The Physics of Conching Chocolate

Taking rheology from the lab to the factory

Wilson Poon

Conching chocolate is a prototypical transition from frictionally jammed solid to flowable suspension with maximal solid content

Never write title by committee!

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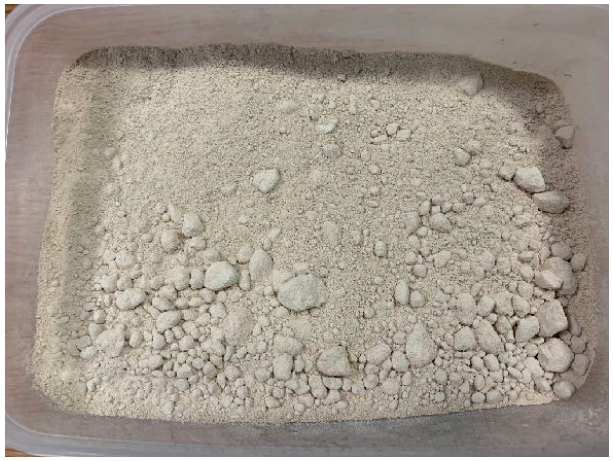
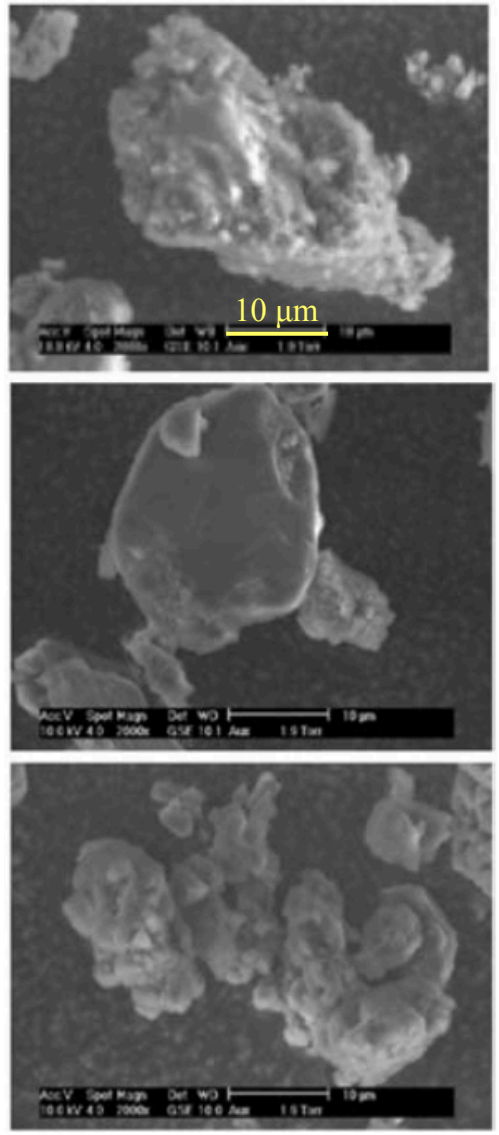
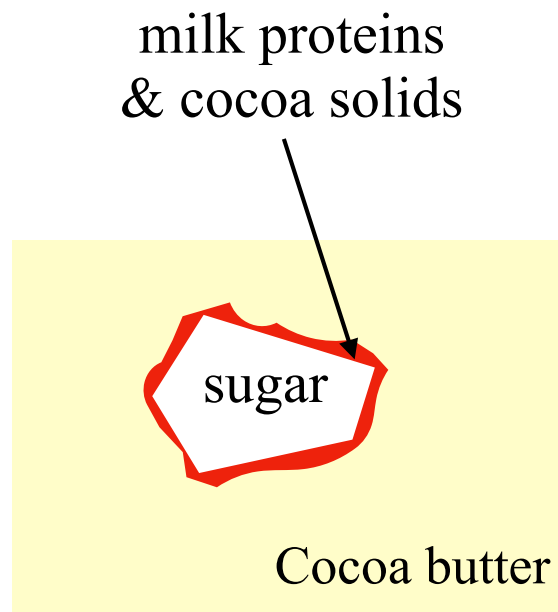
Chocolate ≈ 50% sugar suspension in 50% fat!

Chocolate crumb





Carbonell et al. *J. Food Sci. E* **69** (2004) 465

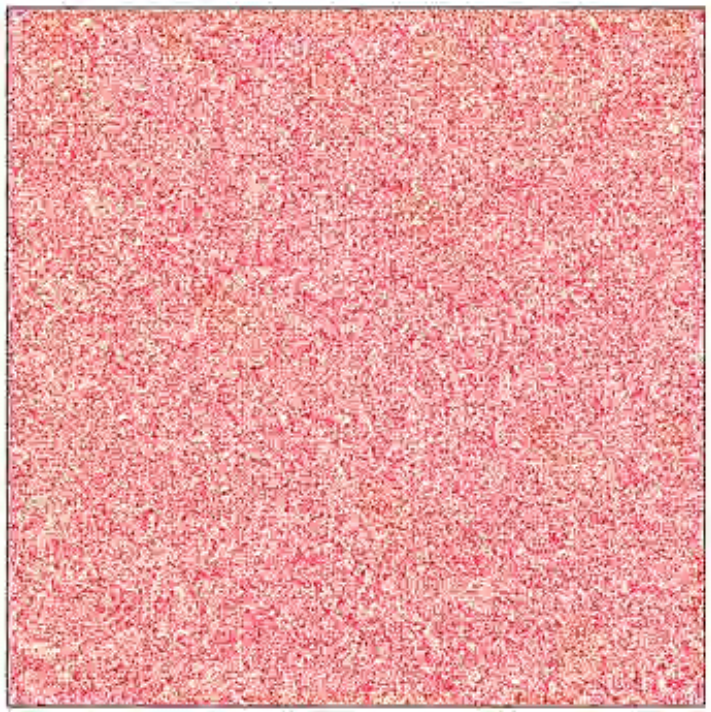


Molten chocolate (in mouth or for processing) = ***non-Brownian*** suspension

Non-Brownian suspension are *triply* nasty!

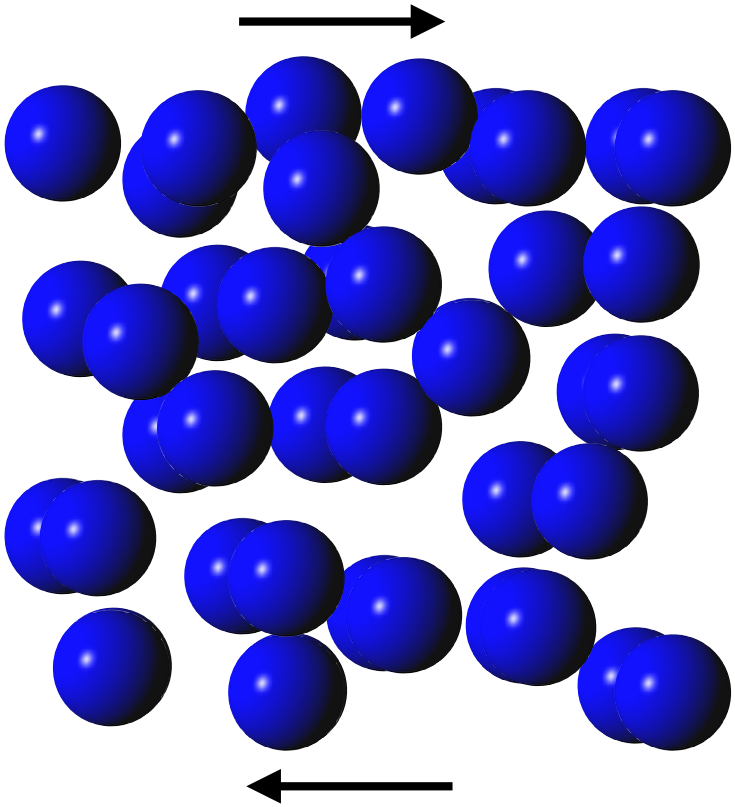
Short-range attraction

Colloids



Brownian motion → aggregation

Attractive colloids



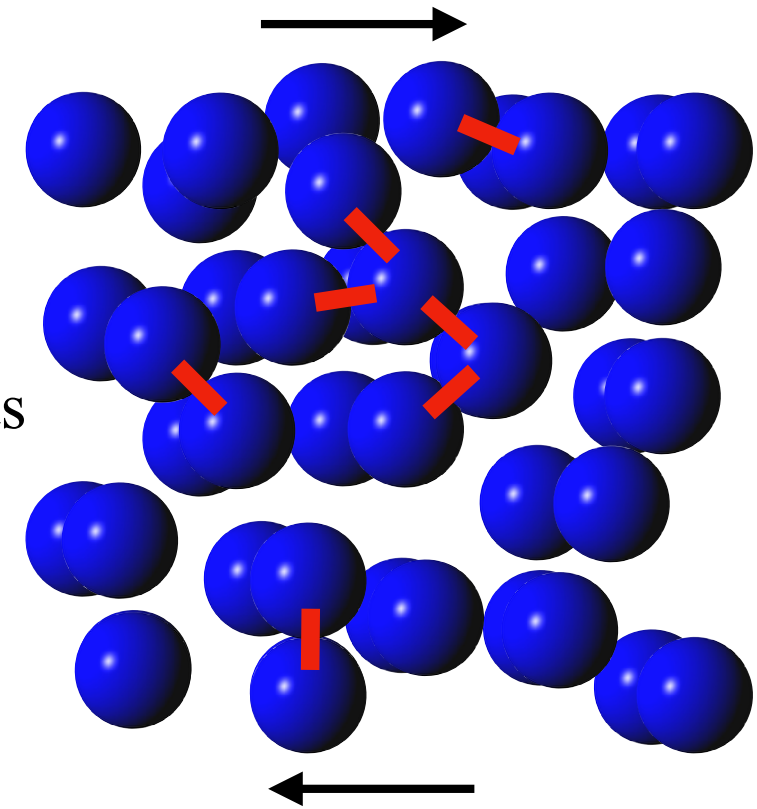
Nothing happens . . .

. . . until we shear it!

Nastiness (1): expect *memory* and therefore *history dependence*!

"Nothing in suspension rheology makes sense except in the light of particle contacts."
Chris Ness (2019)

= particle contacts



Nastiness (2): *surface details* matter!

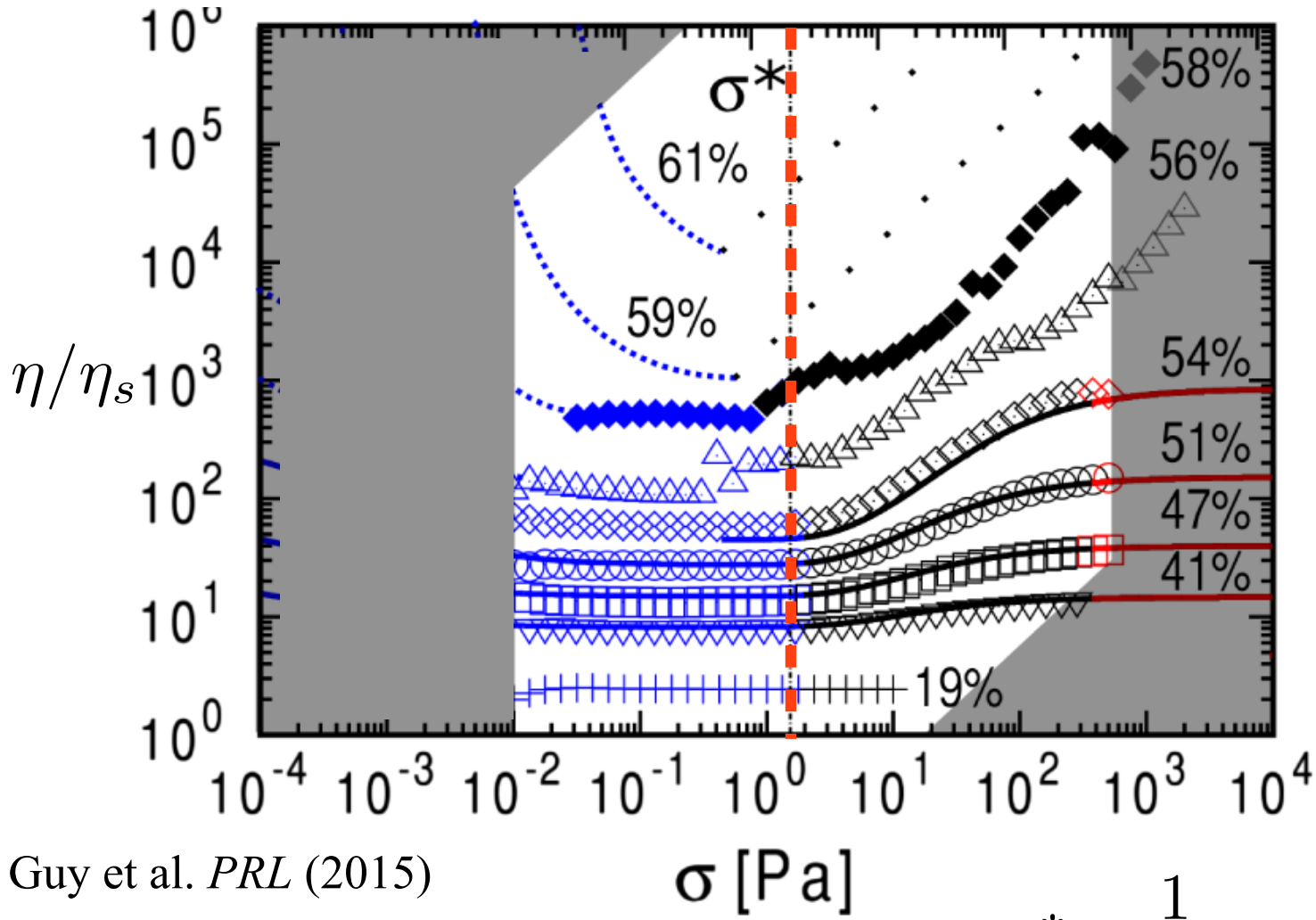
Nastiness (3): *sensitivity* to batch, environment, etc.!

First: review of (relatively) recent advances in *nB*-suspension rheology

Typical phenomenology for *nB*-suspensions of *hard* particles

Cornstarch
Silica
Calcite

Shear thickening starts at fixed σ^*

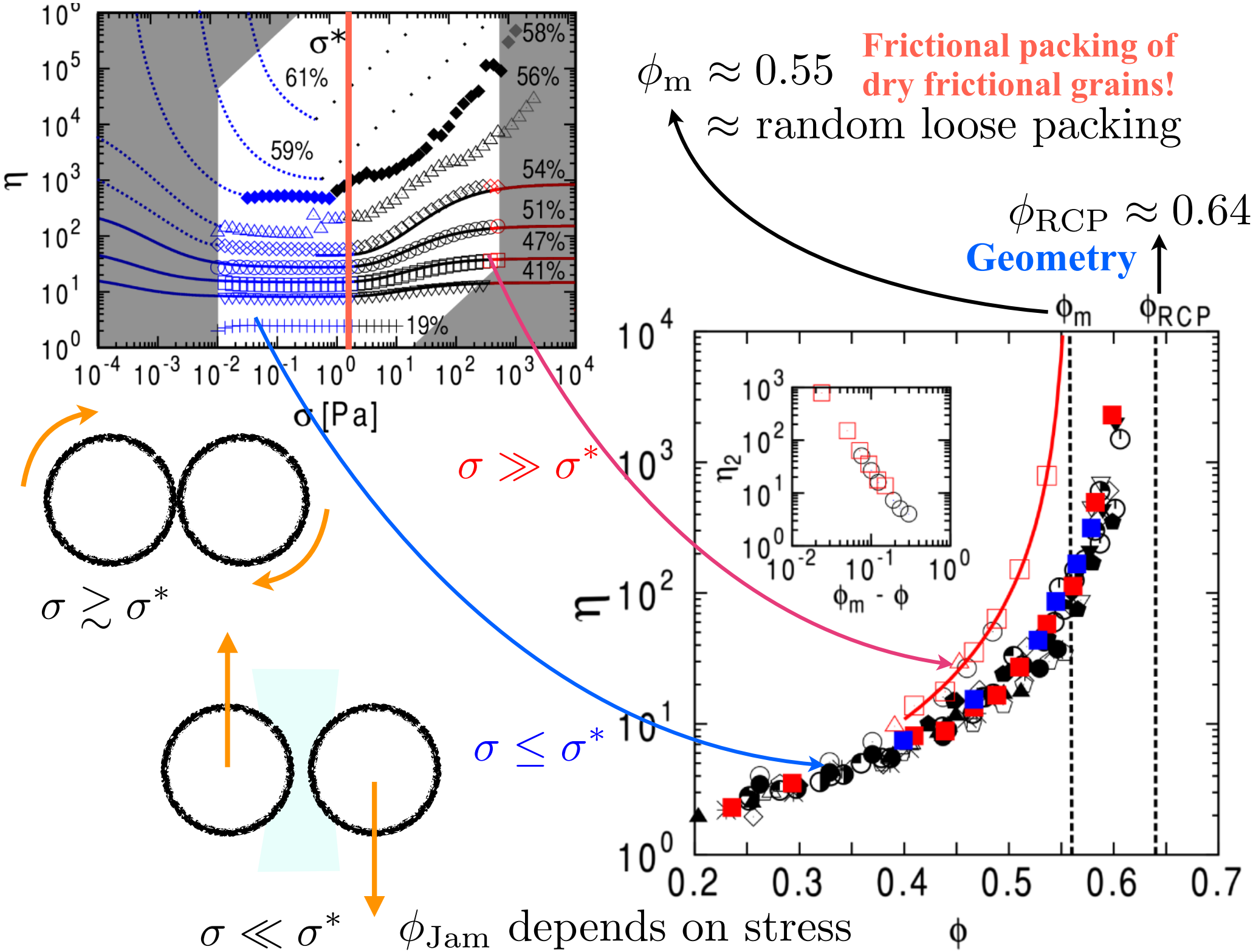


Guy et al. *PRL* (2015)

$$\sigma^* \propto \frac{1}{d^\alpha} \qquad \alpha \approx 2$$

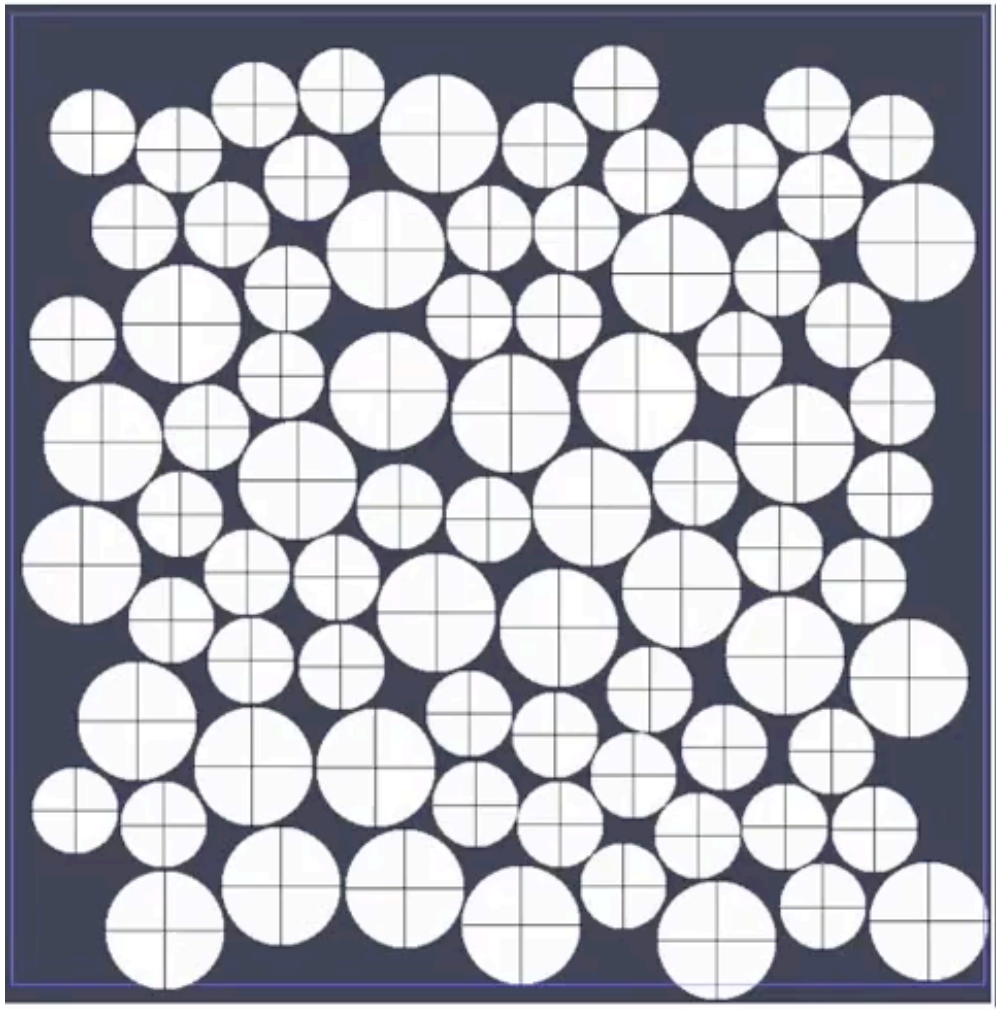
Sterically-stabilised PMMA in decalin; $D \sim 4\mu m$

$\Rightarrow$ granular suspensions are always shear thickened


$\phi_m \approx 0.55$
Frictional packing of dry frictional grains!
$\approx$ random loose packing
$\phi_{RCP} \approx 0.64$
Geometry
σ^*
58%
56%
61%
59%
54%
51%
47%
41%
19%
η
σ [Pa]
$\sigma \gg \sigma^*$
$\sigma \gtrsim \sigma^*$
$\sigma \leq \sigma^*$
$\sigma \ll \sigma^*$
ϕ_m
ϕ_{RCP}
η_2
$\phi_m - \phi$
ϕ
ϕ_{Jam} depends on stress

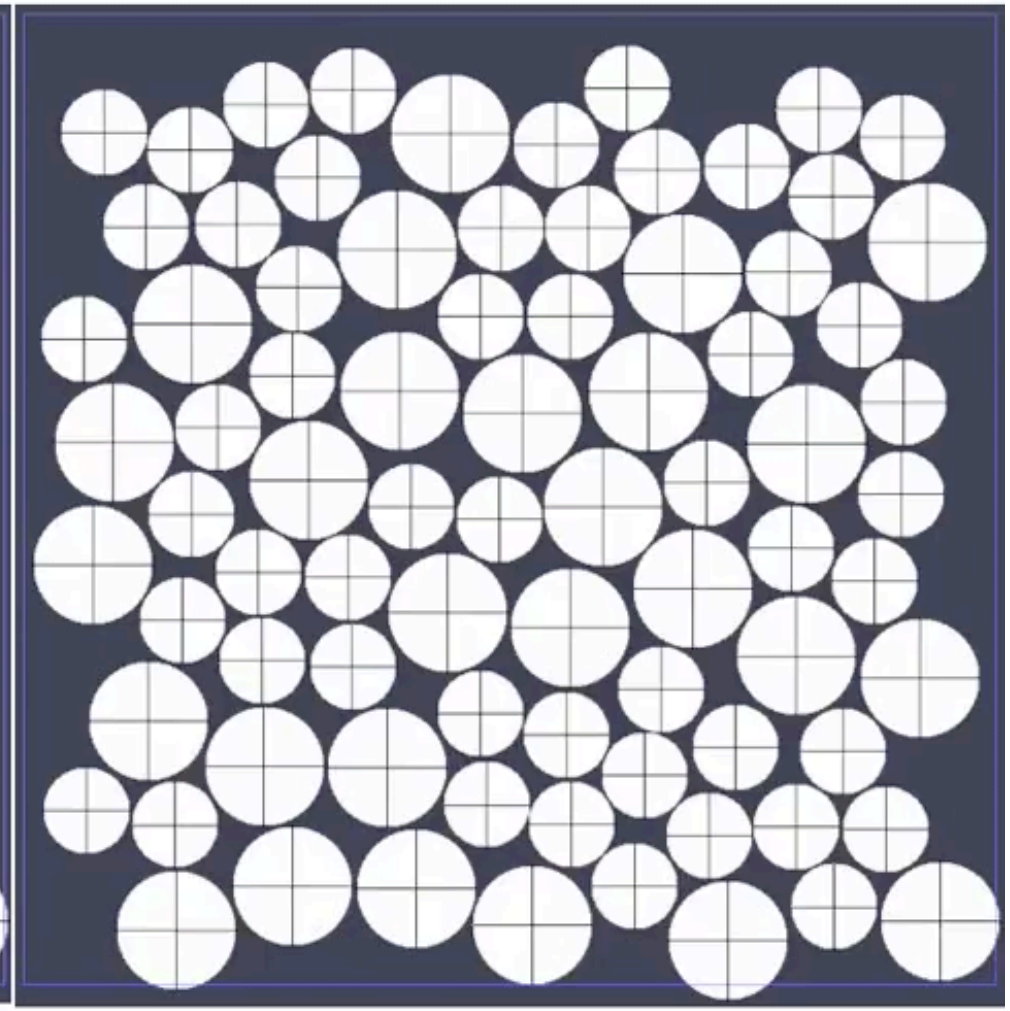
Frictionless

$\mu = 0$



Frictional

$\mu = 1$



Hermes

Particles slip on each other

Particles rotate → extra motion → extra dissipation → higher viscosity

Wyart-Cates theory

$$\eta_r = \left(1 - \frac{\phi}{\phi_J(\sigma)}\right)^{-2}$$

$$\phi_J(\sigma) = f(\sigma)\phi_m + [1 - f(\sigma)]\phi_{\mathrm{RCP}}$$

Fraction of frictional contacts:

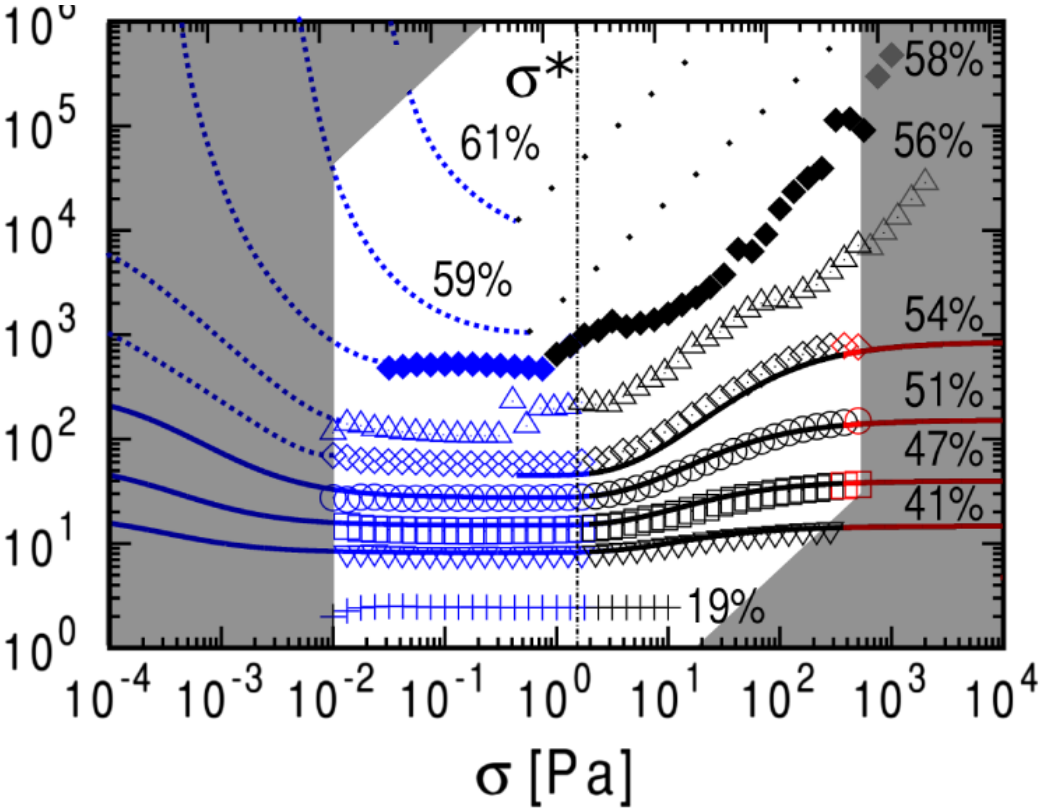
$$f(\sigma) = f(\sigma/\sigma^*) = f(\sigma/\sigma^*(d))$$

$$\rightarrow 0 \text{ if } \sigma \ll \sigma^*$$

$$\rightarrow 1 \text{ if } \sigma \gg \sigma^*$$

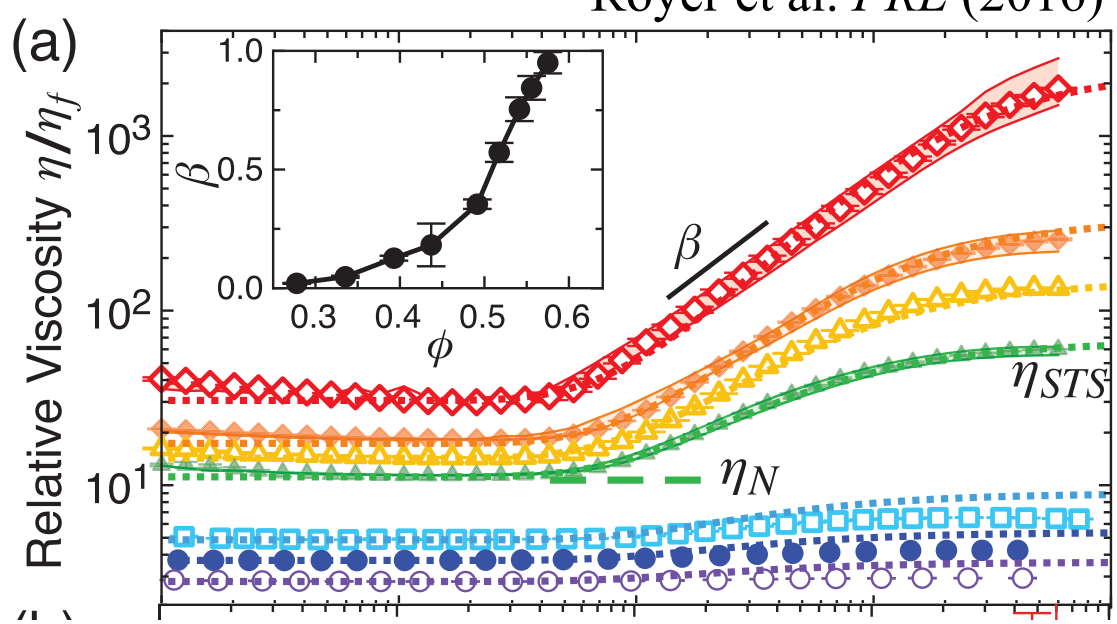
$$\text{Take } f = \exp\left[\left(-\frac{\sigma}{\sigma^*}\right)^{-\alpha}\right]$$

$$\alpha \approx 1$$

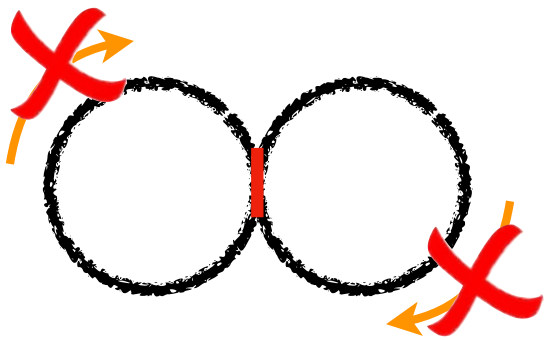


Wyart-Cates model can fit data

Royer et al. *PRL* (2016)



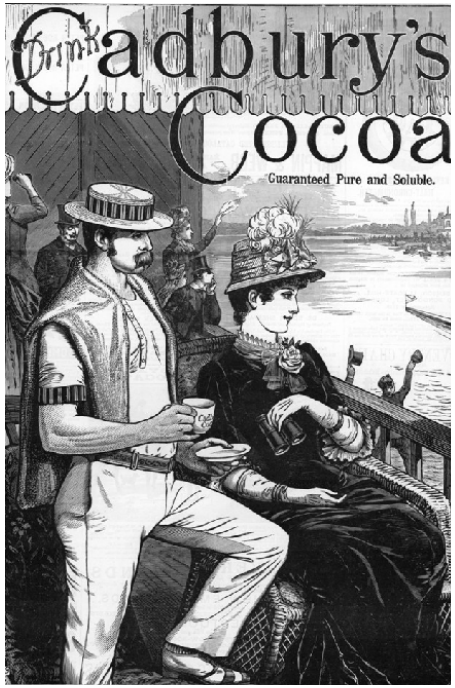
Most *nB*-suspensions (inc. chocolate) contain *sticky* particles …



This talk: concentrate on just friction effects …

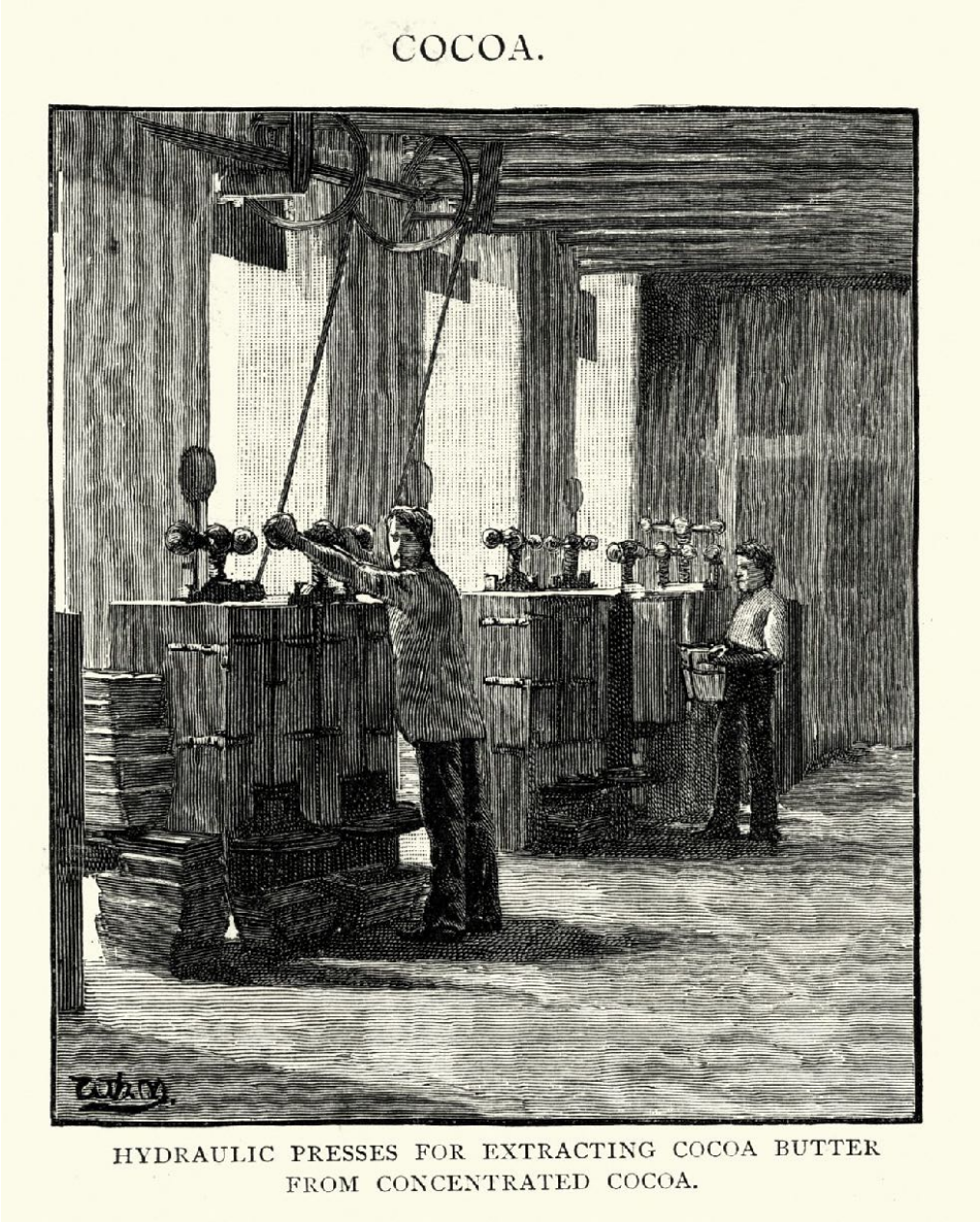
… OK for stresses high enough to break all ‘bonds’

Cacao bean (*Theobroma cacao*)



Cocoa butter

Cocoa powder



Coenraad van Houten (1828)

Joseph, Richard & Francis Fry (1847)

+

+

Mix and pour into a mould …

Daniel Peters (1875)

+ powdered milk

Rudolf Lindt

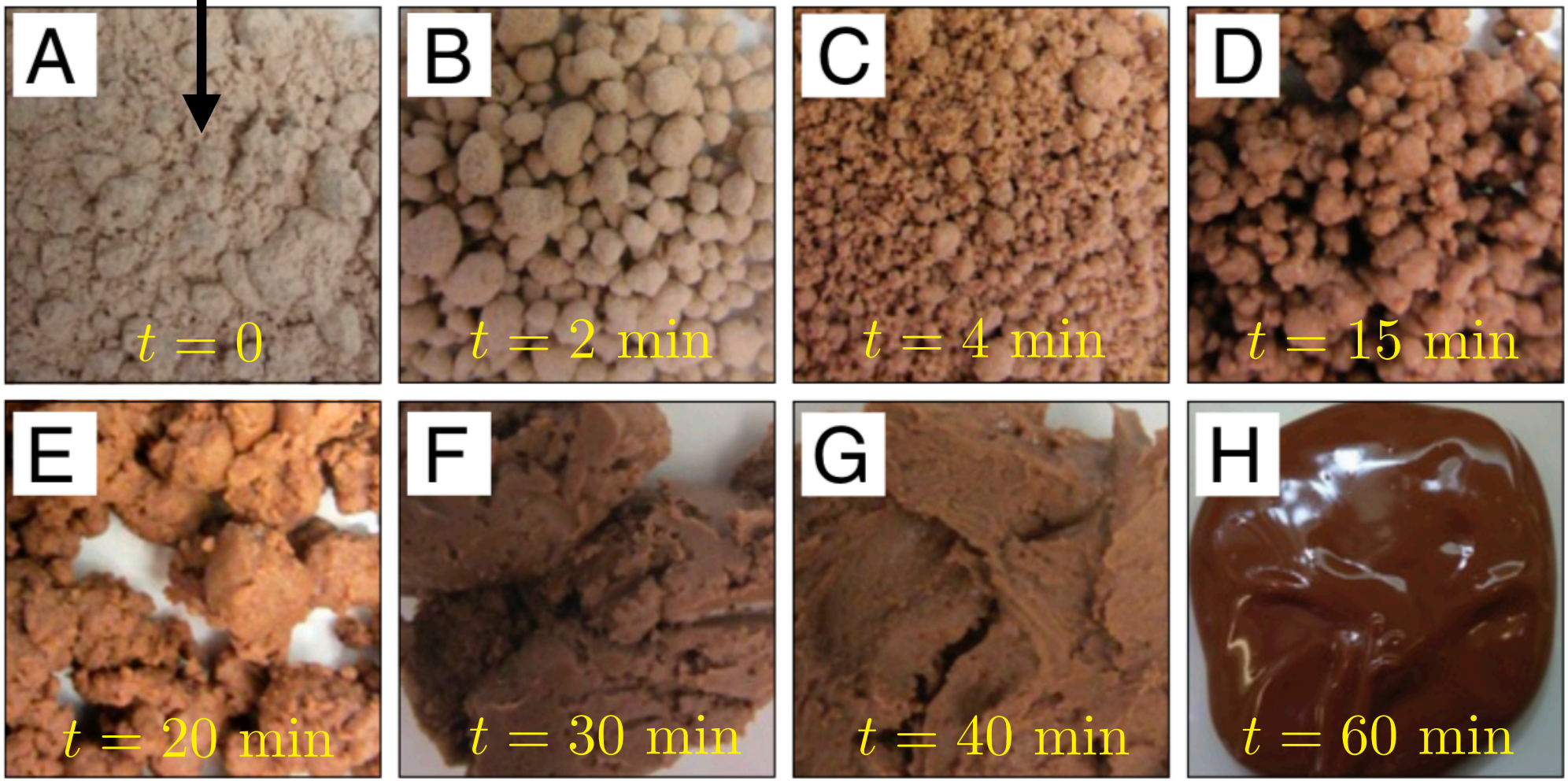
Chocolate used to be gritty!

"Conching"

Conche shell

1879: Prolonged mechanical agitation → 'melt-in-the-mouth' chocolate!

Crumb + sunflower oil + lecithin (lipid mixture)



Contents lists available at ScienceDirect

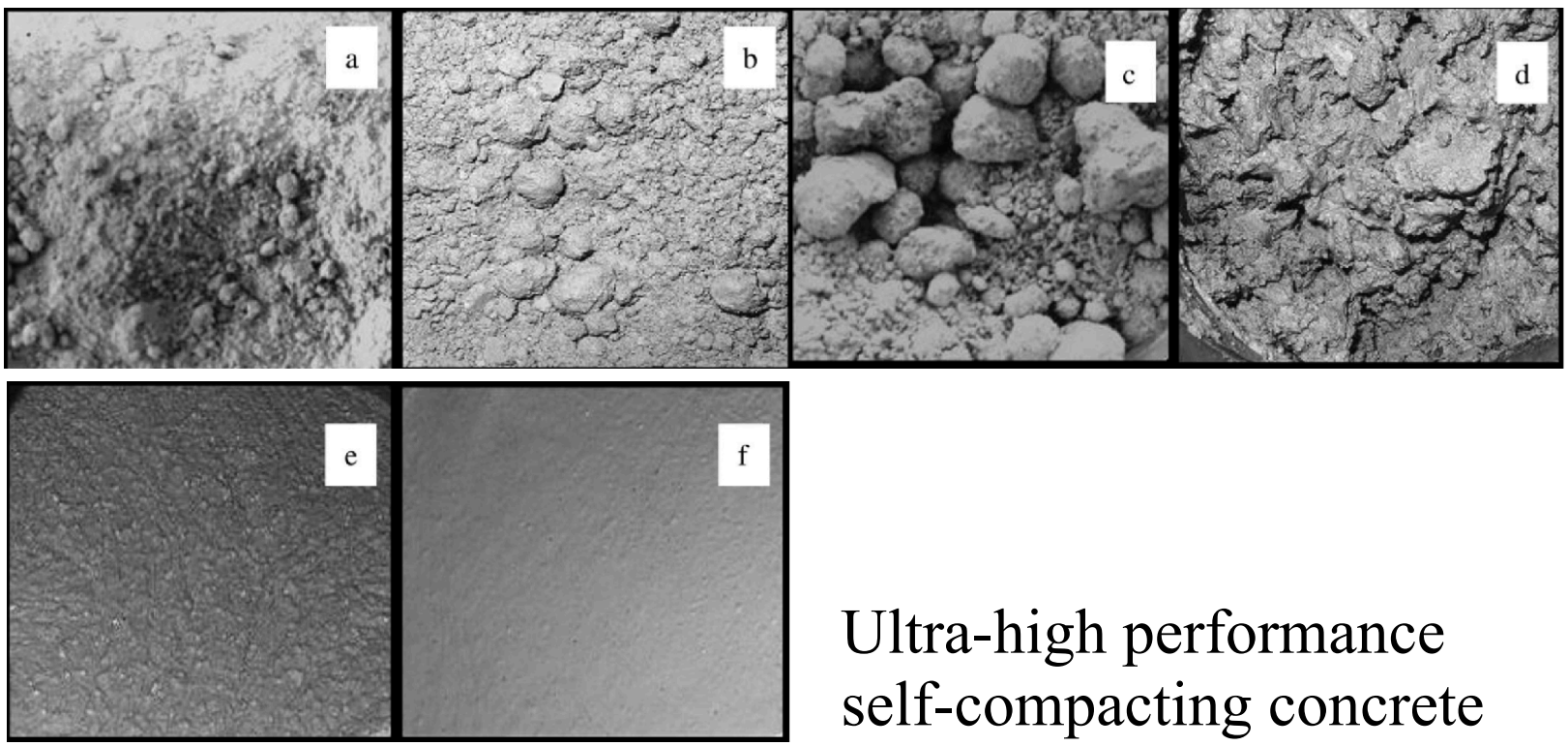
Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Concrete mixing kinetics by means of power measurement

B. Cazacliu *, N. Roquet

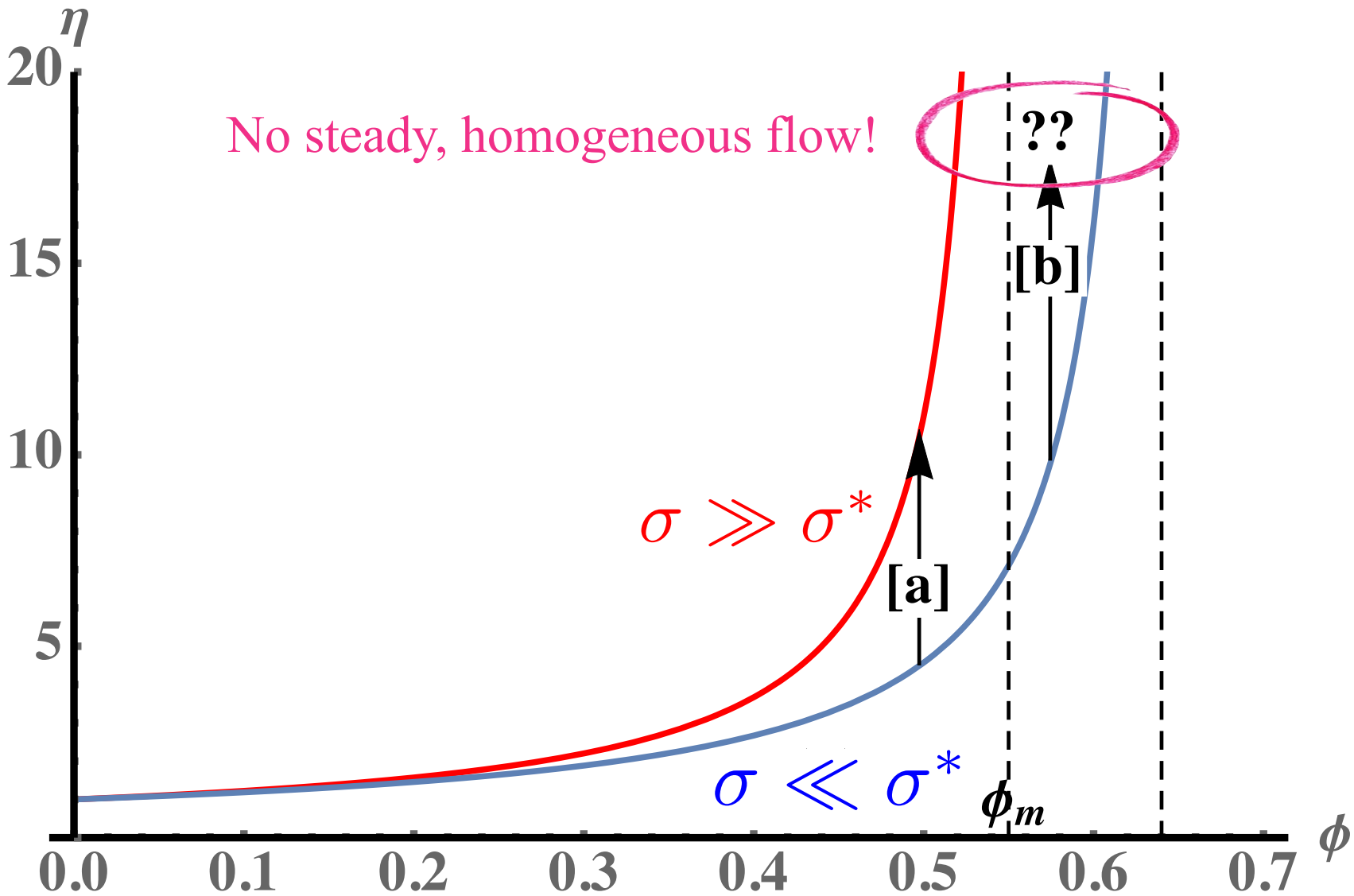
Laboratoire Central des Ponts et Chaussées, BP4129, 44341 Bouguenais Cedex, France



Ultra-high performance self-compacting concrete

Generic: mixing a little liquid with powder to give flowable high-φ suspension …

… is a matter of "φ_m engineering"

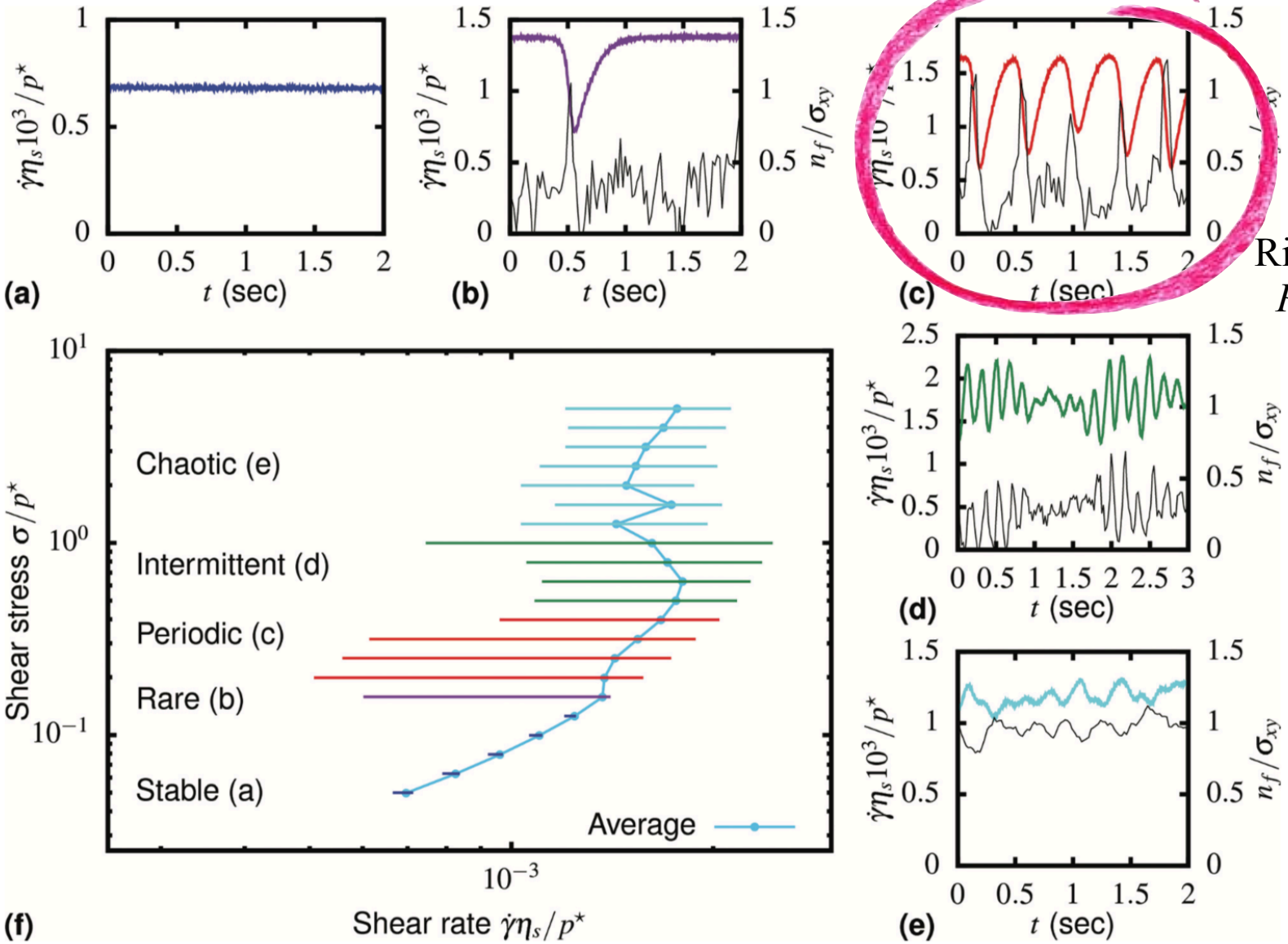


$\phi \geq \phi_{\mathrm{m}}$: shear jamming

Shearing a suspension at $\phi > \phi_{\mathrm{m}} \rightarrow$ instabiities

In rheometer …

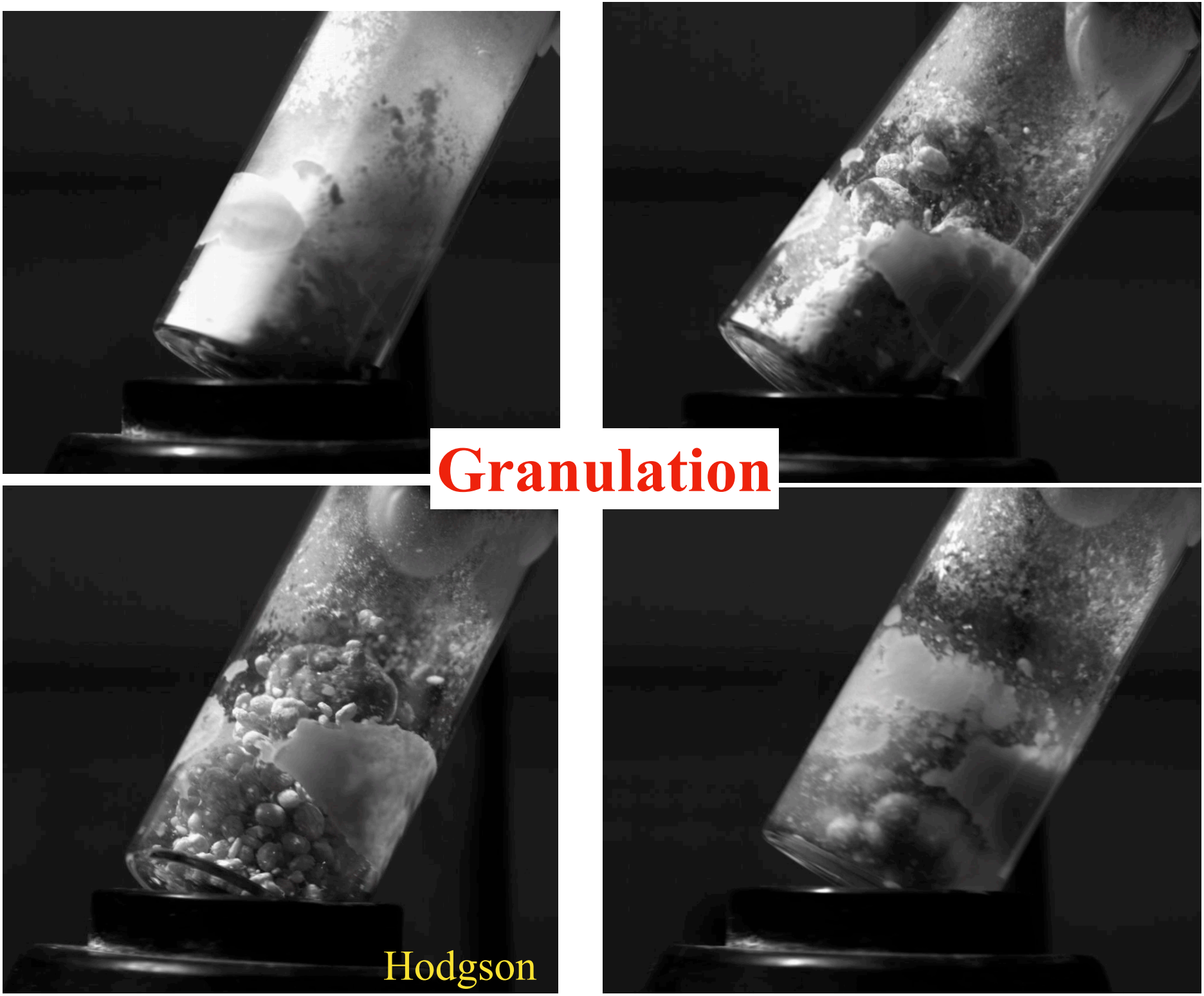
Hermes et al. *J. Rheol.* (2016)



Richards et al. *PRL* (2019)

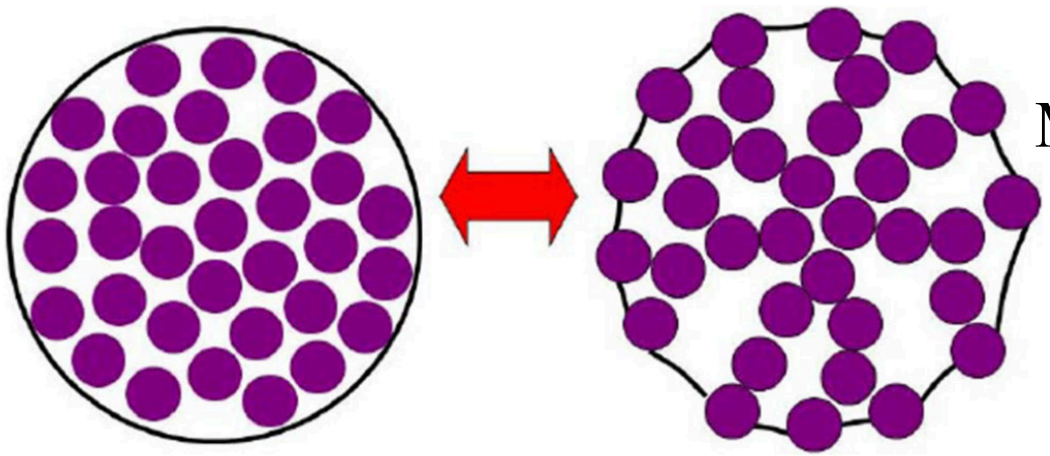
… and with free surface

Spheriglass suspensions



Flow above $\phi_{\mathrm{m}} \rightarrow$ jamming $\rightarrow \sigma \uparrow$

$\sigma > \gamma/a \rightarrow$ protroducing particles

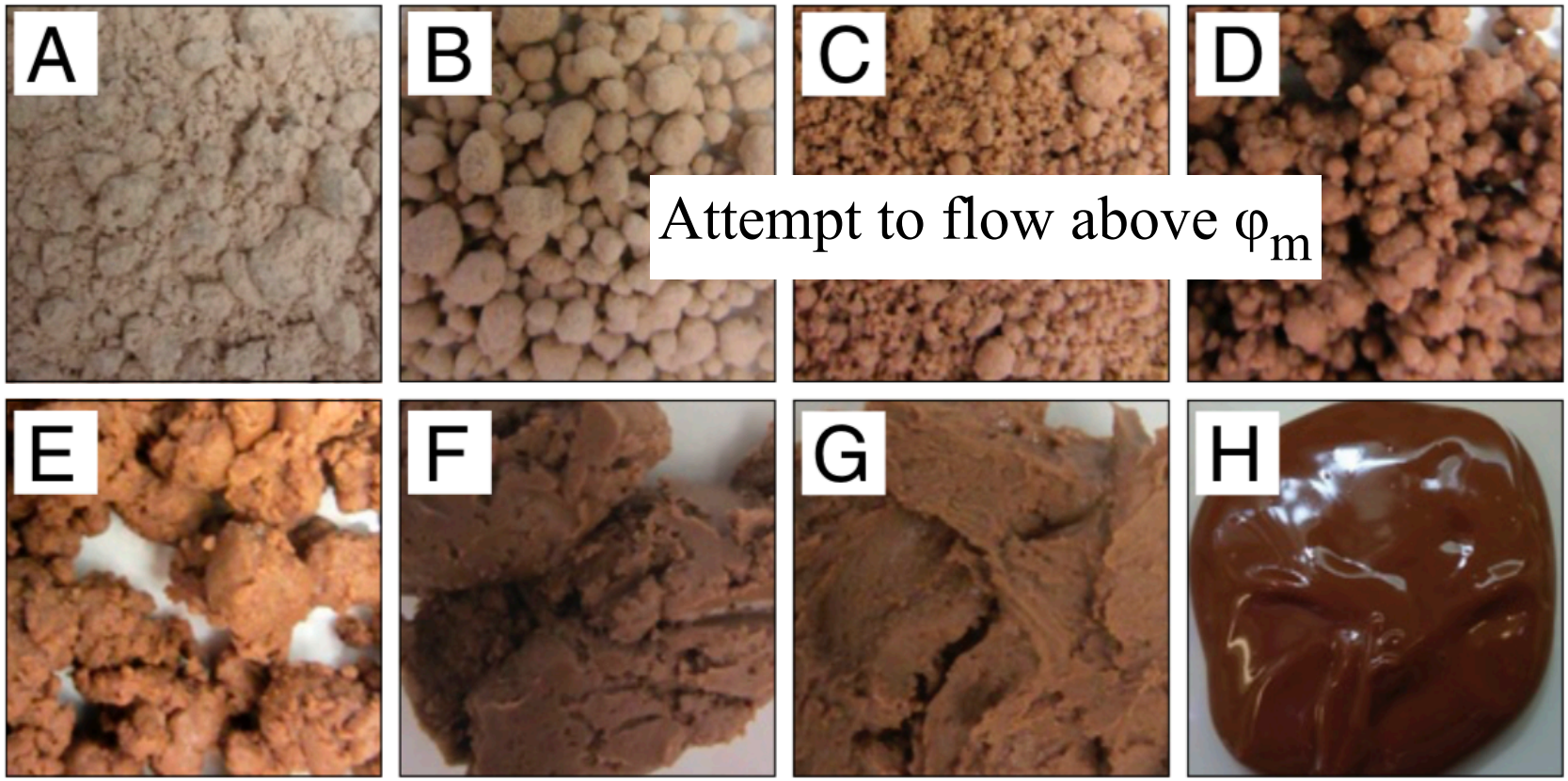


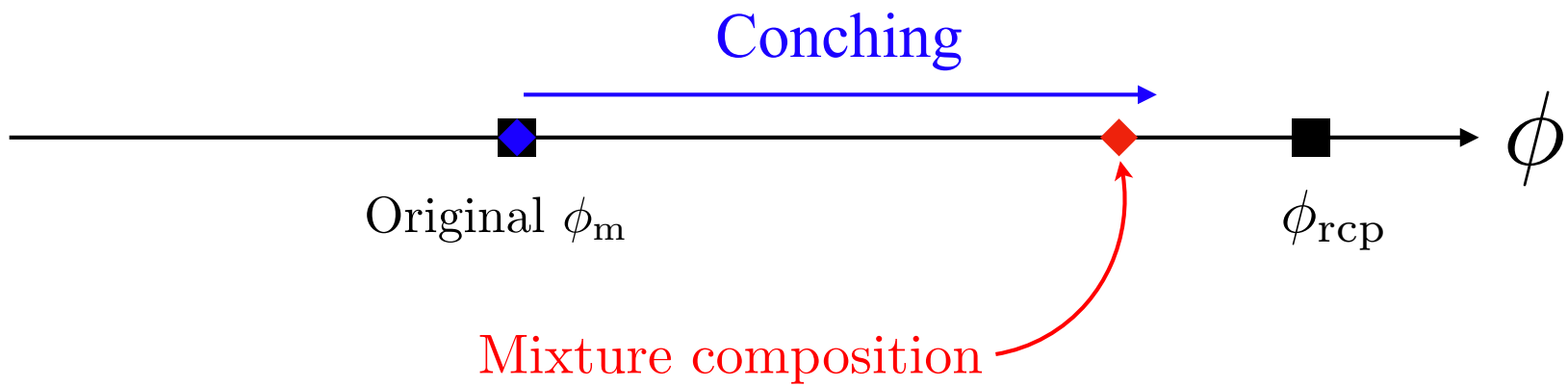
Matt surface!

Remove stress: capillary pressure maintains jamming

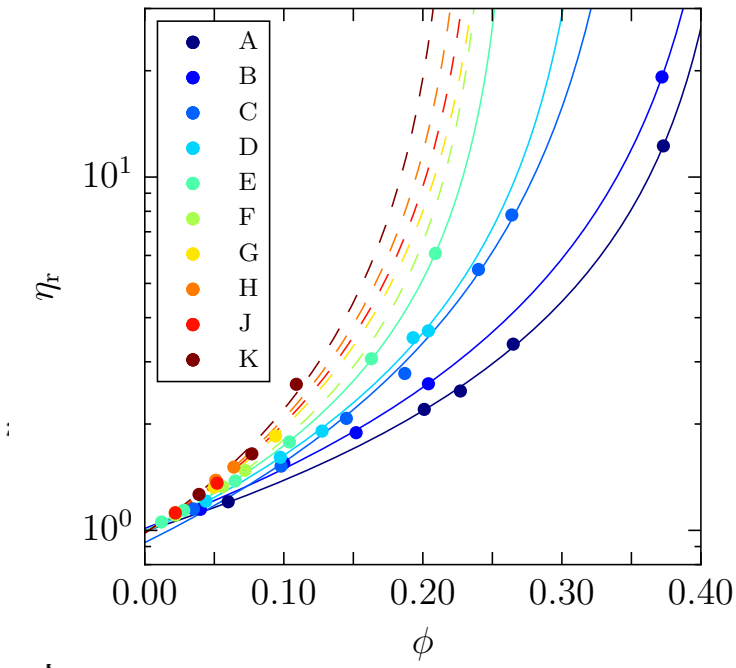
Theory: Cates and others

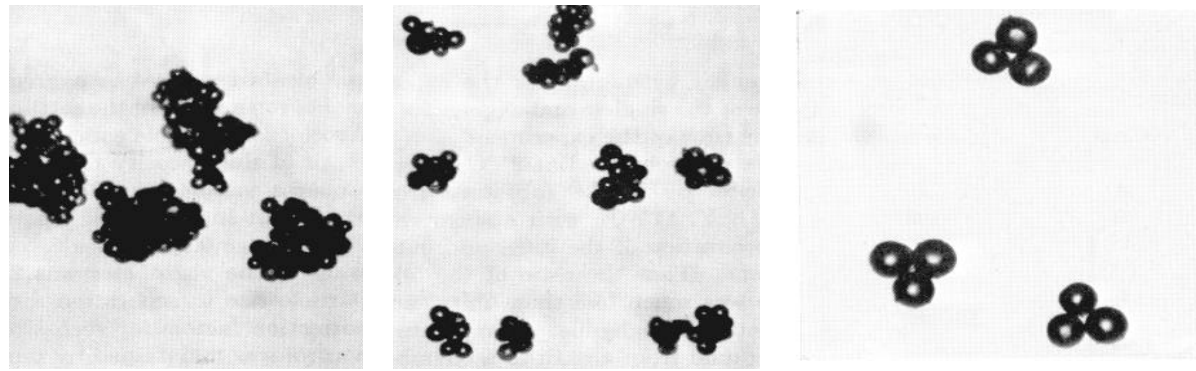
Experiment: Hodgson et al.

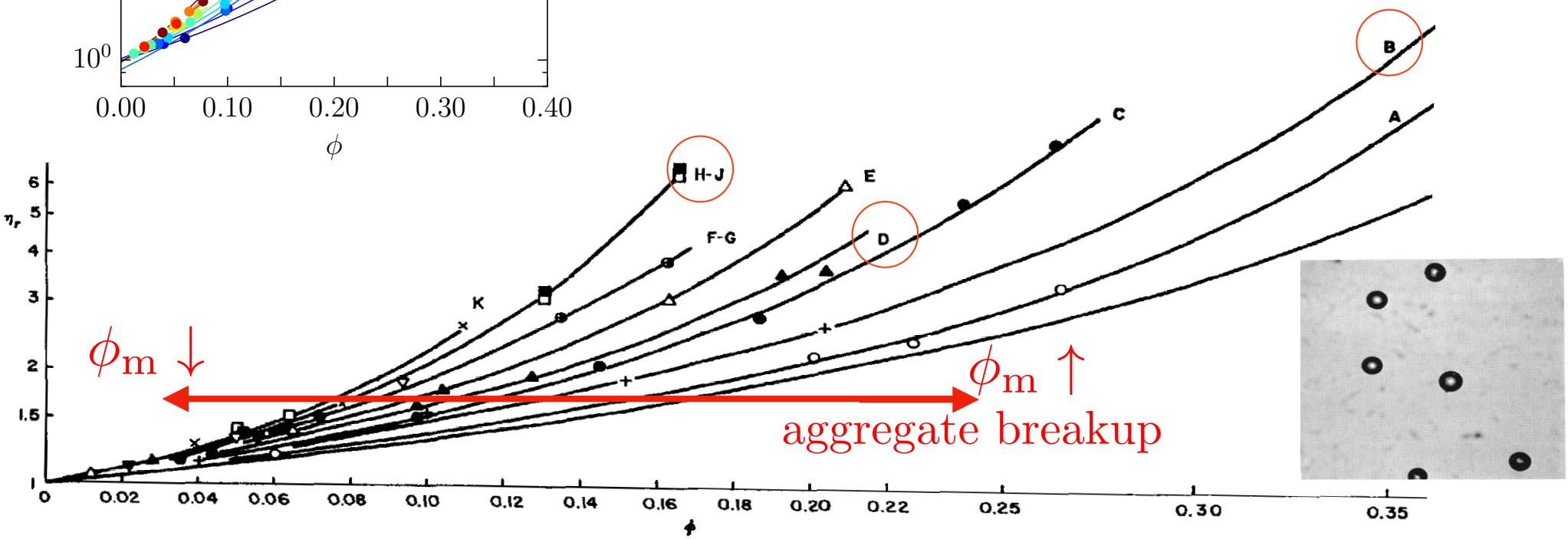

A
B
C
D
Attempt to flow above φ_m
E
F
G
H


Conching
ϕ
Original ϕ_{m}
ϕ_{rcp}
Mixture composition

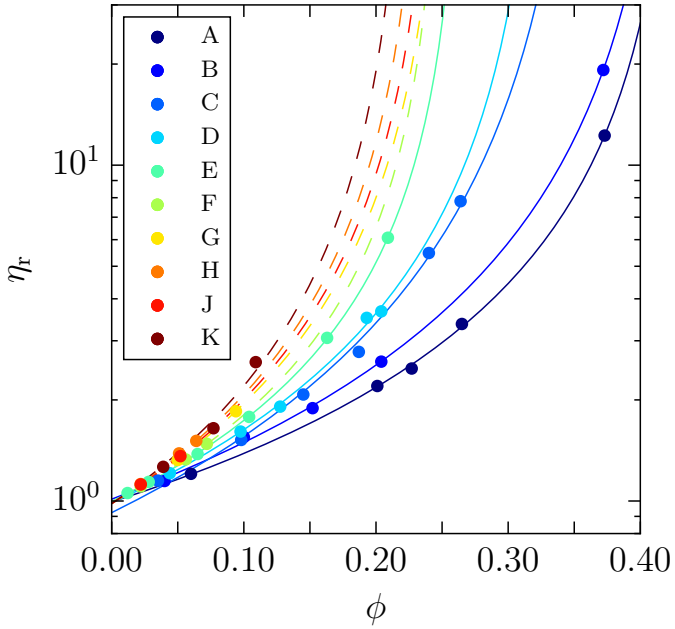
Change aggregation state

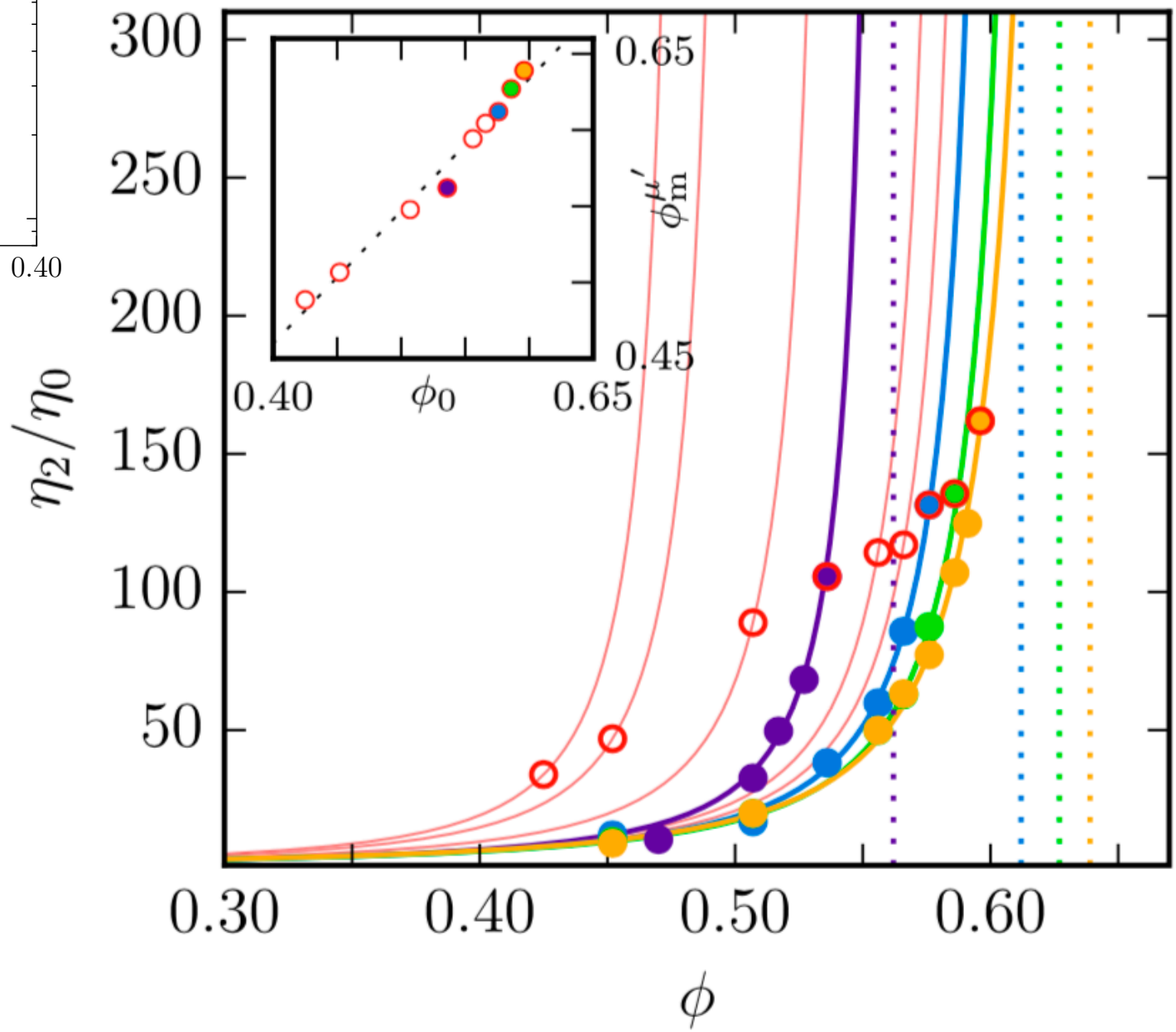




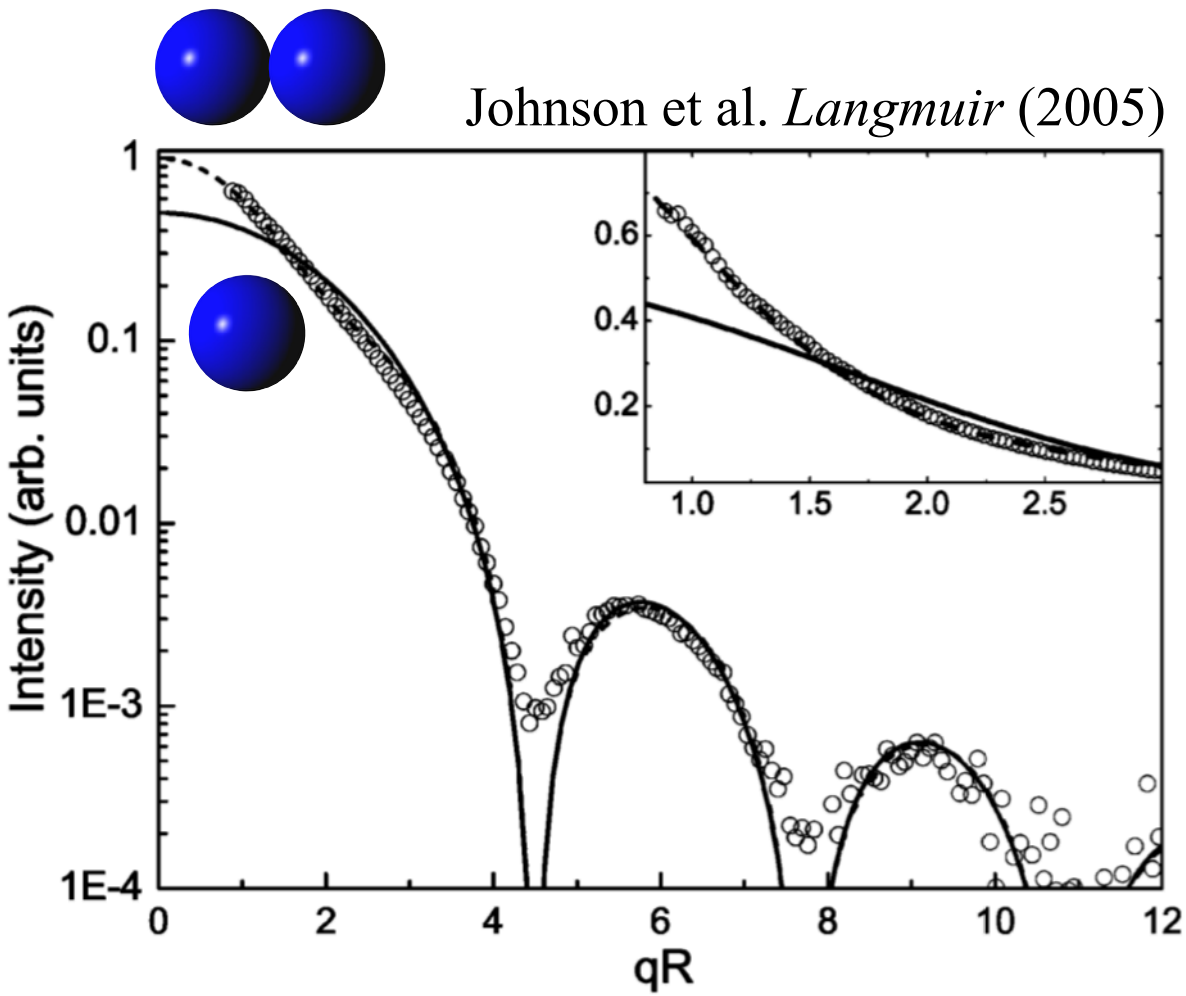


Lewis & Nielson (1968)


A
B
C
D
E
F
G
H
J
K
10^1
10^0
η_r
0.00
0.10
0.20
0.30
0.40
ϕ


300
250
200
150
100
50
η_2/η_0
0.30
0.40
0.50
0.60
ϕ
0.65
0.45
$\phi_m^{\mu'}$
0.40
ϕ_0
0.65

The change in aggregate size *cannot* be detected by scattering …



Why is ϕ_m important in general for many industrial applications?

Because the boss always wants higher solid content!

Stronger materials, lower transport costs, etc.

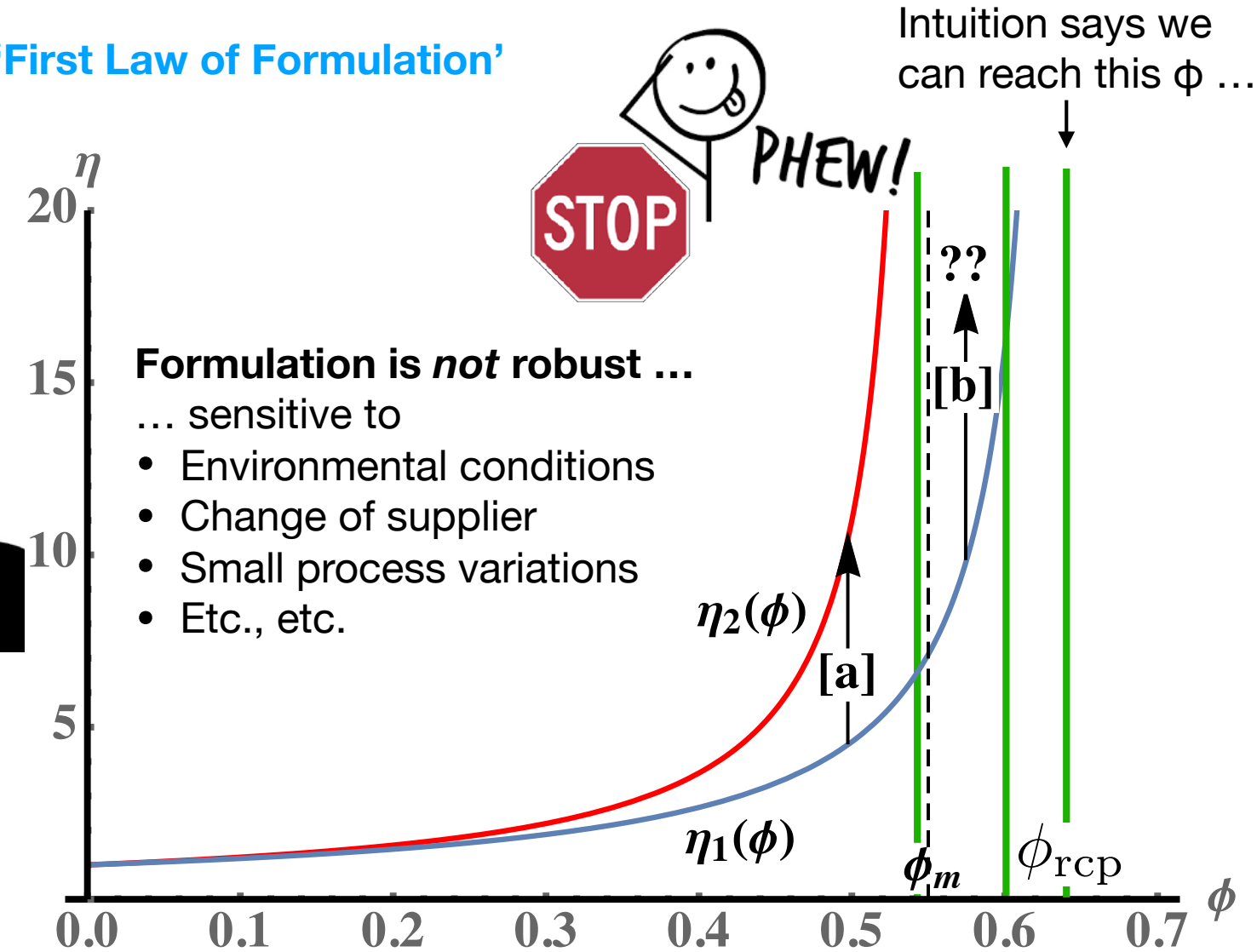
'First Law of Formulation'

Solution 1:
Formulate at lower ϕ

Solution 2:

$\ldots$ increase ϕ_m!

ϕ_m engineering

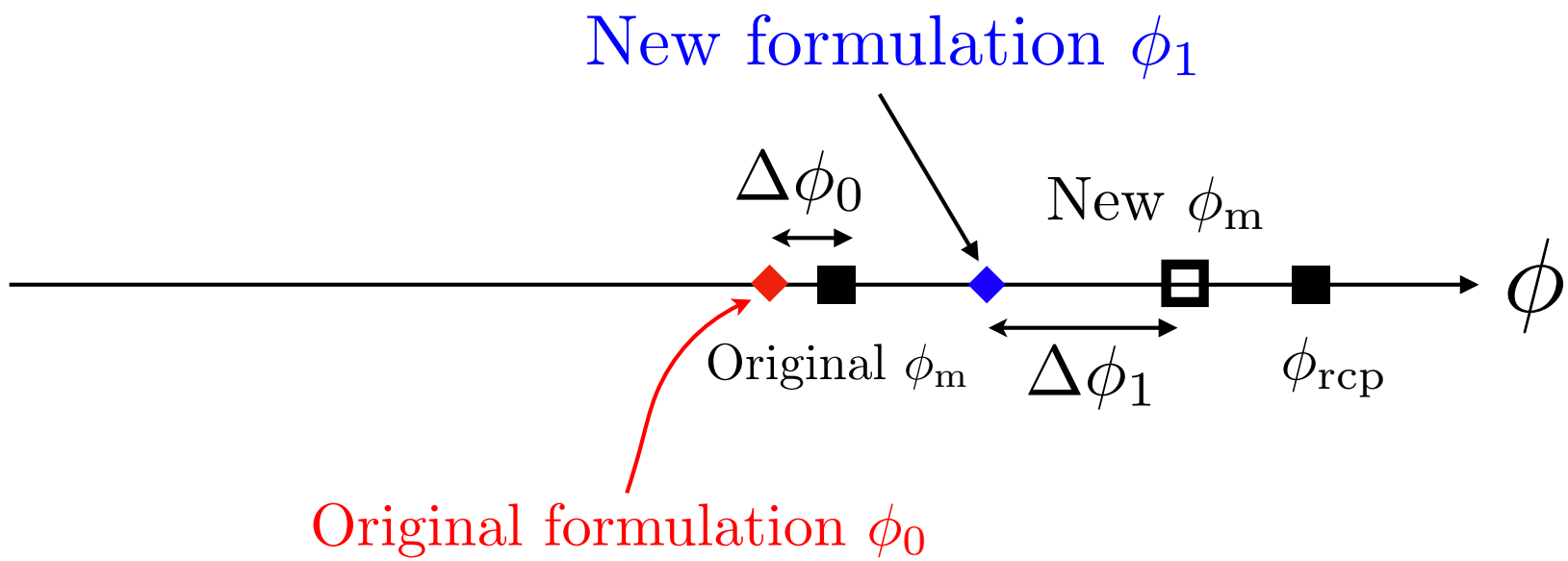


Formulation is *not* robust …

… sensitive to

- Environmental conditions
- Change of supplier
- Small process variations
- Etc., etc.

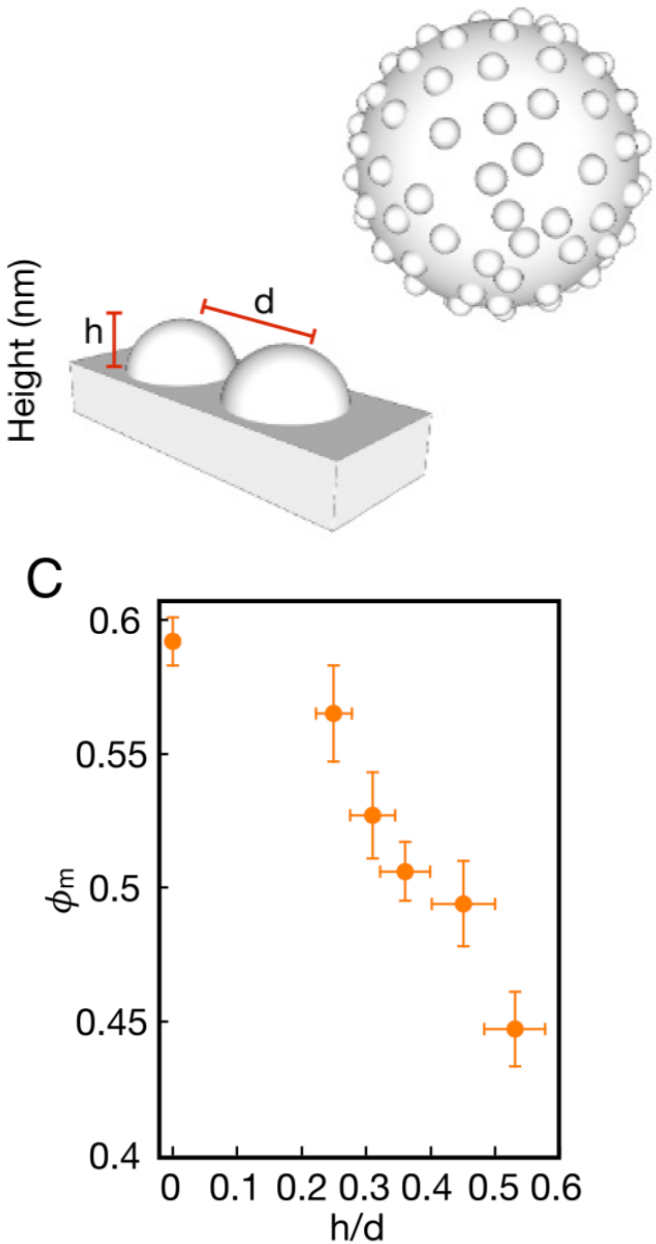
The general principles of φ_m engineering



$\phi_1 > \phi_0$: more solids

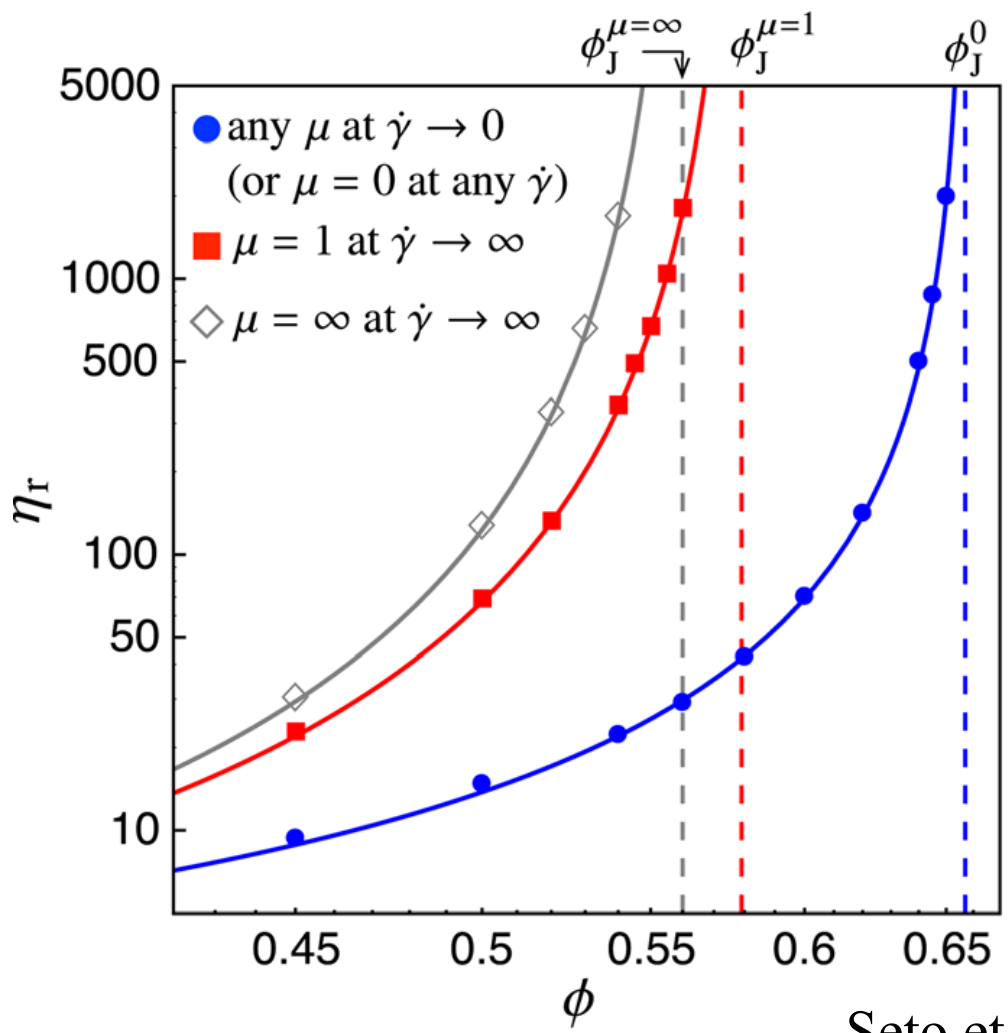
$\Delta\phi_1 > \Delta\phi_1$: more robust

Changing roughness



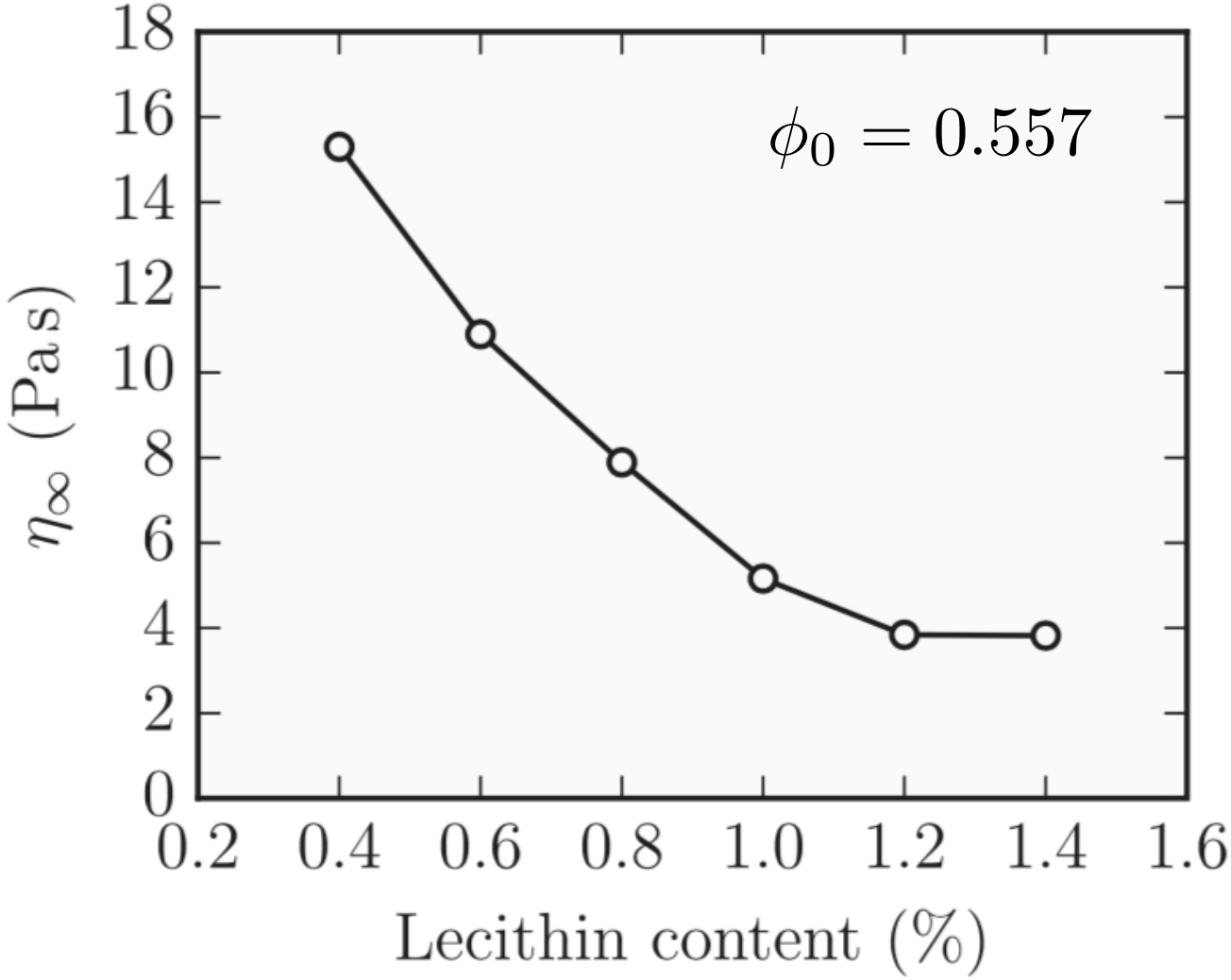
Hsu et al. *PNAS* (2018)

Changing μ

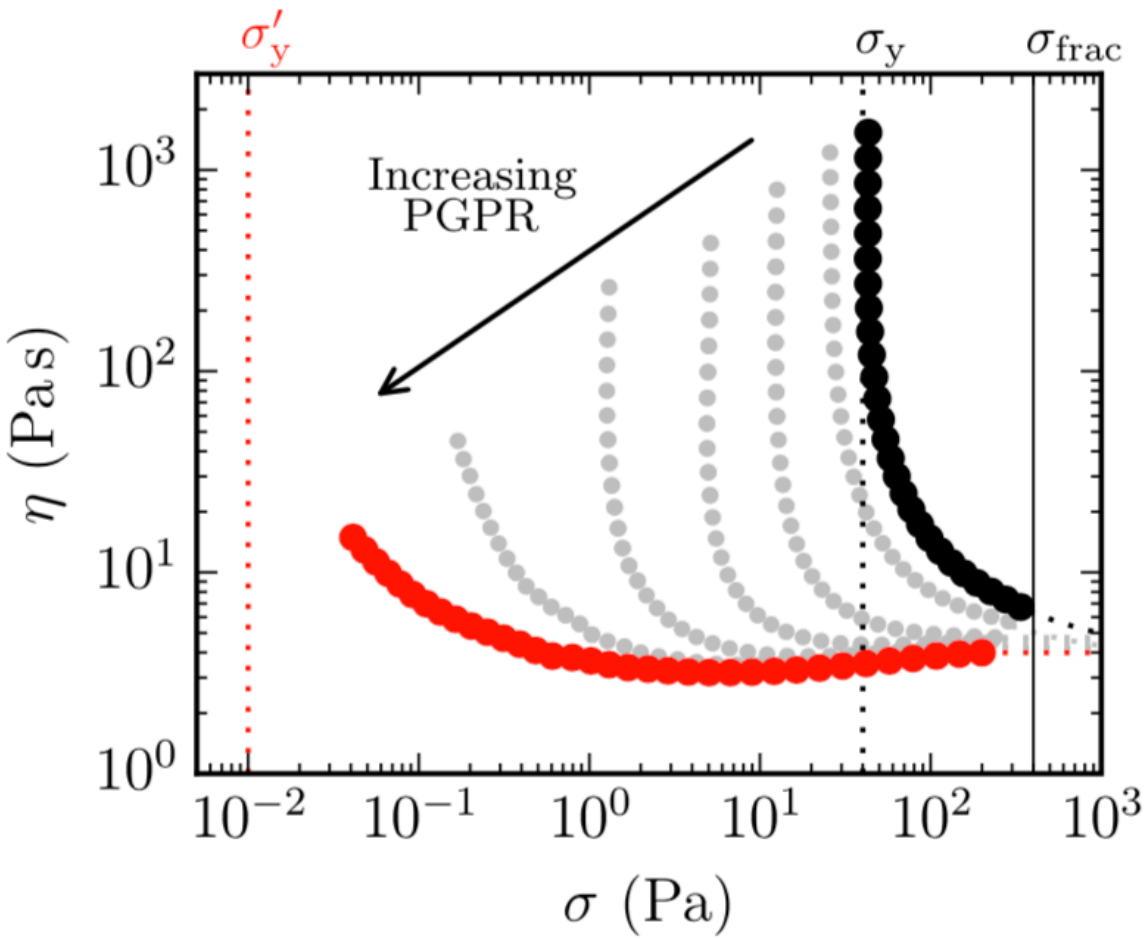


Seto et al. *J. Rheol.*

Surfactants = ‘plasticisers’


$\phi_0 = 0.557$
η_∞ (Pa s)
Lecithin content (%)
0
2
4
6
8
10
12
14
16
18
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6

That's half the story of chocolate rheology …



Tuning adhesive interaction to manipulate yield stress

Summary & conclusions

- Non-Brownian suspension shear thicken very easily
- Shear thickening is due to particles being pressed into frictional contact
- The shear-thickened viscosity diverges at $\varphi_m < \varphi_{rcp}$
- Conching chocolate is a matter of increasing φ_m by breaking up aggregates …
- … and/or decreasing roughness
- φ_m can be also changed tuning μ
- φ_m engineering is important for increasing solid fraction