Introduction to soft materials

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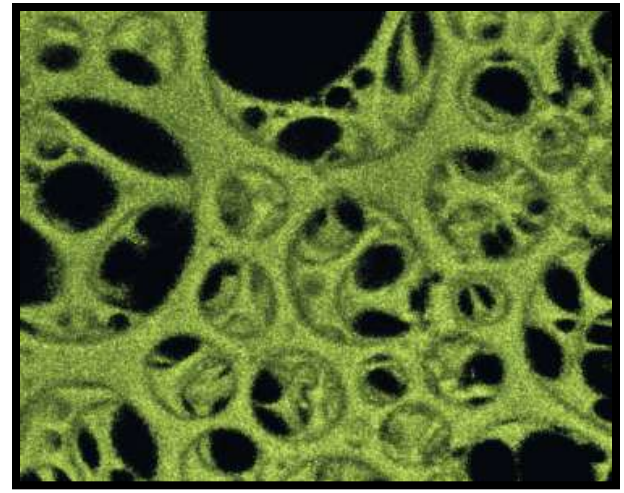
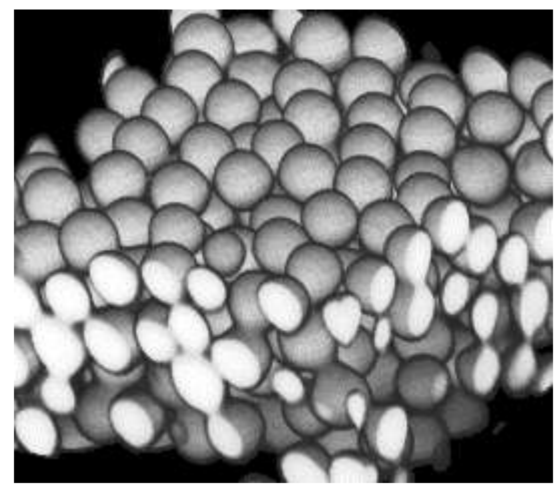


above: emulsion

toothpaste (colloid) and shaving cream (foam)



above: colloid

Examples of soft materials

- food
- toothpaste
- shampoo
- sand piles
- foam

Key theme: often mixtures of various components

Photo: Piotr Habdas

Why study soft materials?

- Lots of cool physics! (some to be discussed in this talk)
- Also some practical reasons…

Why study soft materials?

- Food! (pictures from Canteen #1)

rice noodles (粉丝)

sponge gourd + gluten (丝瓜面筋)

- Make low-fat products with same texture as “normal”
- Improve “shelf-life”: food texture changes with time

Why study soft materials?

- Biology: Understand mechanical properties of cells, tissues

people are soft materials

photo credit: Xin Du

Why study soft materials?

- Biology: Understand mechanical properties of cells, tissues

people are soft materials

- Physics: plenty of interesting physics to do!

photo credit: Xin Du

soft condensed matter

soft condensed matter

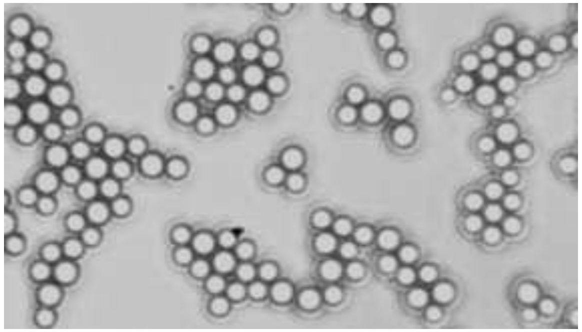
Study of soft systems, often composed of at least two components. Examples: foams, emulsions, colloids, polymers, gels, pastes, food, … Sometimes called "complex fluids".

Key question: how to relate microscopic structure to macroscopic properties.

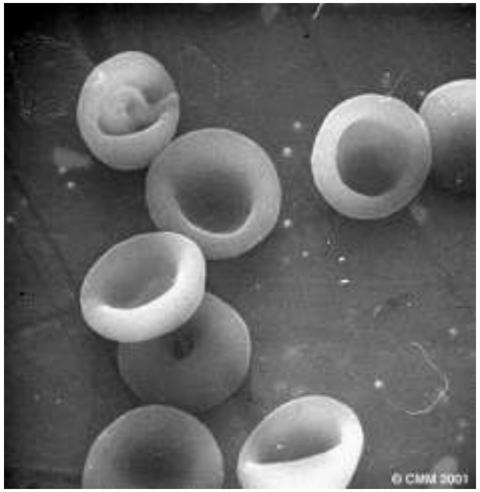
Example A: Colloids

Examples: milk, ink, paint, toothpaste, blood

- 1 nm - 10 μm solid particles in a liquid
- $k_B T$ important
- study with visible light ~ 0.5 μm
  (microscopy, light scattering)
- reasonable time scales



1-2 μm dia. colloids
(E. Weeks & H. Patel)



Red blood cells (5 μm dia.)
(http://www.uq.edu.au/nanoworld/)

Physics of colloids: Brownian motion

Leads to normal diffusion:

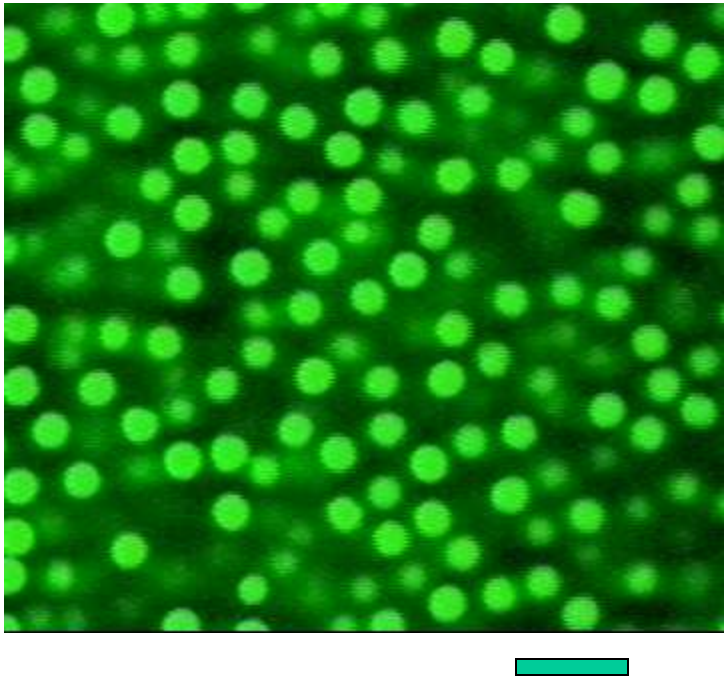
$$\langle \Delta r^2 \rangle = 6D\Delta t$$

$$D = \frac{k_B T}{6\pi\eta a}$$

viscosity η

particle radius *a*

a = 1 μm particles



5 μm

Digression:
Stokes-Einstein-Sutherland equation

$$D = \frac{k_B T}{6\pi\eta a}$$

<u>Derived in 1905:</u>

W. Sutherland, *Phil. Mag.*, **9**. 781.

A. Einstein, *Ann. der Physik*, **17**, 549.

Willian Sutherland in his twentieth year.

www.aapps.org/archive/bulletin/vol15/15_1/15_1_p35p36.pdf
antwrp.gsfc.nasa.gov/ apod/ap000108.html

Digression: Stokes-Einstein-Sutherland equation

$$D = \frac{k_B T}{6\pi\eta a}$$

On the motion of small particles suspended in liquids at rest required by the molecular-kinetic theory of heat
Einstein, *Annalen der Physik*, 17(1905), pp. 549-560.

Implication: Avogadro's number

A dynamical theory of diffusion for non-electrolytes and the molecular mass of albumin
Sutherland, *Philosophical Magazine*, S.6, 9 (1905), 781-785.

Implication: size of albumin

See: www.aapps.org/archive/ bulletin/vol15/15_1/15_1_p35p36.pdf

Calculating mean square displacement

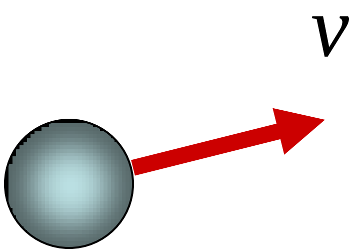
Measure $x_i(t)$ for different particles i

$$\Delta x_i\left(t,\Delta t\right) \equiv x\left(t+\Delta t\right) - x\left(t\right)$$

$$MSD\left(\Delta t\right) = \left\langle \Delta x_i^2\left(t,\Delta t\right)\right\rangle_{t,i}$$

average over all particles i, all initial times t

Physics of colloids: Sedimentation



Stokes drag force: $F_{drag} = 6\pi\eta a v$

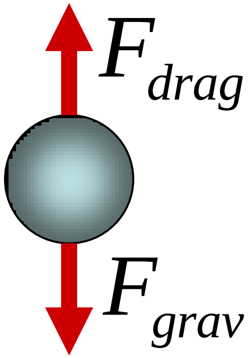
viscosity η

particle radius *a*

Gravitational force: $F_{grav} = mg \rightarrow \left(\frac{4}{3}\pi a^3\right)(\Delta\rho)\, g$

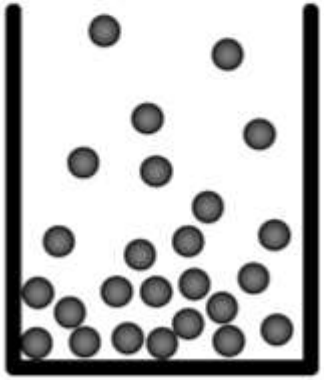
Problem #1: sedimentation & diffusion

Drag force: $F_{drag} = 6\pi\eta a v$



Gravitational force: $F_{grav} = m_{buoy} g = \left(\frac{4}{3}\pi a^3\right)(\Delta\rho)\, g$

Diffusion: $\langle \Delta r^2 \rangle = 6D\Delta t$ $\qquad D = \dfrac{k_B T}{6\pi\eta a}$



1. From balance of forces, find formula for v_{sed}
2. From $m_{buoy} g h = k_B T$, find formula for scale height h
3. Find formula for time to diffuse distance a^2

Answers #1: sedimentation & diffusion

1. From balance of forces, find formula for v_{sed}

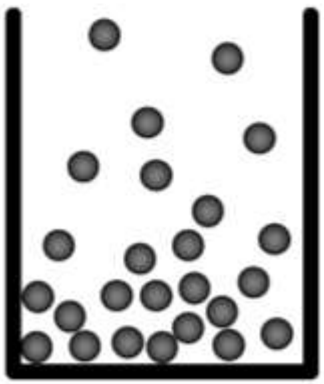
$$v_{sed} = \frac{2}{9}\frac{\Delta\rho a^2 g}{\eta} \propto a^2$$

2. From $m_{buoy}gh = k_BT$, find formula for scale height h

$$h = \frac{3}{4\pi}\frac{k_BT}{\Delta\rho a^3 g} \propto a^{-3}$$

3. Find formula for time to diffuse distance a^2

$$\tau_D = \frac{a^2}{6D} = \frac{\pi\eta a^3}{k_BT} \propto a^3$$



Meaning of Answers #1: sedimentation & diffusion

sedimentation velocity:

$$v_{sed} \propto \Delta\rho a^2 g$$

small particles sediment slowly; use centrifuge to ↑ g

scale height:

$$h \propto \frac{1}{\Delta\rho a^3}$$

strong size dependence of gravity, large particles "bad"

diffusion time:

$$\tau_D \propto a^3$$

small particles move fast

polystyrene particles in water:
$\Delta\rho \sim 0.05$ g/cm^3, $a \sim 1$ µm, $\eta \sim 10^{-3}$ Pa·s, kT=$4\cdot10^{-21}$ J

poly-methyl-methacrylate particles in density-matched solvent:
$\Delta\rho \sim 0.0005$ g/cm^3, $a \sim 1$ µm, $\eta \sim 2\cdot10^{-3}$ Pa·s

sedimentation velocity: $v_{sed} = \frac{2}{9}\frac{\Delta\rho a^2 g}{\eta}$	$\approx 0.1\ \mu$m/s	≈ 1 nm/s
scale height: $h = \frac{3}{4\pi}\frac{k_B T}{\Delta\rho a^3 g}$	$\approx 2\ \mu$m	$\approx 200\ \mu$m
diffusion time: $\tau_D = \frac{\pi\eta a^3}{k_B T}$	≈ 0.8 s	≈ 1.6 s

polystyrene particles in water:
$\Delta\rho \sim 0.05$ g/cm^3, $a \sim 1$ μm, $\eta \sim 10^{-3}$ Pa·s, kT=4·10^{-21} J

large polystyrene particles in water
$\Delta\rho \sim 0.05$ g/cm^3, $a \sim 100$ μm, $\eta \sim 10^{-3}$ Pa·s

sedimentation velocity:

$$v_{sed} = \frac{2}{9}\frac{\Delta\rho a^2 g}{\eta}$$

$\approx 0.1\ \mu$m/s | ≈ 1 mm/s

scale height:

$$h = \frac{3}{4\pi}\frac{k_B T}{\Delta\rho a^3 g}$$

$\approx 2\ \mu$m | ≈ 2 pm

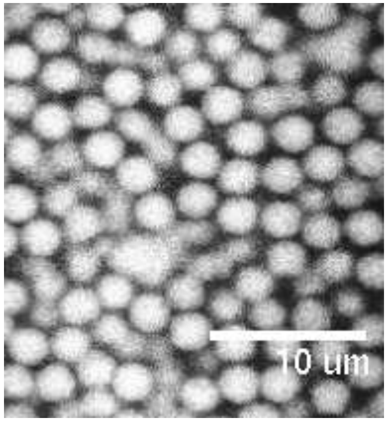
diffusion time:

$$\tau_D = \frac{\pi\eta a^3}{k_B T}$$

≈ 0.8 s | ≈ 9 days

Important points about colloids:

- Small size important
- Understanding scaling with *a* straightforward, useful
- Granular particles (a > 10 μm) aren't thermal



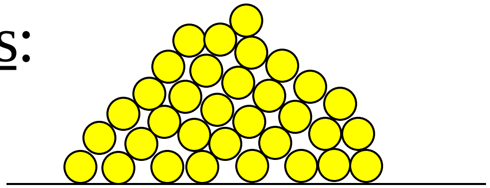
Example B: Granular materials

Definition: large, solid particles in air or vacuum

Solid-like: pile of sand
Liquid-like: pouring sand from bucket
Gas-like: throw sand into the air

Key differences from colloids:

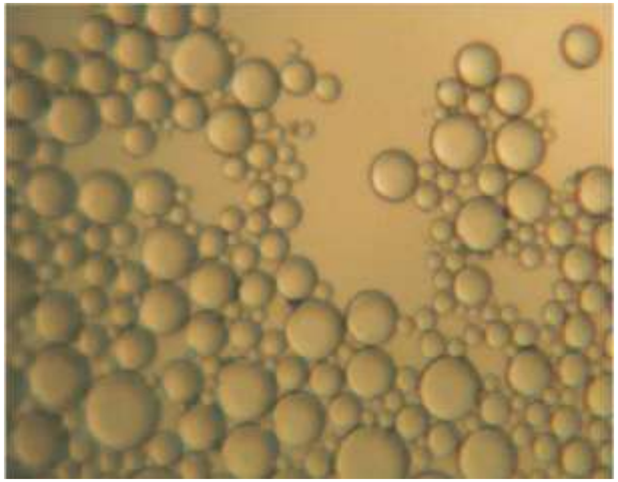
- Friction important
- $k_B T$ not important
- Gravity important (unless 2D horizontal system, or microgravity, or simulation)

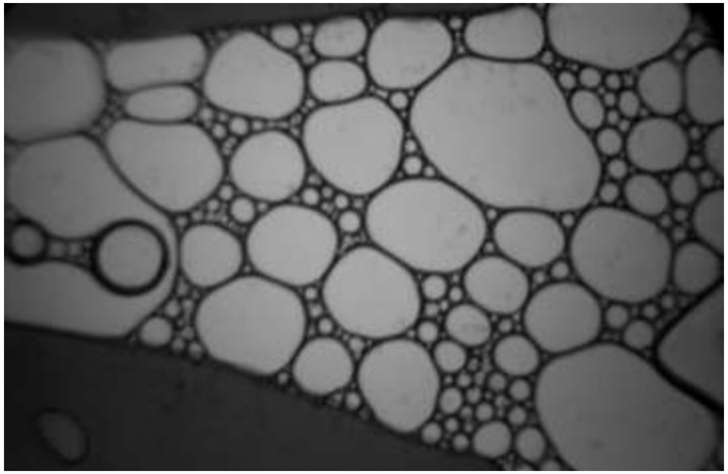


Example C: Emulsions

Definition: Liquid droplets in another liquid (oil & water)
Add surfactant (= soap) to prevent coalescence of droplets

Examples: mayonnaise (surfactant = egg), butter



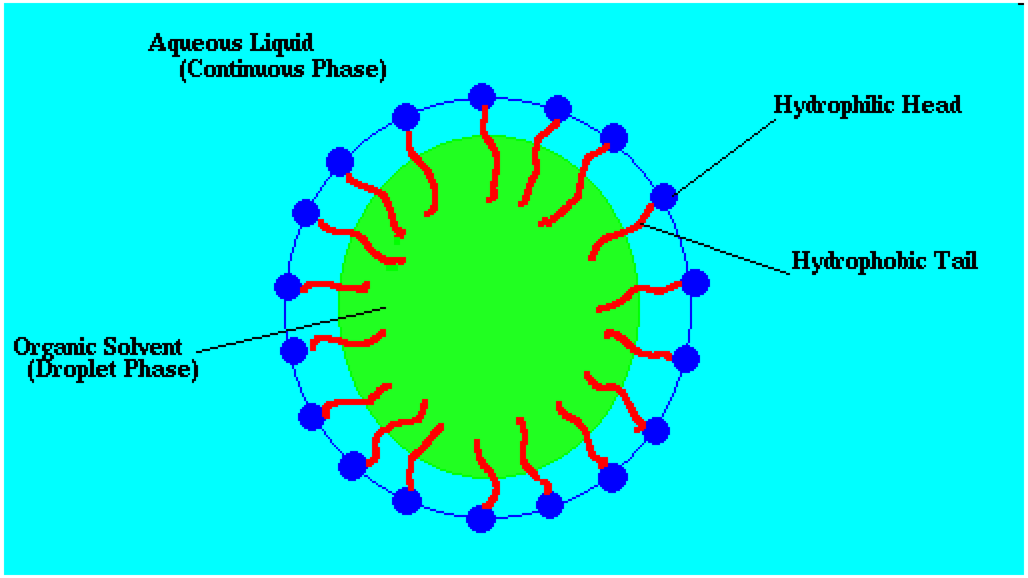


Images taken here in Shanghai.

Example C: Emulsions

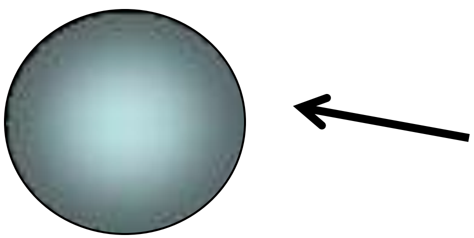
Liquid droplets in another liquid (oil & water)
Add surfactant to prevent coalescence of droplets

Key differences from colloids: droplets can deform; surfactants control surface tension which controls deformability



What is surface tension?

Surface tension γ = energy cost per unit area



Energy of surface ~ γa^2

To make emulsion with droplets of radius a:

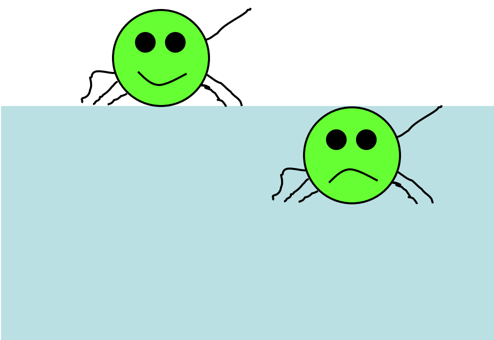
total volume = V, number of droplets $N \sim Va^{-3}$, total area $A \sim Va^{-1}$

→ thus requires energy E ~ $V\gamma/a$ to make emulsion

Question #2:

Why do bugs get to walk on water and not me?

Surface tension γ = energy cost per unit area



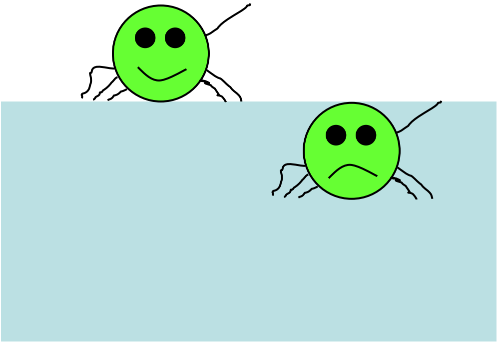
Approximate bug as sphere of radius a.

What is change in gravitational potential energy ΔGPE when bug is immersed?

What is change in surface energy ΔSE when bug is immersed, using water/bug surface tension γ?

How to use ΔGPE and ΔSE to answer top question?

Answer #2:
Why do bugs get to walk on water and not me?



What is change in gravitational potential energy ΔGPE when bug is immersed?

$$\Delta GPE = mga - (-m_{buoyant}ga)$$

$$= \left(\tfrac{4}{3}\pi a^3\right)\left(\rho + \Delta\rho\right)ga$$

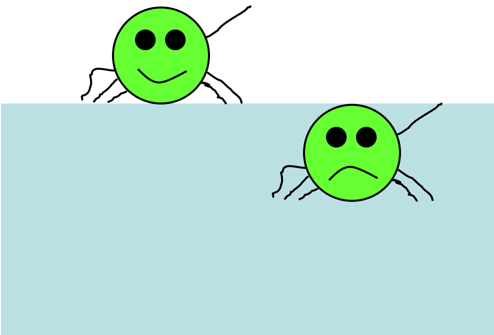
$$\approx \tfrac{4}{3}\pi a^4 g\rho \sim a^4$$

(Assuming $\Delta\rho \sim 0$, bug is density of water)

Answer #2:

Why do bugs get to walk on water and not me?

Surface tension γ = energy cost per unit area

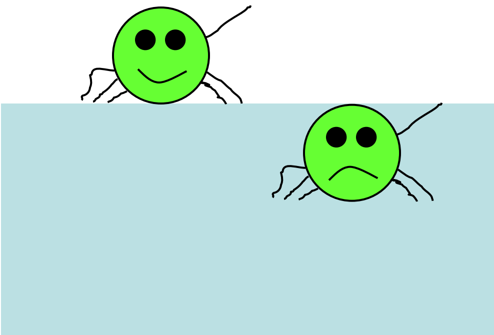


What is change in surface energy ΔSE when bug is immersed, using water/bug surface tension γ?

$$\Delta SE = 4\pi a^2 \gamma \, \square \, a^2$$

Answer #2:

Why do bugs get to walk on water and not me?



How to use ΔGPE and ΔSE to answer top question?

$$\Delta GPE \propto a^4 \qquad \Delta SE \propto a^2$$

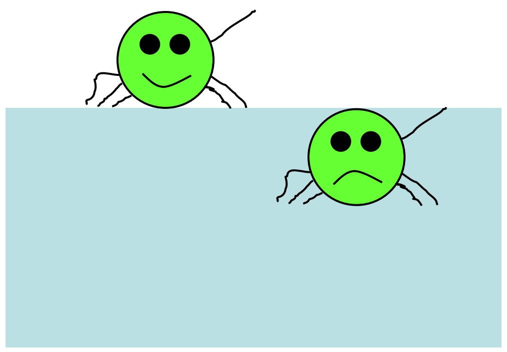
thus, $\Delta GPE / \Delta SE \propto a^2$

if a small enough, SE penalty more significant than GPE reward

Answer #2:

Why do bugs get to walk on water and not me?

How to use ΔGPE and ΔSE to answer top question?



$$\Delta GPE \approx \tfrac{4}{3}\pi a^4 g \rho$$

$$\Delta SE = 4\pi a^2 \gamma$$

$$\Delta GPE / \Delta SE \approx \frac{\rho g}{3\gamma} a^2 \overset{set}{=} 1$$

$$a_0 = \sqrt{\frac{3\gamma}{\rho g}} \approx 4 \text{ mm}$$

Larger than a_0, you sink. ☹

Using $\gamma_{air/water}$ = 0.07 J/m^2

Laplace Pressure of Droplets

Consider balloon: balloon compresses until internal pressure sufficiently high

$$\Delta P = \frac{\gamma}{a}$$

Thus, smaller emulsion droplets are at higher pressure.

image from Wikipedia

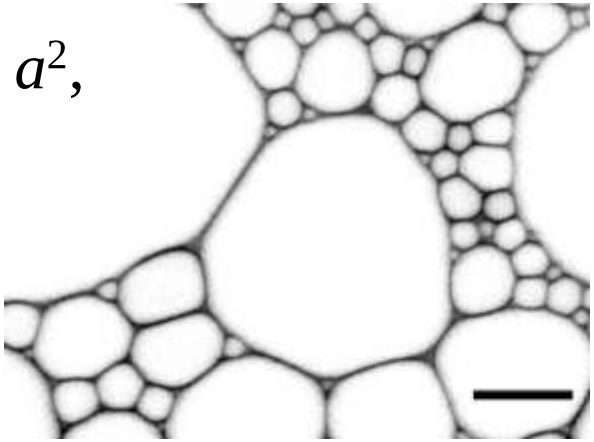
Implications for emulsion droplets:

- Droplets like to be round (minimize surface energy)

- Very large droplets sag under their own weight

- Smaller droplets are stiffer

- Surfactants modify γ, but energy scales as a^2, thus size is more influential



10 μm

picture: C Hollinger & E Weeks

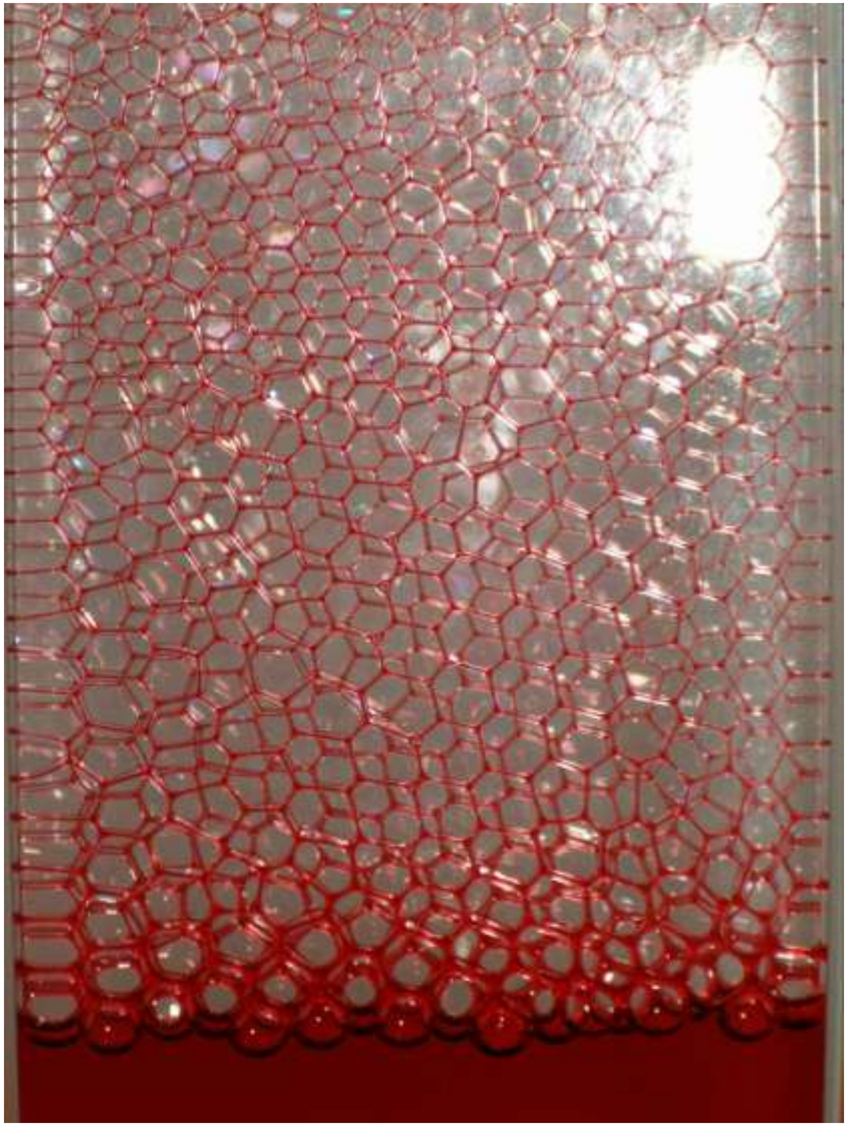
Example D: Foams

Definition: Like emulsions, but gas bubbles rather than droplets. Still need surfactant.

Troubles:

• Foams "coarsen" as gas diffusions from small bubbles to large (due to Laplace pressure)

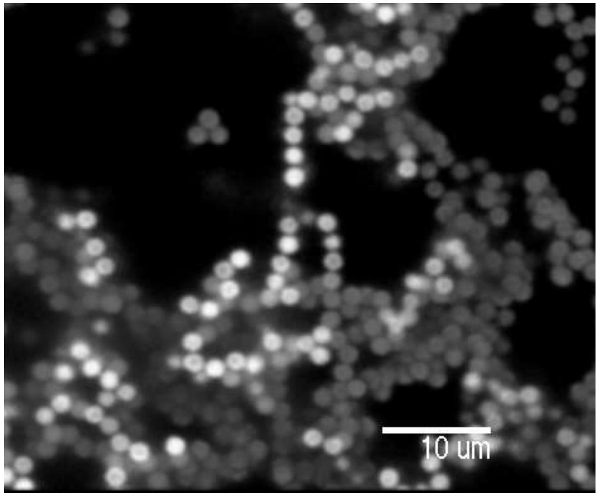
• Foams drain (liquid is heavy)



Picture: G Cianci & E Weeks

Example E: colloidal gels

Many reasons colloids stick together; often trick is to prevent them from sticking!



picture: G Cianci & ER Weeks

These materials are viscoelastic: soft and squishy

Movie: Eric Weeks and Xin Du, from Wednesday

Rheology: measuring response of material to stress

Elastic (Hookean) solid:

$\sigma \sim \gamma$ (stress proportional to strain)

Viscous (Newtonian) fluid:

$\sigma \sim \dot{\gamma}$ (stress proportional to strain rate)

Viscoelastic material:

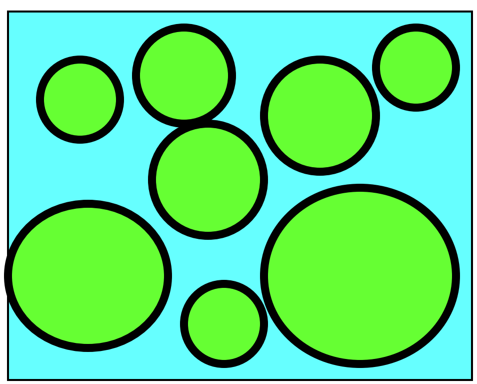
apply oscillating strain $\gamma_0 \sin(\omega t)$, measure stress

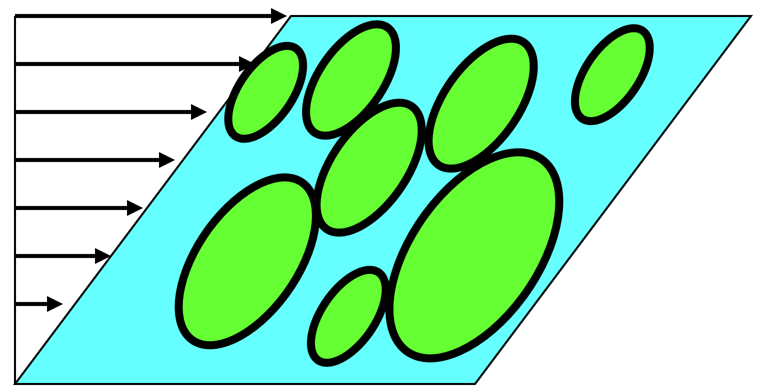
$$\sigma(t) = \gamma_0 \left[G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t) \right]$$

elastic modulus

viscous modulus

Emulsions & foams are viscoelastic due to surface tension

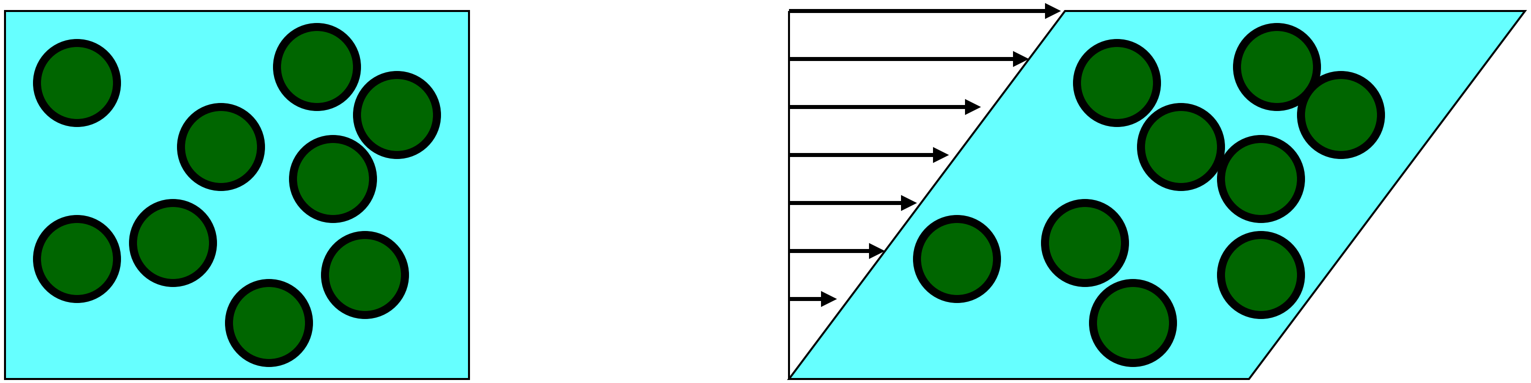




Shearing sample = distorts droplet shapes = increases their surface area = **elastic response**

Fluid moves around = **viscous response**

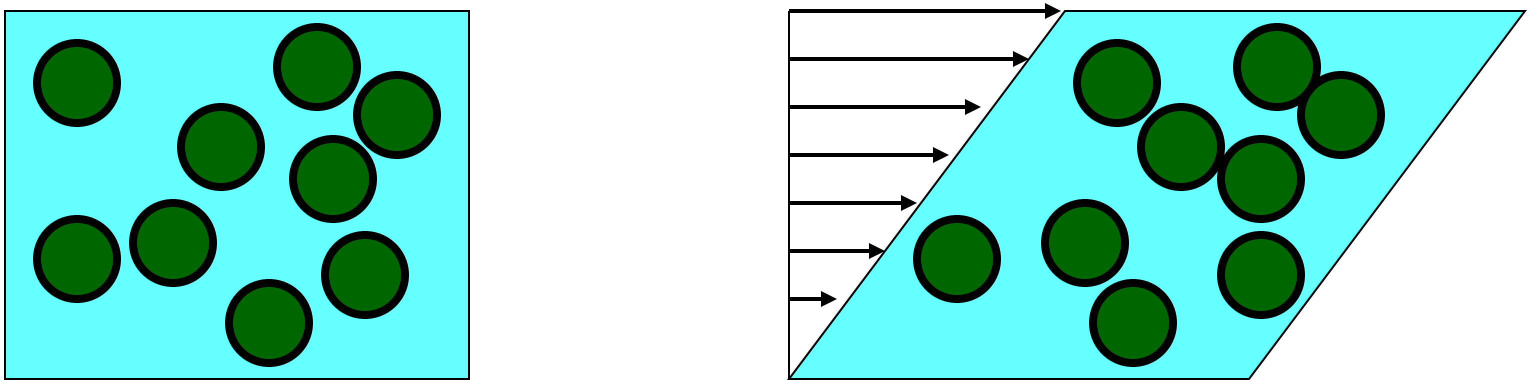
How is a colloidal suspension elastic?



Shearing sample = moves some closer together. If particles have long-range repulsion, this stores energy = **elastic response**

Fluid moves around = **viscous response**

What if particles only have short-range repulsion?



Many colloidal particles act like "hard spheres" and only repel when they touch.

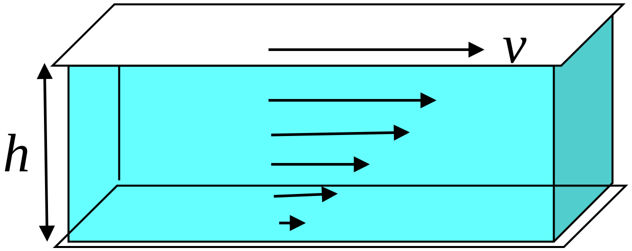
Entropy: sheared configuration has lower entropy = costs free energy = **elastic response**

Fluid moves around = **viscous response**

Péclet number: how fast colloids are sheared

- Time to diffuse: $\tau_D = \dfrac{a^2}{6D}$

- Time to shear: $\tau_S = \dfrac{h}{v} = \left(\dot{\gamma}\right)^{-1}$



$\dot{\gamma}$ is "strain rate"

Péclet number: how fast colloids are sheared

- Time to diffuse: $\tau_D = \dfrac{a^2}{6D}$

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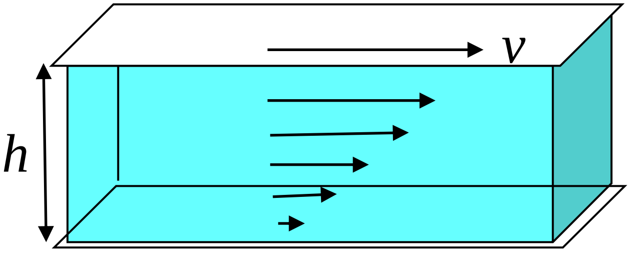
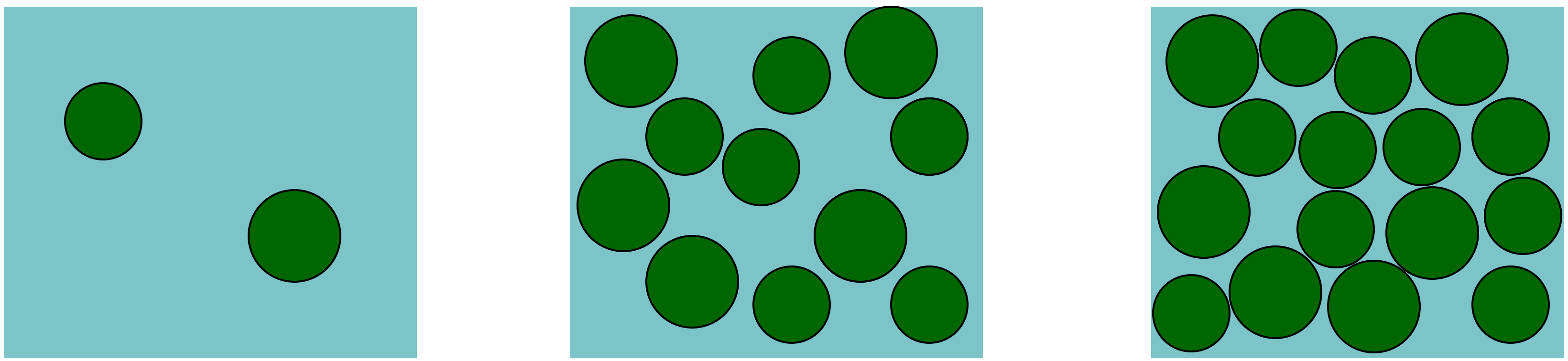


- Ratio: $\mathrm{Pe} \equiv \dfrac{\tau_D}{\tau_S} = \dfrac{a^2\dot{\gamma}}{6D}$

If Pe << 1, expect viscous response. Pe >> 1, elastic response.

Another control parameter: volume fraction ϕ



$\phi \approx 0.1$ $\phi \approx 0.5$ $\phi \approx 0.65$

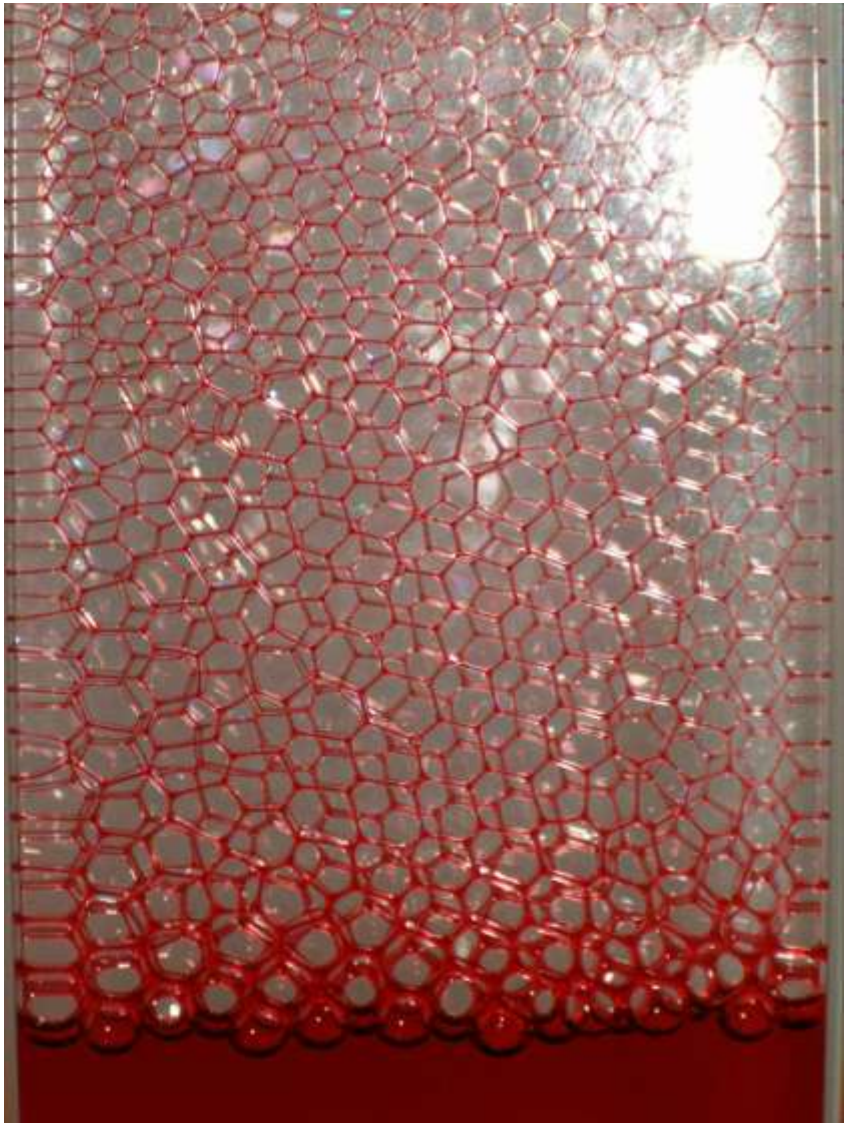
ϕ = fraction of volume occupied by particles (or droplets, or bubbles)

As ϕ increases, elastic response increases. Above $\phi_c \approx 0.6$, becomes solid-like. (Exact value depends on details.)

Example: 3D foam

$\phi \approx 1.00$

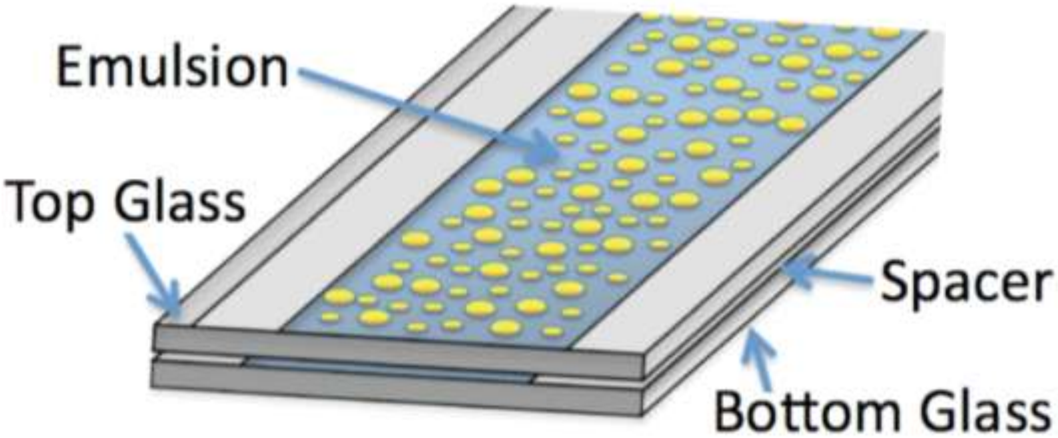
$\phi \approx 0.65$

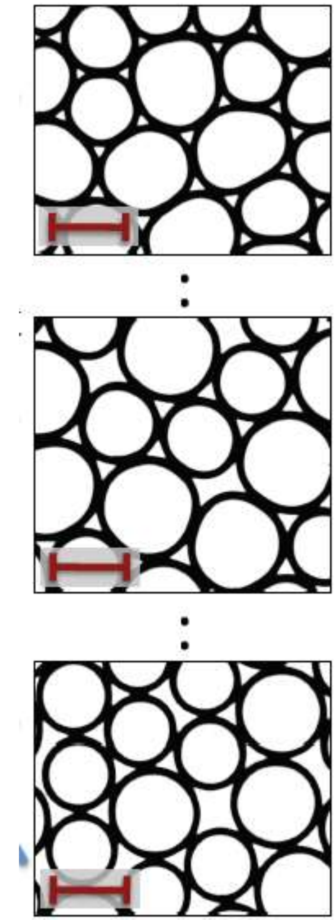


Picture: G Cianci & E Weeks

Example: quasi-2D foam

K. W. Desmond *et al.*, arXiv: 1206.0070



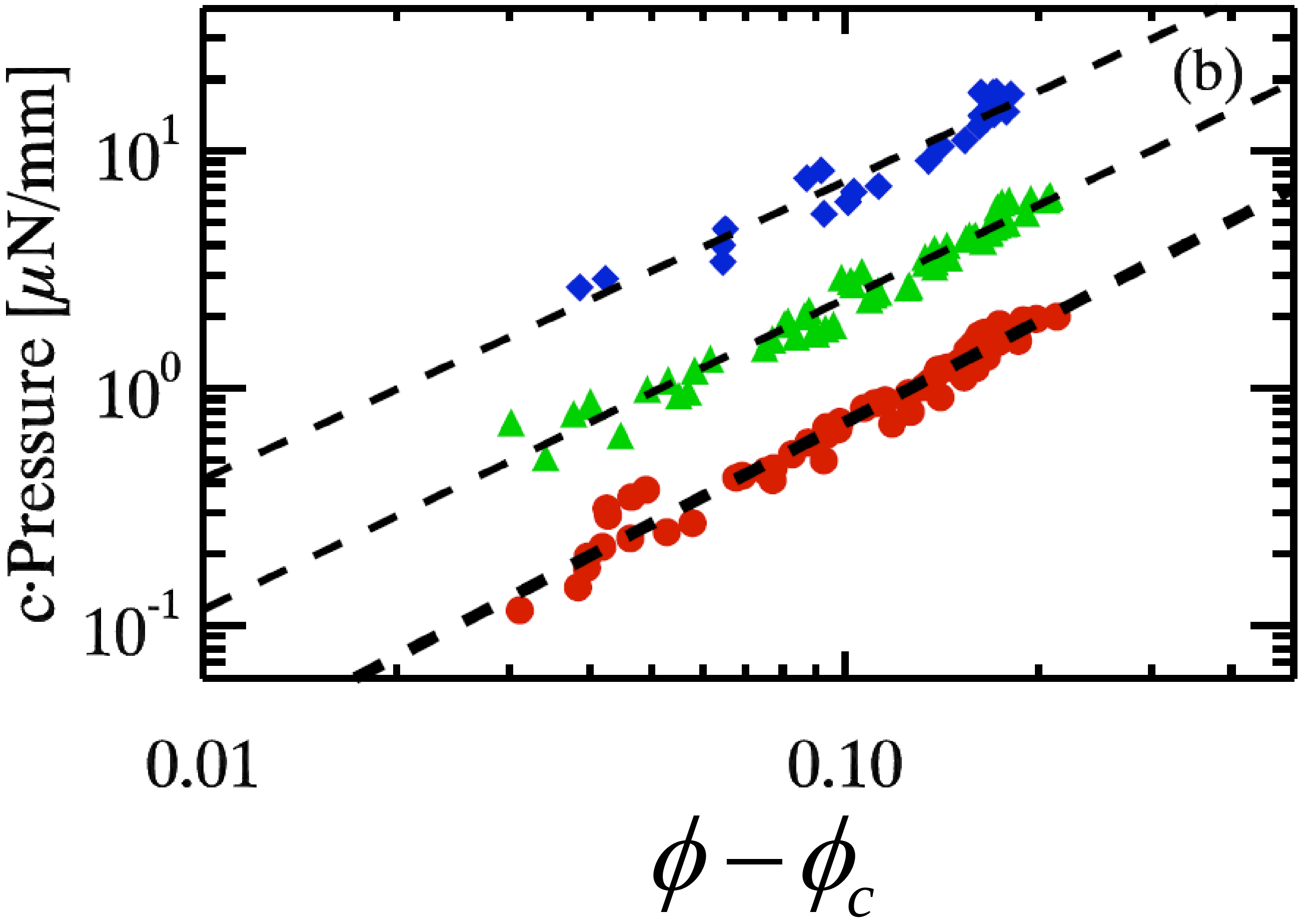


ϕ = 0.96, 0.92, 0.88 (top to bottom)
scale bar = 200 μm

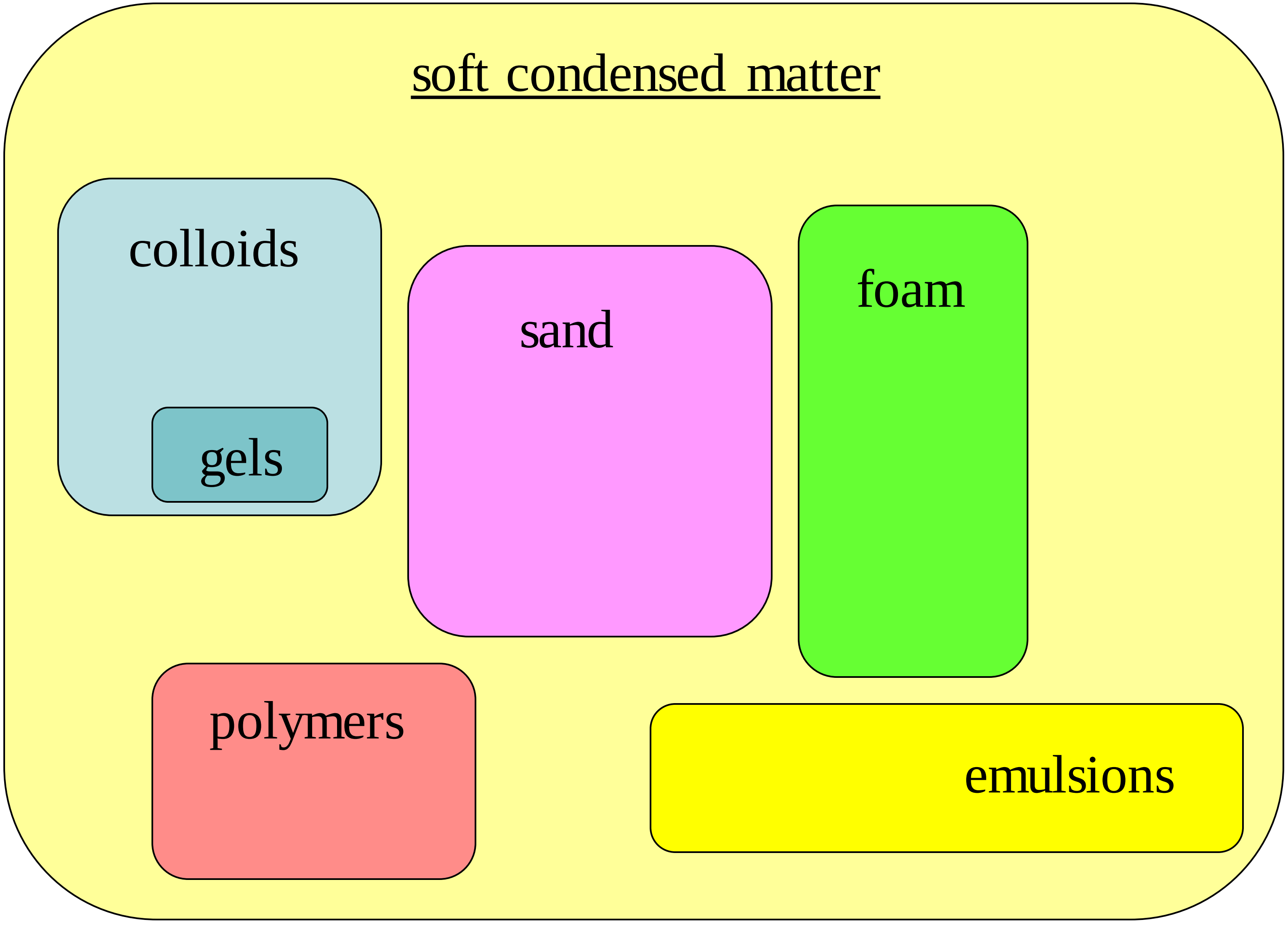
See critical-like scaling of pressure with area fraction ϕ

K. W. Desmond *et al.*, arXiv: 1206.0070

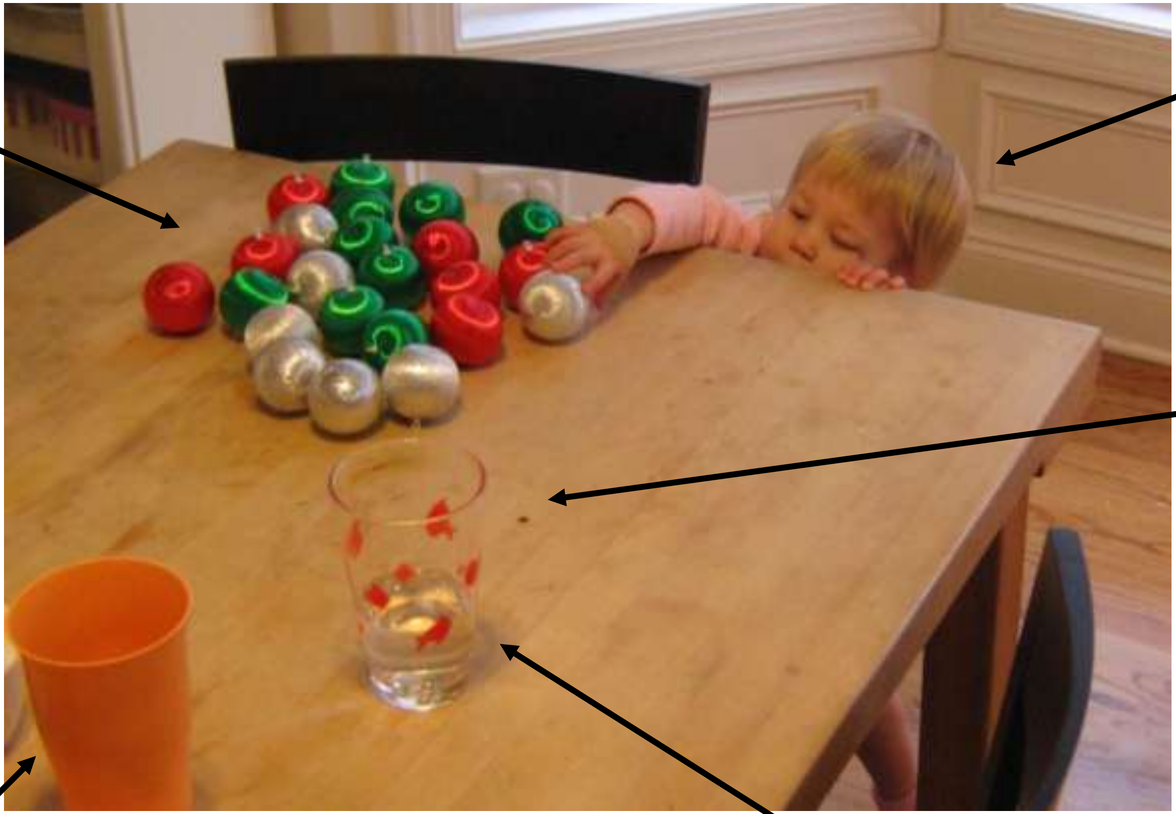
$$P \sim (\phi - \phi_c)^{\beta}, \quad \beta \approx 1.3$$



Different colors for samples with different size ratios


soft condensed matter
colloids
gels
sand
foam
polymers
emulsions

Conclusion:
Life is full of interesting materials



large granular media

biopolymers

glass

polymer glass

liquid

Further Reading

- "The physics of the colloidal glass transition," GL Hunter & ER Weeks, *Rep. Prog. Phys.* **75**, 066501 (2012). Discusses the physics of sedimentation, diffusion, etc.

- "Soft jammed materials," ER Weeks, book chapter in *Statistical Physics of Complex Fluids*, eds. S. Maruyama & M Tokuyama (Tohoku University Press, Sendai, Japan, 2007). Download the preprint version on my website (below). Discusses all of the soft materials mentioned in my talk.

- "Squishy materials," P Habdas, ER Weeks, & DG Lynn, *The Physics Teacher* **44,** 276-279 (May 2006). If you are interested in teaching about these materials. Discusses some simple lab experiments and demos.

- "Video microscopy of colloidal suspensions and colloidal crystals," P Habdas & ER Weeks, *Current Opinion in Colloid and Interface Sci.* **7**, 196-203 (2002). Discussion of microscopy techniques.

- You can download PDF copies of all of these articles here:
  www.physics.emory.edu/~weeks/lab/pubs.html