

# **Colloidal Systems**

(Lecture 1)



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## <u>Outline:</u>

- Examples-Applications
- Main phenomena Forces Time scales
- Phase behavior: Thermodynamic phases, Metastable states (glasses and gels)
- Microscopic Dynamics (Scattering-Microscopy)
- Mechanical properties (Rheology) -> 2<sup>nd</sup> lect.
- Rheology of suspensions and glasses -> 2<sup>nd</sup> lect.
- Rheology of attractive colloids and gels -> 3<sup>nd</sup> lect.



## **Colloidal systems**



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Example: Particles with size few nm to few µm suspended in a liquid



#### Paints, Inks, lubricants, shampoo, foodstuff, blood, ...











Biological systems and applications: Protein crystallisation, macromolecular crowding in biological cells, drug release, etc



Figure 1 Crowded interior. This three-dimensional reconstruction shows part of the cytoplasm of an intact molile Dicrystellium discoideaue. cell. The orange linear complexes are actin filaments: ribosomes and other macromolecular complexes are in grey; membranes are in blue. Reprinted with permission from ref. 3.

#### biomaterials





**Colloidal Systems** 

Which systems are colloidal?



<u>General Definition:</u> Two immiscible component mixtures

Dispersed phase (gas, liquid, solid) in suspending medium (gas, liquid, solid)

<u>Size of dispersed particles: ~10 nm to ~5 µm</u>

Brownian motion keeps

them from sinking

 $\Rightarrow k_B T > m_B g R$  $\Rightarrow radius \ R \le 1 - 5 \ \mu m$ 



#### Examples:

Solid particles suspended in a liquid (paints, blood, milk ...) Liquid particles in a liquid medium (emulsions,...) Solid particles in gas (aerosols,...) Gas in liquid (foams,...).... etc.... all combinations .. but one.







## States: Liquids, Crystals, Glasses, Gels



Concentrated: Colloidal liquid or solid







## The middle world: Mesoscopic phenomena





#### **Brownian Motion : "The restless heart of matter and life"** M.D. Haw





atomic world





0 nanometer



100 picometers 0.2 -

Nucleus of the carbon atom.



10<sup>-14</sup> meters

10 femtometers 0.2 -





"Colloids as large atoms" (P. N. Pusey)

- Collection of interacting particles can tune interactions
- Can reach thermodynamic equilibrium colloidal gases, liquids and solids
- Can be trapped in metastable, non-ergodic states- glasses, gels

•Can study phenomena of generic interest: crystallization, glass formation and melting, ageing etc. Colloidal solids are weak and "slow"







Sterically-stabilised polymethylmethacrylate (PMMA) colloidal "hard spheres"



- Suspend in mixture of organic liquids nearly transparent samples even at high concentrations
- No attraction, nearly hard-sphere repulsion
- Radius  $R \approx 0.2 \text{ to } 1 \mu m$

#### "Plastic Brownian billiard balls"

Other "hard" spheres: Silica particles (small steric layer, PS particles (charged stabilized + salt to screen interactions)



Uniform silica microspheres (1 μm diam, × 10,000).





**Phase behavior** 

**Dynamics of Crystallization** 

Non-ergodic states (glasses, gels)

Flow of glassy and crystalline molecular systems

**Metallic glasses** 











The role of defects. (Top) In crystals, flow is determined by dislocations,





## "Colloid engineering"

- New materials, e.g. photonic or phononic crystals from colloidal precursors
- high precision filters, controlled porosity substrates from colloidal precursors.

Scanning electron microscope pictures of dried sample





(b)

Binary Colloidal Crystal  $AB_2 \quad R_B / R_A = 0.58$ 



Shear induced hard-Sphere FCC Crystal

R.M. Amos et al., PRE **61**, 2929 (2000)





- Nanocomposites (colloids in polymeric matrices) photovoltaics and other applications
- Magnetic particles in 2D,

**Magneto-rheological fluids** 





Primary ZnO nanoparticles

Chu et al. Adv. Materials, 2007

• **Optofluidics (flow induced structures for optical applications)** 





NATURE|Vol 442|27 July 2006|doi:10.1038/nature05060

Developing optofluidic technology through the fusion of microfluidics and optics

Demetri Psaltis<sup>1</sup>, Stephen R. Quake<sup>2</sup> & Changhuei Yang<sup>1</sup>



#### **Applications: Rich Flow properties** (colloids, grains, emulsions, etc)





Wagner and Brady

Non-Newtonian fluids: thixotropy - rheopexy

Applications of shear thickening

Liquid Armor Wagner, (Delaware)



http://www.youtube.com/watch?v=f2XQ97XHjVw







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for colloids time to diffuse their own radius :  $t \approx 1ms...1s$ 

Large particles => Slow diffusion

J. Perrin (Nobel prize, 1926) Used Brownian motion to calculate Avogadro number,  $N_A (=R/k_B) =>$ proved existence of molecules

Mean square displacement of a particle of radius R  $<\Delta r(t)^2 >= 6Dt$  Einstein-Smoluchowksi (1905), for t>t<sub>B</sub> =  $\frac{m}{6\pi\eta R}$  $D_0 = \frac{k_B T}{6\pi\eta R}$  Stokes-Einstein-Sutherland diffusion coefficient



Figure 1.2. Jean Perrin's data, showing the location of colloidal particles released from the center













Sedimentation velocity

$$V_0 = \frac{2}{9} g R^2 \frac{\Delta \rho}{\eta}$$
, isolated sphere

For dilute concentrations  $< \sim 10\% =>$ Hydrodynamic interactions (two body) => slower sedimentation  $\langle V \rangle = V_0 (1 - 6.55\phi)$ , Batchelor (1972)

Large particles => Fast sedimentation

Deviations from Batchelor's prediction at higher  $\phi =$ Multi-particle HI increase velocity









## **Forces - Interactions**







c)



nearly hard spheres

**Attractive (sticky spheres)** 



In bad solvent

Van der Waals attractions

Charged colloids (DLVO potential)



#### **Repulsive colloids: From hard to soft interactions**







Hard spheres (PMMA, silica particles etc.)

**Core-shell microgels:** (example PS-PNIMAM)



Ultra soft multiarm star polymers or Star-like micelles



**Polymer grafted particles** 

**Crosslinked microgels** 

**Charged particles** 

![](_page_19_Picture_0.jpeg)

![](_page_19_Picture_1.jpeg)

![](_page_19_Picture_2.jpeg)

#### van der Waals forces (usually attactive)

#### London or dispersion forces between two induced (fluctuating) dipoles

**Interaction between 2 individual dipoles** 

$$U_{vdW}(r) = -\frac{C}{r^6}$$
, with  $C = \frac{3}{4} \left(\frac{1}{4\pi\varepsilon_0}\right)^2 \alpha^2 \hbar \omega$ 

#### Integrating for colloidal particles

Interaction per unit surface, between 2 semi-infinite solid planes at distance H:

$$U_{vdW}(H) = -\frac{A}{12\pi H^2}$$
, with  $A = \pi^2 \rho^2 C$ , Hamaker constant (usually A>0)

Interaction between 2 spheres of radius R, at surface-surface distance H:

$$U_{vdW}(H) = -\frac{AR}{12H} \left[ 1 + \frac{3H}{4R} + 2\frac{H}{R} \ln(\frac{H}{R}) \right], \text{ for } H \ll R$$

or 
$$U_{vdW}(r) = -\frac{16Aa^{\circ}}{9r^{6}}, \text{ for } r >> R$$

![](_page_20_Figure_0.jpeg)

## **Interactions** Charged particles

![](_page_20_Picture_2.jpeg)

**Screened Coulomb repulsions in the presence of counter-ions** 

**Diffuse double-layer model of Gouy & Chapman** 

![](_page_20_Figure_5.jpeg)

Interaction potential between 2 planes

(semi-infinite solid planes):

$$U_{Cb}(H) = \frac{64n_0k_BT}{\kappa} \tanh^2\left(\frac{ze\psi_0}{4k_BT}\right) \exp(-\kappa H)$$

with  $n_0$  the ion number density, z their valence,  $\psi_0$  the surface potential,

and

 $\kappa^{-1} = (\frac{\varepsilon \varepsilon_0 k_B T}{2e^2 n_0 z^2})^{1/2}$  the Debye Screening length

**Interaction potential between 2 spheres:**  $U_{Cb}(H) = 2\pi \varepsilon R \psi_0^2 \exp(-\kappa H)$  for  $\kappa R < 5$ 

![](_page_21_Picture_0.jpeg)

v

(VR)e

## **Interactions** Charged particles

![](_page_21_Picture_2.jpeg)

![](_page_21_Figure_3.jpeg)

Charged colloids – Total interaction potential DLVO (Derjaguin, Landau, Verwey and Overbeek)

 $\mathbf{U}_{\text{DLVO}}\left(\mathbf{r}\right) = \mathbf{U}_{\text{vdw}}(\mathbf{r}) + \mathbf{U}_{\text{cb}}(\mathbf{r})$ 

**Characteristics:** 

Primary/secondary minimum=>irreversible/reversible aggregation

**Repulsive barrier => particle stabilization** 

**Increasing ion concentration** <= e.g. addition of salt

Weakening of repulsive interactions => decrease of Debye screening length => lowering of the repulsive barrier

half separation Barrier zero @ Critical coagulation concentration (ccc) :

$$c.c.c.\left[mol/lt\right] = \frac{\left(4\pi\varepsilon_{0}\varepsilon\right)^{3}0.107\left(k_{B}T\right)^{5}}{N_{A}A^{2}\left(ze\right)^{6}} \tanh^{4}\left(\frac{ze\psi_{0}}{4k_{B}T}\right)$$

![](_page_22_Picture_0.jpeg)

## Multiarm Star Polymers as model soft colloids

![](_page_22_Picture_2.jpeg)

![](_page_22_Figure_3.jpeg)

$$\frac{f(r)}{kT} = \begin{cases} (5/18)f^{3/2}(1+\sqrt{f}/2)^{-1}(\sigma/r)\exp\left[-\sqrt{f}(r-\sigma)/2\sigma\right] \\ (5/18)f^{3/2}(1+\sqrt{f}/2)^{-1}(\sigma/r)\exp\left[-\sqrt{f}(r-\sigma)/2\sigma\right] \end{cases}$$

good solvent: Likos, Macromolecules, 2008

Likos, Loewen, Richter, PRL, 1998

![](_page_23_Figure_0.jpeg)

## **Depletion Interactions: Attractions in colloid-polymer mixtures**

![](_page_23_Picture_2.jpeg)

Induce attraction between the particles by adding non-adsorbing polymer chains "Depletion": - Unbalanced osmotic pressure pushes particles together

- Overlap of depletion zones gives polymer more free volume (higher entropy)

![](_page_23_Figure_5.jpeg)

Particle radius RPolymer radius of gyration  $r_g$ Overlap zone L~  $r_g$ 

![](_page_23_Figure_7.jpeg)

Asakura-Oosawa (AO) potential

![](_page_24_Figure_0.jpeg)

![](_page_24_Picture_2.jpeg)

- Gravitational:  $F_{gravity} \approx R^3 \Delta \rho g$
- **Brownian:**  $F_{Brownian} \approx k_B T / R$
- Electrostatic:  $F_{coulomb} \approx \varepsilon \varepsilon_0 \zeta^2$
- Viscous (Stokes drag):  $F_{viscous} \approx \eta R \upsilon$
- Van der Waals:  $F_{VdW} \approx A_{eff} / R^2$
- Inertia:  $F_{inertia} \approx \rho R^2 \upsilon^2$

*Example*:  $R = 1 \ \mu\text{m}$ ,  $\eta = 1 \ \text{cp} = 10^{-3}$  Pa s  $\rho = 10^3 \ \text{kg/m}^3$ ,  $\Delta \rho / \rho = 0.01$   $T = 20^{\circ} \text{C}$ ,  $\upsilon = 1 \ \mu\text{m/s}$   $A_{\text{eff}} = 10^{-20} \text{Joule}$ ,  $\zeta = 50 \ \text{mV}$  $g = 10 \ \text{m/s}^2$ ,  $\varepsilon = 100$ ,  $\varepsilon_0 = 8.85 \ 10^{-12} \text{C/Vm}$ 

ratios of forces:

 $\frac{F_{coulomb}}{F_{Brownian}} \approx 100$   $\frac{F_{vdW}}{F_{Brownian}} \approx 1$   $\frac{F_{viscous}}{F_{Brownian}} \approx 1$   $\frac{F_{gravity}}{F_{viscous}} \approx 0.1$   $\frac{F_{inertia}}{F_{viscous}} \approx 10^{-6}, (=\text{Re})$ 

![](_page_25_Picture_0.jpeg)

![](_page_25_Picture_1.jpeg)

![](_page_25_Picture_2.jpeg)

## **Outline:**

- Definitions-Examples-Applications
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![](_page_26_Figure_0.jpeg)

![](_page_26_Figure_1.jpeg)

Alder & Wainwright(1957) Wood & Jacobson (1957) Hoover & Ree (1968) <u>Entropy Driven Crystallisation</u> Crystal has *higher* entropy than metastable fluid at same concentration

**Experiments: Pusey, van Megen, Nature, 1986** 

#### Hard-sphere colloidal crystals and glasses

![](_page_27_Picture_1.jpeg)

Fluid *φ* < 0.494 Fluid + Crystal Crystal  $\phi > 0.545$ 

Glass  $\phi > 0.58$ 

![](_page_28_Picture_0.jpeg)

![](_page_28_Picture_2.jpeg)

![](_page_28_Picture_3.jpeg)

**Decreasing temperature (thermotropic)** 

or increasing concentration (Lyotropic)

**Entropy driven ordering: Isotropic-nematic transition in Hard rods** 

![](_page_29_Picture_0.jpeg)

### Phase behavior – Soft Multiarm Star colloids

![](_page_29_Figure_2.jpeg)

Watzlawek, PRL(1999), Foffi, PRL (2003)

Theoretical phase diagram: Liquid, crystal phases, glasses

![](_page_30_Figure_0.jpeg)

### Phase behavior of repulsive colloids

![](_page_30_Picture_2.jpeg)

![](_page_30_Figure_3.jpeg)

Cloitre, 2000

![](_page_31_Picture_0.jpeg)

![](_page_31_Figure_2.jpeg)

Russel et al. (1989)

#### Long range repulsions =>

Liquid-crystal transition, coexistence and glassy states @ much lower  $\varphi$  than HSs

![](_page_32_Picture_0.jpeg)

## Phase diagram: Depletion attractions

![](_page_32_Picture_2.jpeg)

Schematic experimental phase diagram (colloid-polymer mixtures)

For size ratio,  $\xi > 0.25 =>$  triple coexistence

![](_page_32_Figure_5.jpeg)

![](_page_32_Picture_6.jpeg)

![](_page_33_Picture_0.jpeg)

![](_page_33_Picture_2.jpeg)

#### **Increasing volume fraction**

Free clusters

Interconnected networks

compact clusters -> attractive glass

![](_page_33_Picture_7.jpeg)

Low volume fractions ( $\phi$ <0.2) percolating network Intermediate volume fractions (0.2-0.5):

Interplay with phase separation: •Arrested phase separation •or equilibrium gels High volume fractions (φ>0.58) => attractive glasses

![](_page_34_Picture_0.jpeg)

![](_page_34_Picture_2.jpeg)

Aggregate structures in 3D and 2D

![](_page_34_Figure_4.jpeg)

![](_page_34_Picture_5.jpeg)

n=number of particles within distance R from center of floc  $d_f$  = fractal dimension

High attraction strength=> Diffusion Limited aggregation (DLCA): d<sub>f</sub> = 1.7-1.8

Low attraction strength=> Reaction Limited aggregation

(RLCA): d<sub>f</sub> = 2.0-2.1

Weitz and Huang, PRL 1984

![](_page_35_Picture_0.jpeg)

![](_page_35_Picture_2.jpeg)

![](_page_35_Figure_3.jpeg)

![](_page_36_Figure_0.jpeg)

![](_page_36_Picture_2.jpeg)

![](_page_36_Figure_3.jpeg)

# Macroscopically percolated homogenous structure

Figures from Liu et al., PRL 96 (2006)

# Heterogeneous structure that is arrested due to attraction

![](_page_37_Picture_0.jpeg)

![](_page_37_Picture_1.jpeg)

![](_page_37_Picture_2.jpeg)

Ageing => coarsening of colloidal gel with waiting time

![](_page_37_Figure_4.jpeg)

**FIG. 5.** Evolution of particle microstructure over time for (a) top row, 5 kT gel and (b) bottom row, 6 kT gel. The gel in each snapshot is older than the previous image as indicated.

#### **Brownian Dynamics simulations,** $\phi$ =0.2,

Zia et al, J. Rheol. 2014

![](_page_38_Picture_0.jpeg)

![](_page_38_Picture_1.jpeg)

![](_page_38_Picture_2.jpeg)

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![](_page_39_Picture_0.jpeg)

## **Microscopic Structure and Dynamics**

![](_page_39_Picture_2.jpeg)

#### Light scattering (reciprocal space)

Probe fluctuations at scattering wave vector q.  $q = 4\pi n/\lambda \sin(\theta/2)$ 

<u>Measure structure and particle dynamics</u> of polymers, colloids, emulsions

![](_page_39_Figure_6.jpeg)

![](_page_39_Figure_7.jpeg)

![](_page_39_Picture_8.jpeg)

#### **Optical Microscopy (direct space) Measure structure and particle dynamics**

State of the art: Fast fluorescence confocal microscopy follow dynamics also under shear

![](_page_39_Picture_11.jpeg)

![](_page_39_Picture_12.jpeg)

![](_page_39_Picture_13.jpeg)

![](_page_40_Figure_0.jpeg)

![](_page_40_Picture_2.jpeg)

![](_page_40_Figure_3.jpeg)

![](_page_41_Figure_0.jpeg)

![](_page_41_Picture_2.jpeg)

![](_page_41_Figure_3.jpeg)

(in-cage)

(Van Megen, PRE, 1999)

![](_page_42_Figure_0.jpeg)

![](_page_42_Picture_2.jpeg)

#### **Volume fraction dependence**

![](_page_42_Figure_4.jpeg)

In-cage diffusion decrease towards zero @ rcp ( $\varphi=0.64$ )

![](_page_43_Picture_0.jpeg)

![](_page_43_Figure_2.jpeg)

Long-time (out of cage) dynamics slow down with waiting time near the glass transition

![](_page_43_Figure_4.jpeg)

![](_page_44_Picture_0.jpeg)

![](_page_44_Picture_2.jpeg)

![](_page_44_Figure_3.jpeg)

# **Soft Colloids - Dynamics approaching the glass**

![](_page_45_Picture_1.jpeg)

![](_page_45_Picture_2.jpeg)

t (s)

![](_page_46_Figure_0.jpeg)

![](_page_46_Picture_1.jpeg)

![](_page_46_Picture_2.jpeg)

## END of Lecture 1

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- Mechanical properties (Rheology) => lecture 2

![](_page_47_Figure_0.jpeg)

## **Colloidal systems**

![](_page_47_Picture_2.jpeg)

#### Study questions (Lecture 1)

- 1. Define colloidal systems. Why are colloidal particles defined by size limitations from nanometers to micrometers?
- 2. What is the phase diagram of hard spheres, and how is it changed for soft polymer coated particles?
- 3. What is the role of a polymer in colloidal dispersion stability for a) Grafted or adsorbed polymer b) Dissolved, non-adsorbed polymer?
- 4. Describe the interaction potential and the phase diagram of charged stabilized colloids.
- 5. Calculate the van der Waals interaction per unit area between two semi-infinite planes.
- 6. Determine the critical coagulation concentration (c.c.c) (in mol/L) for two planar surfaces (*use approximately the vdW and screened Coulomb interaction between semi-infinite planes*)
- 7. Calculate the time needed for a colloidal particle with radius, R=0.5  $\mu$ m to diffuse it own diameter in water at 25 C in the dilute limit and at a volume fraction of  $\phi$ =0.1
- 8. Calculate the sedimentation velocity of a particle with R=2 $\mu$ m and  $\rho$ =1.2g/cm<sup>3</sup> in the dilute limit and at  $\phi$ =0.05 and 0.3.
- 9. A colloidal glass of hard spheres with R=100 nm, at  $\varphi$ =0.6 has G'= 80 Pa at  $\omega$ =10 rad/s and T=20 °C. Calculate the G' for a glass at the same  $\varphi$  in the case of HS with R=500 nm at T=40 °C. At which frequency  $\omega$  we should make the comparison?
- 10. Calculate the ratio of main forces in a colloidal suspension with:

 $R = 1 \,\mu\text{m}, \quad \eta = 1 \text{cp} = 10^{-3} \text{ Pa s}, \\ \rho = 10^{3} \text{ kg/m}^{3}, \\ \Delta \rho / \rho = 0.01, \\ T = 20^{\circ}\text{C}, \\ \upsilon = 1 \,\mu\text{m/s}, \\ A_{\text{eff}} = 10^{-20} \text{Joule}, \\ \zeta = 50 \text{ mV}$   $g = 10 \text{ m/s}^{2}, \\ \varepsilon = 100, \\ \varepsilon_{0} = 8.85 \, 10^{-12} \text{C/Vm}$ 

![](_page_48_Figure_0.jpeg)

## **Colloidal systems**

![](_page_48_Picture_2.jpeg)

#### Study questions cont. (Lecture 1)

- 11. You are trying to flocculate a colloidal dispersion in a plant-size operation at 500 K using calcium oxide (CaO). In your laboratory, all you have available at the moment is sodium chloride (NaCl). At room temperature, you find that 2 mol/L NaCl is necessary to induce flocculation. Estimate the concentration of CaO necessary to flocculate the dispersion in your plant operation.
- 12. Determine the crystal-liquid coexistence regime for charged stabilized particles with a Debye screening length  $1/\kappa = 10$  nm and radius R= 150 nm. Assume the particles behave as hard spheres with an effective radius R +  $1/\kappa$ .
- 13. What is the difference between the behavior of power law fluids and Bingham bodies at low stress levels?
- 14. Can you rationalize the dependence of the Debye screening length on the thermal energy, and ion concentration?
- 15. What is a colloidal glass, a colloidal gel and an attractive glass?

![](_page_49_Figure_0.jpeg)

![](_page_49_Picture_2.jpeg)

## Further reading (Lecture 1)

![](_page_49_Picture_4.jpeg)

- W.B. Russel, D.A. Saville, W.R.Schowalter, Colloidal Dispersions, Cambridge University Press, 1989
- R. J. Hunter, Foundations of Colloid Science, Oxford, University Press, New York, 2001
- D. F. Evans, H. Wennerström, The Colloidal Domain, Where Physics, Chemistry, Biology and Technology meet, John Willey and Sons, New York, 1999.
- M.D. Haw "Middle World: The Restless Heart of Matter and Life", 2006

## Reviews:

- P.N. Pusey, in Les Houches Session 51, ed. D. Lesvesque, J. P. Hansen and J. Zinn-Justin, North-Holland, Amsterdam, (1991).
- W. C. K. Poon, J. Phys.: Condens. Matter, (2002), 14, R859–R880.
- C. N. Likos, Physics Reports 348, (2001) 267-439