SFB 1194

Wechselseitige Beeinflussung von Transport- und Benetzungsvorgängen

TECHNISCHE UNIVERSITÄT DARMSTADT

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Max Planck Institute for Polymer Research

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Beyond the Cassie-Baxter Model: New Insights for Predicting Imbibition in Complex Systems

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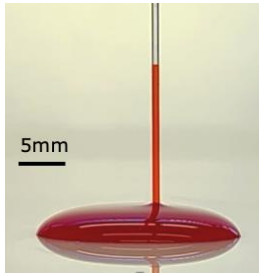
joint work with Lisanne Gossel and Joël De Coninck

SPP 2171 Spring Conference, Mainz, 20.02.2025

Outline

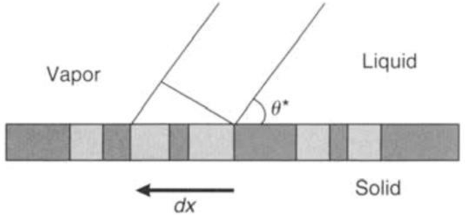
- **Ingredient A:**

  The Lucas-Washburn equation



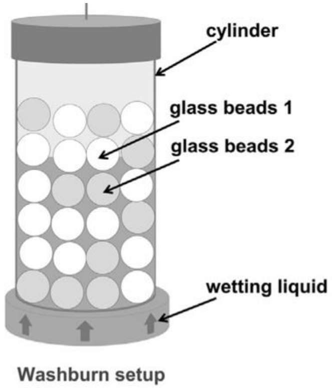
- **Ingredient B:**

  The Cassie-Baxter equation



- **Synthesis:**

  Dynamic wetting of a heterogeneous system



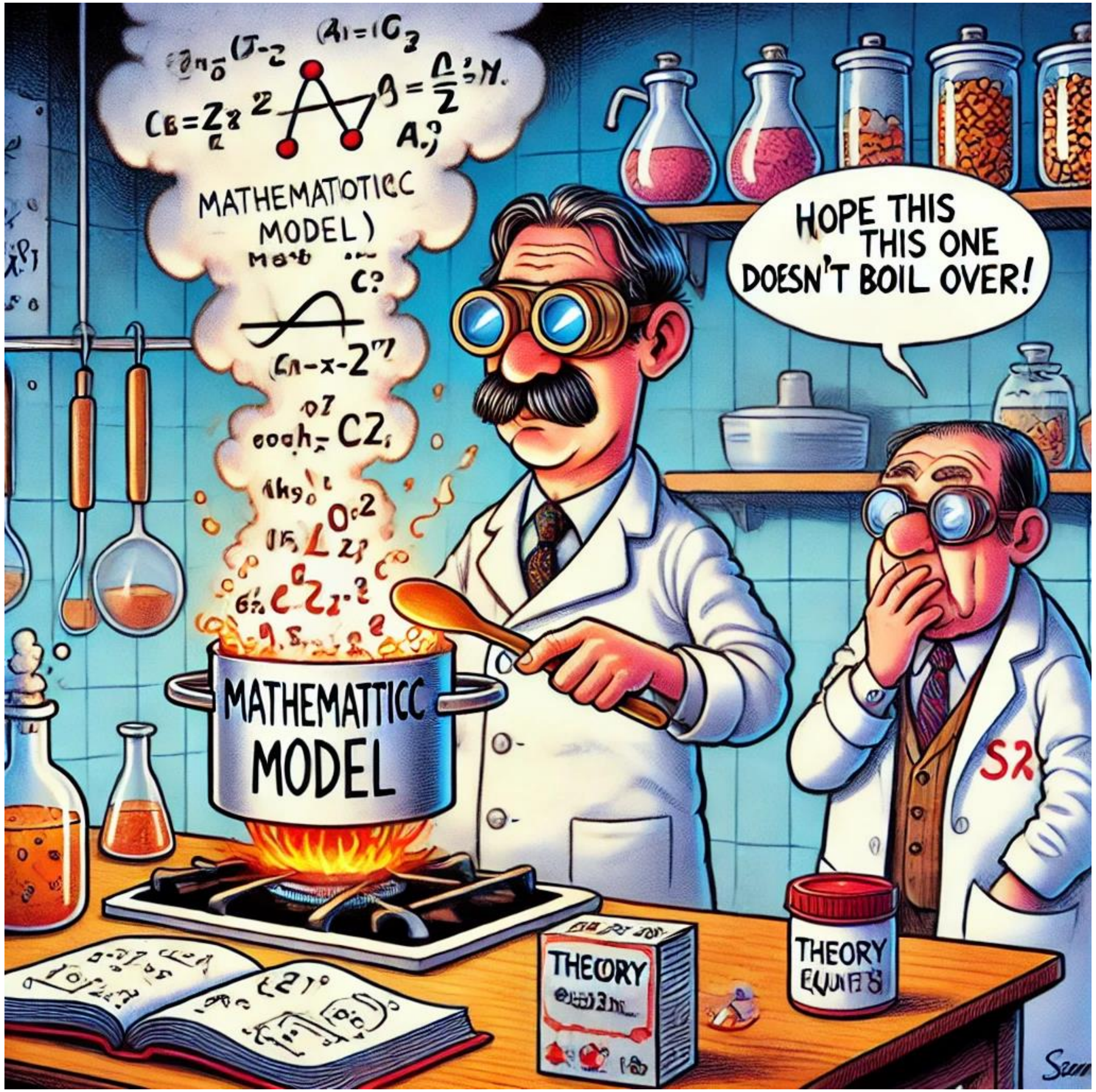
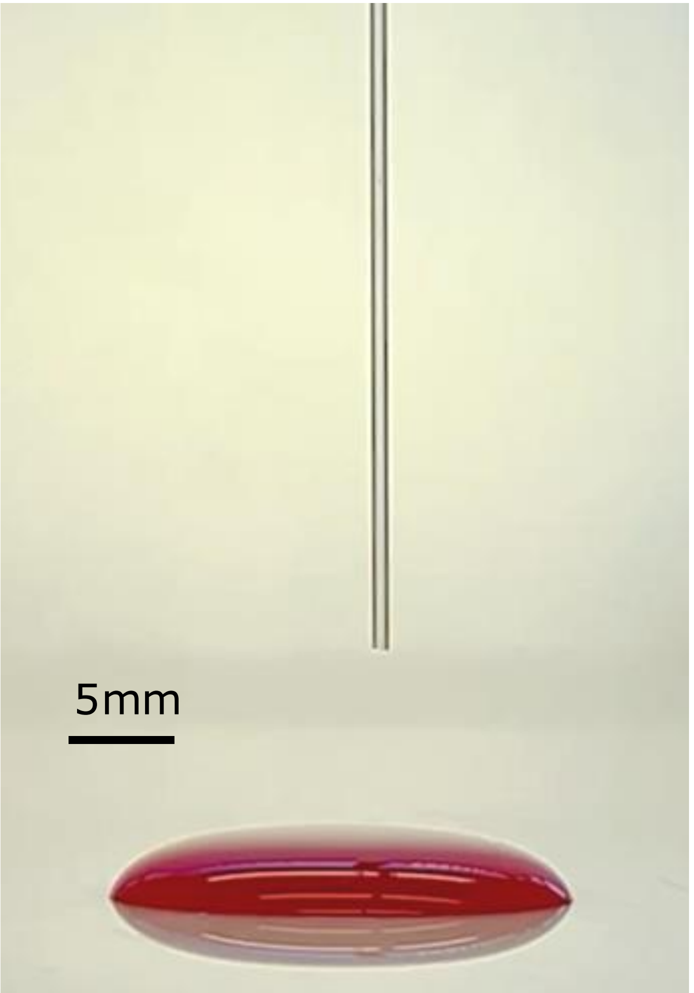


Image created with DALL·E (OpenAI)

Ingredient A: The Lucas-Washburn equation



- Balancing the capillary driving force with viscous friction due to **Poiseuille** flow gives (neglect gravity and inertia):

$$2\pi R\sigma \cos\theta_0 = 8\pi\eta h\dot{h}.$$

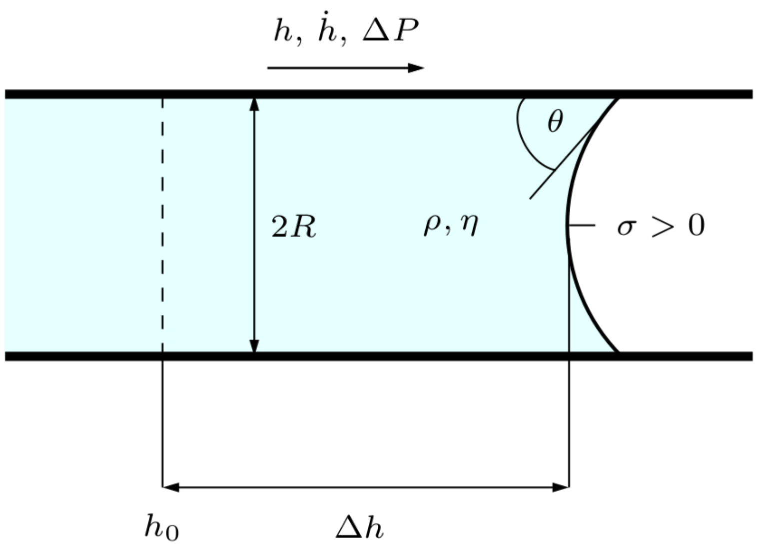
- In non-dimensional form: $(H := h/R, \quad s := t/(4\eta R/\sigma))$

$$H(s)H'(s) = \cos\theta_0.$$

- The well-known solution is:

$$H(s) = \sqrt{2\cos\theta_0\, s} \quad \Leftrightarrow \quad \boxed{h(t) = \sqrt{\frac{R\sigma\cos\theta_0}{2\eta}\, t}}$$

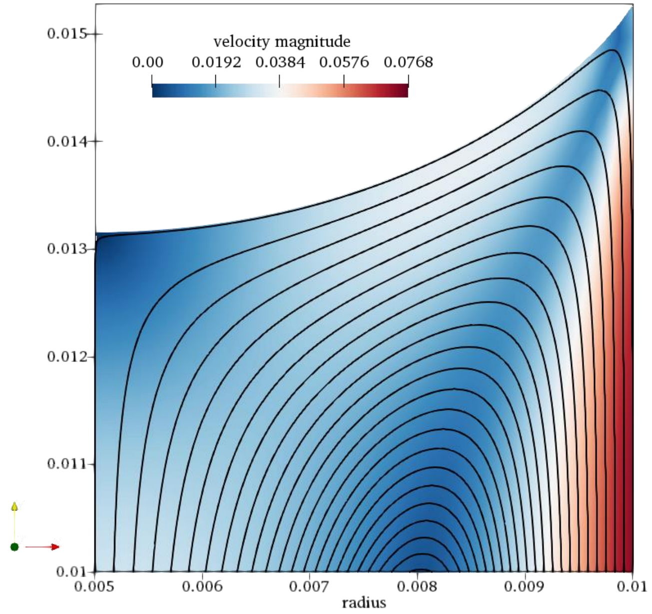
Improved version: Including HDT and MKT



- Lucas-Washburn equation only considers dissipation due to **Poiseuille flow.**
- But, we expect dissipation due to the flow close to the contact line (HDT) **as well as** contact line friction (MKT).
- We can show, that both lead to a **similar term in the model!**

$$\cos\theta_0 = HH' + \frac{1}{32\mathrm{Oh}^2}(HH')' + \beta H'$$

- MKT: $\beta_{\mathrm{MKT}} \sim \zeta/\eta$
- HDT: $\beta_{\mathrm{HDT}} \sim \dfrac{\ln(R/L)}{\theta}$



(Fricke et al., arXiv:2311.11947) and (Fricke et al., Physica D, 2023) see also (Delannoy et al., Soft Matter, 2019).

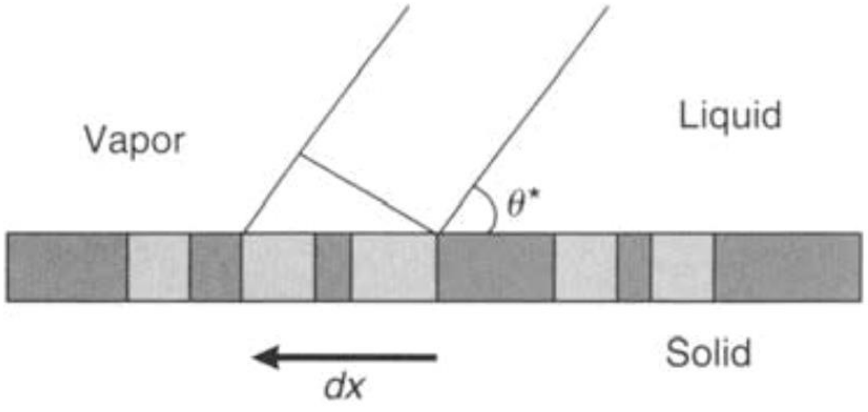
Ingredient B: The Cassie-Baxter equation

- The contact angle on an **ideal** surface is governed by a balance of surface tension forces (Young equation):

$$\sigma_{\mathrm{lg}} \cos\theta_0 + \sigma_{\mathrm{sl}} - \sigma_{\mathrm{sg}} = 0$$

- Model for the static contact angle on <u>**chemically**</u> **textured** surface (Cassie-Baxter equation):

$$\cos\theta_{\mathrm{CB}} = r\cos\theta_1 + (1-r)\cos\theta_2$$



Chemically textured

Image on this slide from de Gennes, Brochard-Wyart, Quere, 2004

Context: Powder Reconstitution

- Preparing a meal for a baby is a highly non-trivial **dynamic wetting** problem!
- Goals: Process speed, avoid air bubbles, product quality, robustness, ….

https://www.youtube.com/shorts/zpyEW7Algf4

Synthesis: Dynamic wetting of a heterogeneous system

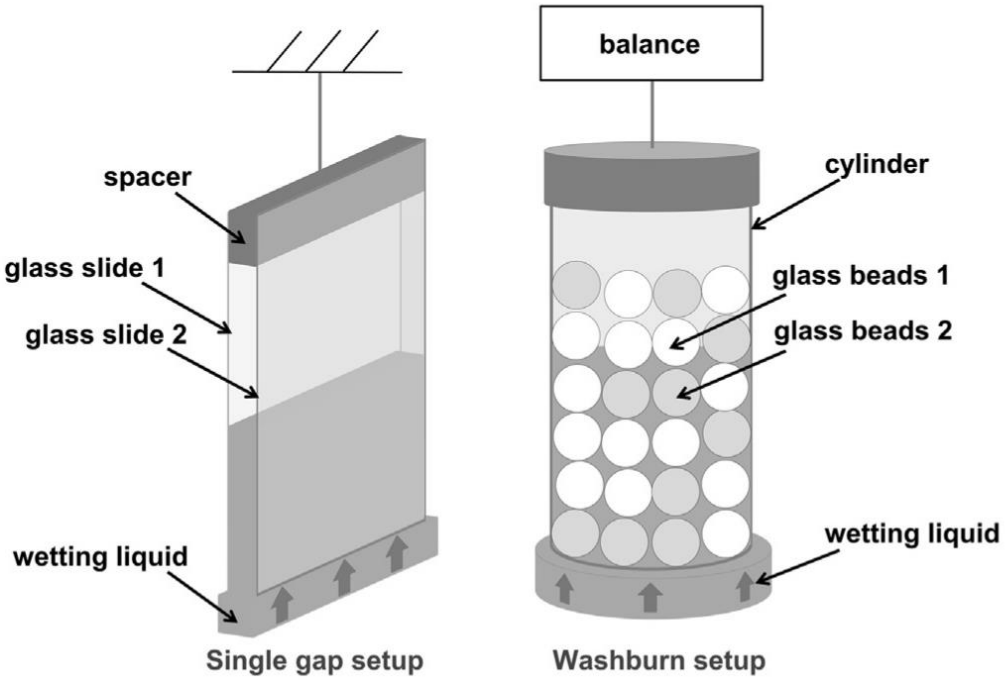


Figure by Kammerhofer et al., Powder Technology 328 (2018).

Can we use the Cassie-Baxter angle to model the imbibition in a mixed powder bed?

$$H(t) = \sqrt{\frac{r_{\mathrm{p,eff}}\,\sigma\,\cos\theta_{\mathrm{CB}}\,t}{2\eta}}.$$

Effective radius

Cassie-Baxter Angle

- Model by Benavente et al. (2002) and Kammerhofer et al. (2018)).

<u>Back to basics:</u> Lucas-Washburn with heterogenity

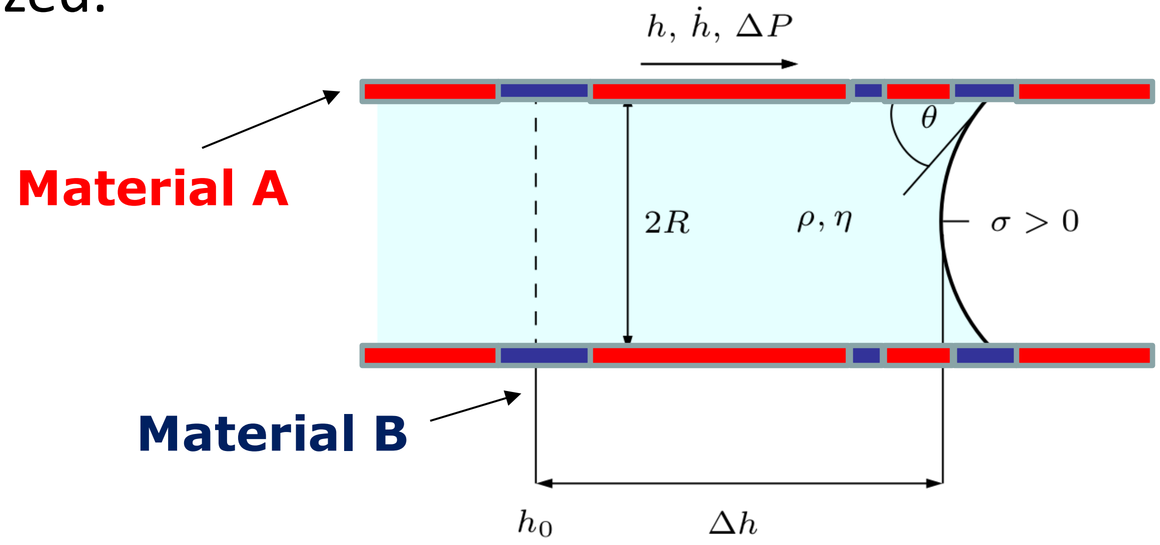
- We revisit the classical Lucas-Washburn model but allow for **heterogeneous** surface, i.e. we study

$$H(s)H'(s) = \cos\theta_0(H(s))$$

- The length of the segments of A and B are **statistically distributed** such that a certain mixture is realized.

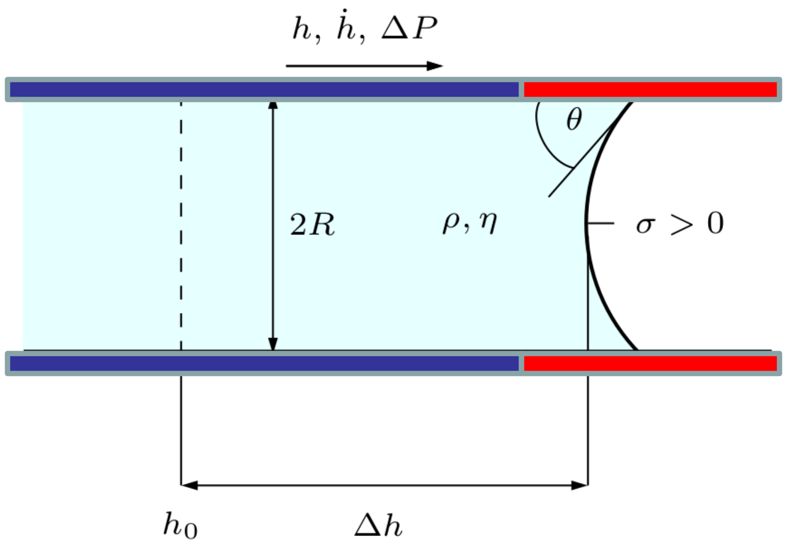
J. De Coninck

Research Question: How should one **arrange** the mixture of A and B to minimize the crossing-time?

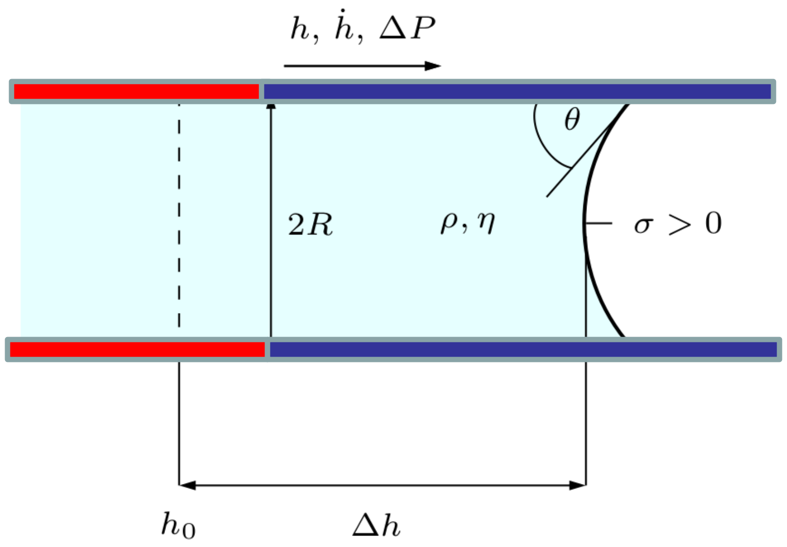


The key question

- Let us assume that **A** is more **hydrophilic** than **B.**
- **What do you think:** Which configuration gives **faster** imbibition?



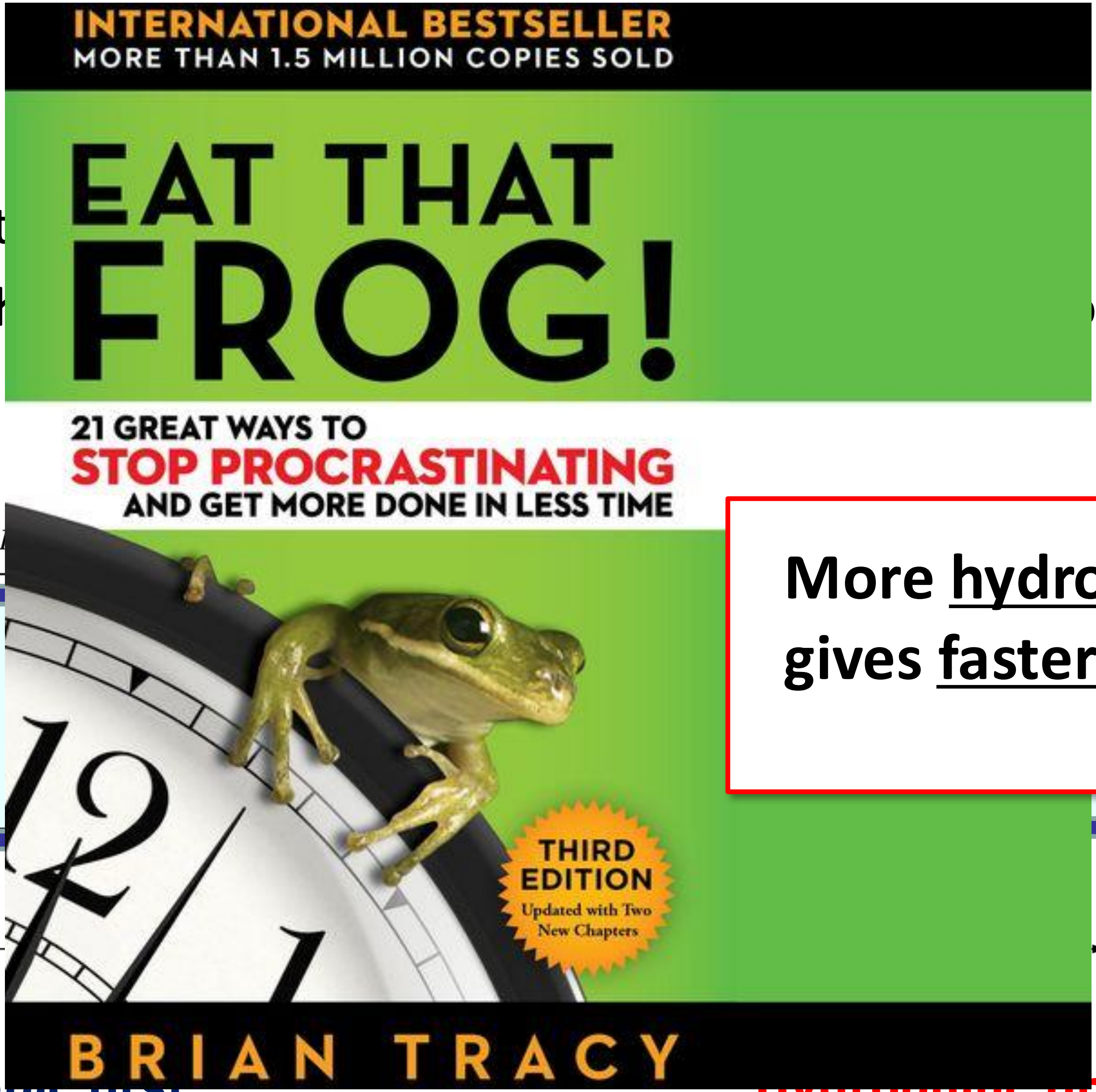
Hydrophobic first

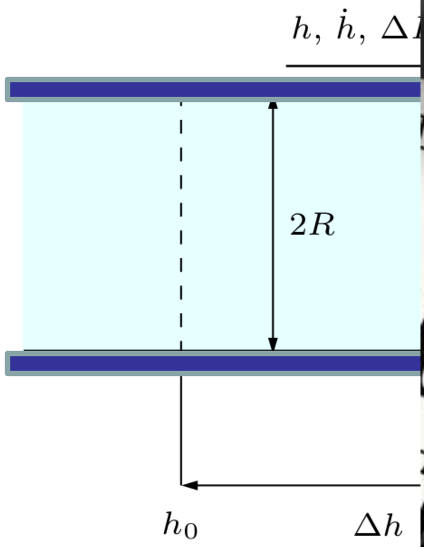


Hydrophilic first

The key questi…

- Let us assume t…
- **What do you th… …n?**





More hydrophobic first gives faster imbibition!

Hydrophobic first

Hydrophilic first

Why does the order matter? A simple exercise …

- Governing equation (non-dimensional form):

$$\cos\theta_0(H) = HH' + \beta(H)H'.$$

Contact Line Friction (depends on material)

- **Solution:** Elapsed time = Integral over inverse speed!

$$s(H) = \int_0^{H} \frac{d\tilde{H}}{V(\tilde{H})} = \int_0^{H} \frac{\tilde{H} + \beta(\tilde{H})}{\cos\theta(\tilde{H})}\, d\tilde{H}.$$

Solution formula

- For <u>piecewise constant</u> properties:

$$s = \sum_i \int_{H_i}^{H_{i+1}} \frac{\tilde{H} + \beta_i}{\cos\theta_i}\, d\tilde{H} = \sum_i \left(\frac{\beta_i}{\cos\theta_i} L_i + \frac{H_{i+1}^2 - H_i^2}{2\cos\theta_i} \right)$$

$$= \frac{\beta_A L_A}{\cos\theta_A} + \frac{\beta_B L_B}{\cos\theta_B} + \sum_i \frac{L_i \bar{H}_i}{\cos\theta_i} =: s_\beta + \sum_i \frac{L_i \bar{H}_i}{\cos\theta_i}.$$

Center coordinate

Invariant

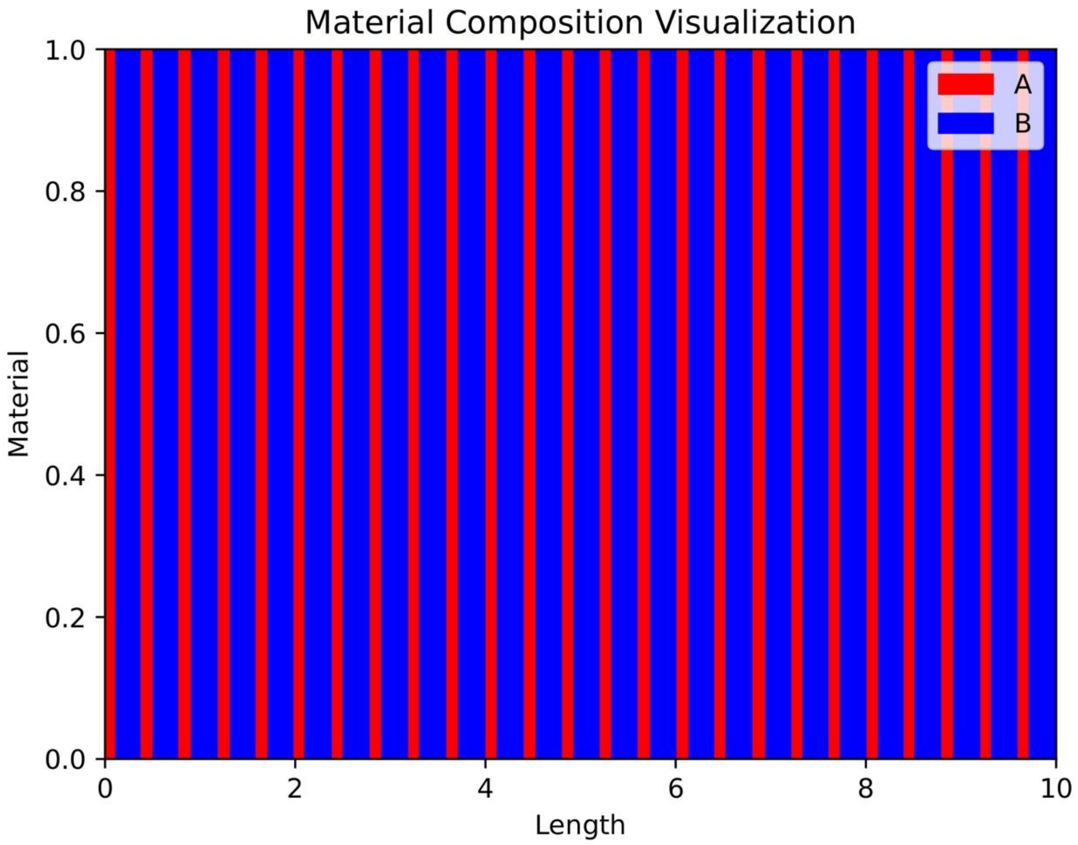
„Poiseuille part" – <u>not</u> invariant

A quantitative example

Python Code:

- Let us look at a concrete example. We choose

$$\theta_A = 30°, \quad \theta_B = 60°, \quad \text{share of A} \quad r_A = 0.3, \quad \text{pore length} \quad L = 10\,R$$



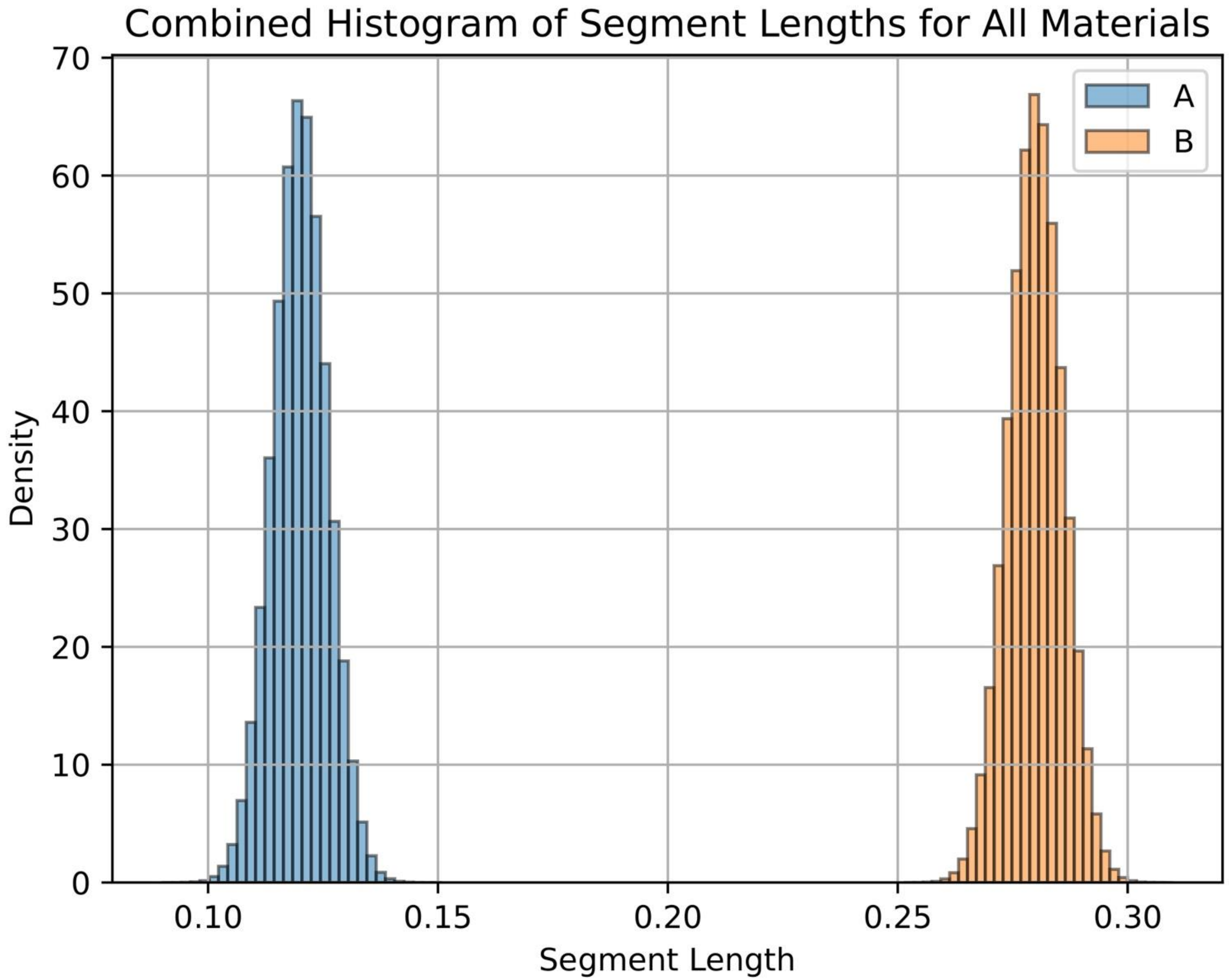
- This yields the Cassie-Baxter angle

$$\cos\theta_{\mathrm{CB}} = 0.3\cos 30° + 0.7\cos 60°$$

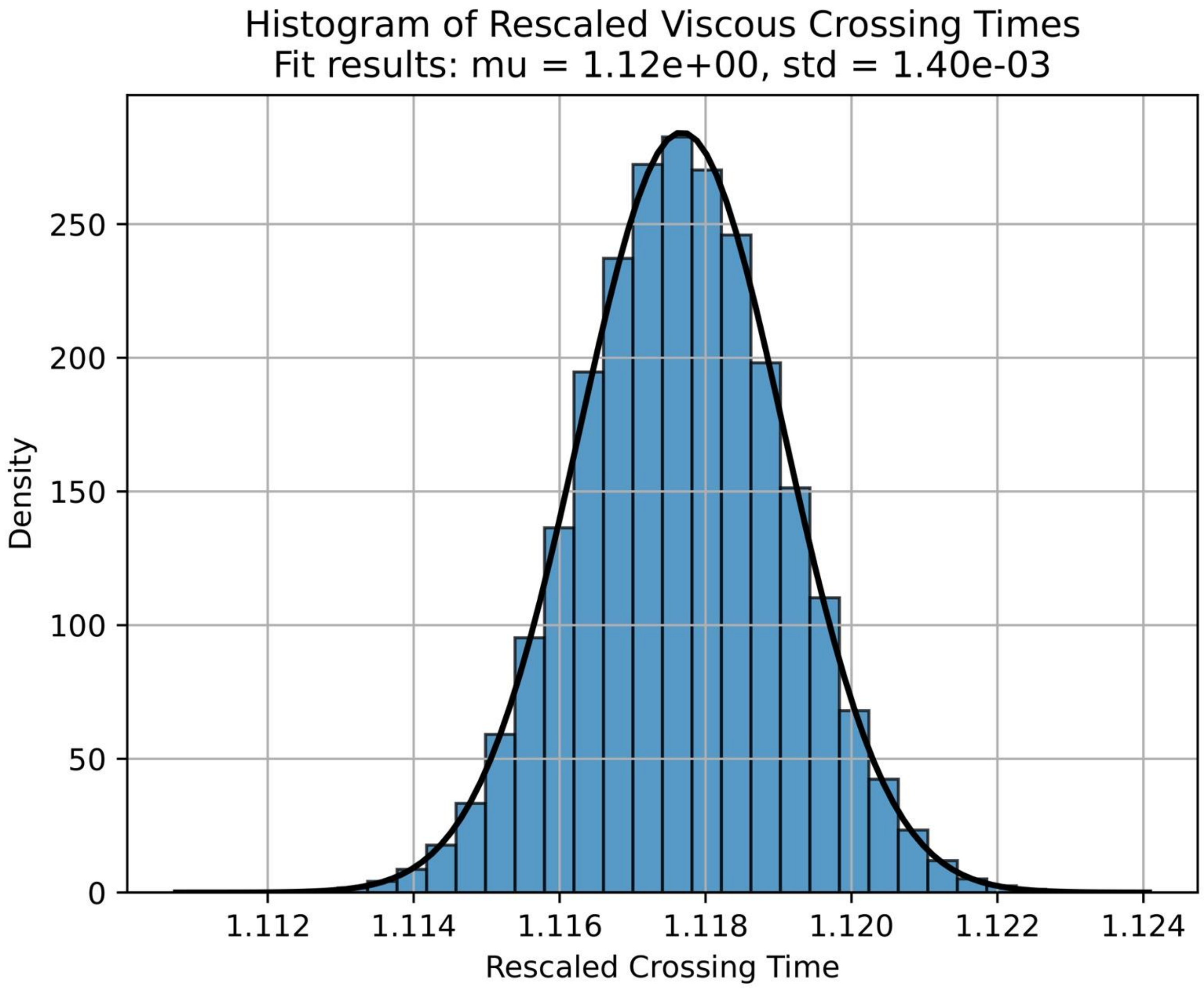
$$\Rightarrow \quad \theta_{\mathrm{CB}} \approx 52.4°$$

- The lengths of the segments follow a **Gaussian** distribution.
- We average over **50k samples** of that material in the following.

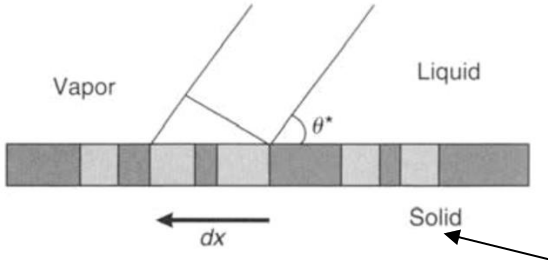
Distribution of segment length (where $r_A = 0.3$)



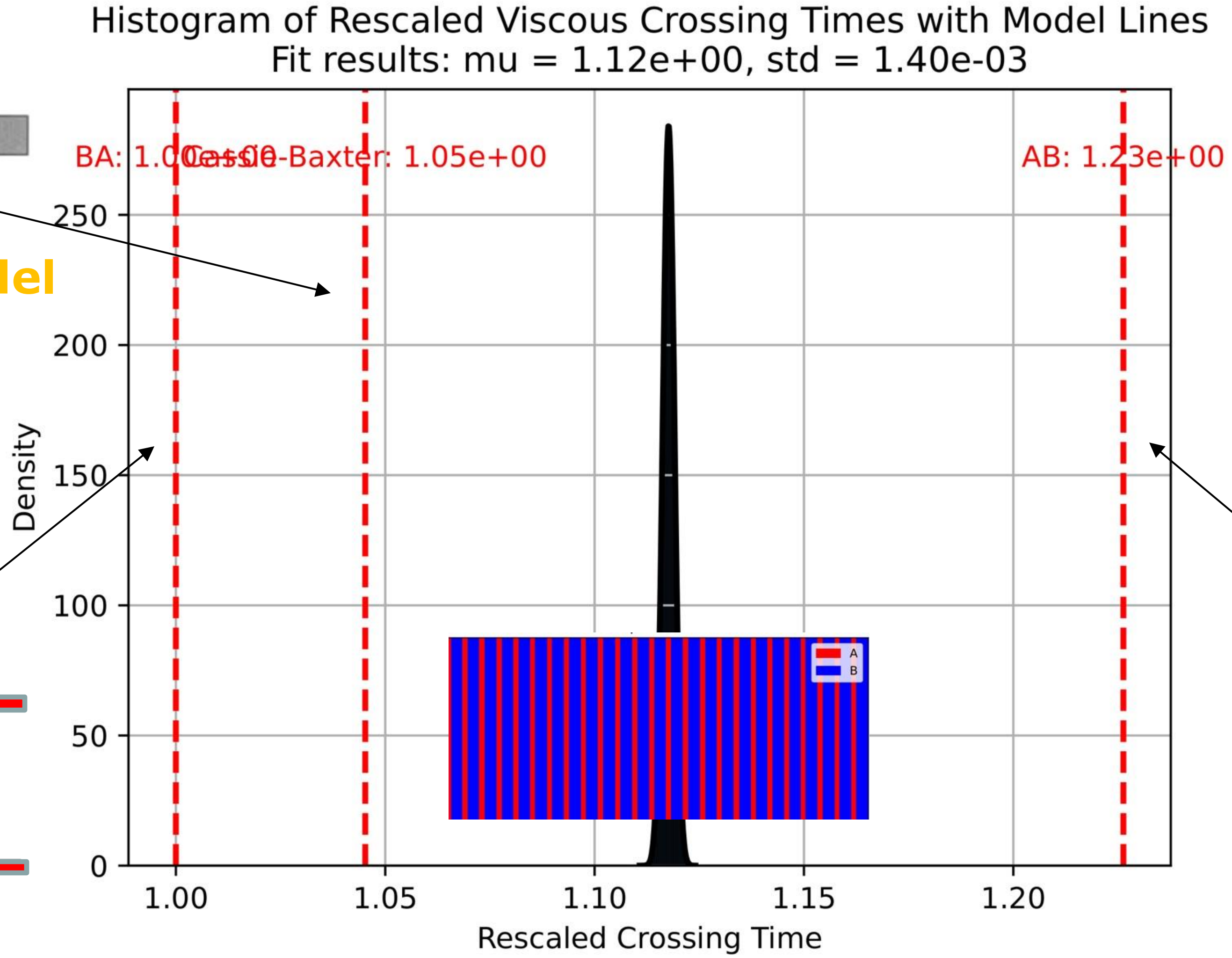
Distribution of crossing time (according to Lucas-Washburn)



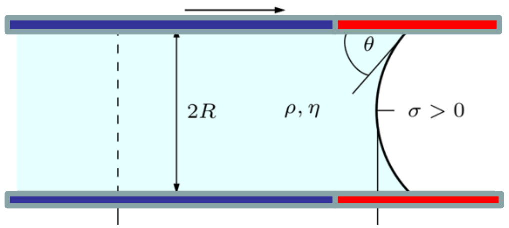
Distribution of crossing time (according to Lucas-Washburn)



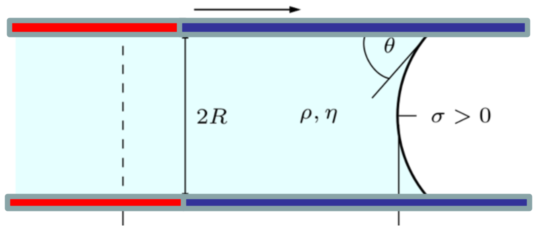
Cassie-Baxter model



Finding: Cassie-Baxter model fails!!



Hydrophobic first



Hydrophilic first

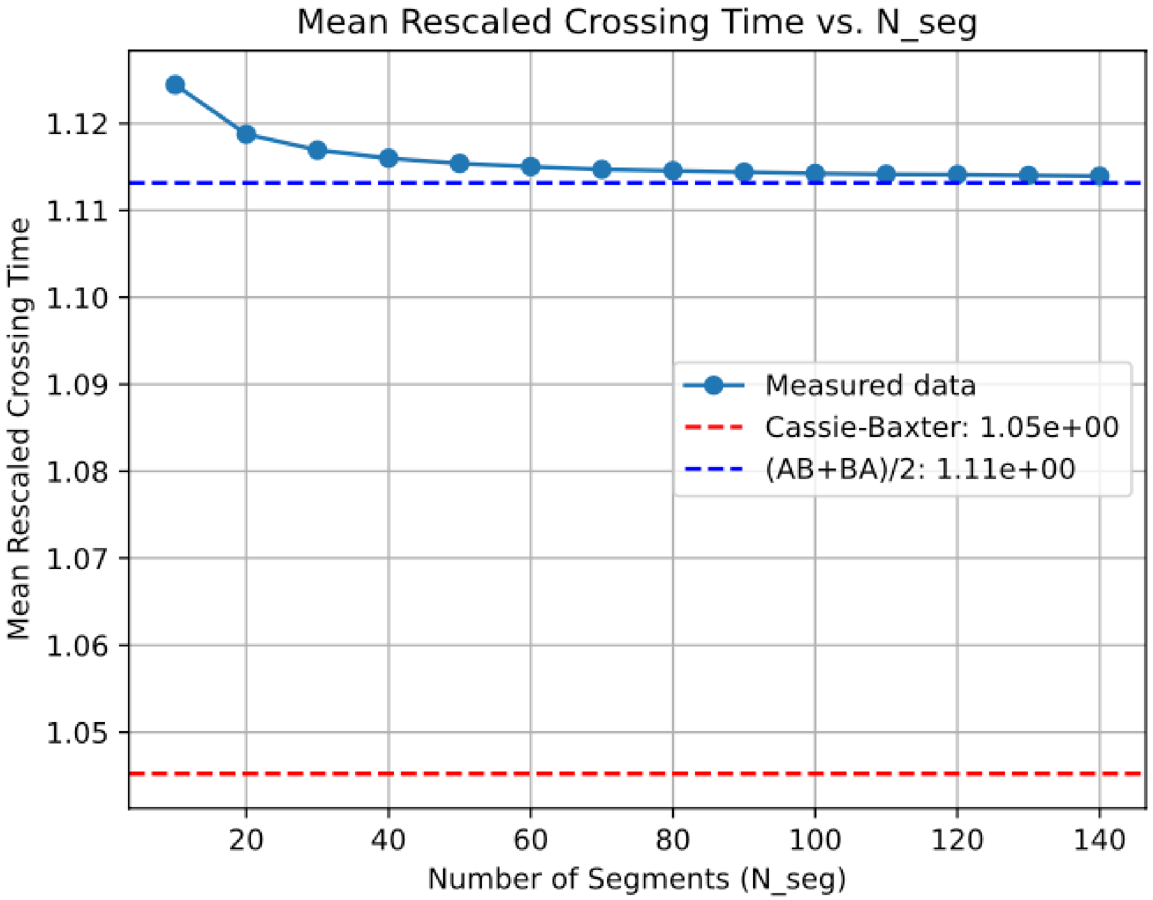
Effective contact angle?

- We can show that the limit is given by:

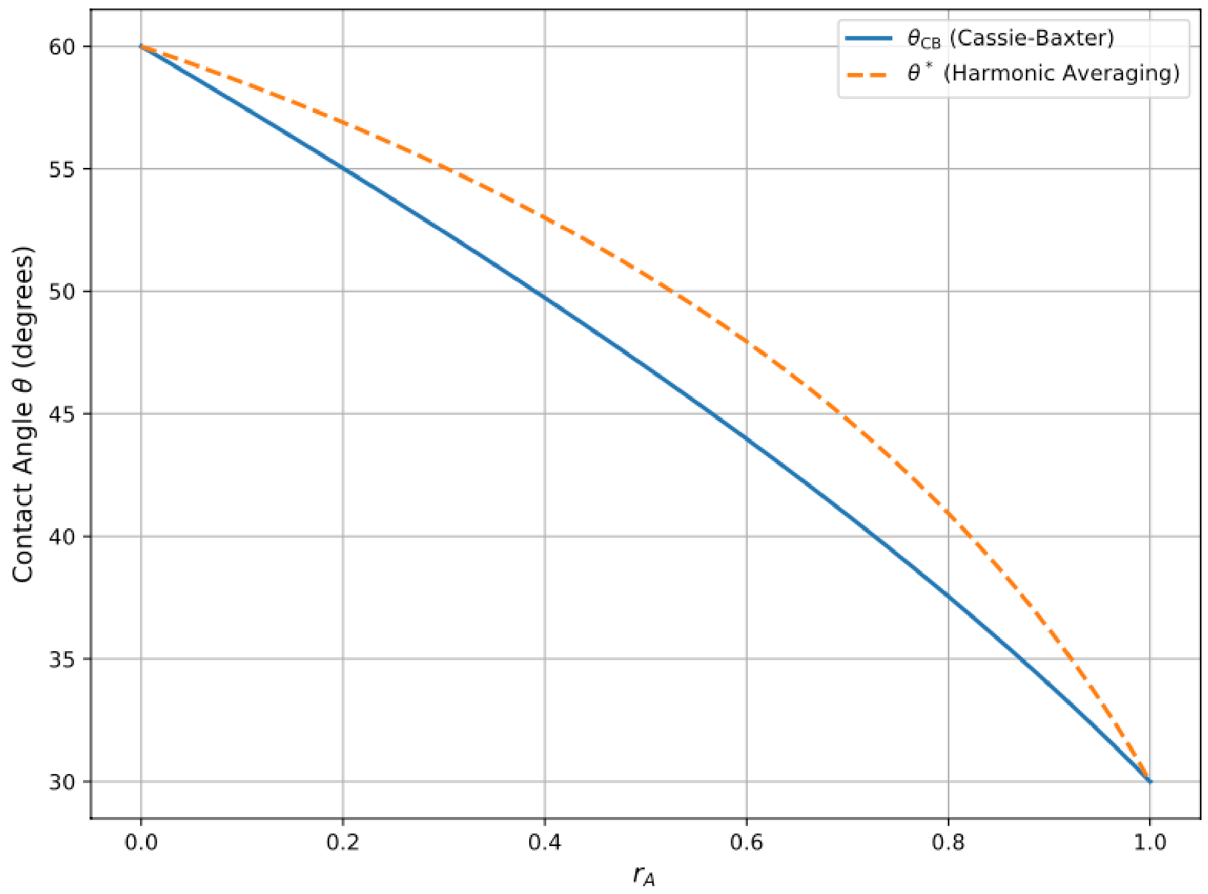
$$s_P^* = \frac{L^2}{2}\left(\frac{r_A}{\cos\theta_A} + \frac{r_B}{\cos\theta_B}\right) = \frac{s_P^{AB} + s_P^{BA}}{2}.$$

- **Arithmetic average** between best and worst case!
- Can we define an effective contact angle?

$$s_P^* = \frac{L^2}{2}\left(\frac{r_A}{\cos\theta_A} + \frac{r_B}{\cos\theta_B}\right) \overset{!}{=} \frac{L^2}{2\cos\theta^*}.$$



Weighted harmonic averaging



- The result is:

$$\cos\theta^* = \left(\frac{r_A}{\cos\theta_A} + \frac{r_B}{\cos\theta_B}\right)^{-1}.$$

- Compare with Cassie-Baxter:

$$\cos\theta_{CB} = r_A\cos\theta_A + r_B\cos\theta_B.$$

- **Observation:** A different type of averaging seems appropriate!

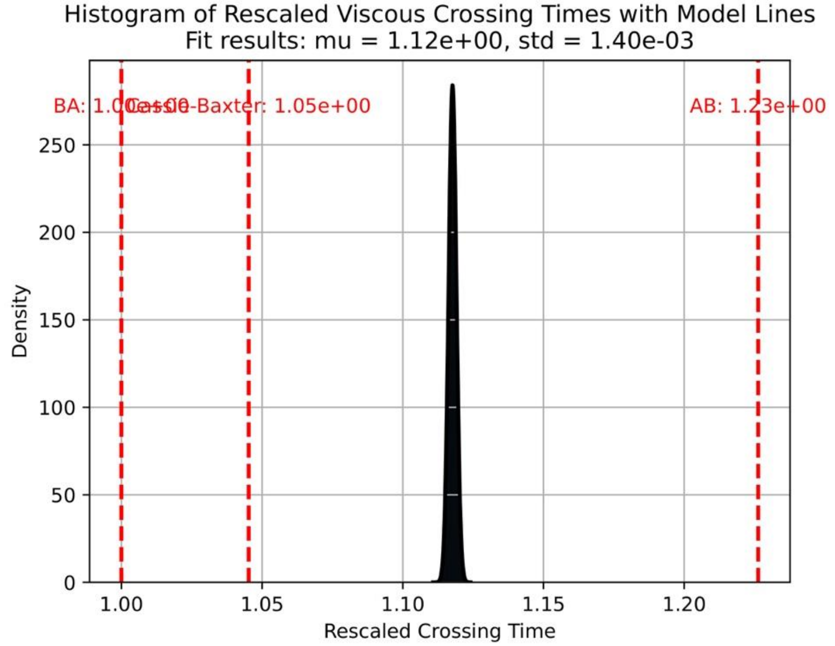
Summary

- We have shown that the **wetting speed** for heterogeneous materials depends (in a non-trivial way) on the **material composition**.

- Suprisingly, Cassie-Baxter theory **fails** for the crossing time!

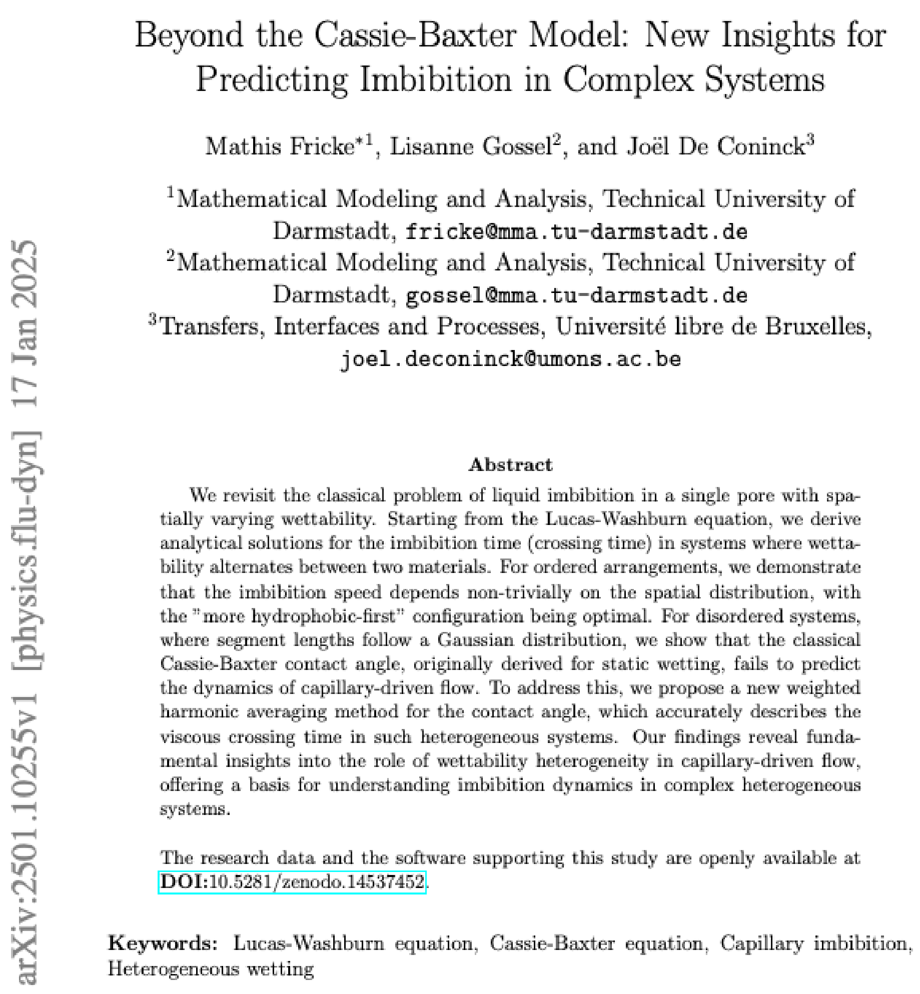
$$M_l(t) = A\,\varepsilon\,\rho\,\sqrt{\frac{r_{\mathrm{p,eff}}\,\sigma\,\cos\theta_{\mathrm{CB}}}{2\eta}}.$$

Effective pore radius compensates for inadequate contact angle value?



- What about **experiments?**
  (Looking for collaboration)

For more details..



Beyond the Cassie-Baxter Model: New Insights for Predicting Imbibition in Complex Systems

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Abstract

We revisit the classical problem of liquid imbibition in a single pore with spatially varying wettability. Starting from the Lucas-Washburn equation, we derive analytical solutions for the imbibition time (crossing time) in systems where wettability alternates between two materials. For ordered arrangements, we demonstrate that the imbibition speed depends non-trivially on the spatial distribution, with the "more hydrophobic-first" configuration being optimal. For disordered systems, where segment lengths follow a Gaussian distribution, we show that the classical Cassie-Baxter contact angle, originally derived for static wetting, fails to predict the dynamics of capillary-driven flow. To address this, we propose a new weighted harmonic averaging method for the contact angle, which accurately describes the viscous crossing time in such heterogeneous systems. Our findings reveal fundamental insights into the role of wettability heterogeneity in capillary-driven flow, offering a basis for understanding imbibition dynamics in complex heterogeneous systems.

The research data and the software supporting this study are openly available at DOI:10.5281/zenodo.14537452.

Keywords: Lucas-Washburn equation, Cassie-Baxter equation, Capillary imbibition, Heterogeneous wetting

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L. Gossel

J. De Coninck

- ArXiv Preprint:
  https://doi.org/10.48550/arXiv.2501.10255
- Research software (Python) is available:
  https://doi.org/10.5281/zenodo.14537452
- Please reach out to me for any questions!

Preprint

Code

This talk:

Thank you very much for your attention!

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