Building College-University Partnerships for Nanotechnology Workforce Development

An Introduction to Colloidal and Self-Assembled Materials

Part 1

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Outline

- Review of Solutions
- Colloids and Colloidal Chemistry
- Self-Assembly

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Solutions

- A homogeneous mixture of two or more substances
- Most common:
  - Solid dissolved in liquid
  - Mixture of two liquids
  - Gas dissolved in liquid
- There are other types as well (solid-solid, gas-solid, etc.)

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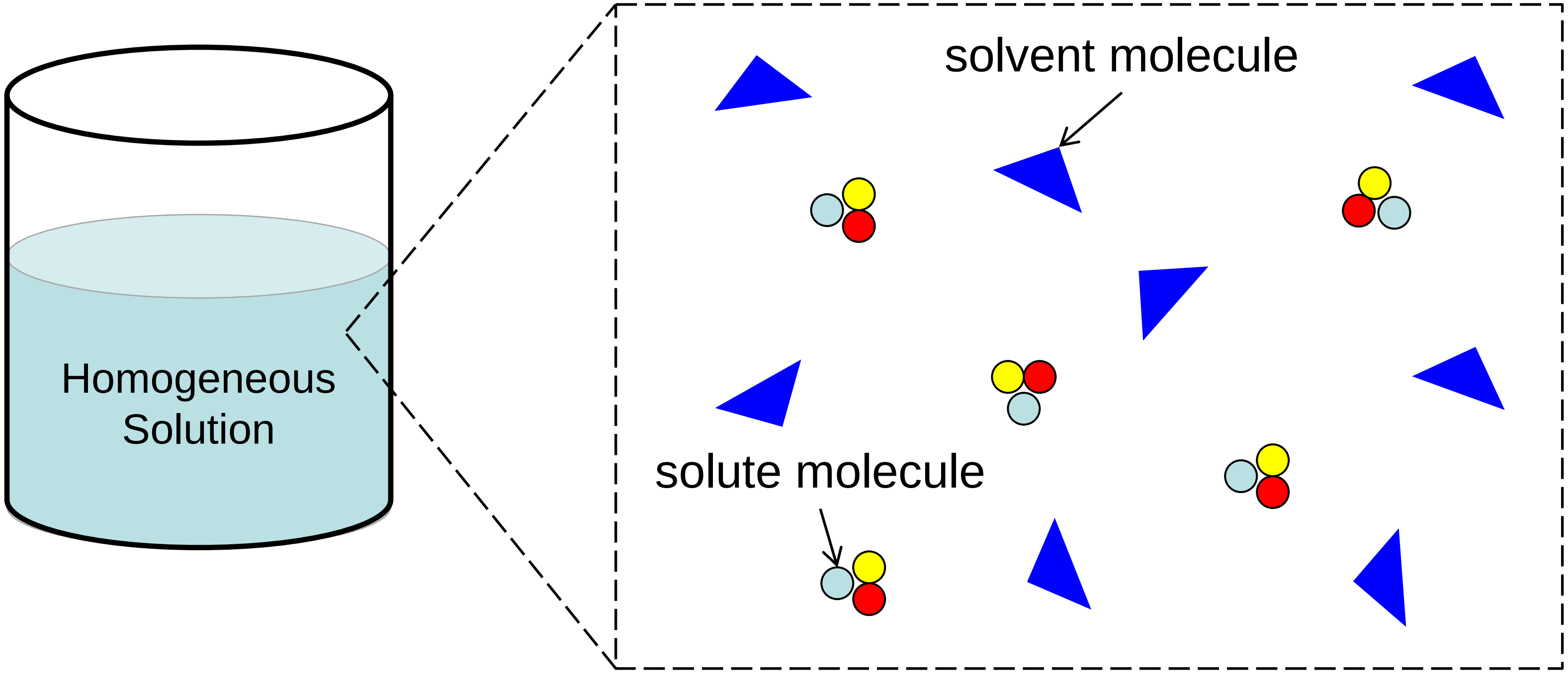
Solution Definitions



Solvent: The substance that dissolves the solute; usually the primary component
Solute: The compound (e.g., salt or sugar) that is dissolved in the solvent

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Properties of Solutions, Solutes, and Solvents

<u>Solutions</u>

- Concentration: reported in several ways
  - Mass basis: $$\text{wt\%} = \frac{\text{mass of solute}}{\text{mass of solute + mass of solvent}}$$
  - Molar basis: $$\text{Molarity (M)} = \frac{\text{Moles of Solute}}{\text{Liters of Solution}}$$
- pH: a measure of the H^+ concentration in an aqueous solution.
  - High pH = basic; low pH = acidic
  - pH is a log scale, not linear

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Properties of Solutions, Solutes, and Solvents

Solutes

- Ionic: dissociate into cations and anions when dissolved in a good solvent (usually water)
  - Examples: table salt (NaCl), NaOH
- Molecular: do not dissociate; remain as whole molecules in solution
  - Examples: sugar (sucrose), ethylene glycol

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Properties of Solutions, Solutes, and Solvents

Solvents

- Each solvent has its own set of properties
  - melting point
  - boiling point
  - polarity
  - density
  - index of refraction
  - possible impurities
  - health and safety

Solvents are chosen for a particular application based on these factors.

Goal: Find the best one for the job while minimizing risks.

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Properties of Solutions, Solutes, and Solvents

- Rule of thumb: “Like dissolves like”
  - This mainly applies to the polarity of solvents vs. solutes.
- For example, which solvent is better suited to cleaning vacuum grease off of a glass fitting? water, acetone, hexanes
- Which pairs of liquids are miscible?
  - water & ethanol, ethanol & IPA, methanol & hexanes, acetone & water, hexanes & pentane, water & pump oil

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Solvent Polarity Index

More Polar

Solvent	Polarity Index	Normal bp(°C)
Water	9	100
DMSO	7.2	189
Acetic Acid	6.2	118
Ethanol	5.2	78
Methanol	5.1	65
Chloroform	4.1	61
Isopropanol	3.9	82
Methylene chloride	3.1	40
Diethyl ether	2.8	35
MTBE	2.5	55
Toluene	2.4	110
Pentane, hexane, heptane	0	35,69,98

Less Polar

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Properties of Solutions, Solutes, and Solvents

Other properties of solvents that may be important to particular applications:

- Halogenated or non-halogenated
- Aromatic vs. non-aromatic
- Hydrogen bonding capability
- Anhydrous (dry) or not (trace water)
- Volatility
- Residues left after evaporation
- Ability to be sublimed
- Stability: ethers decompose over time to form explosive peroxides

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Outline

- Review of Solutions
- Colloids and Colloidal Chemistry
  - What is a Colloid?
  - Types of Colloids and Examples
  - Properties and Applications
- Self-Assembly

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What is a Colloid?

The term colloidal refers to a state of subdivision, implying that the molecules or particles dispersed in a medium have at least one dimension roughly between 1 nm and 1 μm.

http://goldbook.iupac.org/

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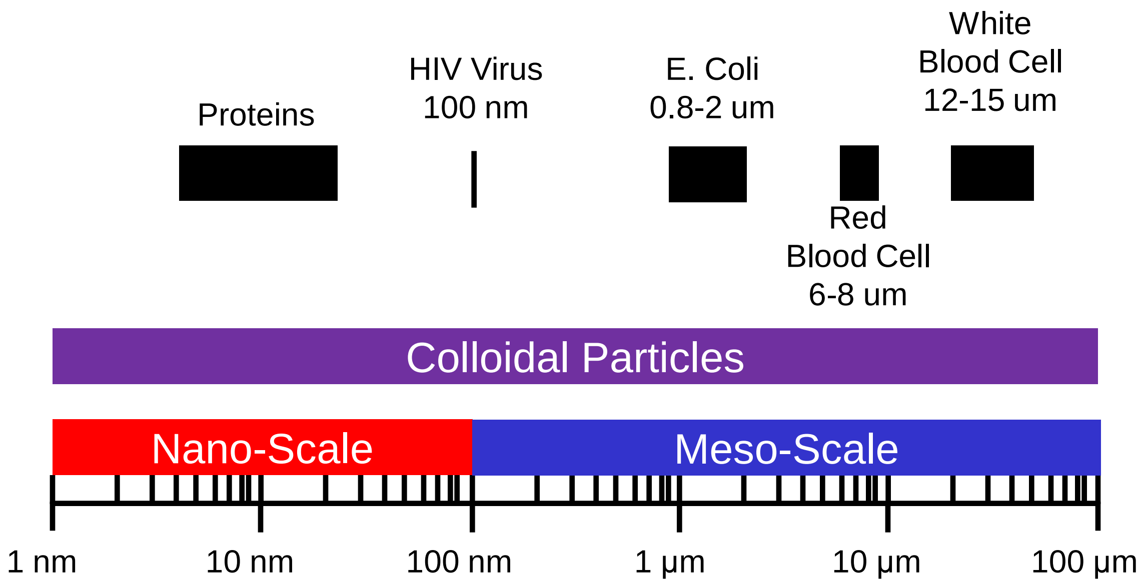
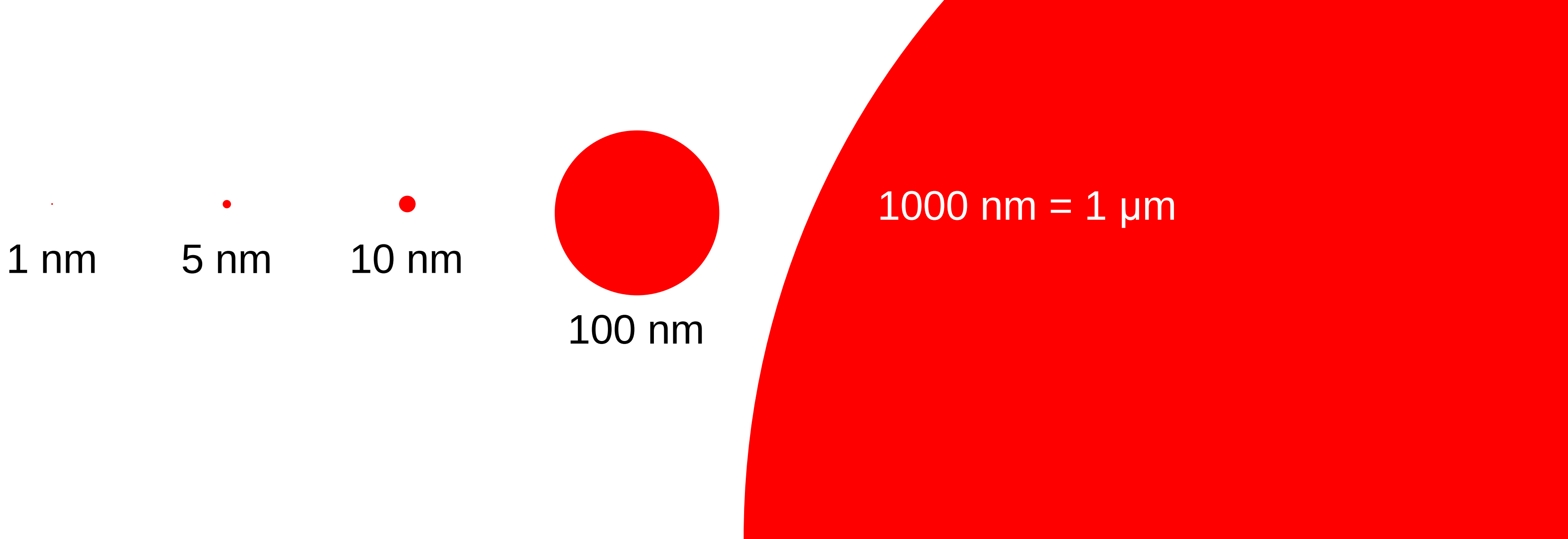
Comparative Size Scale

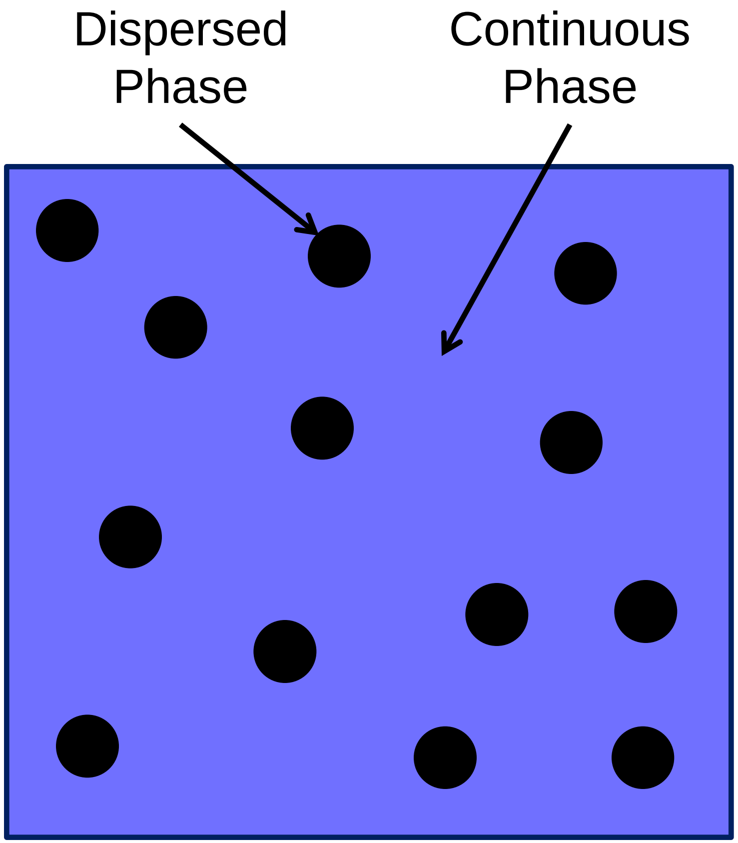


All of these could be classified as colloidal particles



General properties of Colloids

- 2-phase systems: colloids have a dispersed (internal) phase and a continuous (external) phase
- Large interfacial area between the two phases, due to small dimensions of the dispersed phase
- Colloidal particles “are all surface”
- Therefore, surface effects dominate volume effects



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General properties of Colloids

- The particles are not molecularly dissolved in the medium (solvent)
- Colloid ≠ solution
- When properly stabilized, the colloidal particles do not aggregate or settle out over time
- Colloids can be any combination of the three states of matter, but the most common colloidal mixtures consist of solid (or liquid) particles suspended in a liquid medium

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Naming of Colloids

Dispersing Medium	Dispersed Phase	Colloid Name
Solid	Solid	Solid sol
Solid	Liquid	Gel
Solid	Gas	Solid foam
Liquid	Solid	Sol
Liquid	Liquid	Emulsion
Liquid	Gas	Foam
Gas	Solid	Solid aerosol
Gas	Liquid	Aerosol

Paul Davies, School of Chemistry, University of Bristol
http://www.chm.bris.ac.uk/webprojects2002/pdavies/

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Examples of Colloids

Dispersed Phase	Continuous Phase	Type	Example
Liquid	Gas	Aerosol	Fog, Hairspray
Liquid	Liquid	Emulsion	Salad Dressing
Liquid	Solid	Solid Emulsion	Pearl, Opal
Solid	Solid	Solid Suspension	Pigmented Plastics, Stained Glass
Solid	Liquid	Sol or Paste	Ink, Toothpaste
Solid	Gas	Aerosol	Inhalers, Smoke
Gas	Liquid	Foam	Fire Extinguisher, Soap Suds
Gas	Solid	Solid Foam	Pumice, Styrofoam

http://www.rsc.org/ chemistryworld/Issues/2003/February

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Experiment: Finely Dividing a 1 cm^3 Cube

Steps

1. Start with a cube 1 cm on each side
2. Cut it into thin sheets only 10 nm thick
3. Then cut each sheet into 10 sticks
4. Finally cut each stick into nm sized cubes

Calculate

- Total number of pieces arising from original cube
- Surface area of each smaller piece
- Total surface area of all pieces
- Note: volume remains constant (1 cm^3)

http://www.du.edu/~jcalvert/phys/colloid.htm

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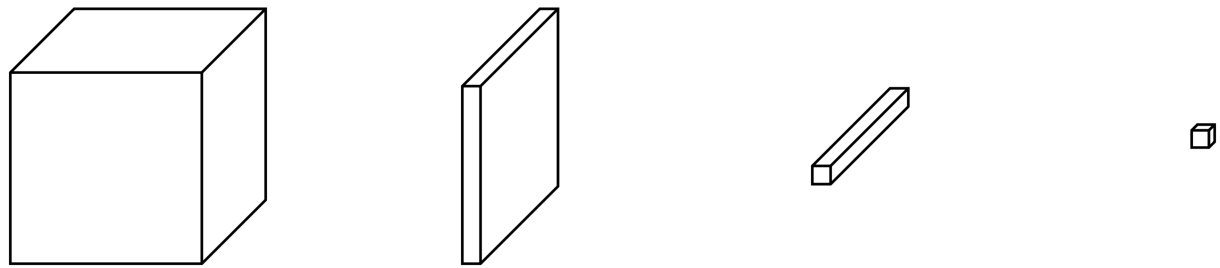
Experiment: Finely Dividing a 1 cm^3 Cube



	Starting Volume (Not Colloidal)	Laminated: Colloid Platelets	Fibrillar: Colloidal Fibers	Corpuscular: Colloidal Particles
Dimensions	1 x 1 x 1 cm	1 cm x 1 cm x 10 nm	1 cm x 10 nm x 10 nm	10 nm x 10 nm x 10 nm
Number of pieces	1	10^6	10^{12}	10^{18}
Surface area per piece (m^2)	6×10^{-4}	2×10^{-4}	4×10^{-10}	6×10^{-16}
Total surface area (m^2)	6×10^{-4}	200	400	600

SA of all pieces needed to make up original volume

Surface area to volume ratio increases as size of particle decreases. Colloids are almost all surface area!

http://www.du.edu/~jcalvert/phys/colloid.htm

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Properties of Colloids

The small size of colloidal particles lends them interesting properties, including:

- They scatter light (solutions do not)
- The particles are subjected to Brownian motion
- The surfaces of particles may become charged, depending on the medium
- Charged colloidal particles can be moved (separated) by an electric field (e.g., electrophoresis of DNA and proteins)

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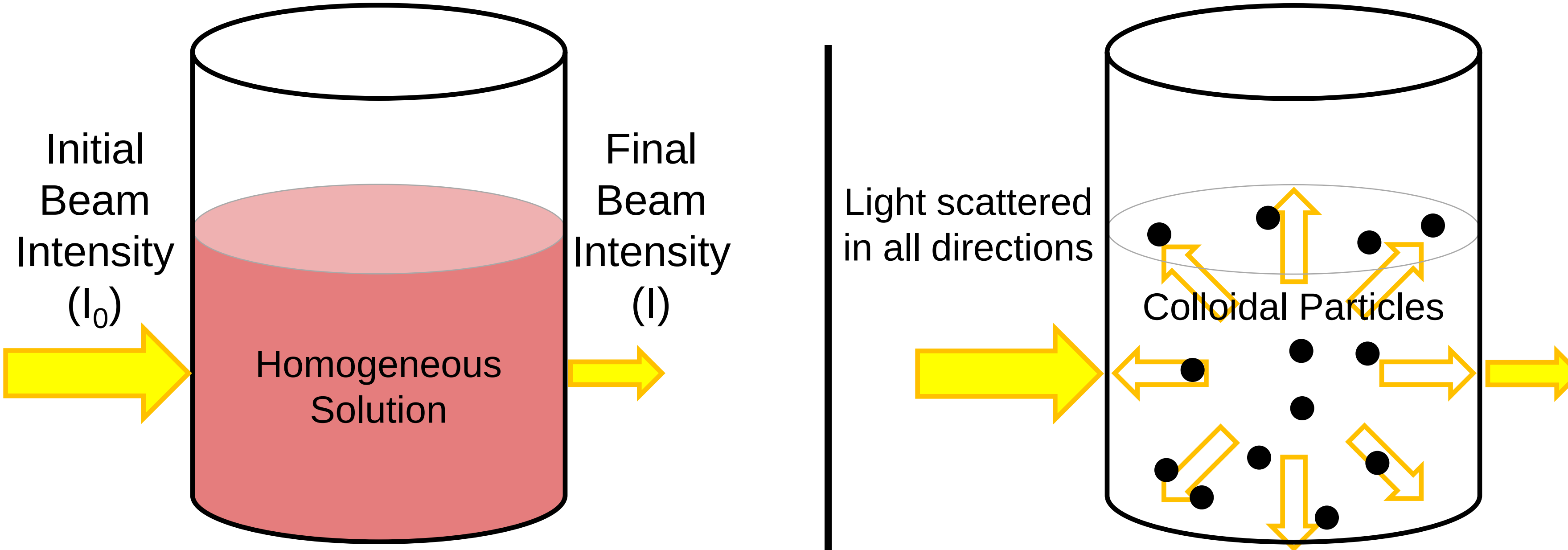
Scattering of Light by Colloidal Particles

Attenuation = Reduced intensity of light passing through a sample due to absorption and scattering. Homogeneous solutions do not scatter light. Colloidal suspensions do scatter light.



Attenuation due only to absorption of light by molecularly dissolved species (chromophores) in the solution

Attenuation due to scattering of incident light by colloidal particles. Absorption may also occur

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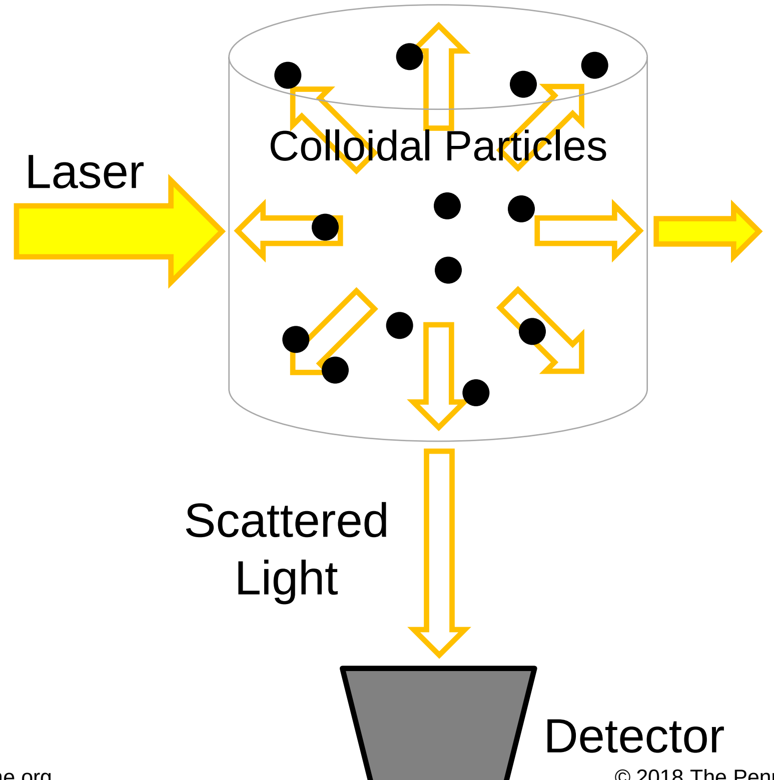
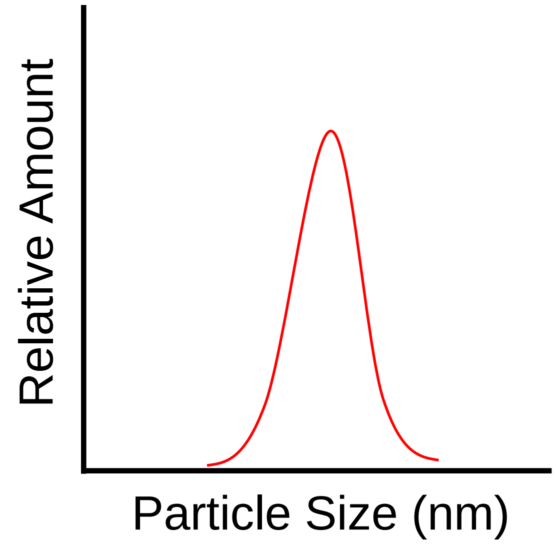
DLS: Dynamic Light Scattering

- The scattering of light by colloidal particles can be put to good use
- Measurements of scattering intensity versus time can be correlated to the Brownian motion of colloidal particles
- Mathematical analysis of the signal is used to calculate the speed of the particles as they diffuse through the sample
- The speed is related to particle size: On average, small particles move faster than larger ones





http://www.malvern.com/

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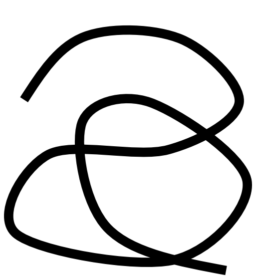
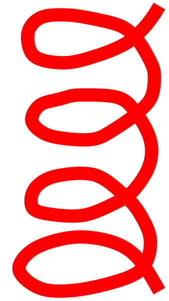
Colloidal Particles in Nanotechnology

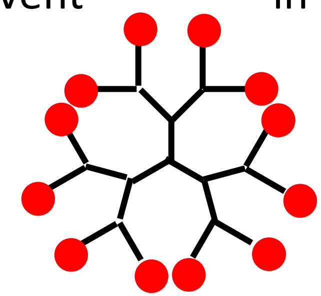


Polymer molecules dispersed in solvent

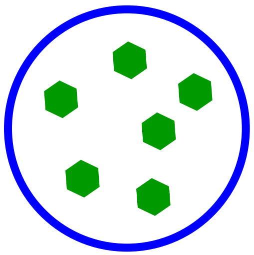


Proteins and DNA in biotechnology

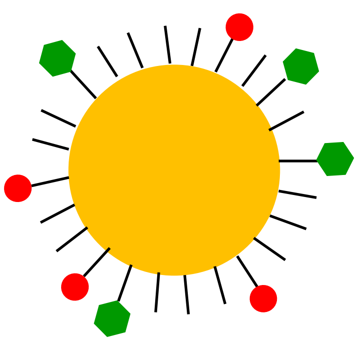
Polymer nano-spheres



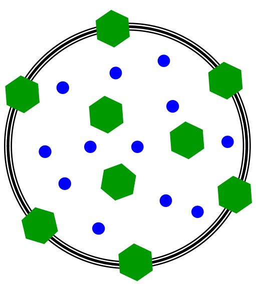
Dendrimer: star-shaped polymer



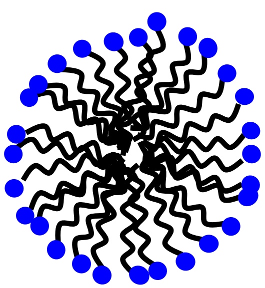
Shell NP: hollow organic, inorganic, or metal sphere



Metal NP



Liposome: hollow particle made from lipids



Emulsion

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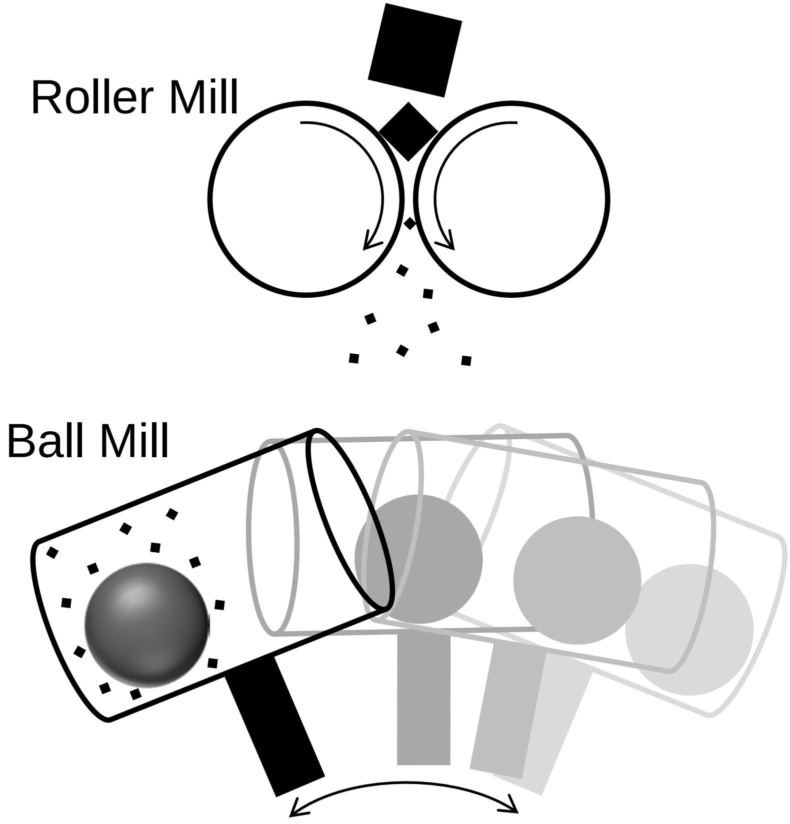
Formation of Colloidal Particles

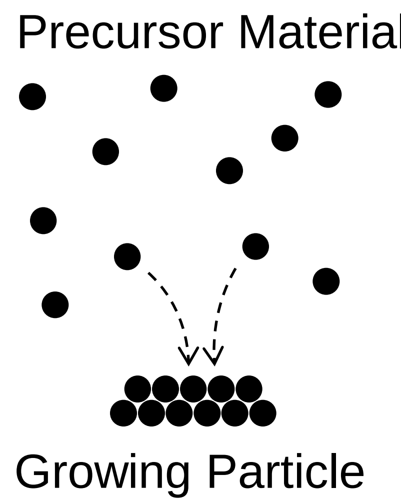
Physical Methods

- Grinding or milling



Condensation Methods

- Flame-spray
- Liquid phase synthesis



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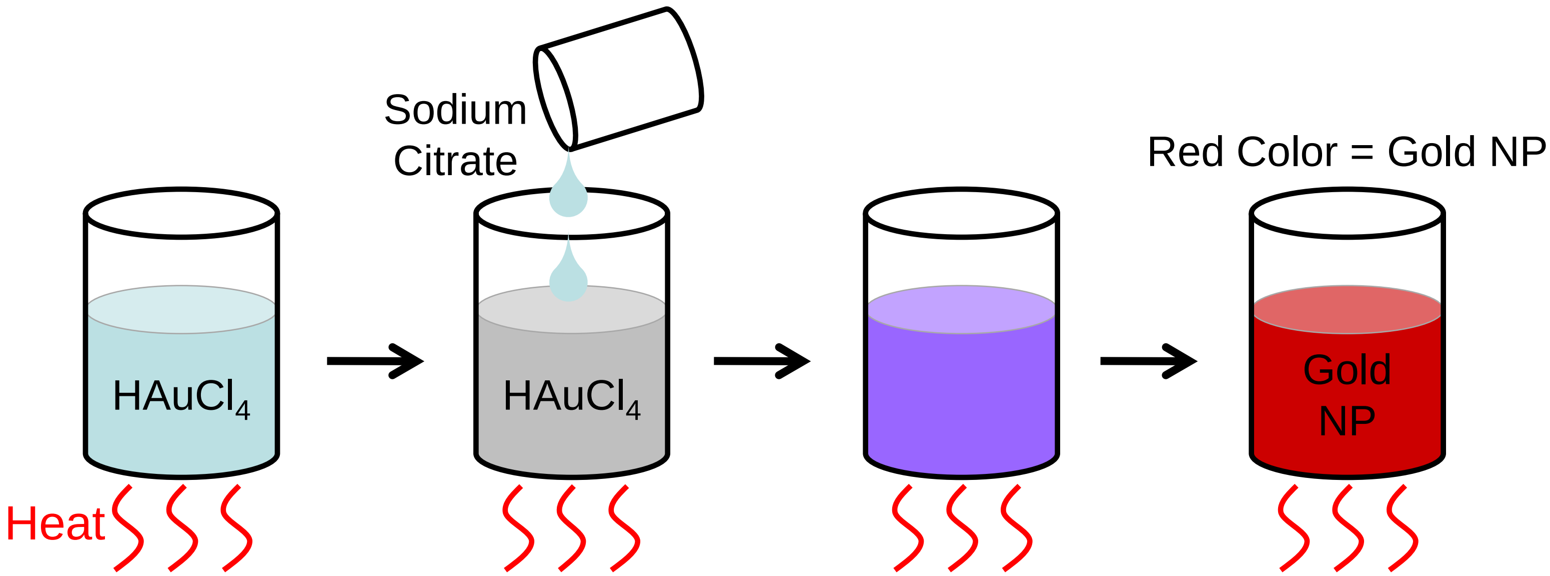
Example: Formation of Gold Nanoparticles



1. Heat a solution of chloroauric acid ($HAuCl_4$) up to reflux (boiling). $HAuCl_4$ is a water soluble gold salt
2. Add trisodium citrate, which is a reducing agent
3. Continue stirring and heating for about 10 minutes
   - During this time, the sodium citrate reduces the gold salt (Au^{3+}) to metallic gold (Au^0)
   - The neutral gold atoms aggregate into seed crystals
   - The seed crystals continue to grow and eventually form gold nanoparticles

http://mrsec.wisc.edu/Edetc/nanolab/gold/index.html
J. Chem. Ed. 2004, 81, 544A.

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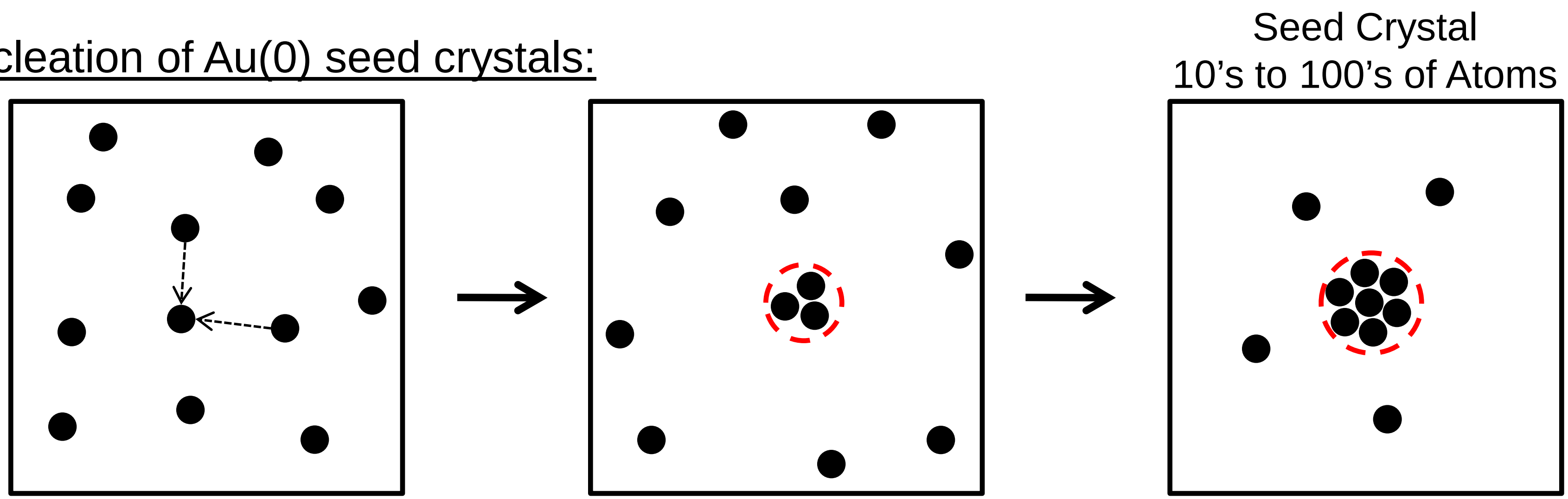
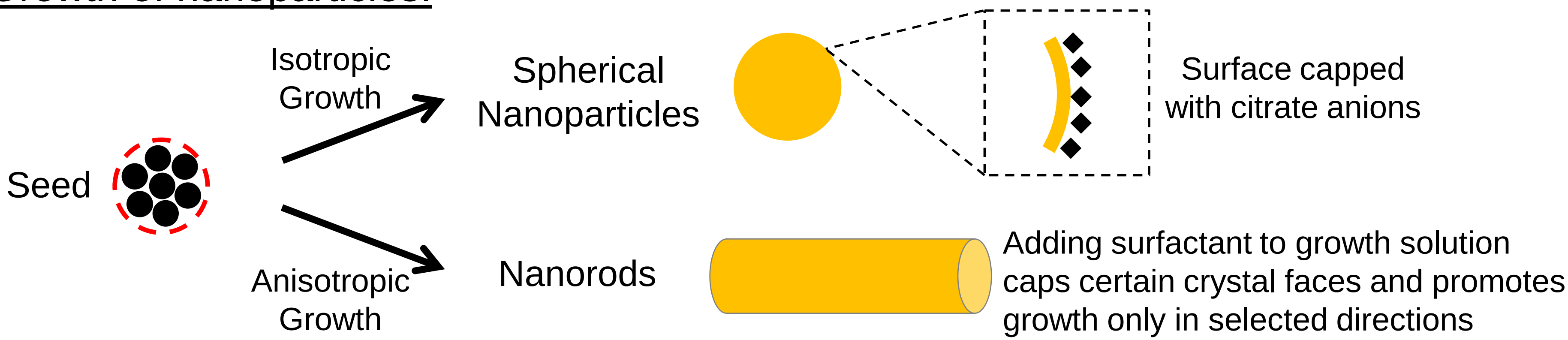
Example: Formation of Gold Nanoparticles

Reduction of gold ions: Au(III) + 3e$^-$ → Au(0)

Nucleation of Au(0) seed crystals:



Growth of nanoparticles:



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Stabilization of Colloids

- Remember: An important aspect of colloidal engineering is the suspension of the particle in a medium – often water
- Colloidal particles can be hydrophobic or hydrophilic.
- Hydrophilic groups generally contain oxygen and nitrogen. They are water loving
- Hydrophobic colloids can be prepared in water only if they are stabilized in some way. The lack of affinity for water will cause them to settle or float
- More general terms are lyophilic (likes the external phase) and lyophobic (dislikes the external phase). These terms are used when the medium is not water

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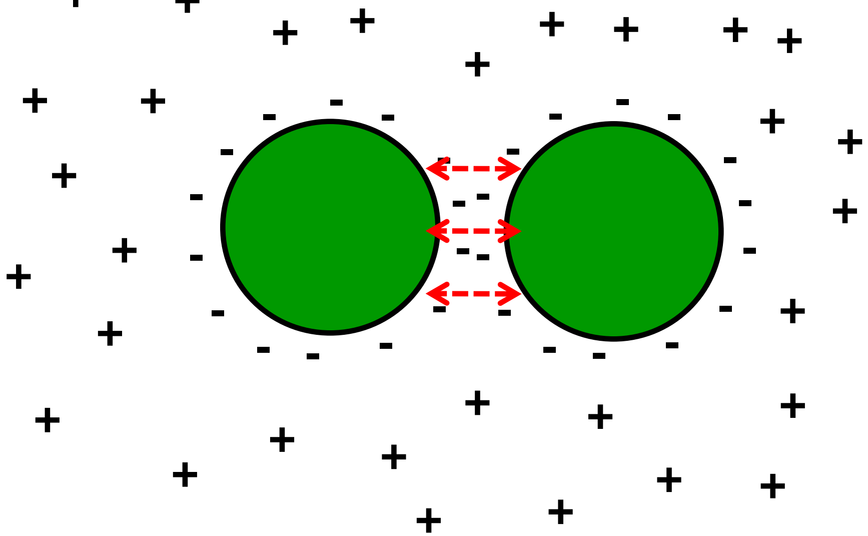
Stabilization of Colloids

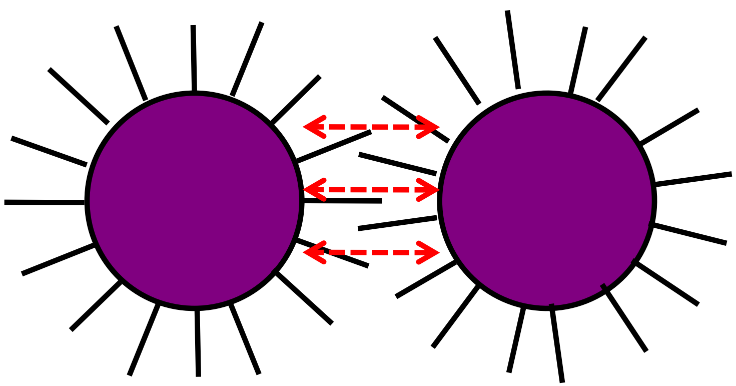
<u>How do the particles remain suspended in solution?</u>

- For such small particles, the forces of Brownian motion exceed the force of gravity, which otherwise would cause the particles to settle out
- Particles suspended in water often acquire a negative surface charge. Particles with charged surfaces repel each other at short distances
- Steric repulsion can also be used to keep particles from aggregating. This is useful for suspending neutral particles in non-polar continuous phases

Electrostatic Repulsion



Steric Repulsion



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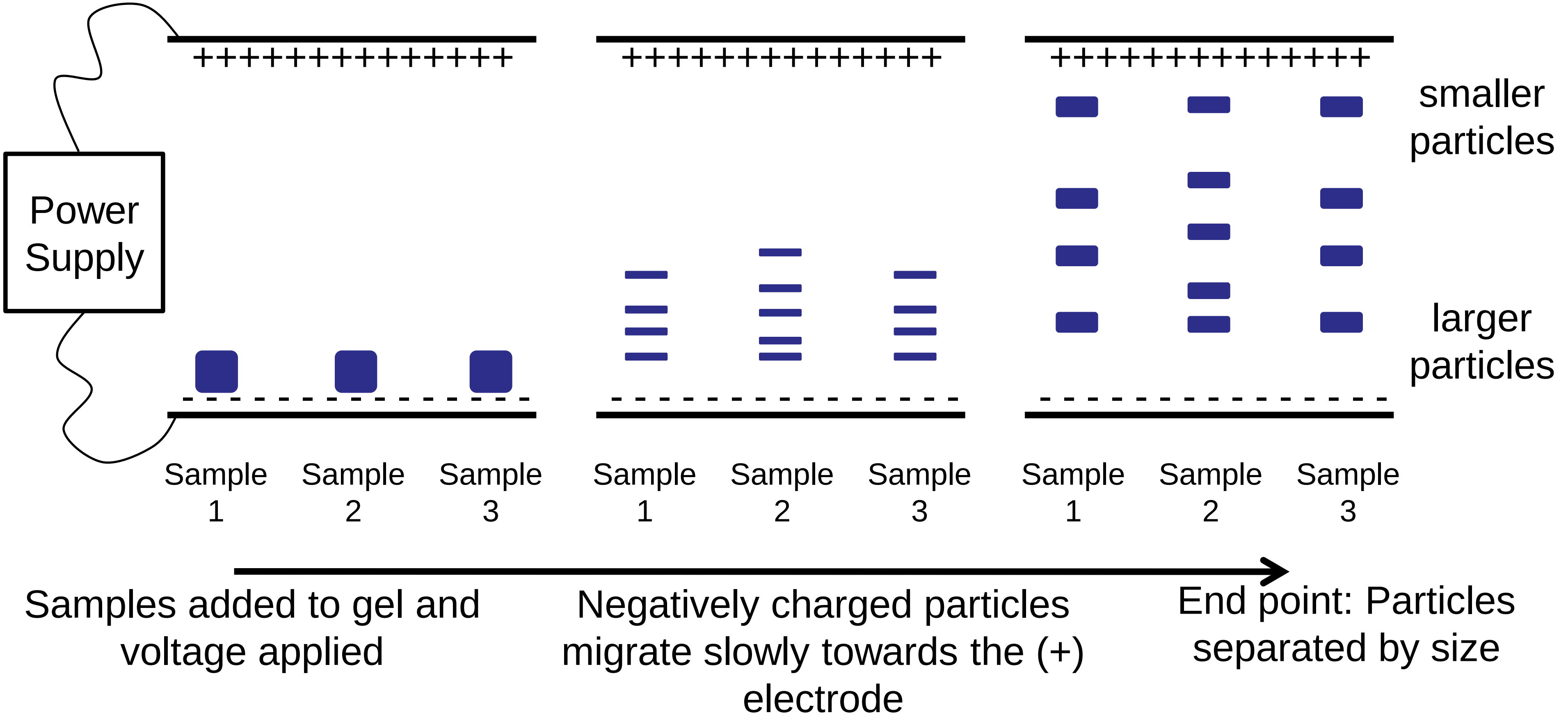
Separating Colloids: Electrophoresis

Colloidal particles commonly take on a negative surface charge when dispersed in water. In the presence of an electric field, the particles move through the surrounding medium. Smaller particles move faster than larger particles. Over time, the colloidal particles become separated according to size

<u>Applications</u>: DNA fingerprinting and protein isolation/purification



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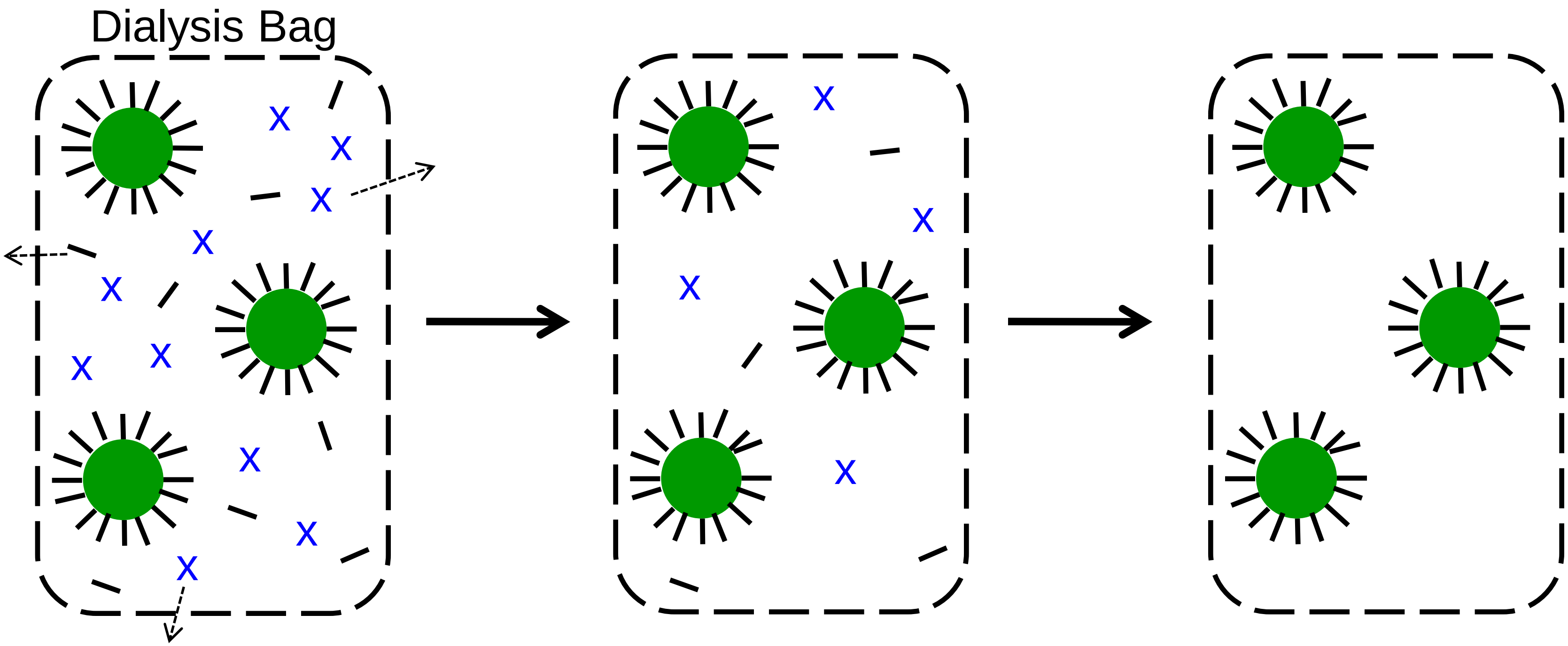
Purifying Colloids: Dialysis

Application: Removing impurities from a colloidal suspension. Impurities could be unreacted starting materials, by-products from particle synthesis, salts, excess capping agents, etc



Semi-permeable membrane allows small molecules to pass. Colloidal particles are too large to pass through the membrane pores. Continuous rinsing with fresh solvent eventually removes all unwanted small molecule impurities

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