Building College-University
Partnerships for Nanotechnology
Workforce Development

An Introduction to Colloidal and Self-Assembled Materials

Part 2

Outline

- Review of Solutions
- Colloids and Colloid Chemistry
- Self-Assembly
  - What is it?
  - Forces and interactions
  - Examples from nature
  - Nanotechnology examples

What is Self-Assembly?

- Ever-evolving definitions
- Sometimes called self-organization
- One possible definition: a reversible process that involves pre-existing, distinct components of an initially disordered structure
- Therefore, self-assembly ≠ formation

"Self-Assembly at All Scales," G.M. Whitesides and B. Grzybowski, *Science* **2002**, *295 (5564)*, 2418.

More on Self-Assembly

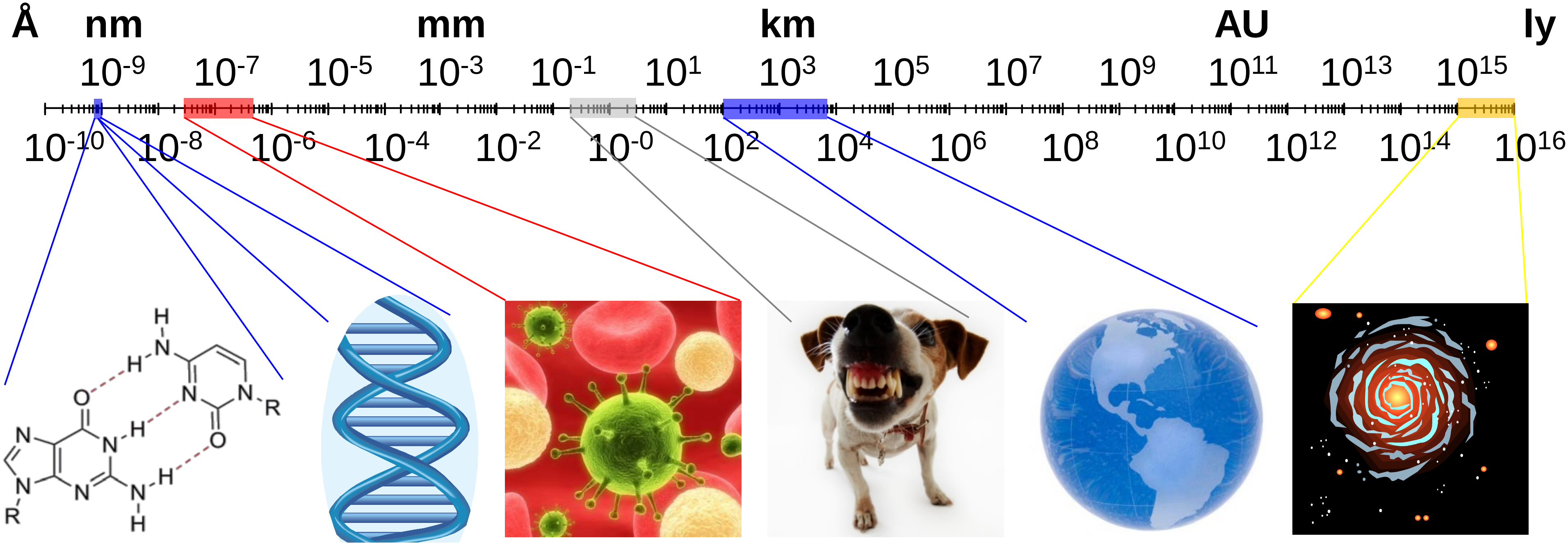
- Has origins in organic chemistry: structures are determined bond-by-bond, but the structures are molecules (less than about 0.5 nm in size)
- However, it is impossible to direct the formation (bond-by-bond) of larger nano- and micro-scale structures
- Lithography is very useful for building larger structures (~100 nm to microns), but is inherently a 2-D process. 3-D structures have to be built layer-by-layer
- Self-assembly fills the processing gap by utilizing specific (usually weak) interactions between molecules to build 2-D and 3-D structures in the 10’s to 100’s nm size range

“Self-Assembly at All Scales,” G.M. Whitesides and B. Grzybowski, *Science* **2002**, *295 (5564)*, 2418.

More on Self-Assembly

- It is not a “brute-force” technique
- You don’t get it by purchasing a tool from a manufacturer
- In fact, it usually requires no tools at all!

Many things (living and non-living) spontaneously organize over many length scales: Å to light year.



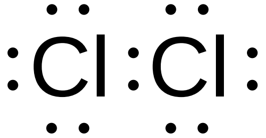
Forces at Work in self assembly

Type or Scale of Self-Assembly		
Molecular	**Nano & Meso Scale**	**Macro-scale**
van der Waals	Brownian Motion	Gravitation
Electrostatics	Capillary Forces	Electromagnetic Fields
Hydrogen Bonds	Entropic Interactions	Magnetic Interactions
Coordination Bonds		

Self-assembly usually occurs in a fluid-like state. The materials (molecules or particles) have to be able to move around. They sample many different orientations and interactions with respect to each other. One orientation (interaction) tends to be more favorable than others. Given enough time, the structural elements optimize their local environments to produce a self-organized structure over a large volume

Bonding and Forces Revisited

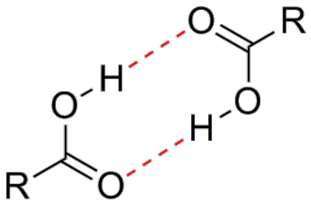
- Covalent Bonds



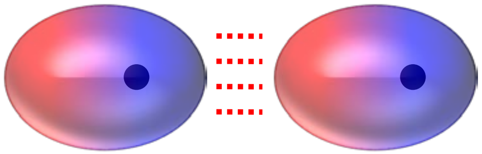
- Ionic (electrostatic)

$$F = \frac{Z_{-}Z_{+}e^{2}}{r^{2}}$$

- Hydrogen Bonding

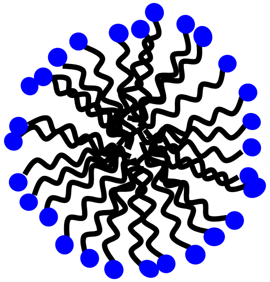


- van der Waals Forces



$$F \propto \frac{1}{r^{6}}$$

- Hydrophobic Interactions



Competition Between Forces

Often, self assembly occurs due to a competition between two types of forces or interactions. Each type of force acts over a characteristic length scale. The table below illustrates the types of self-assembly arising from the interplay of long range repulsions and short range attractions

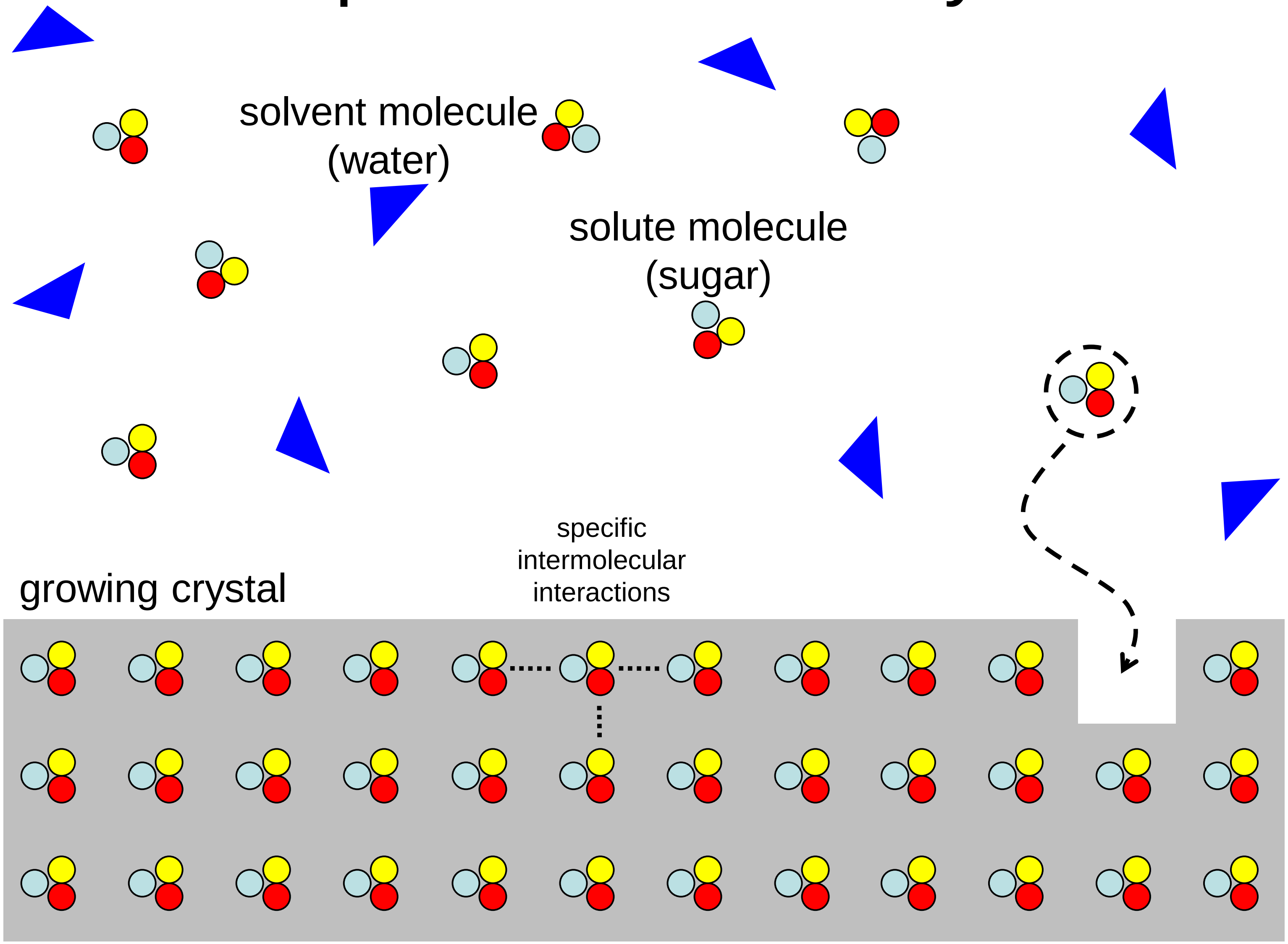
Long-Range Repulsion	**Short-Range Attraction**	**Example of Self-Organized System**
Hydrophobic/Hydrophilic	Covalent Bonding	Micelles, Lyotropic LC
Incompatibility/Insolubility	Covalent Bonding	Block Copolymers
Coulombic Repulsion	Electroneutrality	Ionic Crystals
Excluded Volume	Minimum Space Required	Thermotropic LC
Electric Field	Electric Dipole Interaction	Ferroelectric Domains
Magnetic Field	Magnetic Dipole Interaction	Magnetic Domains

“From Self-Organizing Polymers to Nanohybrid and Biomaterials,” S. Förster and T. Plantenberg, *Angew. Chem. Int. Ed.* **2002**, *41(5)*, 688.

Examples and Applications

- Simple case: crystallization of a compound from solution
- For example: crystals of sugar forming when a heated sugar solution is cooled
- By definition, a crystal is an ordered arrangement of components. In this case, the sugar crystals are comprised of highly ordered sugar molecules
- Each sugar molecule develops specific contacts with neighboring molecules in the growing crystal

Example: Molecular Crystals



Inspiration from Nature

More complicated examples that show the power of self-assembly:

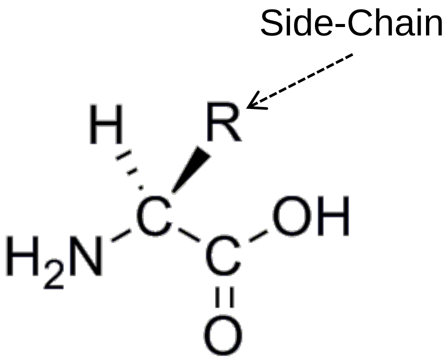
- **DNA double helix**
  - Consists of 2 strands of DNA
  - Each strand contains base pairs covalently bonded to a phosphate backbone
  - The 2 strands are held together by hydrogen bonding between complementary base pairs
- **Protein folding**
  - Proteins are polymers of amino acids
  - They fold into intricate 3-D structures
  - This is discussed on the following slides

Example: Self-Assembly in Nature

Data storage on the molecular level

DNA $\xrightarrow{\text{Transcription}}$ RNA $\xrightarrow[\text{}]{\text{Translation (Ribosome)}}$ Protein

- DNA sequence is the code for protein synthesis
- Codon: 3 adjacent base pairs of DNA that code for one amino acid in the resulting protein
- 20 possible amino acids: each has a different side-chain
- The side-chains have different chemical properties:
  - ✓ large vs. small size (vdW volume and surface area)
  - ✓ hyrdophobic vs. hydrophilic
  - ✓ acidic vs. basic
  - ✓ hydrogen bond donors/acceptors
  - ✓ ability to form disulfide bonds (Cysteine: R-SH + HS-R → R-S-S-R)
  - ✓ ability to coordinate to metal atoms
- Side-chains help guide the protein to fold into a particular structure
- Proteins must be folded properly in order to perform their functions
- Some diseases arise from mis-folded proteins



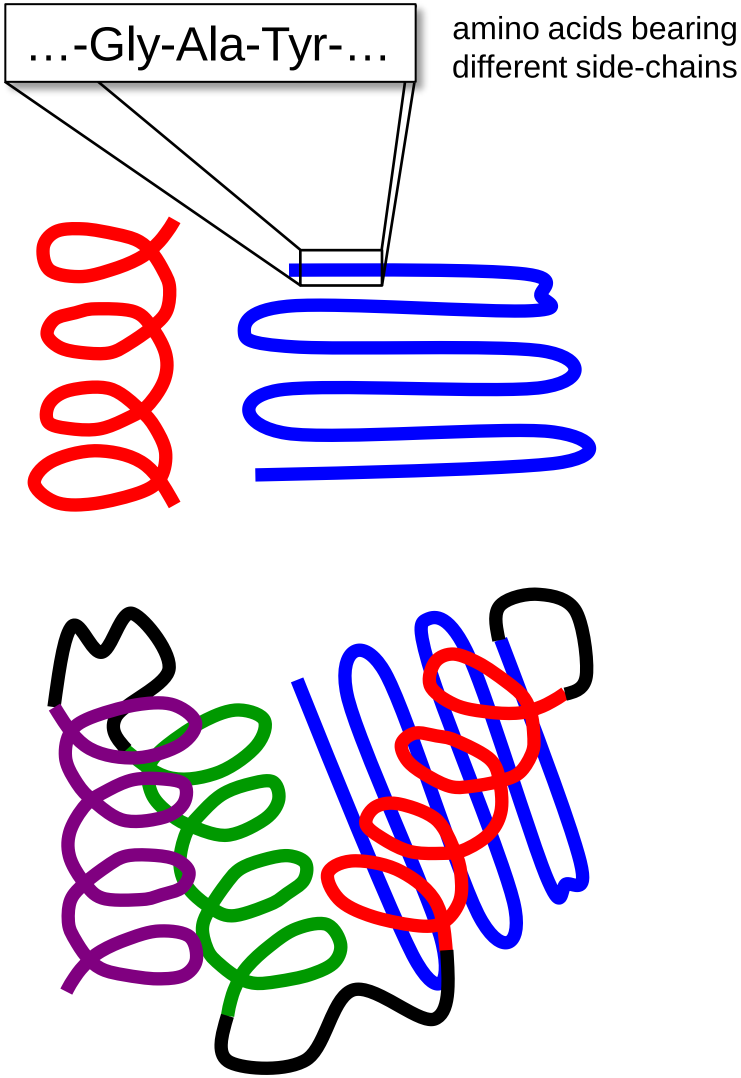
Example: Self-Assembly in Nature

<u>The terminology of protein folding</u>

Primary Structure: The order of amino acids that make up the protein. They are attached, via covalent bonds, into a polymer chain

Secondary Structure: Folding of the backbone chain of the protein into sheet-like or helical structures. This occurs to satisfy the hydrogen bonding capabilities of the back bone amide linkages

Tertiary Structure: Packing together of secondary structure elements to form a functional protein. Hydrophobic side-chains generally pack to the inside of the protein, while hydrophilic side-chains remain on the solvent-exposed surface of the protein. The solvent here is water



Nanotechnology Applications

- The mechanisms involved in protein folding are still being explored by molecular biologists
- But, not all examples of self-assembly are so complex
- In fact, scientists use much simpler versions of self-assembly all the time
- Many applications have found their way into nanotech processes and devices

Applications of Self-Assembly

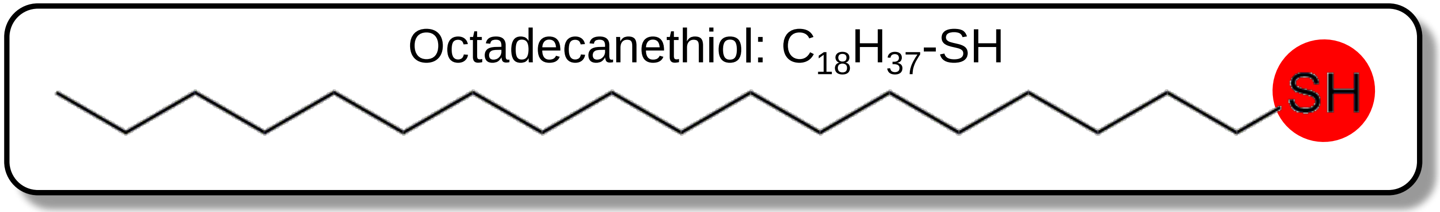
Self-Organizing System	**Application**
Atomic, ionic, and molecular crystals	Materials, optoelectronics
Self-assembled monolayers (SAMs)	Microfabrication, sensors, nano-electronics
Lipid bilayers and lipid films	Biomembranes, emulsions, liposomes for drug delivery
Phase-separated and ionic layered polymers	Nano-structured templates
Liquid crystals	Displays and TVs
Colloidal crystals	Nanosphere lithography, photonic band gap materials

"Self-Assembly at All Scales," G.M. Whitesides and B. Grzybowski, *Science* **2002**, *295 (5564)*, 2418.

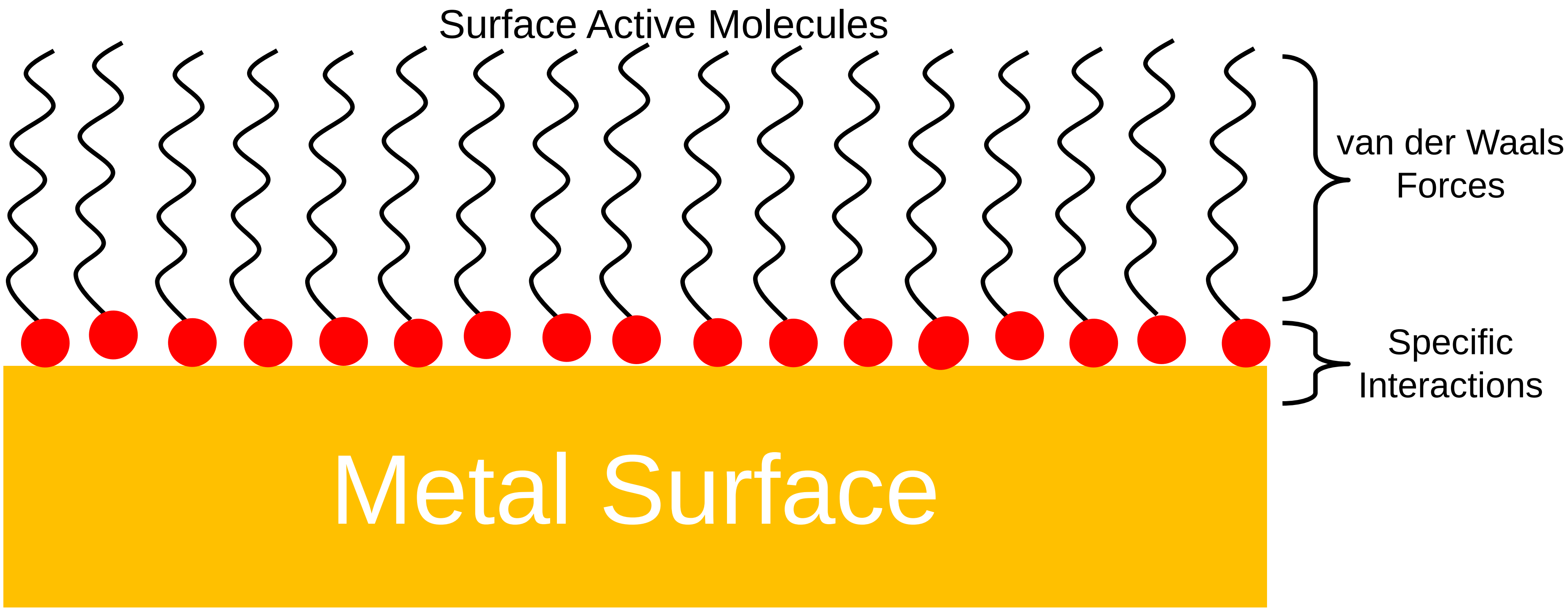
Example: Self-Assembled Monolayers

- Self assembled monolayers (SAMs) refer to the organization of extremely thin films (one molecule thick) on solid surfaces
- Common examples: thiols on gold; silanes on oxide surfaces
- The molecules that form SAMs are like surfactants. They have two distinct regions: One part is attracted to the surface; the other is not
- The molecules are sometimes called “Ligands,” especially when talking about SAMs on metal surfaces.
- Applications: improved PDMS mold release; altered hydrophobicity of surfaces

Example: Self-Assembled Monolayer (SAM)



Octadecanethiol: $C_{18}H_{37}$-SH

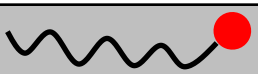


Specific example: alkane thiols on gold. These molecules have a long greasy tail and an –SH head group. The –SH is attracted to the gold while the hydrocarbon tail is exposed to the solvent or air

SAMs: Choosing the Best Ligand

- Ligands have to be chosen so that they will bind and assemble on a surface
- Some ligands work on many surfaces
- Others work best only on selected surfaces
- If a ligand does not bind well to a surface, then it can be easily rinsed off and a SAM does not form
- When designed properly, SAMs are durable surface treatments

Ligands for Various Surfaces

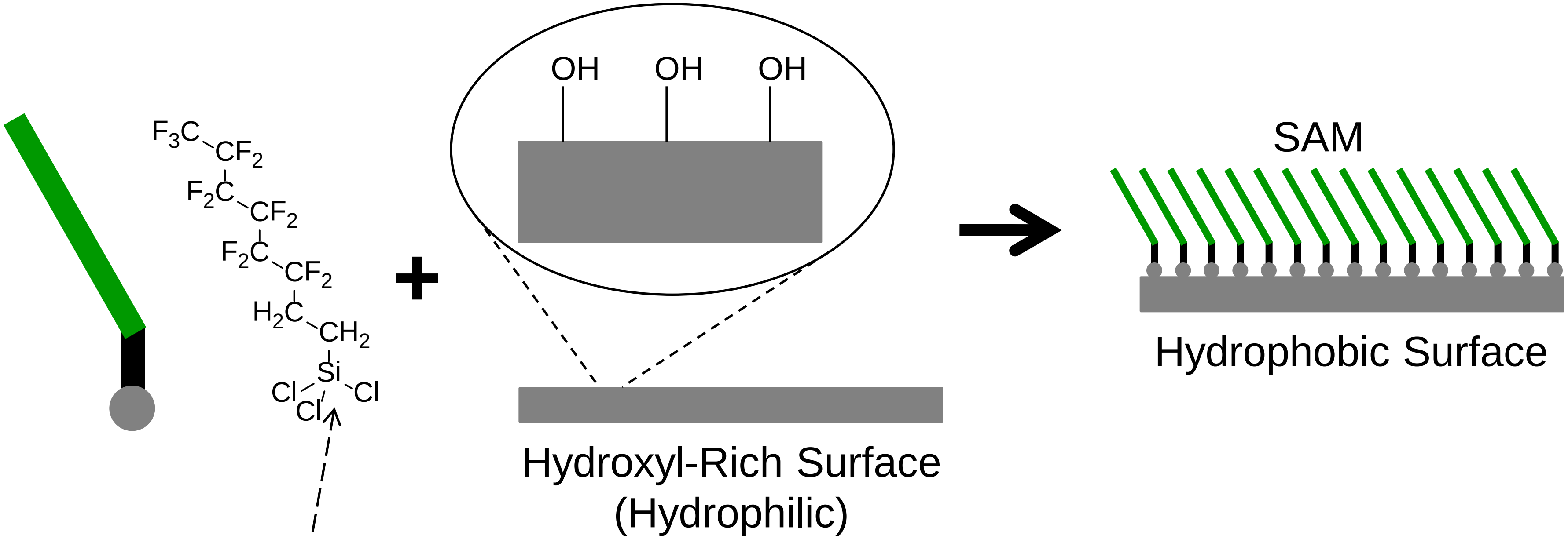
✓ = Yes SAM ✗ = No SAM **Surface**	**Alkylated Ligand** 					
	Thiol R-SH	**Sulfide** R-S-R	**Phosphine** R_3P	**Isonitrile** R-NC	**Carboxylic Acid** R-COOH **Phosphonic Acid** $R\text{-}PO(OH)_2$	**Alcohol** R-OH **Amine** $R\text{-}NH_2$ **Amide** $R\text{-}CONH_2$
Cr, Ni, Fe, Al	✗	✗	✓	✓	✓	✓
Pt	✓	✗	✓	✓	✓	✓
Cu, Ag	✓	✗	✓		✓	
Au	✓	✓	✓	✓	✗	✗
Zn	✓	✗	✓	✓	✓	✓

Other Surfaces	
Metal & Silicon Oxides	✓ Silanes $R\text{-}SiCl_3$

Adsorption generally follows "Hard-Soft-Acid-Base" rules: Carboxylic and phosphonic acids adsorb onto any metal oxide surface. Thiols and isonitriles adsorb onto soft metals (Cu, Ag, Au, Pt). However, phosphines (which are considered soft) form monolayers on many surfaces (soft or hard). This could be due to their oxidation to phosphine oxides

Pure and Applied Chemistry **1991**, *63(6),* 821-828.

Application: Surface Modification



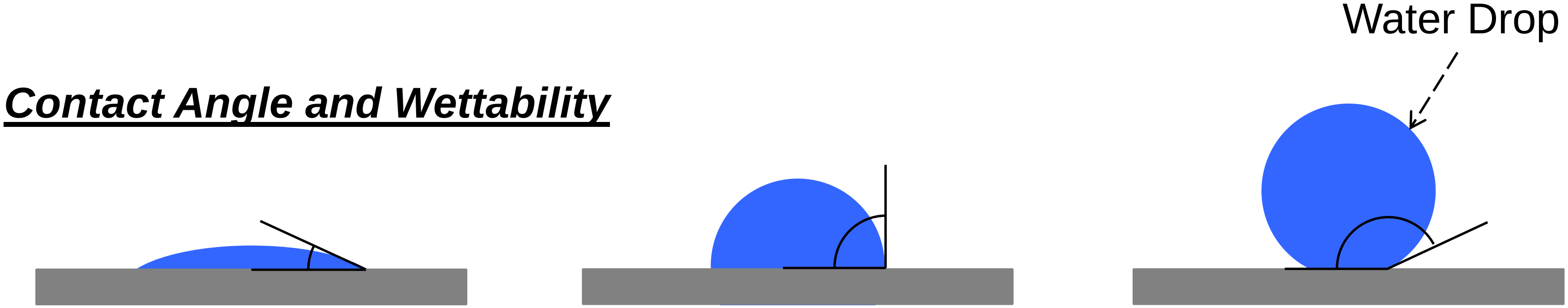
Reacts with hydroxyls

Hydroxyl-Rich Surface
(Hydrophilic)

SAM

Hydrophobic Surface

Contact Angle and Wettability

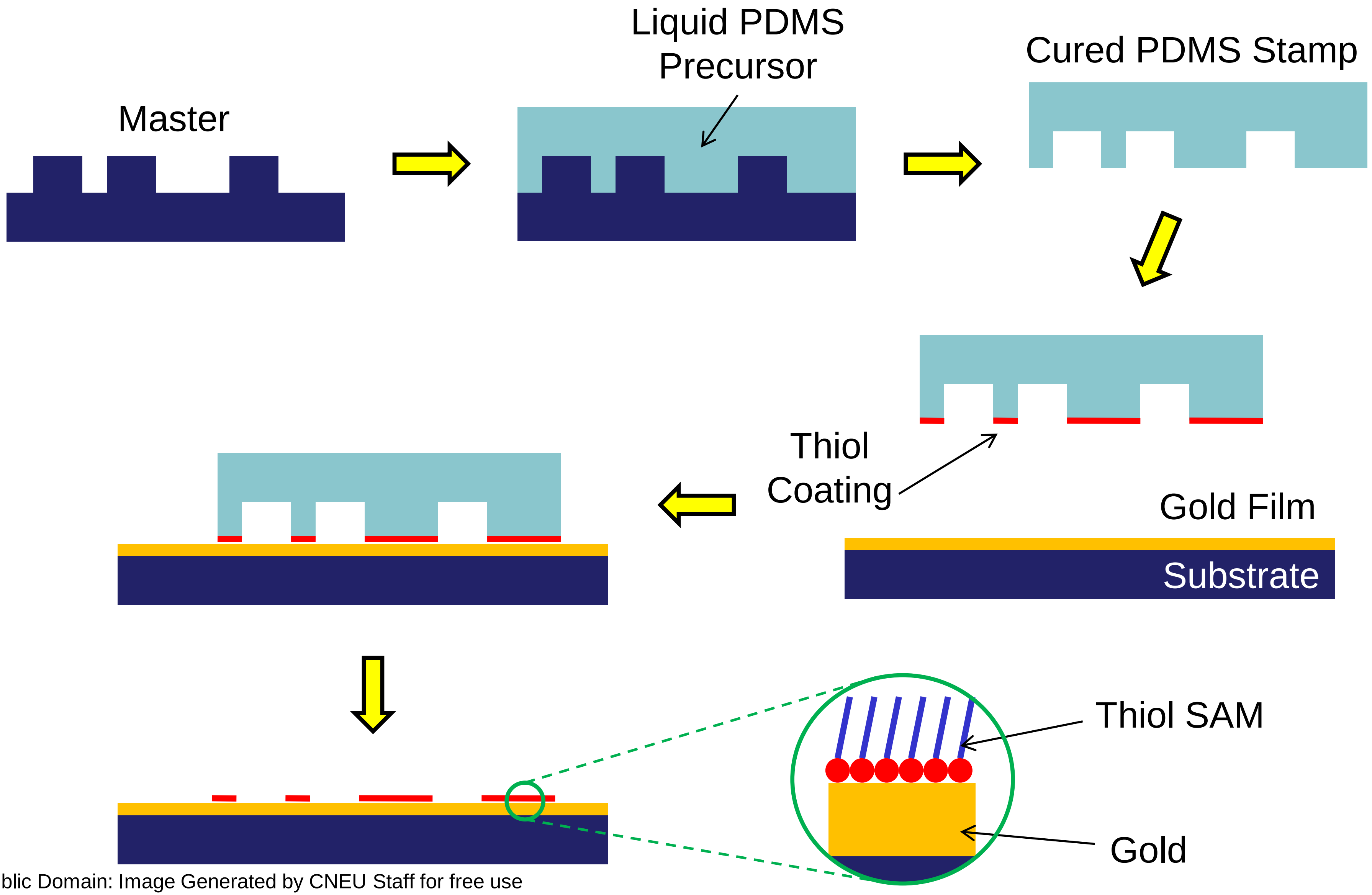

Water Drop

Hydrophilic
<30°

Hydrophobic
>90°

Super Hydrophobic
>150°

Application: Microcontact Printing



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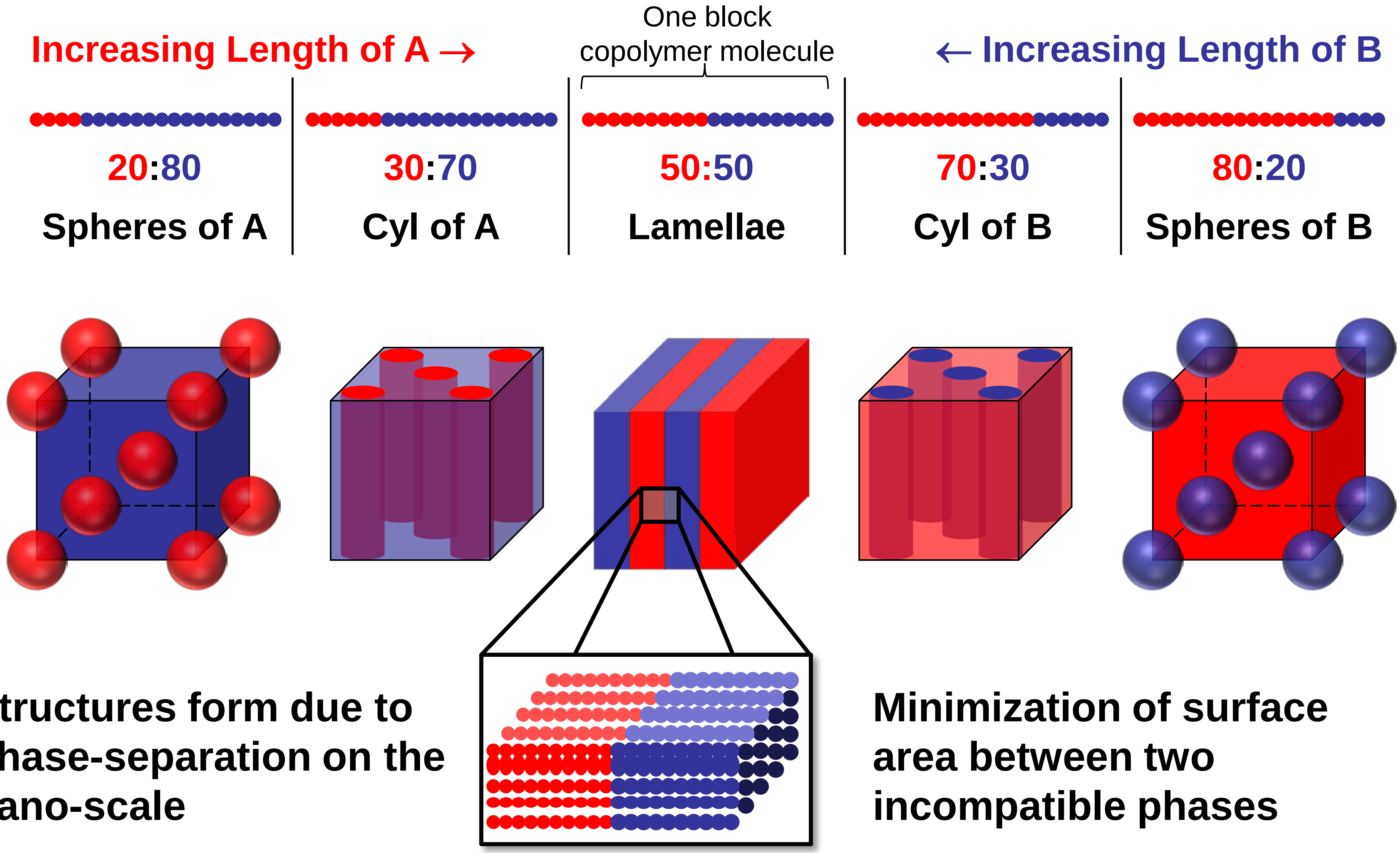
Example: Block Copolymers

- Block copolymers are similar to surfactants in that they have two chemically dissimilar parts
- When cast into films, the two blocks do not want to mix with each other (like oil and water)
- But the blocks are covalently attached to each other, so they cannot move too far apart
- This causes a phase separation on the nanoscale.
- Nanoscale domains form a pattern that is characteristic of the block copolymer composition (spheres, cylinders, lamellae)
- Changing the ratio (1:2) changes the pattern

One Block Copolymer Molecule

Block 1 Block 2

Example: Block Copolymers



Increasing Length of A →

One block copolymer molecule

← Increasing Length of B

20:80	30:70	50:50	70:30	80:20
Spheres of A	**Cyl of A**	**Lamellae**	**Cyl of B**	**Spheres of B**

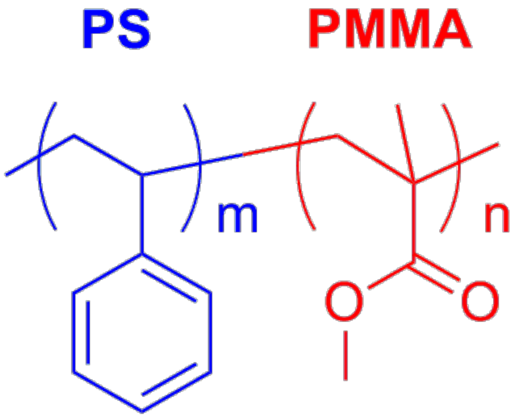
Structures form due to phase-separation on the nano-scale

Minimization of surface area between two incompatible phases

Example Process for Block Copolymers

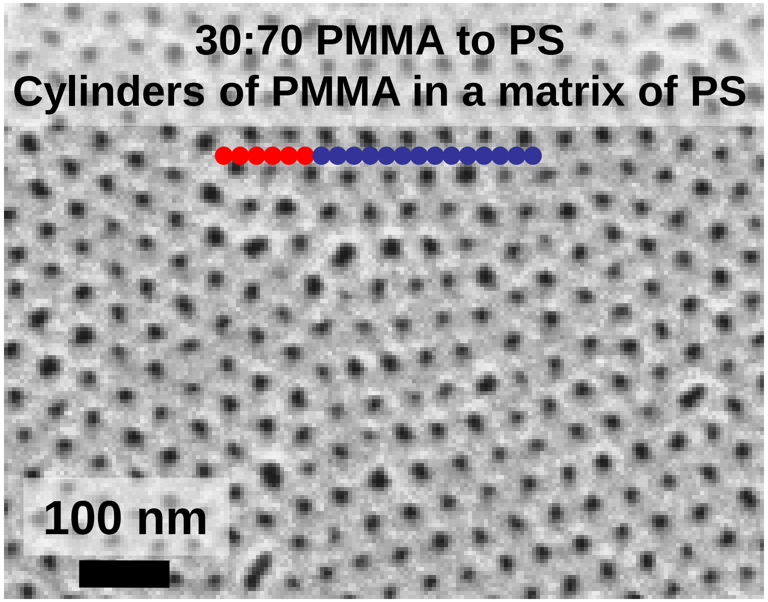
The exact process route depends on the properties of the block copolymer being used to create the pattern. This example is for PS-*b*-PMMA, which self-assembles when heated to about 175 °C (above the T_g of both blocks, but not totally melted)

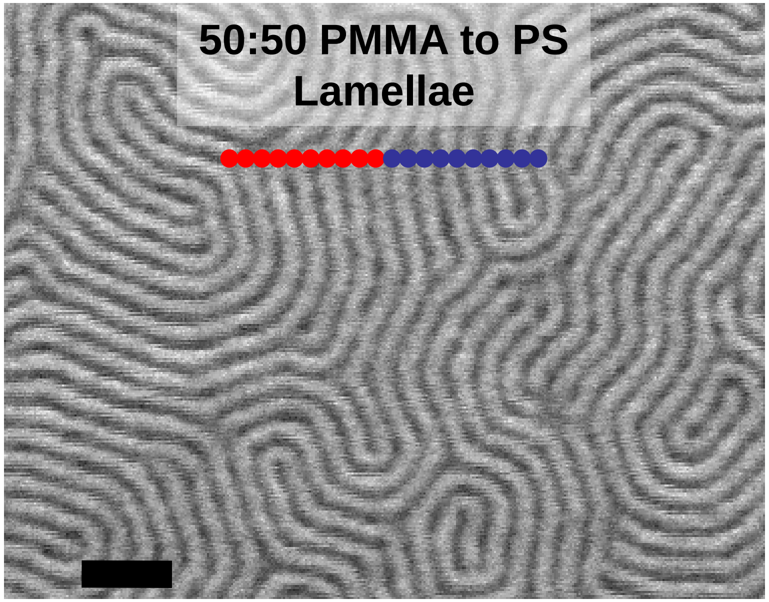
- Clean the substrate to remove any contamination
- Neutralize (randomize) the surface so that both blocks (PS and PMMA) have an equal affinity for the surface. In other words, neither block will preferentially wet or stick to the substrate surface
- Dissolve the polymer in a solvent (toluene or PGMEA) to make a dilute solution of the polymer (1 wt% works well)
- Spin coat a thin film (35 nm) of PS-*b*-PMMA onto the randomized substrate
- Anneal (heat) the sample in a 175 °C vacuum oven for approximately 24 hours
- Cool the sample back to rt and verify the self-assembled pattern via FESEM or AFM

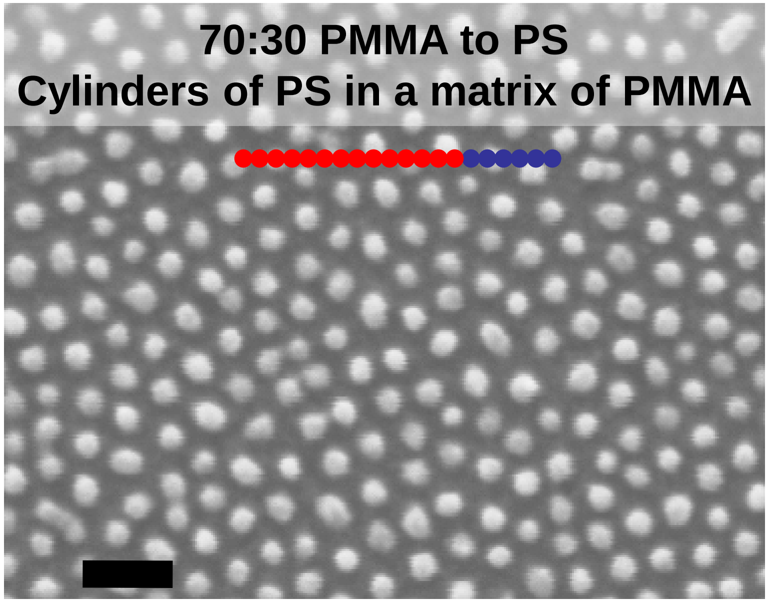


http://www.internano.org

Images of Block Copolymers







Increasing size of **PMMA block**

Decreasing size of **PS block**

Overall size (PS + PMMA) remains constant

Light gray: PS
Dark gray: PMMA

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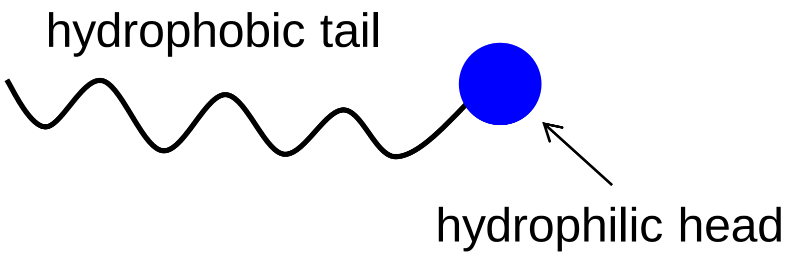
Surfactants

- Soaps and detergents are common examples of surfactants
- Each molecule has a hydrophobic tail and hydrophilic head
- When dissolved in water, surfactants self-assemble into micelles to minimize interactions between the hydrophobic tails and the water



Surfactants can be classified according to their head group:

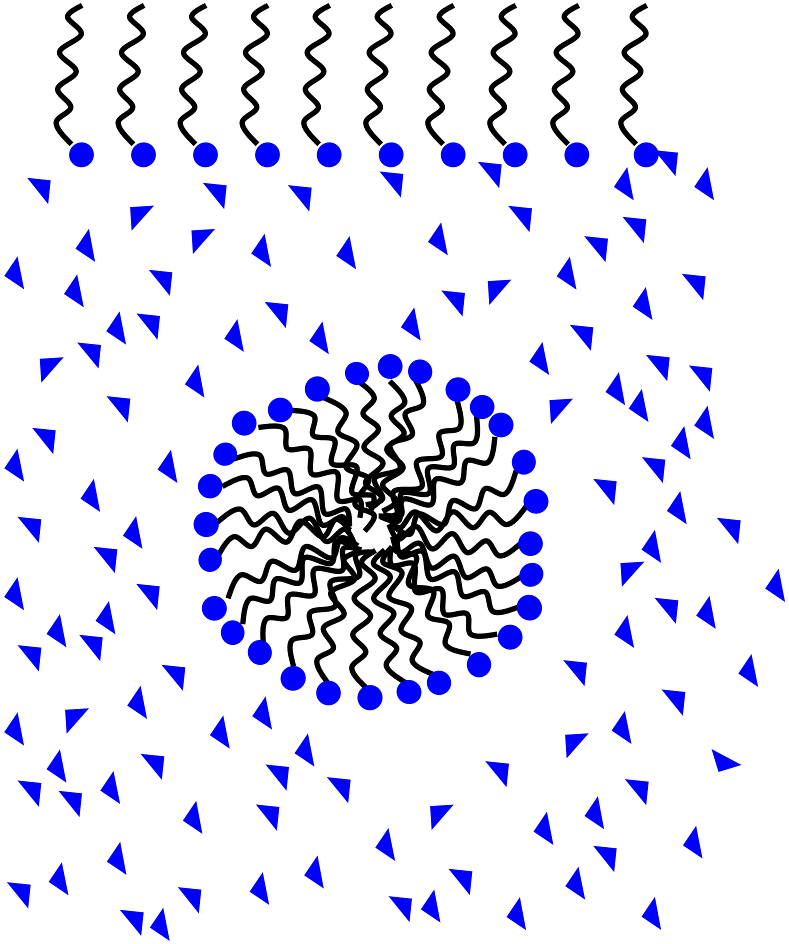
- Anionic – negative charge
- Cationic – positive charge
- Non-ionic – no charge
- Zwitterionic – both (+) and (-)

The choice of surfactant depends on the application:

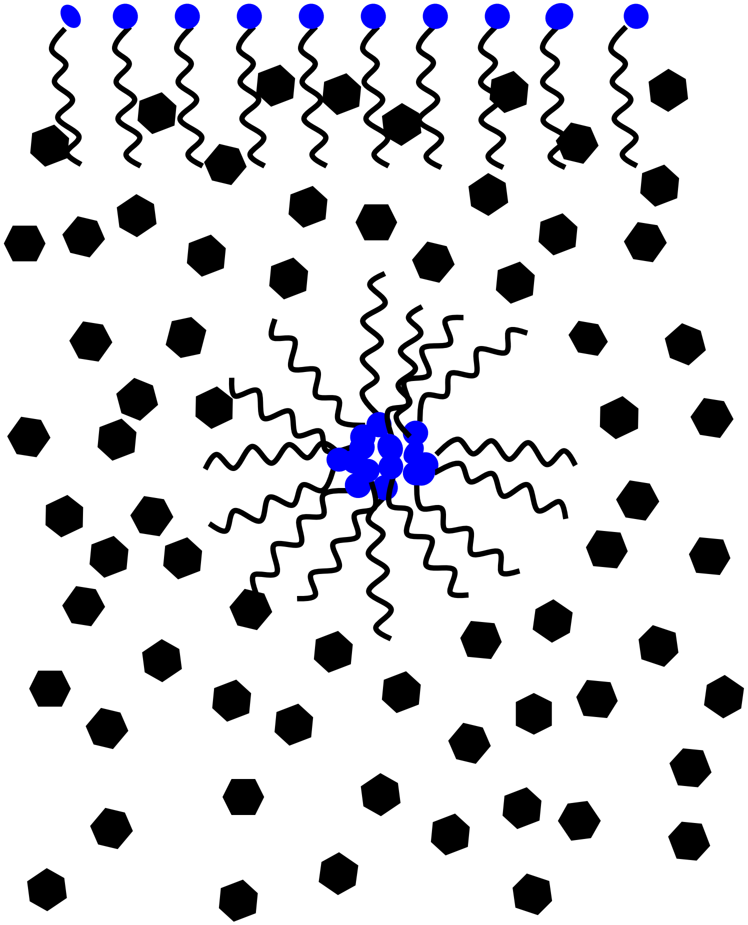
- Common soaps: anionic (good cleansing and high foaming)
- Baby shampoo: zwitterionic (mildness)
- Laundry detergent: non-ionic (lower foam and less sensitive to hardness ions)

Example: Micelle and Reverse Micelle

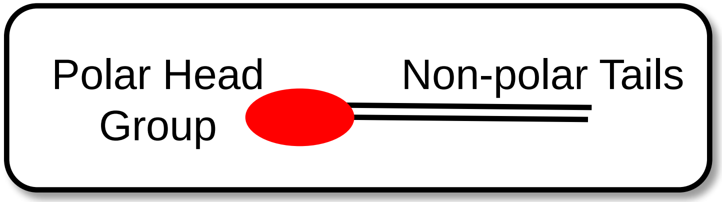
Polar Solvent (Water)



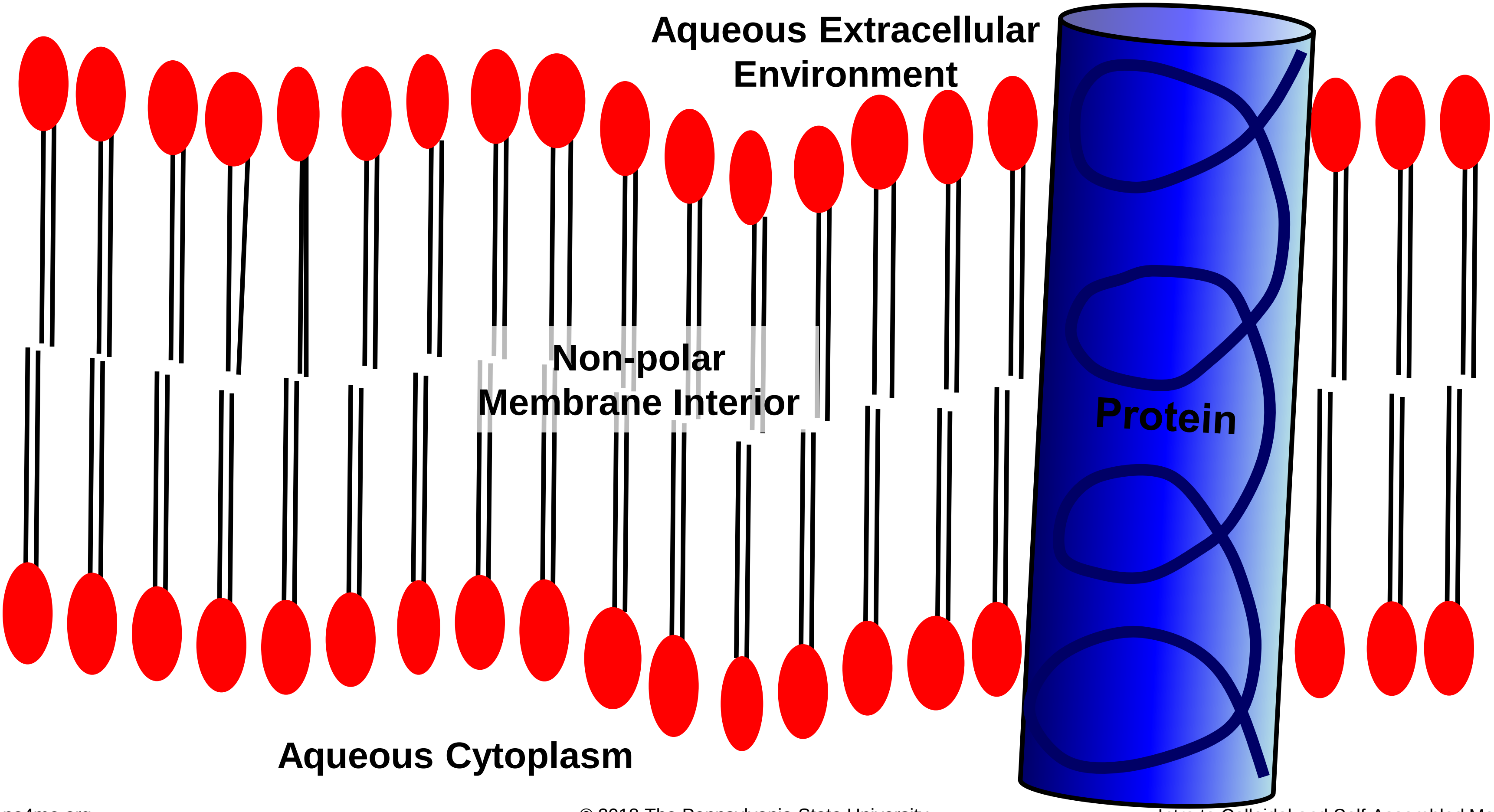
Non-Polar Solvent (Oil)



Example: Lipid Bilayers



Lipids are natural surfactants that self-assemble into cell membranes



Liquid Crystals

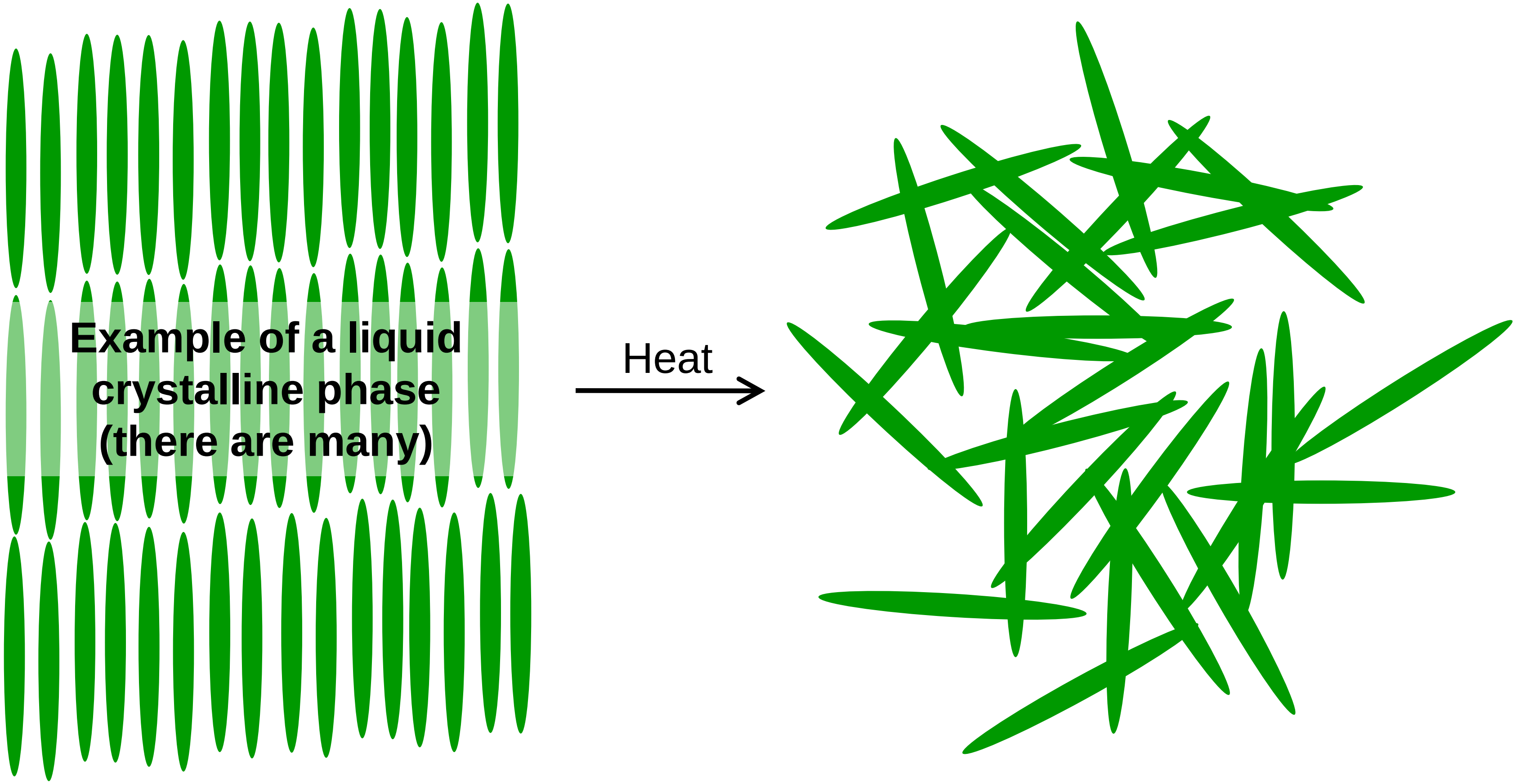
- Liquid crystals exist somewhere between a solid crystal (very ordered) and an isotropic liquid (no order)
    - Kind of like an organized liquid
    - The molecules arrange themselves so that they stack into a highly ordered pattern
    - But the material is still fluid-like
- Phase change = transition from one state (arrangement of molecules) to another state

Liquid Crystals

- Two general types of liquid crystals (LC):
  - **Thermotropic LC:** change phase as temperature increases/decreases
  - **Lyotropic LC:** phase changes induced by addition of solvent (change in concentration)
- Some liquid crystals have an interesting property: they rotate the plane of polarization of light. This property is used in some LCD displays

Example: Liquid Crystals (LC)

<u>Thermotropic LC:</u> change phase as temperature increases/decreases
<u>Lyotropic LC:</u> phase changes induced by addition of solvent (change in concentration)

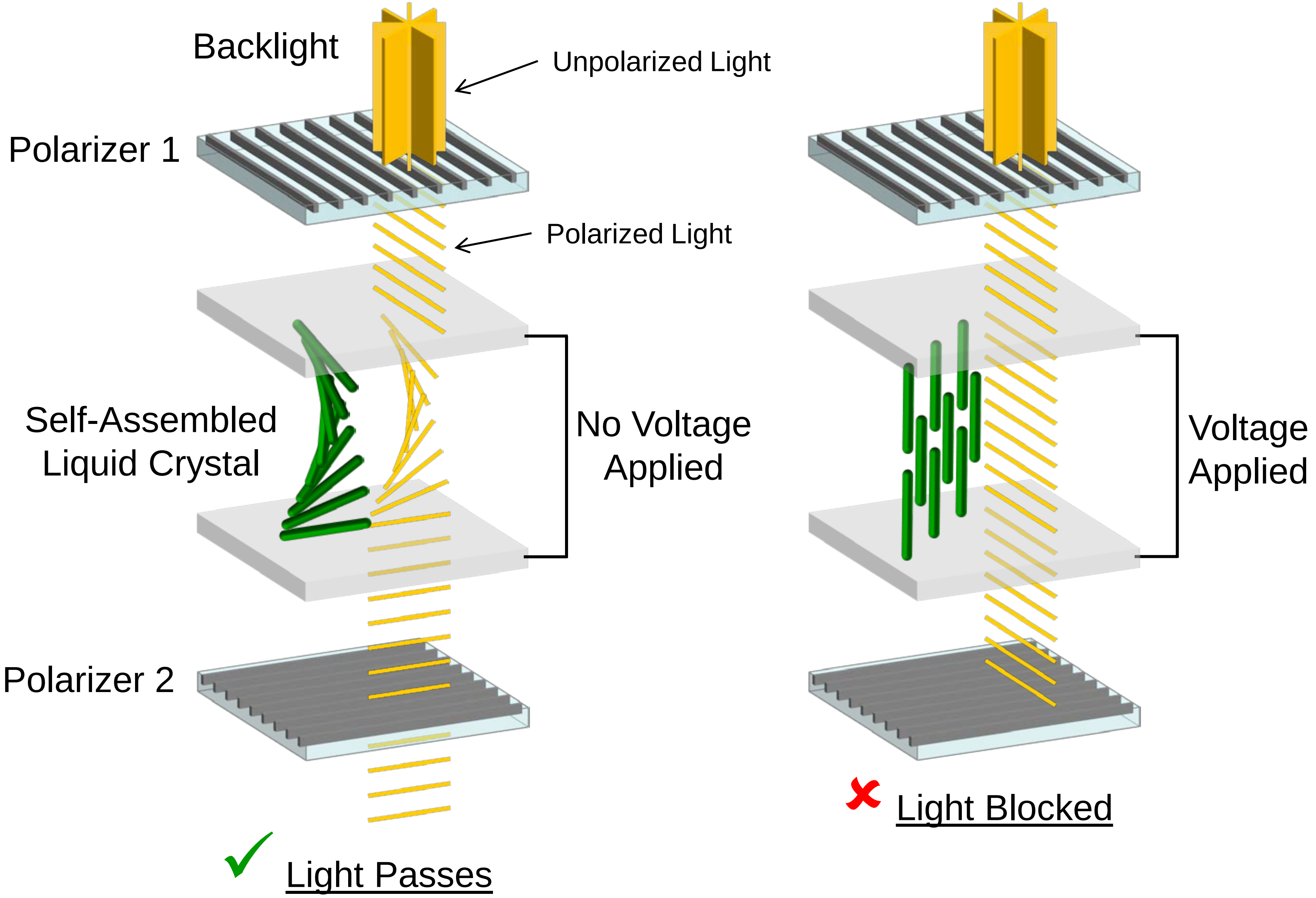


Example of a liquid crystalline phase (there are many)

<u>Liquid Crystal</u>
Long range order but still behaves like a fluid

<u>Isotropic liquid</u>
no long range order

Application: TFT LCD



Backlight

Unpolarized Light

Polarizer 1

Polarized Light

Self-Assembled Liquid Crystal

No Voltage Applied

Voltage Applied

Polarizer 2

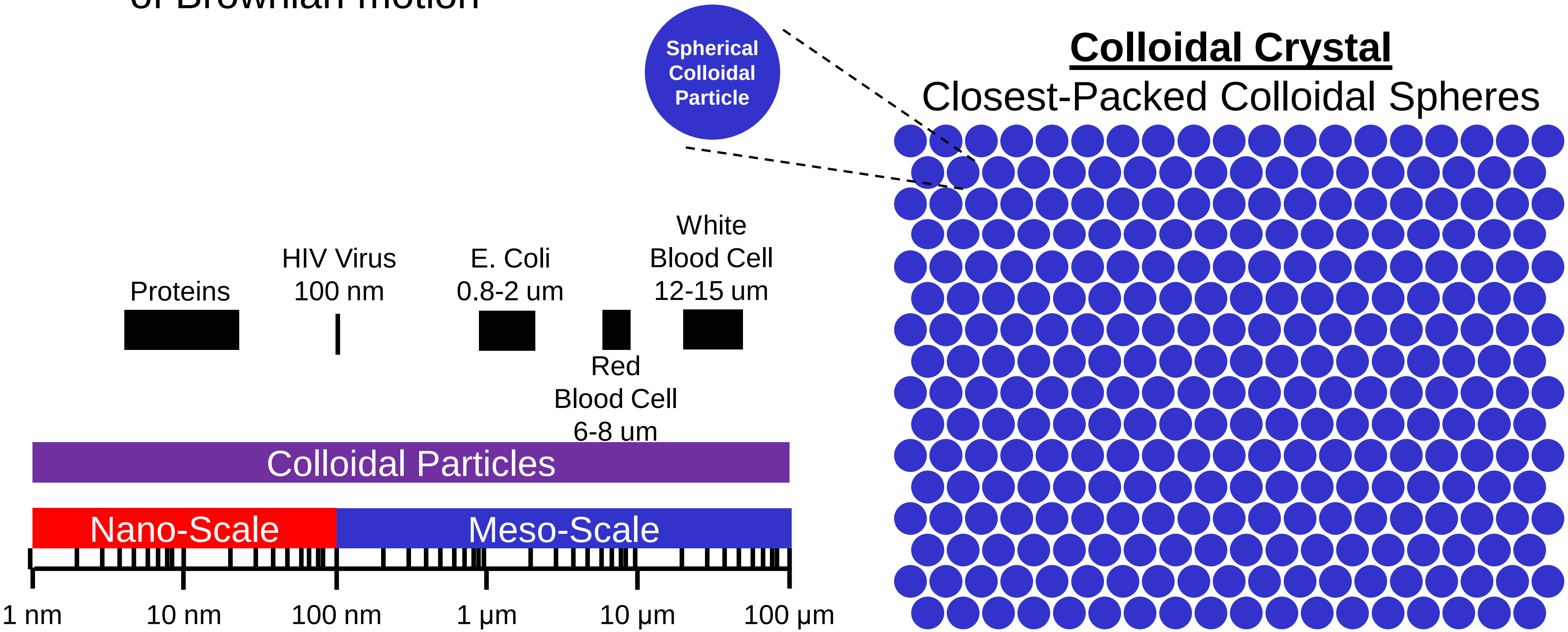
✓ Light Passes

✗ Light Blocked

Example: Colloidal Crystals

Similar to atomic and molecular crystals, except that the size of the building blocks are much larger and the forces holding them together are much weaker (compared to the size of the particles)

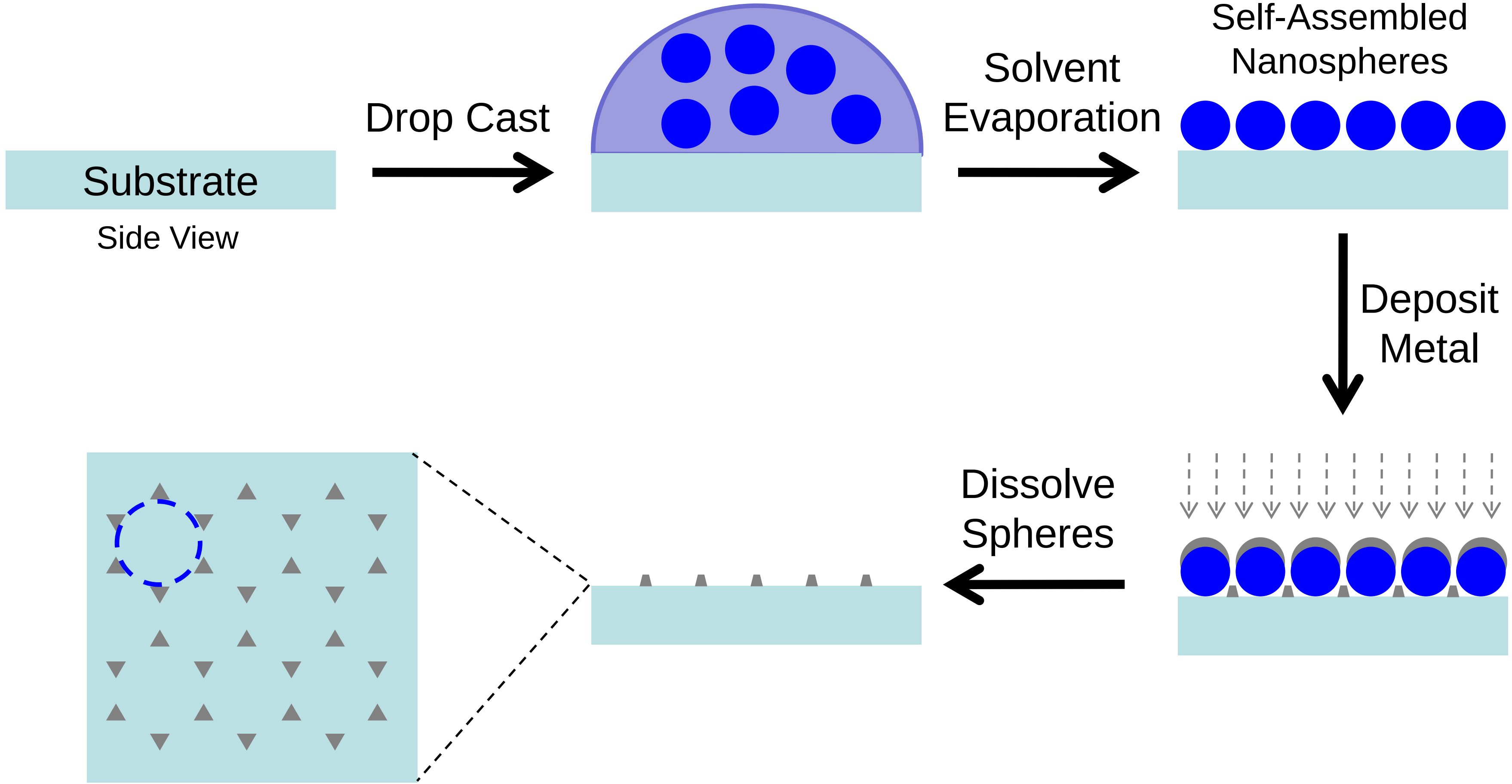
Colloidal: encompasses particles that have at least one characteristic dimension in the 1 nm to 1 um range – small enough to be the subjects of Brownian motion



Colloidal Crystal

Closest-Packed Colloidal Spheres

Application: Nanosphere Lithography



Colloidal Solution of Nanospheres

Substrate

Side View

Drop Cast

Solvent Evaporation

Self-Assembled Nanospheres

Deposit Metal

Dissolve Spheres

Top View

Feature spacing can be tailored by adjusting size of colloidal spheres

Summary

- Colloid: refers to small size of objects; encompasses nano- and meso-scale
- Colloids scatter light; homogeneous solutions do not scatter light
- There are many everyday examples of self-assembly: soaps, proteins, LCDs
- Emerging nanotech applications rely heavily on self-assembling molecules, polymers, and particles
- Advances in self-assembly may eventually lead to true “bottom-up” manufacturing