# Preview – Complex Colloids

**Willem Kegel**
*Van 't Hoff Laboratory*
*Utrecht University*
*The Netherlands*

**Finite-size equilibrium structures <-> macroscopic phase separation (part I)**

Colloidal molecules (**Statphys** – brief summary here)

Equilibrium clusters & periodic structures in systems with long-range repulsion and short-range attraction

Emulsification by colloids – Solid-stabilized or 'Pickering' emulsions.

Free energy of dispersed matter in capillary approximation:

Finite size –micro- *versus* macroscopic phase separation

$$F = F_0 + \gamma S$$

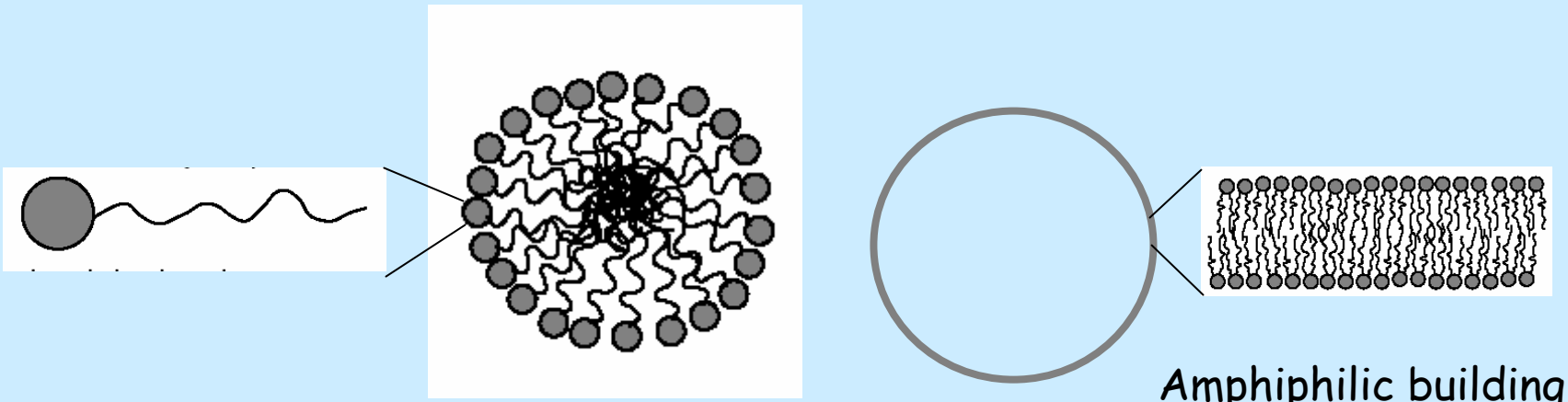
Bulk

Surface

Minimize $F$ by minimizing surface area $S$ → macroscopic phase separation

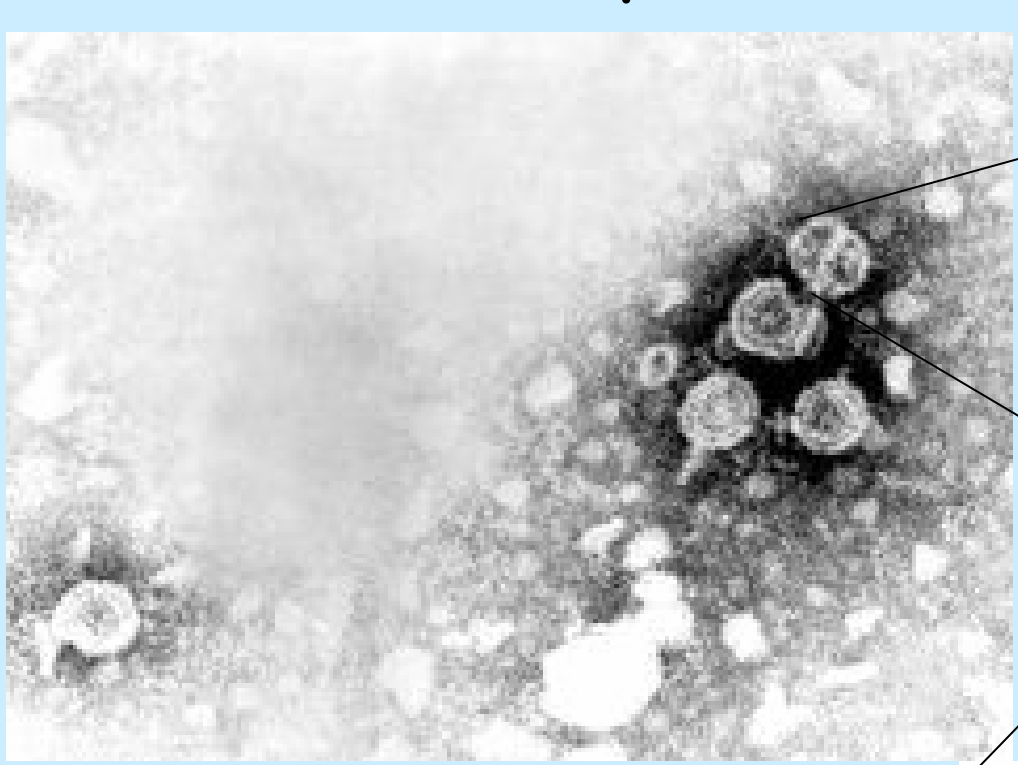
**'Micro' phase separation: internal constraints**

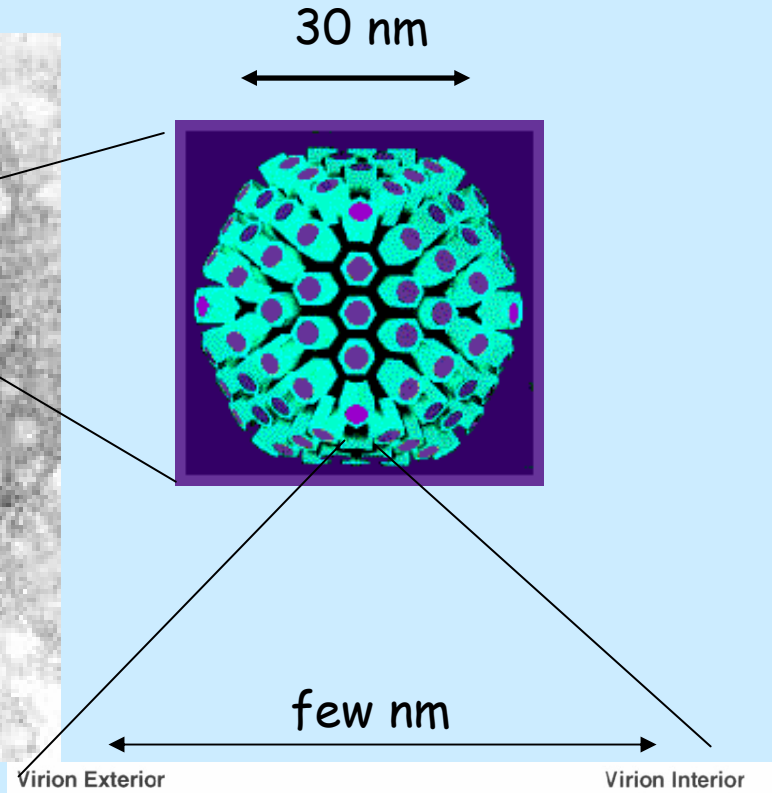
Micelles, microemulsions, vesicles, diblock copolymers…



Amphiphilic building blocks

# ...virus capsids ~ 'coats' of viruses

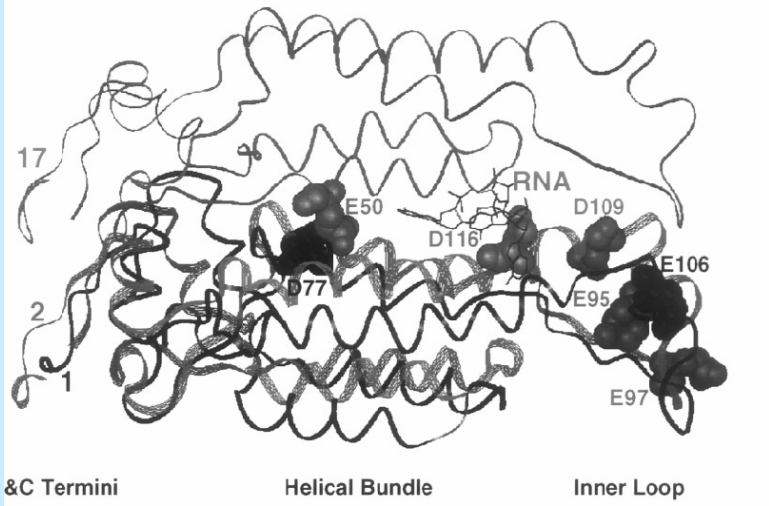




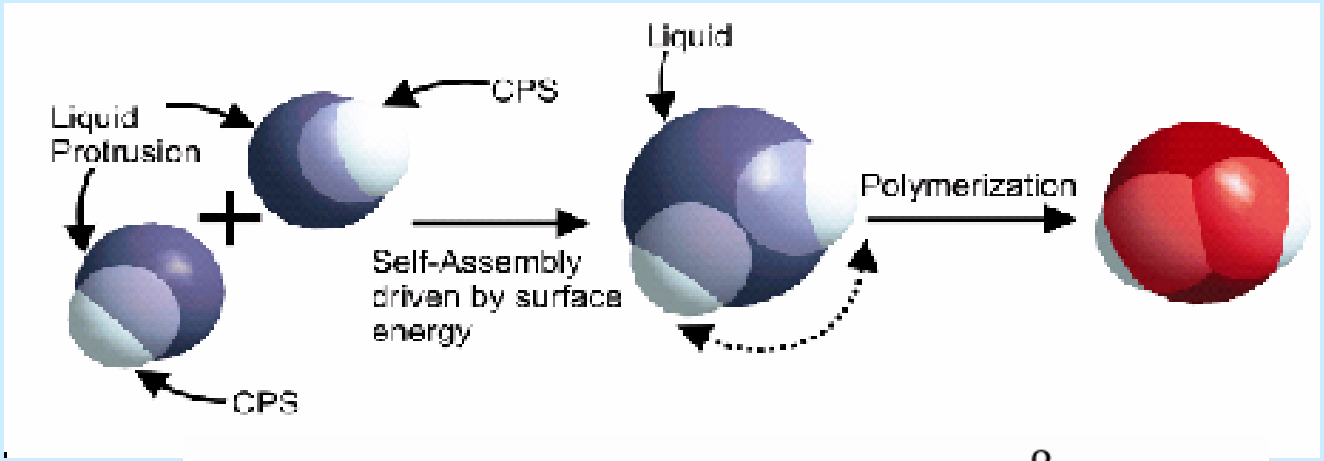

(Un)coating regulated by:
* Hydrophobic interactions between apolar **patches** on protein surface

•Screened-Coulomb interactions

[WKK & P. vd Schoot, BPJ 2004; 2006]



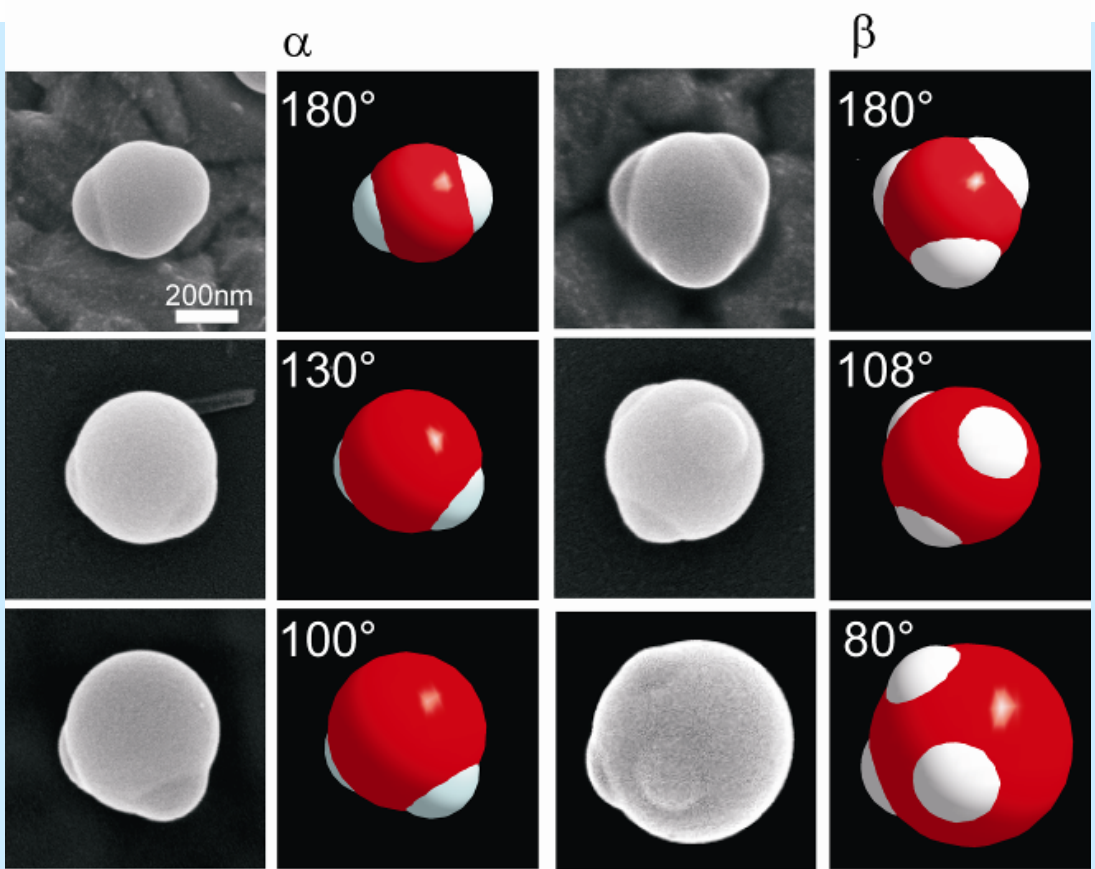
# Colloids with tunable geometry



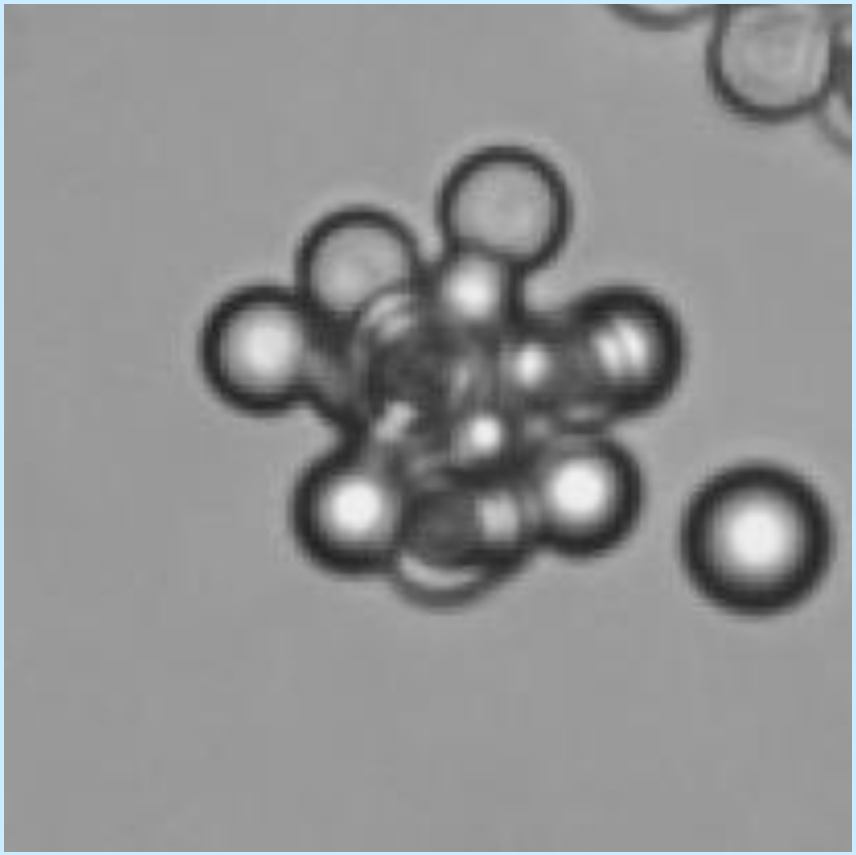

Plausible mechanism:

Depletion forces generated during polymerization

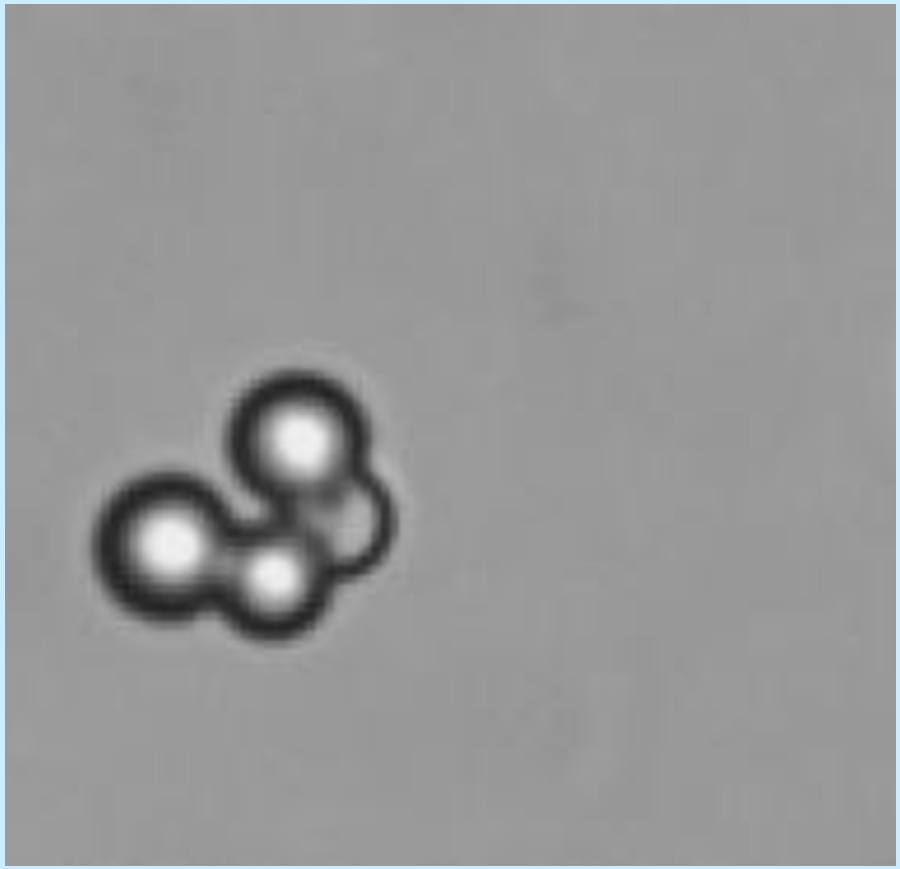
DJ Kraft ea
JACS, Soft Matt 2009

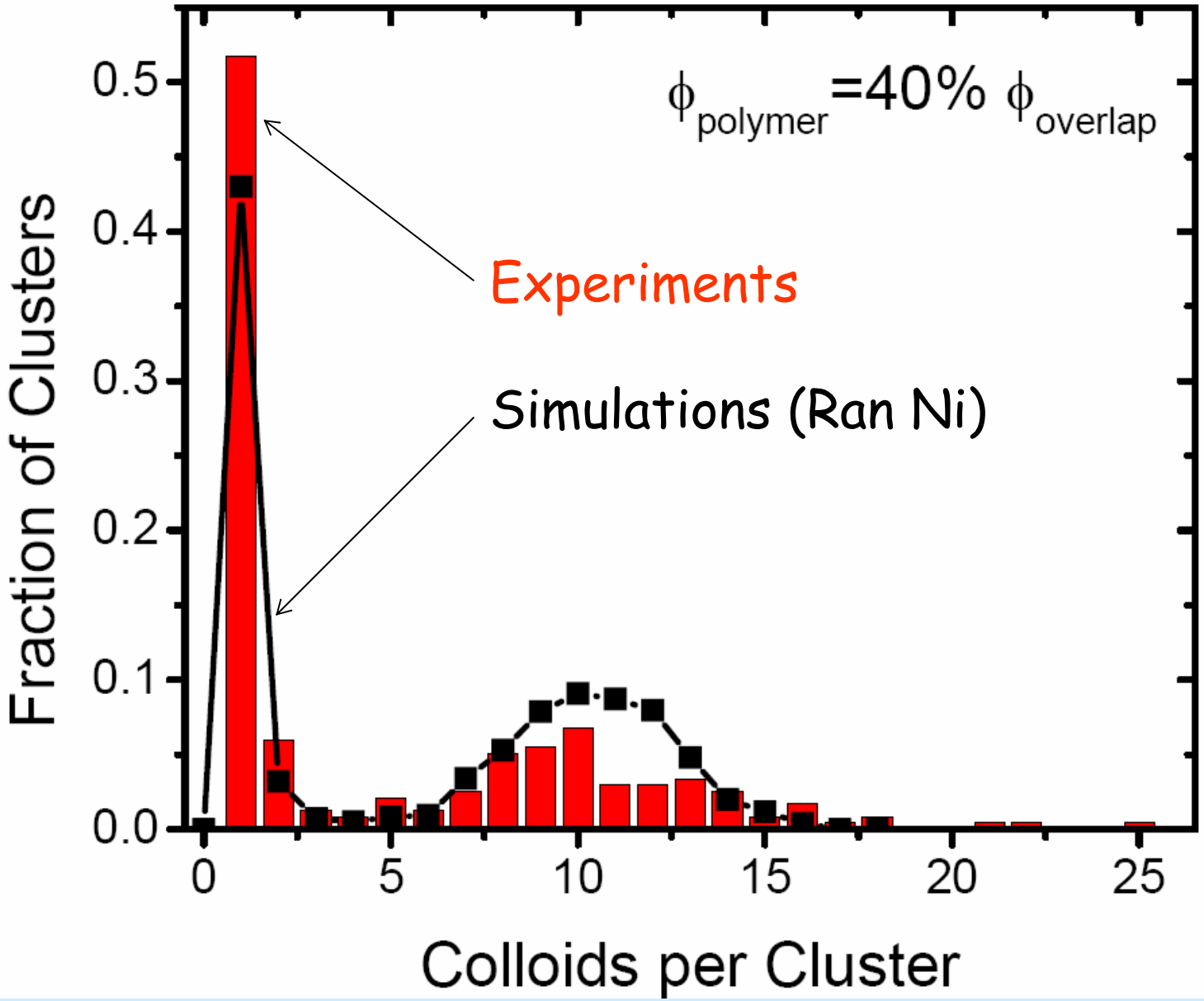


Colloidal micelle



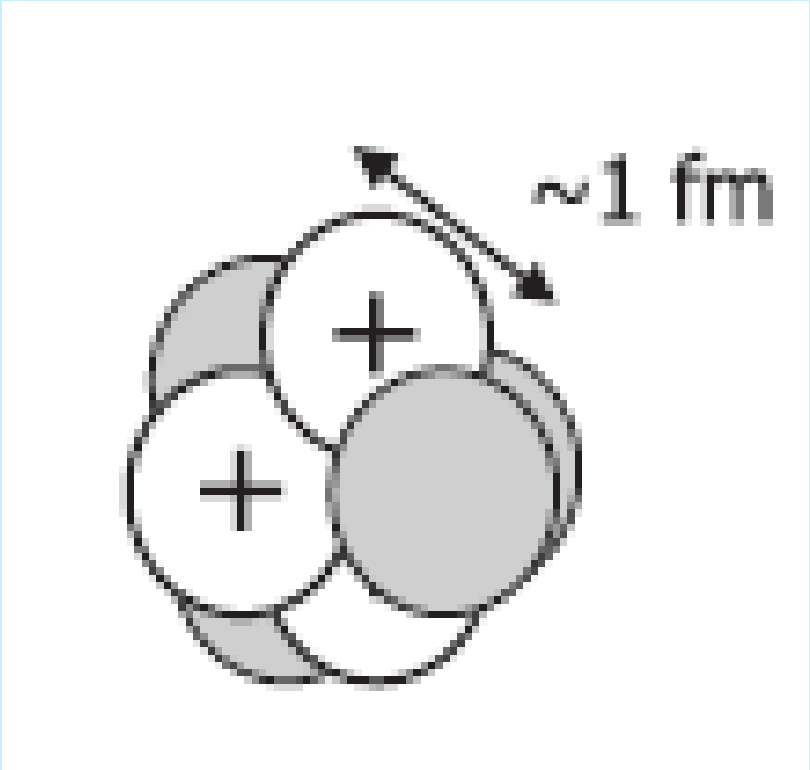
Colloidal dimer




$\phi_{polymer}$=40% $\phi_{overlap}$
Experiments
Simulations (Ran Ni)
Fraction of Clusters
0.0
0.1
0.2
0.3
0.4
0.5
0
5
10
15
20
25
Colloids per Cluster

Atomic nuclei –

internal constraint = long-range Coulomb repulsion



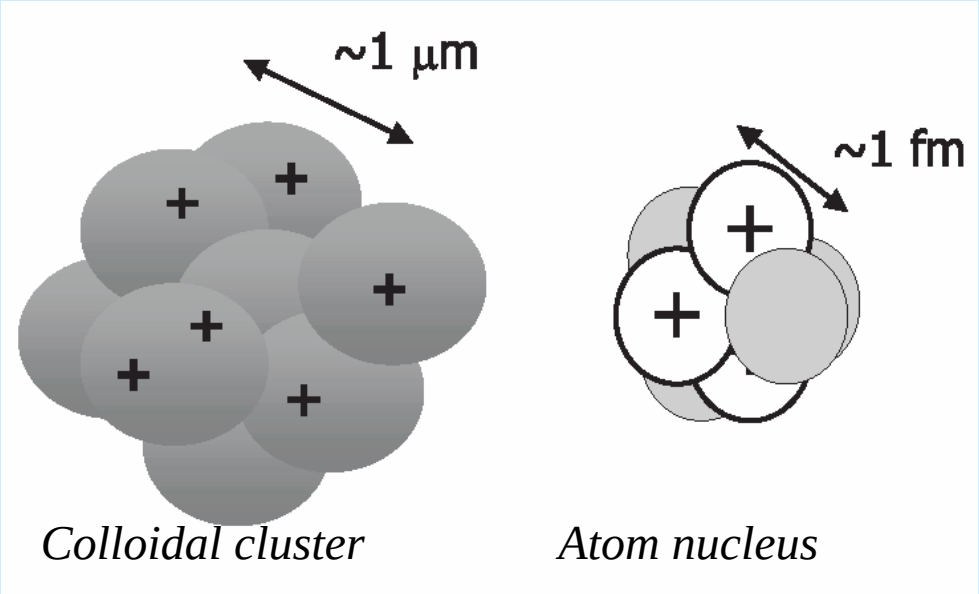
# Part I: Colloids as nucleons

# Outline

- Weakly charged colloids, low screening: **colloids as nucleons** Why low screening? High screening has been done: **DLVO**
- Cluster phases in colloids & proteins – controversies
- Higher densities – link with dense nuclear matter

# Colloids & nucleons

[J. Groenewold & WKK. *J. Phys. Chem. B* **105**, 11702 (2001); *J. Phys.: Condens. Matter* **16** S4877 (2004) ]

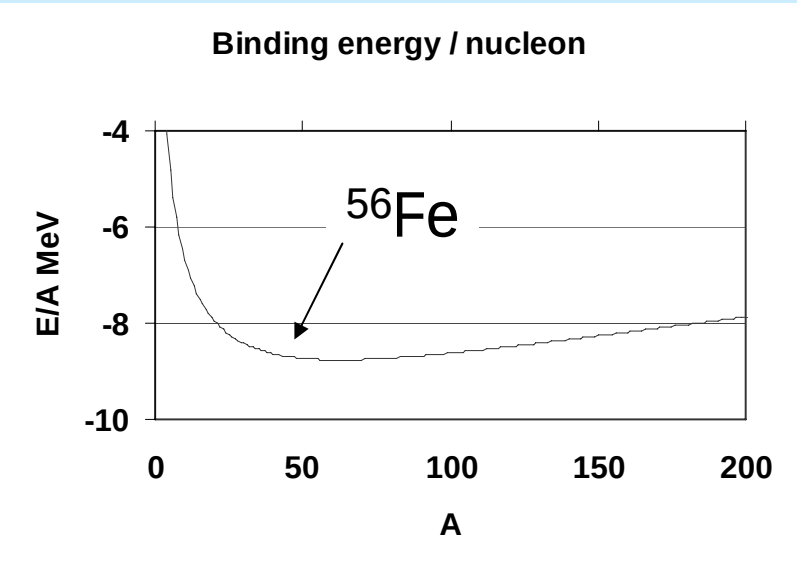


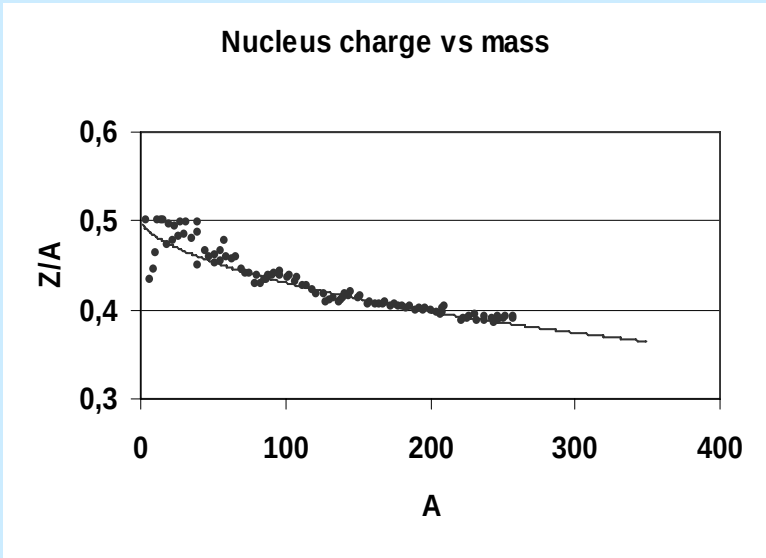

| | | |
|---|---|---|
| Short-range attraction | Van der Waals / depletion | Strong nuclear force |
| + | | |
| long-range repulsion | (Screened) Coulomb | Coulomb |

Mass formula (nuclei of atomic number A, nuclear charge Z):

$$F/A = -a_{vol} + a_{sym}\left(1 - \frac{2Z}{A}\right)^2 + a_{surf}A^{-1/3} + a_{Coul}Z^2A^{-4/3}$$

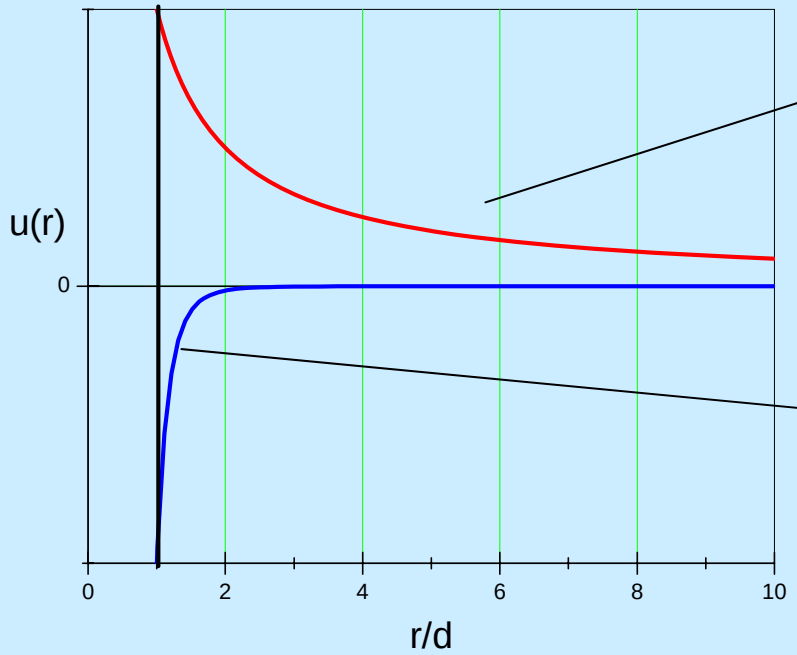
(neglect pairing term)




electron capture: $p + e^- \rightarrow n + \nu$

Colloidal equivalent:




Charged colloids in solvents with small dielectric constant: long-range repulsion (long screening length)

Attractive **potential of mean force** by (e.g.,) depletion of polymers

Ionic dissociation at low dielectric constants: dissociation energy $kT\lambda_B/b$ – ionization due to increased translational entropy of counter ions.

Bjerrum length

bond length

"ion capture": $C^{(n+1)+} + i^- \rightarrow C^{n+}$

Free energy density of spherical colloidal cluster of radius R:

$$f = f_0 + 3\gamma R^{-1} + \frac{4\pi}{5}\lambda_B\rho^2 R^2 + 2\rho\left(\ln(\rho/\rho_0) - 1\right)$$

Surface tension

Charges/ volume

Entropy (ions + combinatorial)

$$\rho_0^2 \approx \frac{e^{-\lambda_B/b}\sigma}{rb^3\phi}$$

# Intermezzo: site-binding model

Ions can be bound to colloid surface with energy $-\lambda_B / b$
or translate freely in bulk

*Free energy $F = -\ln Q = -\ln Q_{ads} Q_{bulk}$

$$\lambda_B = \frac{e^2}{4\pi\varepsilon\varepsilon_0 kT}$$

$$Q_{ads} \approx \frac{Z_{\max}!}{Z!(Z_{\max} - Z)!}\left(e^{\lambda_B / b}\right)^{(Z_{\max} - Z)}$$

$$Q_{bulk} \approx \frac{V^Z}{Z! b^{3Z}}$$

Take $Z \ll Z_{max}$

$$\longrightarrow \quad f = \frac{F}{V_{cluster}} = 2\rho\left(\ln(\rho / \rho_0) - 1\right)$$

$$\sigma = Z_{\max} / 4\pi r^2$$

$$\phi = \frac{n v_{colloid}}{V}$$

$$\rho_0^2 \approx \frac{e^{-\lambda_B / b}\sigma}{r b^3 \phi}$$

*Minimum ρ *
(without Coulomb term)

r ≡ colloid radius

'Entropic' term $\equiv$ charge - generating

Similar role as symmetry term in mass formula:

Expand around $\rho_0$:

$$2\rho\left(\ln(\rho/\rho_0)-1\right) \approx -2\rho_0 + \frac{1}{\rho_0}(\rho_0-\rho)^2$$

Now cluster free energy *isomorphic* to 'mass formula' !

→ Map cluster free energy onto mass formula. Result:

$$A \to 4\pi R^3 / 3v$$

$$Z \to 4\pi R^3 \rho / 3v\rho_0$$

$$a_{vol} \to -f_0 v + 2\rho_0 v$$

$$a_{surf} \to 4.84\gamma v^{2/3}$$

$$a_{sym} \to kT\rho_0 v$$

$$a_{Coul} \to 0.48kT\lambda_B \rho_0^2 v^{5/3}$$

Numbers comparable for: $\sim 1\ \mu\mathrm{m}$ colloids in solvent $\varepsilon \approx 10$ and sufficient charge density

…experimentally observed?

First indications:
Segre ea, PRL **86**, 6042, (2001)

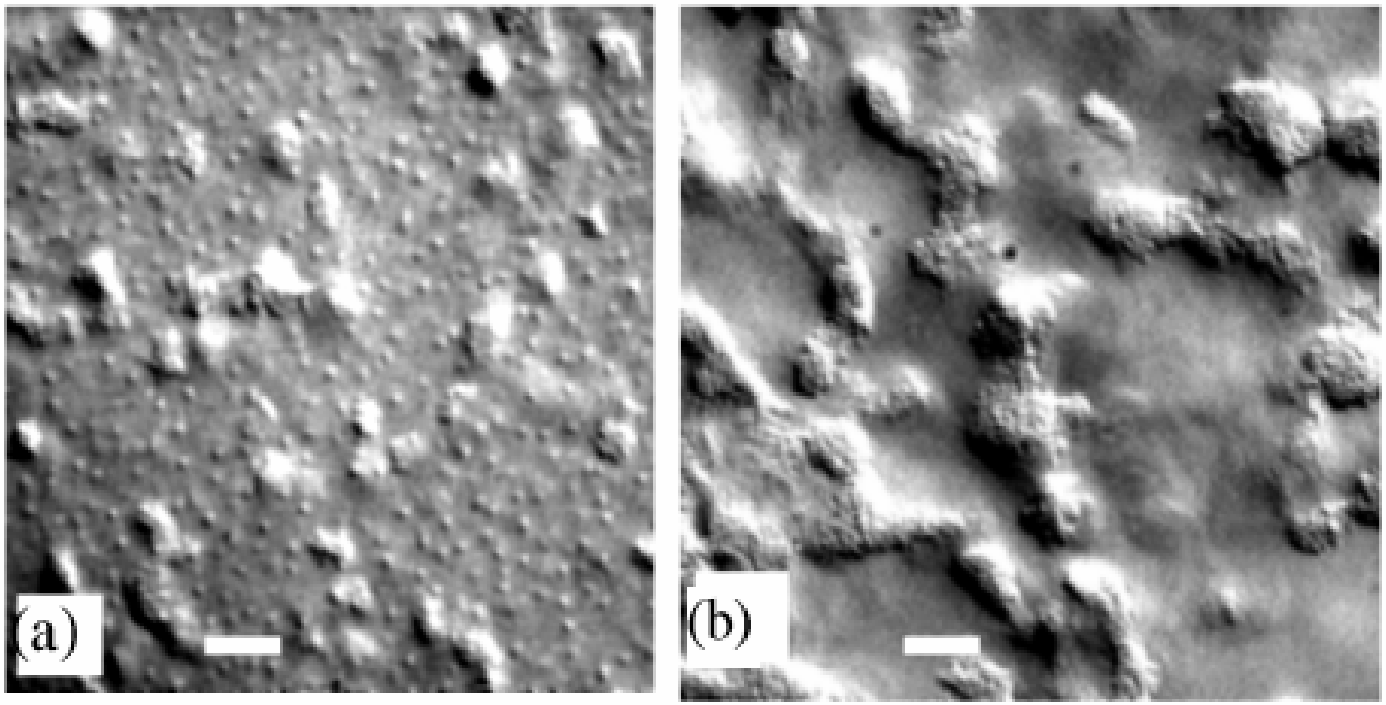
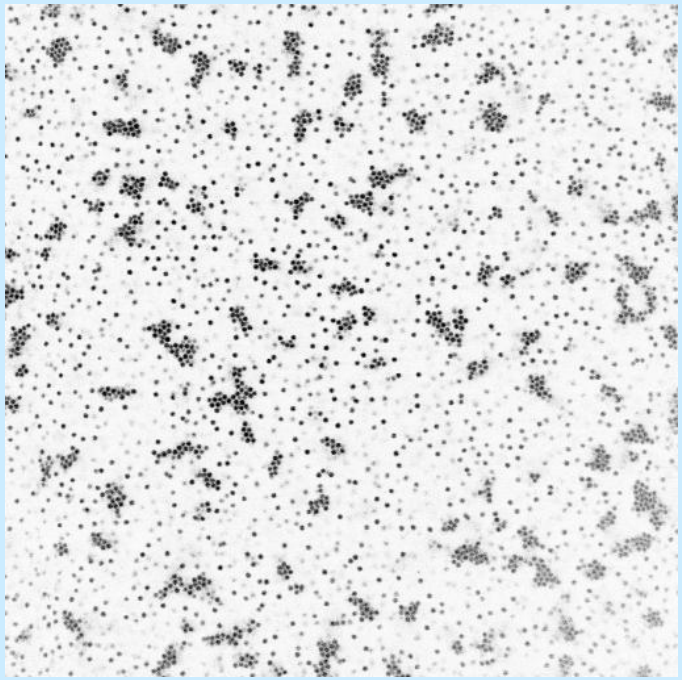
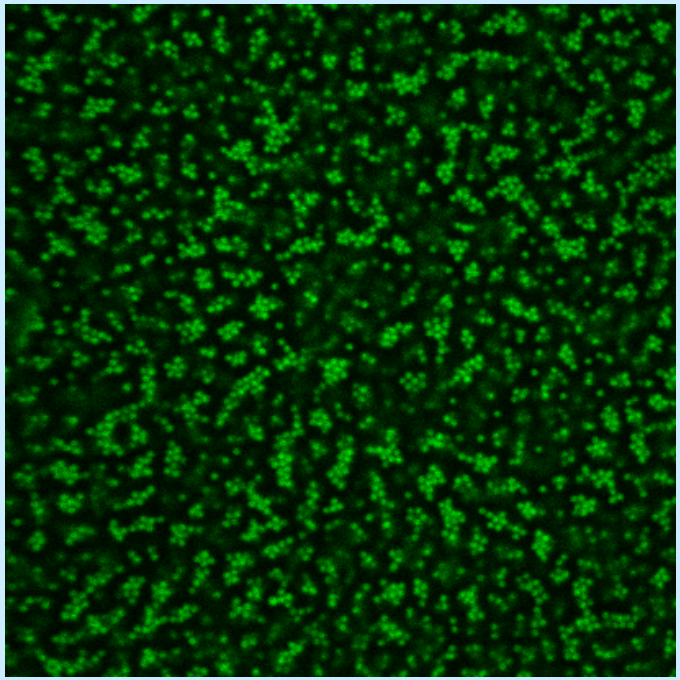



FIG. 2. DIC microscope images of (a) fluidlike and (b) solid-like phases. The attractive interactions are the same in both samples, $U \approx 4k_BT$, but the volume fractions are different, $\phi_a = 0.06$ and $\phi_b = 0.12$. The lines are 2.5 $\mu$m long.

[Segre ea, PRL **86**, 6042, (2001)]

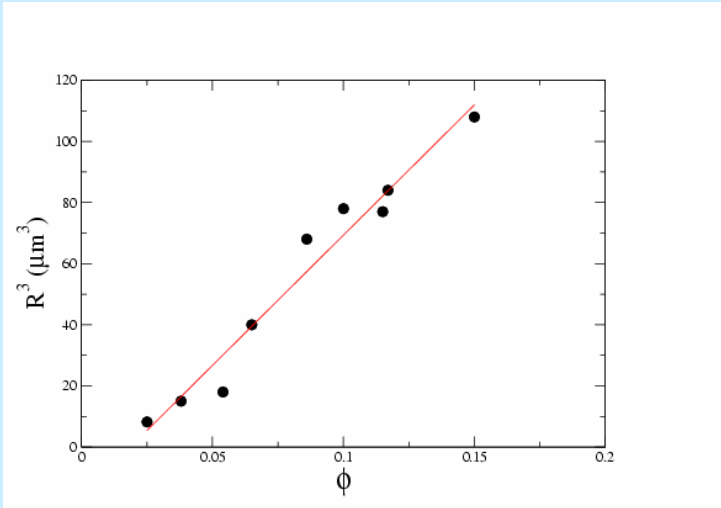


[Sedgwick ea , J. Phys.: Condens. Matt. **16**, S4913, (2004)
Stradner ea Nature **432**, 492, (2004)]

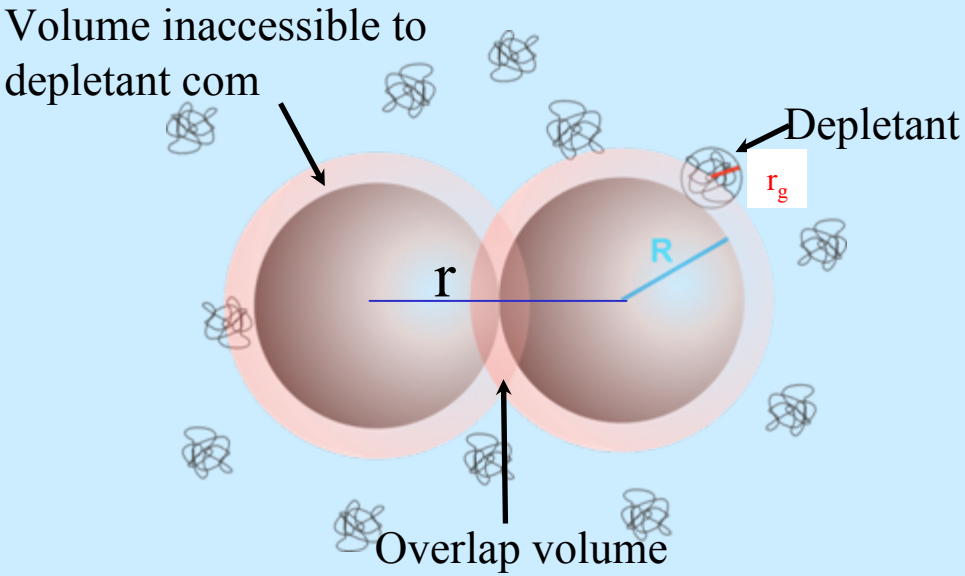


[M. van Schooneveld ea JPCB 2009]

# Model prediction: optimum cluster radius $R_*^3 \propto \phi$



# Origin of attraction: depletion interaction




$$U = -\Pi \cdot V_{overlap}$$

Pairwise:

$$U = -kT\rho_p \frac{4\pi}{3}\sigma^3\left(1 - \frac{3}{4}\frac{r}{\sigma} + \frac{1}{16}\left(\frac{r}{\sigma}\right)^3\right)$$

(Asakura-Oosawa (AO) potential)

$$\sigma = R + r_g$$

Why $R_*^3 \propto \phi$ ?

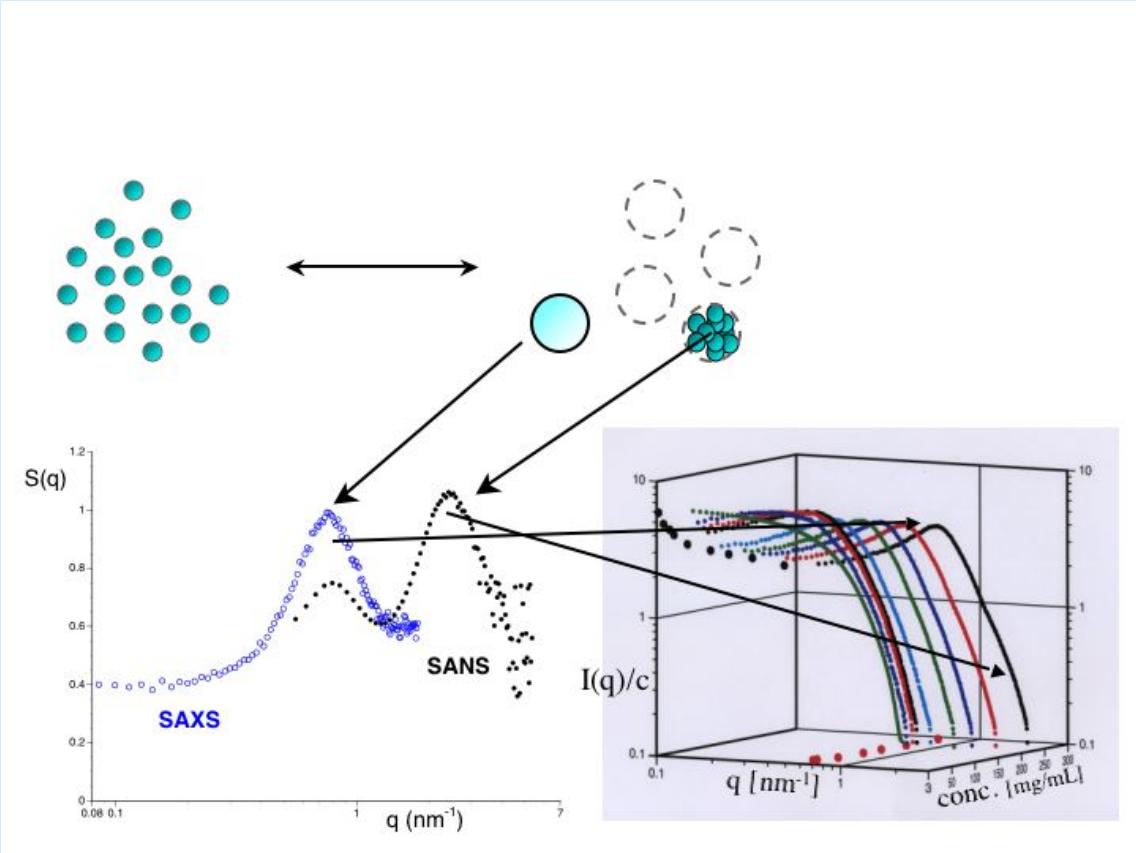
Minimize free energy density - result

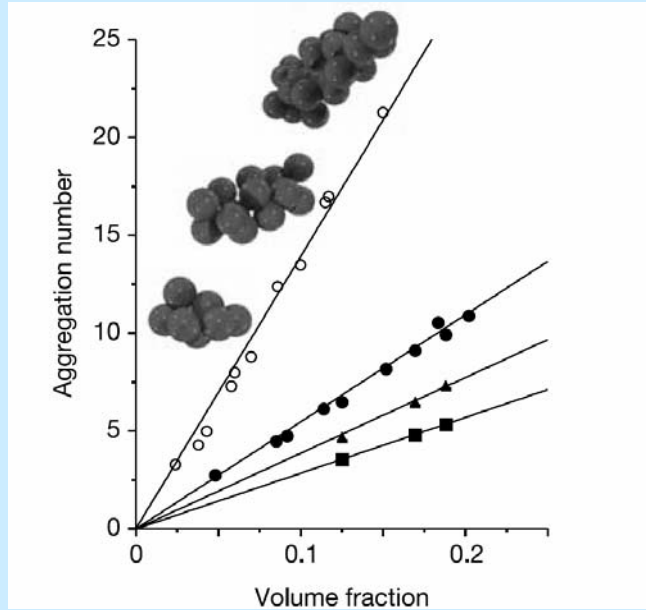
$$R_*^3 = \frac{15}{8\pi}\frac{\gamma}{\lambda_B \rho^2}$$

As long as $\rho \approx \rho_0$, and $\rho_0^2 \approx \frac{e^{-\lambda_B/b}\sigma}{rb^3\phi}$

→ QED

# Stable clusters also observed in aqueous protein solutions (without added salt)




$$Aggr.\# \propto R_*^3 \propto \phi$$

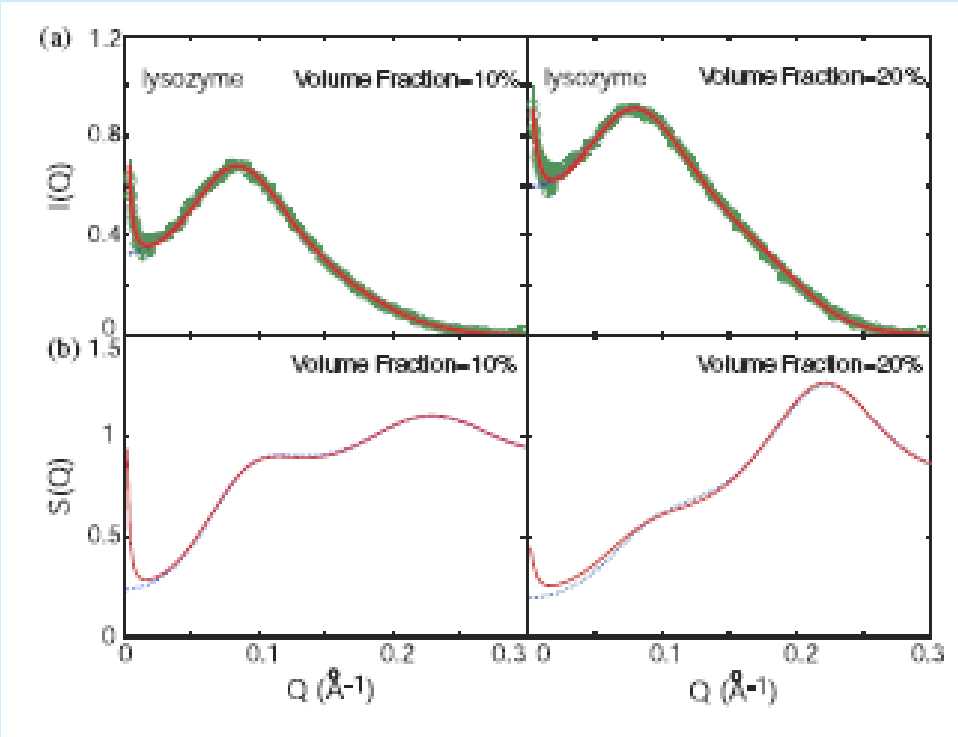
[Stradner ea Nature **432**, 492, (2004)]

Numbers (small R, large ε) make sense
Cluster size cannot (much) exceed Debye length

# Controversies related to equilibrium protein clusters

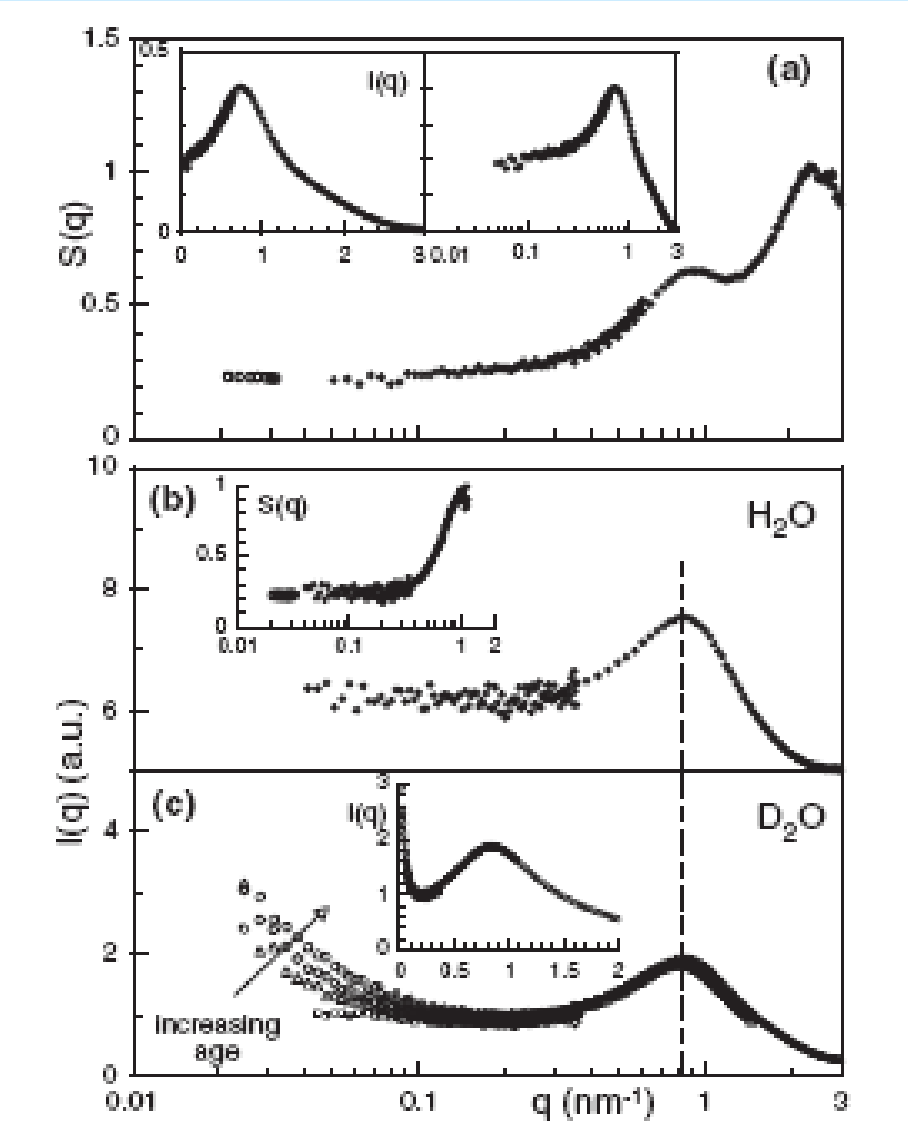
- 1 Zero-Q peak: Long-range attraction in protein solutions

[Y. Liu, E. Fratini, P. Baglioni, R-R Chen, S.H. Chen, PRL **95**, 118102, (2005)]



# Zero Q peak appears several days after sample preparation, related to impurities

[A. Stradner, F. Cardinaux, P. Schurtenberger, PRL **96**, 219801, (2006)]

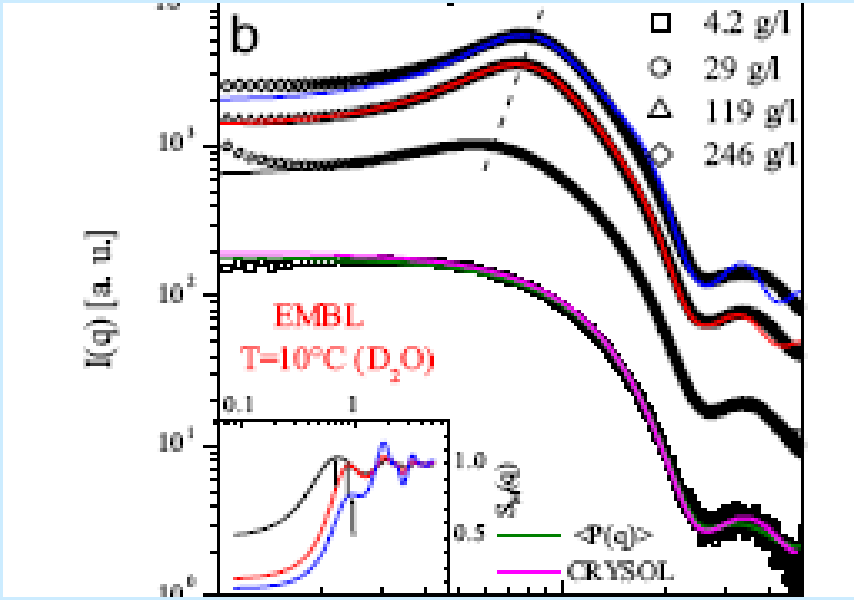


2.

# Absence of equilibrium cluster phase in concentrated lysozyme solutions

Anuj Shukla*, Efstratios Mylonas†, Emanuela Di Cola*, Stephanie Finet*, Peter Timmins‡§, Theyencheri Narayanan*§, and Dmitri I. Svergun†§¶

[PNAS **105**, 5075, (2008)]

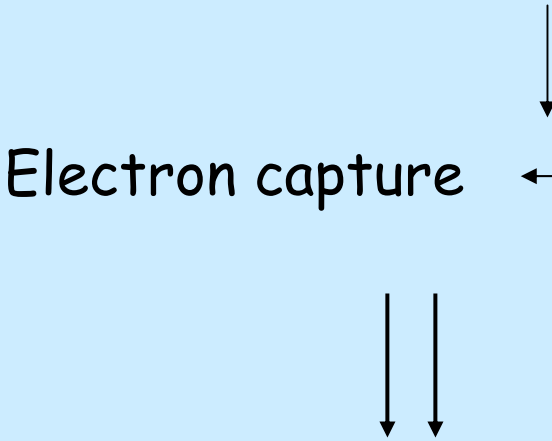



In case of clusters: expect *constant* peak with lysozyme concentration

…but 'critical cluster concentration' ≈ 200 g/l !

# Higher nuclear densities (>$10^6$ g/cm$^3$)

Electron energy comparable to nucleon binding energy




## Increasing size of most stable isotope

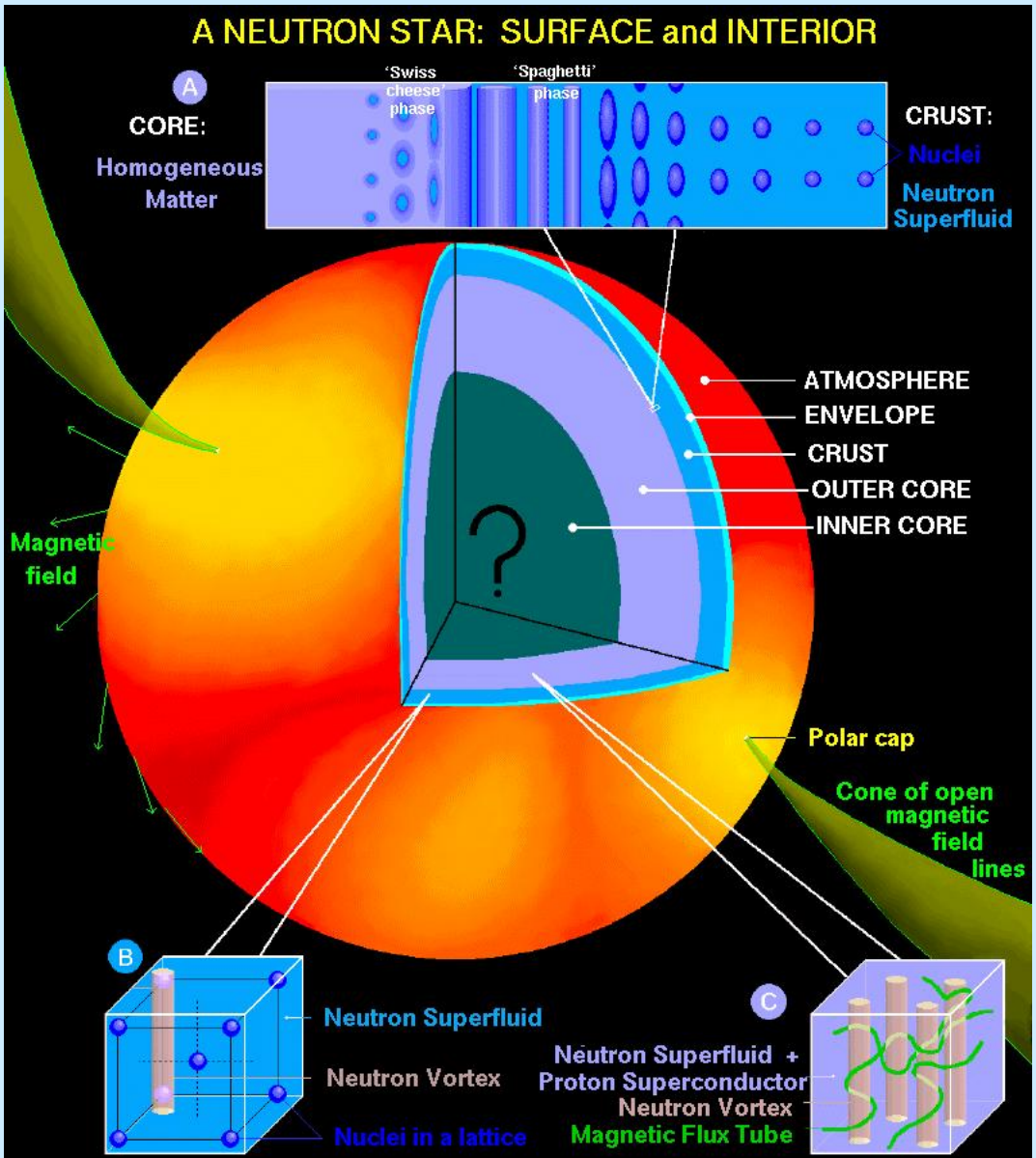
[Haensel (2001), *Physics of Neutron Star Interiors*, D. Blaschke ea (ed), Springer]

Qualitatively comparable to stable colloidal cluster size $R_*^3 \propto \phi$

caused by $a_{sym} \leftrightarrow \rho_0 \sim \phi^{-1/2}$

# Large nuclear densities: neutron star interiors

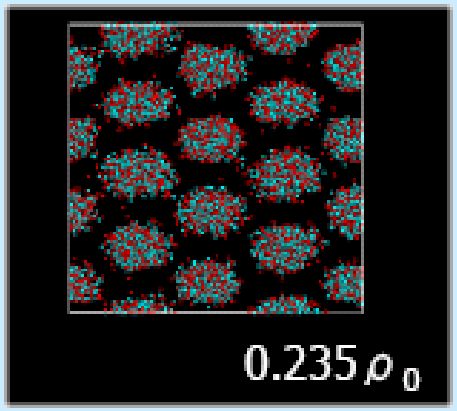
Several scenarios; first attempt: [Baym, Bethe & Pethick, Nucl. Phys. **A175**, 225, (1971)]



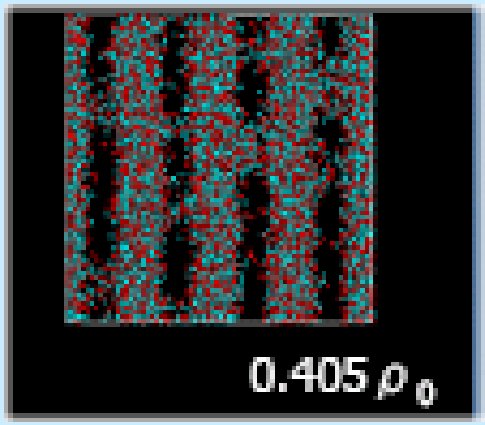

Core:
Density $10^{14}$ gcm$^{-3}$

Nuclear matter at high density : several predictions, e.g.,

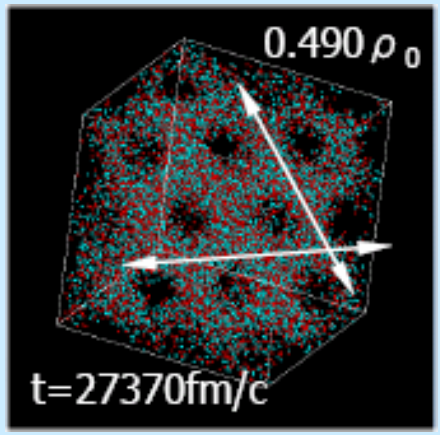
## nuclear "pasta"




"Spaghetti"




"Lasagna"

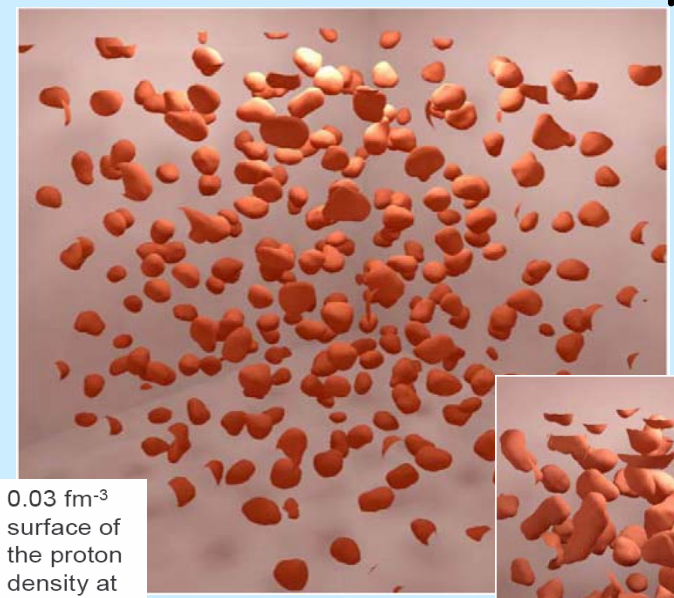



"anti – spaghetti"

[Watanabe, Sato, Yasuoka, Ebisuzaki, Phys. Rev. **C66**, 012801, (2002); **68**, 035806, (2003)]

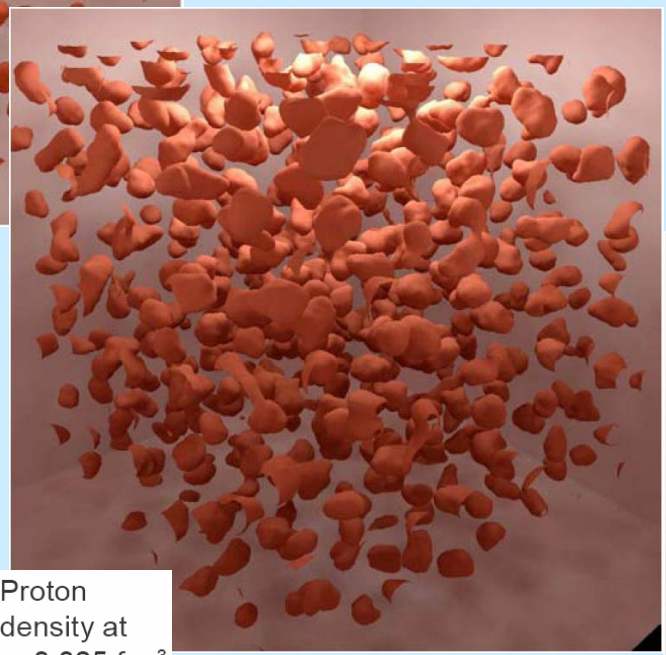
# Other predictions (simulation):

[Horowitz ea, Phys. Rev. **C69**, 045804, (2004)]

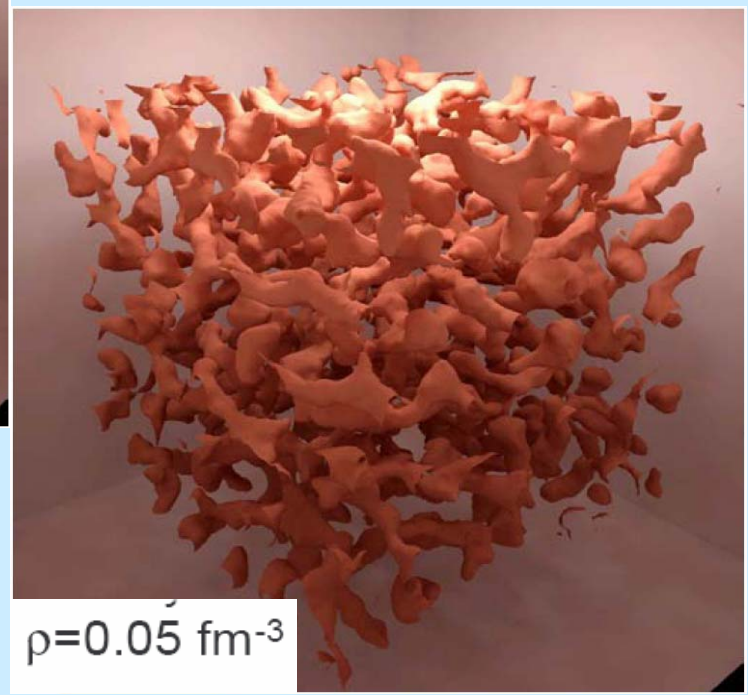


0.03 $fm^{-3}$ surface of the proton density at $\rho$=0.01 $fm^{-3}$

$\sim 10^{13}$ g/cm$^3$



Proton density at $\rho$=0.025 $fm^{-3}$



$\rho$=0.05 $fm^{-3}$

# Periodic structures from MD simulation of 'colloidal' system

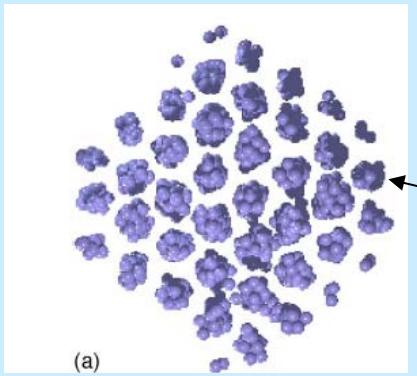
[A. De Candia ea, PRE **74**, 010403(R), (2006)]

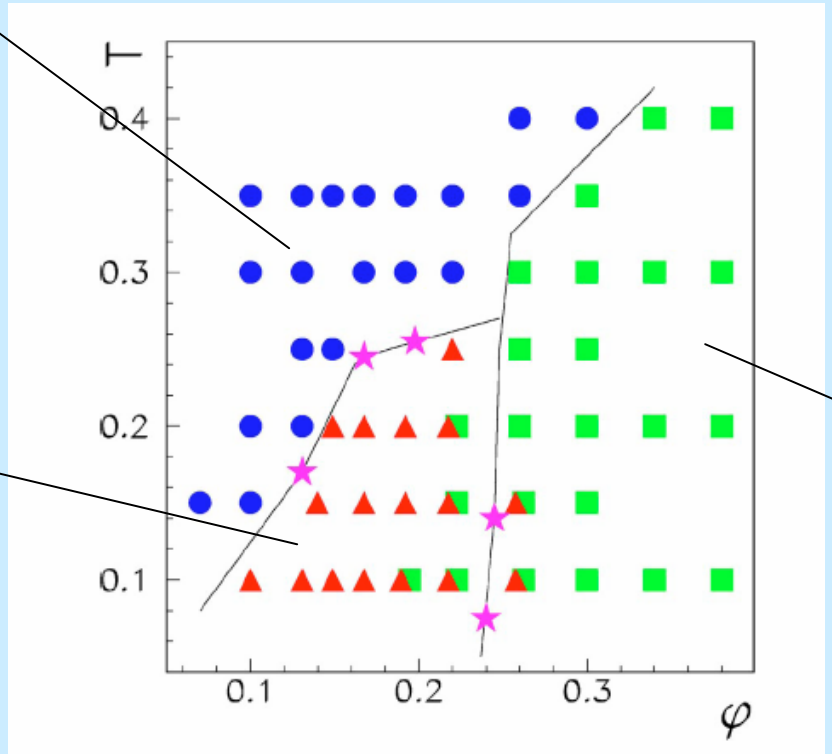
Model potential

$$V(r) = \epsilon\left[ a_1\left(\frac{\sigma}{r}\right)^{36} - a_2\left(\frac{\sigma}{r}\right)^{6} + a_3 e^{-\lambda(r/\sigma-1)} \right]$$

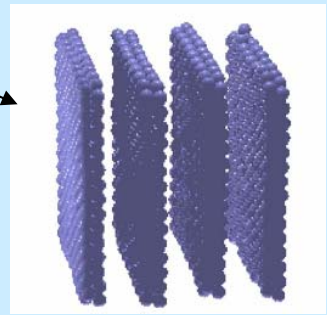
'disordered'

columnar

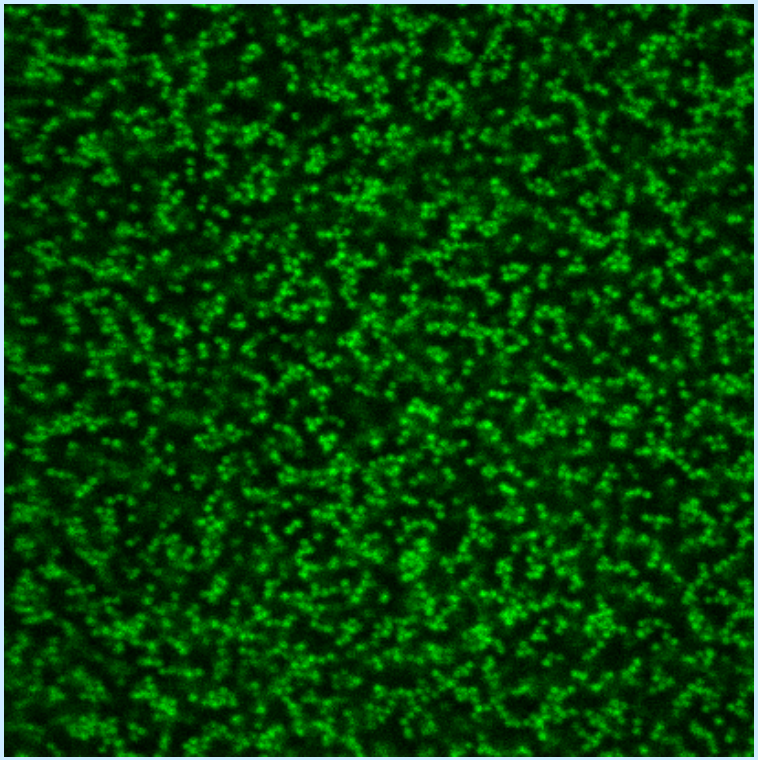



lamellar



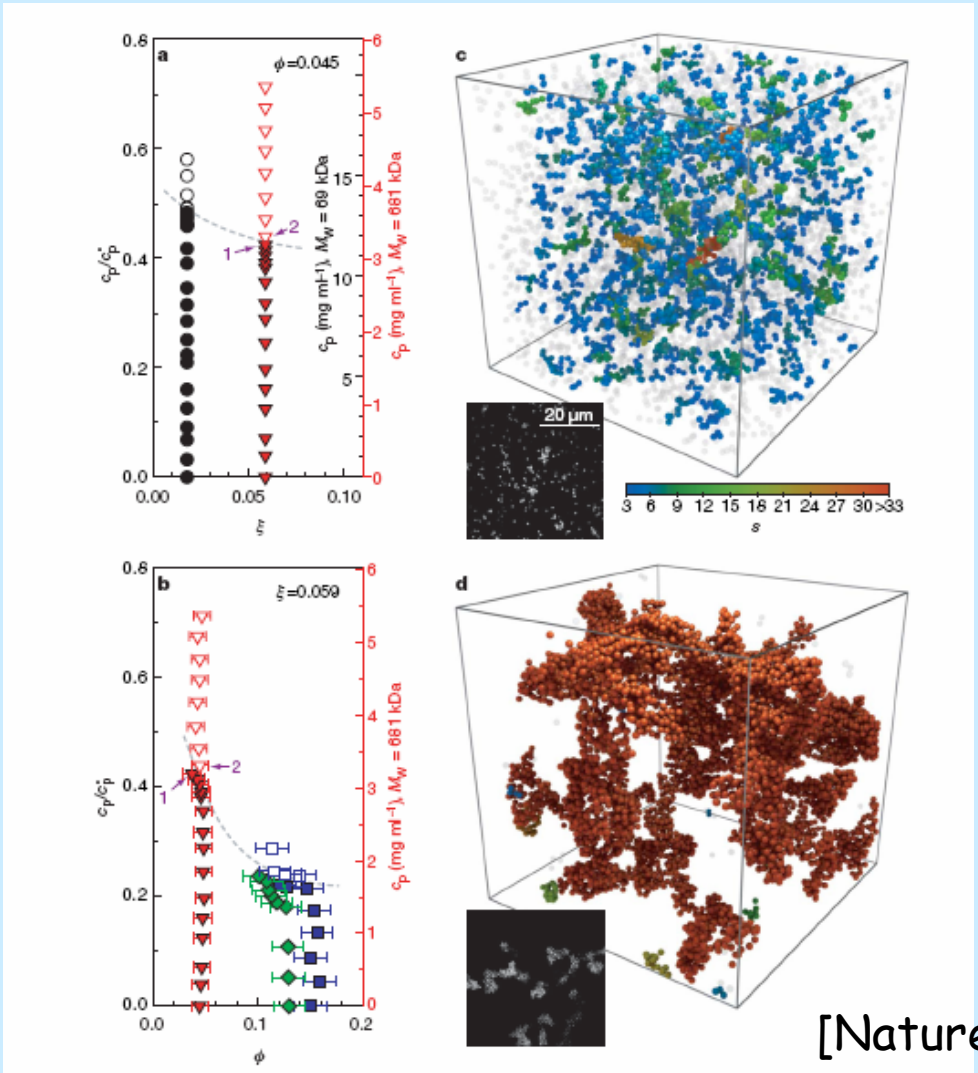
Experiments: 'gel' at higher volume fraction of colloids



# Gelation of particles with short-range attraction

Peter J. Lu[1], Emanuela Zaccarelli[3,4], Fabio Ciulla[3], Andrew B. Schofield[5], Francesco Sciortino[3,4] & David A. Weitz[1,2]

Claim: Low – density gels are 'arrested gas-liquid instabilities'

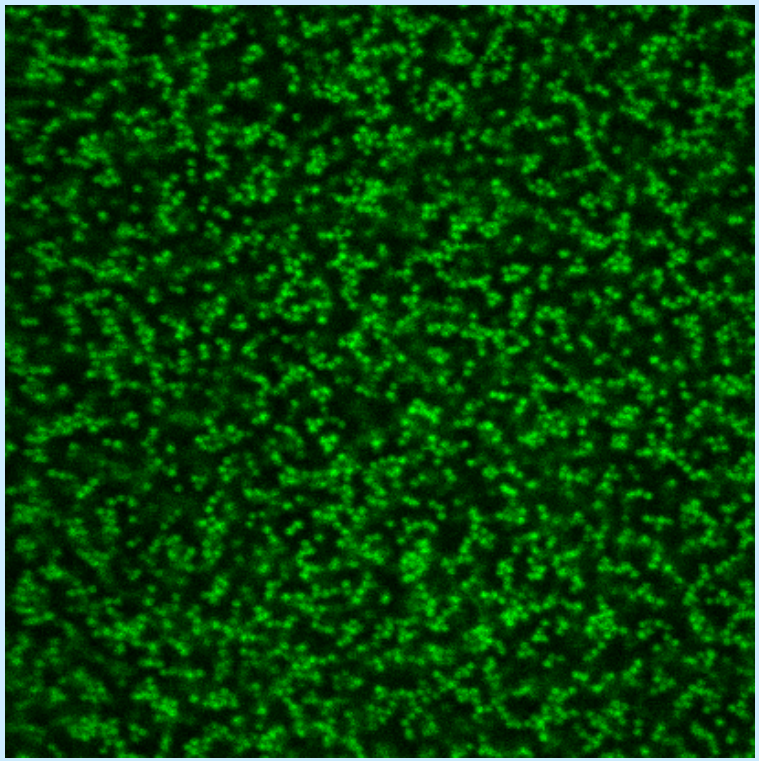



[Nature **453**, 499, (2008)]

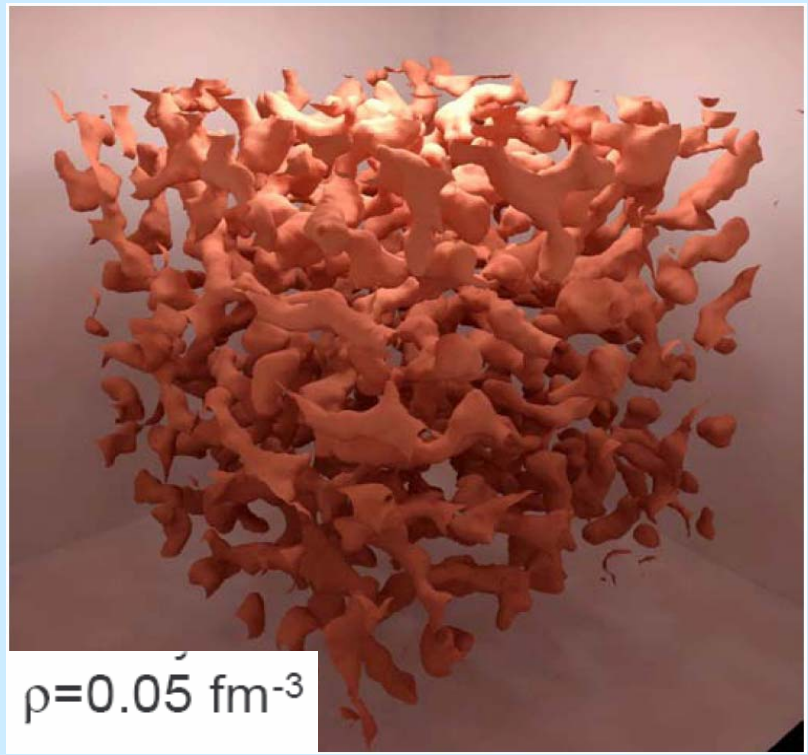
Here instability is due to transition between clusters and …

…periodic structure?

…or…



?



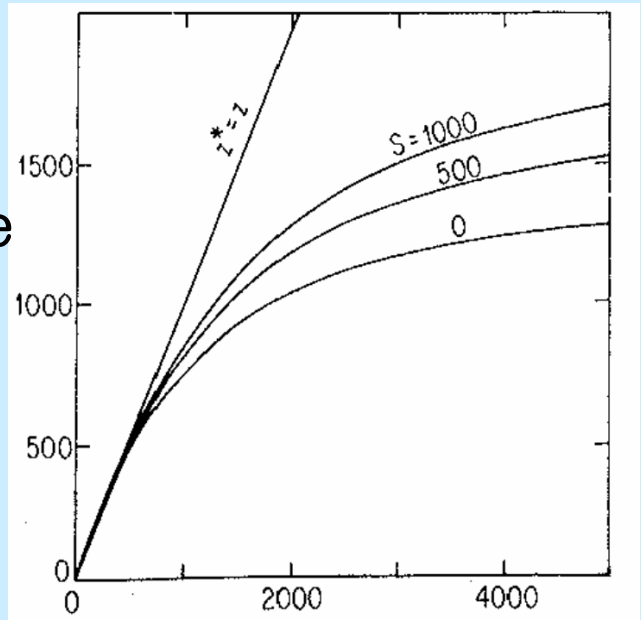
# Colloidal cluster stability

- Larger clusters: larger surface- or zeta potential

$$\zeta \propto R^2 \rho_0 \lambda_B$$

- If ζ > (several kT): expect unstable clusters due to **counter-ion condensation**. condensation of counter-ions in 'Gouy' layer

Effective Charge Z




'saturation value' determined by surface potential+sphere size

(S=added ion pairs/ macroion)

# chargable groups

Use Debye-Huckel with renormalized charge

[Alexander et al. JCP **80**, 5776, (1984)]

# Colloidal cluster stability

- Find stability boundary

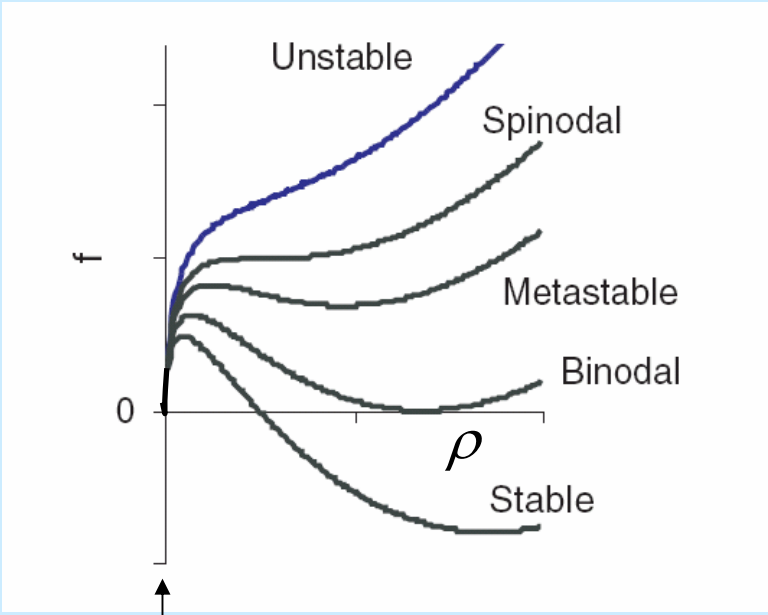
Insert equilibrium radius into cluster free energy: $R_*^3 = \frac{15}{8\pi}\frac{\gamma}{\lambda_B \rho^2}$

$$f(\rho) = c\gamma^{2/3}\lambda_B{}^{1/3}\rho^{2/3} + 2\rho\left(\ln(\rho/\rho_0) - 1\right)$$ (c=5.34 for spherical clusters)

Plot for several values of

$\rho_0 \gamma^{-2} \lambda_B{}^{-1}$ ↓

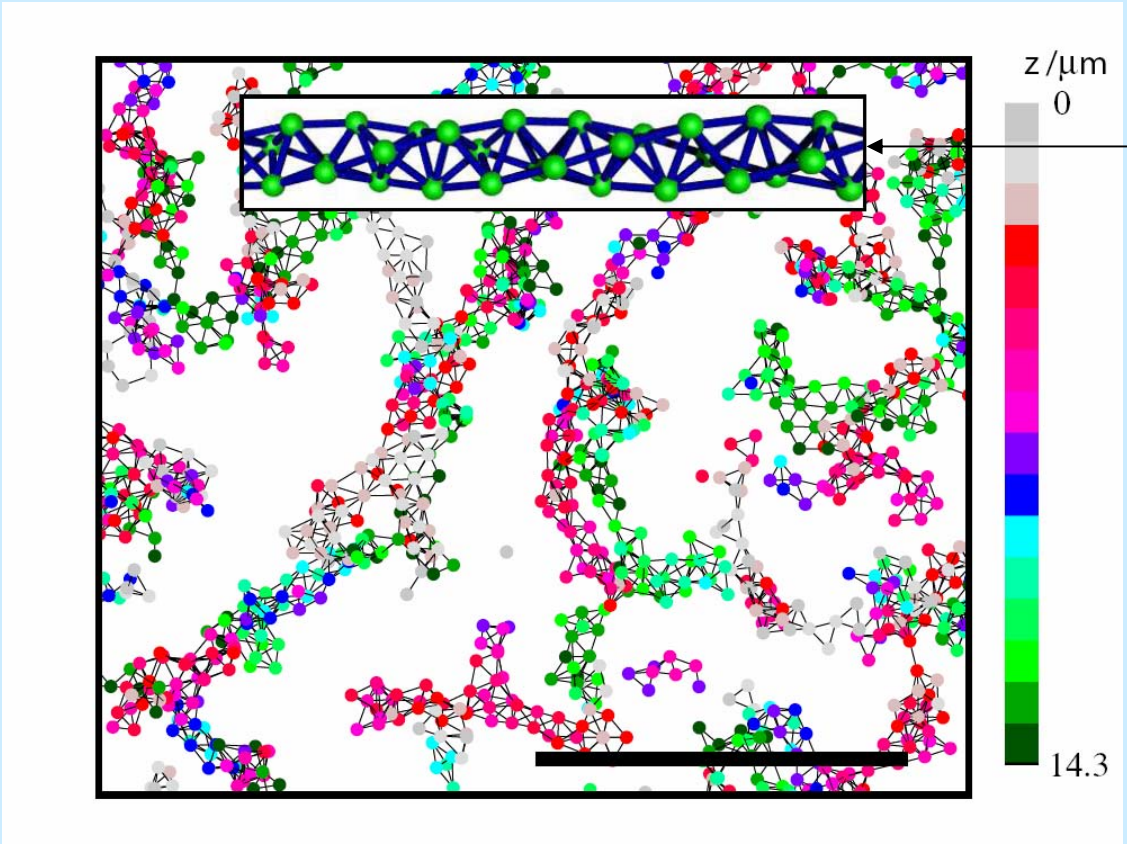
increasing




$\infty$ cluster

# Gel stucture

Dense chains of particles constructed from face-sharing tetrahedral clusters [Campbell ea, PRL 94, 208301, (2005)]




Spirals grow due to instability in single plane [Sciortino ea, Cond-matt/0505453v1]

⟶ Directional growth from spherosymmetrical objects & potentials

# Is gel state thermodynamically stable?

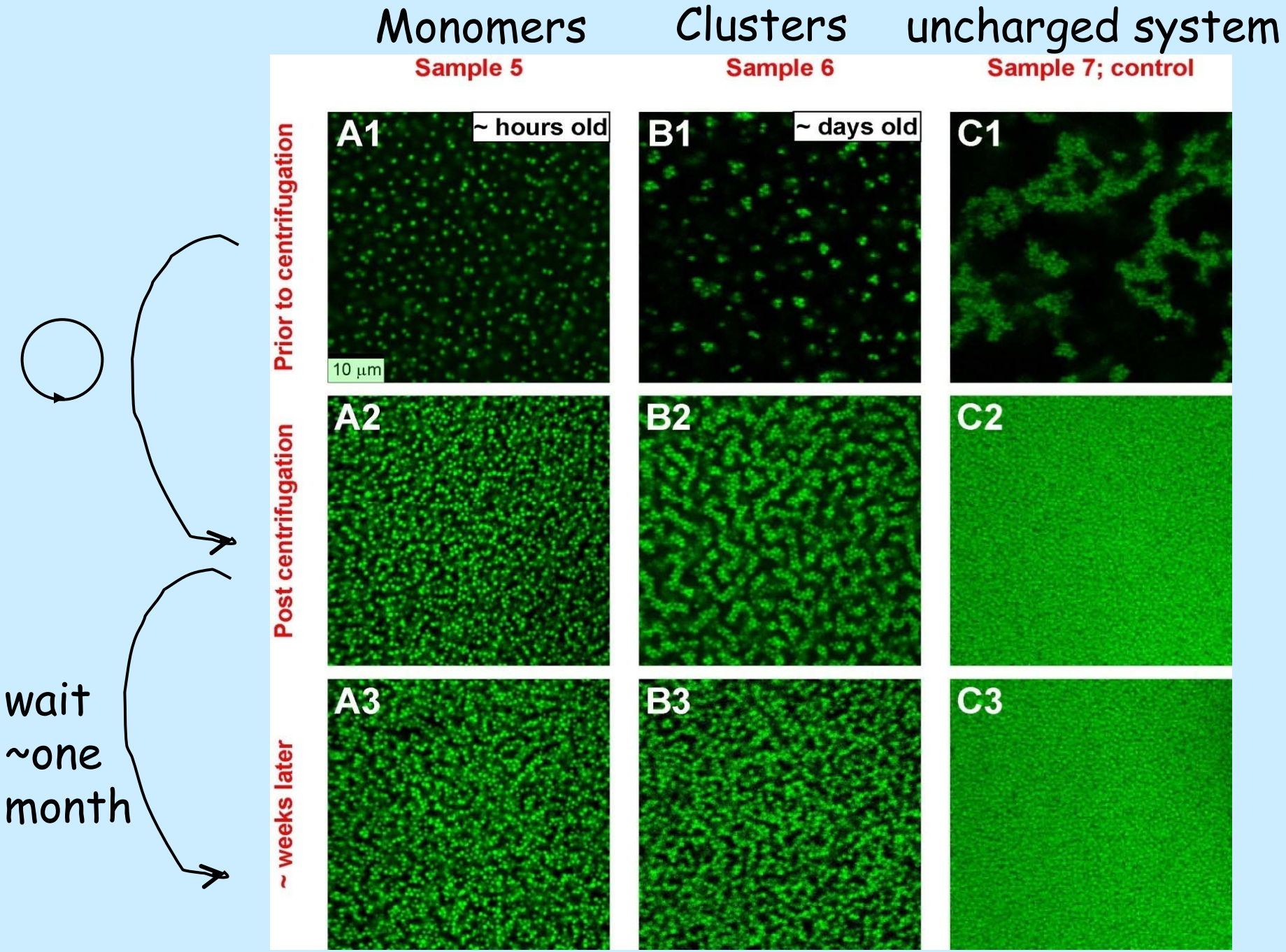
Generate high(er) densities by centrifugation

Start with monomers (centrifugate immediately after preparation)

Start with equilibrium clusters

Follow structures in time

Results [van Schooneveld ea JPCB 2009] ....


Monomers
Clusters
uncharged system
Sample 5
Sample 6
Sample 7; control
Prior to centrifugation
Post centrifugation
~ weeks later
A1
~ hours old
B1
~ days old
C1
10 μm
A2
B2
C2
A3
B3
C3
wait
~one
month

- Initial gel structure depends on quenched state;

- Different gels (slowly) evolve towards similar structure:

REVERSIBLE GEL STATE

# Further work

I. Improve theory:

- beyond spherical clusters
- inhomogeneous charge distributions
- interactions between clusters
- allow for dielectric constant variation

II. Experimental:

- ground state at high volume fractions:
  look for periodic / inverted structures
- Carefully check phase boundary scaling(s)

# Part II: (Spontaneous) emulsification induced by colloids

Can oil and water be mixed … forever?

Yes: in microemulsions. Requires special (mixtures of) surfactants.

-> Other way(s)?

From Henk Lekkerkerker:


70 % vet

EURO 1,25

35 % vet

EURO 1,55

25 % vet

EURO 1,88

**More water, more expensive!**

Unilever

Outline

1. Intro: why dispersed drops are in general unhappy
(part II)

1. Solid-stabilized / Pickering emulsification: wetting etc

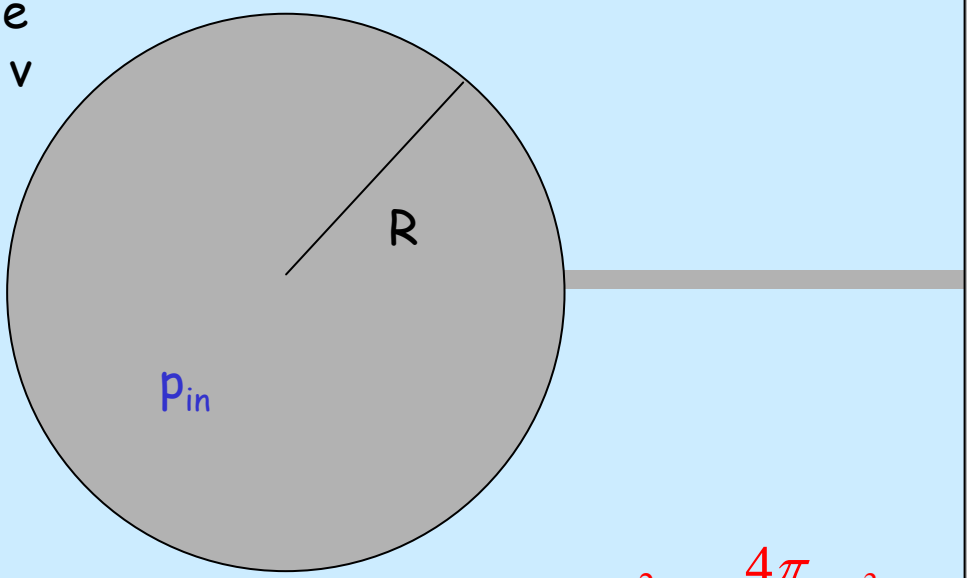
2. Type of emulsions: O/W or W/O

3. Examples:
   Stimulus- responsive particles
   bio-particles (spores, viruses, bacteria)
   emulsification of partly miscible liquids
   phase-transfer catalysts

5. Equilibrium solid-stabilized emulsions

# Bare drop (O/W or W/O or gas/liquid)

* N molecules inside
* molecular volume v




(Gibbs) free energy $F = \gamma A_{ow} - \Delta p V_d = 4\pi R^2 \gamma - \frac{4\pi}{3} R^3 \Delta p$

$\Delta p = p_{in} - p_{out}$

Minimize $\longrightarrow$ $\Delta p = \frac{2\gamma}{R}$

$\frac{F_{\min}}{N} = \frac{\gamma v}{R}$ (big = good)

Young- Laplace

**Mechanical stability iff R -> ∞**

# Emulsification: delay demixing

- Surfactants: adsorb at O/W interface

delay coalescence by electrostatics (O/W) or
steric repulsion (W/O) STILL RIPENING

- Add insoluble / involatile compound ('trapped species')
to emulsified phase :

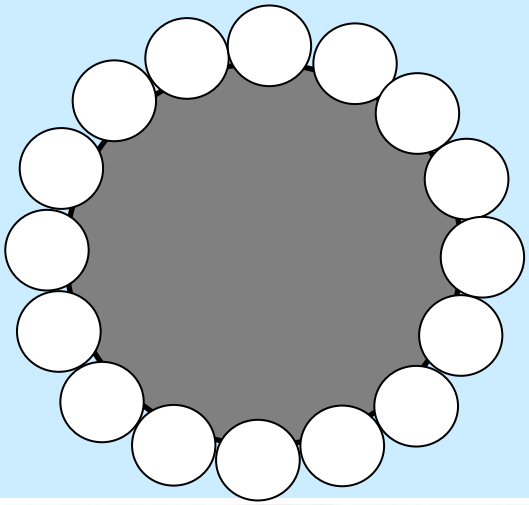
osmotic pressure can balance Laplace pressure: NO growth by ripening. STILL COALESCENCE!

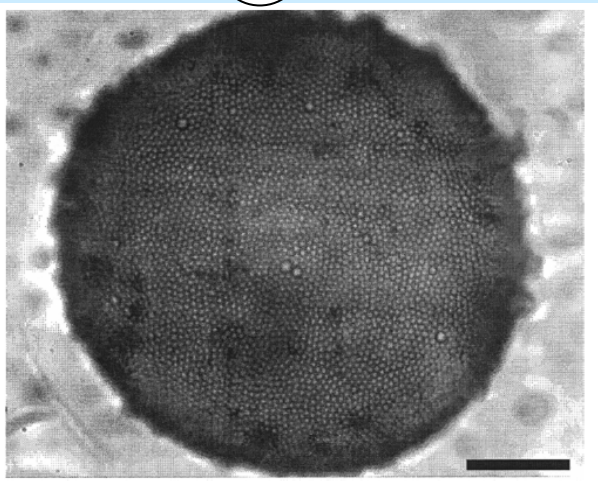
(stability of fog with salt as trapped species)

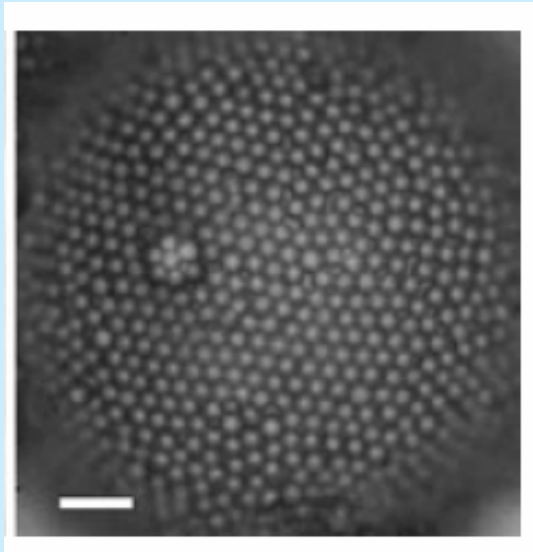
# Solid – stabilized or 'Pickering' emulsions:

[Ramsden 1903, Pickering 1907]

**Metastable** oil drops in water or water drops in oil
'stabilized' by a layer of adsorbed particles

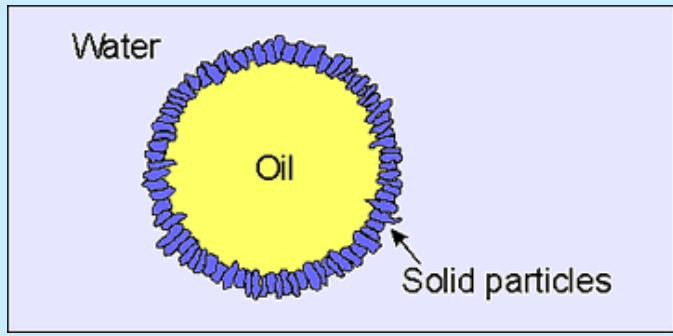


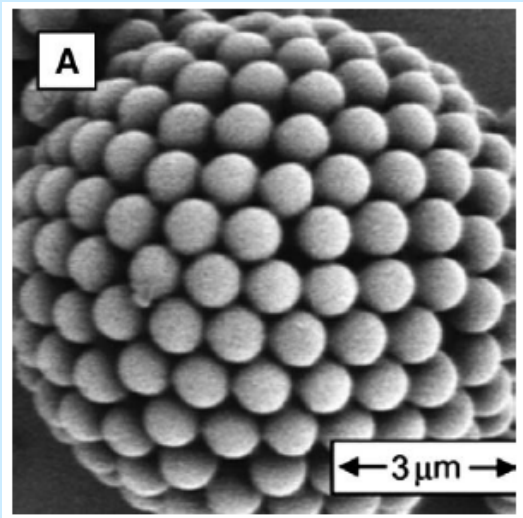




Hsu MF,

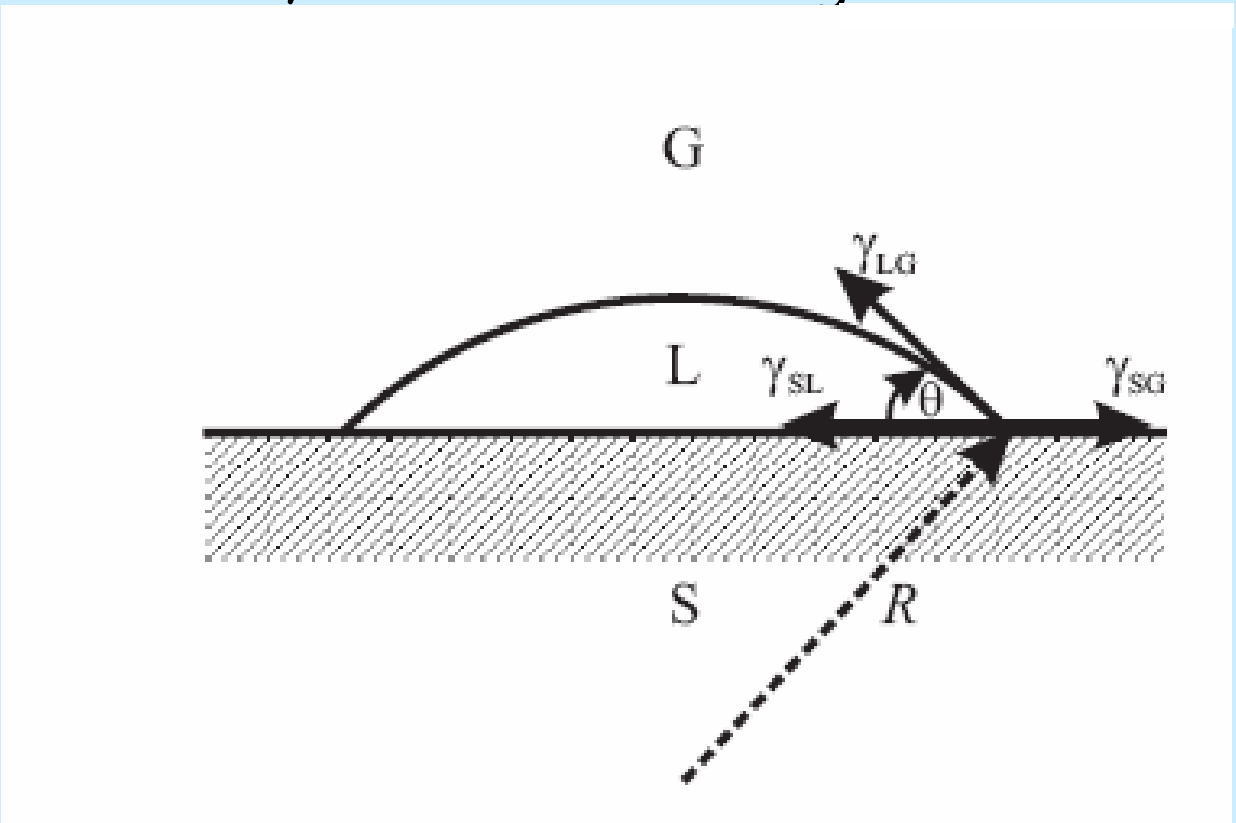
Langmuir 2005;21:2963–70.



**Why colloids may adsorb @ interfaces:**

non-0, non-π contact angle between 3 materials




Force balance or (surface) free energy minimal:

$$\gamma_{SL} + \gamma_{LG} \cos\theta = \gamma_{SG}$$

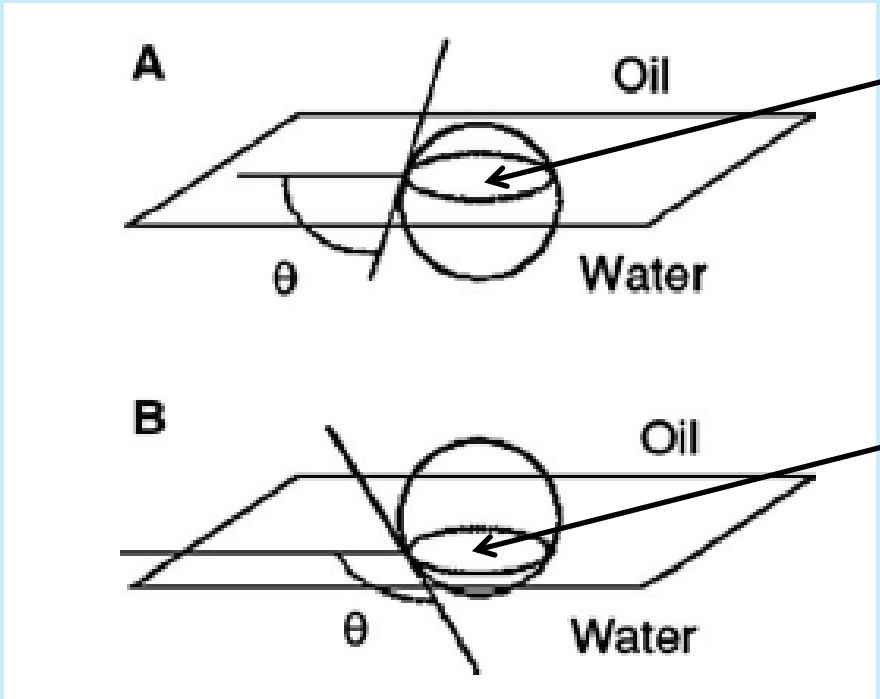
Contact angle determined by interfacial tensions:

$$\cos\theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}$$

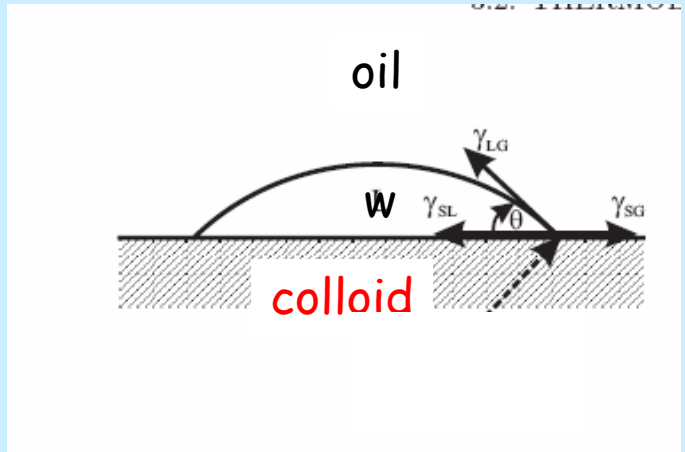
Young (- Dupré)

# Driving force for colloid adsorption @ OW interface:

## Reduction of bare O/W interfacial energy (~$\gamma_{ow}A_{ow}$)




$A_{ow}$




Adsorption energy per colloid ~ $\gamma_{ow}a^2$; $\gamma_{ow}$ ~ 1 - 10 kT/nm$^2$

a = 10 nm -> $\gamma_{ow}a^2 \approx 10^2 - 10^3$ kT / colloid

a= 1 μm -> $\gamma_{ow}a^2 \approx 10^6 - 10^7$ kT / colloid

Even for close-packed layers of adsorbed colloids:

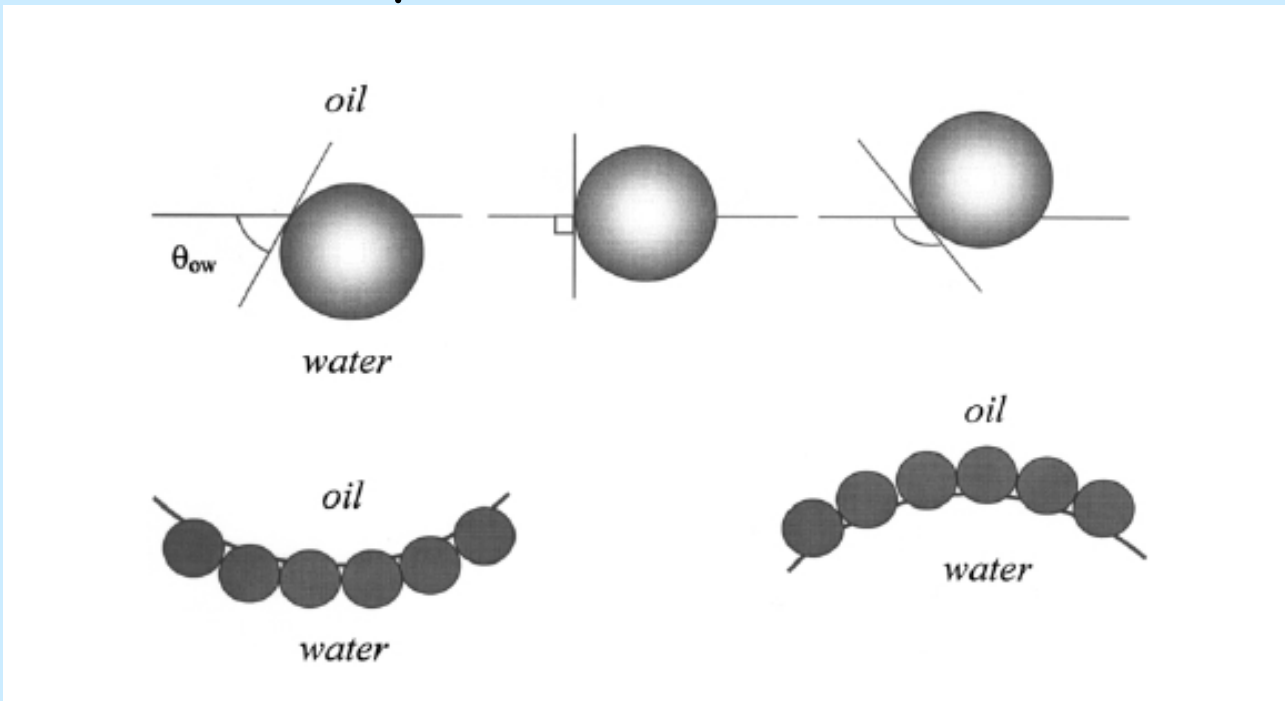
~ 10% bare O/W interface

PE (**usually**) NOT TD stable

# O/W or W/O ?

Emperical rule (Pickering 1907):

liquid that forms drop interior least wets the colloid surface



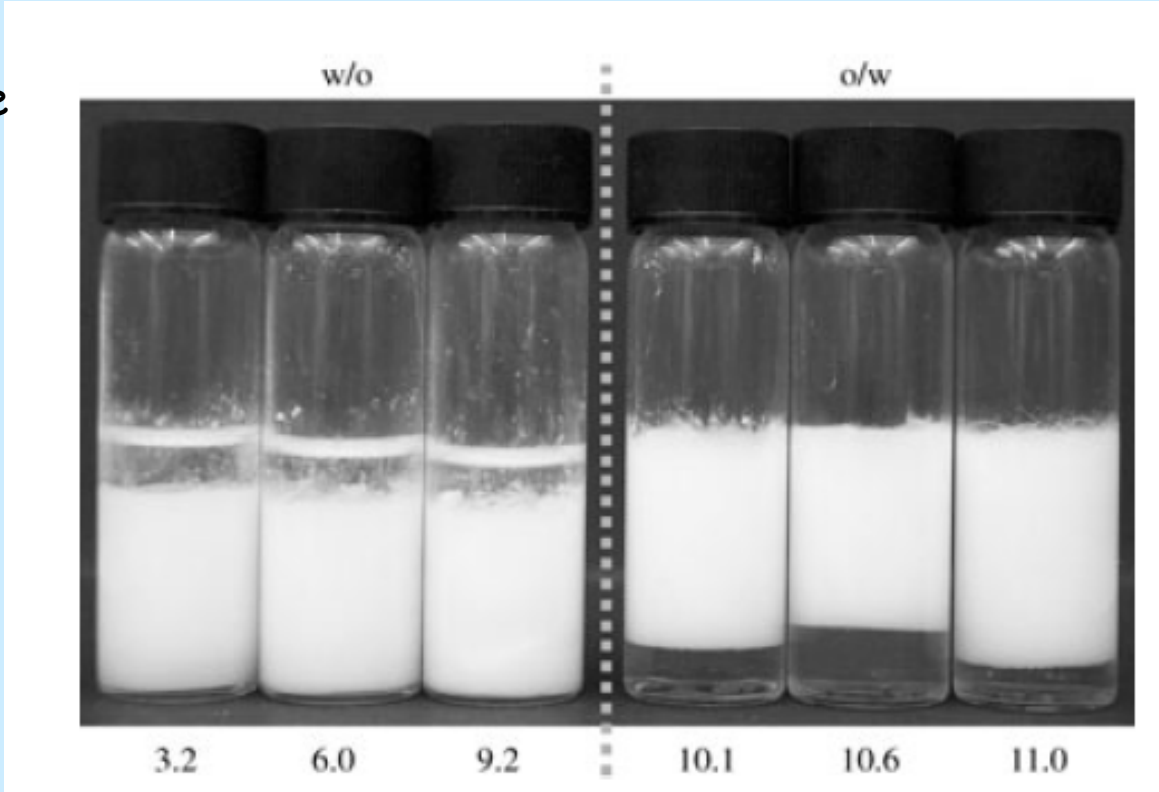

O/W

W/O

- Phase inversion from W/O (water drops in oil) to O/W (oil drops in water) possible

*Bernard P. Binks* and Jhonny A. Rodrigues* *Angew. Chem.* **2005**, 117, 445–448

(charged) polystyrene colloids




→ pH

Increasing pH -> more charge -> lower free energy -> lower $\gamma_{cw}$ -> smaller $\theta$

# Influence of salt concentration

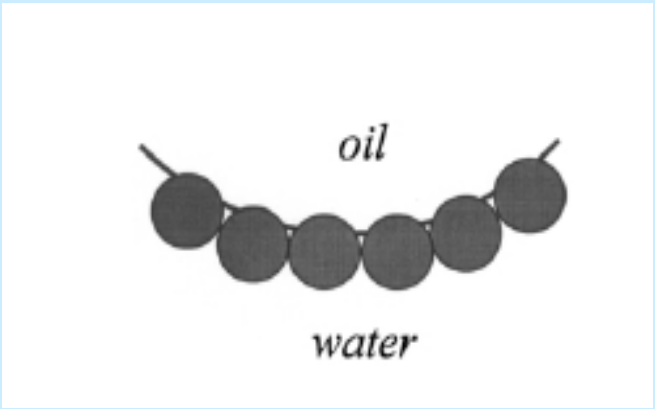
***Table 1:*** Effect of salt concentration on the conductivity ($\kappa$) and type of emulsions prepared.[a]

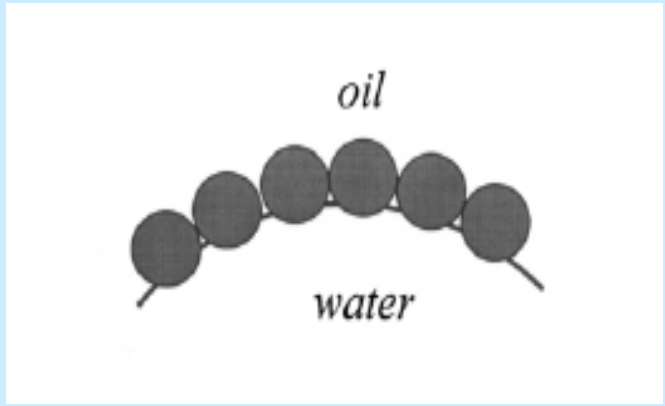
| NaCl [M] | $\kappa$ [$\mu S\,cm^{-1}$] | Type |
|---|---|---|
| 0.30 | 20.5 | w/o |
| 0.42 | 26.8 | w/o |
| 0.47 | 33.4 | w/o |
| 0.54 | 34.2 | w/o |
| 0.66 | 17720 | o/w |
| 0.79 | 21200 | o/w |
| 1.15 | 31500 | o/w |
| 2.15 | 49500 | o/w |

[a] From hexadecane and aqueous NaCl (1:1) containing 2 wt% of carboxy-coated polystyrene latex particles (200 nm diameter) at pH 10.6 at 25 °C.

More salt -> lower electrostatic free energy -> lower $\gamma_{cw}$ -> smaller $\theta$

# Rationalization of 'Pickering rule':
n colloids @ curved O/W interface

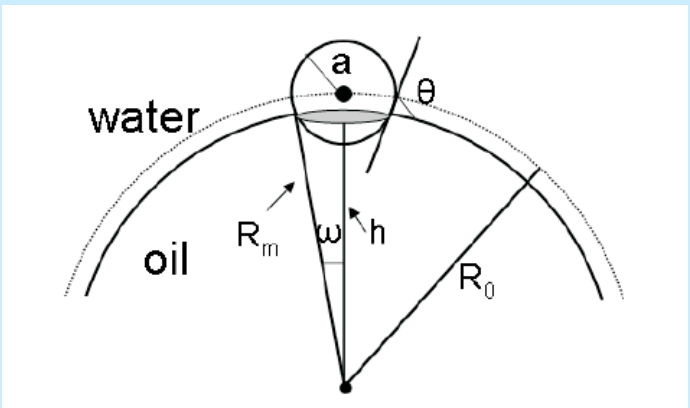



minimize drop free energy per adsorbed colloid

$$F/n = \gamma_{cw}A_{cw} + \gamma_{co}A_{co} + \gamma_{ow}A_{ow} - \Delta p v_d$$

Areas of curved interfaces




$$A_{cw} = 2\pi a^2[1 + cos(\theta - \omega)]$$

$$A_{co} = 2\pi a^2[1 - cos(\theta - \omega)]$$

$$nA_{ow} = 4\pi R_m^2 - 2\pi R_m^2 n(1 - cos\ \omega)$$

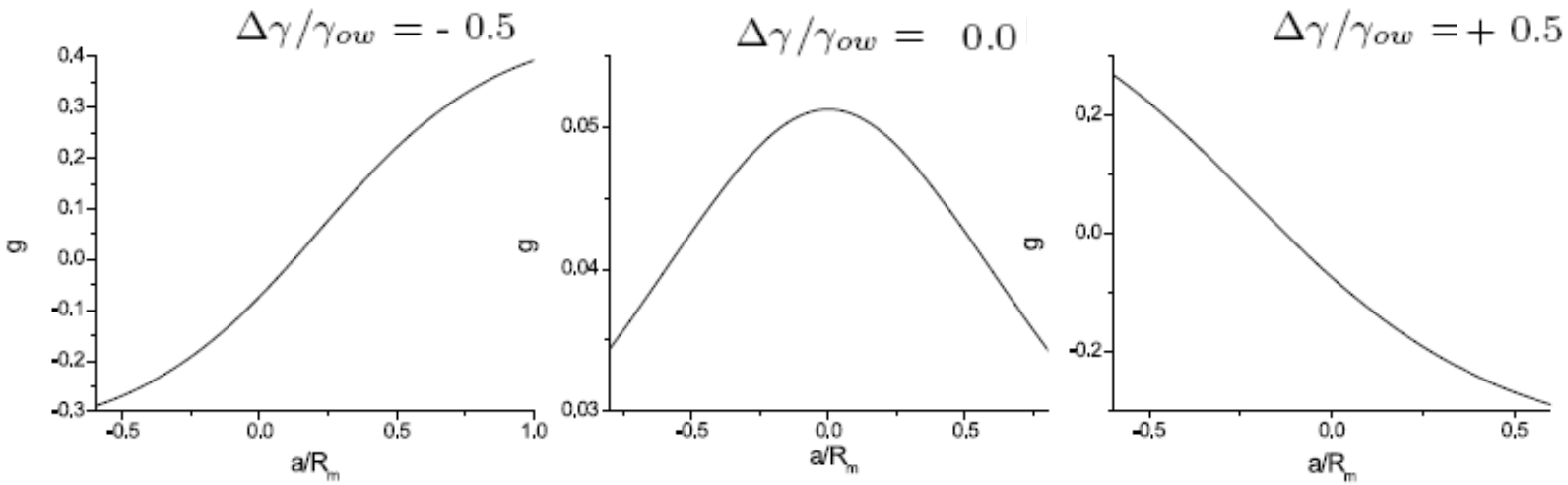
explains old (1907) emperical rule by Pickering :

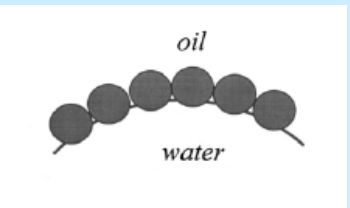
liquid that forms drop interior least wets the colloid surface

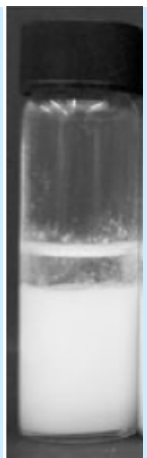
$\Delta\gamma = \gamma_{co} - \gamma_{cw}$

$R_m > 0$ : O/W
$R_m < 0$ : W/O

g =reduced F/n

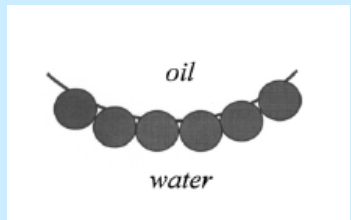


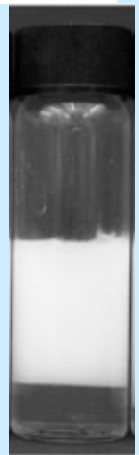



'double' emulsions

Equilibrium TD rules
in non-equilibrium system!



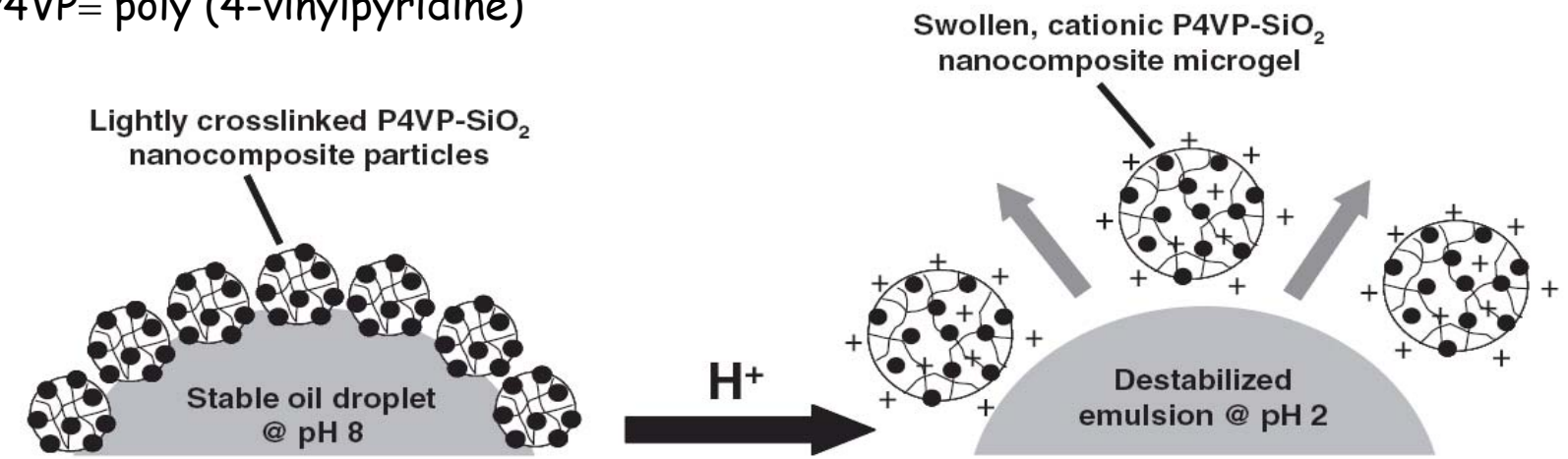



# Complex stuff @ interfaces

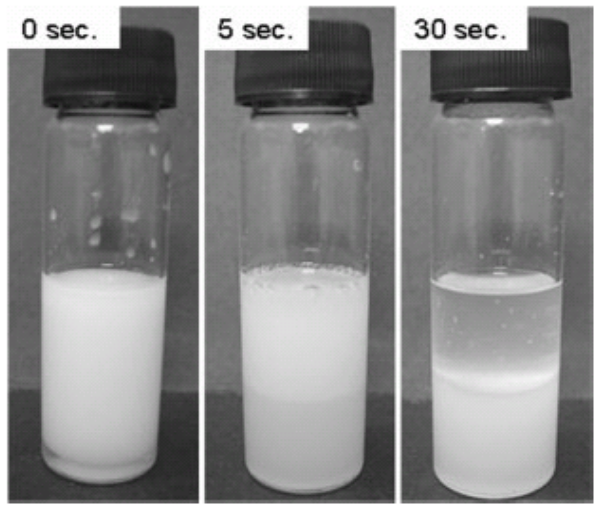
# Stimulus- responsive emulsifiers:

## Nanocomposite microgel particles [Fuji ea, Adv. Mater. **17**, 1014, (2005)]

P4VP≡ poly (4-vinylpyridine)

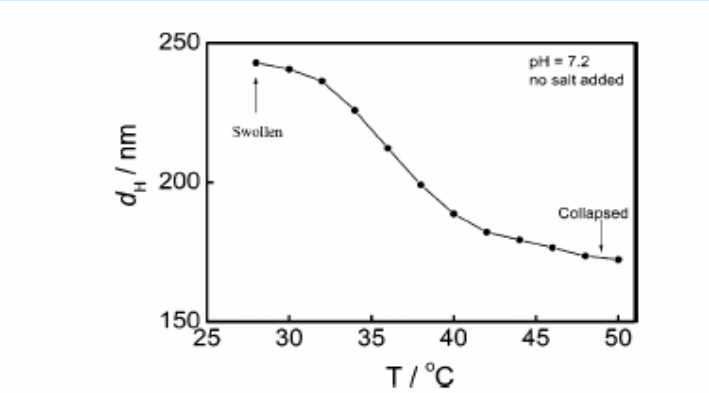



Rapid macroscopic phase separation
After quenching pH=8.9 ->2 at t=0

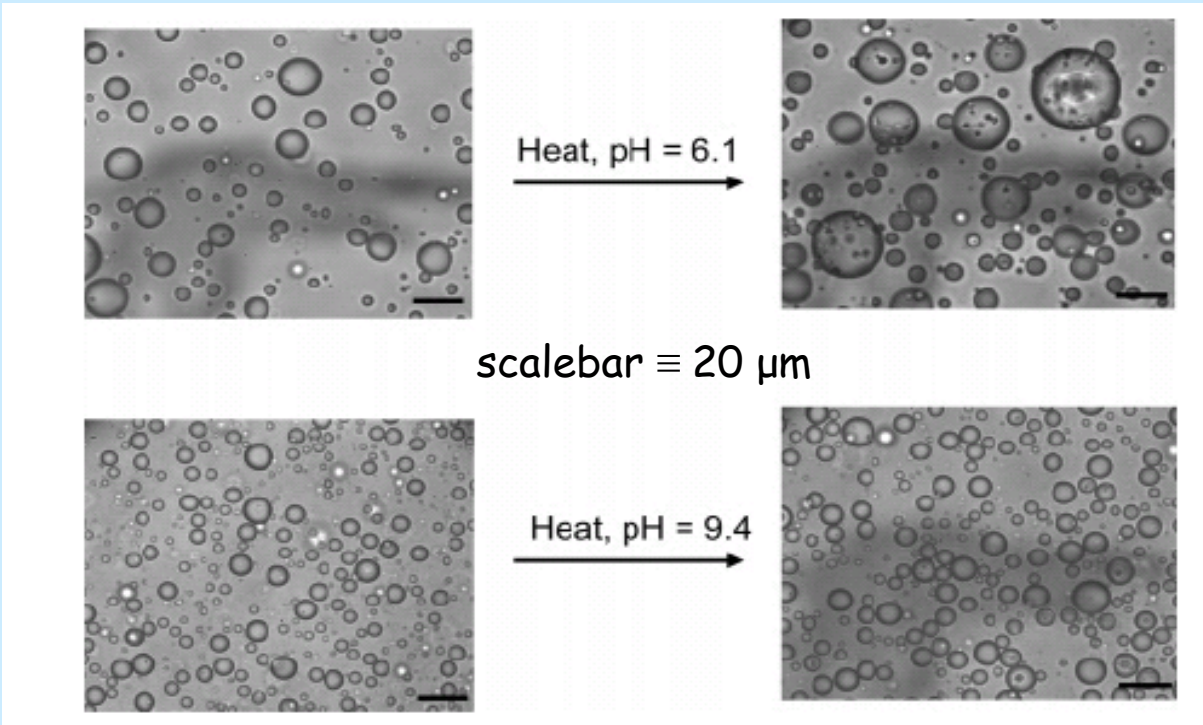


# Additional degree of freedom: temperature

[Ngai ea, Macromolec. **39**, 8171, (2006)]

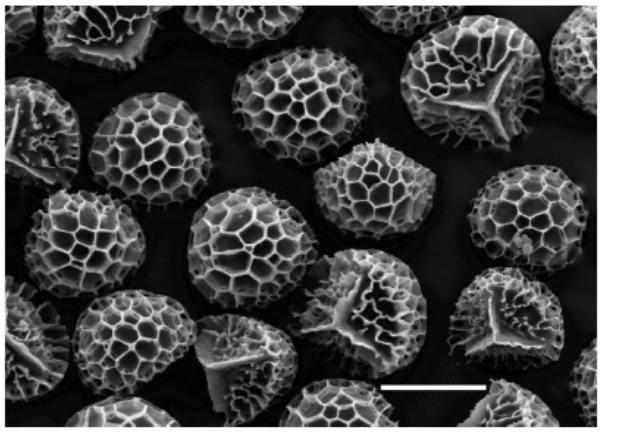



PNIPAM poly(N-isopropylacrylamide) microgel particles

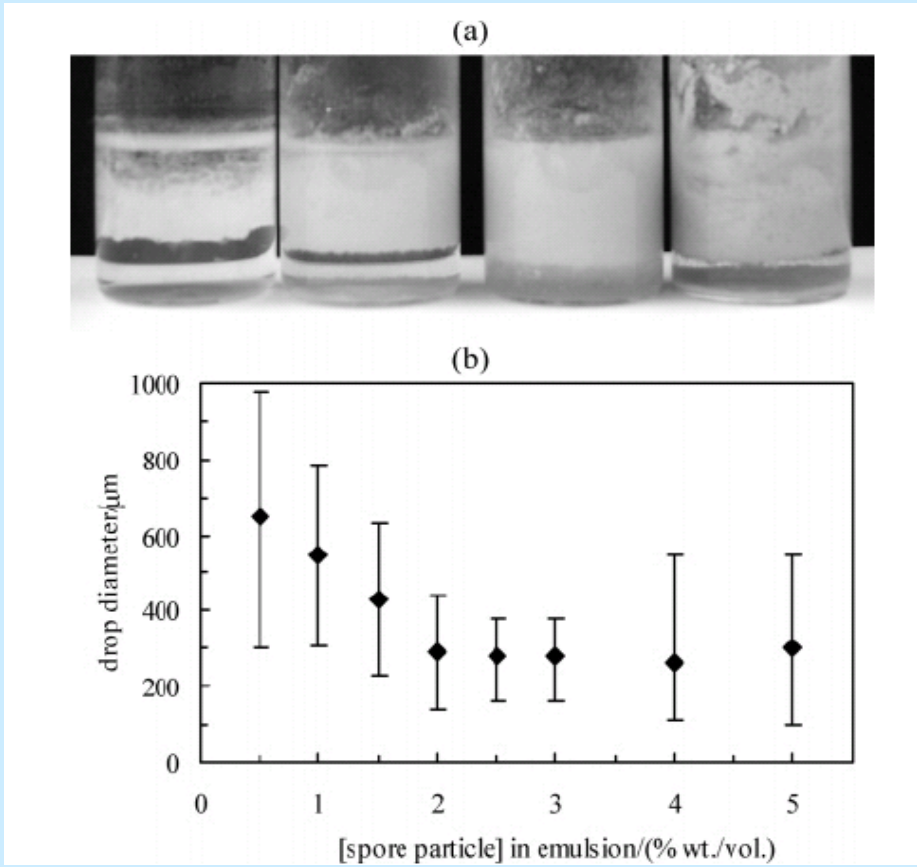


# Bio - stuff

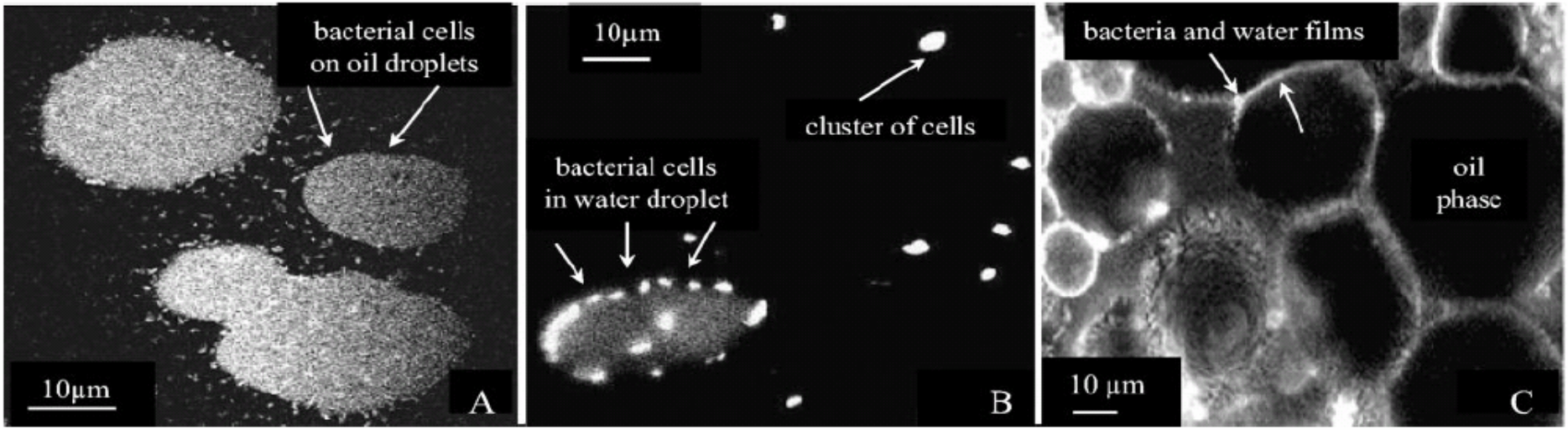
## 1. Spore particles [Binks ea, Langmuir **21**, 8161, (2005)]



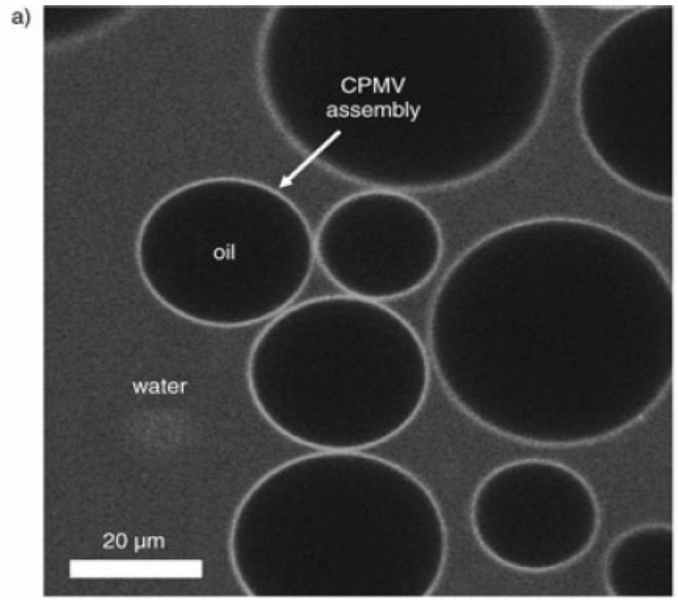
25 μm

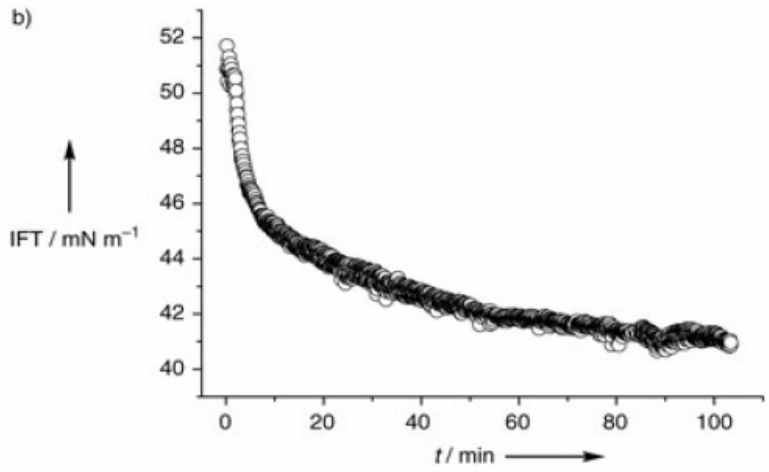


# 2. Bacteria [Dorobantu ea, Appl. Environm. Microbiol. **70**, 6333, (2004)]



# 3. Virus capsids [Russell. Angew. Chem. Int. Ed. **44**, 2420, (2005)]



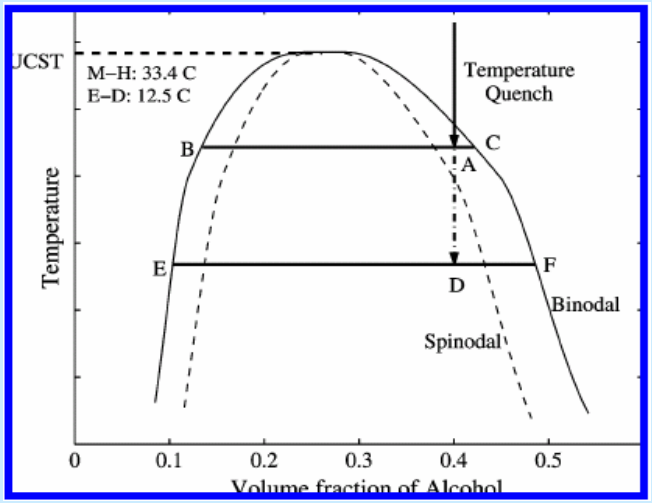

CPMV ≡ cowpea mosaic virus

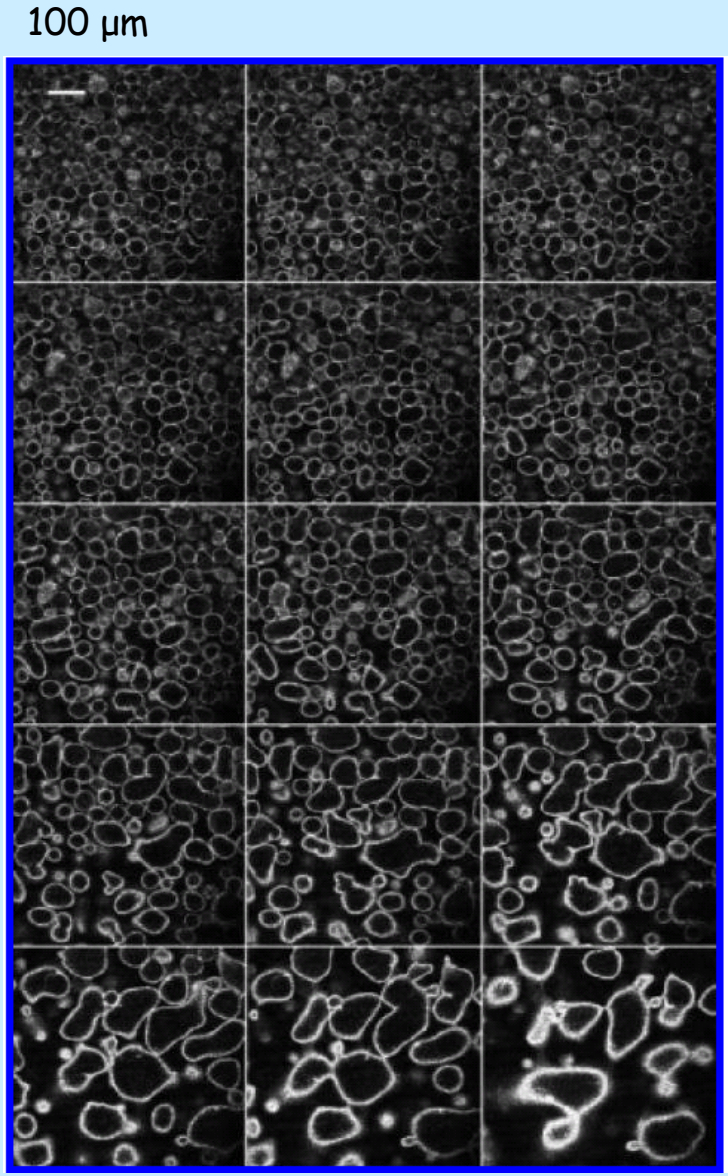
Subsequent cross-linking of virus monolayers:
stable capsules

# Emulsions with weird shapes: partly miscible liquids

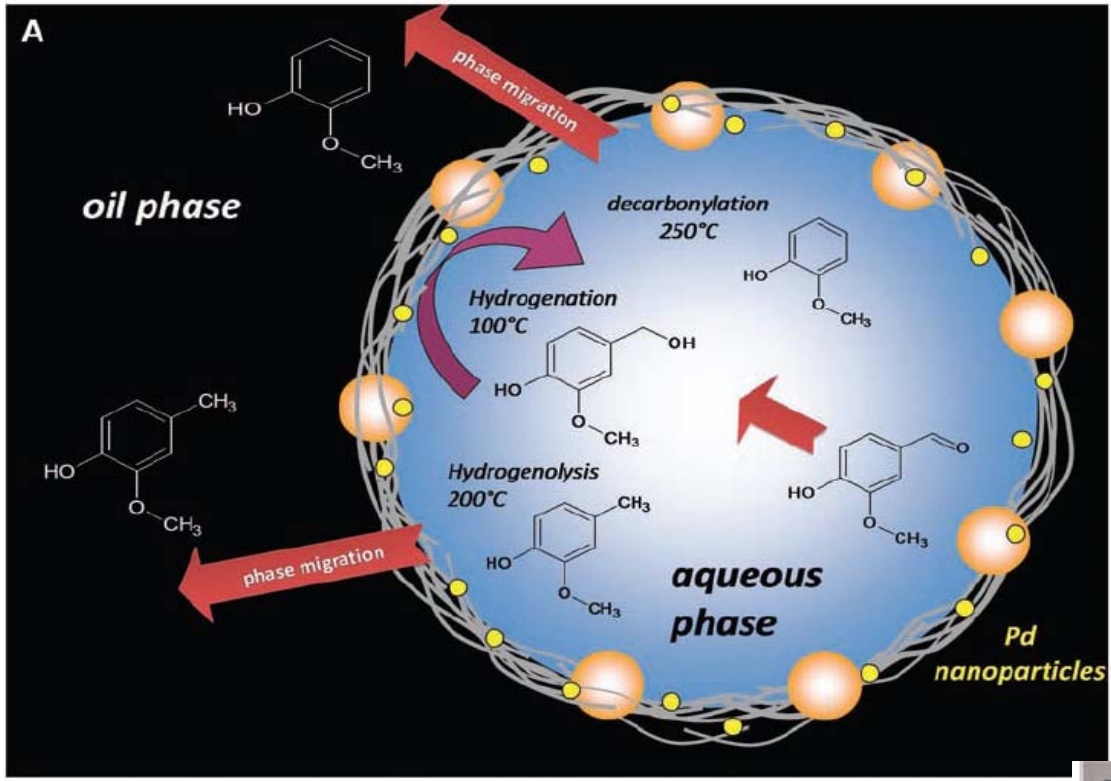
[Clegg ea, Langmuir **23**, 5984, (2007)]

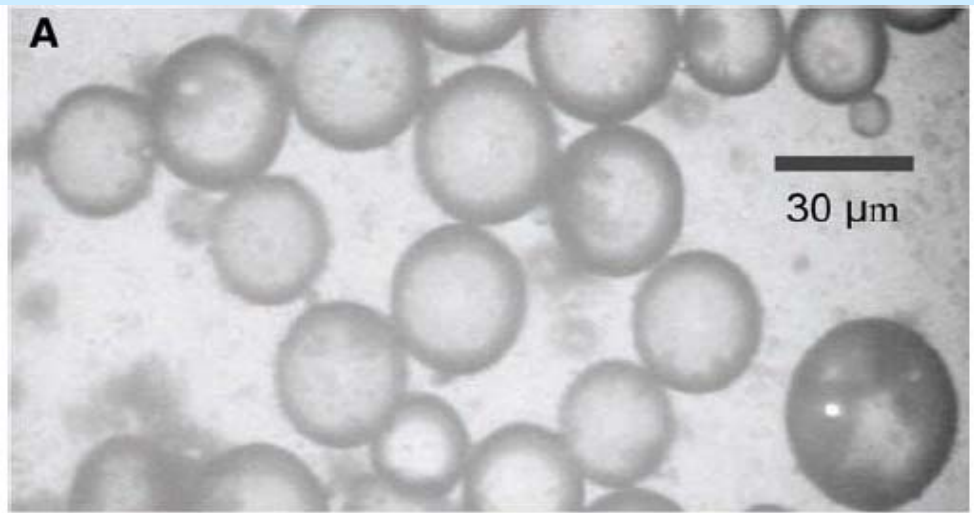
## Ethanol – dodecane

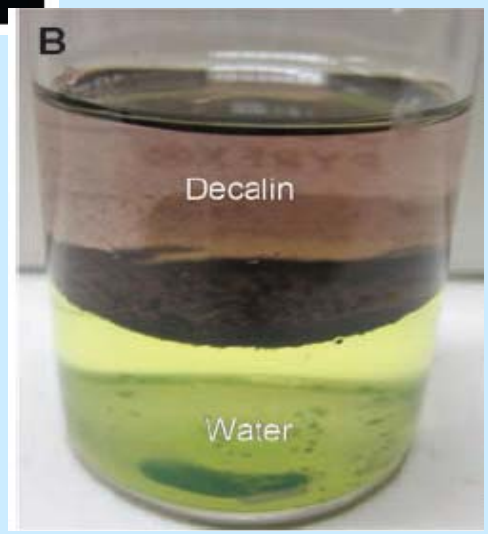


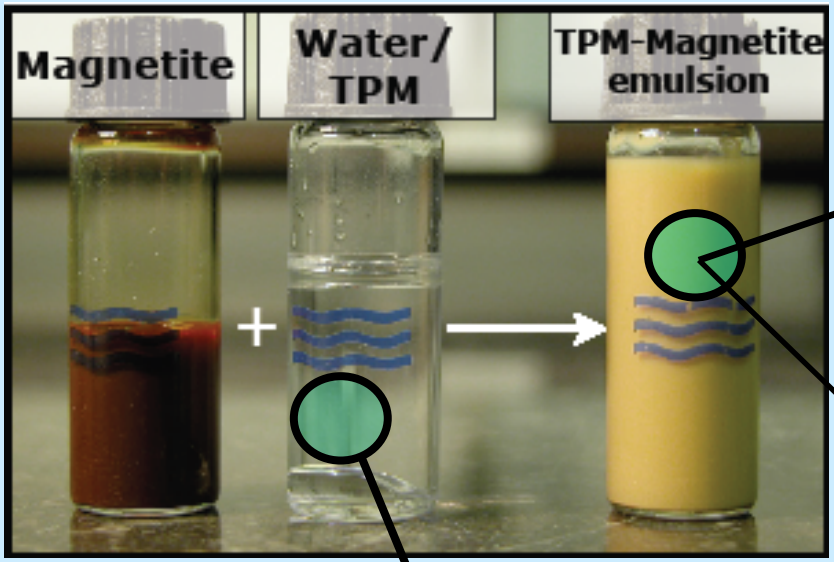
# ..as phase-transfer catalysts [Crossley ea Science **327**, 68, (2010)]

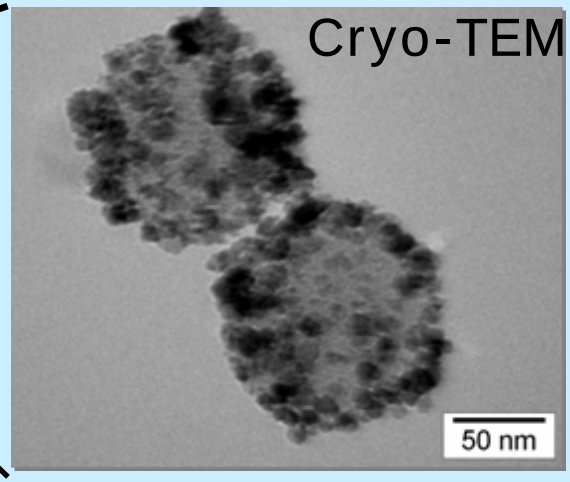



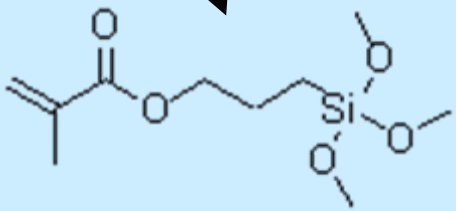



# **Equilibrium** solid - stabilized emulsions




Oil in water Pickering emulsion



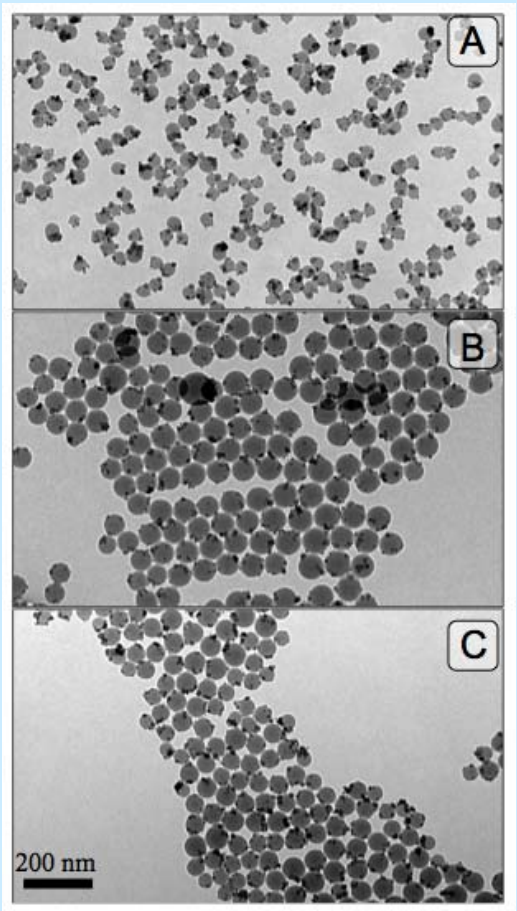



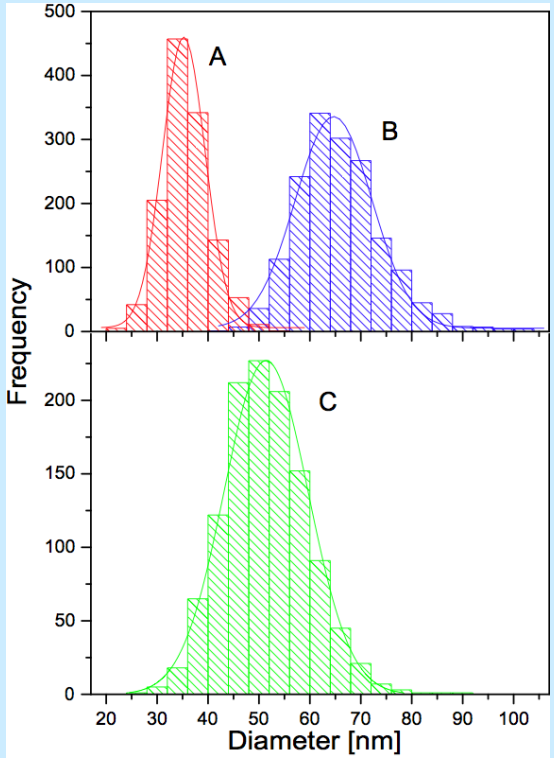

TPM
3-(Trimethoxysilyl)propyl methacrylate

- S. Sacanna, WKK, A. P. Philipse, PRL **98**, 158301 (2007)

# Thermodynamic stability

mix



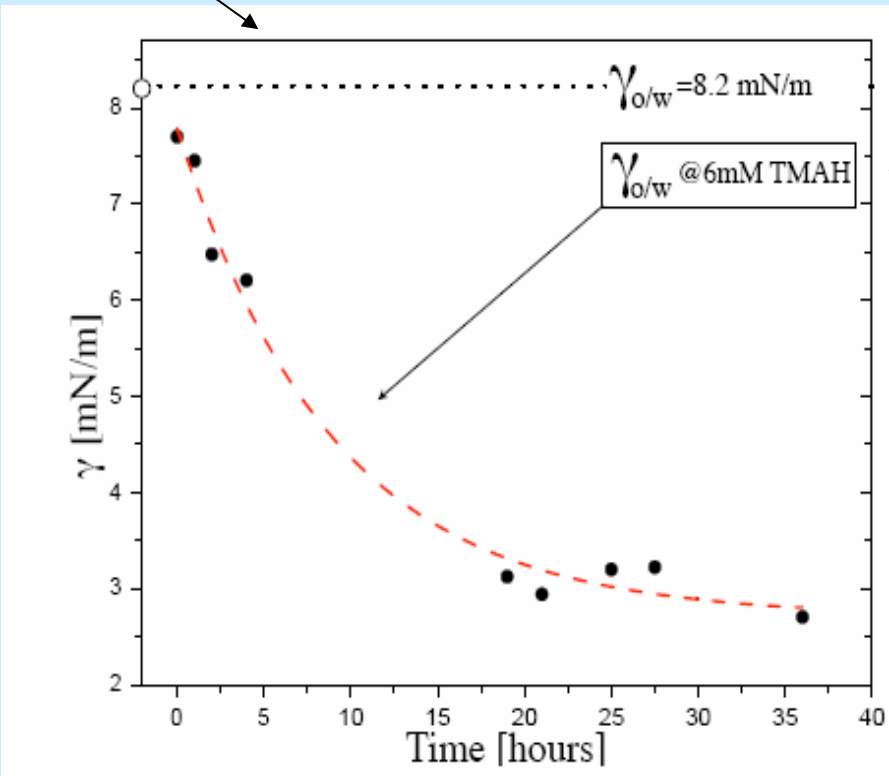




Spontaneous formation of intermediate droplet size

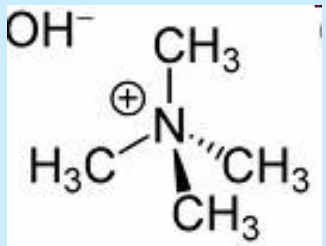
# Requirements for TD stable Pickering emulsions:

[S. Sacanna, WKK, A. P. Philipse, Langmuir (2007)]
[DJ Kraft, B. Luigjes ea, Submitted]

Colloid size < ~100 nm
Charged
Colloids have preference for oil
Influence of nature of counterions
Low O/W interfacial tension
(but NOT as low as for microemulsions)




(TMAH ≡ Tetramethylammonium hydroxide)



# Condition(s) for TD stability?

## Create oil/water/colloid interface:

- **Cost** = AT LEAST ~ 10% bare oil-water interface

per unit (emulsion-drop) area ~ $\gamma_{ow}/10$

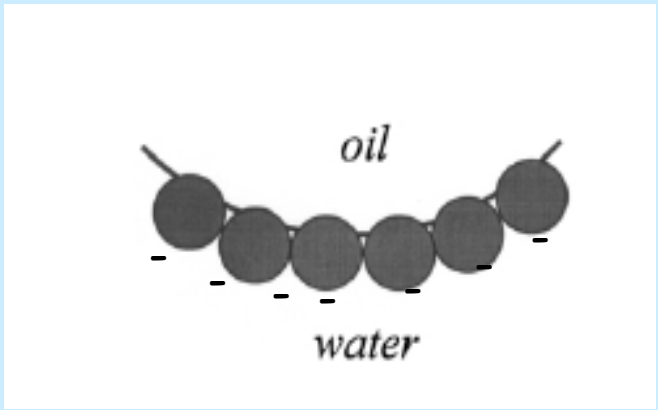
Potential **gain** = ION ENTROPY

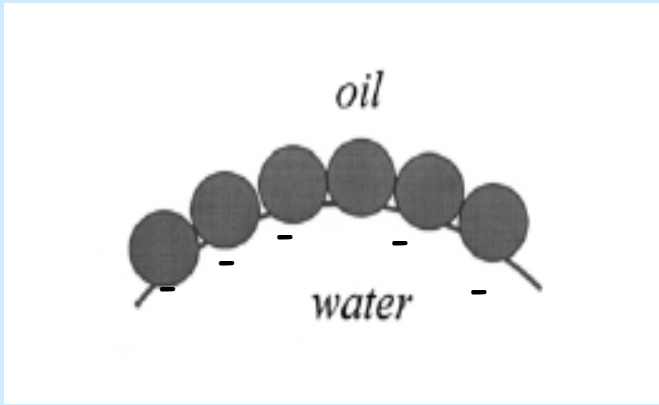
upon adsorption of colloids with chargable groups onto O/W interface (initially in oil).

Must be < ~ - $\gamma_{ow}/10$ (per unit area)

Expect competition between adsorbed state and dispersed state in oil or water

# n **charged** colloids @ curved O/W interface




Take perturbation on HS : [WKK & J. Groenewold, PRE(R) 2009]

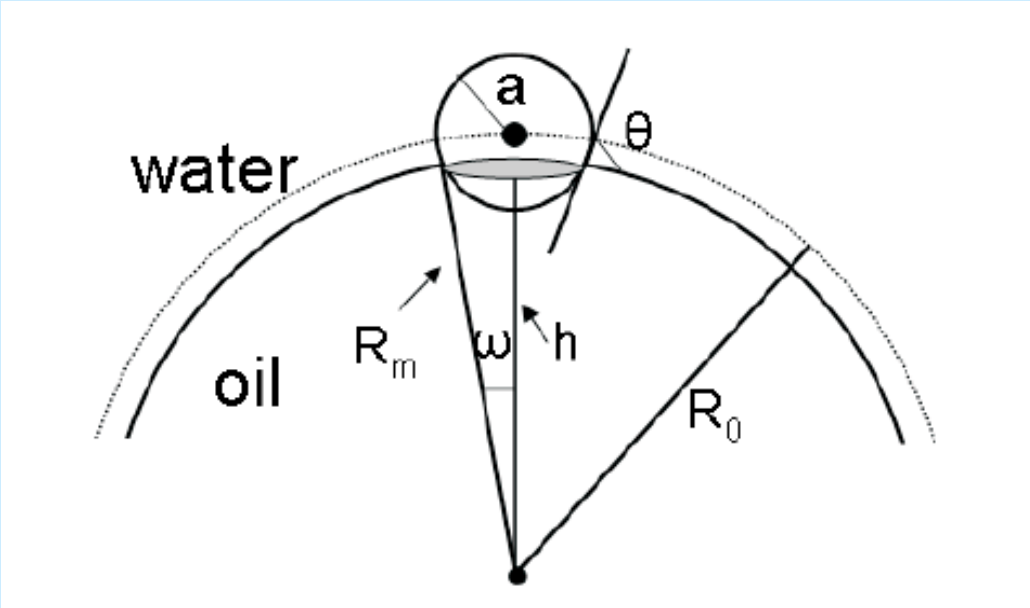
close-packed layers with added electrostatic contribution

…adsorption energy per colloid ~ $\gamma_{ow}a^2$ >(>) 100 kT

$$F/n = \gamma_{cw}A_{cw} + \gamma_{co}A_{co} + \gamma_{ow}A_{ow} - \Delta p v_d + f_{el}$$

Stabilizing iff sub-linear in interfacial area's

# Areas of spheres @ curved interfaces



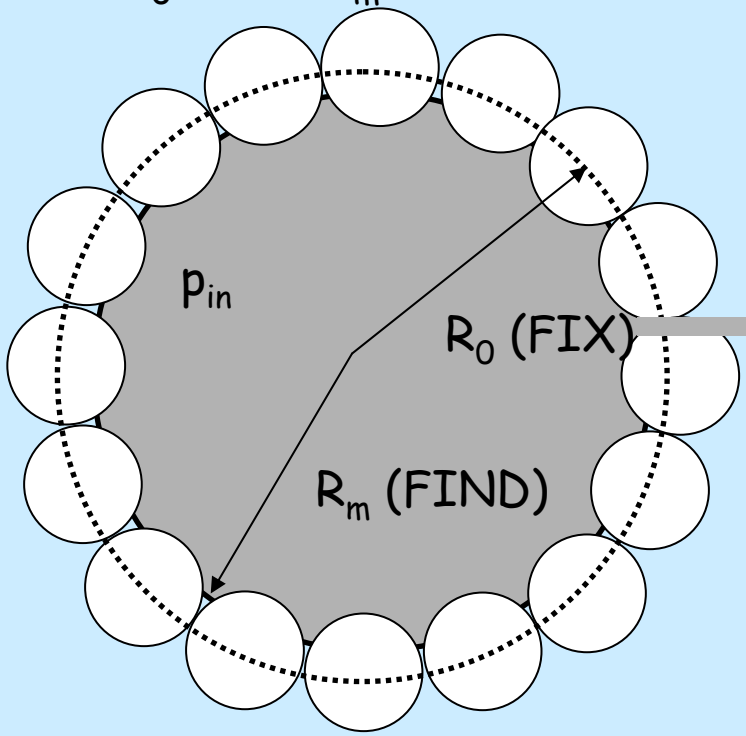

$$A_{cw} = 2\pi a^2[1 + cos(\theta - \omega)]$$

$$A_{co} = 2\pi a^2[1 - cos(\theta - \omega)]$$

$$nA_{ow} = 4\pi R_m^2 - 2\pi R_m^2 n(1 - cos\ \omega)$$

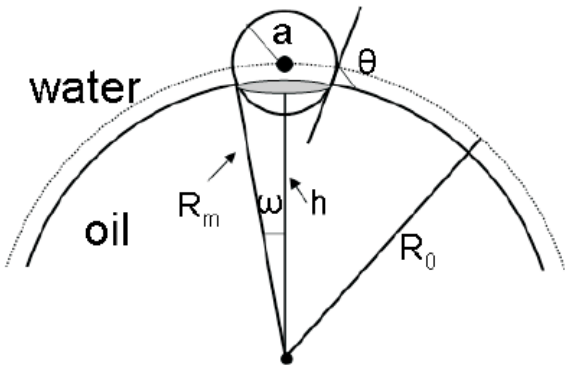
# Ensemble & constraints

Create a drop: Fix $R_0$, find $R_m$




Reservoir

$p_{out}$




Minimize F/n

Obtain contact angle (areas) by (geometrical) relation between $R_0$, $R_m$

$$a\ cos\theta = \frac{R_0^2 - R_m^2 - a^2}{2R_m}$$

## Special case: n = constant ≡ no interactions

(as in, e.g., Kralchevski ea, Langmuir 2005)

Condition:

$$\left(\frac{\partial F/n}{\partial R_m}\right)_{R_0} = \left(\frac{\partial F/n}{\partial R_0}\right)_{R_m} = 0$$

Result:

$$R_m = \frac{-a\Delta\gamma \pm \left(\Delta\gamma^2 a^2 + \gamma_{ow}^2 (R_0^2 - a^2)\right.}{\gamma_{ow}}$$

$\Delta\gamma = \gamma_{co} - \gamma_{cw}$

$$\cos\theta = \frac{\Delta\gamma}{\gamma_{ow}}$$ Young

$$\Delta p = \frac{2\gamma_{ow}}{R_m}$$ Young - Laplace

→ Mechanical stability ($\Delta p = 0$) iff $R \to \infty$

# Close Packing

Constraint ≡ relation between n, $R_0$

*Impose* mechanical equilibrium

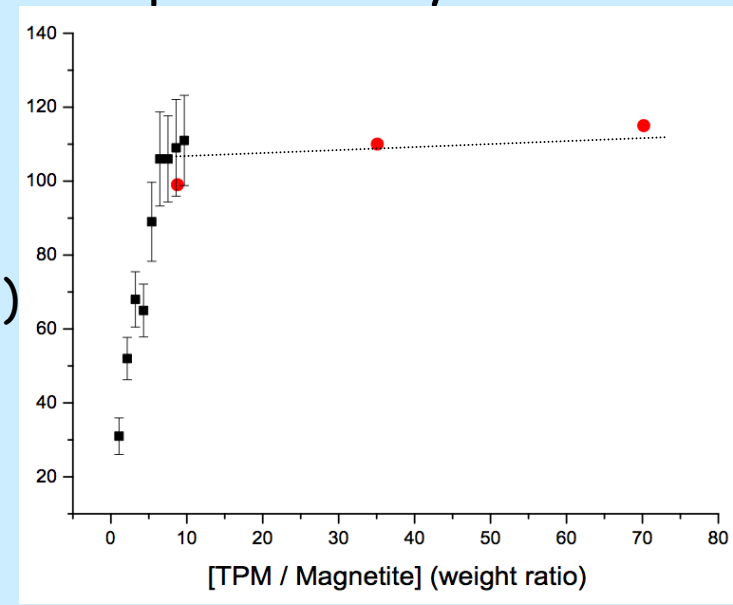
$$\Delta p = 0$$

Implies zero mean curvature!

PE may coexist with 'excess' droplet interior


Excess oil phase

as experimentally observed:




Points to PREFERRED CURVATURE of O/W/colloid interface

Find $R_m$ by

$$\left(\frac{\partial\, F/n}{\partial R_m}\right)_{R_0(n)} = 0.$$

# Electrostatics

# electrical charges z

$$f_{el} = z \ln\left(\frac{z}{z_{max}}\right) + bz + cz^2$$

(per colloid; in kT)

Combinatorial (ion) entropy

Dissociation energy

$$b \approx \lambda_B / d_{bond}$$

Self-energy (DH)

$$c \approx \frac{\lambda_B}{2a(1+\kappa a)}$$

Neglect interactions between charges @ different colloids  OK for $\kappa^{-1} < a$.

Effective # dissociable sites $z_{max} = \rho_c A_{cw}$: NO dissociation @ oil side

Coupling with contact angle:

$$A_{cw} = 2\pi a^2 n(1 + cos(\theta - \omega))$$

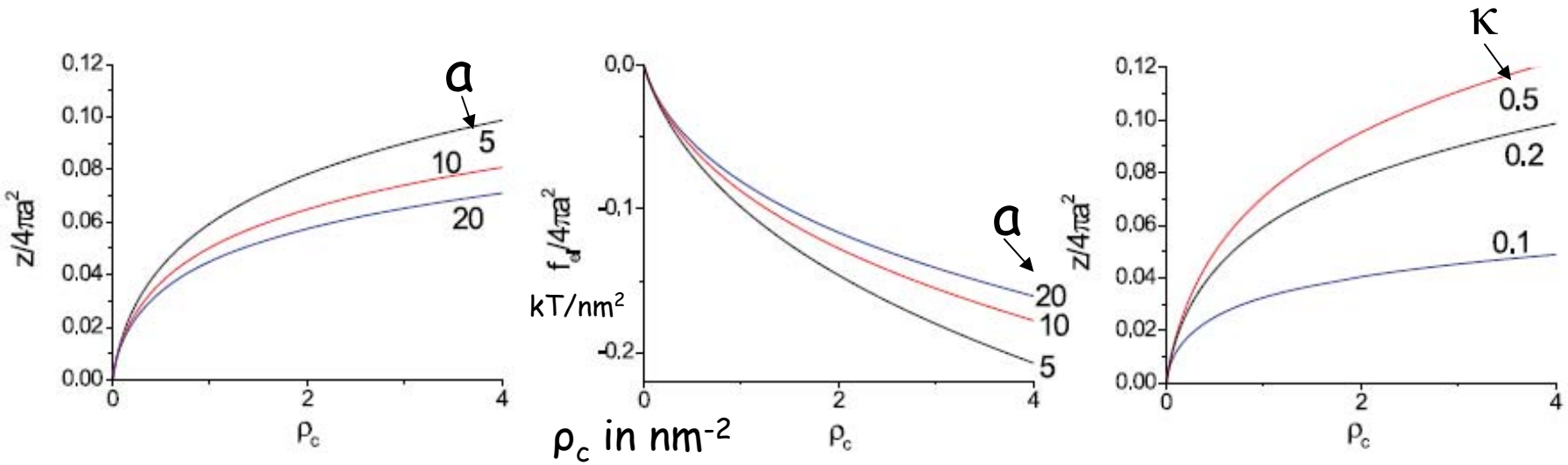
Includes charge renormalization: optimal z depends on a, κ, ….

$$z = \frac{W\left(2c\, e^{-(b+1)} z_{max}\right)}{2c}$$

Lambert function

$$x = W(x)e^{W(x)}$$

Example: colloids fully immersed in water

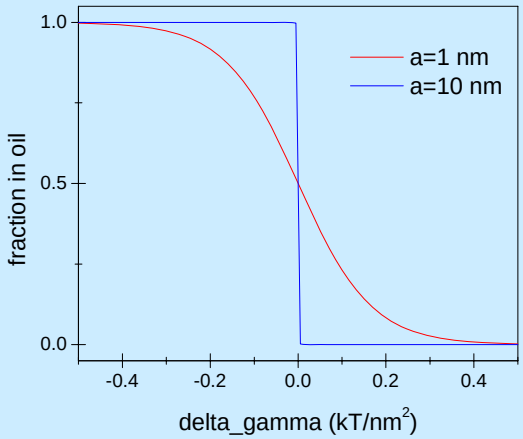



$\rho_c = z_{max}/4\pi a^2$

z is far-field or renormalized charge [Alexander ea JCP 1984]

# Calculate FE relative to appropriate **reference state**

No O/W interface: fraction colloids in oil $\approx \dfrac{e^{-4\pi a^2 \Delta\gamma / kT}}{1+e^{-4\pi a^2 \Delta\gamma / kT}}$




or: |transfer colloid from O -> W| (usually) >> kT

Define free energies relative to reference states in O and W

$$\Delta f_o = \frac{F}{n} - 4\pi a^2 \gamma_{co}$$

$$\Delta f_w = \frac{F}{n} - 4\pi a^2 \gamma_{cw}^{(1)}$$

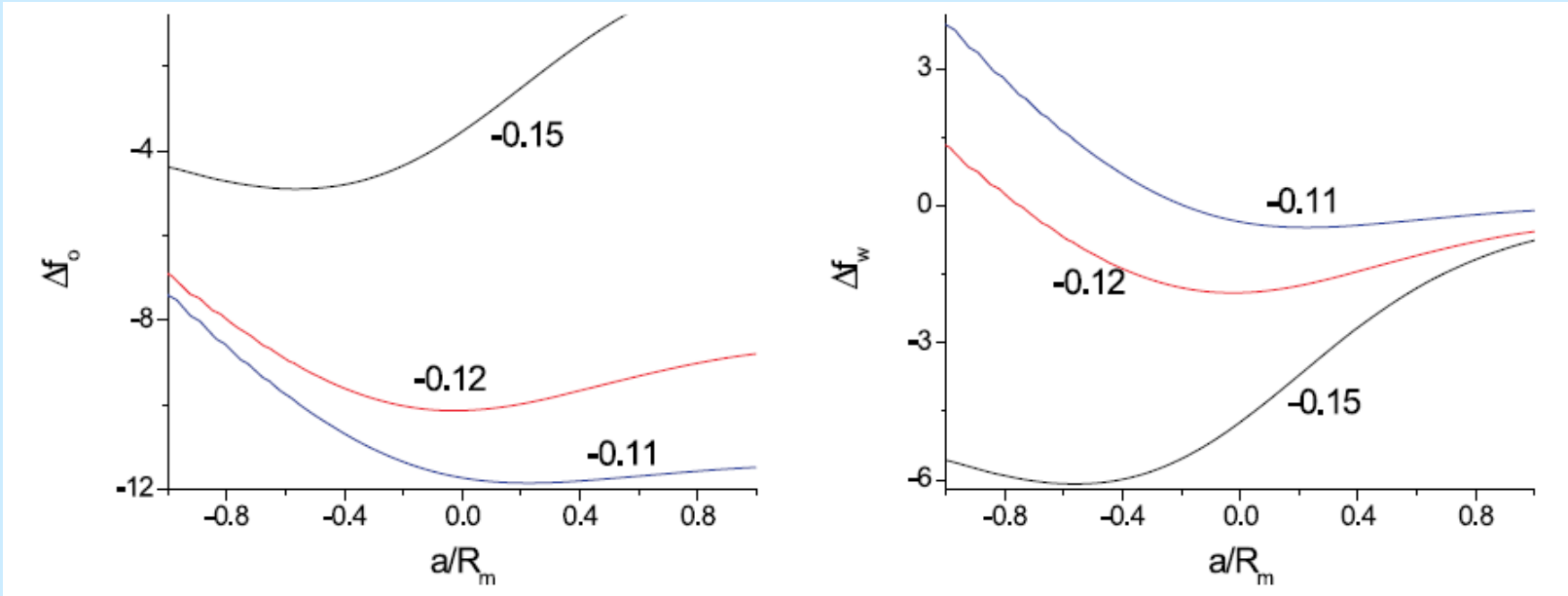
$$\gamma_{cw}^{(1)} = \gamma_{cw} + \frac{f_{el}(\theta = 0)}{4\pi a^2}$$

Condition for TD stability:

$$(\Delta f_o < 0) \quad \wedge \quad (\Delta f_w < 0)$$

Results (#'s are $\Delta\gamma$ in kT/nm$^2$ )

$$\Delta\gamma = \gamma_{co} - \gamma_{cw}$$




$\gamma_{ow}$= $0.5\ kT/nm^2,\ \rho_c = 2\ nm^{-2},\ a = 5\ \mathrm{nm},\ b = 0.5\ kT,\ \kappa = 0.2\ nm^{-1}$

→ TD stability iff $\Delta\gamma < 0$ : colloids prefer oil

→ Presence of O/W interface allows ion dissociation: entropy gain

→ $\kappa^{-1}$ too small: colloids to water.

Too large: colloids to oil (charge too expensive)

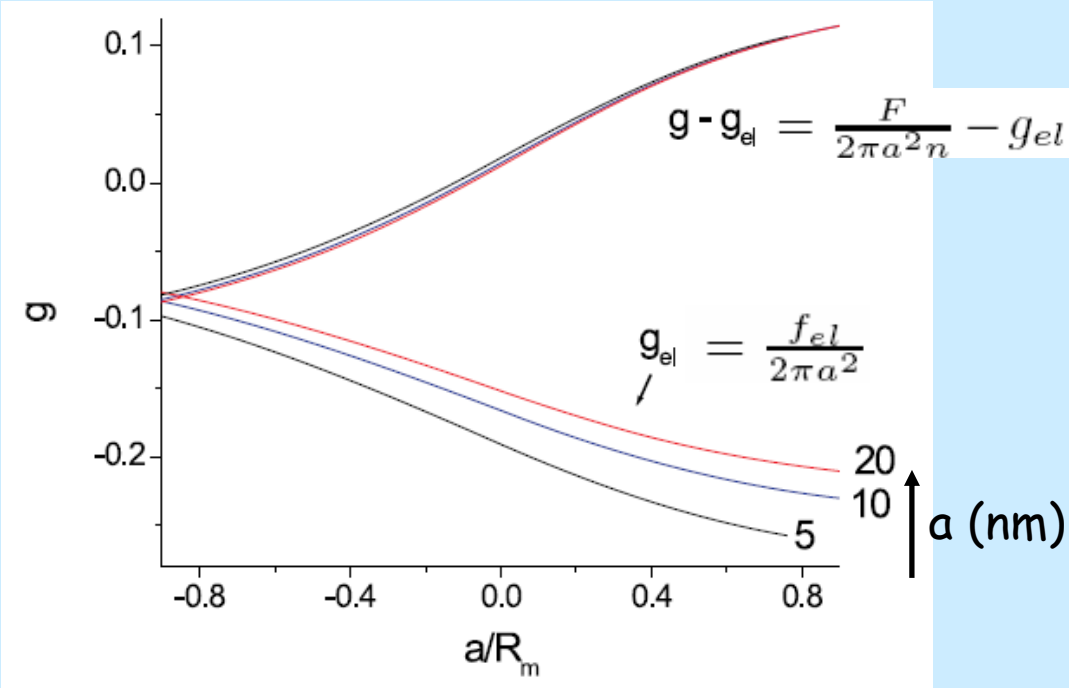
In charge renormalization regime, drop energy

$$F \sim \alpha_1 a^2 - \alpha_2 a^{2-\delta}$$

$\alpha_1, \alpha_2, \delta > 0$

Surface terms

Electrostatics




Negative 'Line tension term' arises naturally from ion entropy

**Predictions wrt TD stability consistent with experiments:**

- Small colloid size (max order 100 nm)
- High density of chargeable groups (order $1/nm^2$)
- Low O/W interfacial tension (order 1 kT / $nm^2$)
- Without O/W interface, colloids prefer oil over water

Difference between experiment & theory in details

e.g., influence ionic strength on equilibrium R

## further work / what's cooking?

- Equilibrium shape of O/W interface
- More realistic electrostatic interactions (2 length scales)
- Theory with generalized interactions
- other colloid shapes
- Experiments with different oils

# THANX

Stefano Sacanna
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Bob Luigjes
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Jos Zwanikken
Michiel Hermes
Marcus Bier
Martin Oettel

& You!