# Mechanics of particulate interfaces

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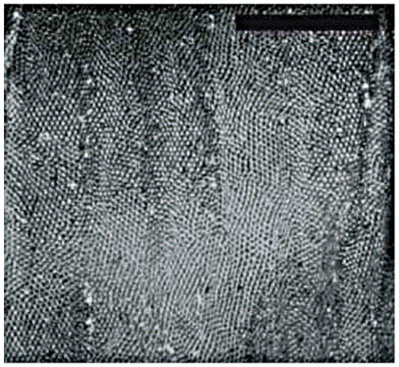
- Where ? Why ?
- Monolayers & particle rafts
  - unusual 2-d solid
    - buckling
    - cracking
    - encapsulation

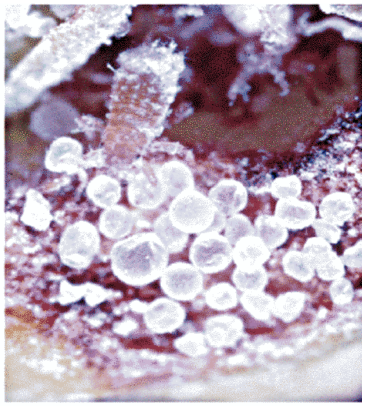
D. Vella
P. Aussillous
D. Richard

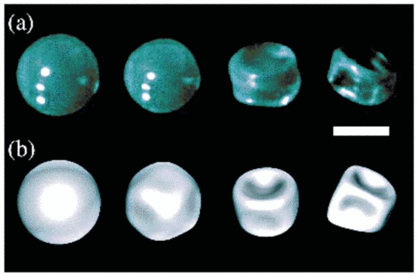
- Multi-layered films & shells
  - formation & mechanical instabilities

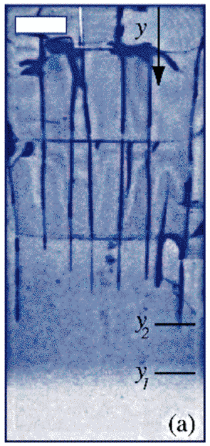
E. Dufresne
C. Riera
D. Weitz

- Interfaces of suspensions
  - dynamic interfacial tension ??

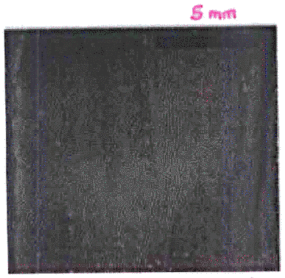




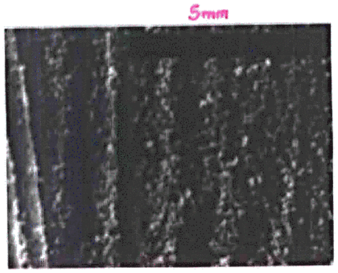




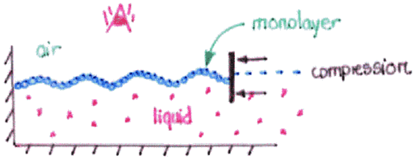
2-d particle rafts of non-Brownian particles on water (Vella, D.; Aussillous, P.; LM; 2004)



30μm particles



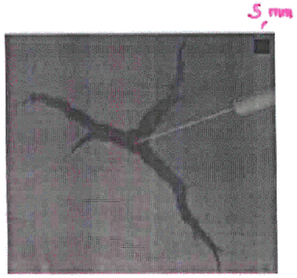
wrinkles when compressed



$\gamma$ = interfacial tension (air-water)

d = particle diameter

+ surfactant →



cracks when pulled apart

· intermittent motion : 2 time scales $\begin{cases} \text{crack motion (fast)} \\ \text{surfactant diffusion (slow)} \end{cases}$

i.e. Particle rafts behave like 2-d solids

i.e. non-zero shear modulus (zero frequency!)

- water-air-solid interface is crucial!
  - cohesive (capillary) interaction
- steric interaction between particles is crucial!
  - supports anisotropic stresses

e.g

buckling

cracking

· qualitatively different from a dry powder (no cohesion) in 2-d!

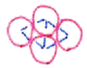
· " " " Langmuir monolayers (no $k_BT$)

· " " " bubble rafts (no stacking)

walks & talks like a solid .... elastic properties ?

∴ it is a 2-d solid ?

Young's modulus $E$ / Poisson ratio $\nu$



· central forces

· hexagonal close packing $\phi_{solid} = \pi/2\sqrt{3}$

→ $\nu = 1/\sqrt{3}$ ( geometry ! )

$$E = \frac{\gamma}{d} \cdot \underbrace{(1-\nu)}_{\text{areal elasticity}} \cdot f(\phi)^{?} \quad ?$$

dimensional analysis

2-d elasticity : $\underset{\bar{\sigma}}{\underset{\parallel}{(\sigma_{11}+\sigma_{22})}} = \frac{E}{(1-\nu)}\underset{\bar{\epsilon}}{\underset{\parallel}{(\epsilon_{11}+\epsilon_{22})}}$

$\therefore \quad d\bar{\epsilon}/d\bar{\sigma} = (1-\nu)/E \quad \Rightarrow \quad d\bar{\epsilon}/d\tau = (1-\nu)/E\underset{\text{particle diameter}}{d}$

& $\tau = \bar{\sigma} d$

but $d\bar{\epsilon}/d\tau = \underset{\text{interface area}}{1/A} \cdot dA/d\tau = \frac{1}{A_l + A_s} \cdot \frac{d}{d\tau}(A_l + A_s)$ (Lucassen, 1990)

$A_l$ = area covered by liquid ; $A_s$ = area covered by solid = constant !

i.e. $d\bar{\epsilon}/d\tau = \frac{1}{(1 + A_s/A_l)} \cdot \frac{dA_l}{A_l\, d\tau}$

if $A_s = \underset{\text{solid area fraction}}{\phi} . A$ , $A_l = (1-\phi)A$ & $\frac{dA_l}{A_l . d\tau} \simeq \frac{1}{\gamma}$

then, $(1-\nu)/Ed \cong (1-\phi)/\gamma \Rightarrow E \sim \frac{\gamma}{d}\,\frac{(1-\nu)}{(1-\phi)}$

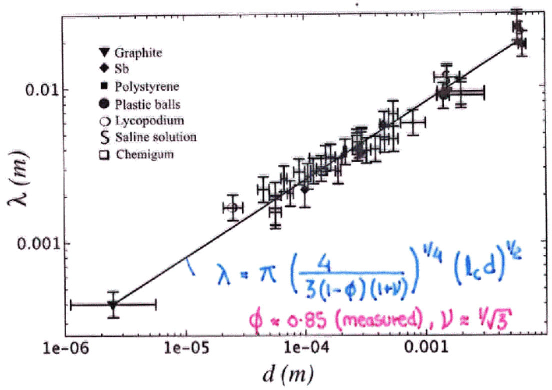
i.e. $E \approx 4.5 . \frac{\gamma}{d}$ $\left[\nu \sim 1/\sqrt{3} , \phi_{cp} \sim \pi/2\sqrt{3}\right]$

Experiment ? buckling assay

$\underset{\text{bending elasticity (short }\lambda)}{Ed^3/12(1-\nu^2) \cdot d^4h/dx^4} + \underset{\text{compression}}{T\, d^2h/dx^2} + \underset{\text{gravity (long }\lambda)}{\rho g h} = 0$ ; periodic b.c.

sub. $h = A \sin 2\pi x/\lambda \Rightarrow T = T(\lambda) \leftarrow$ minimization

$\Rightarrow \underset{\checkmark}{\lambda} = \pi\left(4\underset{?}{E}\overset{\checkmark}{d}^3/3\overset{\checkmark}{\rho}\overset{\checkmark}{g}(1-\nu^2)\right)^{1/4}$



$\lambda = \pi\left(\frac{4}{3(1-\phi)(1+\nu)}\right)^{1/4}(l_c d)^{1/2}$

$\phi \approx 0.85$ (measured), $\nu \approx 1/\sqrt{3}$

since $E \sim \frac{\gamma}{d}$

$\lambda \sim \left(\frac{\gamma d^2}{\rho g}\right)^{1/4}$

$\sim (d\, l_c)^{1/2}$

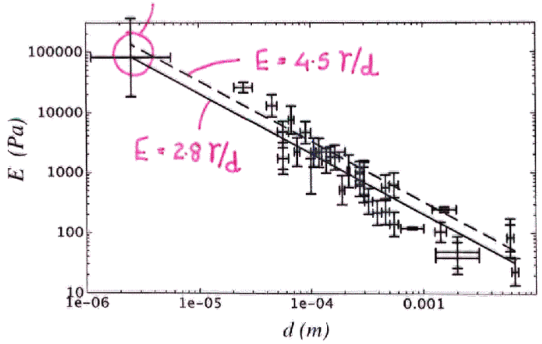
where

$l_c \sim \gamma/\rho g$

- capillary length

$\lambda = \lambda(d) \Rightarrow E = E(d)$

Brownian !

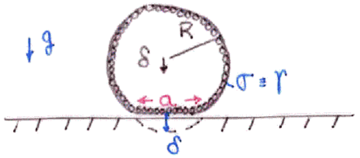


$E = 4.5\ \gamma/d$

$E = 2.8\ \gamma/d$

cracking ? encapsulation ?

## Statics:



$$\rho g R^3 \cdot \delta \sim \sigma \cdot \Delta A$$

↑ area change due to flattening

· parabolic contact (weakly deformed, i.e. $\rho g R^3 \leq \sigma R \Rightarrow R < l_c$)

$l_c = (\sigma/\rho g)^{1/2}$

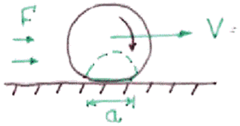
$\Rightarrow \quad a^2 \sim \delta R$

Then, $\Delta A \sim a^4/R^2 \sim \delta^2$ & $\delta \sim \rho g/\sigma \cdot R^3$

$$\Rightarrow \left.\begin{array}{l} \delta \sim R^3/l_c^2 \\ a \sim R^2/l_c \end{array}\right\} \text{static}$$

## Dynamics:

ROLLING !



viscosity $\mu$

$Ca = \mu V/\sigma \ll 1$

$\Rightarrow$ shape changes due to motion are not significant !

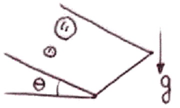
$$F V \sim \mu \cdot \left(\frac{Va}{R}/a\right)^2 \cdot a^3$$

↓ power

↓ dissipation rate

$$\Rightarrow \quad V \sim F/\mu \cdot l_c^3/R^{\cancel{4}}$$

e.g.



$F \sim \rho g \sin\theta \cdot R^3$

$$\Rightarrow \quad V \sim \frac{\rho g \sin\theta}{\mu} \cdot l_c^3/R_{/\!/} \leftarrow$$

smaller is faster !

## How aphids lose their marbles : ancient non-stick droplets in nature

encapsulation of liquid by particulate layer (hydrophobic)

⇓

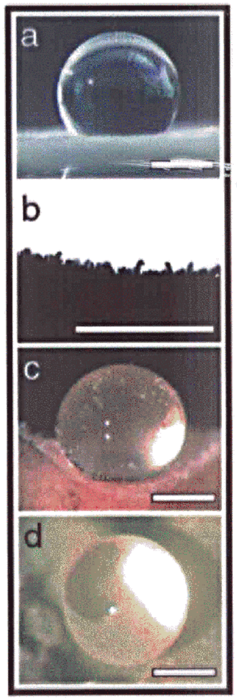
unusual static/dynamic behavior [non-wetting drops : LM ; Y. Pomeau, 1999]

(N. Pike, D. Richard, W. Foster, LM, 2002)

Life at small scale ⇒ interfacial forces are dominant !

Insects need non-stick / non-wetting 'solutions'

WAX



Scale bar : 1mm

Ⓘ • chemically hydrophobic

$\theta_{eq.} \sim 110°$. (on smooth surfaces)

Ⓘⓘ • waxy tufts → mechanically rough GALL surfaces → $\theta^* > \theta_{eq.}$

Ⓘⓘⓘ • waxy tufts → coating of droplets → $\theta^* > \theta_{eq.}$ ⊕ no coalescence

↓

non-stick scat !

Ⓘⓥ Dynamics :

Velocity $V \sim \frac{F\, l_c^3}{\mu R^4}$ [rolling]

F - force

$l_c \sim \sqrt{\sigma/\rho g}$ - capillary length

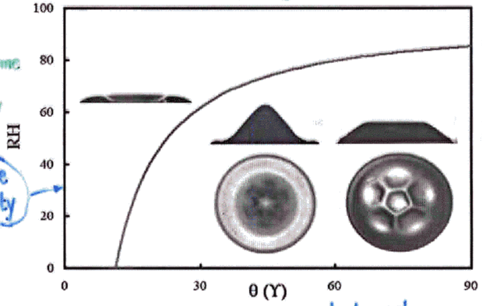
\# of droplets $\sim R^{-3}$

→ time taken $\sim R^{-3}/R^{-4} \sim R$ ! i.e. parcelling + rolling yields a dynamical advantage

Drying of sessile colloidal drops : Skin formation + capillary consolidation + elastic shell

(C. Riera, LM; 2004)

Constant area + Reduction in volume
⇓
buckling instability

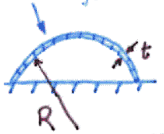


relative humidity →

(Pauchard, Allain; 2003)

(50-100nm latex particles, $\phi_i \sim 20\%$)

multi-layered



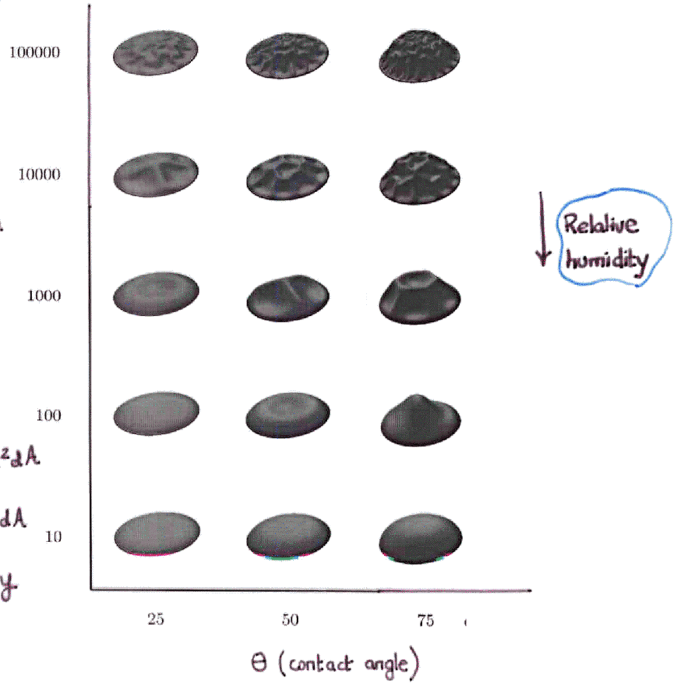
$(R/t)^2 \approx U_s/U_b$

Bending energy

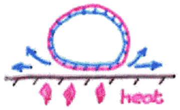
($U_b \sim Et^3 \int \underline{K}^2 dA$

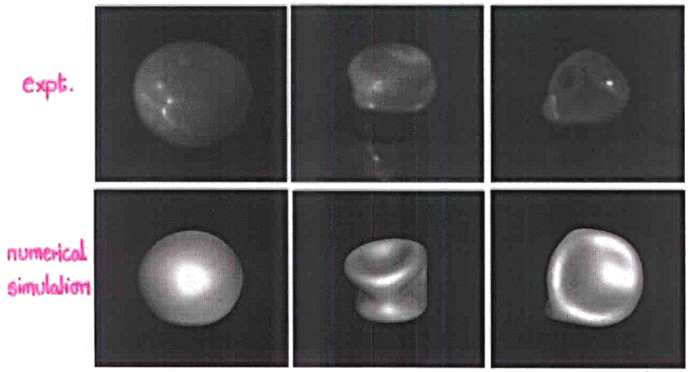
($U_s \sim Et \int \underline{\underline{\epsilon}}^2 dA$

Stretching energy



## Drying of levitating colloidal drops



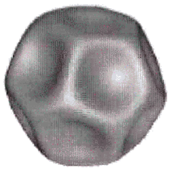


(N. Tsapis, E. Dufresne et al., 2004)

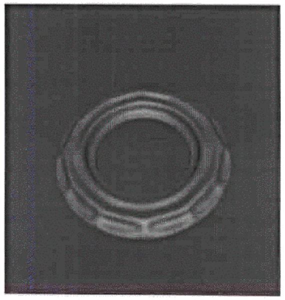
(C. Riera; 2004)

$(R/t)^2 \sim 100$

$(R/t)^2 \sim 10^3$



semi-Toroidal sessile elastic ring



- boundary conditions + geometry determine morphology
  (modulus only determines instability threshold!)

## Drying of a colloidal suspension (confined)

20 nm particles

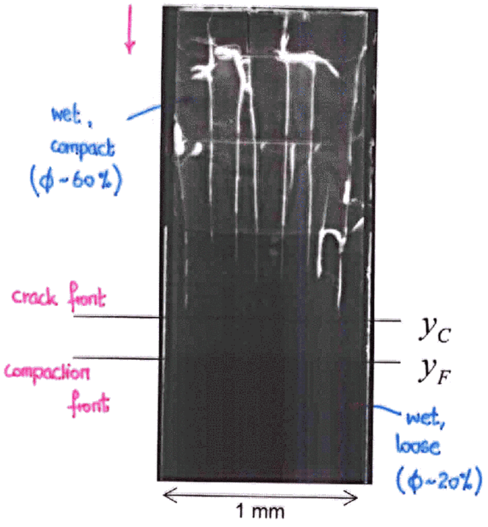
(E. Dufresne, J. Ashmore, ... D. Weitz, LM; 2004)

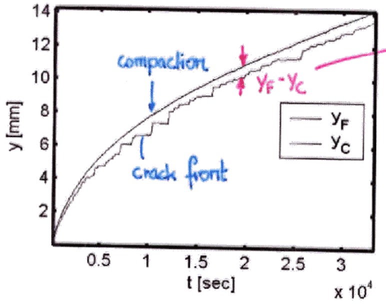
capillary stresses

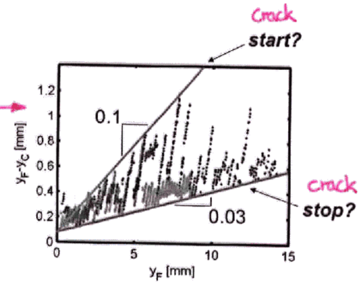
$$p \sim -\gamma/r_m \sim -\frac{10^{-1}\ \mathrm{N/m}}{10^{-8}\ \mathrm{m}} \sim -10^{7}\ \mathrm{Pa} \approx -100\ \mathrm{atm.!}$$

↓

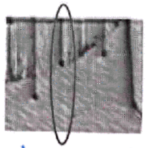
propensity for cracking



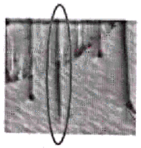




Why 2 critical stresses ? →



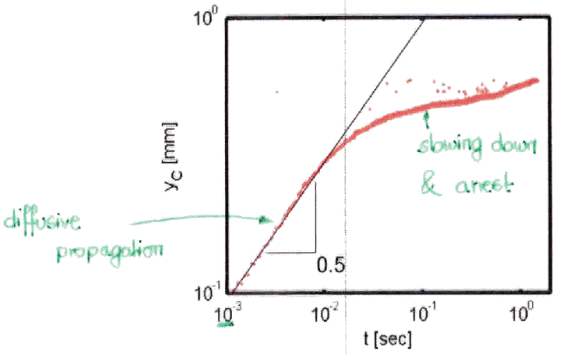
blunt crack (initiation)

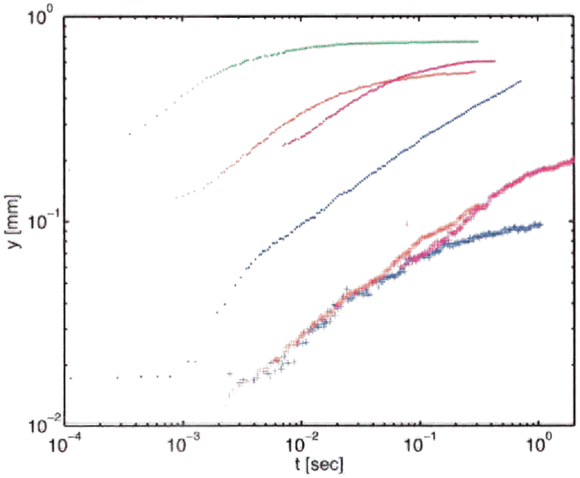


sharp crack (propagation)

Motion of individual cracks ?

high-speed video





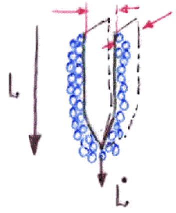
??

Elasticity & fracture of a fluid-filled porous network ! (Biot; 1941)

Energy balance : Elastic power = Viscous dissipation + Interfacial energy rate

$w$ = crack opening displacement

$h$ = film thickness ~ crack spacing



$$\sigma^2/E \cdot h^2 \dot{L} \approx \eta \cdot \left(\dot{L}/r_p\right)^2 \cdot w \cdot h \cdot L + \Gamma \cdot h \dot{L}$$

particle size ($r_p$)

$\Gamma = 2\gamma$ = interfacial energy/area

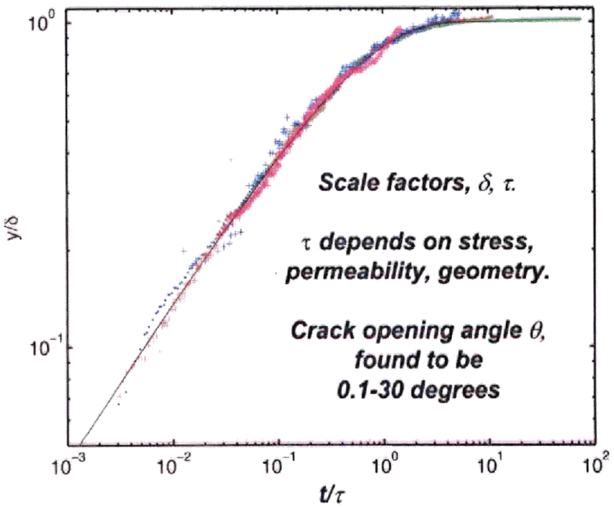
for a single crack $w = \sigma/E \cdot h$

$$\therefore \quad \dot{L} \sim \underbrace{r_p^2/\eta}_{\text{hydraulic permeability}} \left[1 - (\sigma_c/\sigma)^2\right] \sigma/L \quad ; \quad \sigma_c \sim \sqrt{E\Gamma/h}$$

$(k/\eta)$ hydraulic permeability

critical stress (starting !)

$\Rightarrow$ if $\sigma \gg \sigma_c$ ; $L\dot{L} \sim c$ i.e. $L \sim \sqrt{t}$



**Scale factors, $\delta$, $\tau$.**

**$\tau$ depends on stress, permeability, geometry.**

**Crack opening angle $\theta$, found to be 0.1-30 degrees**

## Conclusions / Lessons / Questions

- Monolayer particle rafts exhibit solid-like behavior
  - plasticity ?
  - shear banding/localization ?
  - dynamic fracture ?
- Capillary/evaporation driven consolidation
  → colloidal shells for encapsulation
  - Flow/irreversible behavior ??
  - evaporation/diffusion control of thickness ?
- Cracking of stressed poroelastic networks
  - playground for Biot 'slow' wave propagation ?
  - origin of $\sigma_c$ (start) / $\sigma_c$ (stop) ?
  - aggregate/suspension → solid ?

Puzzle : Can one have both cracking & buckling in the same specimen ?