Emulsions:
Fundamentals & Applications

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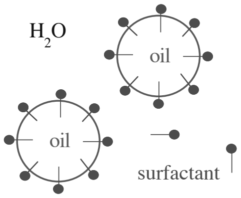
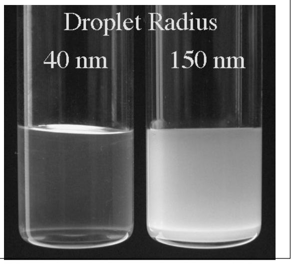




Mayonnaise: An Edible Elastic Emulsion

"Mayonnaise":	corruption of "*moyeunaise*"
	old French word "*moyeu*" - egg yolk

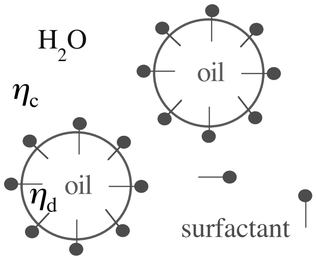
An emulsion of egg yolks and oil (essential)
salt, pepper, vinegar, or lemon juice (added for taste)

Larousse Gastronomique

Recipe:
Add 3 yolks, 1 tblsp. vinegar, 1 tsp. salt in bowl & mix gently
Add 2.5 cups of olive oil, drop by drop at first, then in a thin trickle, *beating constantly* with a whisk or wooden spoon.

Emulsion "sets": it attains an elasticity that can overcome gravity
Emulsion is made elastic by raising droplet volume fraction ϕ

Emulsions: Metastable Dispersions of Liquid Droplets



Droplets of one liquid dispersed
into a different immiscible liquid
by mechanical shear

radius: a droplet volume fraction: ϕ
surface tension: σ viscosity: η

Surfactant inhibits coalescence; lowers σ

Continuous phase:	liquid in which droplets are dispersed	(e.g. H_2O)
Dispersed phase:	liquid inside droplets	(e.g. oil)

Emulsions do not form without mechanical agitation

Strong interfacial repulsion and strong insolubility of liquids
allow droplets to remain dispersed over many years

Multi-phase Materials: Meet the Family

Dispersions

One material phase distributed in a different fluid phase
Non-equilibrium systems; not thermodynamic states

Dispersions in Liquids

Emulsion	Liquid in Liquid	mayo, lotion, …
Foam	Gas in Liquid	shaving cream, …
Particulate	Solid in Liquid	clay, paint, …

Dispersions in Gases

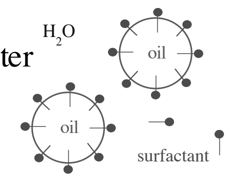
Aerosol	Liquid in Gas	fogs, mists, …

Dispersions are <u>not</u> solutions

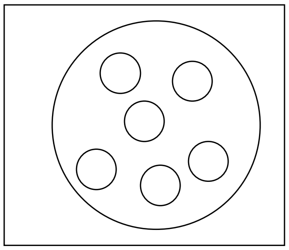
Solution is a spontaneous mixture of miscible components
Example: solution of a polymer in a good solvent
Solutions are thermodynamic equilibrium states

Emulsions: Basic Nomenclature

“Oil-in-water” (O/W) or “direct” emulsions
droplets of non-polar oil dispersed in polar water



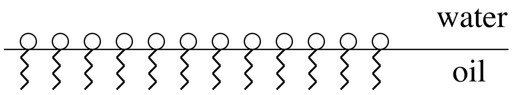
“Water-in-oil” (W/O) or “inverse” emulsions
droplets of polar water dispersed in non-polar oil

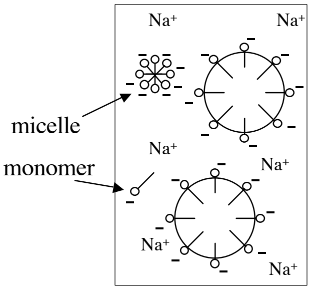


“Double emulsions”
droplets of water dispersed in oil
dispersed in water: (W/O/W)

“Multiple emulsions”
droplets of water dispersed in oil
dispersed in water dispersed in oil: (W/O/W/O)

Surfactants: SURFace ACTive AgeNTs





Amphiphilic molecules
e.g. oil-loving hydrocarbon tail,
+ water-loving head group

Inhibits coalescence of the emulsion

Provides repulsive interaction potential between droplet interfaces

Generally soluble in continuous phase and very insoluble in dispersed phase

Lowers surface or “interfacial” tension, σ, somewhat but not close to zero

σ provides a restoring force- opposes increase in surface area, A

Classes of Surfactants

Ionic – charged head group

- Anionic – negative charge (e.g. sodium dodecyl sulfate: SDS)
- Cationic – positive charge (e.g. ammonia groups: CTAB)
- Zwitterionic – both positive and negative charges

Non-ionic – polar headgroup (e.g. nonyl-phenol ethoxy7: NP-7)

Polymeric – provide a steric barrier (e.g. poly-vinyl-alcohol: PVA)

Excess surfactant is generally in the continuous phase
structures: monomers or micelles

Surfactant mixtures are typically used in commerical products

Surfactant compatibility is an issue for double/multiple emulsions

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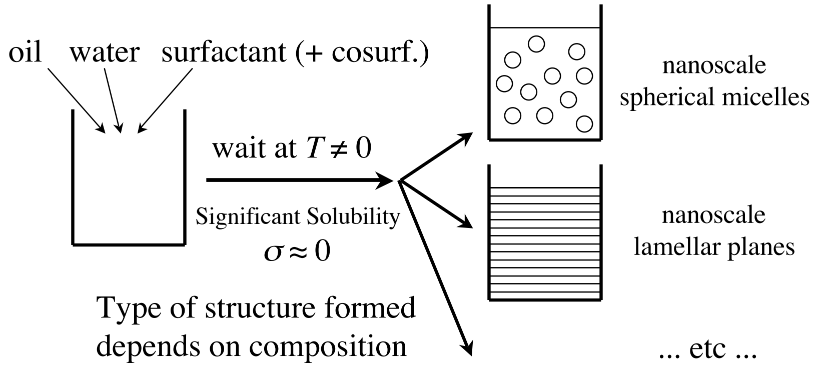
Microscale Emulsions are **not** "Microemulsions"

Lyotropic liquid crystalline phases of oil/water/surfactant mixtures

-Also called "Mesophases"-

Lowest energy thermodynamic state

Self-organized nanoscale structures form spontaneously



oil water surfactant (+ cosurf.)

wait at $T \neq 0$

Significant Solubility

$\sigma \approx 0$

nanoscale
spherical micelles

nanoscale
lamellar planes

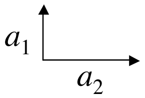
... etc ...

Type of structure formed
depends on composition

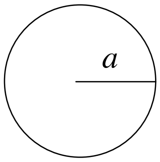
Control of type of structure and volume fraction, ϕ,
is limited by phase transitions

Deforming Droplets: Laplace Pressure

General Expression for curved interface



Laplace Pressure: $\Pi_L = \sigma[1/a_1 + 1/a_2]$



No Applied Stress:
Surface tension minimizes
surface area for a given volume
-> sphere

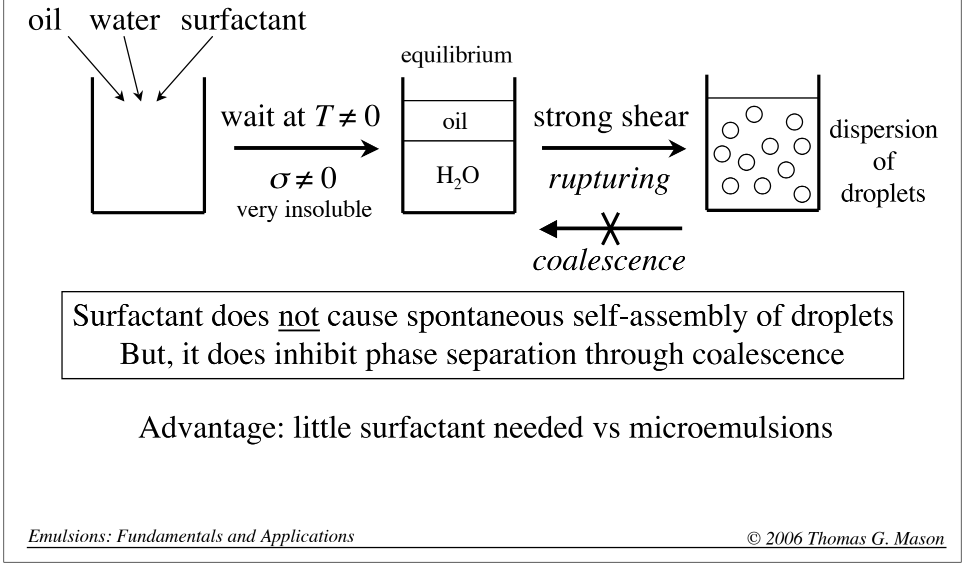
Laplace Pressure: $\Pi_L = 2\sigma/a$

Laplace Pressure Scale: σ/a

To deform and rupture droplets- must overcome Laplace Pressure

Emulsification: Basic Idea

Out-of-equilibrium dispersion of liquid droplets



oil water surfactant

wait at $T \neq 0$

$\sigma \neq 0$
very insoluble

equilibrium

oil

H_2O

strong shear
rupturing

coalescence

dispersion
of
droplets

Surfactant does not cause spontaneous self-assembly of droplets
But, it does inhibit phase separation through coalescence

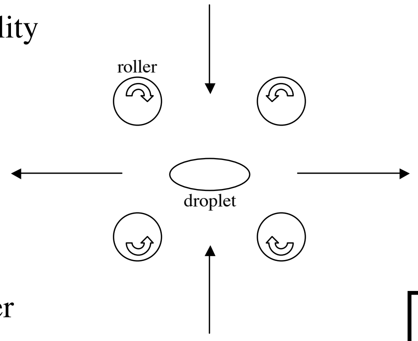
Advantage: little surfactant needed vs microemulsions

Rupturing of Isolated Droplets in a Shear Flow

Extensional Shear: 4-Roll Mill

G.I. Taylor, *Proc. Royal Soc.* **A146**, 501 (1934).

Capillary Instability



As rate increases the droplet:

deforms
elongates
breaks up

Capillary Number

Taylor's Formula

$$Ca = \frac{\text{viscous stress}}{\text{Laplace pressure}} \approx \frac{\eta_c \dot{\gamma}}{(\sigma / a)} \xrightarrow[\text{neglect } \eta_d]{Ca \approx 1} \boxed{a \approx \frac{\sigma}{\eta_c \dot{\gamma}}}$$

Stability of Emulsions

Stability against creaming (gravity-driven inhomogeneity in ϕ)

minimize density difference between droplets
take advantage of Brownian motion

Thermal-Gravitational Height (h_{tg}):
Law of atmospheres (Boltzmann factor): $\exp[-mgh/(k_B T)]$
$1/e$ value -> $h_{tg} = k_B T/(\Delta\rho V g)$, $V = 4\pi a^3/3$
microscale and nanoscale droplets cream/settle slowly
density matching can reduce creaming

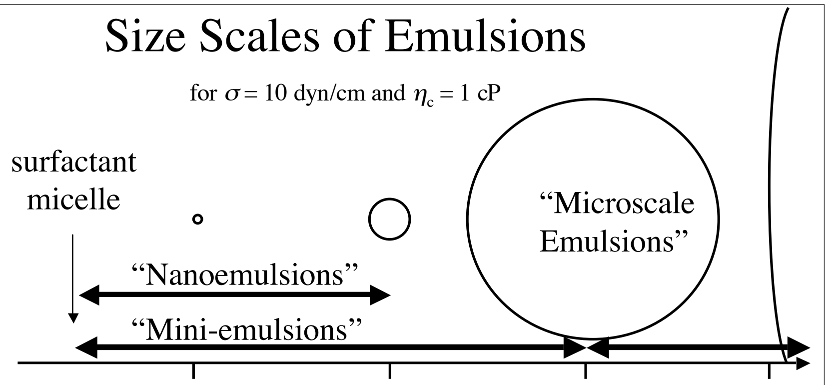
Stability against coarsening (growth of average droplet size)

Coalescence: rupturing of thin films of continuous phase
overcome critical disjoining pressure Π_c^*

Ostwald ripening:
diffusion of dispersed phase through continuous phase
controlled by solubility (use higher M_W oil to reduce)

Size Scales of Emulsions

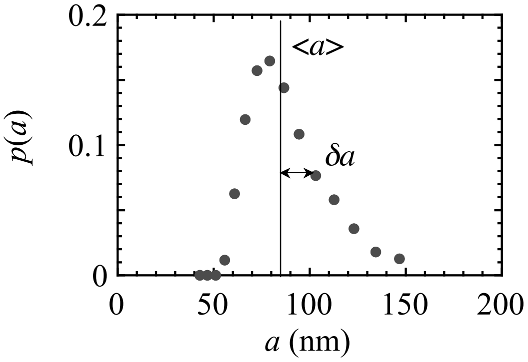
for $\sigma = 10$ dyn/cm and $\eta_c = 1$ cP



Radius (nm)	10	10^2	10^3	10^4
Volume/droplet (L)	10^{-21} (zepto)	10^{-18} (atto)	10^{-15} (femto)	10^{-12} (pico)
Laplace Pres. (atm)	10^2	10^1	10^0	10^{-1}
Shear Rate (1/s)	10^9	10^8	10^7	10^6

Emulsion Size Distributions

Probability distribution of droplet sizes



Weighting is important

Number-weighted:
each droplet has the same weight regardless of size

Volume-weighted:
smaller droplets receive very little weight

Build up a histogram of droplet sizes through measurements

Polydispersity: $\delta a/<a>$ "monodisperse" < 10%

$$\overline{\delta a}/\bar{a} = \left[\overline{a^2} - \bar{a}^2\right]^{1/2}/\bar{a}$$

Measuring Emulsion Size Distributions

Scattering Methods

Dynamic Light Scattering: (random walk of droplets)
Static Small Angle Light, Neutron, or X-ray Scattering
(SALS, SANS, and SAXS)

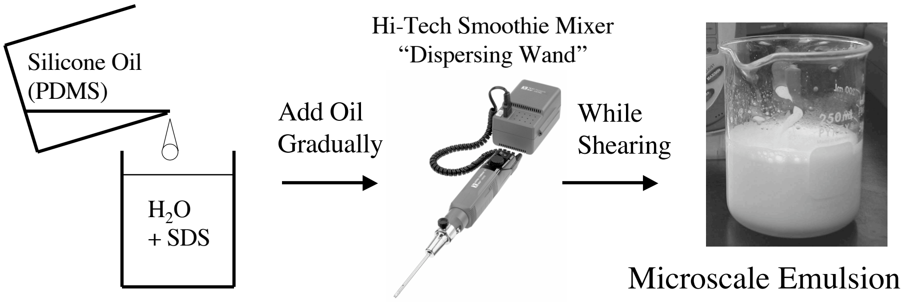
Advantages: ensemble averages over many droplets
Disadvantages: generally assume a smooth peaked distribution

Microscopy Methods

Optical microscopy (0.5 μm and larger)
Cyro-Scanning electron microscopy (SEM)
Transmission electron microscopy (TEM)

Advantages: can see bimodal or unusual distributions
Disadvantages: hard to get good ensemble-averaged statistics
cryo-handling is more difficult

Making Microscale Emulsions: High-Throughput



Silicone Oil (PDMS)

H_2O + SDS

Add Oil Gradually

Hi-Tech Smoothie Mixer
“Dispersing Wand”

While Shearing

Microscale Emulsion

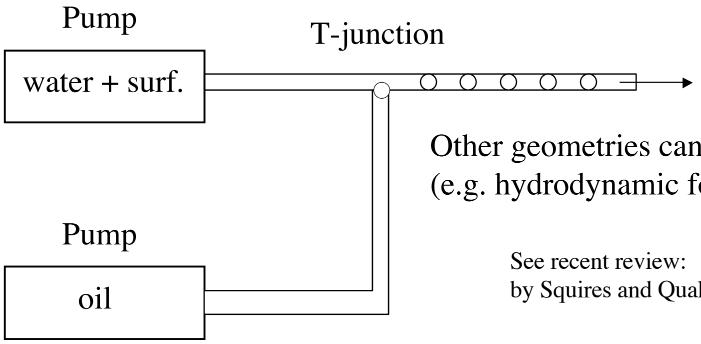
Control Composition: “Direct” Oil-in-Water Emulsion
Oil: type, volume fraction ϕ, viscosity η_d
Surfactant: type, concentration C

Advantages:
high-throughput suitable for commercial production

Disadvantages:
polydispersity in size can be large- inhomogenous shear
typically requires large volumes of liquids

Microfluidic Emulsification: Low-Throughput

Modern Variation of Traditional Droplet Production by Micropipettes



Pump

T-junction

water + surf.

Pump

oil

Other geometries can be used
(e.g. hydrodynamic focusing)

See recent review:
by Squires and Quake

Advantages:
- produces highly monodisperse droplets
- small liquid volumes required (good for expensive materials)

Disadvantages:
- very low volume throughput of droplets (not macroscopic)

Macroscopic Properties of Emulsions

Once made, it is possible to raise and lower the volume fraction over a very wide range, from dilute to concentrated

Dilute emulsions:	low ϕ	liquid-like
Concentrated emulsions:	high ϕ	solid-like

Want to understand bulk <u>macroscopic properties</u> of many droplets

Use Thermodynamics!

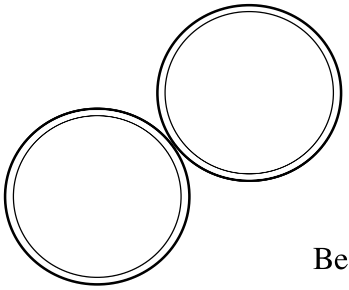
Effective Volume Fraction of Droplets

Anionically-stabilized droplets have a larger effective ϕ
due to the screened charge repulsion between surfaces

Debye screening length λ_D creates a larger effective volume fraction

$\phi_{\text{eff}} \approx \phi\,[1 + (\lambda_D/a)]^3$ $\lambda_D \approx 3\ \text{Å}/C^{1/2}$

Microscale Droplets: Assume there is a rigid film of thickness λ_D



Negatively charged
droplet surfaces

Na^+ screening
cations in H_2O

$\phi_{\text{eff}} \approx 0.6\,[1 + (30\ \text{Å}/5000\ \text{Å})]^3 \approx \mathbf{0.61}$

Becomes more significant for smaller droplets

Osmotic Pressure Π of Emulsions

Dilute Emulsions:

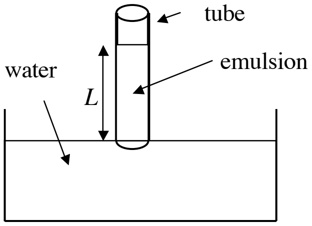
Ideal Gas Law: number density

$\Pi = n_d k_B T$

$\Pi = \rho g L$

$n_d = N/V$
$= N/(\pi R^2 L)$

$n_d = \phi/(4\pi a^3/3)$



Source of Osmotic Pressure is Thermal Motion of Droplets

Concentrated Emulsions:

$\Pi \approx (\sigma/a)\,(\phi - \phi_c^*)$, where ϕ_c^* is a critical packing volume fraction

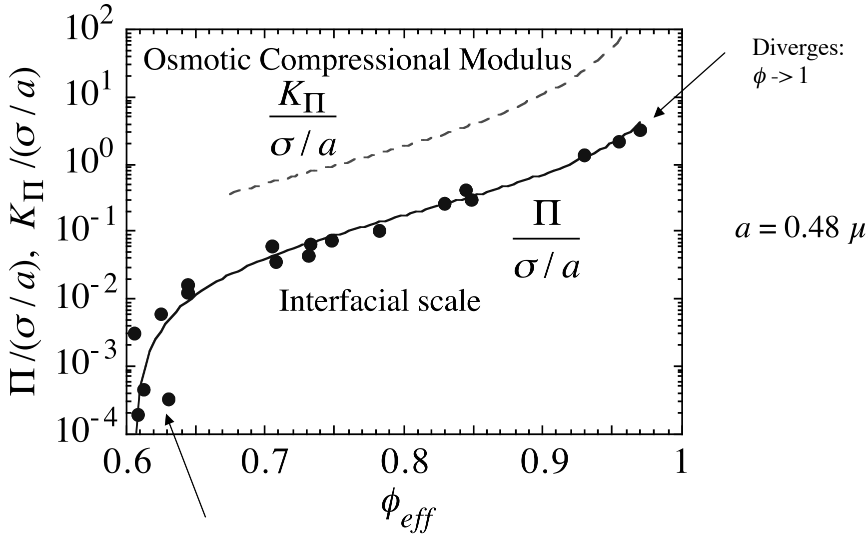
Source of Osmotic Pressure is Droplet Deformation

Helmholtz Free Energy: $F = N[\sigma(\pi a^2)(\phi - \phi_c^*)^2 - 3k_B T \ln(\phi_c^* - \phi)]$

$V = V_d + V_c$ $\Pi = -\left.\frac{\partial F}{\partial V}\right|_{V_d} = \frac{\phi^2}{V_d}\left.\frac{\partial F}{\partial \phi}\right|_{V_d}$

Osmotic Equation of State for Emulsions

Real microscale O/W emulsion of repulsive oil droplets stabilized by SDS



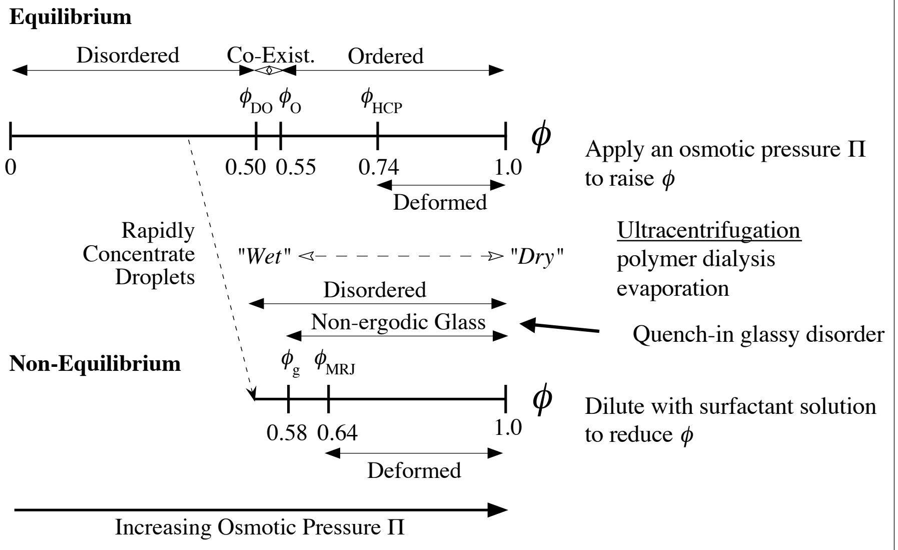
$a = 0.48\ \mu\text{m}$

"Maximal Random Jamming" of Spheres = "Random Close Packing"

Structure of Deformable Monodisperse Droplets

"Hard" droplet surfaces deform only when direct contact is made

T.G. Mason, et al., *J. Phys: Cond. Matt.* (submitted)



Equilibrium

Disordered Co-Exist. Ordered

ϕ_{DO} ϕ_O ϕ_{HCP}

0 0.50 0.55 0.74 1.0 ϕ

Deformed

Apply an osmotic pressure Π to raise ϕ

Rapidly Concentrate Droplets

"*Wet*" ⊲– – – – – – – – – ⊳ "*Dry*"

Disordered

Non-ergodic Glass

Ultracentrifugation
polymer dialysis
evaporation

Quench-in glassy disorder

Non-Equilibrium

ϕ_g ϕ_{MRJ}

0.58 0.64 1.0 ϕ

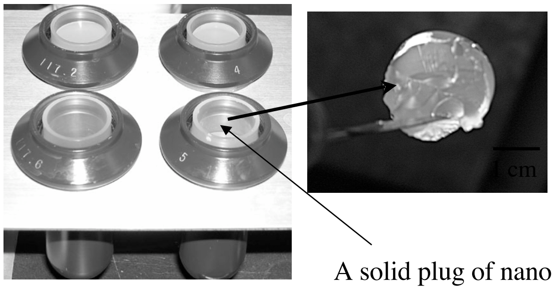
Deformed

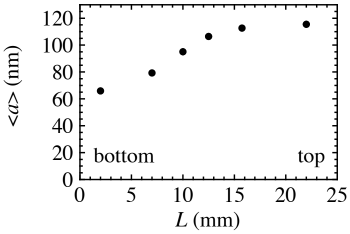
Dilute with surfactant solution to reduce ϕ

Increasing Osmotic Pressure Π

Ultracentrifugal Size Fractionation of Nanoemulsions

Larger droplets cream faster $$v \approx \frac{2\Delta\rho g a^2}{9\eta_c}$$





A solid plug of nanoemulsion taken from the top of the centrifuge tube

Disperse droplets to $\phi = 0.1$
Ultracentrifuge (20,000 RPM for 3 hrs)
Divide concentrated plugs & combine same sections

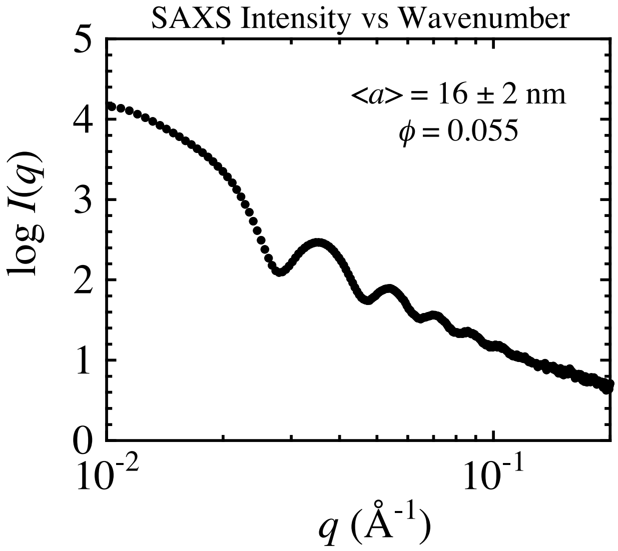
Repeat

Concentrated Nanoemulsion of Uniform Droplets

T.G. Mason, et al., *Condensed Matter Phys.* **9** 193 (2006).

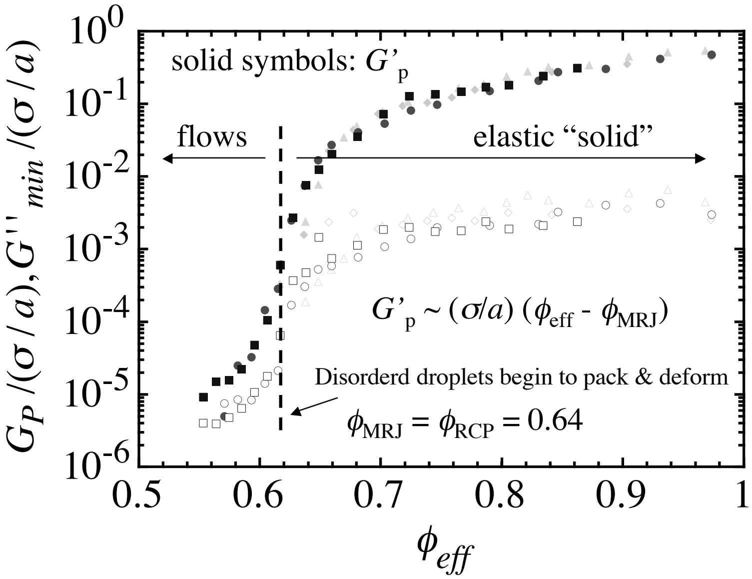
X-Ray Scattering From Fractionated Nanoemulsions

Many oscillations in form factor -> High monodispersity



Linear Rheology of Microscale Emulsions

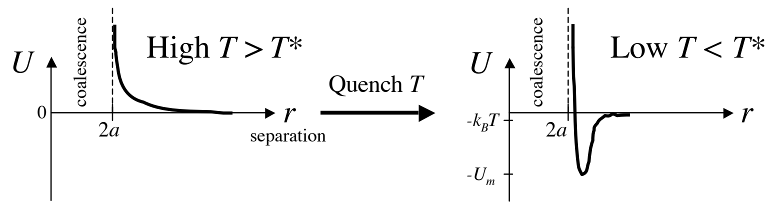
T.G. Mason & D.A. Weitz *PRL* **75** 2051 (1995)



Attractive Emulsions: Aggregation of Slippery Droplets

What happens if you suddenly turn on a very strong slippery attraction that doesn’t cause droplet coalescence?

Raising [NaCl] higher than we have shown: causes droplets to aggregate

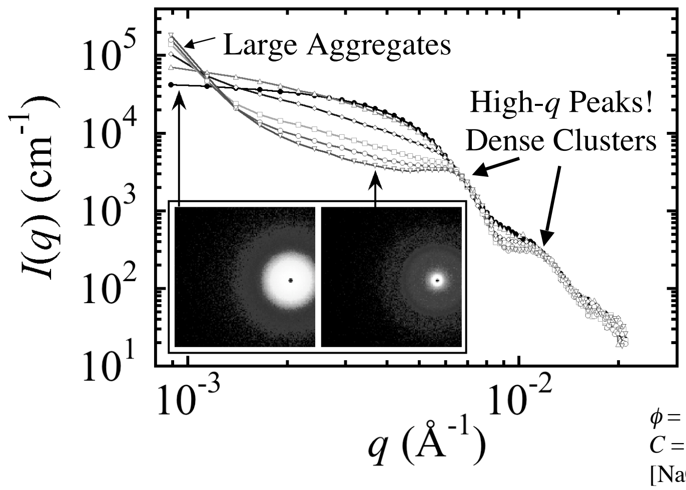


Screened Coulomb Repulsion
Droplets Are Uniformly Dispersed

Strong Short-Range Attraction
Droplets do Not Coalesce
Thin Film of Water Persists

Time Resolved-SANS: Evolution of Structure of Attractive Nanoemulsions

Quench: $T = 50$ °C to $T = 45$ °C $T^* = 47$ °C



time after quench

t (s)

0

239

482

724

968

2100

$\phi = 0.12$
$C = 10$ mM
[NaCl] ≈ 0.67 M
$\langle a \rangle = 51$ nm (16% PD)

J.N. Wilking, S.M. Graves, C.B. Chang, K. Meleson, M.Y. Lin, T.G. Mason, *PRL* **96** 015501 (2006)

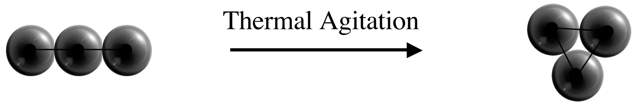
Shear-Rigid Bonds vs Slippery Bonds

Shear Rigid Bonds: Bond Shear Elasticity $G' \gg k_BT$

Examples: gold colloids, silica colloids, soot…

“Classic DLCA”

Slippery Bonds: Bond Shear Elasticity $G' = 0 \ll k_BT$



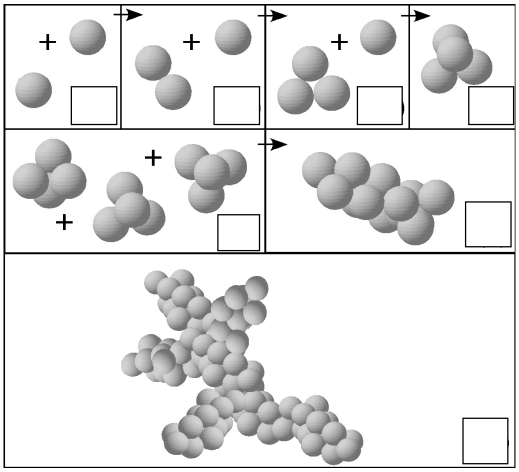
Examples: nanoemulsions…

“Slippery DLCA”

Rearrangement after touching

Space-Filling Gels from Slippery DLCA

Attractive Jamming of Non-Coalescing Droplet Clusters



Monomers
-> Tetrahedra

Tetrahedra
-> Larger Cluster

Larger Clusters
-> Tenuous Aggregate
-> Space Filling Gel

J.N. Wilking, S.M. Graves, C.B. Chang, K. Meleson,
M.Y. Lin, T.G. Mason, *PRL* **96** 015501 (2006)

Emulsions: Summary

Long-lived Non-equilibrium Dispersions of Droplets

Fluid mechanics is critical in their formation and destruction
droplet rupturing and coalescence

Macroscopic properties are governed by thermodynamics

Rapidly quenched concentrated emulsions have disordered structures
First clear example of a “soft glassy material”

Osmotic pressure: “Equation of State” for emulsions

Rheology… more to come in a future lecture