Statistical mechanics of hysteretic capillary phenomena: predictions of contact angle on rough surfaces and liquid retention in unsaturated porous media

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الصندوق القطري لرعاية البحث العلمي
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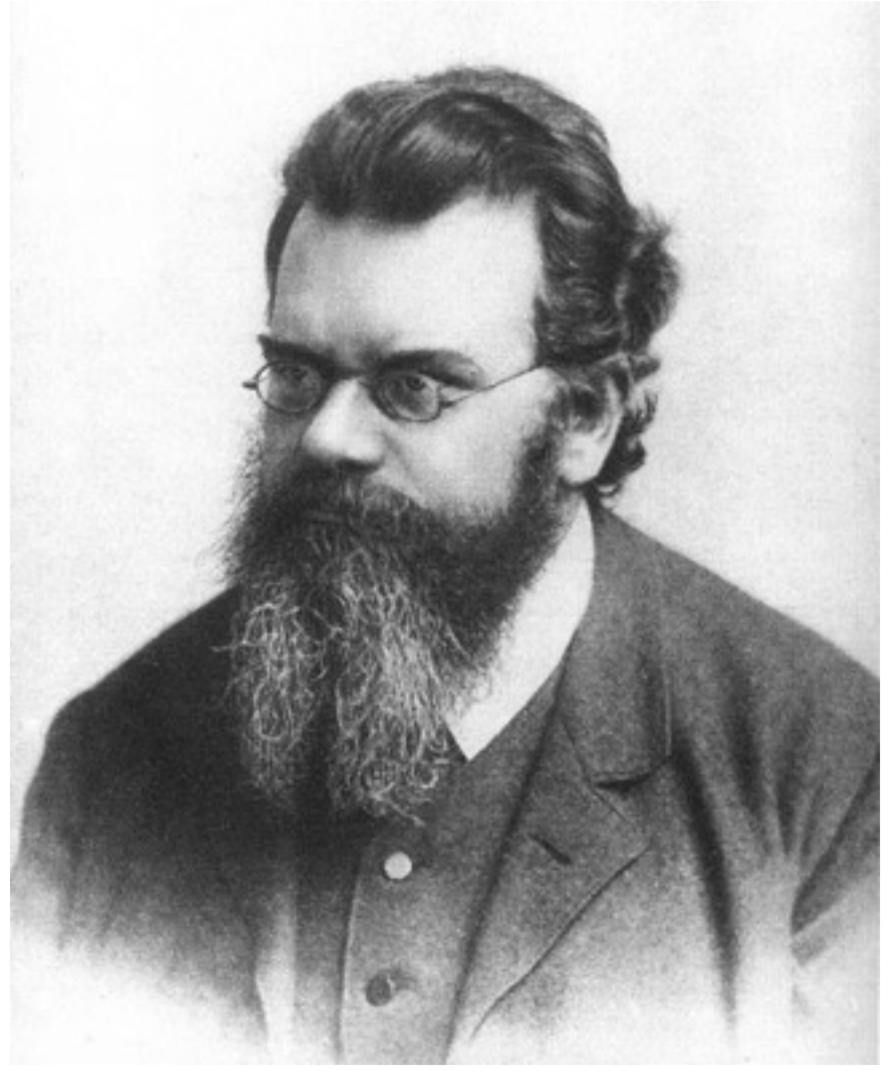
Member of Qatar Foundation

http://grainflowresearch.mae.cornell.edu/

InterPore 2017, Rotterdam, May 10, 2017



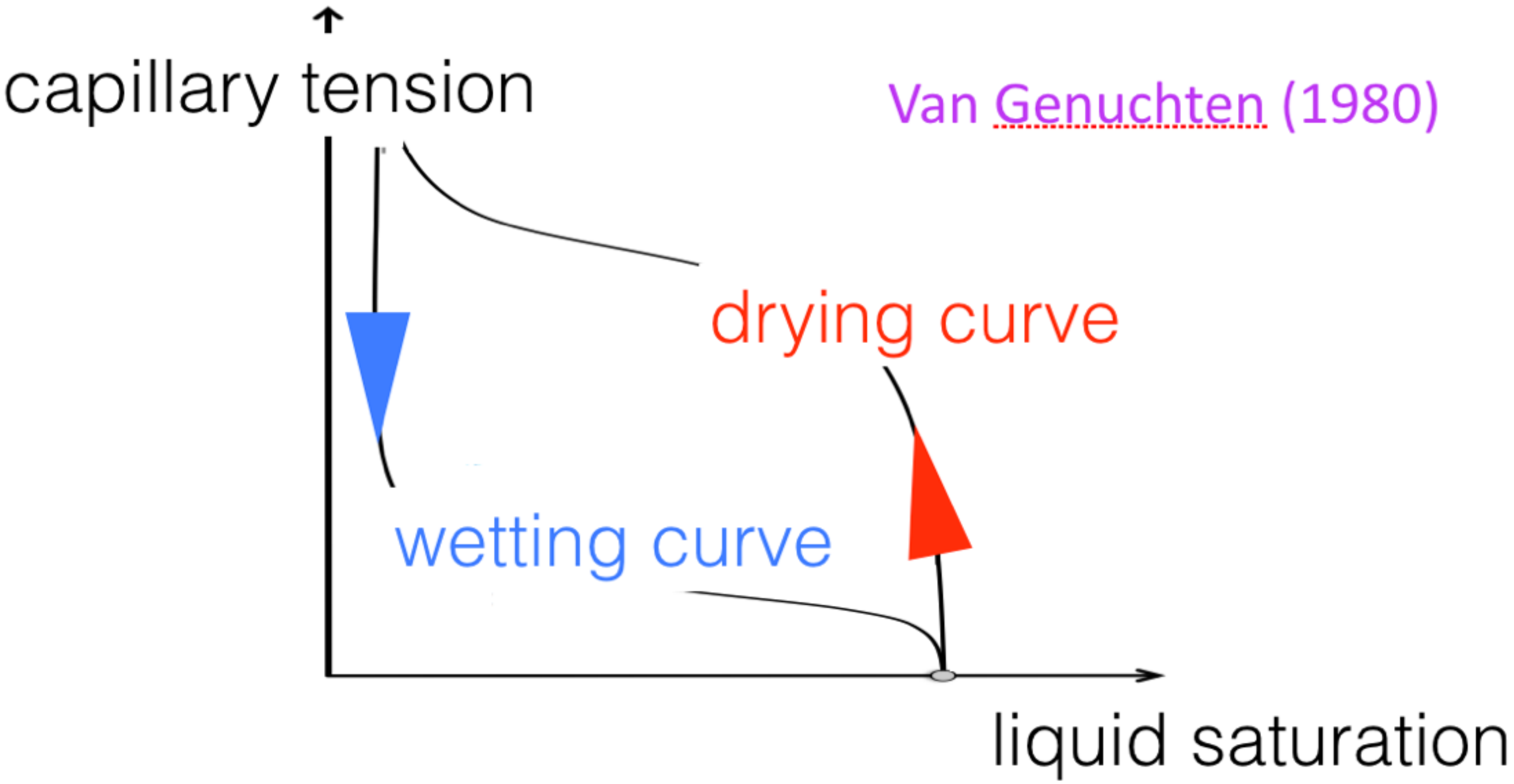
Ludwig Eduard Boltzmann
(February 20, 1844 – September 5, 1906)

Hysteresis

Collective interactions

Statistical Mechanics

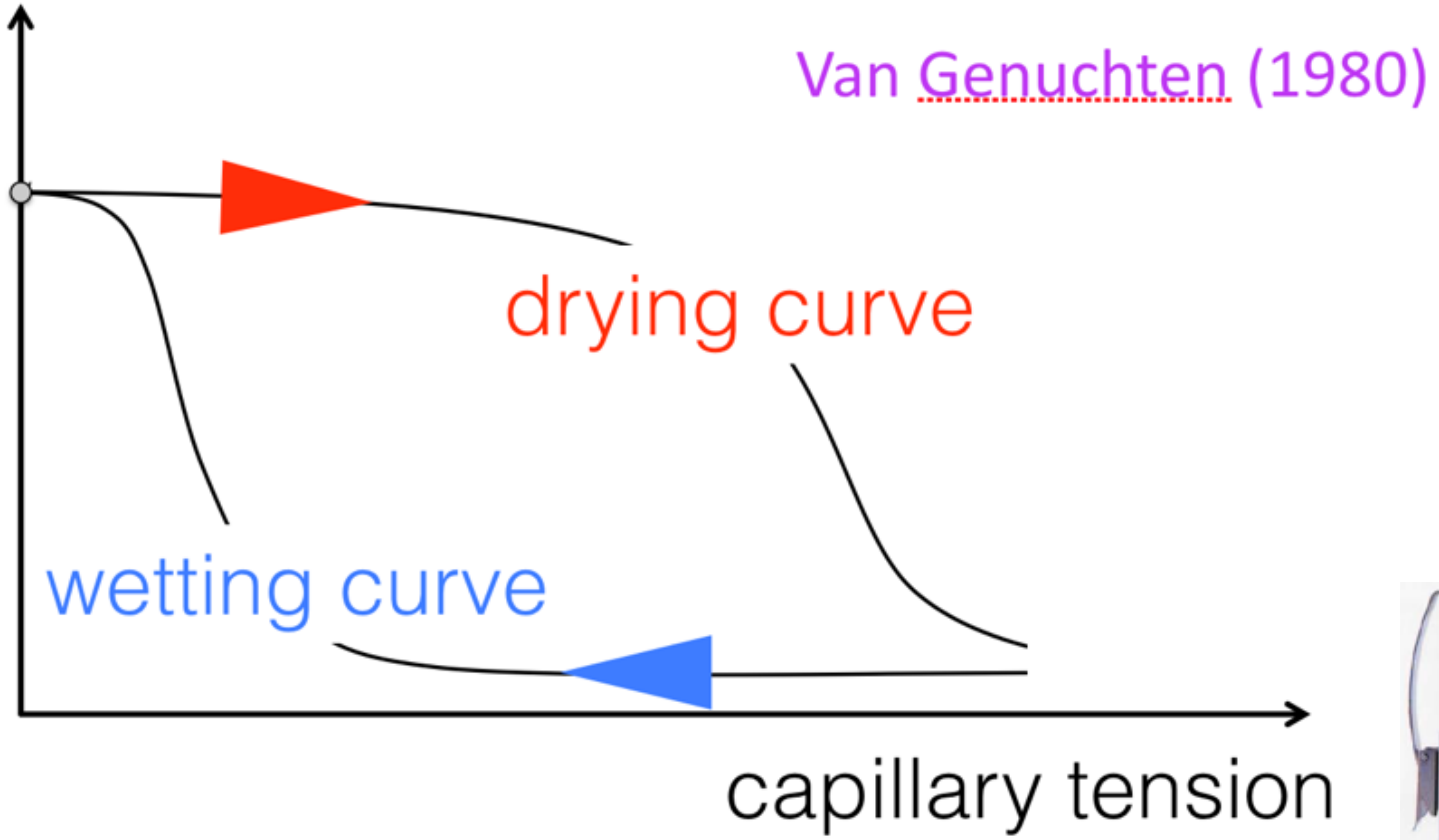
Statistical Mechanics of Unsaturated Porous Media



Van Genuchten (1980)

Jin Xu and Michel Louge, Phys. Rev. E 92 (2015)

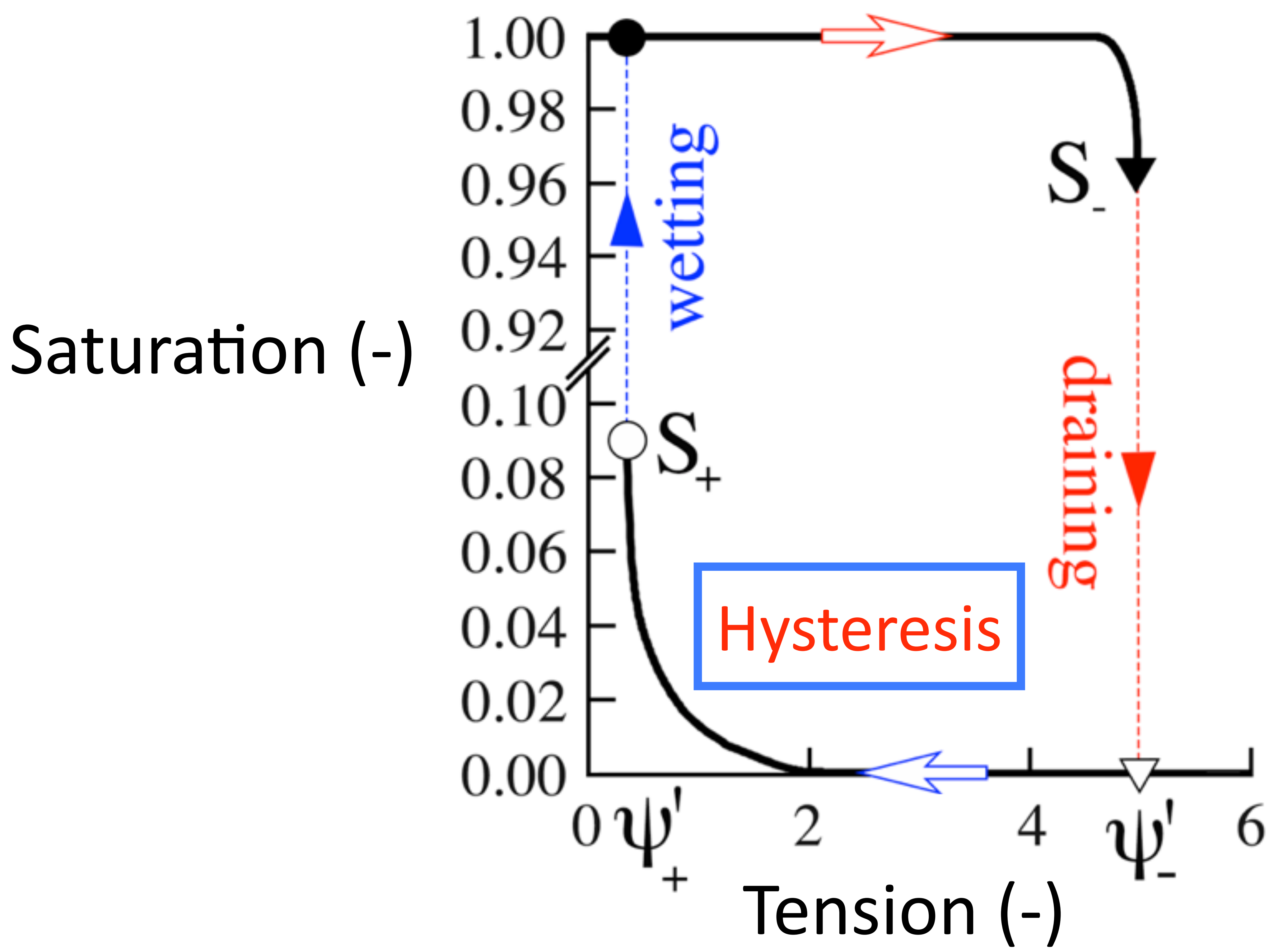
Statistical Mechanics of Unsaturated Porous Media

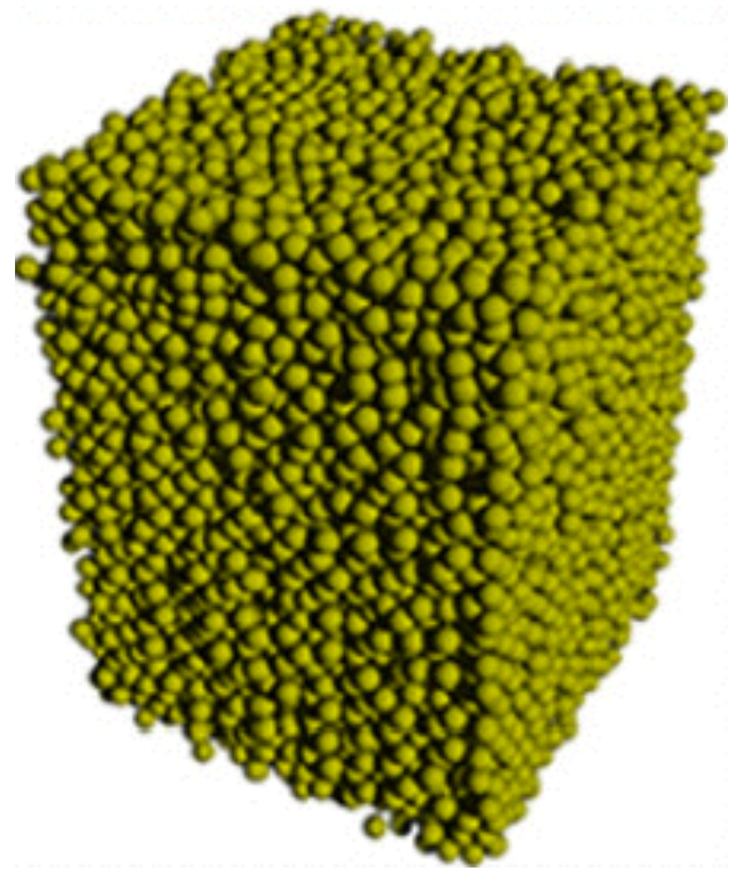


Jin Xu and Michel Louge, Phys. Rev. E 92 (2015)

Statistical Mechanics of Unsaturated Porous Media

Predict the retention curve
from pore geometry and surface energies
with an equilibrium theory

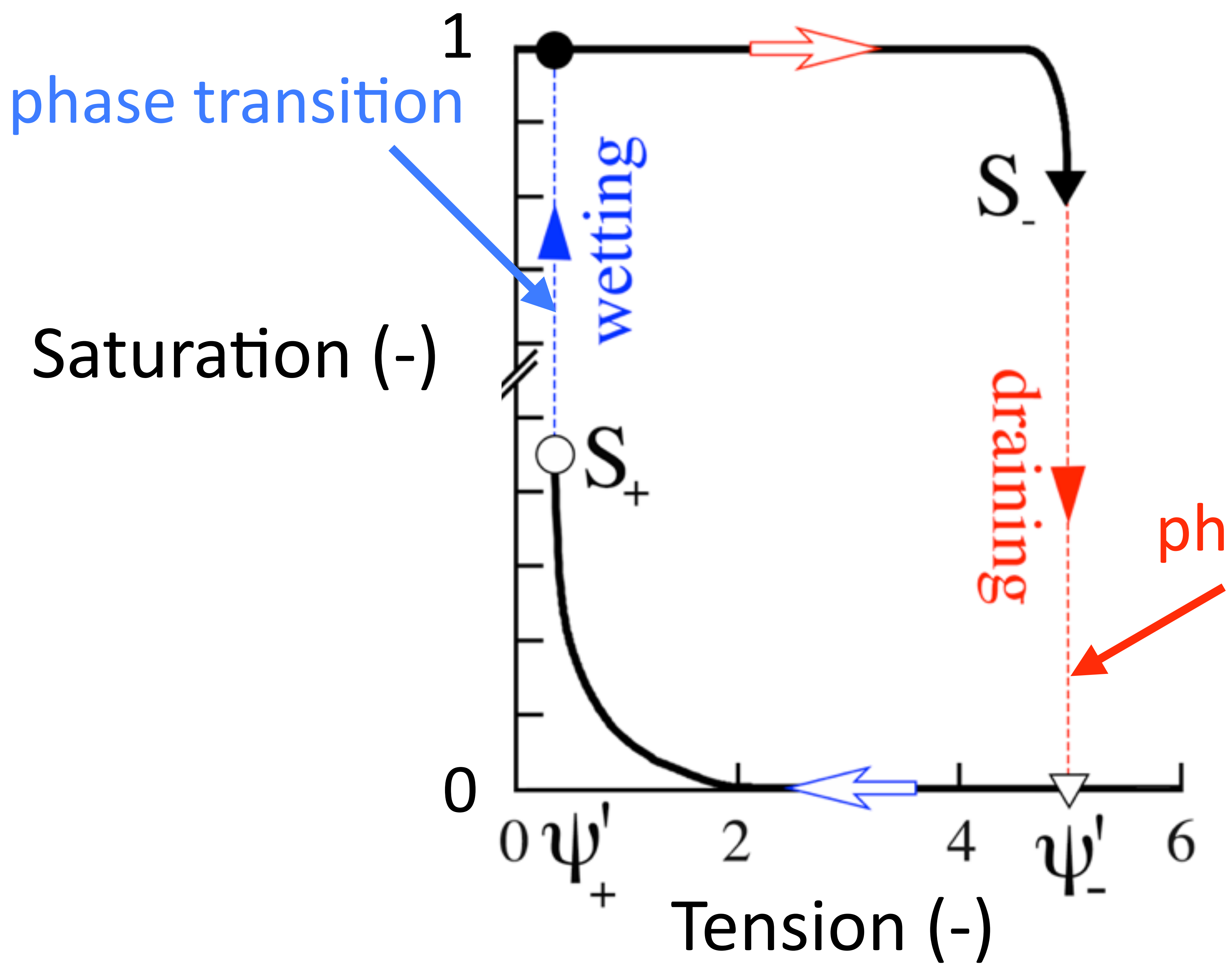


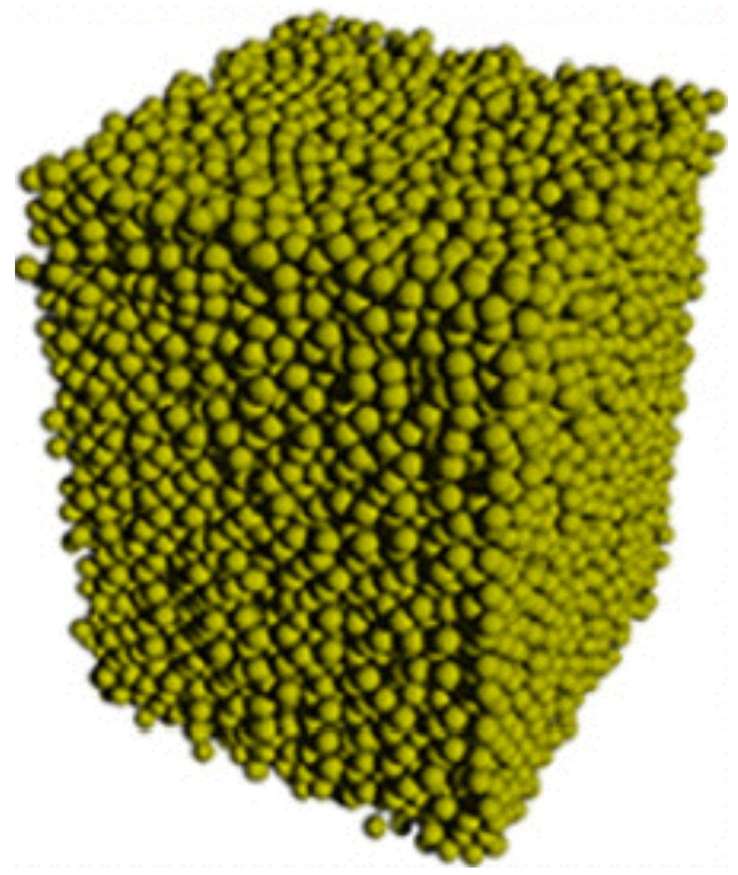


Jin Xu and Michel Louge, Phys. Rev. E 92 (2015)

Statistical Mechanics of Unsaturated Porous Media

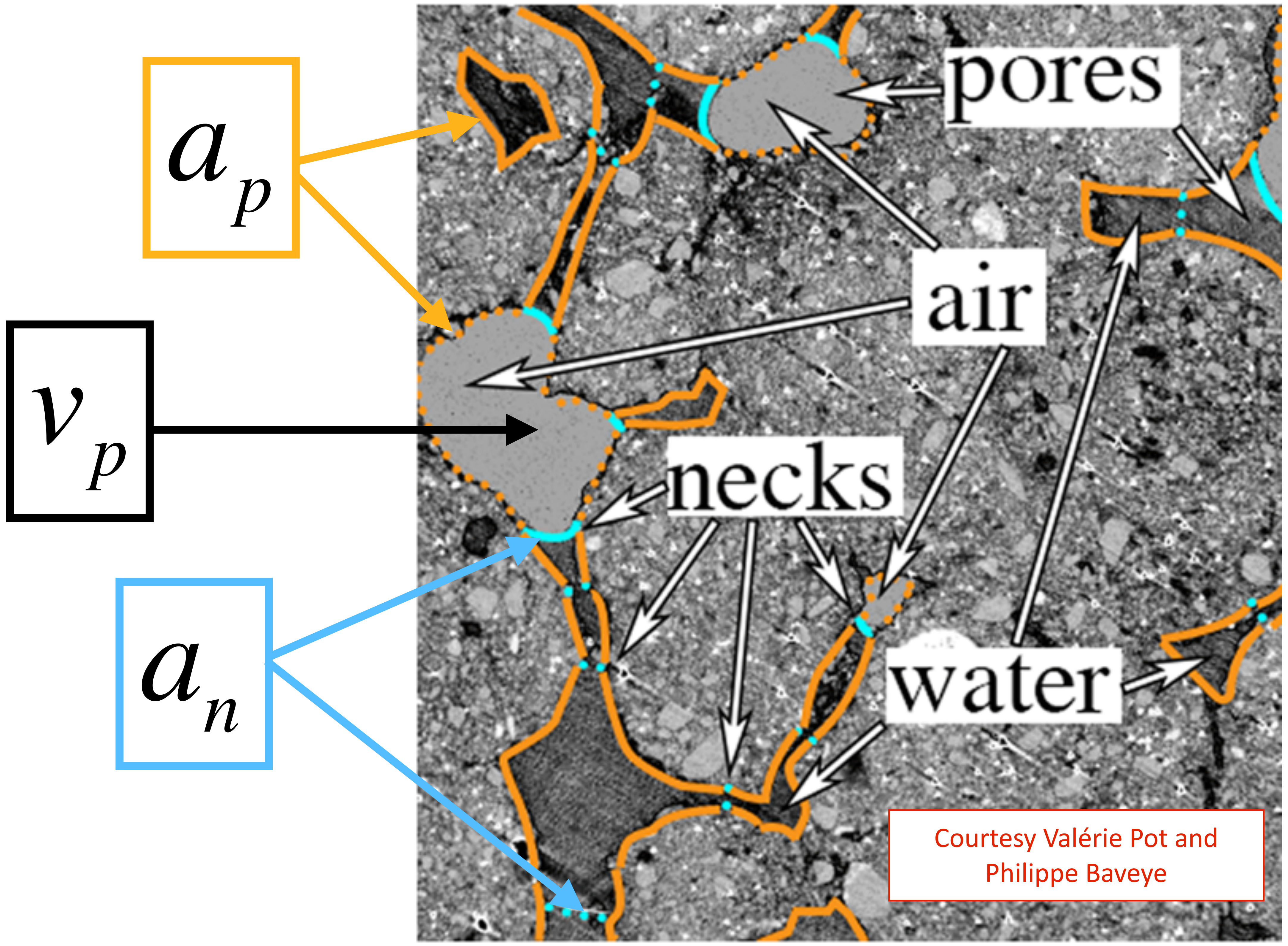
Drainage and imbibition are first-order phase transitions





Jin Xu and Michel Louge, Phys. Rev. E 92 (2015)

Geometry: pores and necks



Pot, et al
Adv. Water Res.(2015)

Pore volume v_p pore surface area a_p

each pore has several necks with overall cross-section a_n

Ising model: the simplest statistical mechanics

filling state σ → $\sigma = -1$ pore full of liquid

filling state σ → $\sigma = +1$ pore full of gas

Filling state variable

Saturation

filling state σ → $\sigma = -1$ pore full of liquid

filling state σ → $\sigma = +1$ pore full of gas

Degree of Saturation *S*

$$0 \leq \left[S = \frac{\theta}{1-\nu} = \frac{1-\bar{\sigma}}{2} \right] \leq 1$$

θ = liquid volume fraction

ν = solid volume fraction

Two state variables: pore filling and tension

filling state σ

$\sigma = -1$ pore full of liquid

$\sigma = +1$ pore full of gas

mean field $\bar{\sigma} = f(\psi^*)$

gas-liquid interfacial energy $\gamma_{\ell g}$

relative tension

$$\psi^* = \frac{\psi \bar{v}_p^{1/3}}{\gamma_{\ell g}}$$

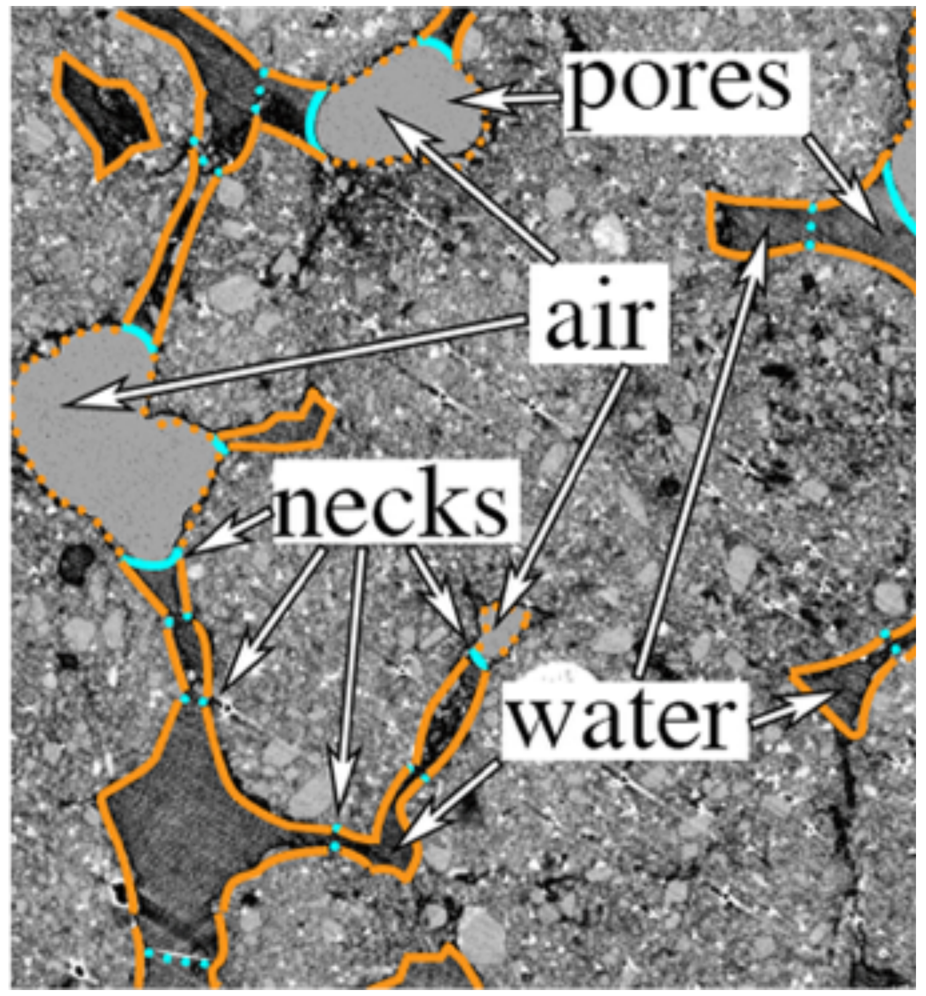
Energy of a single pore

$$E = \frac{\sigma}{2}\left(-\psi \times v_p + \gamma_{\ell g} a_p \cos\theta_e - \gamma_{\ell g} a_n \bar{\sigma}\right)$$

pressure work

pore wall energy

neck interface energy



Young contact angle $\cos\theta_e = \frac{\gamma_{gs} - \gamma_{s\ell}}{\gamma_{\ell g}}$

$$E^* = \frac{E}{\gamma_{\ell g} \bar{v}_p^{2/3}}$$

Dimensionless energy of a single pore

$$E^* = \frac{\sigma}{2}\left(-\psi^* + \alpha\cos\theta_e - \lambda\bar{\sigma}\right)$$

pressure work

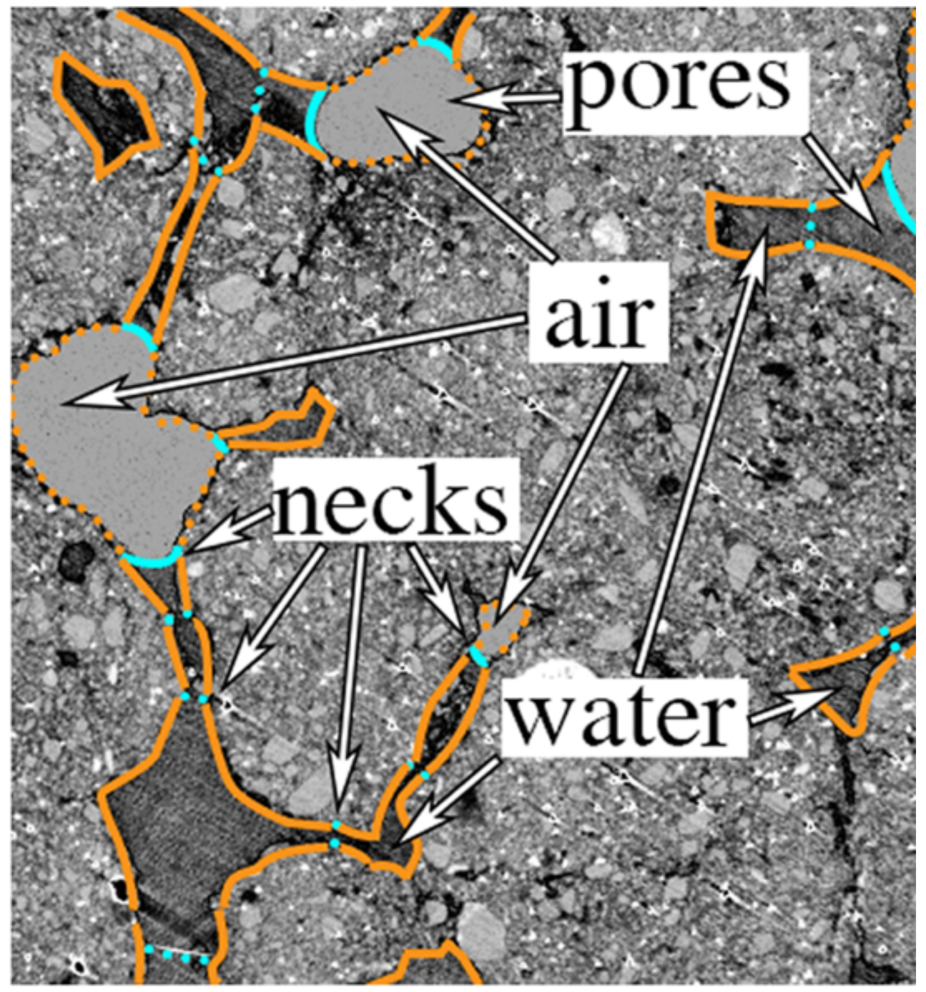
pore wall energy

neck interface energy

Young contact angle θ_e

$$\alpha \equiv \frac{a_p \bar{v}_p^{1/3}}{v_p}$$

specific pore wall area

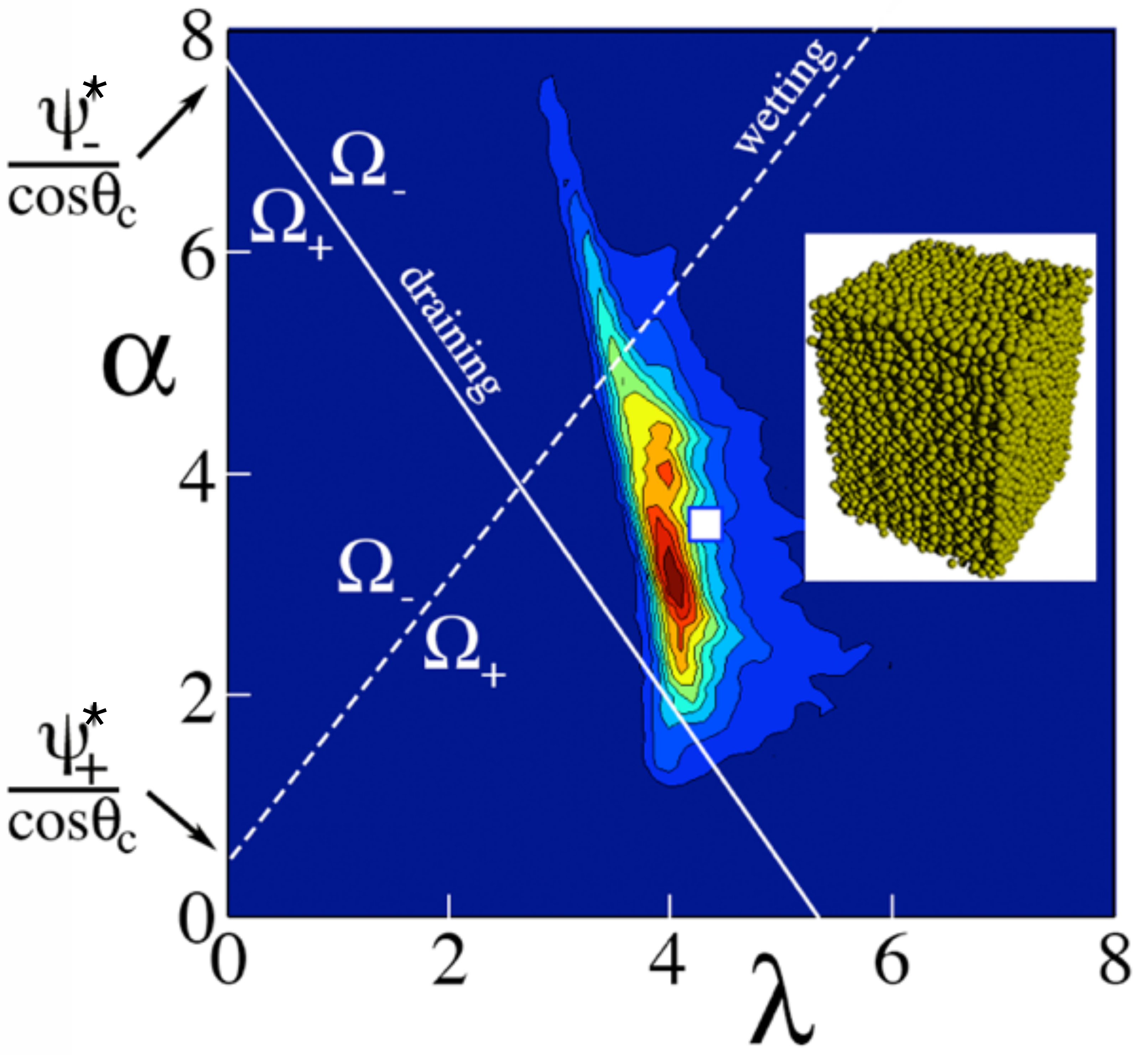


$$\lambda \equiv \frac{a_n \bar{v}_p^{1/3}}{v_p}$$

specific neck cross section

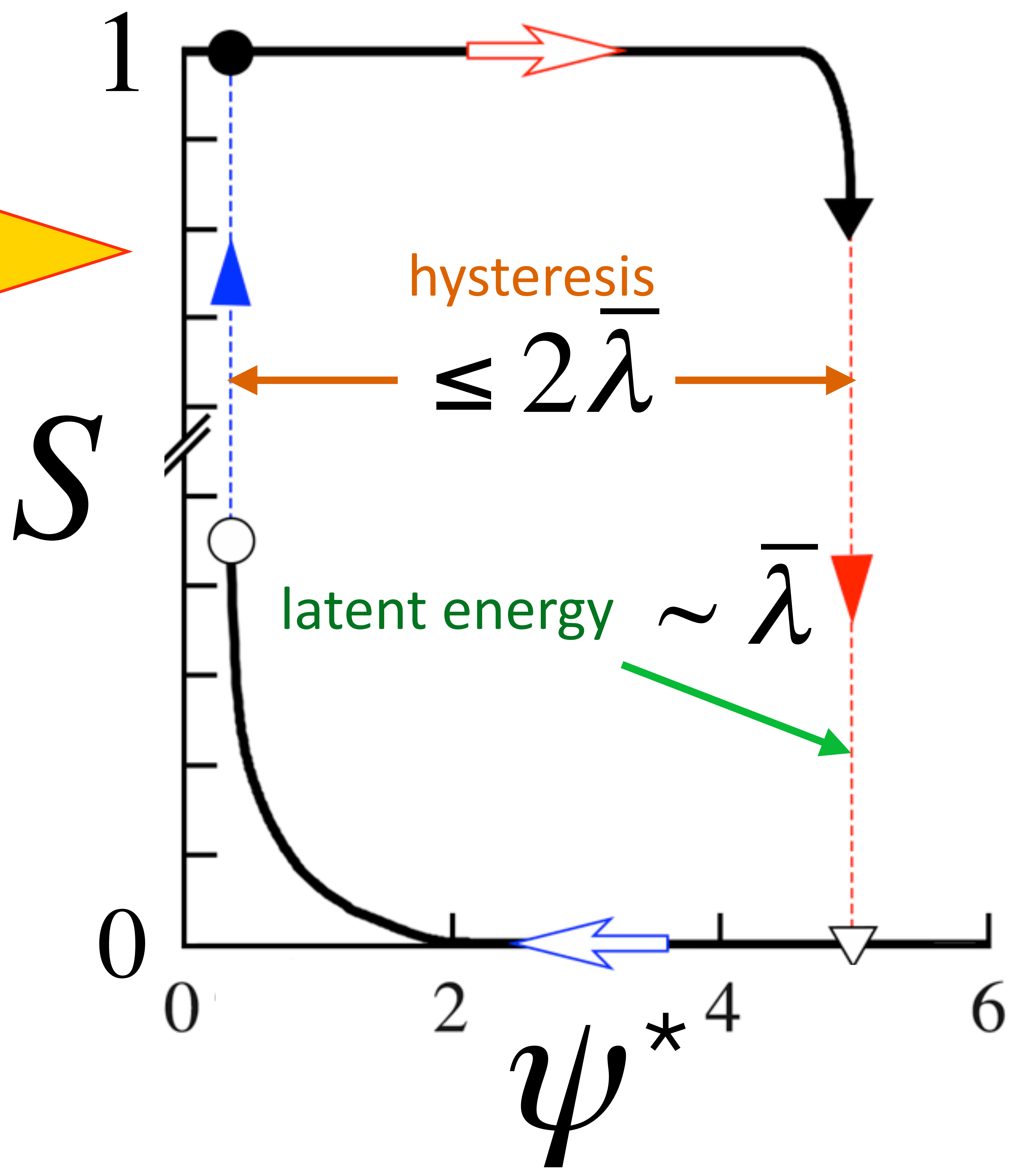
Collective interactions

distribution of α and λ

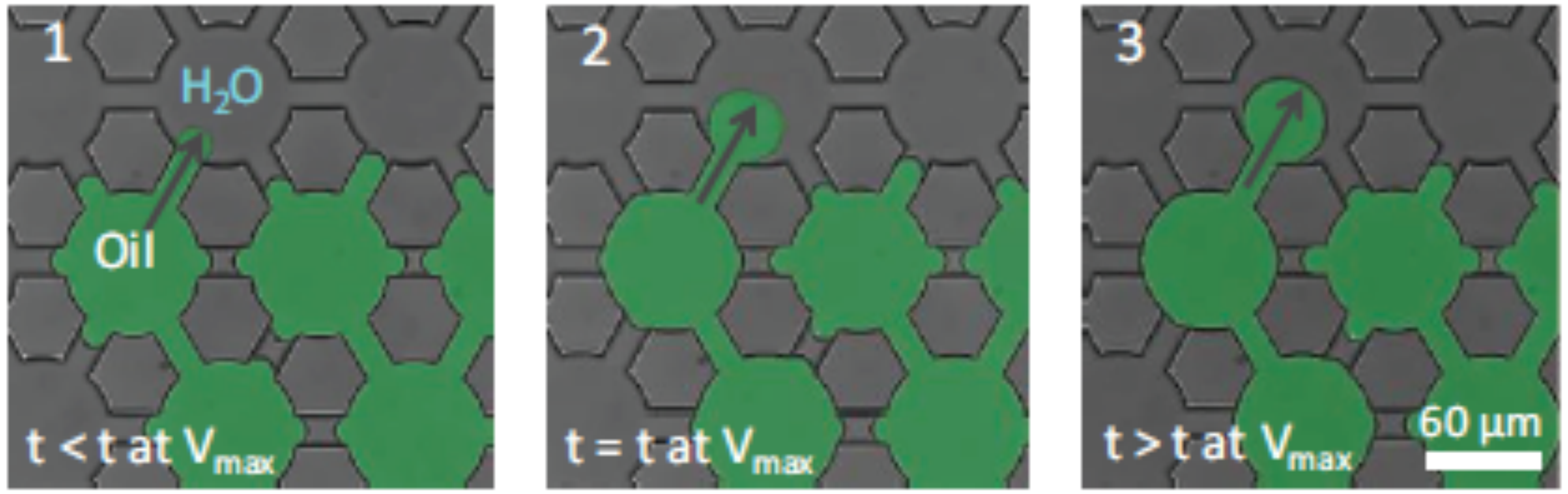


numerical simulations
of Patrick Richard

IFSTTAR

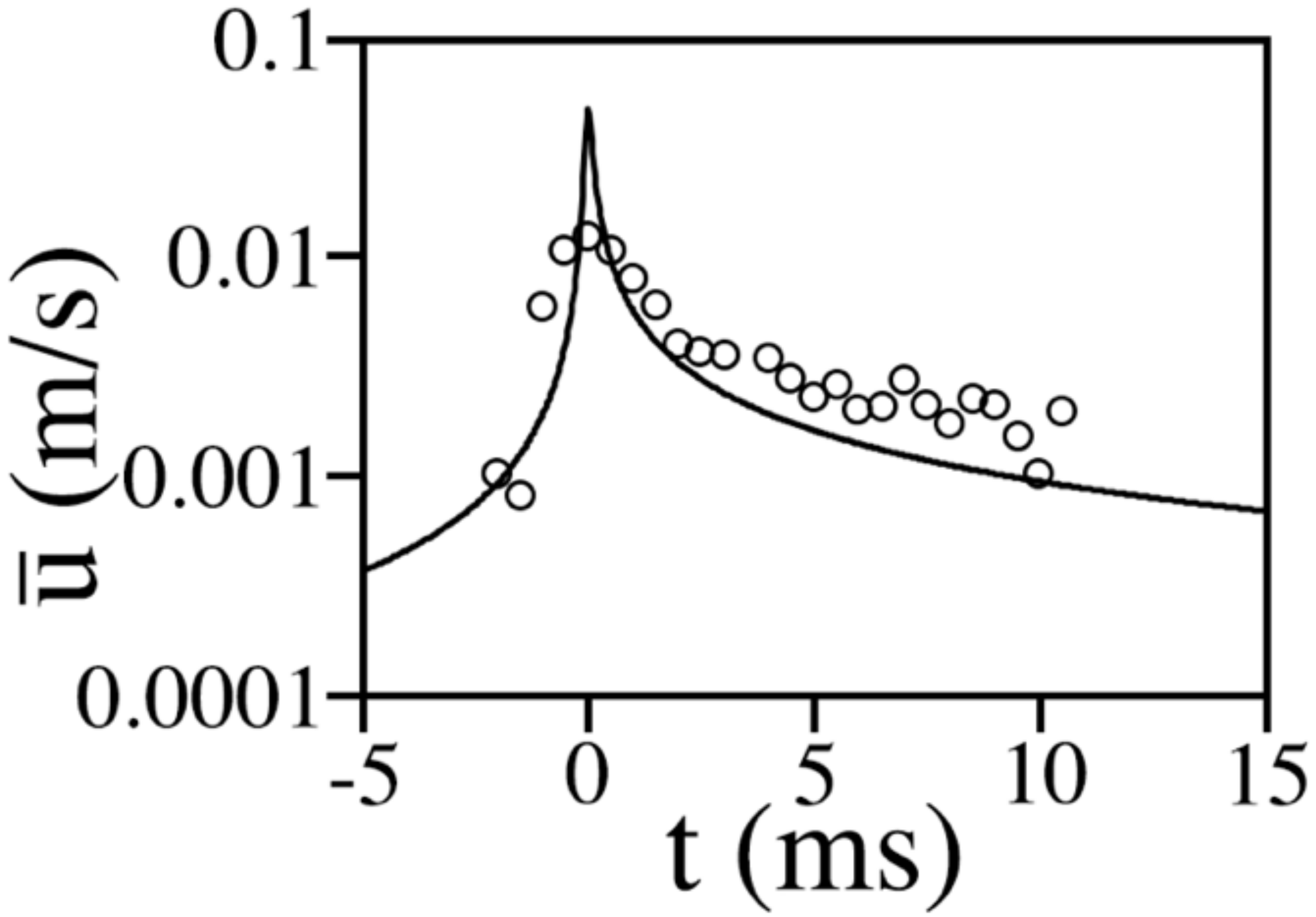


Haines jumps: latent energy dissipation

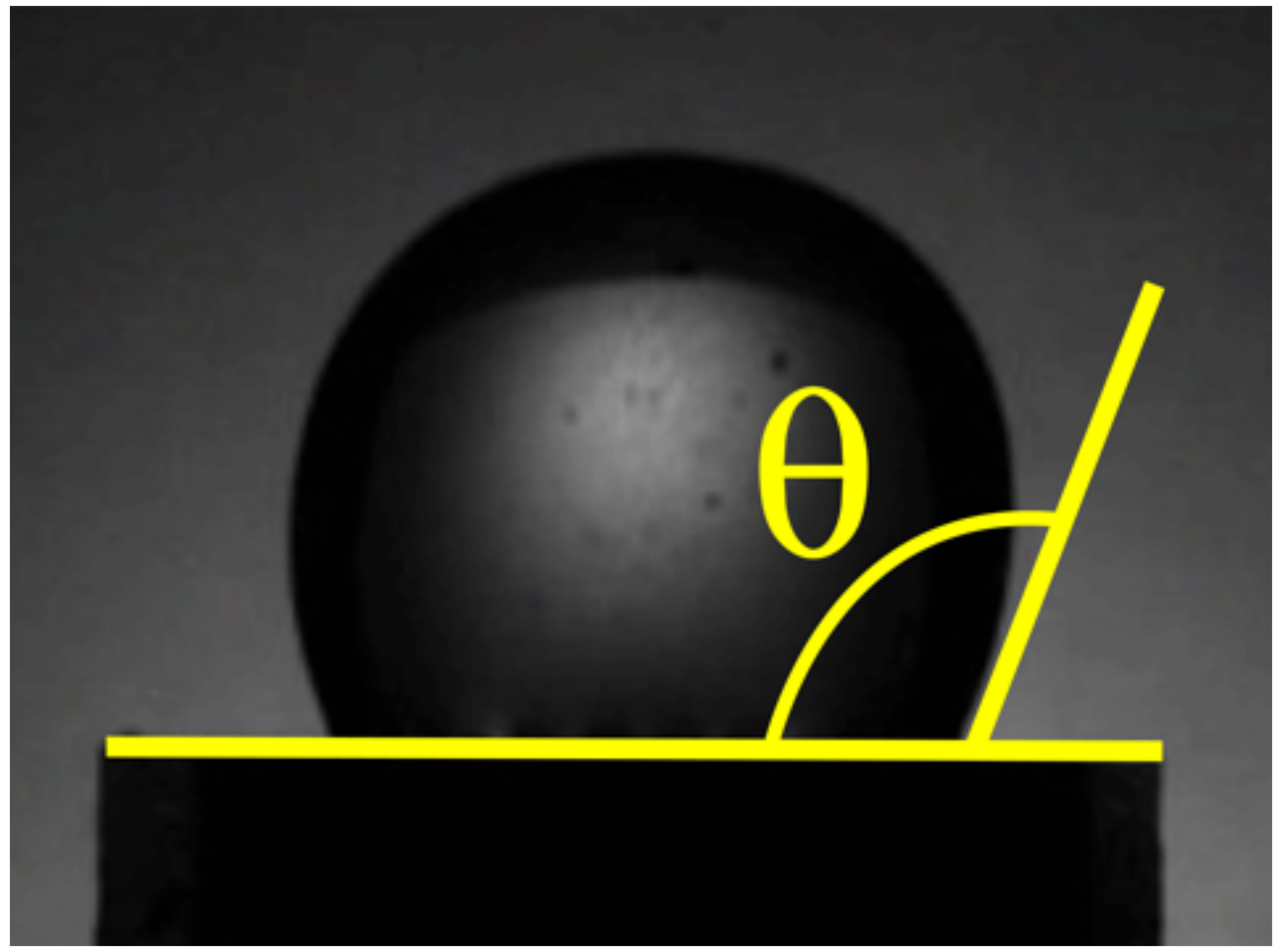


data of Armstrong & Berg, Phys. Rev E 88 (2013)

model: mass conservation and viscous dissipation of latent energy



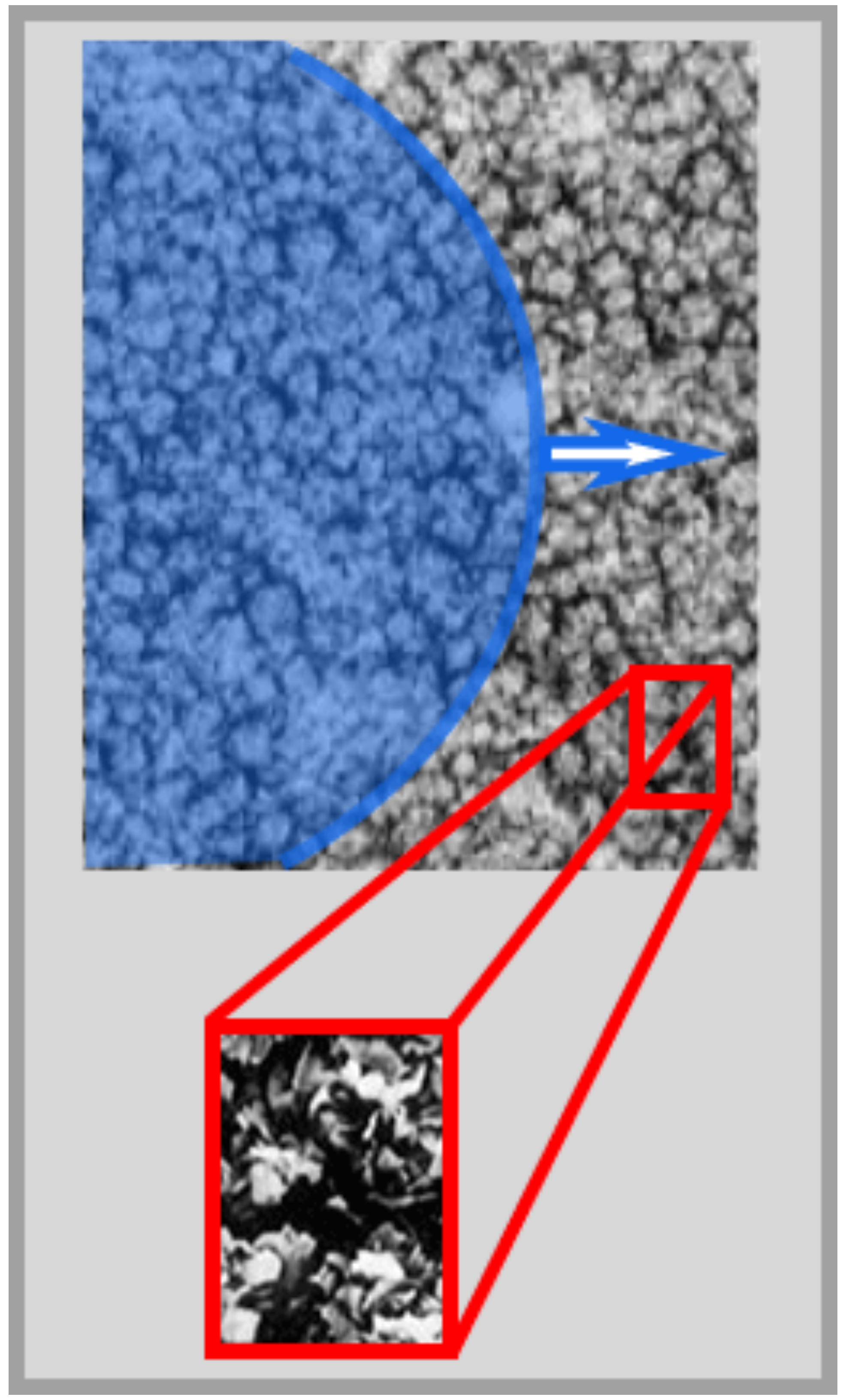
Statistical Mechanics of the Triple Gas-Solid-Liquid Contact Line



Michel Louge, Phys. Rev. E 95 (2017)

Statistical mechanics of the contact line

Predict advancing and receding contact angles
from surface cavity geometry and surface energies
with an equilibrium theory



advancing contact line

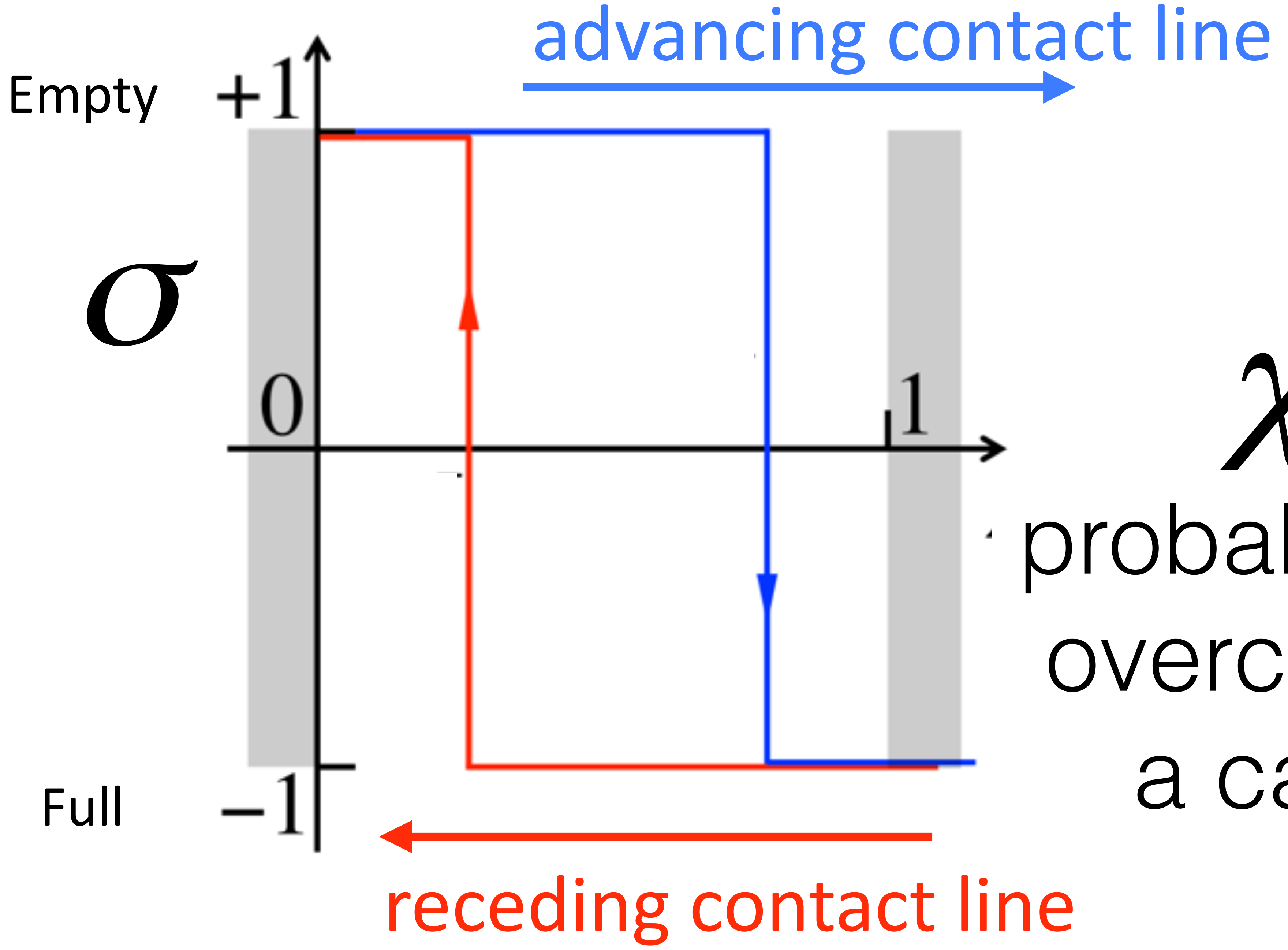
data of Shibuishi, et al (1996)

State variables

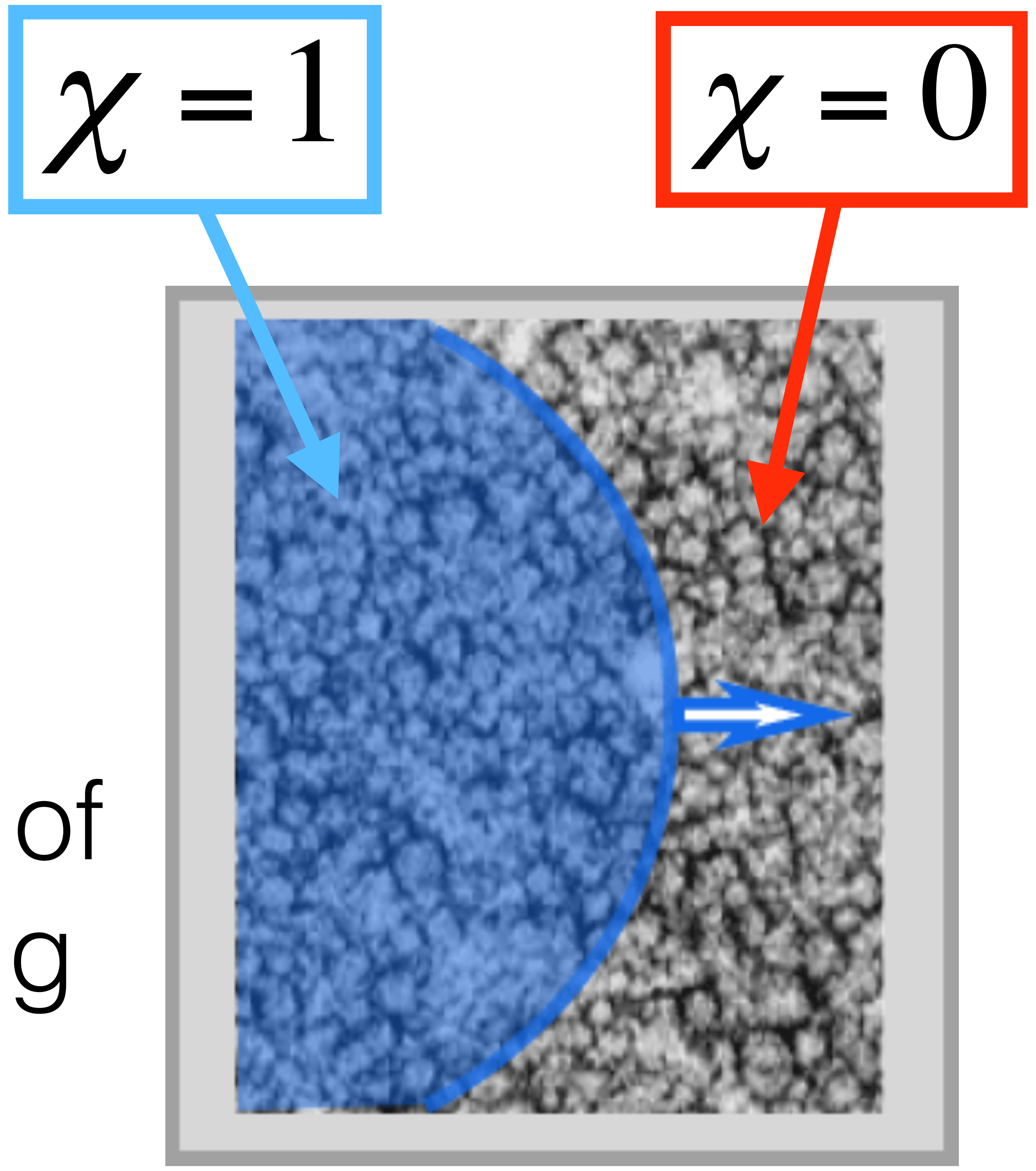
$\sigma = +1$ cavity full of gas

$\sigma = -1$ cavity full of liquid

cavity filling state

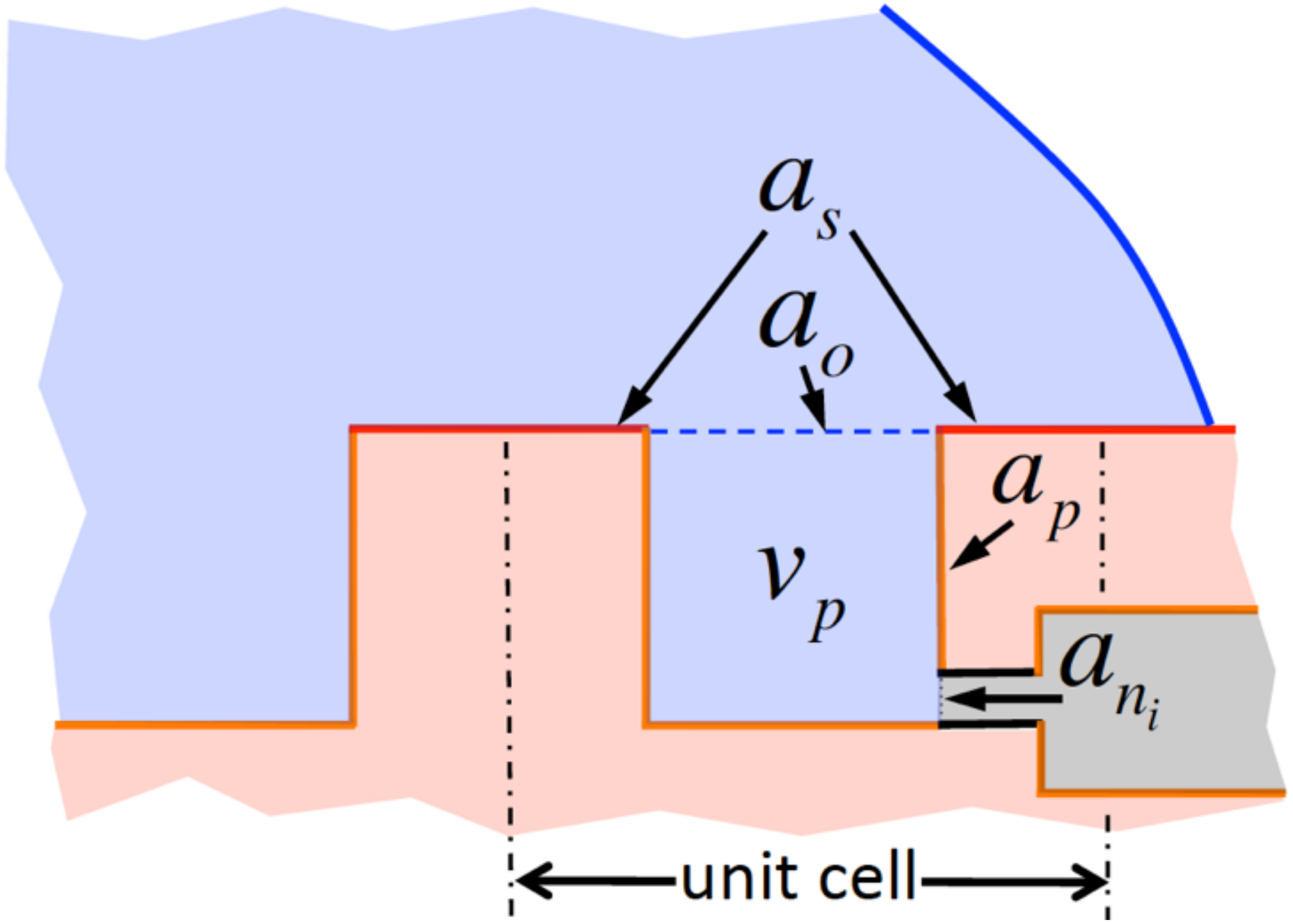


χ
probability of overcoming a cavity



data of Shibuishi, et al (1996)

Geometry of a rough surface: cavities and necks

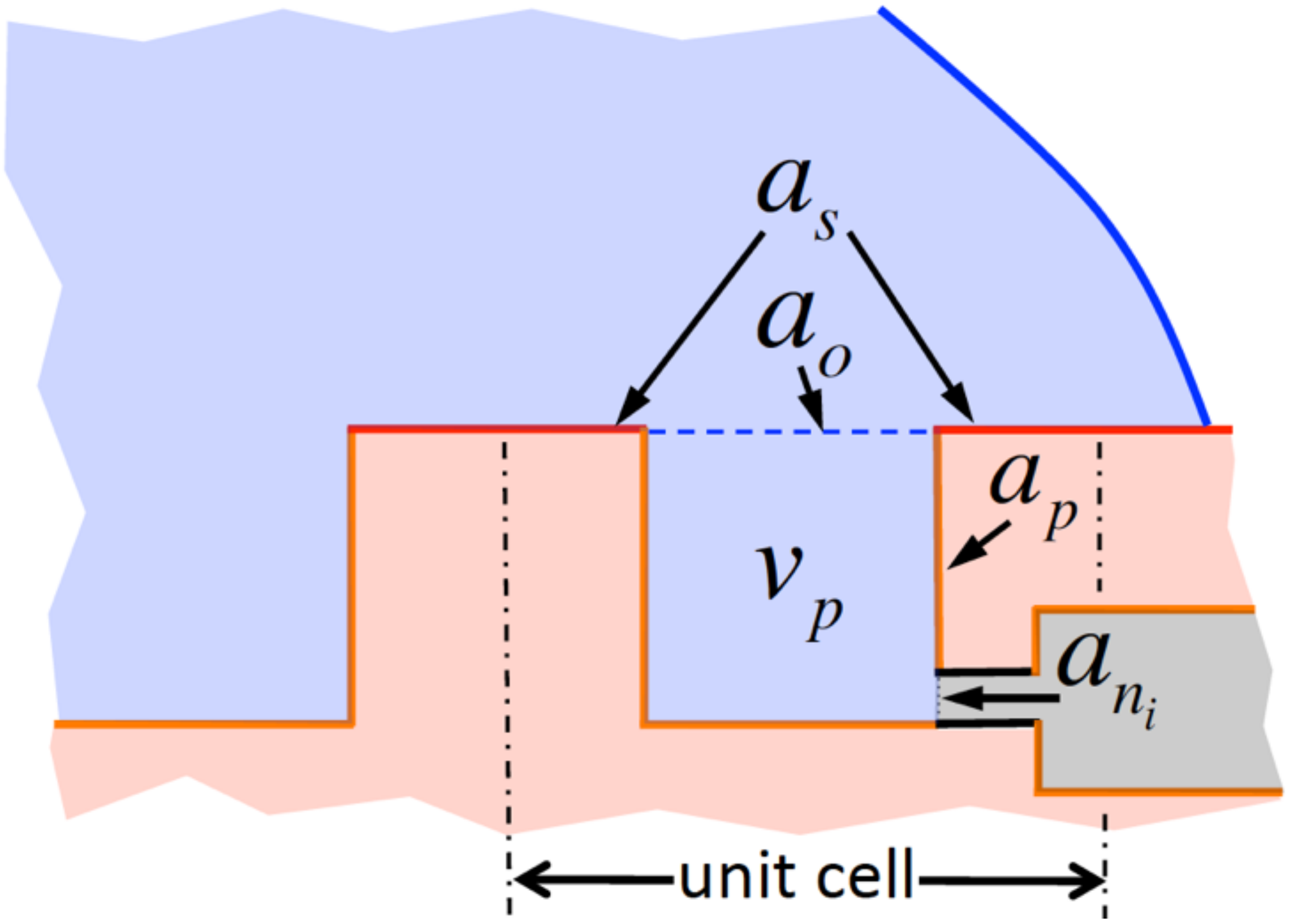


cavity volume v_p ; cavity opening area a_0 ; cavity surface area a_p

solid surface area a_s

several necks of of index (i) and cross section $a_{n,i}$

Energy of a single surface cavity



$$E = \gamma_{\ell g} \frac{\sigma}{2}\left[\left(2\chi - 1\right) a_0 + a_p \cos\theta_e - a_n \bar{\sigma}\right]$$

$$E^* \equiv \frac{E}{\bar{a}_0 \gamma_{\ell g}}$$

relative energy

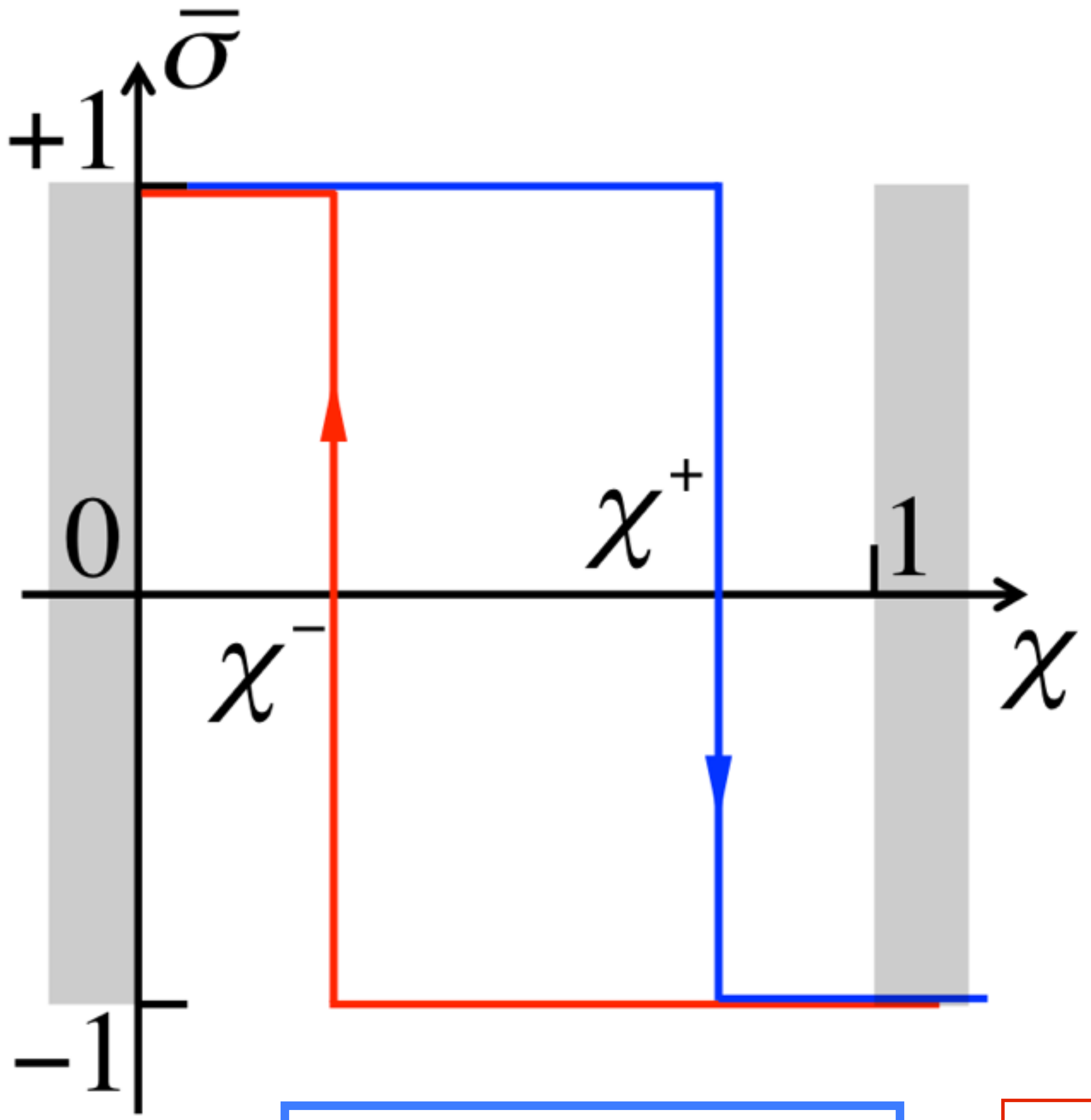
$$\alpha \equiv \frac{a_p}{\bar{a}_0}$$

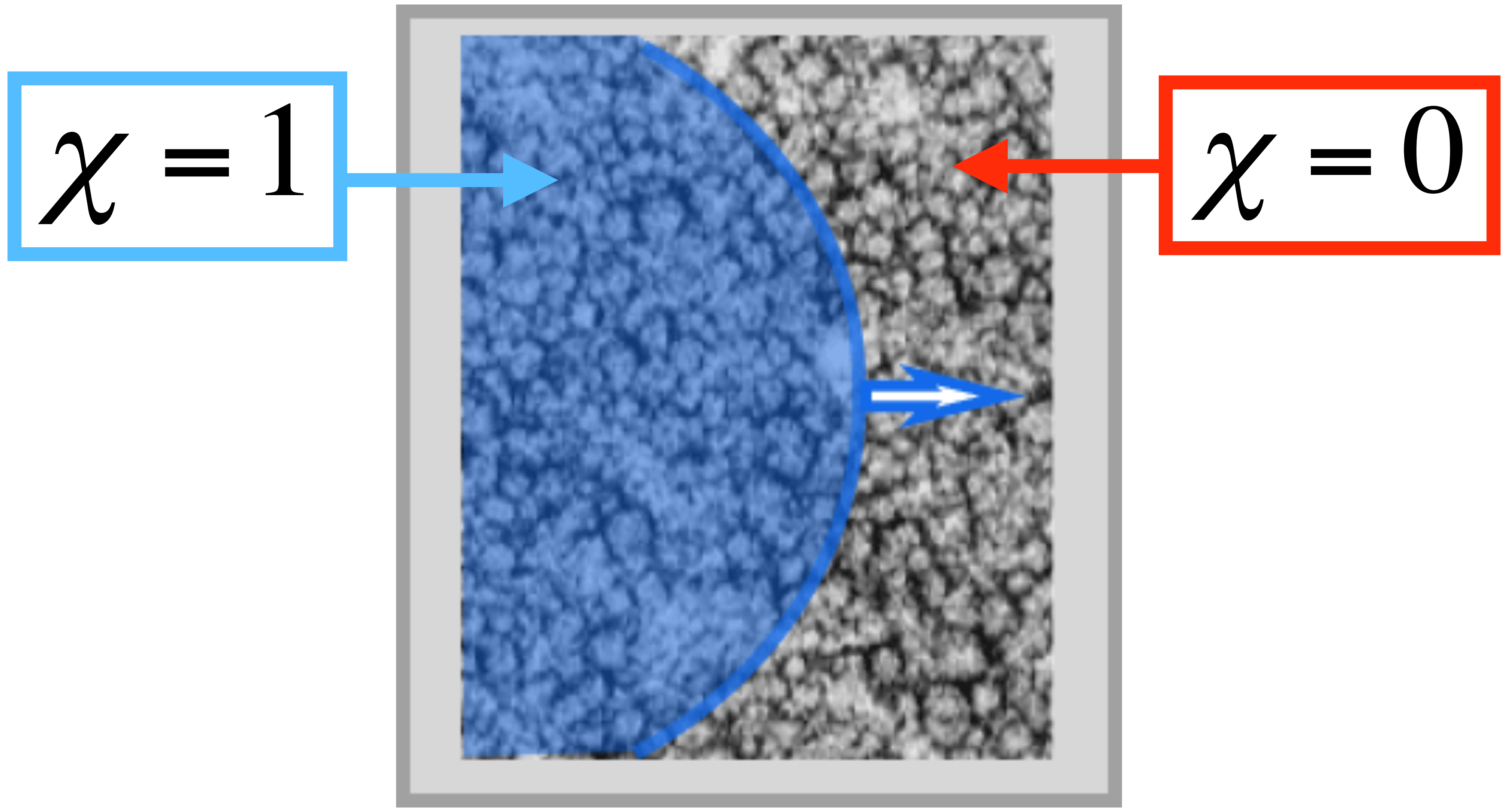
cavity area

$$\lambda \equiv \frac{a_n}{\bar{a}_0}$$

neck cross-section

First-order phase transition



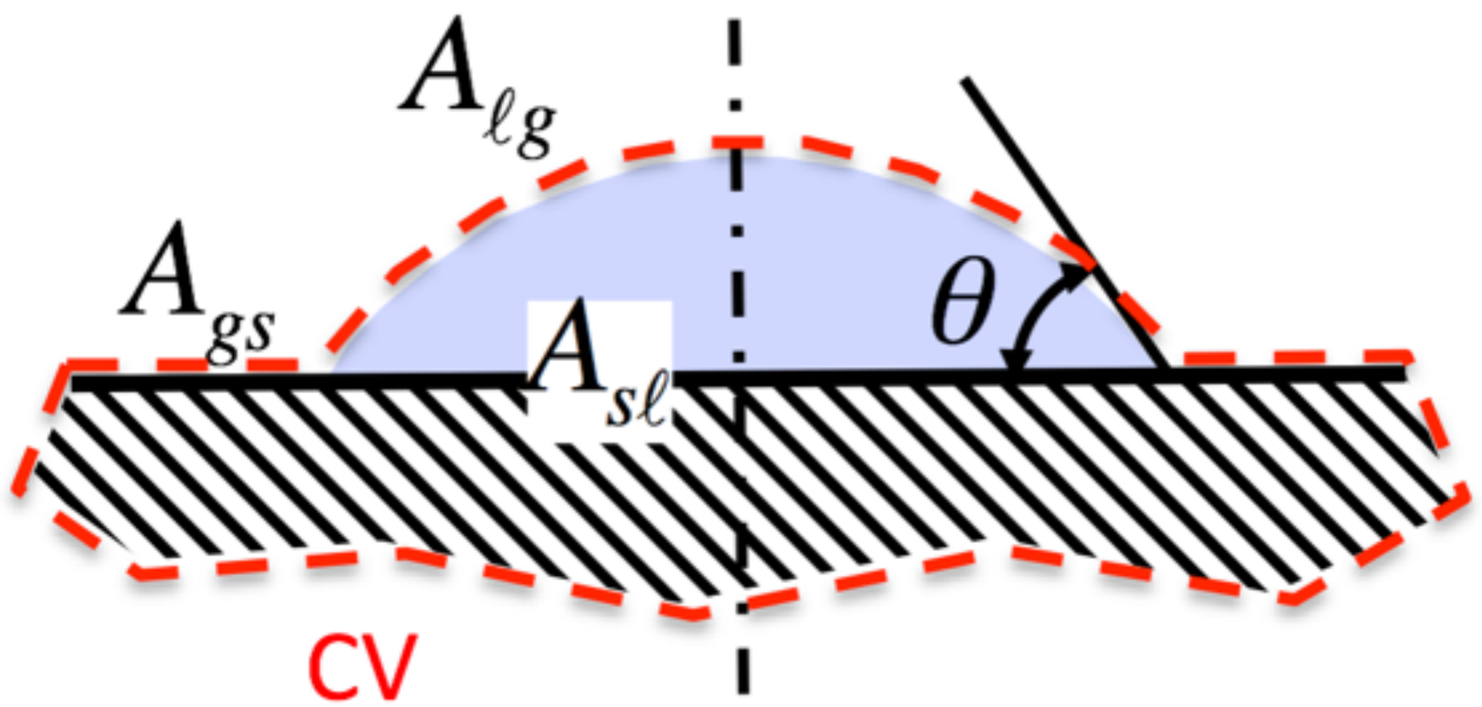


$$\Delta E^* = -\lambda$$

Latent energy

Energy required for line displacement

without surface cavities

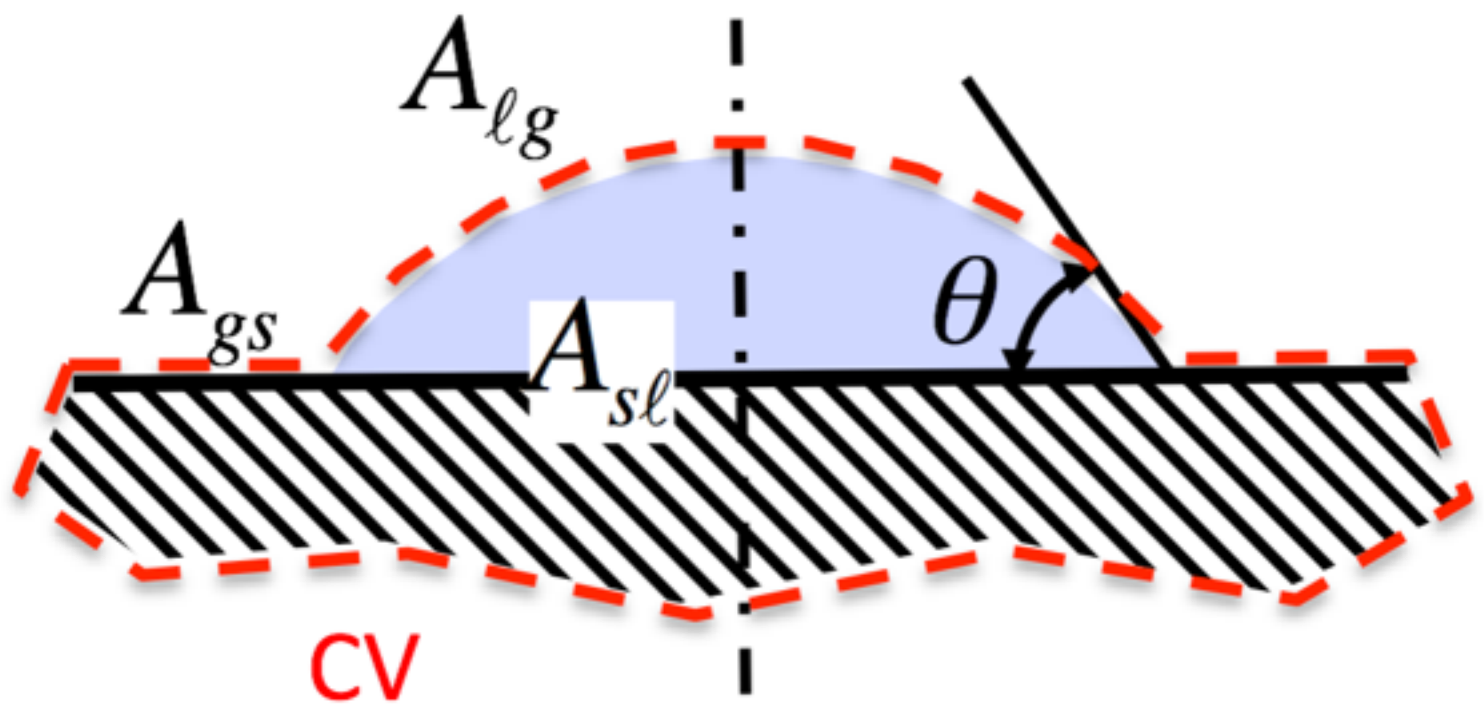


Tadmor (2004)

$$dG = \gamma_{s\ell} dA_{s\ell} + \gamma_{\ell g} dA_{\ell g} + \gamma_{gs} dA_{gs}$$

Energy required for line displacement

without surface cavities



Tadmor (2004)

$$dG = \gamma_{s\ell} dA_{s\ell} + \gamma_{\ell g} dA_{\ell g} + \gamma_{gs} dA_{gs}$$

constant volume
spherical cap

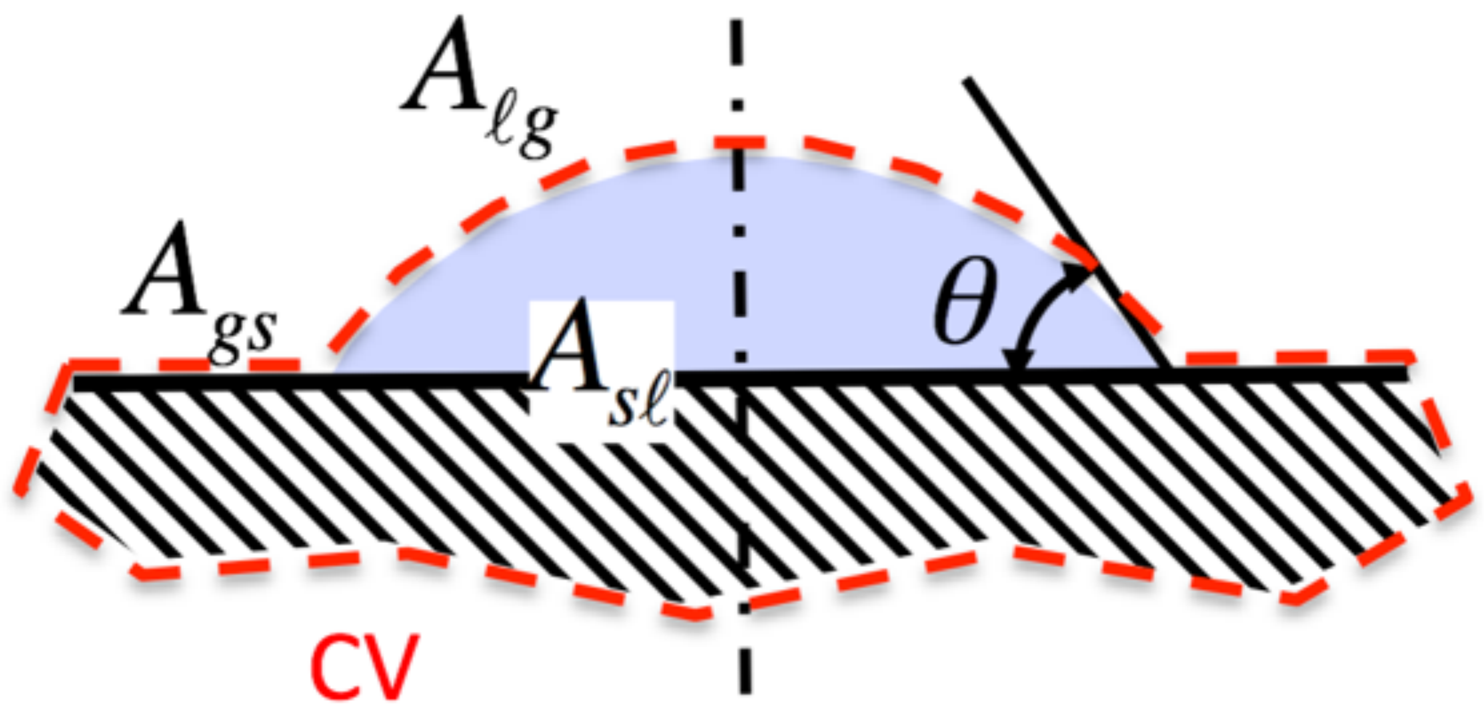
$$\frac{dA_{gs}}{dA_{s\ell}} = -1$$

$$\frac{dA_{\ell g}}{dA_{s\ell}} = \cos\theta$$

$$\cos\theta_e = \frac{\gamma_{gs} - \gamma_{s\ell}}{\gamma_{\ell g}}$$

Energy required for line displacement

without surface cavities



Tadmor (2004)

$$dG = \gamma_{s\ell} dA_{s\ell} + \gamma_{\ell g} dA_{\ell g} + \gamma_{gs} dA_{gs}$$

constant volume spherical cap

$$\frac{dA_{gs}}{dA_{s\ell}} = -1 \qquad \frac{dA_{\ell g}}{dA_{s\ell}} = \cos\theta \qquad \cos\theta_e = \frac{\gamma_{gs} - \gamma_{s\ell}}{\gamma_{\ell g}}$$

potential energy change upon incrementing $dA_{s\ell}$

$$dG = \gamma_{\ell g} dA_{s\ell} \left(\cos\theta - \cos\theta_e \right)$$

With surface cavities

Advance

$$dG = \gamma_{\ell g} \, dA_{s\ell} \left(\cos\theta - \cos\theta_a \right)$$

$$\cos\theta_a = \left(1 - \varepsilon\right)\cos\theta_e - \varepsilon \int_0^1 \bar{\sigma} \, d\chi + \varepsilon \Delta E$$

checkered solid surface

cavity filling

latent energy

Advancing vs receding line

Advance

$$dG = \gamma_{\ell g} dA_{s\ell} \left(\cos\theta - \cos\theta_a \right)$$

$$\cos\theta_a = \left(1-\varepsilon\right)\cos\theta_e - \varepsilon \int_0^1 \bar{\sigma}\, d\chi + \varepsilon\Delta E$$

different sign

Recession

$$dG = \gamma_{\ell g} dA_{s\ell} \left(\cos\theta - \cos\theta_r \right)$$

$$\cos\theta_r = \left(1-\varepsilon\right)\cos\theta_e - \varepsilon \int_0^1 \bar{\sigma}\, d\chi - \varepsilon\Delta E$$

latent energy

Six distinct regimes

regime	χ_c^+	χ_c^-	$\cos\theta_a - (1-\epsilon)\cos\theta_e$ (Advancing angle)	$\cos\theta_r - (1-\epsilon)\cos\theta_e$ (Receding angle)
I	$\in [0,1]$	$\in [0,1]$	$+\epsilon(\alpha\cos\theta_e - 2\lambda)$	$+\epsilon(\alpha\cos\theta_e + 2\lambda)$
II	$\in [0,1]$	< 0	$+\epsilon(\alpha\cos\theta_e - 2\lambda)$	$+\epsilon$
III	> 1	$\in [0,1]$	$-\epsilon$	$+\epsilon(\alpha\cos\theta_e + 2\lambda)$
IV	< 0	< 0	$+\epsilon$	$+\epsilon$
V	> 1	< 0	$-\epsilon$	$+\epsilon$
VI	> 1	> 1	$-\epsilon$	$-\epsilon$

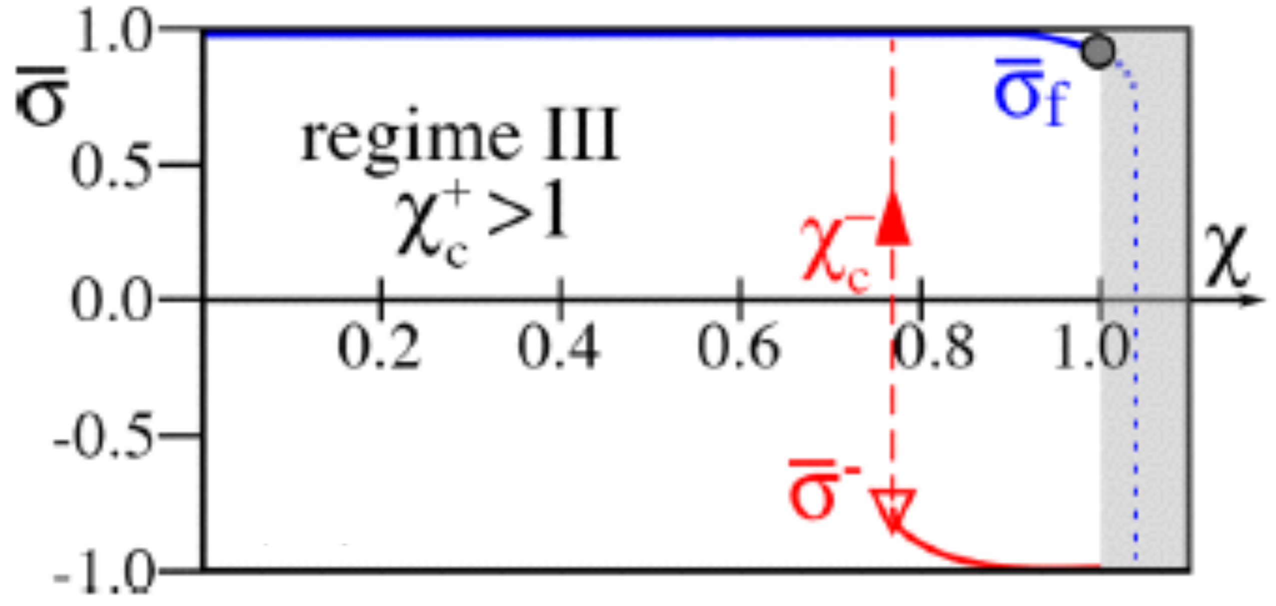
Each regime allows zero, one or two transitions.

Six distinct regimes

Advancing angle — Receding angle

regime	χ_c^+	χ_c^-	$\cos\theta_a - (1-\epsilon)\cos\theta_e$	$\cos\theta_r - (1-\epsilon)\cos\theta_e$
I	$\in [0,1]$	$\in [0,1]$	$+\epsilon(\alpha\cos\theta_e - 2\lambda)$	$+\epsilon(\alpha\cos\theta_e + 2\lambda)$
II	$\in [0,1]$	< 0	$+\epsilon(\alpha\cos\theta_e - 2\lambda)$	$+\epsilon$
III	> 1	$\in [0,1]$	$-\epsilon$	$+\epsilon(\alpha\cos\theta_e + 2\lambda)$
IV	< 0	< 0	$+\epsilon$	$+\epsilon$
V	> 1	< 0	$-\epsilon$	$+\epsilon$
VI	> 1	> 1	$-\epsilon$	$-\epsilon$

Example: regime III



No phase transition with advancing line

Six distinct regimes

			Advancing angle	Receding angle
regime	χ_c^+	χ_c^-	$\cos\theta_a - (1-\epsilon)\cos\theta_e$	$\cos\theta_r - (1-\epsilon)\cos\theta_e$
I	$\in [0,1]$	$\in [0,1]$	$+\epsilon(\alpha\cos\theta_e - 2\lambda)$	$+\epsilon(\alpha\cos\theta_e + 2\lambda)$
II	$\in [0,1]$	< 0	$+\epsilon(\alpha\cos\theta_e - 2\lambda)$	$+\epsilon$
III	> 1	$\in [0,1]$	$-\epsilon$	$+\epsilon(\alpha\cos\theta_e + 2\lambda)$
IV	< 0	< 0	$+\epsilon$	$+\epsilon$
V	> 1	< 0	$-\epsilon$	$+\epsilon$
VI	> 1	> 1	$-\epsilon$	$-\epsilon$

allowed transitions

Six distinct regimes

Advancing angle   Receding angle

regime	χ_c^+	χ_c^-	$\cos\theta_a - (1-\epsilon)\cos\theta_e$	$\cos\theta_r - (1-\epsilon)\cos\theta_e$
I	$\in [0,1]$	$\in [0,1]$	$+\epsilon(\alpha\cos\theta_e - 2\lambda)$	$+\epsilon(\alpha\cos\theta_e + 2\lambda)$
II	$\in [0,1]$	< 0	$+\epsilon(\alpha\cos\theta_e - 2\lambda)$	$+\epsilon$
III	> 1	$\in [0,1]$	$-\epsilon$	$+\epsilon(\alpha\cos\theta_e + 2\lambda)$
IV	< 0	< 0	$+\epsilon$	$+\epsilon$
V	> 1	< 0	$-\epsilon$	$+\epsilon$
VI	> 1	> 1	$-\epsilon$	$-\epsilon$

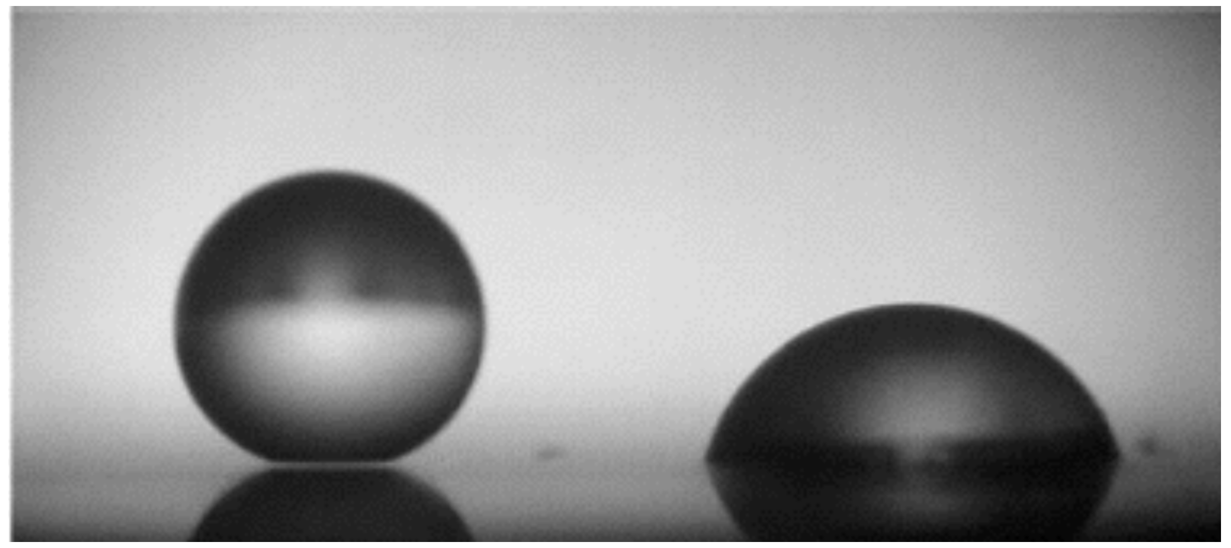
"Cassie-Baxter state" (1944)

Six distinct regimes

Advancing angle — Receding angle

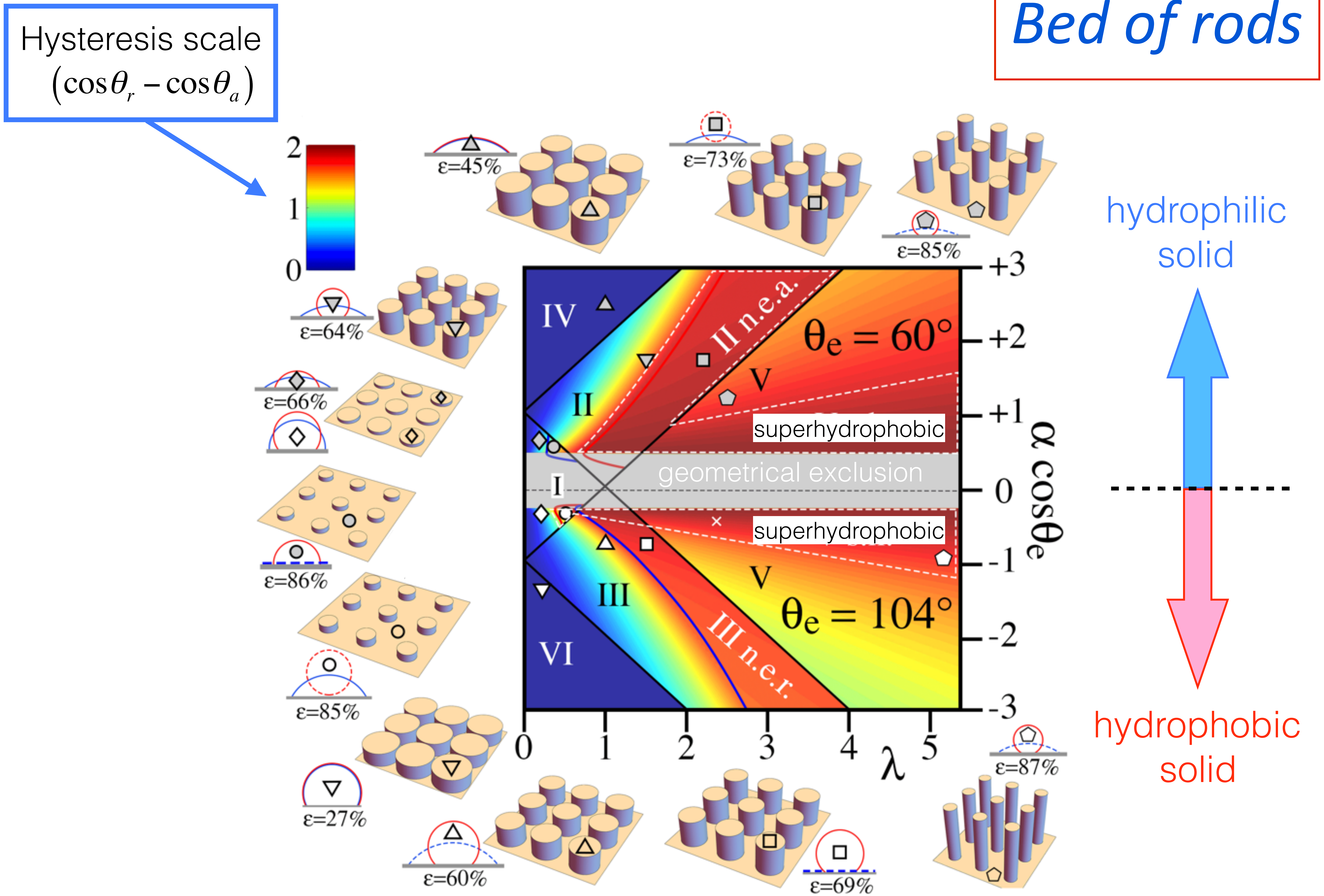
regime	χ_c^+	χ_c^-	$\cos\theta_a - (1-\epsilon)\cos\theta_e$	$\cos\theta_r - (1-\epsilon)\cos\theta_e$
I	$\in [0,1]$	$\in [0,1]$	$+\epsilon(\alpha\cos\theta_e - 2\lambda)$	$+\epsilon(\alpha\cos\theta_e + 2\lambda)$
II	$\in [0,1]$	< 0	$+\epsilon(\alpha\cos\theta_e - 2\lambda)$	$+\epsilon$
III	> 1	$\in [0,1]$	$-\epsilon$	$+\epsilon(\alpha\cos\theta_e + 2\lambda)$
IV	< 0	< 0	$+\epsilon$	$+\epsilon$
V	> 1	< 0	$-\epsilon$	$+\epsilon$
VI	> 1	> 1	$-\epsilon$	$-\epsilon$

'Metastable' states: cavities do not fill spontaneously before recession



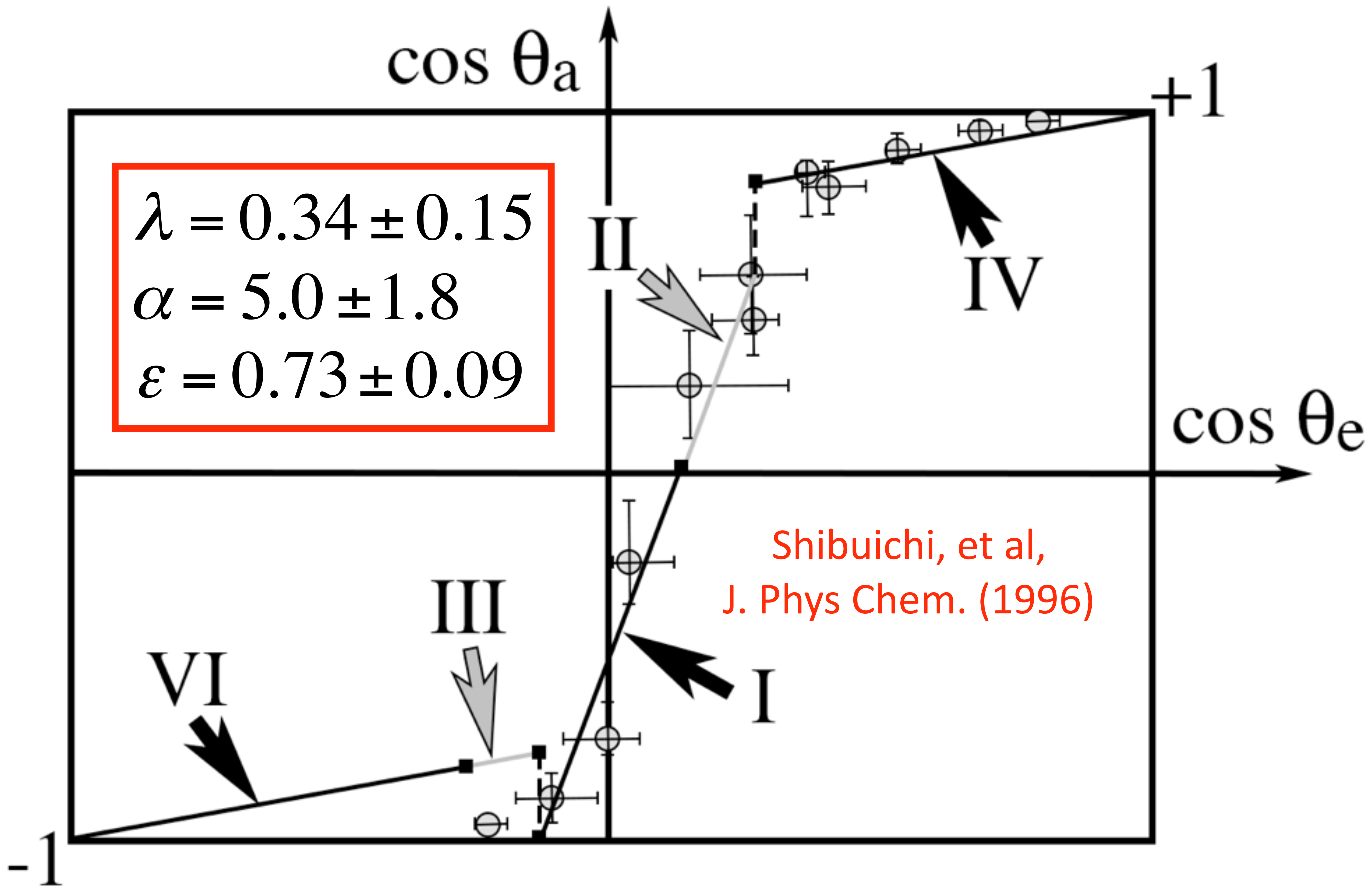
Callies and Quéré, Soft Matter (2005)

Bed of rods



Hysteresis scale
$(\cos\theta_r - \cos\theta_a)$
2
1
0
ε=45%
ε=73%
ε=85%
ε=64%
ε=66%
ε=86%
ε=85%
ε=27%
ε=60%
ε=69%
ε=87%
IV
II
II n.e.a.
V
$\theta_e = 60°$
superhydrophobic
geometrical exclusion
I
superhydrophobic
III
V
$\theta_e = 104°$
III n.e.r.
VI
+3
+2
+1
0
-1
-2
-3
$\alpha \cos\theta_e$
0
1
2
3
4
5
λ
hydrophilic
solid
hydrophobic
solid

Comparison with data



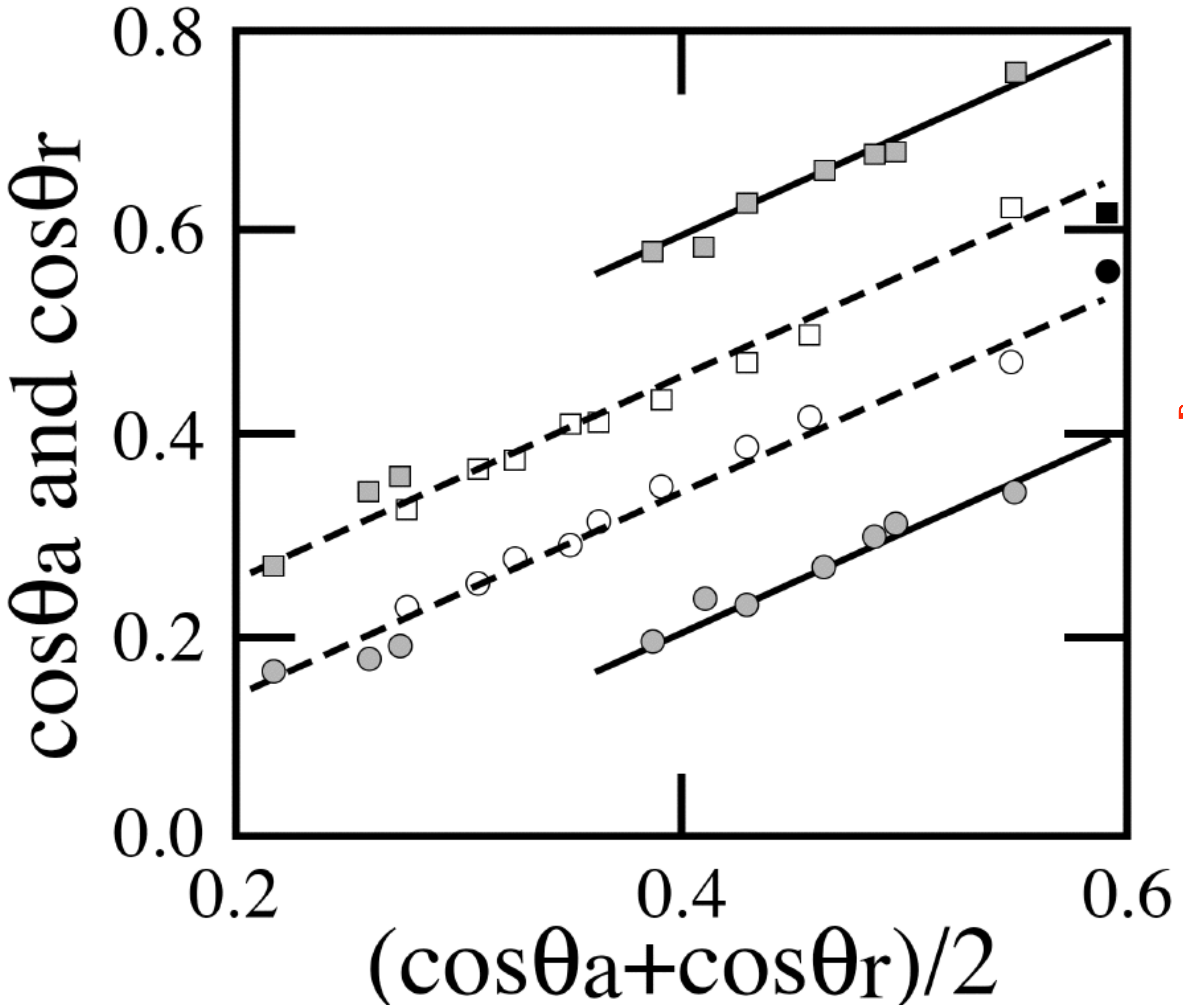
mixtures of water and 1,4 dioxane
on surfaces of alkylketene dimer (AKD)
and dialkylketone (DAK)

Comparison with data

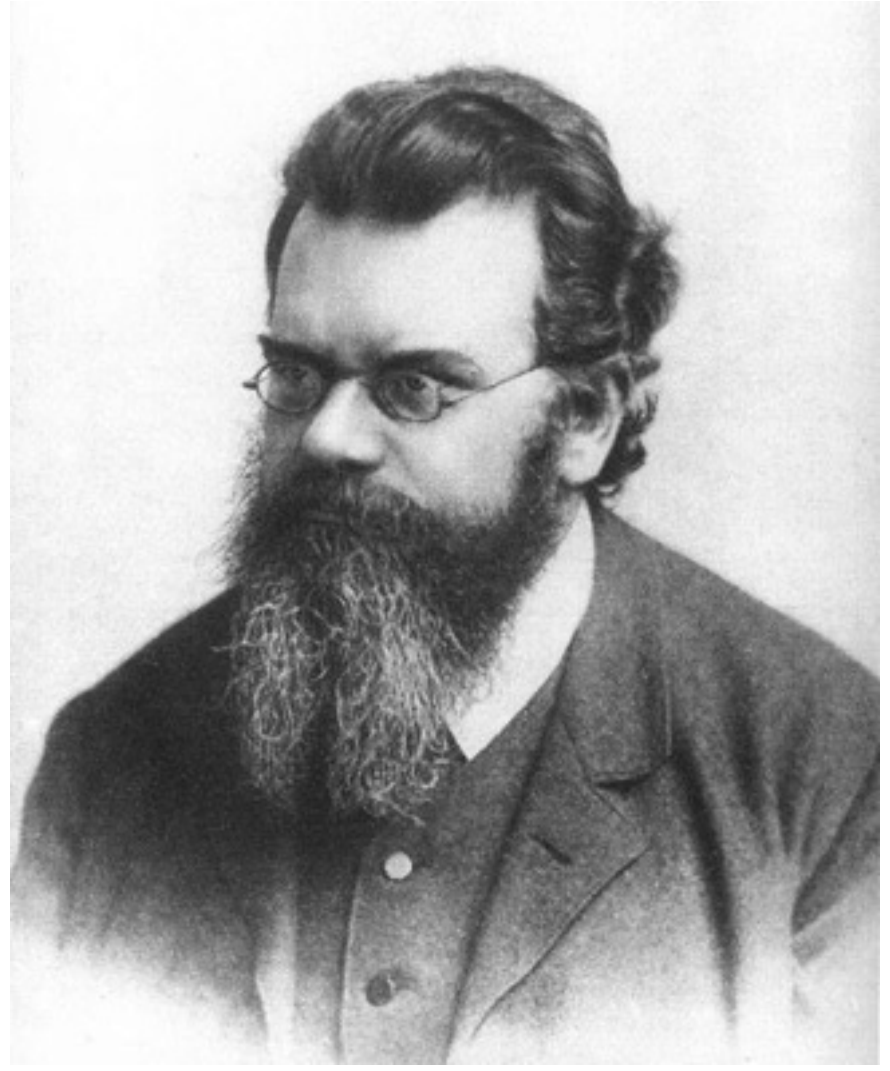
Regime I $\cos\theta_r - \cos\theta_a = 4\lambda\varepsilon$

Lam, et al, Adv. Colloid Interface Sci (2002)

FC-732-coated silicon wafer <100> surface



“Wenzel state”

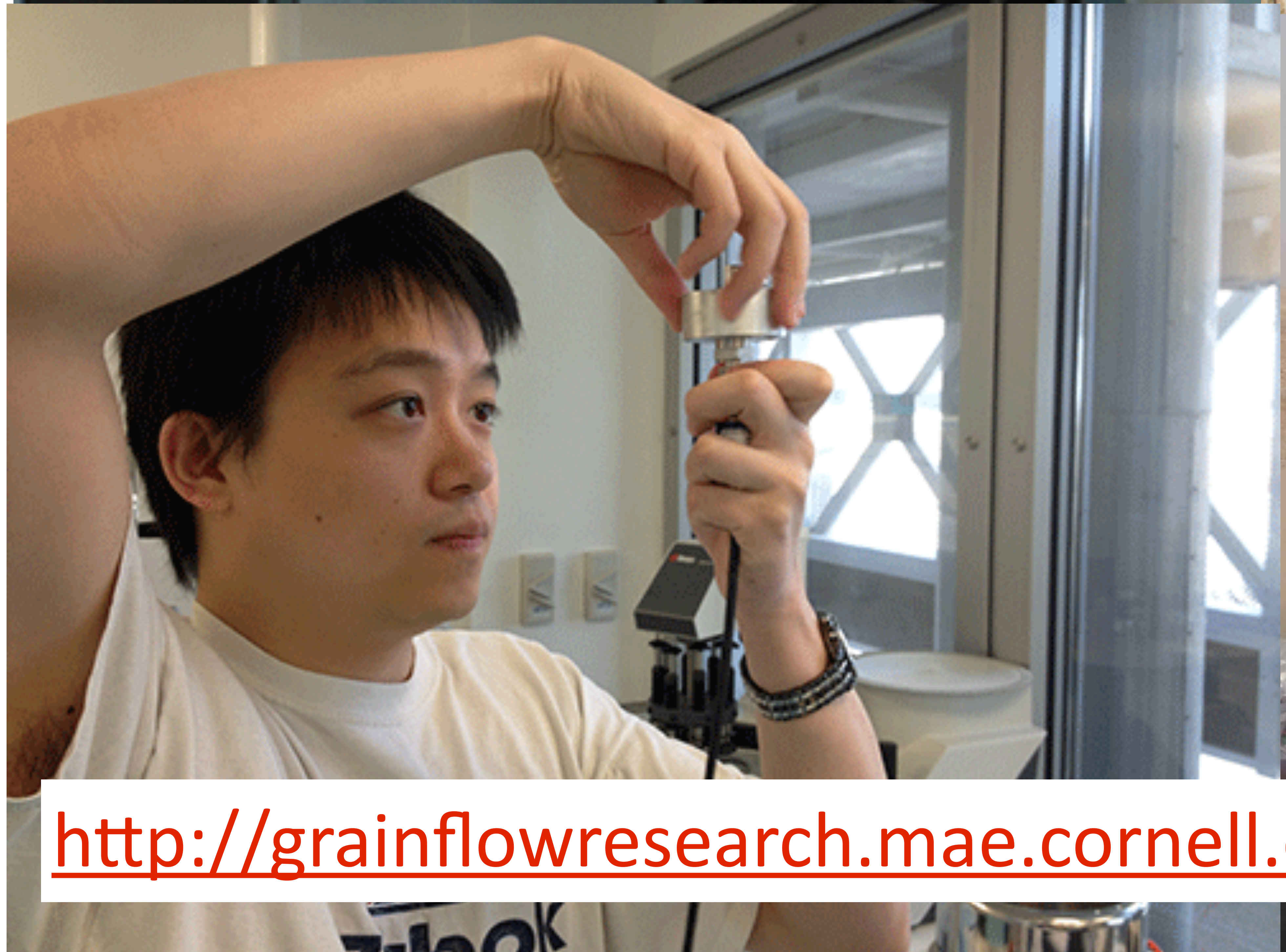


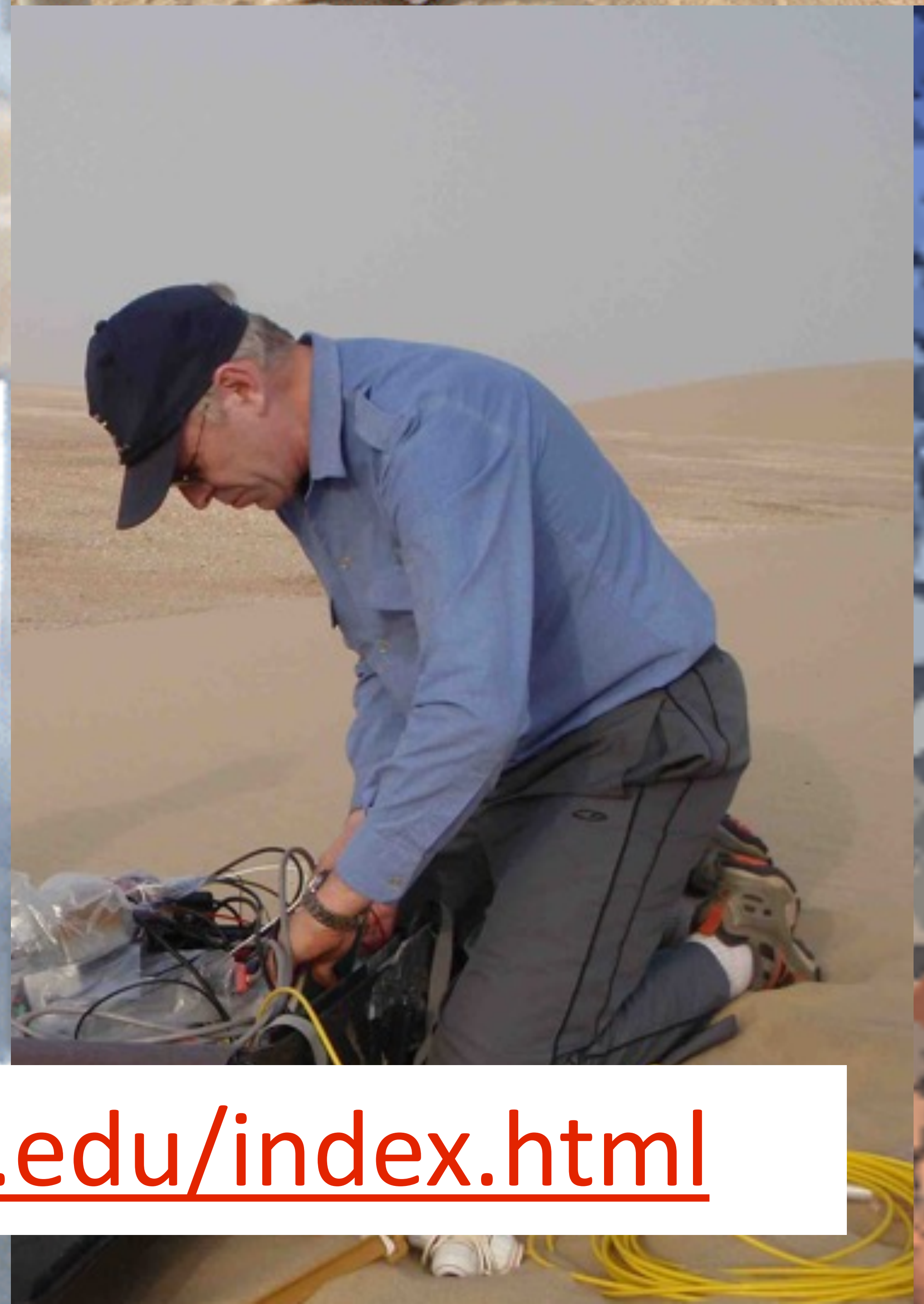
Ludwig Eduard Boltzmann
(February 20, 1844 – September 5, 1906)

Statistical Mechanics is a useful framework for analyzing capillary phenomena.

Jin Xu and Michel Louge, Phys. Rev. E 92 (2015)

Michel Louge, Phys. Rev. E 95 (2017)





http://grainflowresearch.mae.cornell.edu/index.html