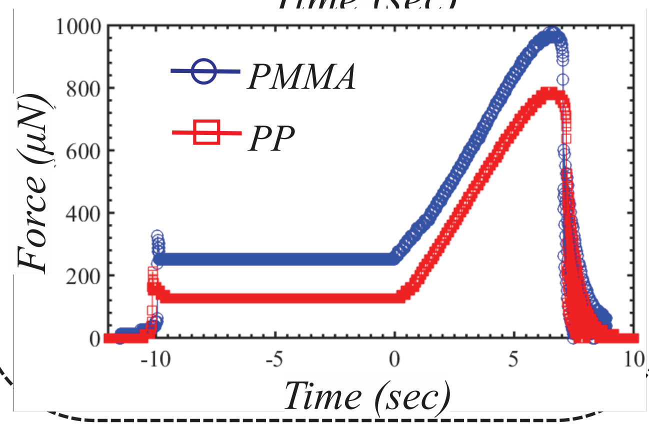
S. Misra

Revisiting limitations of existing adhesion measurement techniques

How to use the technique for characterizing high-energy surfaces, where a complete pull-off of the probe droplet could not be observed?

Adhesion measurement on a high-energy surfaces such as a PMMA substrate



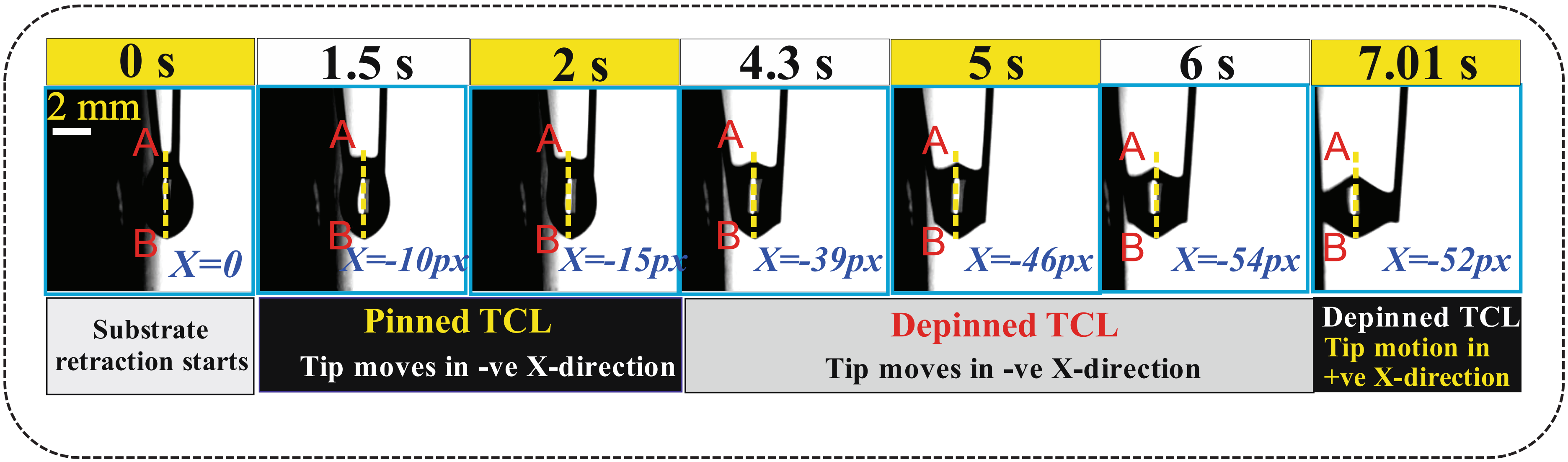


For such case, what point in the force-time curve should we infer as the maximum adhesion force?

S. Shyam*, S.Misra*, S.K. Mitra, *Journal of Colloid And Interface Science* **2022**, 630, 322-333

A modified technique

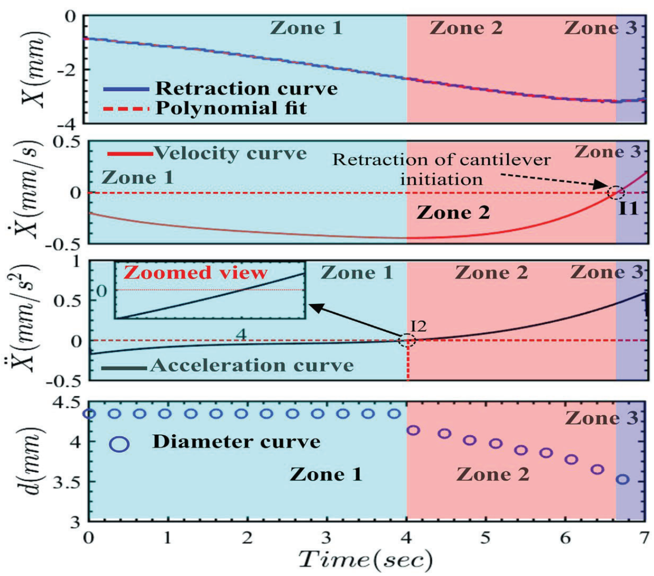
- Even for high-energy substrate a clear depinning could be observed
- Can we use the force corresponding to the point of depinning as the maximum adhesion force.



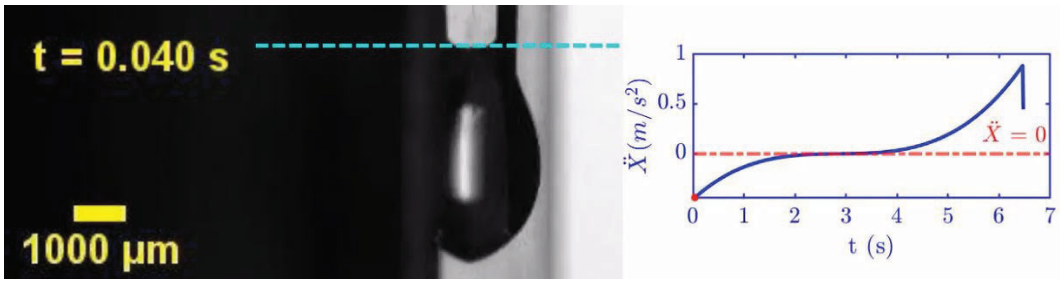
S. Shyam*, S.Misra*, S.K. Mitra, *Journal of Colloid And Interface Science* **2022**, 630, 322-333

A modified technique

Even if depinning is the criteria, how do you correlate the motion of the cantilever with the onset of depinning?



Temporal variation of the displacement (X), velocity ($\dot{X}$), acceleration ($\ddot{X}$) of the cantilever tip and the contact diameter of the probe droplet during the retraction of the test substrate

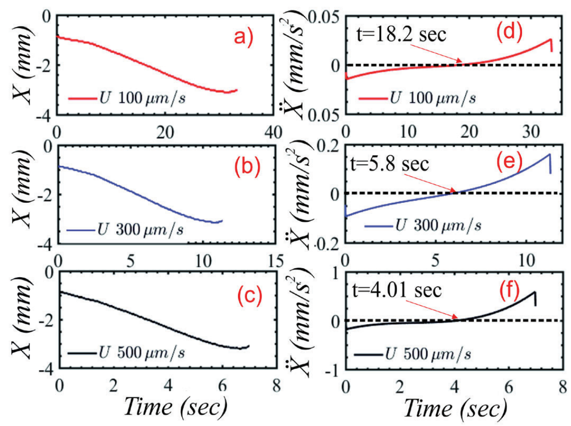


Onset of depinning corresponds to $\ddot{X} = 0$

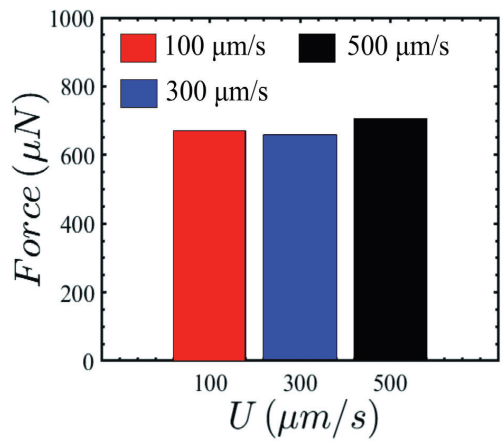
S. Shyam*, S.Misra*, S.K. Mitra, *Journal of Colloid And Interface Science* **2022**, 630, 322-333

Universality of the technique

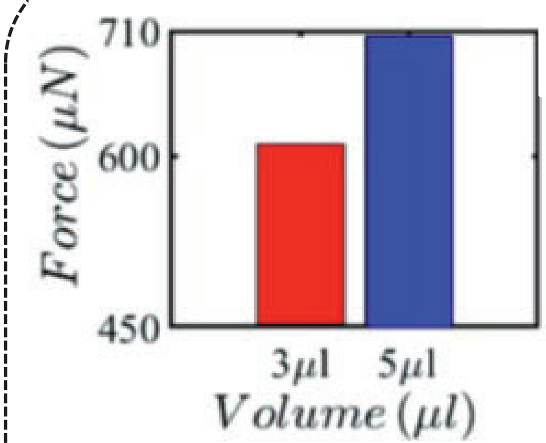
Force corresponding to the onset of depinning is the characteristic adhesion force.



The retraction and the corresponding acceleration curves for various substrate velocities



Adhesion force corresponding to the various substrate velocities



Adhesion force corresponding to various volumes of probe droplet

S. Shyam*, S.Misra*, S.K. Mitra, *Journal of Colloid And Interface Science* **2022**, 630, 322-333

Wetting of 2D materials

The debate

nature materials LETTERS
PUBLISHED ONLINE: 22 JANUARY 2012 | DOI: 10.1038/NMAT3228

Wetting transparency of graphene

Javad Rafiee[1†], Xi Mi[2†], Hemtej Gullapalli[3], Abhay V. Thomas[1], Fazel Yavari[1], Yunfeng Shi[2], Pulickel M. Ajayan[3★] and Nikhil A. Koratkar[1,2★]

We report that graphene coatings do not significantly disrupt the intrinsic wetting behaviour of surfaces for which surface–water interactions are dominated by van der Waals forces. Our contact angle measurements indicate that a graphene monolayer is wetting-transparent to copper, gold or silicon, but not glass, for which the wettability is dominated by short-range chemical bonding. With increasing number of graphene layers, the contact angle of water on copper gradually transitions towards the bulk graphite value, which is reached for ~6 graphene layers. Molecular dynamics simulations and theoretical predictions confirm our measurements and indicate that graphene's wetting transparency is related to its extreme thinness. We also show a 30–40% increase in condensation heat transfer on copper, as a result of the ability of the graphene coating to suppress copper oxidation without disrupting the intrinsic wettability of the surface. Such an ability to independently tune the properties of surfaces without disrupting their wetting response could have important implications in the design of conducting, conformal and impermeable surface coatings.

Graphene is a single-atom-thick sheet of sp^2-hybridized carbon atoms arranged in a hexagonal honeycomb lattice. It possesses a unique combination[1,2] of high specific surface area, chemical

film was transferred onto both Si and Au substrates. Films with a varying number of graphene layers (N), from monolayer to $N > 10$, were also deposited on Cu and glass substrates. Control of the number of layers was carried out by varying the growth time in CVD, as demonstrated in our previous work[19]. Atomic force microscopy was used to measure the film thickness, which gave estimates of the number of graphene layers in each sample. Graphene-coated Cu and glass samples with N values ranging from 1, 1–2, 2–3, 4–6, 6–9, 8–12 and 10–15 were prepared. Figure 1a–c shows optical micrographs of large-area graphene film deposition on Cu, glass and Si, respectively. The deposited graphene is several cm in in-plane dimensions and forms a uniform conformal coating with no physical breaks. A Raman spectroscopy study (using 514 nm wavelength excitation) was used to confirm the approximate number of graphene layers on the Cu substrates. Figure 1d shows measured Raman spectra for the 2D peak for graphene films with a varying number of layers. A clear shift in the position of the 2D peak with number of layers is observed (Fig. 1d,e), from ~2,680 cm^{-1} for monolayer graphene to ~2,715 cm^{-1} for the $N > 10$ sample. These results are consistent with the literature; for example, Ferrari *et al.*[20] have reported that, as the number of layers in graphene films is reduced, the 2D peak shifts towards a lower frequency range, and for single-layer graphene it appears between 2,650 and 2,700 cm^{-1}

Wetting transparent?

PRL **109,** 176101 (2012) PHYSICAL REVIEW LETTERS week ending 26 OCTOBER 2012

Breakdown in the Wetting Transparency of Graphene

Chih-Jen Shih,[1] Qing Hua Wang,[1] Shangchao Lin,[1,2,*] Kyoo-Chul Park,[2] Zhong Jin,[1] Michael S. Strano,[1] and Daniel Blankschtein[1,†]
[1]*Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA*
[2]*Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA*
(Received 21 August 2012; published 24 October 2012)

We develop a theory to model the van der Waals interactions between liquid and graphene, including quantifying the wetting behavior of a graphene-coated surface. Molecular dynamics simulations and contact angle measurements were also carried out to test the theory. We show that graphene is only partially transparent to wetting and that the predicted highest attainable contact angle of water on a graphene-coated surface is 96°. Our findings reveal a more complex picture of wetting on graphene than what has been reported recently as complete "wetting transparency."

DOI: 10.1103/PhysRevLett.109.176101 PACS numbers: 68.08.Bc, 68.03.Cd, 68.65.Pq

Partially transparent?

Wettability of Graphene

Rishi Raj,[†] Shalabh C. Maroo,[‡] and Evelyn N. Wang[*,†]
[†]Device Research Laboratory, Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States
[‡]Department of Mechanical and Aerospace Engineering, Syracuse University, Syracuse, New York 13244, United States

Our results which indicate that the underlying substrate has a negligible effect on the wettability of graphene-coated copper, silica, and glass substrates is now explained in the context of similar results in literature. For copper where van der Waals forces dominate, the experimental contact angle values for graphene coated copper in our work agrees with those reported in Rafiee et al.[6e] However, the contact angle used for bare copper substrates differs in the models, which lead to discrepancies in the interpretation of the substrate effect. While we demonstrated through the comparison of our simulation results (using fundamental LJ parameters from literature[17]) and previously reported controlled experiments[12] that pristine copper underneath the CVD grown graphene is superhydrophilic with apparent contact angles of 0°, Rafiee et al.[6e] used the large experimental contact angle values (84–85°) on copper with native oxide layer and contaminates in ambient as the bare substrate wettability in their model. Accordingly, if the fundamental LJ parameters[17] resulting in pristine copper substrate wettability[12] was used, the effect of the underlying substrate on the wettability even for a monolayer graphene coating on copper would be negligible.

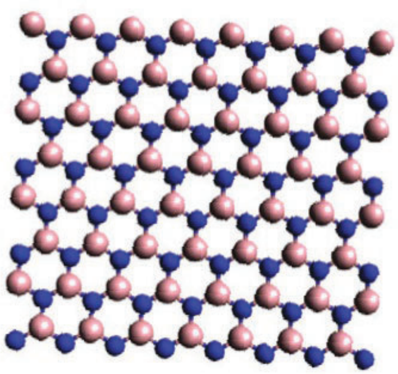
In literature for monolayer graphene on glass and SiO_2 (where both van der Waals and electrostatic forces due to partial charges dominate), static contact angle measurements

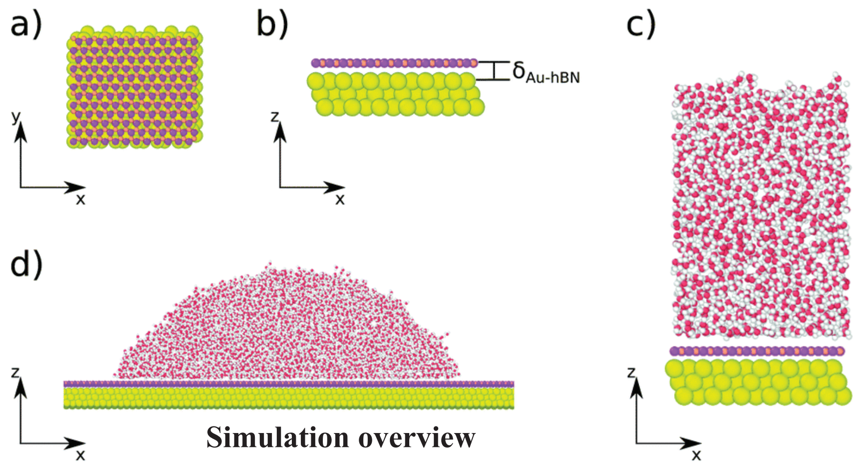
cleaned silica surface in Shih et al.,[6m] however, demonstrate the potential of unobtrusive graphene coatings for surface wettability. Physical understanding of wettability on such plasma cleaned surfaces with free charges remains absent in literature and requires additional theoretical and modeling efforts to elucidate the underlying physics.

Conclusions. We demonstrated that copper, glass, and silica substrates coated with an atomically thin 2D material graphene matches the wettability of 3D bulk graphite. The advancing contact angle was found to be independent of the number of layers of graphene sheets and was in good agreement with our molecular dynamics simulation and theoretical calculations. The receding contact angle, however, was governed by the defects in as-grown and transferred graphene sheets, leading to significant contact angle hysteresis. As a result, static contact angle measurements for wettability and surface energy characterization on such surfaces cannot solely be used. Continuum models for interfacial and adsorption energy calculations were shown to be inaccurate due to the underestimation of the solid–liquid equilibrium distances in graphene-coated substrates. The fundamental understanding of graphene–water interactions elucidated in this study is an important step towards developing graphene assisted surface-coatings for heat transfer and microfluidics devices.

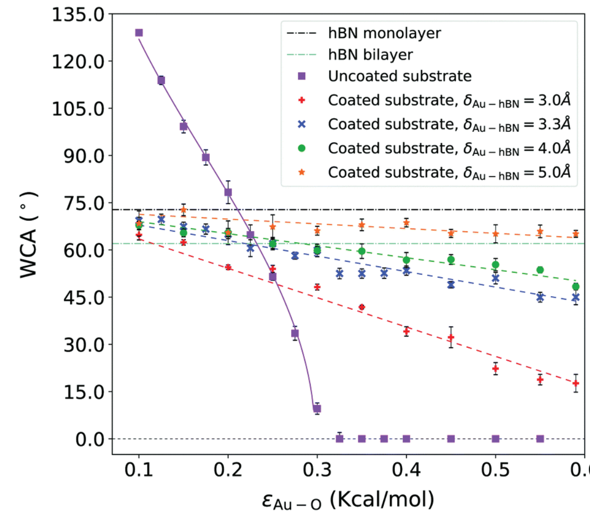
Or opaque?

hBN: looking ahead of graphene





Wetting translucency effect is observed On unstructured surfaces

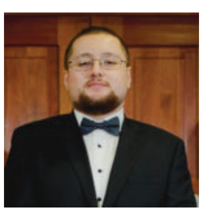


Despite similar interfacial structure, hBN presents higher friction to water compared to carbon-based nanostructures (CNT and Graphene)

Electrostatic interactions between water and hBN atoms play a key role

What about the wetting of nanostructured hBN surfaces?

Tocci, et al. *Nano letters* 14.12 (2014): 6872-6877.
Joseph and Aluru. *Nano letters* 8.2 (2008): 452-458.



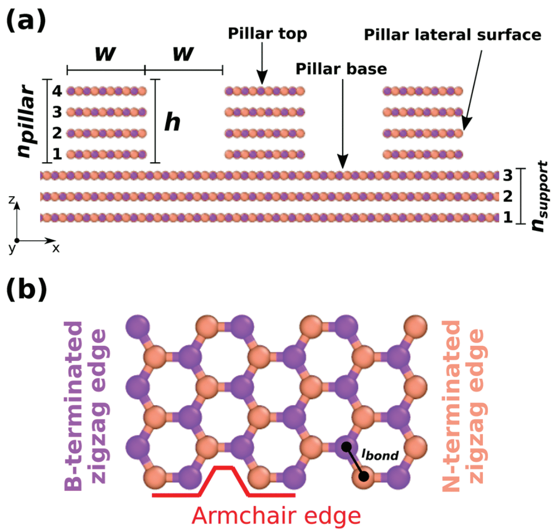
E. Wagemann

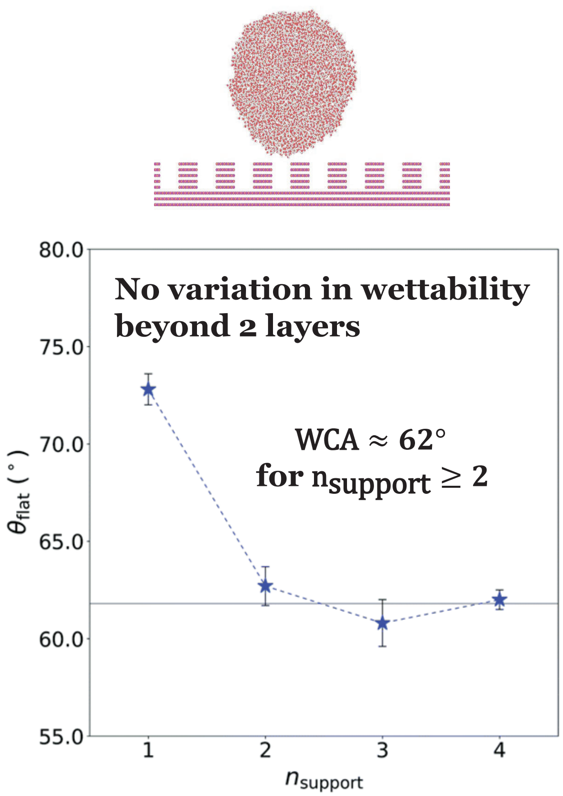
WATERLOO INSTITUTE FOR nanotechnology

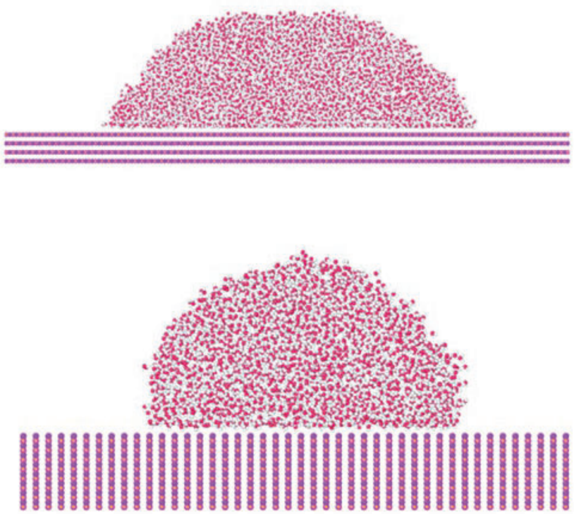
UNIVERSITY OF WATERLOO

Wagemann et al., *Phys. Chem. Chem. Phys.* **2020**;22(15):7710-7718

Nanostructured hBN – tunable wettability regime





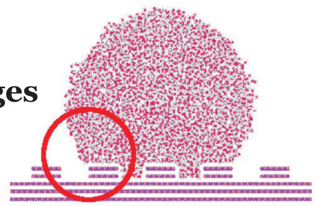


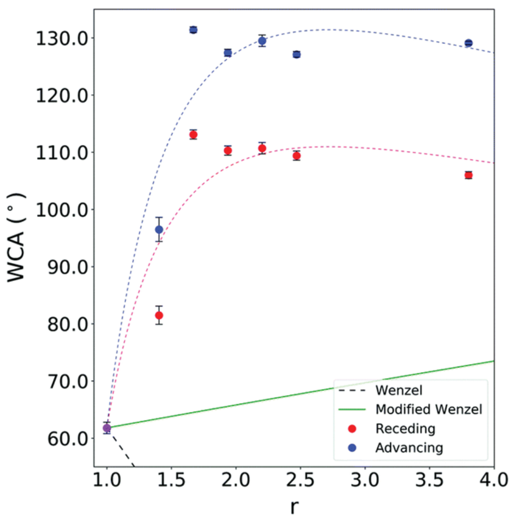
Hydrophobic lateral (armchair) walls

Wagemann et al., *Phys. Chem. Chem. Phys*. **2020**, *22*(4), 2488-2497

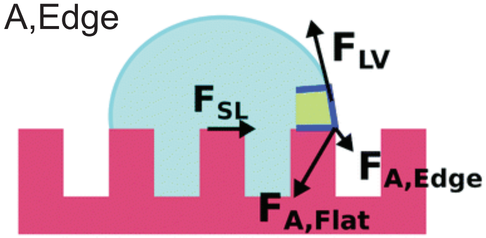
Effect of nanostructured edges - armchair vs zigzag

Armchair edges



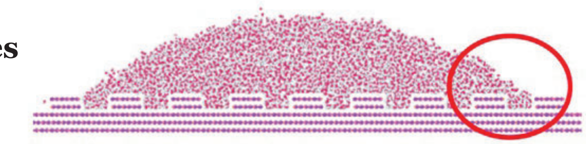


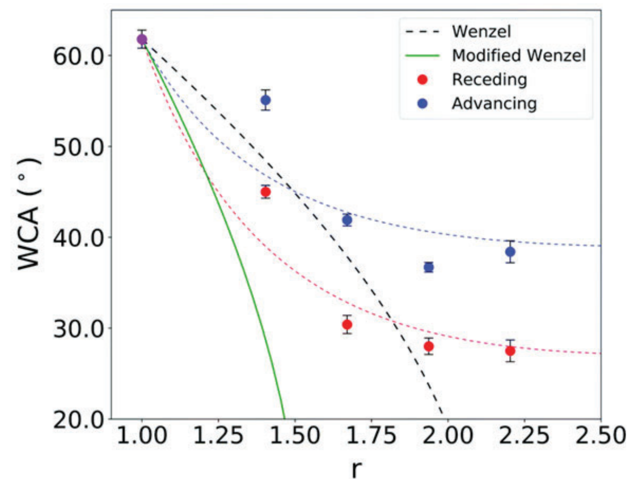
$F_{A,Flat} > F_{A,Edge}$

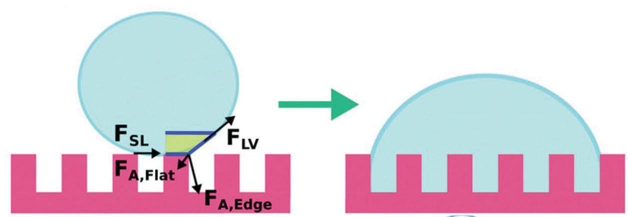


vs.

Zigzag edges





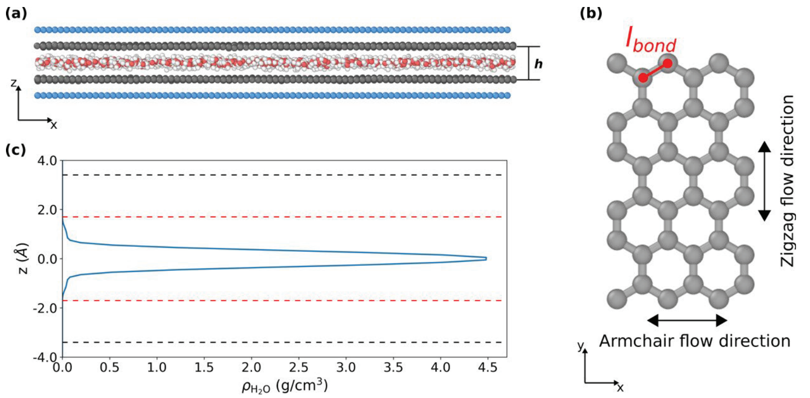


$F_{A,Flat} < F_{A,Edge}$

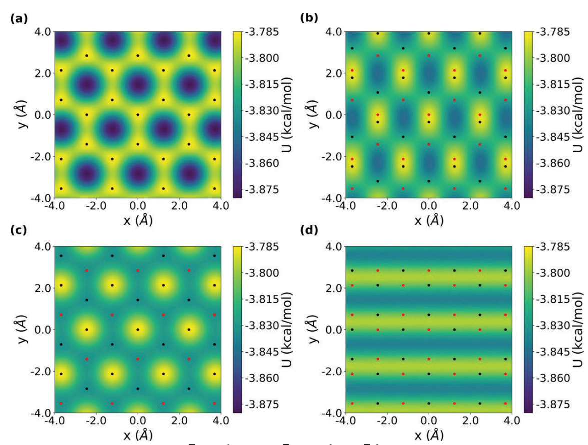
Wenzel transition

Wagemann et al., *Phys. Chem. Chem. Phys.* **2020**, *22*(4), 2488-2497

Water friction inside Ångström confinements

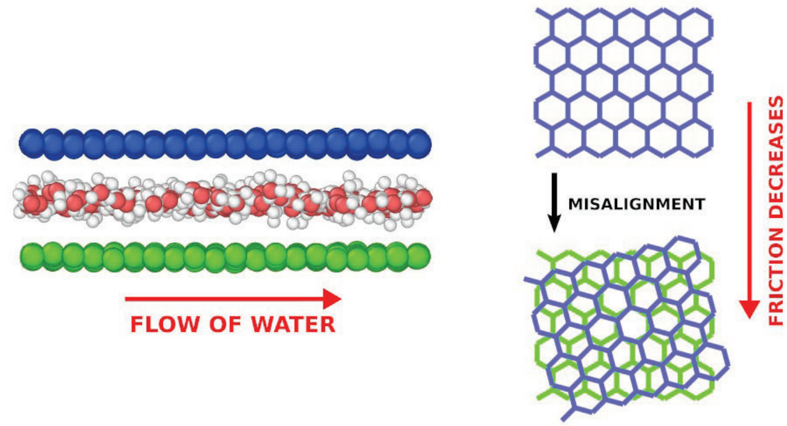


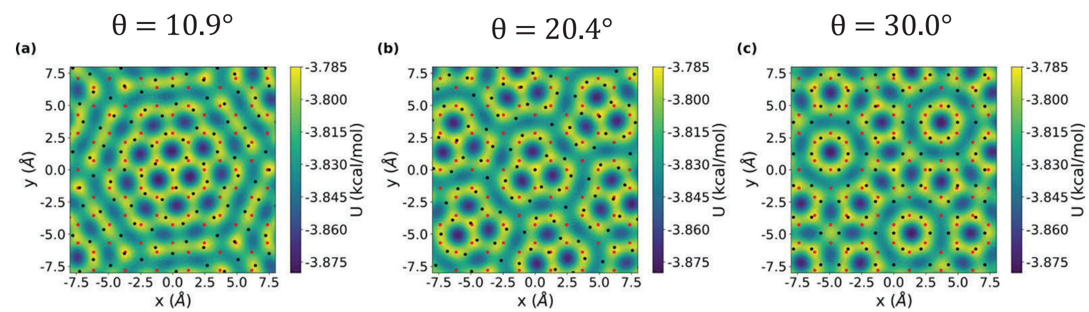
Potential energy landscape



Translational misalignment

Types of misalignment: translational vs rotational





Rotational misalignment

Design efficient transport mechanism through Ångström channels via misalignment

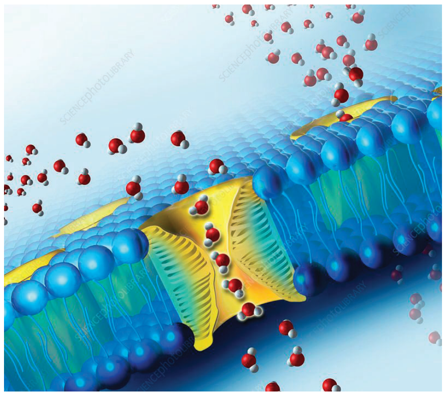
Wagemann et al., *ACS Appl. Mat. & Interfaces* **2020** *12* (31), 35757-35764

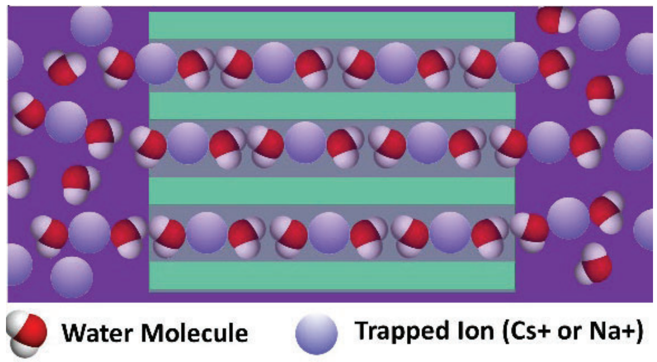
MNT Micro & Nano-Scale Transport Laboratory

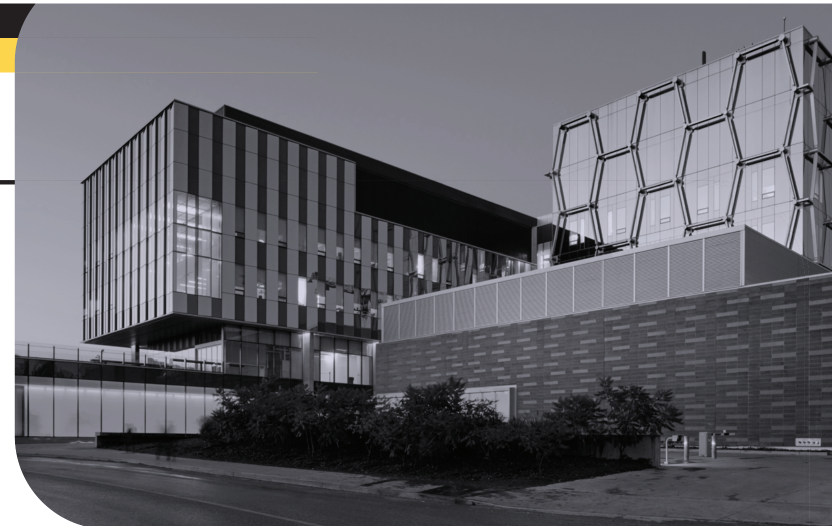
WATERLOO INSTITUTE FOR nanotechnology

UNIVERSITY OF WATERLOO

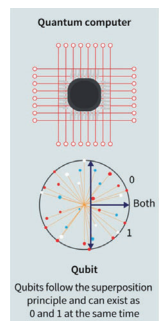
Commercialization pathway







Aquabits – *Revolutionizing Trapped ion technology*



Aquabits
www.AquabitsQ.com
skmitra@uwaterloo.ca

Patents:
US 2021/0308624 A1 Published: October 7, 2021
PCT WO 2021/195788 A1 Published: October 7, 2021

MNT Micro & Nano-Scale Transport Laboratory

WATERLOO INSTITUTE FOR nanotechnology

UNIVERSITY OF WATERLOO

Thank you

Micro & Nano-scale Transport Laboratory
Rm 1512, Mike & Ophelia Lazaridis Quantum-Nano Centre
200 University Avenue West
Waterloo, ON, Canada N2L 3G1