

# COLLOIDS

- type of mixture containing dispersed particles 1-1000nm in diameter
- one substance is evenly distributed in another

## CLASSIFICATION:

Type	Dispersed substance & medium	Examples
Sol	Solid in a liquid	Ruby glass, paints
Emulsion	Liquid in a liquid	Milk (solid): Cheese, pearl
Foam	Gas trapped in liquid/solid	Whipped cream, soap suds
Aerosol	Liquid/solid dispersed in gas	Smoke, mist

Hydrocolloid: when water is the dispersion medium ex. Jello

Tyndall Effect: in solution, light passes through clearly // in colloidal solutions, light is scattered/reflected in all directions

## DNA-GRAFTED PARTICLES:

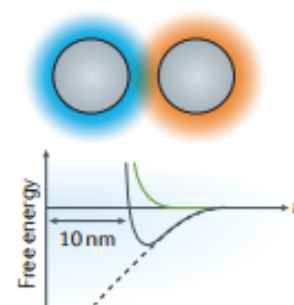
### I. NANOSCALE

Oligonucleotides attached to gold nanoparticles through a thiol functional group (most common)

Noble Metals	Oxides	Semi-Conductors
Au	$\text{Fe}_x\text{O}_y$	CdSe
Ag	$\text{SiO}_2$	CdS
Pd	$\text{TiO}_2$	PdS

Length of DNA  $\approx$  size of particle

- > wide potential minimum
- > overall hydrodynamic radius of a DNA NP dictates the packing and assembly behavior of the system
- > Melting temperature ( $T_m$ ) of NP aggregates depend on the size of the NPs
- > DNA NP superlattices are very compressible, capable of transforming between different structures ex. an isotropic transformation can result in up to 80% volume reduction



Steric stabilization: by adding a *lyophobic* material to a colloid provides a protective “shield” and prevents particles from approaching close enough to join // *synthetic polymers* can be used for this purpose

### II. MICROSCALE:

Oligonucleotides attached to polymer / silica particles

- ligand-receptor binding
- physical grafting
- covalent attachment (SPAAC)

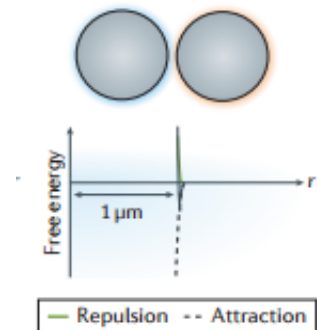
Particles	Polystyrene Polymethyl methacrylate Silica Silica-methacrylate hybrid Titania TPM
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Synthesis reactions:

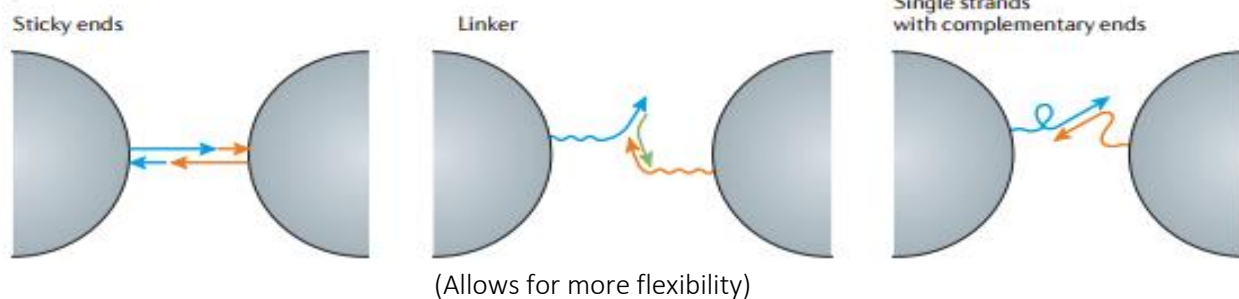
- *Avidin-biotin*: strongest non-covalent interaction
- *Water-soluble carbodiimide / covalent bonding*: strongest interaction, includes amide linkage between carboxylate group and amine group, or azide-alkyne interactions (SPAAC)
- *PEG modification, swelling/deswelling*: polymer-based colloids only, triblock polymers connect DNA to the colloid
- *Solid colloids with surface-mobile linkers*: utilizes small unilamella vesicles (SUVs) to integrate hydrophobically modified linkers // this method and swelling/deswelling results in small, 2D crystalline structures

Length of DNA  $\approx$  1% particle size

- often “hit or stick” binding, must attain *smooth surfaces* or *high density of surface-functional anchors* so equilibrium structures (minimize free energy) can be formed
  - > “hit and stick” binding results in kinetically trapped amorphous aggregates
  - > thin coating of DNA means a greater sensitivity to particle roughness and inhomogeneity
  - > *smooth surfaces* allow for homogenous interaction potential
- DNA shorter than particle diameter, and dsDNA never crystallized, but ssDNA always created crystals



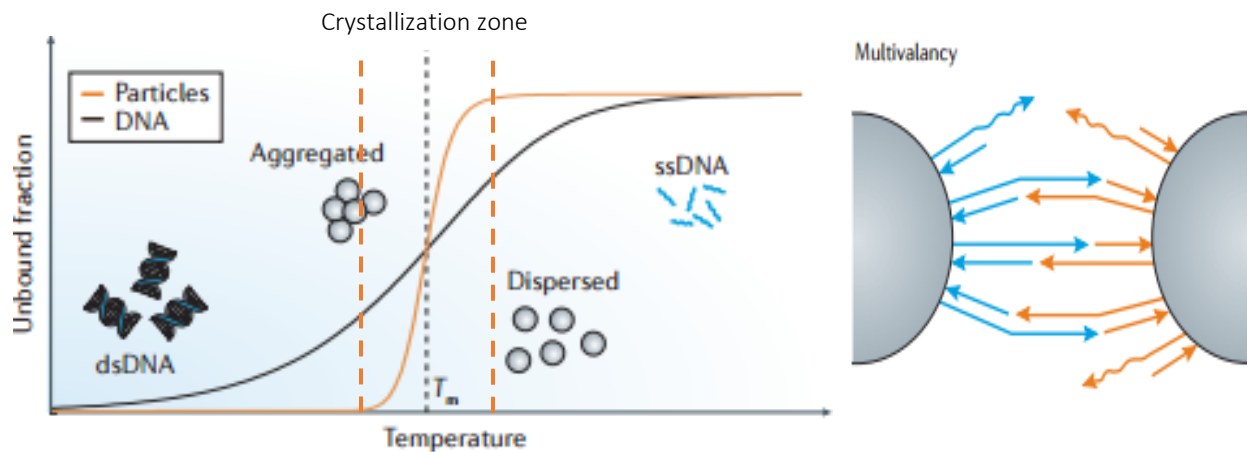
DNA bridges: *how particles attract one another*



**DNA HYBRIDIZATION:**

- stability achieved through base-pairing, but more importantly through base stacking
  - > Base stacking: a hydrophobic, electrostatic interaction
    - partly inter-strand, partly intra-strand
    - these interactions increase with increased salt concentrations
- hybridization becomes thermodynamically favorable at lower temperatures
- $T_m$  of particles grafted with complementary strands can be higher or lower than  $T_m$  of DNA strands in solution

- Nearest neighbor predictions of hybridization of free energy
  - > controls strength and  $T_m$  of each DNA bridge
  - > Observed trend (@ 37°C):
    - $G-C > C-G > G-G > G-A \approx G-T \approx C-A > C-T > A-A > A-T > T-A$
  - > DNA stability depends on percentage of G-C bonds: G-C base pairs have the greatest stability (3 H bonds)
    - increasing G-C content raises the  $T_m$  at which complementary strands dissociate
    - influenced by neighboring base pairs ex.) A-T surrounded by G-C = stability
- An INCREASE in base pairs = INCREASE in  $T_m$



- Melting transition from aggregated to dispersed state of the colloidal particles is steeper because of multivalency
  - > Multivalency: the ability to form >1 DNA bridge at a time
- curves shift to LOWER temperatures as *linker density* decreases, but shifts to HIGHER temperatures as *molecular mass* decreases
  - > larger molecular mass keeps particles further apart, and reduces the number of links
- $p_{\text{unbridged}}(r) = (1 - p)^N$ 
  - > p: probability
  - > N: total number of bridges that can form
  - > because of multivalency, N is much greater than 1 // this means that the attraction between particles varies from negligible to irreversible in just a few °C

#### Attaining Equilibrium:

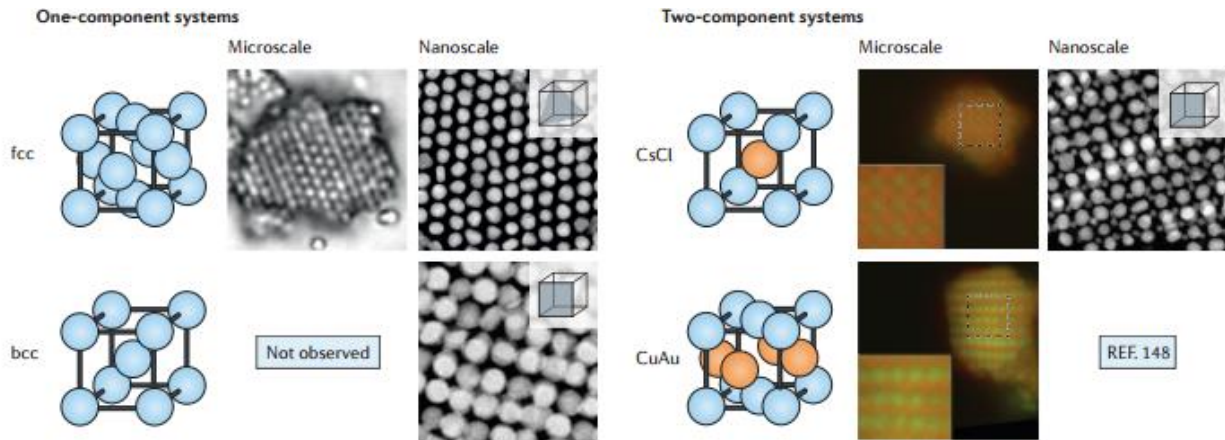
- conduct at the correct temperature, usually a few °C below the  $T_m$  // a non-equilibrium state is attained when procedures are conducted at temperatures well below  $T_m$  of the particles
- decrease van der Waals forces by increasing salt concentration
- create an assembly where particles aggregate with a high number of strands that bind together weakly
- minimize free energy:  $F = U_{\text{total effective potential}} - TS_{\text{entropy}}$ 
  - > F can be minimized by maximizing the number of attractive pair interactions between particles

Buffer solutions with different *ionic strengths*

NaCl concentration	Interparticle spacing	Reasoning
LOW	LARGE spacing	Particle-particle repulsion strong
MED (0.05 – 0.7M)	Small spacing increases, ex. $\sim 1.7\text{nm}$ change for a 24-mer linked NP	
HIGH	Particles assemble closely	Cations screen the negative charge of DNA Mask repulsion between 2 negatively charged phosphodiester backbones

- linear relationship between  $T_m$  and salt concentration, decreases van der Waals forces
- a higher NaCl concentration = faster aggregation and often higher grafting density, but also lowers the stabilization against aggregation
  - > stepwise addition of salt and DNA may prevent this

### TYPE OF CRYSTALS



- Assembly structures maximize the total number of hybridized DNA interconnects between particles
- Binding group mobility = less dramatic dissociation transition
  - > attained by anchoring DNA to a lipid-coated particle surface
  - > bridges gap between hard nano/microparticles with covalently coupled immobile binding groups & soft “floppy” objects with mobile binding groups
- Crystal structures determined by: particle size, stoichiometry, sticky-end sequences
  - > thickness depends on: initial particle concentration, particle size, particle density

### CRYSTAL CHARACTERIZATION

Crystals follow the rule for equilibrium crystals (complementary contact model), meaning that contact between spheres with complementary strands is maximized

$$F = U - TS$$

U is minimized when there are a maximum number of attractive pair interactions

#### EXCEPTIONS:

1. long-ranged interactions: U is no longer proportional to the number of nearest-neighbor pairs
2. large entropic contribution (TS) ex. “soft” vibrational modes

*Cesium-chloride (CsCl)*

- 2 interpenetrating simple cubic lattices
- if particles weren't distinguished, the assembly would have the *bcc* structure
  - › *bcc structure*: favored if next-nearest-neighbor interactions are possible

*Copper-Gold (CuAu)*

- each particle has 8 neighbors of the opposite type
- if particles weren't distinguished, the assembly would have the *fcc* structure

CuAu favored over CsCl for all but the weakest A-A, B-B attraction strengths

If A-A, B-B strengths are great enough CuAu will form because of greater interacting pairs of particles

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