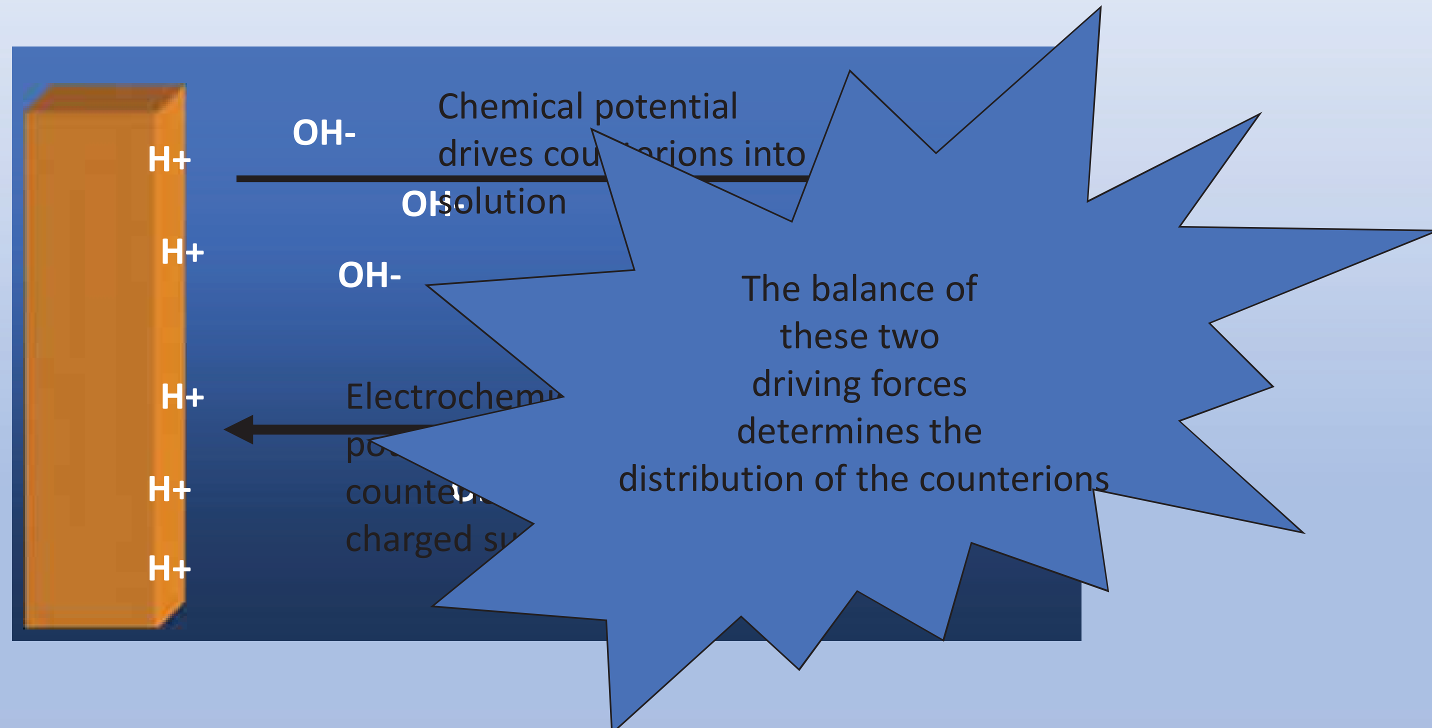
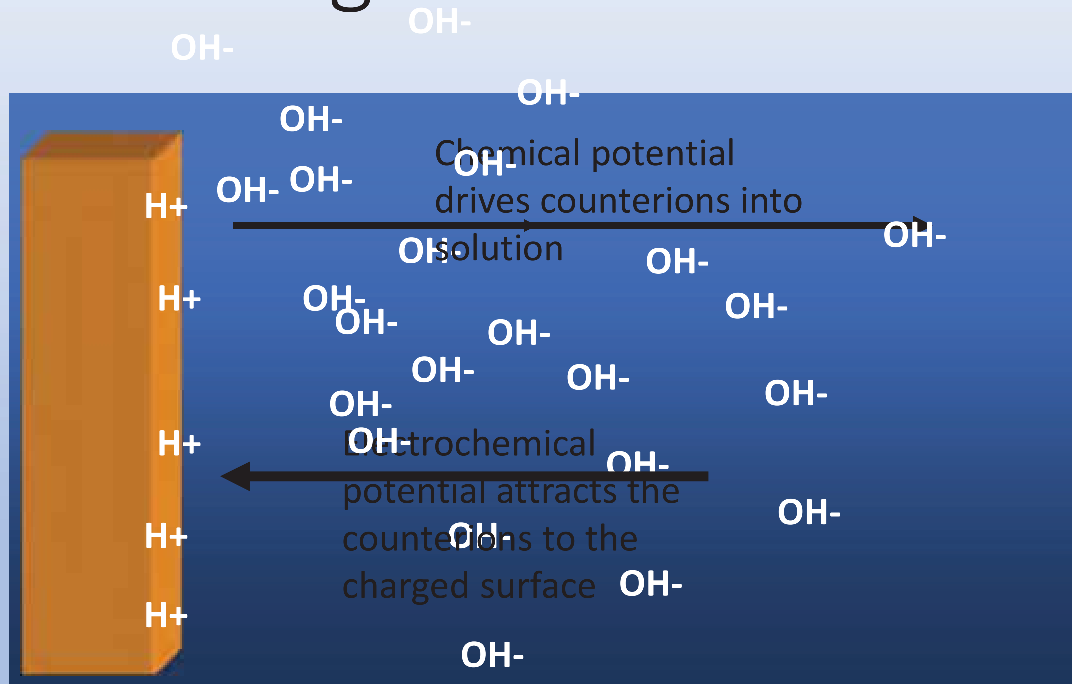
Electrical Charges Associated with Surfaces



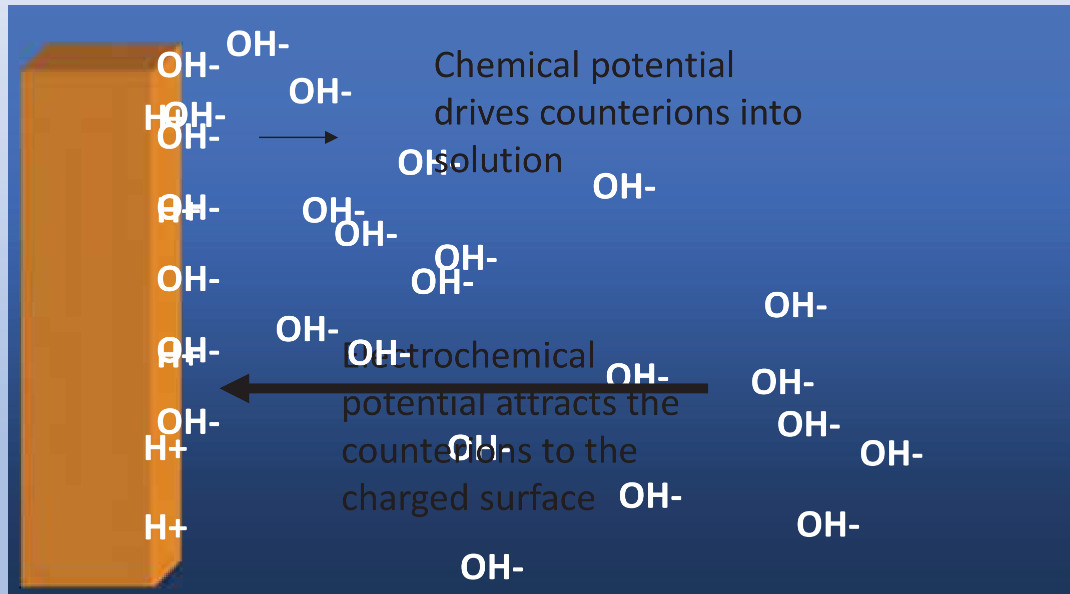
The balance between chemical potential and electrochemical potential establishes a Donnan Equilibrium

Electrical Charges Associated with Surfaces



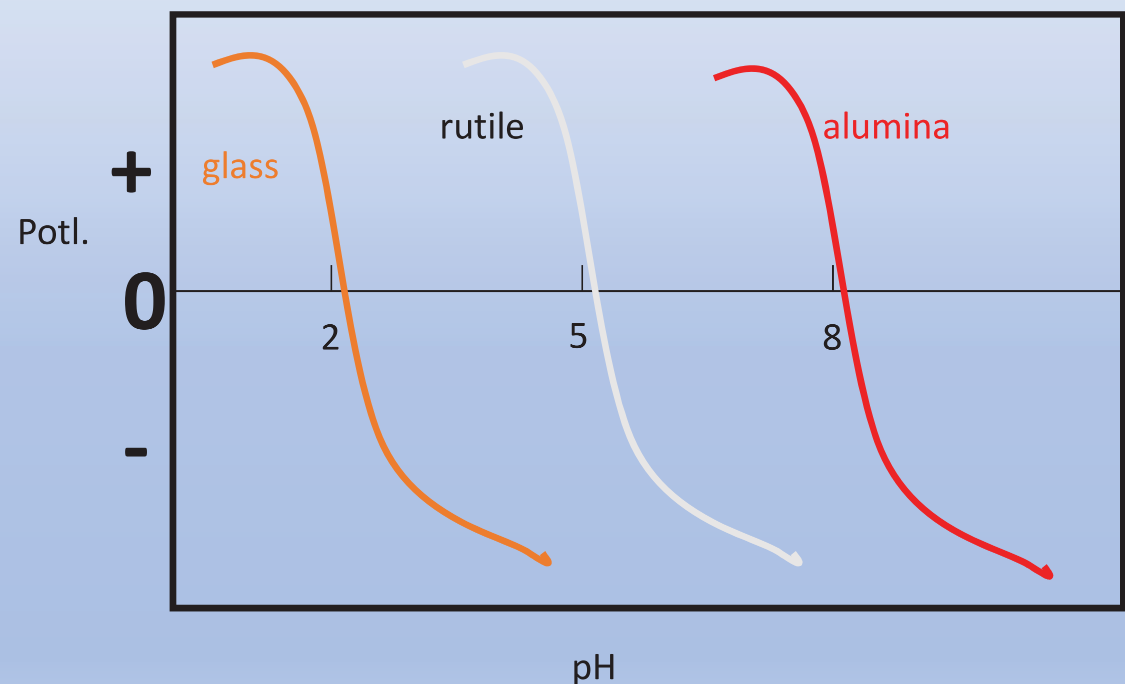
If the pH is raised by adding more hydroxyl ions, the chemical potential drive is decreased and the distribution of counterions favors more electroneutralization of the surface potential

Electrical Charges Associated with Surfaces



If excess base is added, the surface charge will reverse in sign, from positive to negative

Electrical Charges Associated with Surfaces



Every material surface possesses a characteristic Point of Zero Charge

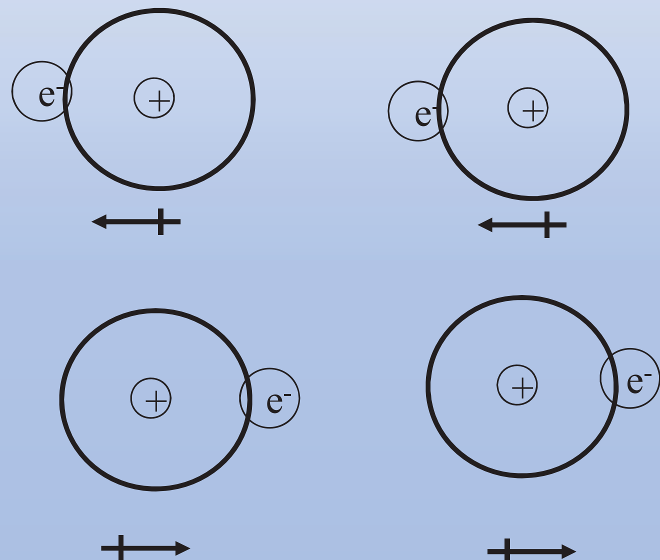
Dispersion Instability

- Attractive Energy
- Repulsive Energy
- Total Energy
  - Sum of Attractive and Repulsive Forces

Attractive Forces

- Sources of attractive forces
  - Permanent dipole
  - Dipole-induced dipole
  - Induced dipole-induced dipole
- Forces vary inversely with intermolecular distance[6]
- Dependent on the polarizability and density of atoms and solvent
- Attraction for particles decreases in water
- Attraction weakest when dispersed molecules are chemically similar to solvent

Theory of London Attraction



Summation of transitory dipoles leads to zero net permanent dipole moment, however, in both configurations, the atoms are mutually attractive

Van der Waals Forces Between Colloidal Particles

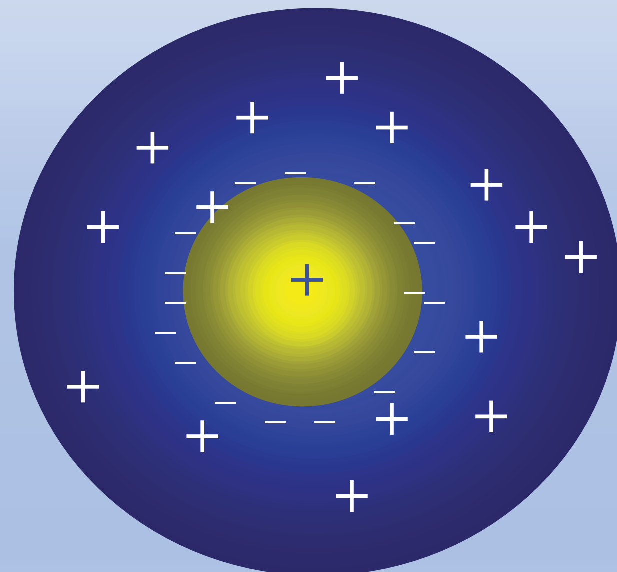
- For a colloidal particle, each atom or molecule of one particle attracts every atom in the other particle
- Each particle has 10^6-10^{10} atoms

Net effect of adding a myriad of possible atomic interactions is a generation of long range attraction (5-10 nm) between particles that is of considerable strength

Electrical Colloidal Stability of Latexes

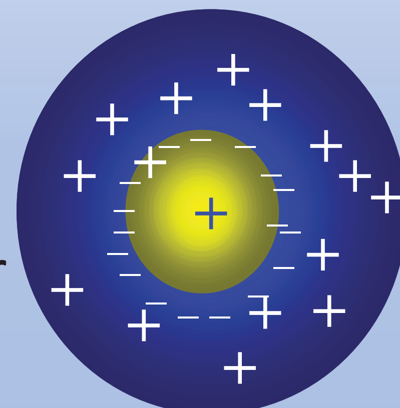
- **Provided by surfactants**
  - **anionic, cationic, nonionic**
  - **surfactants can interfere with coating performance**
- **Copolymerization with ionic monomers**
  - **water-soluble products are made in this process and they remain in the latex**
- **Interfacially adsorbed polyelectrolyes**
  - **excellent stability and little effect on the coatings performance**
  - **sometimes polyelectrolyte is desorbed (under shear) causing poor deposition of film (competition for interface)**

What Forms the Repulsive Barrier?
1. Electrical Double Layer



Electrical Double Layer

- Composed of two layers
  - An inner layer that may include adsorbed ions
  - Diffuse layer
    - Thermal energy
    - Electrical forces
- Thickness of double layer
    - Concentration of ions



Heimenz, P. Principles of Colloid and Surface Chemistry. 2nd ed. Marcel Dekker, New York. 1986.

Example of Double Layer Thickness

- Double layer thickness decreases with increasing ion strength
- Ionic strength given by

$$I = \frac{1}{2} \cdot \sum_i c_i \cdot z_i^2$$

Where c_i-concentration
z_i-ion charge

Example:
For $I = 10^{-1}$M, DLC=1nm
For $I = 10^{-3}$M, DLC =10nm

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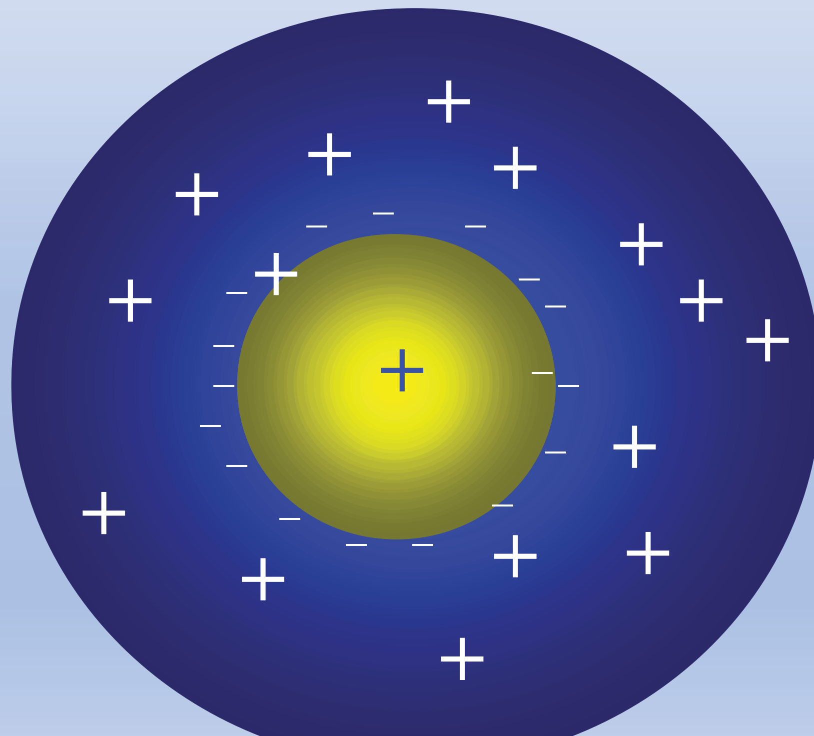

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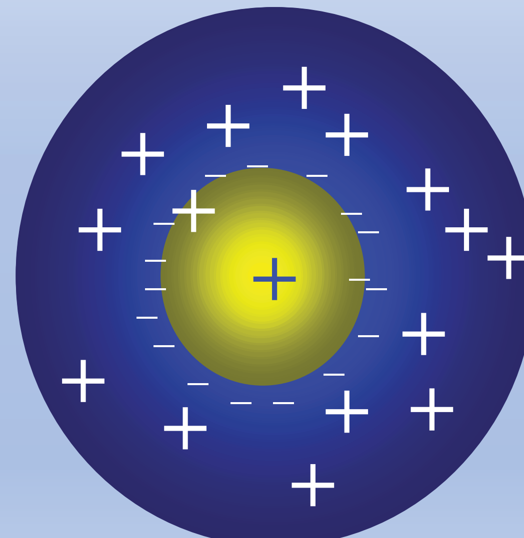

Heimenz, P. Principles of Colloid and Surface Chemistry. 2nd ed. Marcel Dekker, New York. 1986.

Example of Double Layer Thickness

- Double layer thickness (κ^{-1}) decreases with increasing ion strength
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Where c_i-concentration
z_i-ion charge

Example:
For I=10^{-1}M, κ^{-1}=1nm
For I=10^{-3}M, κ^{-1}=10nm

Schramm, L. <u>Emulsions: Fundamentals and Applications in the Petroleum Industry</u>. Chapter 1. (Schramm, L. L. Ed.) American Chemical Society, Washington D.C. 1992.

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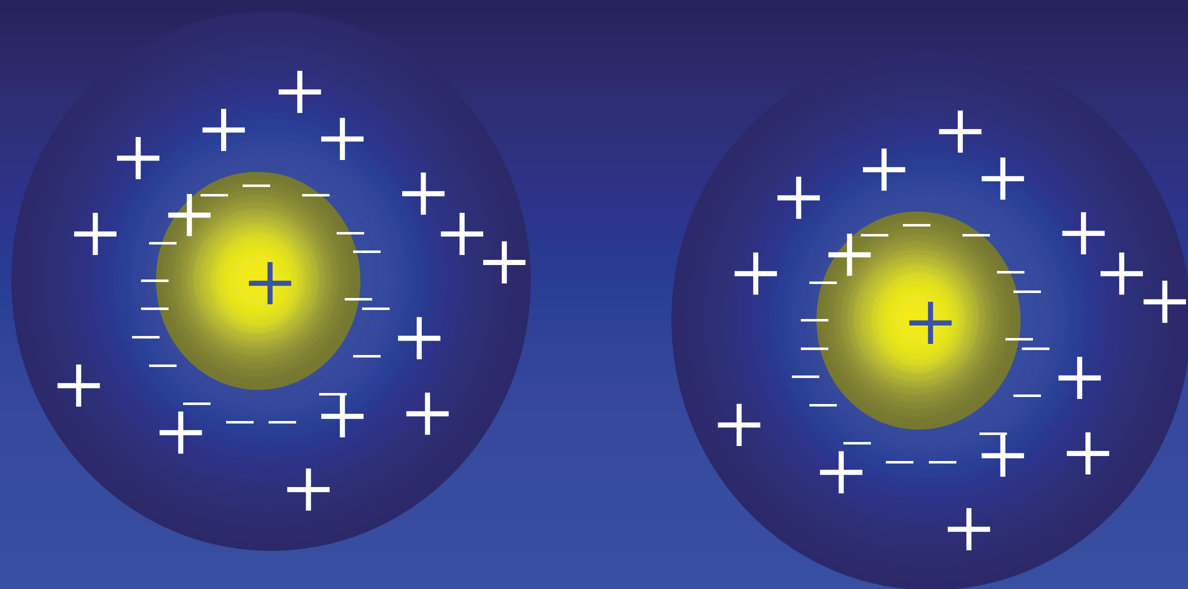
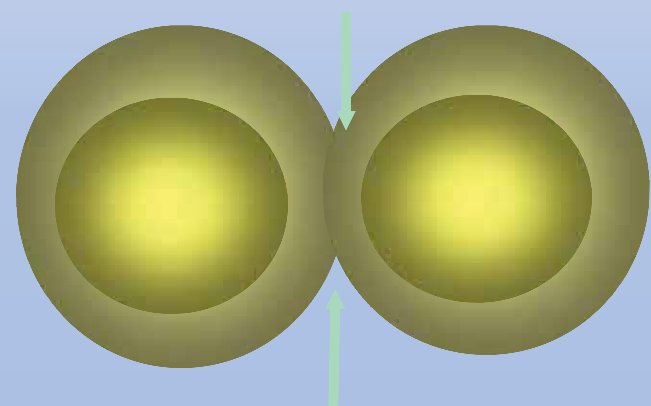
DLVO STABILITY



Stabilization by the Electric Double Layer

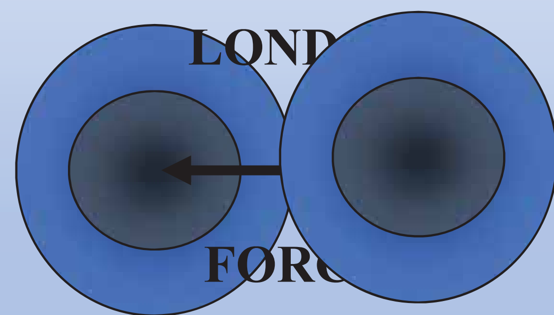
Repulsion as the double layers overlap



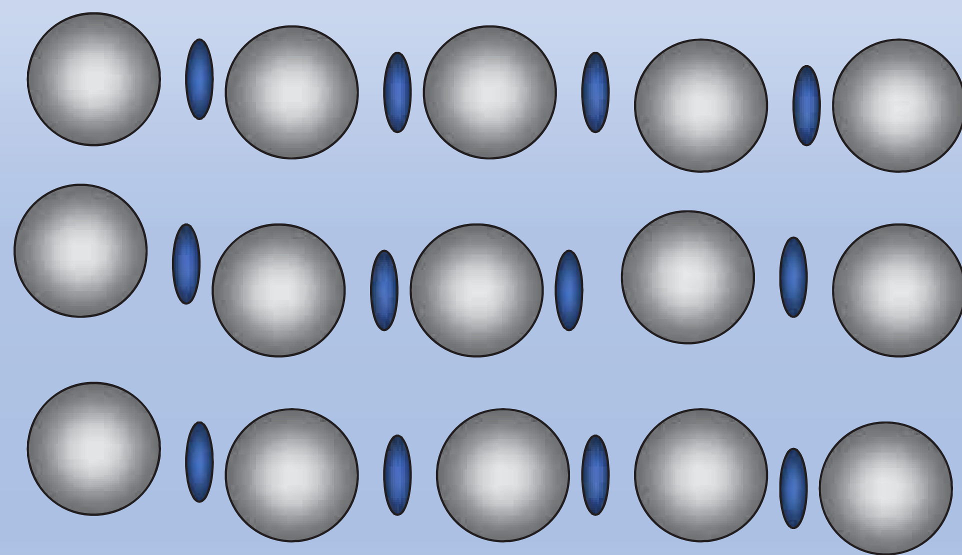
Stability of dispersions

- Complex:
  - attractive and repulsive forces act simultaneously
    - depend on physical conditions
    - pH, ionic strength, temperature, concentration
  - usually thermodynamically unstable
  - kinetically stable

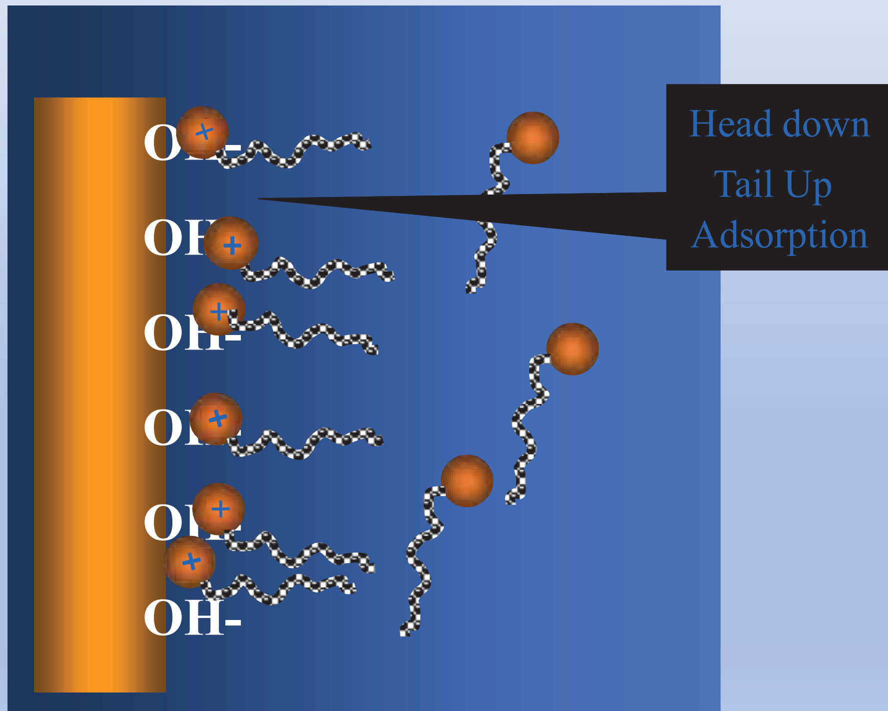
DLVO THEORY



ISE THEORY



Surfactants and Conditioning



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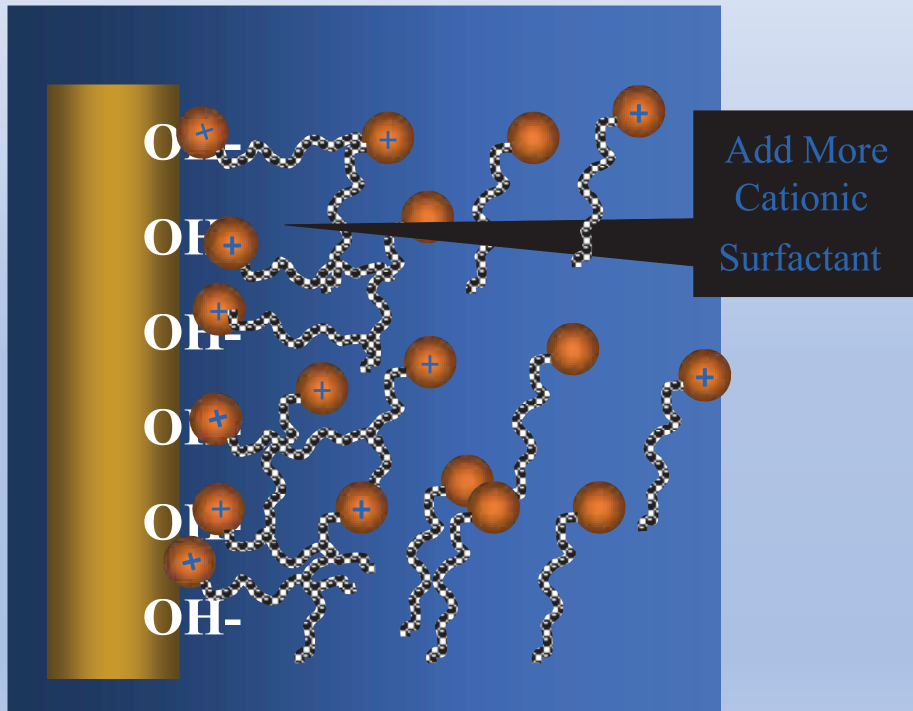

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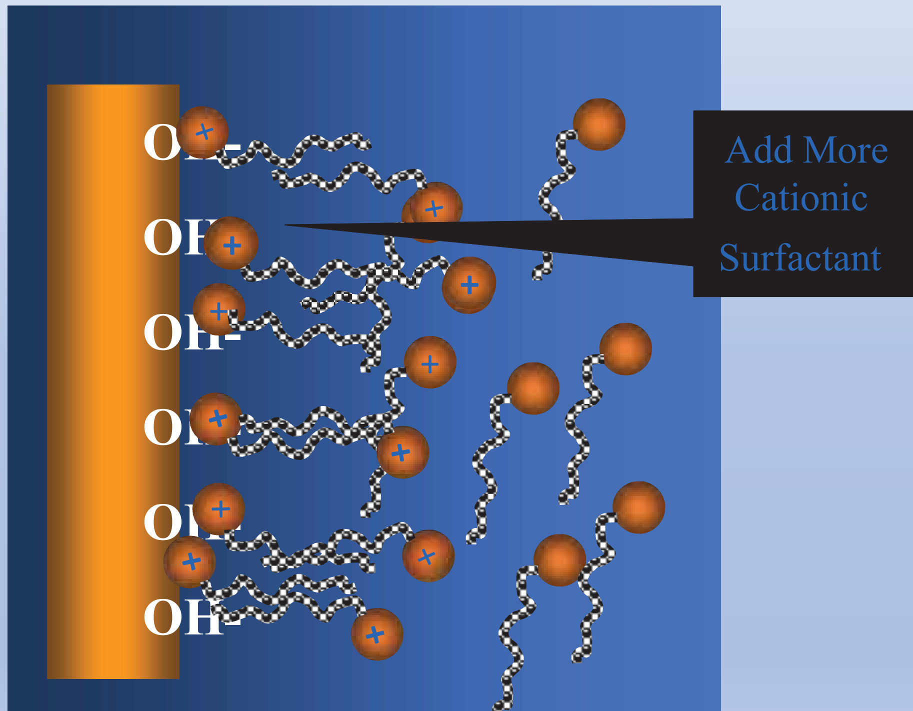

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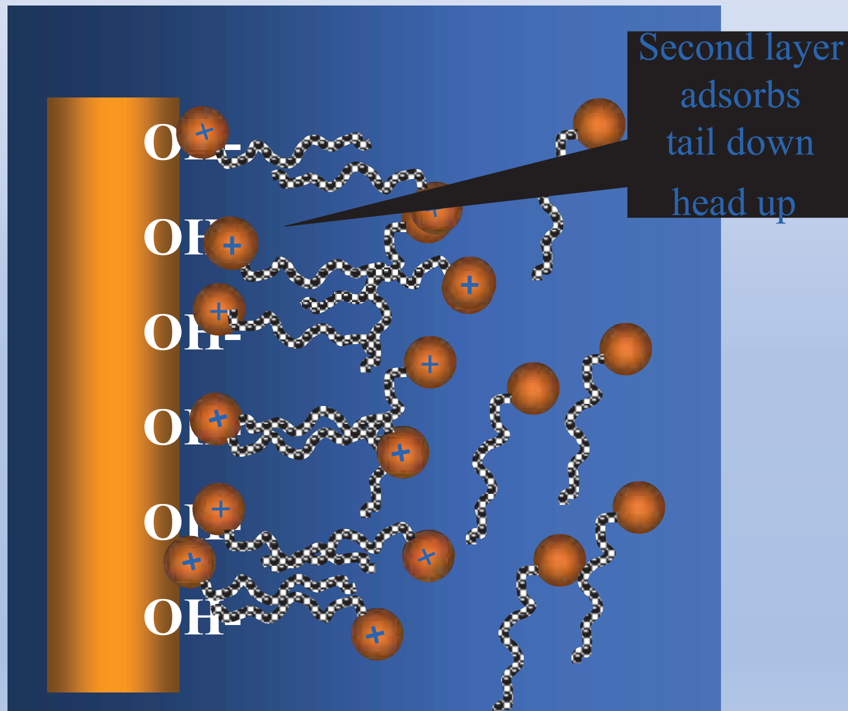
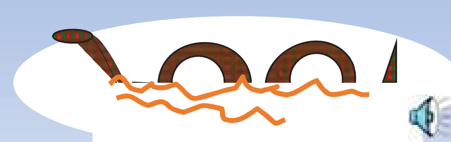
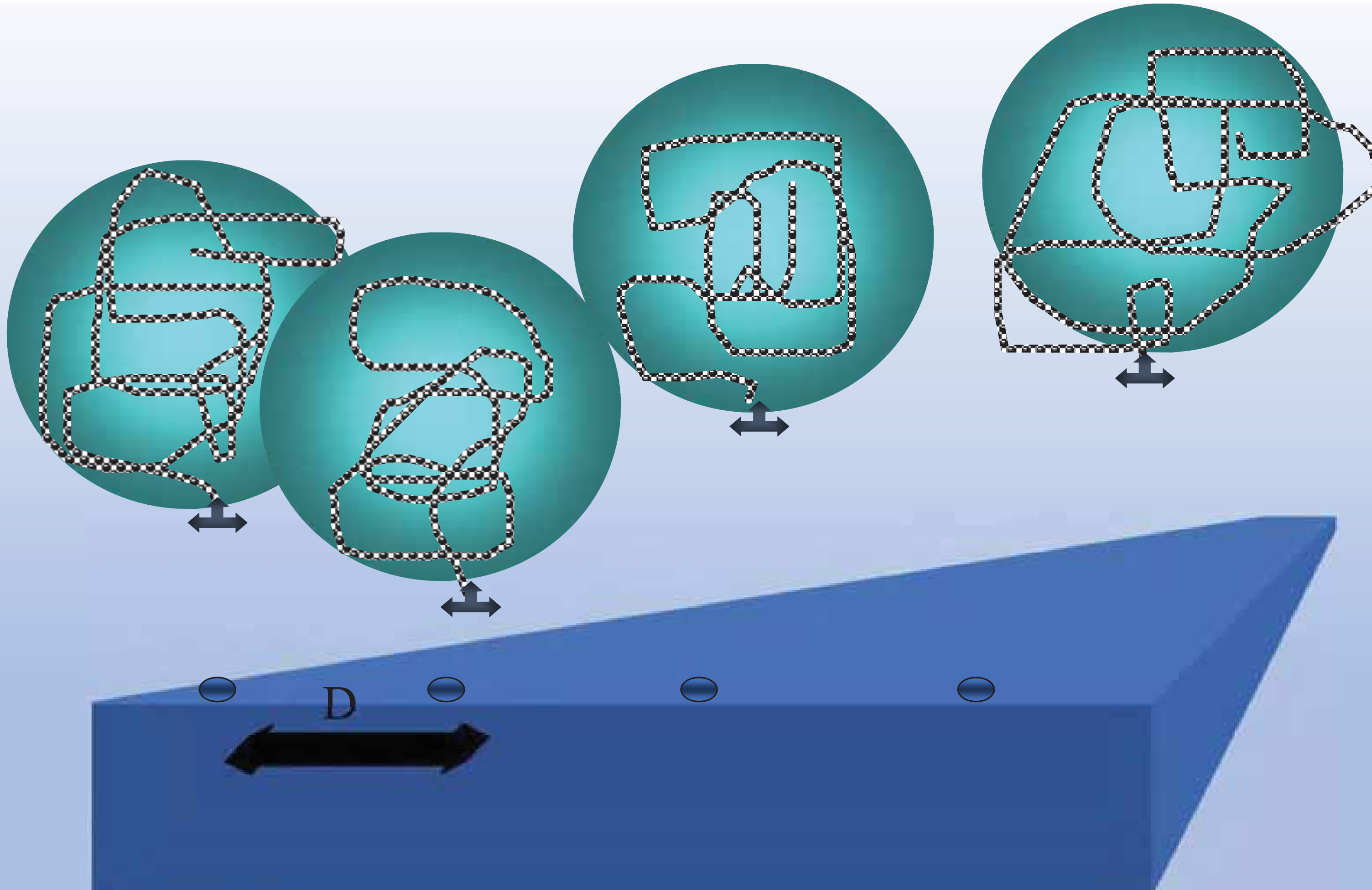
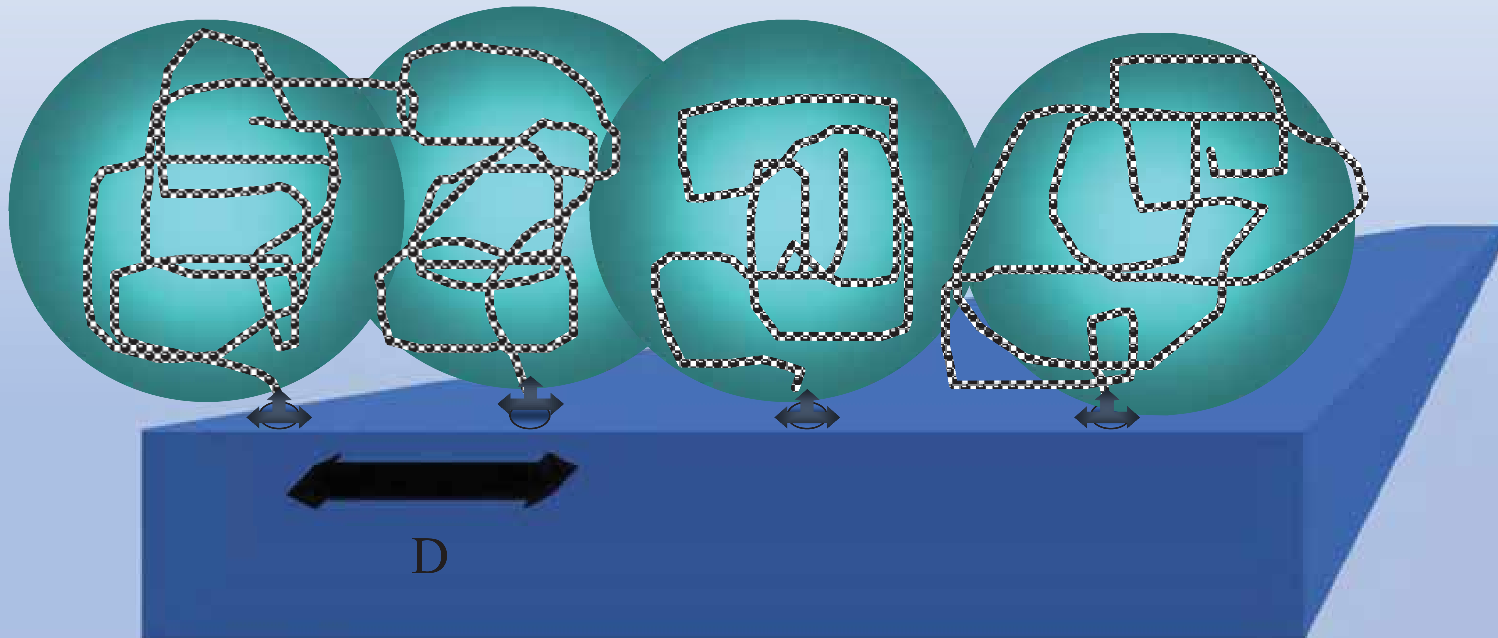


WATER -SOLUBLE AND SWELLABLE POLYMERS AT INTERFACES





ADSORPTION AS MUSHROOMS



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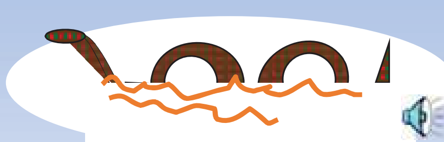

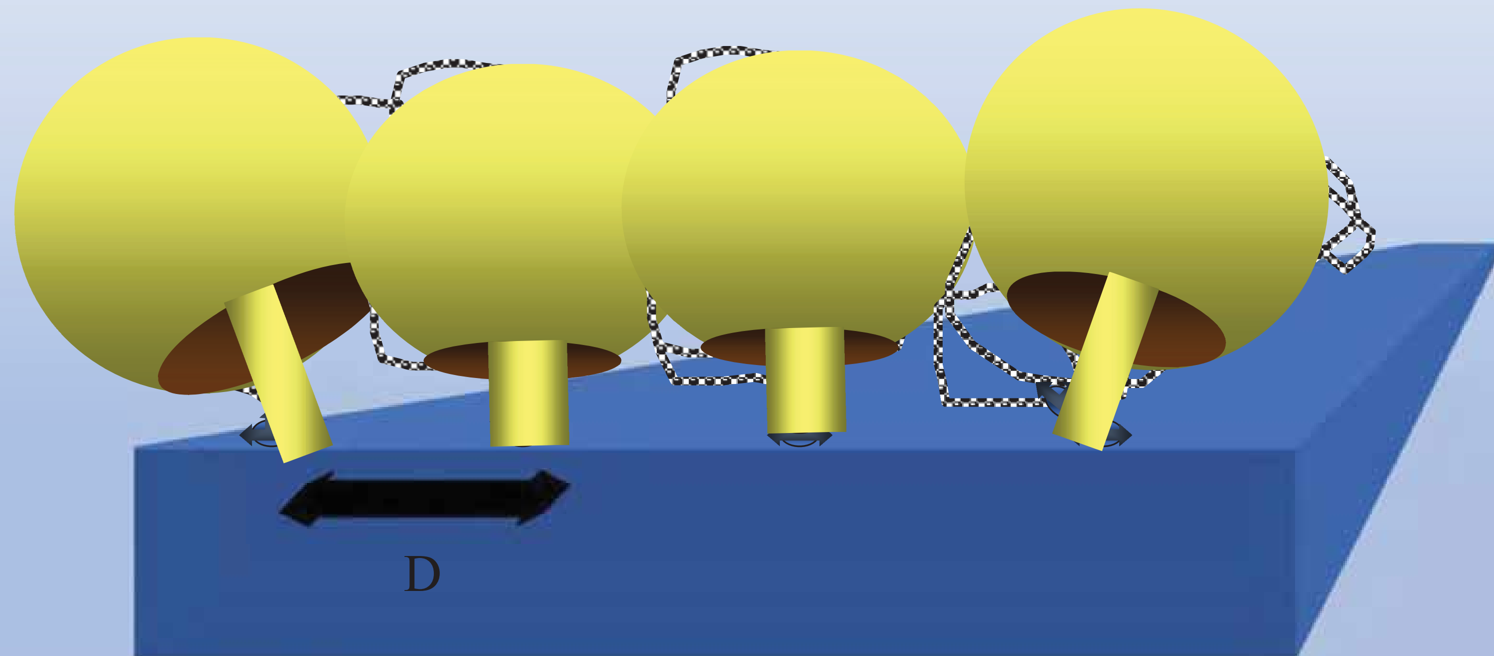

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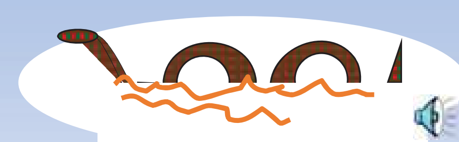

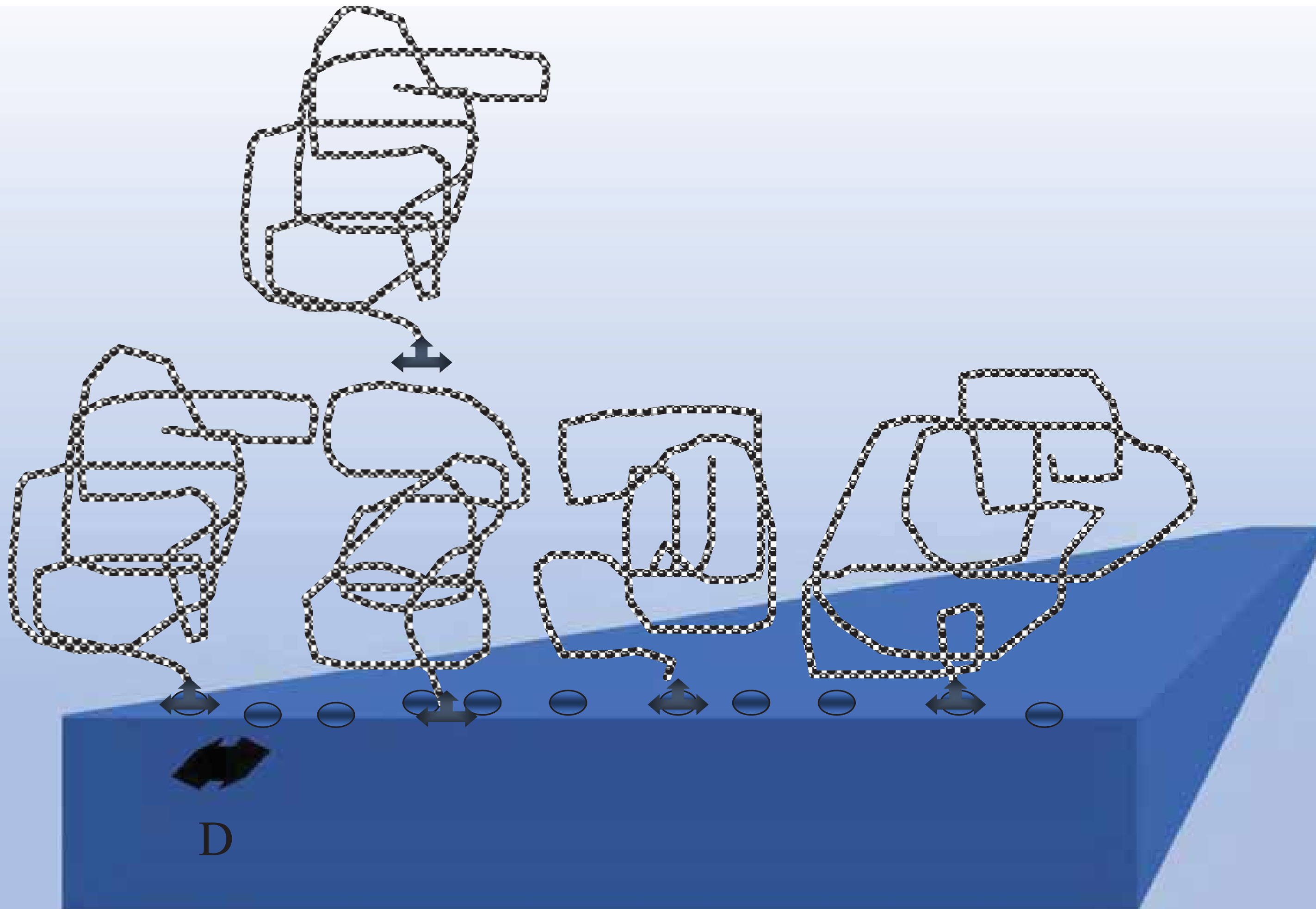

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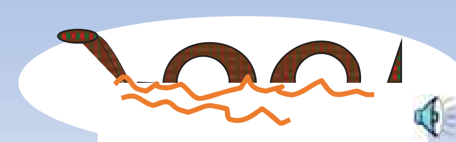
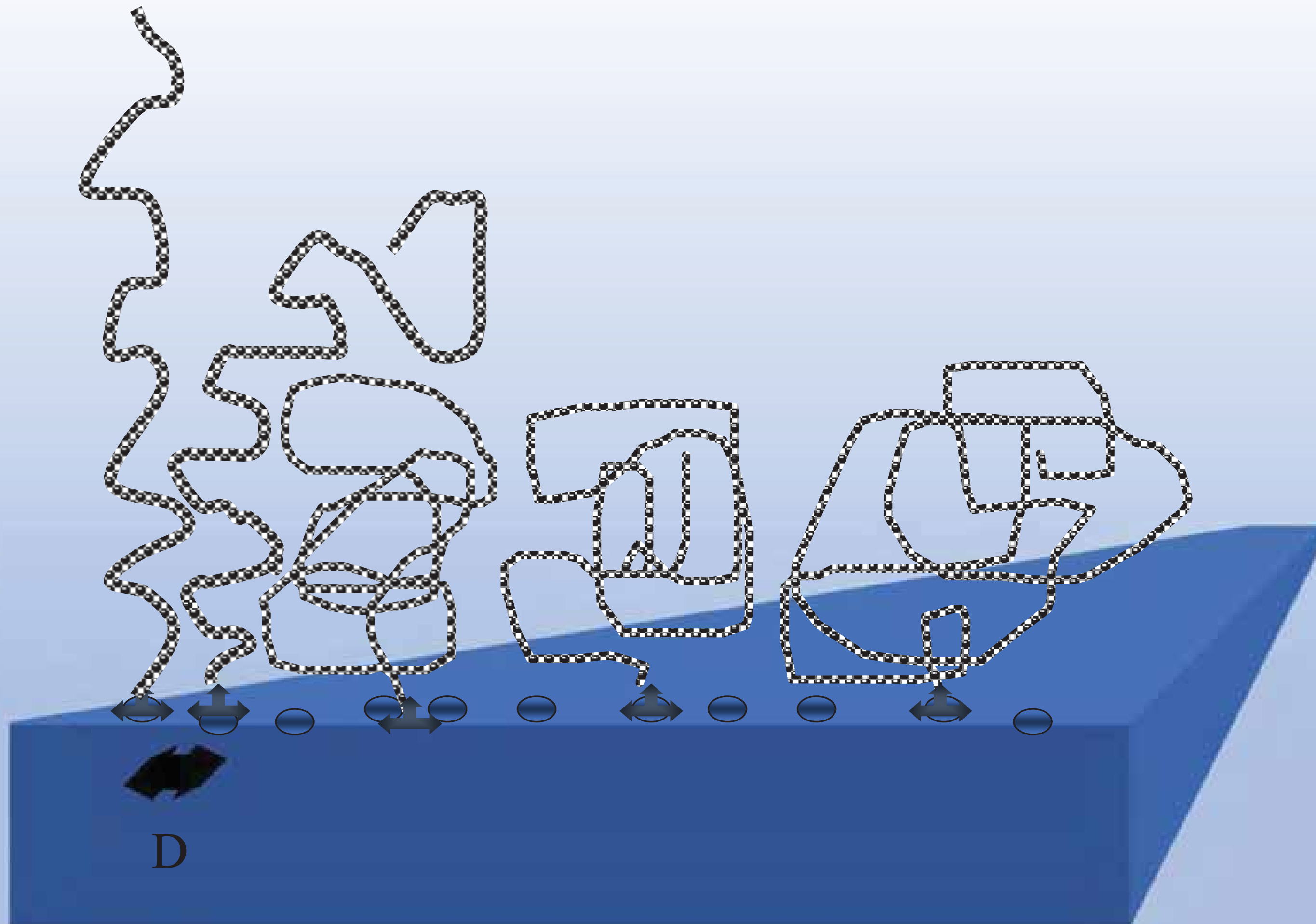
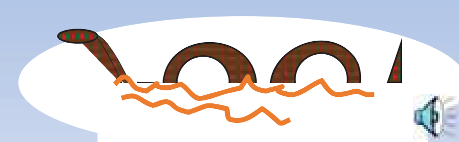
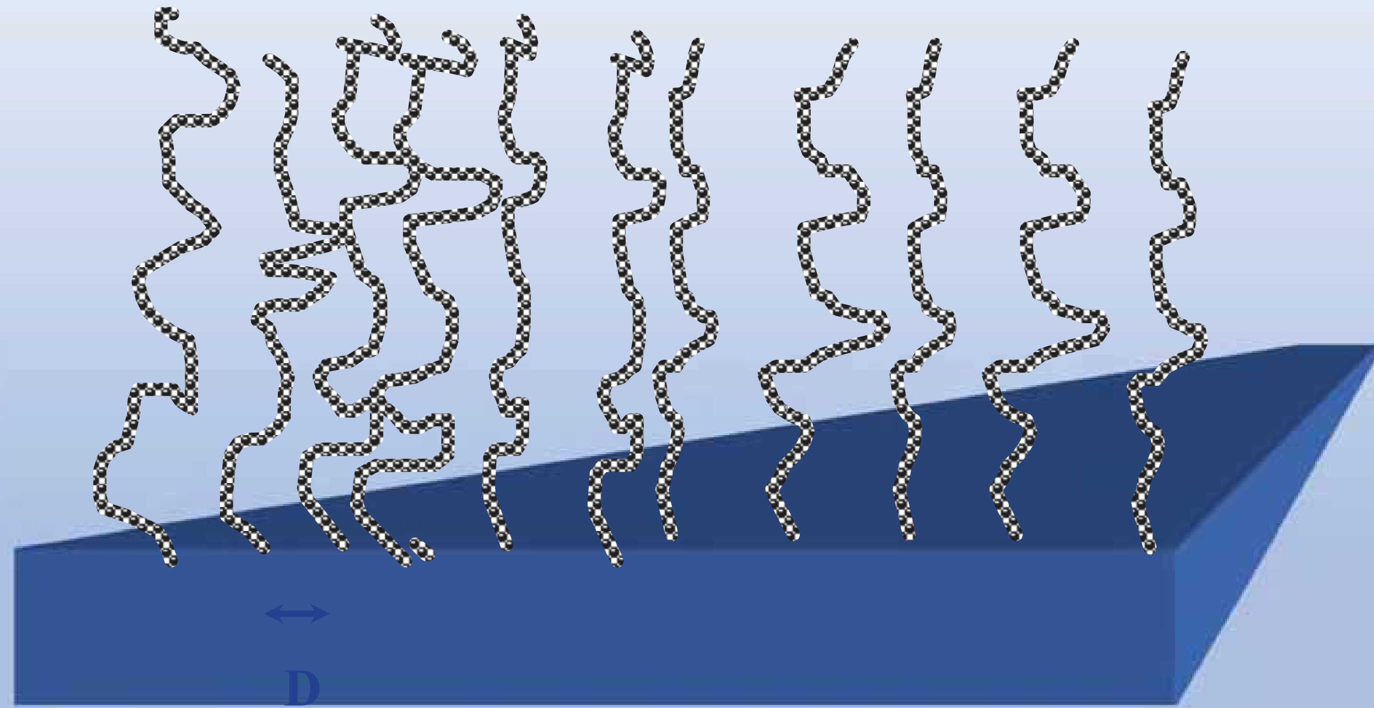




ADSORPTION AS BRUSHES





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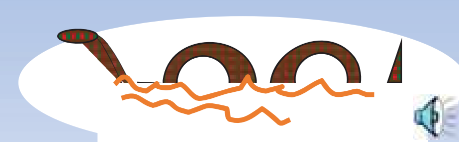
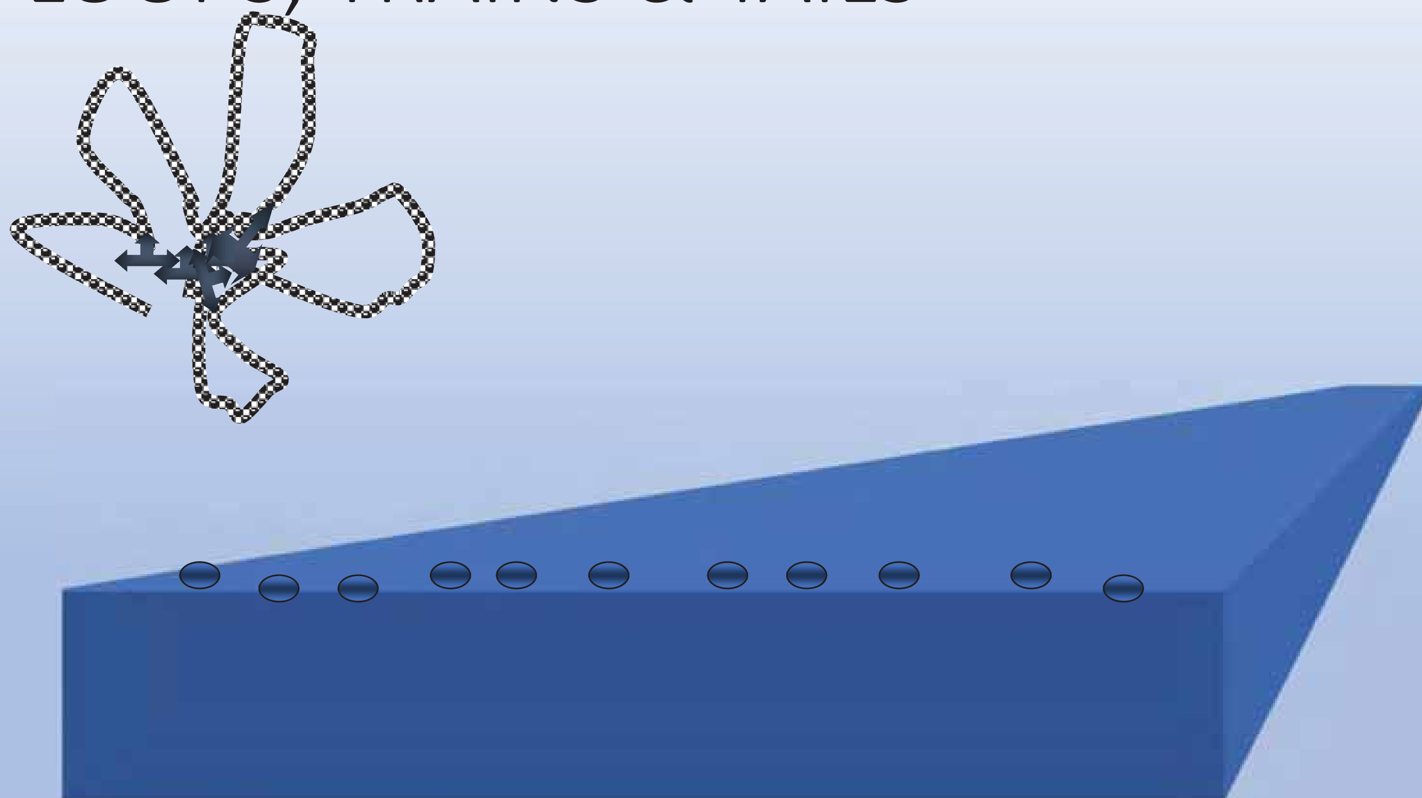
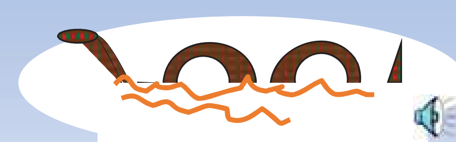


LOOPS, TRAINS & TAILS





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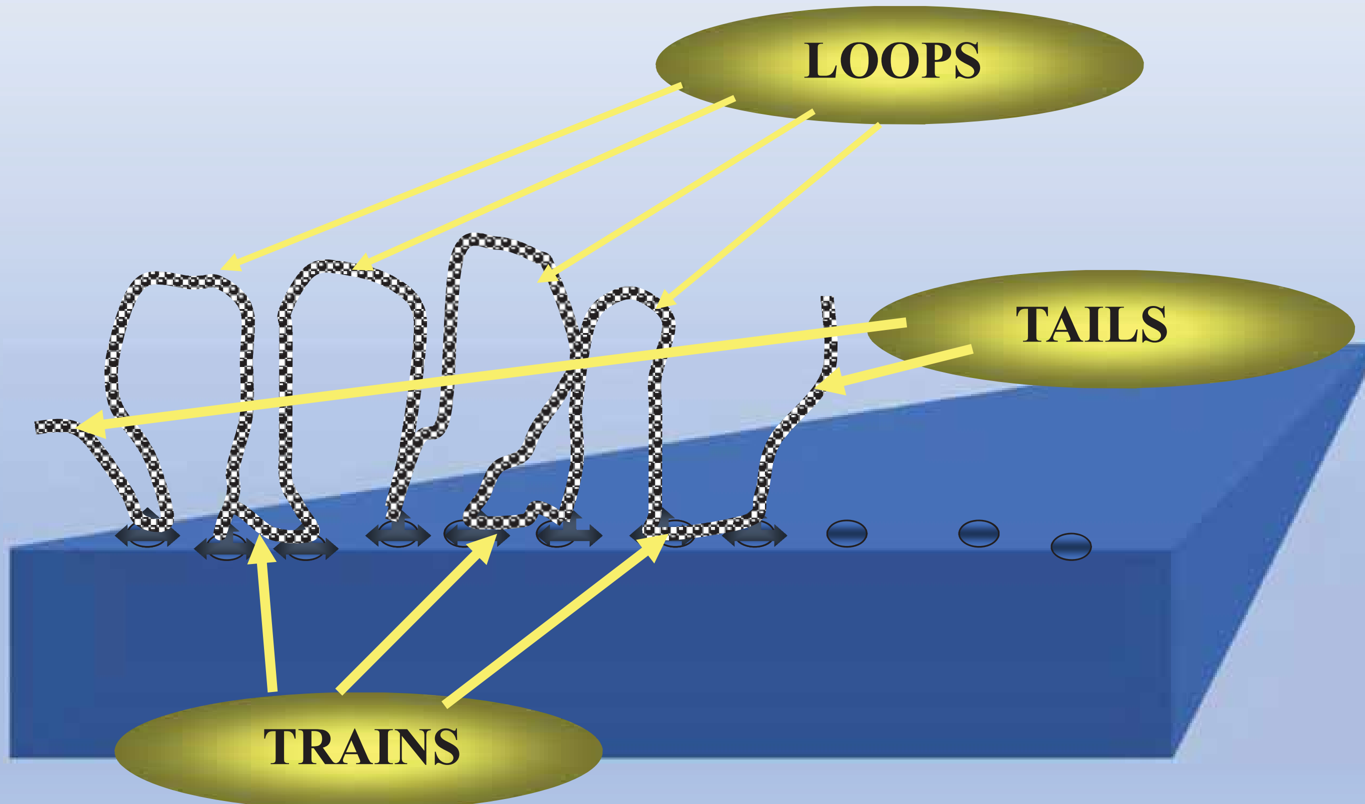
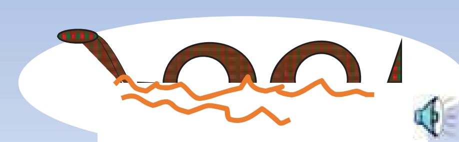
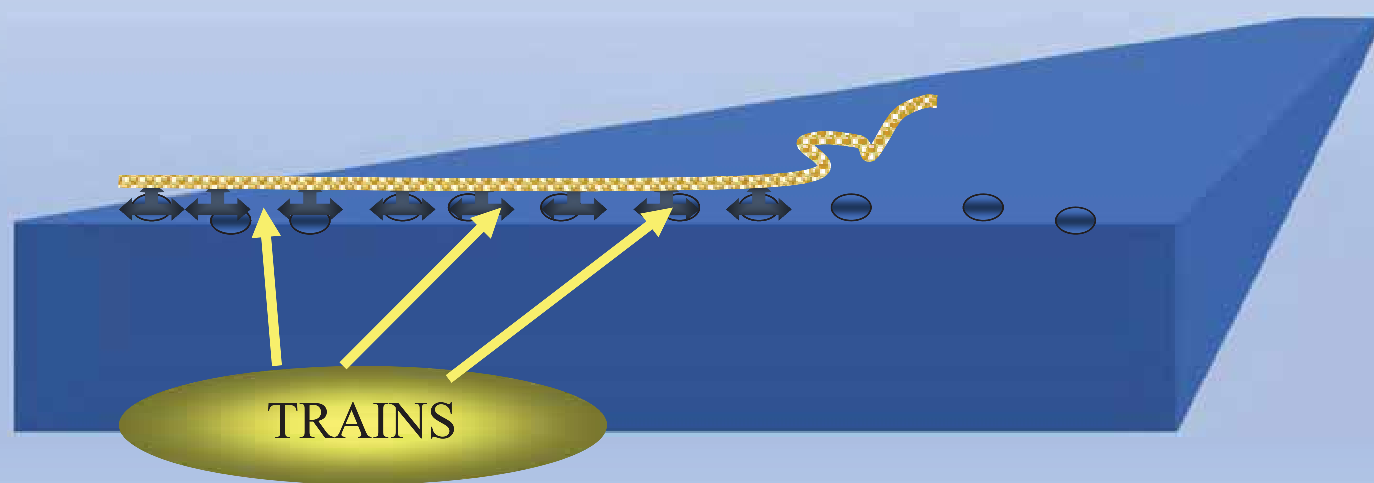
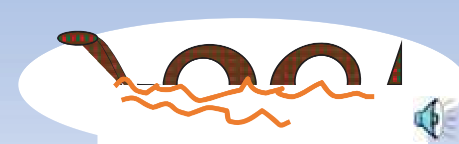




Strong Interaction





Vinylpyrrolidone/ dimethylaminoethylmethacrylate Copolymer

- The isoelectric point of hair is ~pH 5
- Cationic polymers show enhanced substantivity to hair
- Control ionic repulsion at hair surface
- Note:
  - Flyaway arises from triboelectric charging

QUATERNIZED PVP/DIMETHYLAMINOETHYL METHACRYLATE COPOLYMER *(Polyquaternium 11)*

- Quaternization assures substantivity to hair under alkaline conditions-Important when formulating high pH cold wave lotions
- Cationic polymers used in conditioning and soft-setting formulations:
  - Aid in detangling during combing of wet hair
  - Easily removed by shampoo

QUATERNIZED PVP/DIMETHYLAMINOETHYL METHACRYLATE COPOLYMER *(Polyquaternium 11)*

- Ideally suited for styling lotions (commonly called glazes), gels and aerosol foams (mousses) because of good wet combing and easy setting
- When dry, they can give a crisp shiny curl (wet look)
  - These curls can be combed out with minimum of flaking, resulting in a conditioned styled look
- Improve condition of damaged hairs. Making their surfaces smooth and increasing strength

Polyquaternium-6
(Merquat 100 –Nalco)

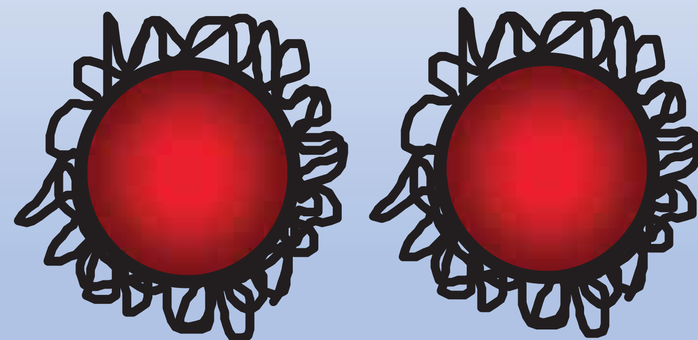
- Polydiallyldimethylammonium chloride)
- Excellent substantivity to skin and hair
  - Confers conditioning benefits
- Does not form films
- Poor compatibility with anionic ingredients

Polyquaternium-7

(Merquat 550 & S –Nalco)

- Poly(acrylamide-*co*-diallyldimethylammonium chloride)
- Excellent substantivity to skin and hair
  - Confers conditioning benefits
- Forms films
- Good compatibility with anionic surfactants

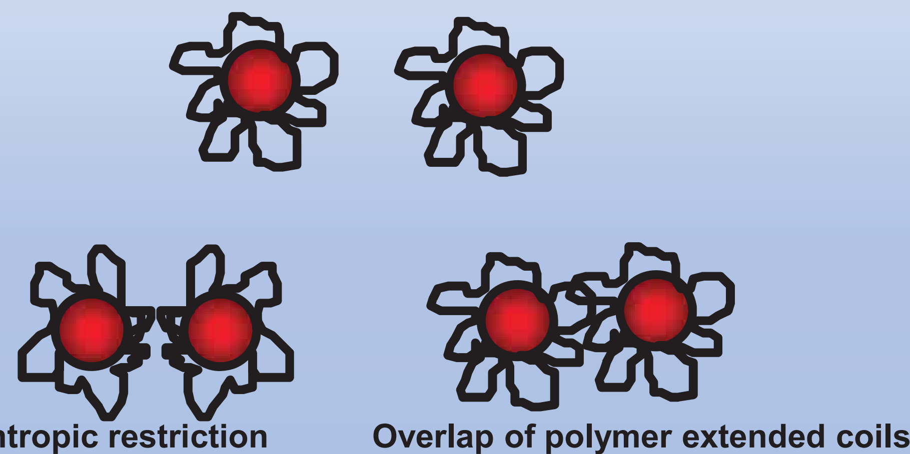
Steric Stabilization



The stabilization of emulsions by polymer adsorbed at the interface between the dispersed and continuous phases

Napper, D.H.; Polymeric Stabilization of Colloidal Dispersions, **Academic Press, 1983**
Vincent, B.; Whittington, S.; In Colloid and Surface Science; **Matijevic, E., Ed.; Plenum: 1982**

Mechanisms of Steric Stabilization



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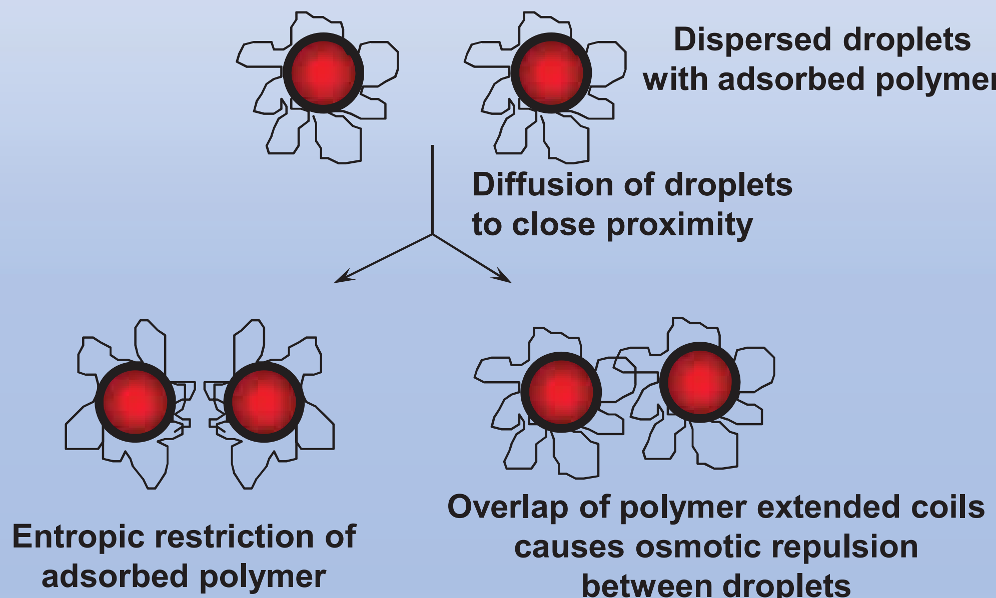
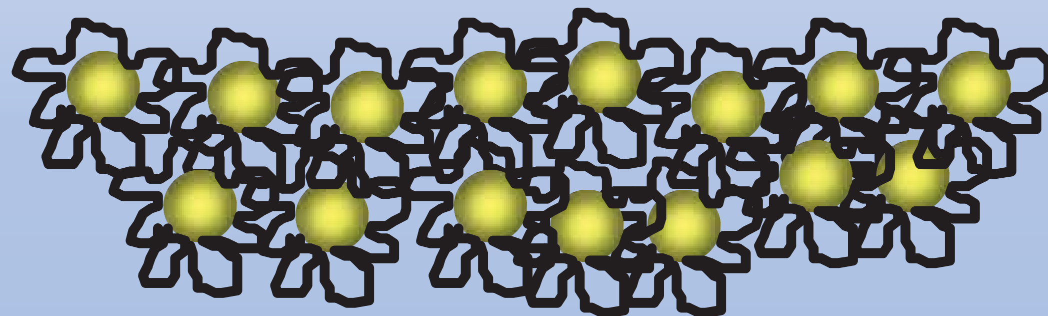
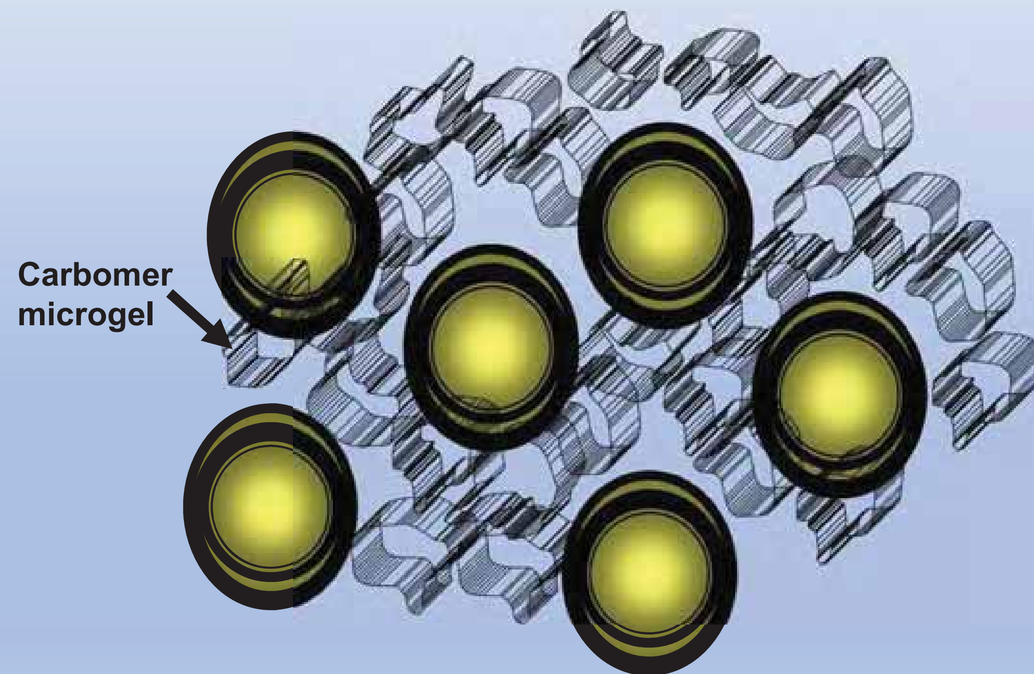


…but Steric Stabilization Does Not Stabilize Against Creaming or Sedimentation

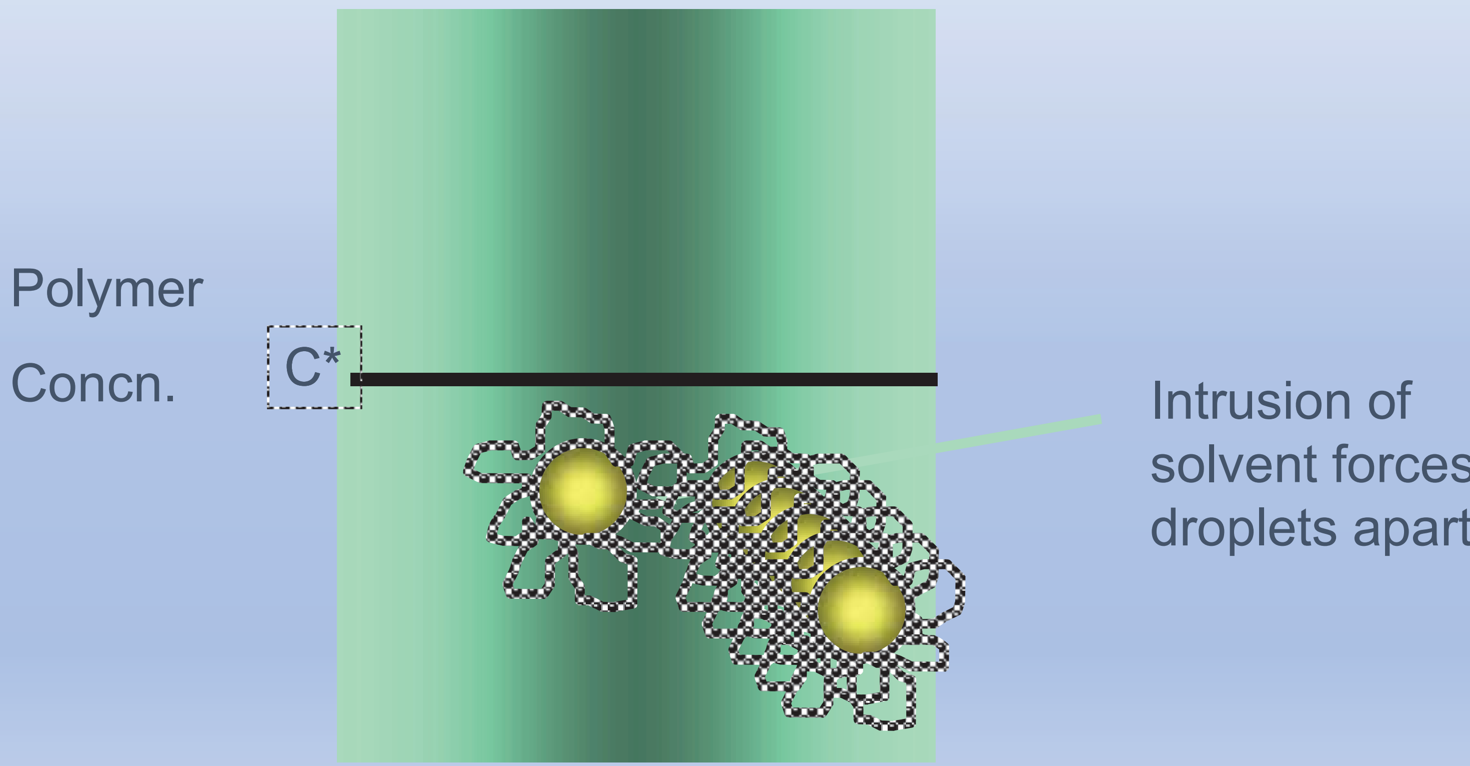


…Microgel Thickeners Can Be Used to Stabilize Against Creaming



Polymeric Emulsifiers

The Consequence of Critical Overlap on Steric Stabilization



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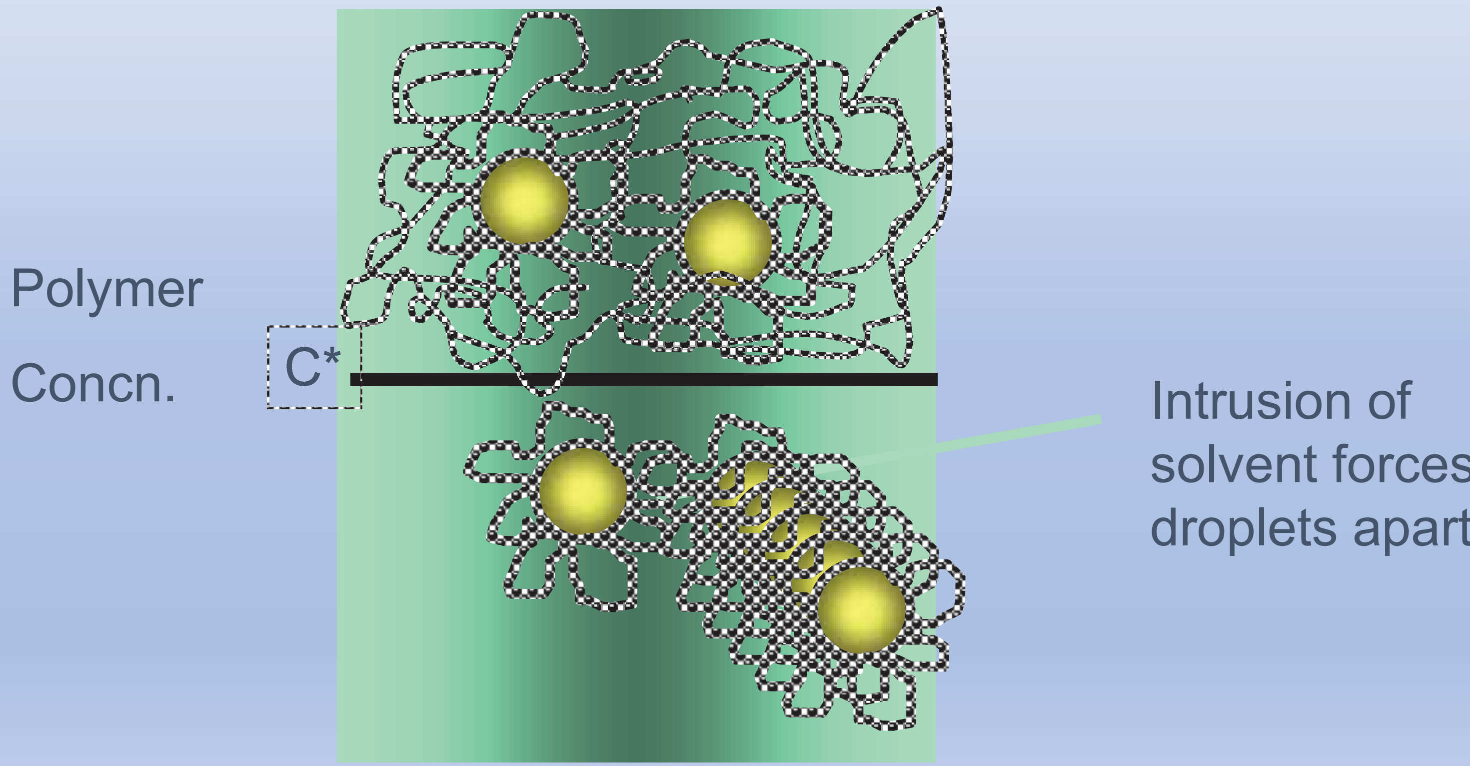

HUGGIN'S PLOT BY CONTRAVES FOR AQUEOUS HMPAA AT pH = 5.5