Colloidal Systems
(Lecture 1)

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Colloidal systems

Outline:

- **Examples-Applications**
- **Main phenomena - Forces - Time scales**
- **Phase behavior: Thermodynamic phases, Metastable states (glasses and gels)**
- **Microscopic Dynamics (Scattering-Microscopy)**

- Mechanical properties (Rheology) -> 2nd lect.
- Rheology of suspensions and glasses -> 2nd lect.
- Rheology of attractive colloids and gels -> 3rd lect.
Colloidal systems

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Colloids – Examples

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
Colloidal Systems
Which systems are colloidal?

**General Definition:** Two immiscible component mixtures

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

Size of dispersed particles: ~10 nm to ~5 μm

Brownian motion keeps them from sinking

\[ k_B T > m_B g R \]

\[ \Rightarrow \text{radius } R \leq 1 - 5 \mu m \]

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

Dilute: Colloidal "gas"

Concentrated: Colloidal liquid or solid
The middle world: Mesoscopic phenomena

Macro-world

10 nm – 10 μm

Middle-world

Brownian Motion: “The restless heart of matter and life”
M.D. Haw

atomic world
“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 poly-methylmethacrylate (PMMA) colloidal “hard spheres”

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

“Plastic Brownian billiard balls”

Other “hard” spheres: Silica particles (small steric layer, PS particles (charged stabilized + salt to screen interactions)
Colloids as “Large Atoms”

Phase behavior

Dynamics of Crystallization

Non-ergodic states (glasses, gels)

Flow of glassy and crystalline molecular systems

Metallic glasses
Applications - Why are colloids interesting?

• “Colloid engineering”

New materials, e.g. photonic or phononic crystals from colloidal precursors

high precision filters, controlled porosity substrates from colloidal precursors.

Binary Colloidal Crystal

\( AB_2 \quad R_B/R_A = 0.58 \)

R.M. Amos et al., PRE 61, 2929 (2000)
More applications of colloidal systems

- **Nanocomposites** (colloids in polymeric matrices), photovoltaics and other applications

- **Magnetic particles in 2D**, Magnoeto-rheological fluids

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

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Developing optofluidic technology through the fusion of microfluidics and optics

Demetri Psaltis, Stephen R. Quake & Changhuei Yang

Figure 1 | A generalized layer construction of an optofluidic device.
Applications: Rich Flow properties (colloids, grains, emulsions, etc)

Non-Newtonian fluids: thixotropy - rheopexy

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

Applications of shear thickening

Liquid Armor
Wagner, (Delaware)
Colloidal systems

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• Mechanical properties (Rheology)
Main phenomena – Brownian motion

Mean square displacement of a particle of radius $R$

\[ <\Delta r(t)^2> = 6Dt \]  \hspace{1cm} \text{Einstein-Smoluchowksi (1905), for } t > t_B = \frac{m}{6\pi \eta R} \]

\[ D_0 = \frac{k_B T}{6\pi \eta R} \]  \hspace{1cm} \text{Stokes-Einstein-Sutherland diffusion coefficient}

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

Large particles $\Rightarrow$ Slow diffusion

\textbf{J. Perrin (Nobel prize, 1926)}

Used Brownian motion to calculate

Avogadro number, $N_A (= R/k_B) \Rightarrow$

proved existence of molecules

Figure 1.2. Jean Perrin’s data, showing the location of colloidal particles released from the center at time zero and measured at time $t$. The right figure shows a typical trajectory of a 0.53 μm particle.

Mewis and Wagner, Colloidal suspension rheology, Cambridge, 2012
Main phenomena – Sedimentation

Sedimentation velocity

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

For dilute concentrations < ~10% =>

Hydrodynamic interactions (two body) => slower sedimentation

\[ \langle V \rangle = V_0 (1 - 6.55\phi), \quad \text{Batchelor (1972)} \]

Large particles => Fast sedimentation

Deviations from Batchelor’s prediction at higher \( \phi \) =>

Multi-particle HI increase velocity
**Time scales**

\[ \langle \Delta r(t)^2 \rangle = 6D t \]

Stokes-Einstein-Sutherland diffusion

\[ D = \frac{k_B T}{6\pi \eta R} \]

\( (Atomic: t \approx 10^{-12} - 10^{-10} \text{s}) \)

\[ t \approx 1\text{ms}...1\text{s} \]

**Mechanical response**

\[ G \propto \frac{k_B T}{R^3} \]

\[ G \approx 1 - 1000 \text{N/m}^{-2} \]

\( (Metals: G \approx 10^9 - 10^{12} \text{N/m}^{-2}) \)

**Length scale**

\( d \approx \lambda \)

(wavelength of light)

Large Enough =>

good for microscopy and light scattering
Forces - Interactions

- Nearly hard spheres
- Attractive (sticky spheres)
- In bad solvent
- Van der Waals attractions
- Charged colloids (DLVO potential)
- Sterically stabilized

Coulomb repulsions

V/k_B T
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**

**Diagram:**
- Polymer grafted particles
- Crosslinked microgels
- Charged particles
Interactions

van der Waals forces (usually attractive)

London or dispersion forces between two induced (fluctuating) dipoles

Interaction between 2 individual dipoles

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

Integrating for colloidal particles

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

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

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

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

or \[ U_{vdW}(r) = -\frac{16Aa^6}{9r^6}, \quad \text{for} \ r >> R \]
Interactions
Charged particles

Screened Coulomb repulsions in the presence of counter-ions

Diffuse double-layer model of Gouy & Chapman

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

\[ \kappa^{-1} = \left( \frac{\varepsilon \varepsilon_0k_BT}{2e^2n_0z^2} \right)^{1/2} \]

the Debye Screening length

Interaction potential between 2 spheres: \( U_{cb}(H) = 2\pi\varepsilon R\psi_0^2 \exp(-\kappa H) \) for \( \kappa R < 5 \)
Interactions
Charged particles

Charged colloids – Total interaction potential

DLVO (Derjaguin, Landau, Verwey and Overbeek)

\[ U_{DLVO}(r) = U_{vdw}(r) + U_{cb}(r) \]

**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

**Barrier zero @ Critical coagulation concentration (ccc):**

\[
c.c.c. [mol/lt] = \left( \frac{4\pi\varepsilon_0\varepsilon}{N_A A^2 (ze)^6} \right) 0.107 \left( \frac{k_B T}{4k_B T} \right)^5 \tanh^4 \left( \frac{ze\psi_0}{4k_B T} \right)
\]
Multiarm Star Polymers as model soft colloids

Parameters:
Functionality (number of arms) $f$
Molecular weight of arm $M$
Solvent quality

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

Likos, Loewen, Richter, PRL, 1998

good solvent: Likos, Macromolecules, 2008
Depletion Interactions: Attractions in colloid-polymer mixtures

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)

Can control
- range – size ratio \( r_g/R \)
- strength – polymer concentration

\[
V_{ov} = \frac{4\pi}{3} (R + L)^3 \left(1 - \frac{3r}{4(R + L)} + \frac{r^3}{16(R + L)^3}\right)
\]

\[
F_{dep} = -P_{osm} V_{ov} \quad \text{with} \quad P_{osm} = \frac{N}{V} k_B T
\]

Asakura-Oosawa (AO) potential

Particle radius \( R \)
Polymer radius of gyration \( r_g \)
Overlap zone \( L \sim r_g \)
Colloidal systems: Scale of main forces:

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

**Example:**

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

**ratios of forces:**

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

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Phase behavior – Brownian Hard Spheres

One-dimensional phase diagram

\[ \phi = \frac{N}{V} \left( \frac{4}{3} \pi R^3 \right) \]

PMMA spheres Sterically stabilized with PHSA

Entropy Driven Crystallisation
Crystal has higher entropy than metastable fluid at same concentration


Computer simulations:
Alder & Wainwright (1957)
Wood & Jacobson (1957)
Hoover & Ree (1968)
Hard-sphere colloidal crystals and glasses

- After mixing
  - Fluid $\phi < 0.494$
  - Fluid + Crystal
  - Crystal $\phi > 0.545$
  - Glass $\phi > 0.58$

- One day
- Four days
Isotropic liquid

Nematic-liquid crystals

Smectic-Liquid Crystals

Crystal

Decreasing temperature (thermotropic)

or increasing concentration (Lyotropic)

Entropy driven ordering: Isotropic-nematic transition in Hard rods
Phase behavior – Soft Multiarm Star colloids


**Theoretical phase diagram:** Liquid, crystal phases, glasses
Phase behavior of repulsive colloids

Suspension \( \Phi_F \)  
Crystal \( \Phi_G \approx 0.58 \)  
Glass \( \Phi_C \approx 0.64 \)  
Jammed

Thermally activated dynamics

Contact forces

Cloitre, 2000
Long range repulsions =>

Liquid-crystal transition, coexistence and glassy states @ much lower $\phi$ than HSs
Phase diagram: Depletion attractions

Schematic experimental phase diagram (colloid-polymer mixtures)

For size ratio, $\xi > 0.25 \Rightarrow$ triple coexistence
Metastable states: Colloidal gels

Increasing volume fraction

- Free clusters
- Interconnected networks
- Compact clusters -> attractive glass

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 ($\phi>0.58$) -> attractive glasses
Low volume fractions: Fractal microstructure (flocs)

Aggregate structures in 3D and 2D

\[ n \propto R^{d_f} \]

- \( n \) = number of particles within distance \( R \) from center of floc
- \( d_f = \) fractal dimension

High attraction strength =>
Diffusion Limited aggregation
(DLCA): \( d_f = 1.7-1.8 \)

Low attraction strength =>
Reaction Limited aggregation
(RLCA): \( d_f = 2.0-2.1 \)

Weitz and Huang, PRL 1984
Phase transition – gelation kinetics

Metastable: Nucleation & growth

Unstable: Spinodal decomposition

Gels through Arrested phase separation

Zaccarelli, JPCM, 2007

Verhaegh et al. Physica A

Schematic for long(er) range attractions
Evolution of structure during gelation

adhesive hard-spheres (AHS) (one component)

φ = 0.09

Gel formation (cooling)

Colloid-polymer mixture (two components)

φ = 0.15

Gel formation (higher cφ)

Snapshots courtesy of Castañeda-Priego

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

Macroscopically percolated homogenous structure

Heterogeneous structure that is arrested due to attraction
Metastable states: Colloidal gels

Ageing => coarsening of colloidal gel with waiting time

Brownian Dynamics simulations, $\phi=0.2$,

Zia et al, J. Rheol. 2014
Colloidal systems

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Microscopic Structure and Dynamics

Light scattering (reciprocal space)

Probe fluctuations at scattering wave vector \( q \).

\[ q = \frac{4\pi n}{\lambda} \sin(\theta/2) \]

Measure structure and particle dynamics of polymers, colloids, emulsions

Optical Microscopy (direct space)

Measure structure and particle dynamics

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

DLS for HS’s at 0.49<φ<0.59

• As φ increases the particles are caged more and more

• At φ ~ 0.58, fluctuations partly freeze and crystallization is suppressed

van Megen & Underwood, PRE, 1994

\[
f(q,t) = \frac{1}{N} \sum_{j=1}^{N} \sum_{i=1}^{N} < \exp(iq \cdot (\bar{r}_i(0) - \bar{r}_j(t))) >
\]

\[
q = 4\pi n/\lambda \sin(\theta/2)
\]

Mode Coupling Theory (MCT) predicts a transition to a dynamically arrested non-ergodic state (repulsive glass)

Götze 1980
Mean Square displacement

\[ \left\langle \Delta r^2(t) \right\rangle / R^2 \]

\[ \sqrt{\left\langle \Delta r^2(t) \right\rangle} \approx 0.28R \]

\[ \sqrt{\left\langle \Delta r^2(t) \right\rangle} \approx 0.16R \]

\[ \phi = 0.466 \] (out of cage)

\[ \phi = 0.583 \]

Caging: particles cannot escape nearest neighbour cage

Short time dynamics (in-cage) (Van Megen, PRE, 1999)

Long time dynamics
Hard Spheres: Short-time self diffusion

Volume fraction dependence

Batchelor’s prediction
Hydrodynamic effect at low $\phi$,
(pair wise contributions)

Dilute limit: $\phi \rightarrow 0$

$D_0^s(\phi) \sim D_0(1 - 1.83\phi)$

Close packing:

$\varepsilon = 1 - \phi/\phi_{rcp} \rightarrow 0$

$D_0^s(\phi) \sim D_0/\ln(1/\varepsilon)$

In-cage diffusion decrease towards zero @ $rcp$ ($\phi=0.64$)
Long-time (out of cage) dynamics slow down with waiting time near the glass transition.
Re-entrant glass transition: repulsive to attractive glass

Pham et. al. Science, 2002

Attractive glass

Repulsive glass
Soft Colloids - Dynamics approaching the glass

Multiarm Stars

Caging with increasing c or T

\[ \varphi_g \]

\[ \phi_{\text{eff}} = 0.06 \]
\[ \phi_{\text{eff}} = 0.50 \]
\[ \phi_{\text{eff}} = 0.72 \]
\[ \phi_{\text{eff}} = 1.02 \]
\[ \phi_{\text{eff}} = 1.48 \]

\[ \text{Angle=150°, } q=0.0325 \text{ nm}^{-1} \]
Colloidal systems

END of Lecture 1

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• **Mechanical properties (Rheology)** => lecture 2
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 μm to diffuse its own diameter in water at 25 C in the dilute limit and at a volume fraction of φ=0.1
8. Calculate the sedimentation velocity of a particle with R=2μm and ρ=1.2g/cm³ in the dilute limit and at φ=0.05 and 0.3.
9. A colloidal glass of hard spheres with R=100 nm, at φ=0.6 has G’ = 80 Pa at ω=10 rad/s and T=20 °C. Calculate the G’ for a glass at the same φ in the case of HS with R=500 nm at T=40 °C. At which frequency ω we should make the comparison?
10. Calculate the ratio of main forces in a colloidal suspension with:

\[ R=1 \mu m, \quad \eta = 1 \text{cP} = 10^{-3} \text{ Pa s}, \quad \rho = 10^3 \text{ kg/m}^3, \quad \Delta \rho / \rho = 0.01, \quad T = 20^\circ \text{C}, \quad \nu = 1 \mu m/s, \quad A_{\text{eff}} = 10^{-20} \text{Joule}, \quad \zeta = 50 \text{ mV} \]

\[ g=10 \text{ m/s}^2, \quad \varepsilon=100, \quad \varepsilon_0=8.85 \times 10^{-12} \text{C/Vm} \]
Colloidal systems

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?
Colloidal systems

Further reading (Lecture 1)

**Books:**
- M.D. Haw “Middle World: The Restless Heart of Matter and Life”, 2006

**Reviews:**