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14. ABSTRACT
Although the breakthrough pressure needed for liquids to penetrate re-entrant surface textures has been considered typically as simply a dependent parameter arising from the combination of geometry and thermodynamic interaction characteristics of the surface, it has the advantage of often being one of easiest parameters to determine experimentally with good precision. In fact, for many types of textures, including "random" media such as fibrous filters, or textures formed by growth or deposition of nanoparticles, it is far easier to quantify the breakthrough pressure than to quantify the geometry or the equilibrium contact angle. This presentation will explore the use of experimentally-determined breakthrough pressures (in combination with surface imaging and apparent contact angle measurements) to infer important geometric and thermodynamic characteristics of liquid repellent surfaces. Data are presented for two relevant examples, silicone coated "phase separator" membranes and silane-treated aluminum oxide "nanograss" textures.

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BREAKTHROUGH PRESSURE AS A TOOL TO PROBE THE CHARACTERISTICS OF SILICON-CONTAINING LIQUID-REPELLENT SURFACES

15 December 2014

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Outline

- Background
  - Overview of Breakthrough Pressure Calculations
- Specific Examples of Breakthrough Pressure
  - Precisely Patterned Surfaces
  - “Semi-Random” Fabric Membranes
  - “Random” Media
- Methods to Infer Surface Thermodynamics from Breakthrough Pressures

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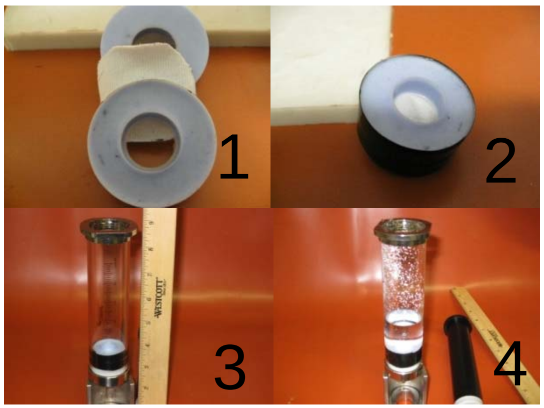
AFRL Mission

Background: Breakthrough Pressure



Measured experimentally

Liquid Property

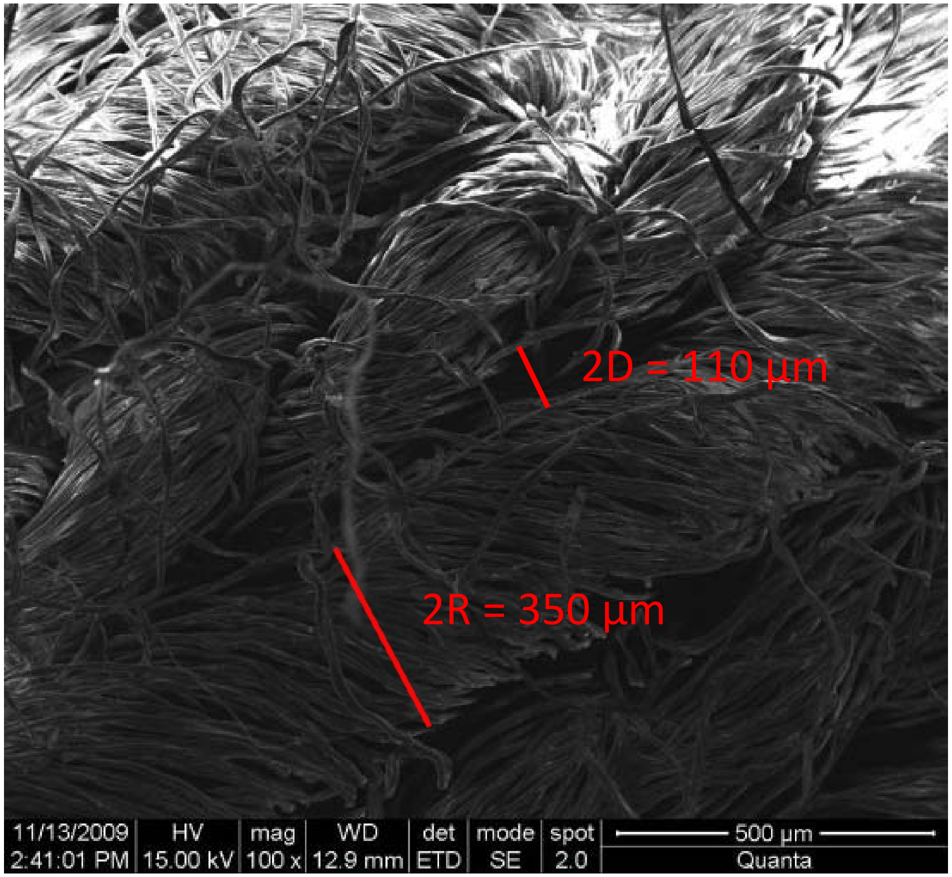
$$P_{bt} = \frac{2R\gamma_{lv}(1-\cos\theta)}{D^2 + 2DR\sin\theta}$$

Estimated "equilibrium" contact angle of liquid drop in contact with surface

Determined by surface analysis

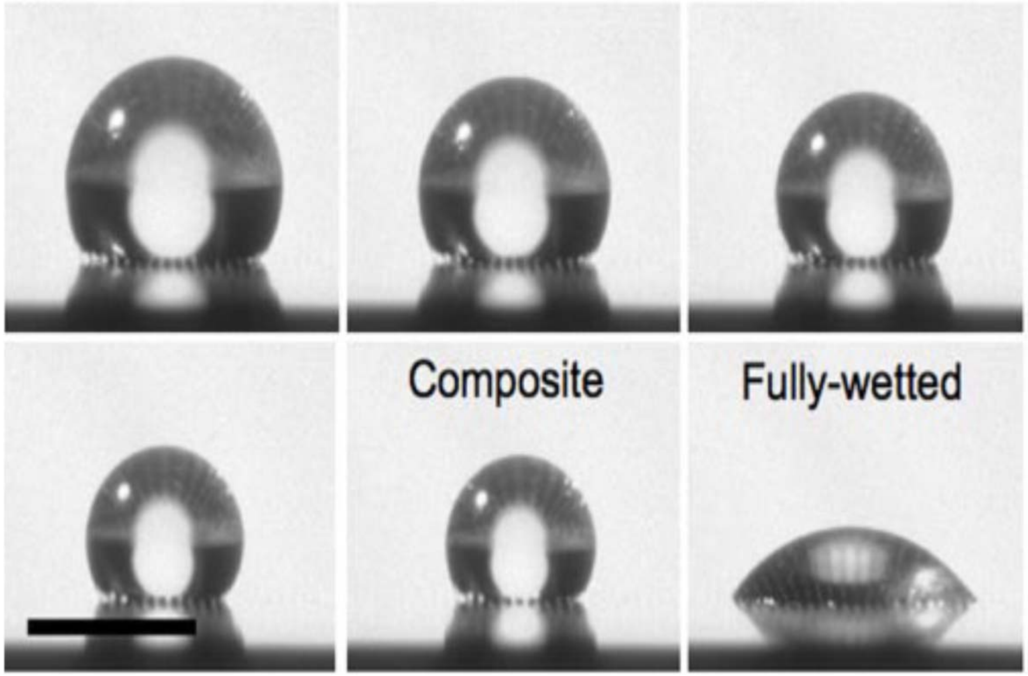
- Typically, a liquid-solid surface contact angle is estimated from existing data, then geometric parameters of the surface are measured, then these are related to liquid properties and the breakthrough pressure by an equation that depends on the type of surface (the above equation is for arrays of cylinders)

Example: Breakthrough Pressure for Array of Cylinders



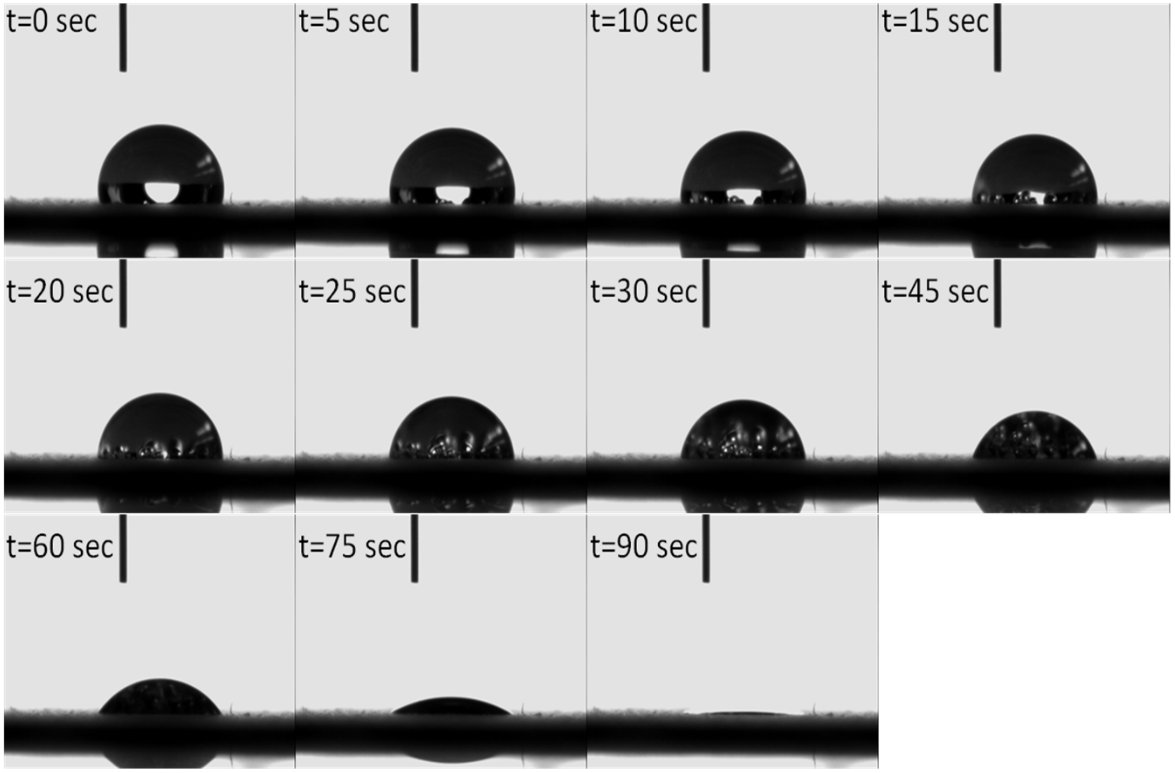
- The geometric factors required are the gap distance between fiber bundles (D) and the size of fiber bundles (R). Equivalent parameters are used for different types of surfaces.

Breakthrough Pressure of Precisely Patterned Surfaces



- Select still images of a droplet of methanol evaporating on a superoleophobic surface textured with micrometer-sized features possessing re-entrant curvature; At a discrete pressure, the droplet transitions to the fully wetted Wenzel-state (from Tuteja et al., Proc. Nat. Acad. Sci. USA, **2008**, *105*, 18200-18205).

Breakthrough Pressure of "Random" Surfaces



- Images of a chloroform droplet evaporating/infusing into an 80 wt% FF-silica surface displaying the progressive collapse of the metastable solid-liquid-air interface as a result of the increasing Laplace pressure within the droplet.
- The gradual transition from the Cassie-state to the fully wetted Wenzel-state indicates that no single value of the breakthrough pressure exists.

Determination of Surface Thermo-dynamic Parameters from P_{bt}

$$P_{bt,1} = \frac{2R\gamma_{lv}(1 - \cos\theta_1)}{D^2 + 2DR\sin\theta_1}$$

$$P_{bt,2} = \frac{2R\gamma_{lv}(1 - \cos\theta_2)}{D^2 + 2DR\sin\theta_2}$$

- In principle, if one knows the geometric parameters D and R, one can solve the equations independently for each value of θ given each value of P_{bt}.

Example: Breakthrough Pressure for Array of Cylinders

- In this case, measured data are compared to predictions (dashed lines) based on possible values of R, D, and an assumed value of 125° for the equilibrium contact angle between water and the treated surface.
- The upper dashed line is a prediction based on bundle geometry, the bottom dashed line is a prediction based on individual fiber geometry

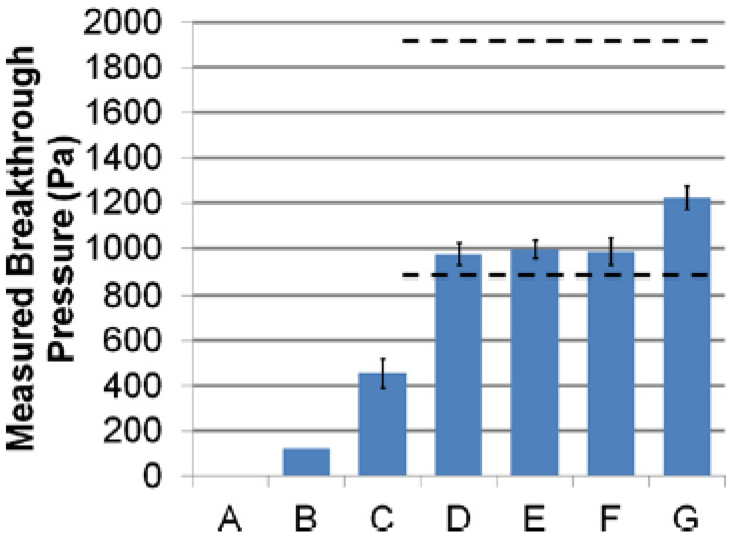


Fig. 3. Breakthrough pressure results for the following dip coating solutions: (A) AK225G only, (B) no treatment, (C) 1 wt% Tecnoflon in AK225G, (D) 1 wt% F-POSS in AK225G, (E) 1 wt% Tecnoflon in AK225G, then 1 wt% F-POSS in AK225G, (F) 1 wt% F-POSS in AK225G, then 1 wt% Tecnoflon in AK225G, G) 1 wt% of mixed solids (50 wt% F-POSS and 50 wt% Tecnoflon) in AK225G.

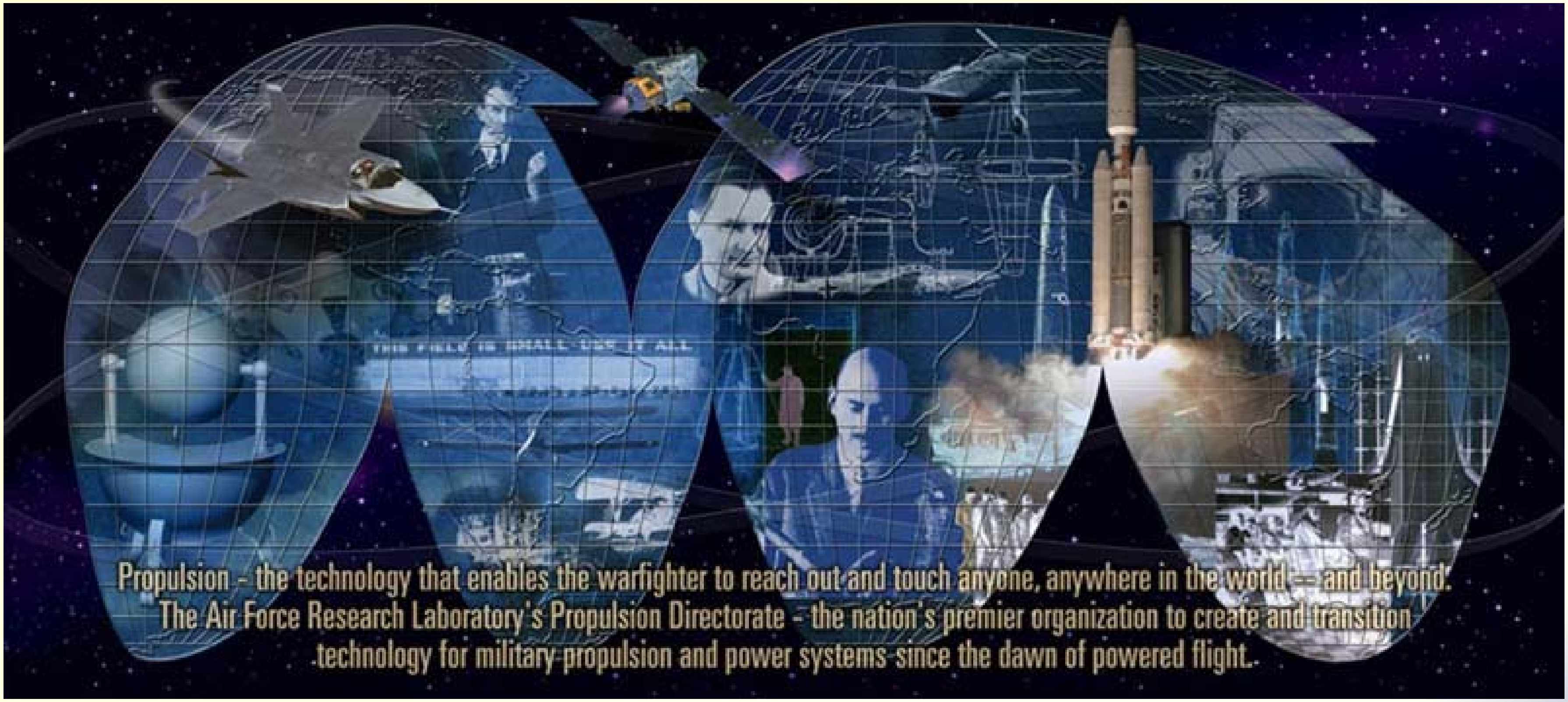
Example: Calculation of Contact Angles for Treated Fabric Surfaces

Treatment	P_{bt} (Pa)	Θ (deg)	Comment
None	130 ± 50	39 ± 8	Reasonable
1% Technoflon	460 ± 110	79 ± 11	Low end of expected range
1% F-Decyl POSS	980 ± 90	133 ± 9	High end of expected range
1% Technoflon, then 1% F-Decyl POSS	1000 ± 100	135 ± 11	High end of expected range
1% F-Decyl POSS, then 1% Technoflon	990 ± 120	134 ± 14	Within error bounds
0.5% F-Decyl POSS and 0.5% Technoflon (simultaneous)	1220 ± 80	166 ± 18	Likely too large

- The inverse procedure provides a rough estimate of contact angle that is reasonable in most cases as a rough guess; errors in geometric parameter measurement compound errors in breakthrough pressure measurement

Summary

- Breakthrough pressures represent an easily measured characteristic of the performance of liquid repellent surfaces
- On surfaces with well-defined geometries, the breakthrough pressure takes on a definite value. On surfaces with stochastic topographies, that is, surfaces where the characteristics of some features are randomly distributed, then the breakthrough pressure may take on a range of values rather than a definite single value
- In principle, it is possible to use the breakthrough pressure (which is readily quantified) to estimate surface parameters, such as the “equilibrium” contact angle, that are easy to understand theoretically but difficult to determine in practice
- Initial studies of the use of breakthrough pressures to estimate thermodynamic properties of surfaces shows that while rough guesses may be obtained reliably, errors in the determination of surface geometrical parameters significantly increase the uncertainty



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