What Are Colloids? [pln3]

Particles dipersed in some medium. The particles and the medium can be solid, liquid, or gaseous. Many combinations are realized.

particles	medium	type	realizations
liquid	gas	liquid aerosol	fog, spray
solid	gas	solid aerosol	smoke, dust
gas	liquid	foam	foams, froths
liquid	liquid	emulsion	milk, mayonnaise
solid	liquid	sol, dispersion	paints, ink, blood
		suspension	
gas	solid	solid foam	styrofoam, pumice
liquid	solid	solid emulsion	tarmac, ice cream
		gel	jelly, gelatin
solid	solid	solid suspension	opal, pearl
			pigmented plastic

Classification: [table adapted from Hamley 2007]

Shapes:

- liquid droplets are mostly spherical (interfacial tension balanced by pressure),
- gas bubbles are spherical at low density and tend to be polyhedral at high density (in foams),
- solid particles tend to have many different shapes,
 - compact (roughly spherical or polyhedral),
 - elongated (rod-like),
 - flat (plate-like).

Maximum size:

- solid colloids have diameter $\lesssim 1\mu m$,
- grains have diameter $\gtrsim 1\mu m$,
- motion of colloids driven by thermal fluctuations,
- motion of grains driven by mechanical agitation (e.g. shaking).

Size distribution:

- monodispersity (narrow distribution),
- *polydispersity* (broad distribution).

Sols:

- Solid particles dispersed in liquid.
- Preparation:
 - milling,
 - ultrasound,
 - condensation from vapor,
 - nucleation from solution.
- Challenge: control of polydispersity.
- Relation to solvent: lyophobic versus lyophilic.

Gels:

- In rheological terms gels are Bingham fluids. Dispersion medium is elastic; it does not flow.
- Sol-gel transition induced at critical concentration, perhaps assisted by chemically enhanced aggregation.
- Some gels consist of soft bridging networks grown via flocculation.
- Gels may absorb fluids due to osmotic effect and swell. Swelling saturates if network is strong or breaks up weak networks.
- Syneresis: gels may form in one structure and then age into a different, more compact structure, releasing liquid in the process.

Clays:

- Colloidal suspension of ($\sim \mu m$ -sized) plate-like mineral particles.
- Formation of layered structures via adhesive VDW or H-bond forces.
- Some clays have layers of water between platelets.
- Some clays have positive charges (broken covalent bonds) along edges of platelets and negative charges across flat surfaces. The charges may then produce a gel structure.

Foams:

- Gas bubbles in liquid or solid medium with shapes changing from spherical toward polyhedral as crowding increases.
- Stability of gas/liquid foams is precarious:
 - 1. Liquid drains, driven by gravity. Walls become thinner. Thin walls tend to pop. Interior bubbles merge and get bigger in the process. Exterior bubbles disappear.
 - 2. Liquid drains out of walls toward wall junctions (plateau borders), driven by surface tension. Surface tension lowers pressure at junctions relative to walls. Pressure differential induces liquid flow from walls toward junctions. Walls get thinner and junctions wider. Bubbles pop with consequences as stated.
- Gibbs-Marangoni effect: presence of surfactant molecules reduces surface tension, which slows down wall thinning.



Emulsions:

- Dispersions of immiscible liquids, homogenized e.g. by stirring, shaking, or ultrasonification.
- Homogenization increases interfacial area, which adds (positive) interfacial free energy.
- Dispersed droplets of minority liquid will merge in due time and thus lower the free energy.
- Emulsifiers (surfactant additives) reduce surface tension and thus prolong lifetime of homogenized state.

Estimate of interfacial free energy:

- N: number of droplets of minority liquid,
- R: average radius of droplets,
- γ : interfacial tension,

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$$V = \frac{4\pi}{3}R^3N$$
: estimated total volume of droplets,

•
$$A = 4\pi R^2 N = \frac{3V}{R}$$
: estimated total interfacial area,

•
$$\Delta G = \gamma \frac{3V}{R}$$
: estimated free energy.

Some relevant facts:

- Microemulsions (of diameters $\sim 1 100$ nm) tend to be thermodynamically more stable than macroemulsions (of diameters $\sim 0.1 10\mu$ m).
- The same combination of substances with minority/majority reversed yields diverse products, e.g. margerine (water/oil) or milk (oil/water).
- Distinguish *dispersed* microemulsions, where only the majority liquid is connected macroscopically, from *bicontinuous* microemulsions, where both liquids form macroscopic networks.
- Colloids tend to produce non-Newtonian viscous behavior, e.g. shear thinning or shear thickening.

Stability of colloids:

- Stability against ...
 - sedimentation (settling at the bottom),
 - creaming (rising to the top),
 - aggregation (in the bulk).
- Types of aggregation are
 - *flocculation* (mostly reversible),
 - coagulation (irreversible and irregular),
 - *coalescence* (irreversible and regular).
- Monodisperse colloids tend to crystallize (coalesce) and polydisperse colloids tend to coagulate.
- Stability often is a matter of time scale.

Interactions between colloids:

- Interaction range tends to be small compared to particle size (unlike for atoms or small molecules).
- Some interaction energies tend to be large compared to $k_{\rm B}T$ and cause irreversible aggregation.
- Some interaction energies are controllable by modifications of the medium.

Agents of change:

- Agents of aggregation are
 - gravity, buoyancy,
 - short-range attractive forces.
- Agents of dispersion are
 - Brownian motion (thermal fluctuations),
 - electrostatic repulsion (charge stabilization),
 - modified particle surfaces (steric stabilization).

Separate topics:

- association colloids (amphiphiles)
- polymer solutions
- network colloids (porous solids)