COLLOIDAL SELF ASSEMBLY II:
PACMEN & MULTIVALENT
COLLOIDS

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Outline of lectures on colloids

• Lecture I: Yesterday
  ‣ Overview of colloids (sizes, materials)
  ‣ Self-assembly of colloids: (colloidal liquids, crystals, & glasses)
    • photonic crystals (& the diamond lattice)
    • need for directional interactions
  ‣ van der Waals interactions (fluctuating electric dipoles)
  ‣ Electrostatic interaction: Poisson-Boltzmann & Debye-Hückel, DLVO
  ‣ Depletion interaction
  ‣ DNA hybridization

• Lecture II: Today
  ‣ Lock & key colloids
  ‣ Colloids with valence
  ‣ Colloidal molecules: to infinity and beyond

Wednesday, July 25, 12
Lock & Key Colloids

Drawing inspiration from proteins ...

Pac-Man Particles
Lock & Key Colloids

PROTEINS

COLLOIDS
Pacman particle synthesis

Oil = “TPM” = 3-methacryloxypropyl trimethoxysilane

Make emulsion
(oil droplets in water)
Pacman particle synthesis

Oil
Water

Oligomerize oil

Oligomerize Si-O groups (pH↑) N~1-10

TPM =
Pacman particle synthesis

TPM =

Polymerize shell
- Oligomerize Si-O groups (pH↑) N~1-10
- Polymerize methacrylate groups (free radical)
  - Creates porous shell
  - Nucleates TPM nanoparticles in solution outside of TPM droplets

O/W emulsion

Shake

Water

Oil
Pacman particle synthesis

TPM =

Polymerize shell
- Oligomerize Si-O groups (pH↑) N~1-10
- Polymerize methacrylate groups (free radical)
  - Creates porous shell
  - Nucleates TPM nanoparticles in solution outside of TPM droplets
  - Osmotic imbalance sucks small oligomers out of TMP droplets (through shell)

And ...
Pacman particle synthesis

Oil

Water

Shell buckles

o/w emulsion

Shake

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Pacman particles

TEM

SEM

2 μm
Pacman particles

\[ r_c \propto d_i \]

\[ d_i = 1.5 \text{ – } 3.5 \, \mu m \]
Monodisperse pacman particles

diameter (\(\mu m\))

\begin{align*}
\text{diameter} &= 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 \\
\text{H} &= 0, 1, 2, 3, 4, 5 \\
\text{Diameter} &= 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 \\
\text{H} &= 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7
\end{align*}
Pacman lock & key

\[ S \sim n_{\text{poly}} \ln V \]

depletion zones

non adsorbing polymer

Solvent

Lock

Key
Pacman lock & key

\[ S \sim n_{\text{poly}} \ln V \]

- depletion zones
- Max overlapping volume
- can tune interaction strength
- key too small

\[ \Delta S \sim n_{\text{poly}} \frac{\Delta V}{V} \]

non adsorbing polymer
Pacman depletion movie

Watch this pac-man

Particle (key) binds to PacMan (lock)
Size selectivity

small spheres bind with big pac-men

big spheres bind with big pac-men

diameter (µm)
Pacman depletion movie

Watch this pac-man

Colloidal couplings

Monomer

Dimer

Trimer
Lock-and-key binding model

\[ \mathcal{L} + \mathcal{K} \rightleftharpoons \mathcal{LK} \]  
chemical equilibrium between locks & keys

\[ \mu_L + \mu_K = \mu_{LK} \implies \frac{n_{LK} n_0}{n_L n_K} = e^{-\left[E_b + k_B T \ln\left(\frac{V_b n_0}{v_u}\right)\right]/k_B T} \]

\[ E_b = -k_B T n A \left(2r_p - r_0 - \kappa^{-1}\right) \]

Lock & key binding energy: balance between electrostatic repulsion and depletion attraction

Entropy: binding volume vs unbound volume per key

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Lock-and-key binding data

\[ \mu_L + \mu_K = \mu_{LK} \quad \Rightarrow \quad \frac{n_{LK} n_0}{n_L n_K} = e^{-\left[ E_b + k_b T \ln(V_b n_0) \right]} / k_B T \]

\[ \kappa^{-1} = 3.0 \text{ nm} \]

different key sizes

\[ d_{\text{key}} = 1.57 \mu\text{m} \]

\[ 1.86 \mu\text{m} \]

\[ 2.47 \mu\text{m} \]

fitting parameters

\[ A \approx 0.5 \mu\text{m}^2 \]

\[ \approx 1/15^{th} A_{\text{sphere}} \]

\[ V_b \approx 0.005 \mu\text{m}^3 \]
Tunable depletion attraction

\[ \Delta S \sim n_p \frac{\Delta V}{V} \]

NIPAM gel particles shrink when heated above 39°
Melting

Start at 25°C, then heat to 40°C

Particle pairs dissociate at 40°C
Towards a more perfect pacman

Heterogeneous nucleation

Monodisperse seeds (PS, PMMA, silica, etc.)

Cartoon
The real colloids

seeds

TPM on seeds

old pacmen

pacmen
Lock & key interaction

\[ \mu_L + \mu_K = \mu_{LK} \Rightarrow \frac{n_{LK} n_0}{n_L n_K} = e^{-\left[\frac{E_b+k_B T \ln(V_b n_0)}{k_B T}\right]} \]

binding energy

binding volume (entropy)
Self-replicating pacmen

cycle of colloidal life

T=40°
T=30°
T=40°
T=30°
Colloids with directional bonds

How can we make colloids with multiple direction bonds?

\[ \text{CO}_2 \quad \text{CH}_4 \quad \text{SO}_2 \]

Start by assembling colloids in a controlled way ...
How to make colloidal clusters

water + surfactant

EMULSIFY

swollen sphere

toluene droplet

toluene
monodisperse lightly cross-linked acid terminated polystyrene spheres (they swell in oil)

van der Waals keeps us together
Coulomb keeps us apart

suck out toluene
Emulsion pictures

particle-in-oil in water emulsion

swollen particle bound to droplet interface

toluene droplet
Emulsion & cluster pictures

particle-in-oil in water emulsion

clusters after removal of oil

swollen particle bound to droplet interface

toluene droplet

solid particle cluster
Cluster formation

particles are confined to droplet surface, not the interior

capillary force pulls spheres towards center

2 µm

particles move at surface
particles touch and jam
droplet deforms
Rearrangement
drying
$M_2 = \sum_{0}^{n} (r - r_{cm})^2$

John Conway*
(Princeton)

* Conway, Sloane, et al.
Discrete Comp. Geom.
14, 237 (1995)

Manoharan et al.
Science 301, 483 (2003)
Separating clusters

\[ \Delta mg = 6\pi \eta R_{hyd} v_{sed} \]

\[ \Rightarrow v_{sed} = \frac{\Delta \rho}{\eta} R_{hyd}^2 g \]

It's a race

Clusters with large hydrodynamic radius sediment faster
It's a race

Clusters with large hydrodynamic radius sediment faster

\[ \Delta mg = 6\pi \eta R_{hyd} v_{sed} \]

\[ \Rightarrow v_{sed} = \frac{\Delta \rho R_{hyd}^2}{\eta} g \]
Making patchy particles

amidinated PS spheres → cluster → swell cluster with styrene (emulsion) → amidinated patchy sphere

swell with styrene

polymerize styrene
Patchy particles

amidinated PS spheres -> cluster -> swell cluster with styrene (emulsion) -> amidinated patchy sphere

clusters

patches
Functionalizing patchy particles

- Amidinated PS spheres
- Cluster
- Swell cluster with styrene (emulsion)
- Amidinated patchy sphere

- NHS biotin
- Biotinated patchy particle
- Streptavidin-biotin with sticky DNA
- Fluorescent streptavidin
Functionalizing patchy particles

patches

fluorescent

NHS biotin

biotinated patchy particle

streptavidin-biotin with sticky DNA

fluorescent streptavidin

=
Purified patchy particles

2 patches

3 patches
Linking up: it’s specific!

scale bar = 800 nm

AB

AB₂

AB₃

AB₄

Alternating copolymer/oligomer
Colloidal molecules

small patches
AB$_4$ formation kinetics
Colloidal polymerization kinetics
Controlling patch size

decreasing patch size

Linking with complementary particles

Ethylene-like

big patches