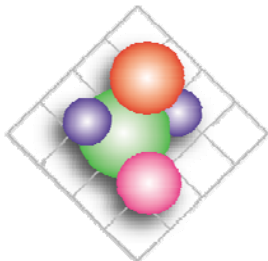


# Basic Forces in Particle Adhesion

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# Course Outline

## Adhesion of Particles to Surfaces

- Overview of forces of adhesion

- Forces in dry systems



- Forces in aqueous systems



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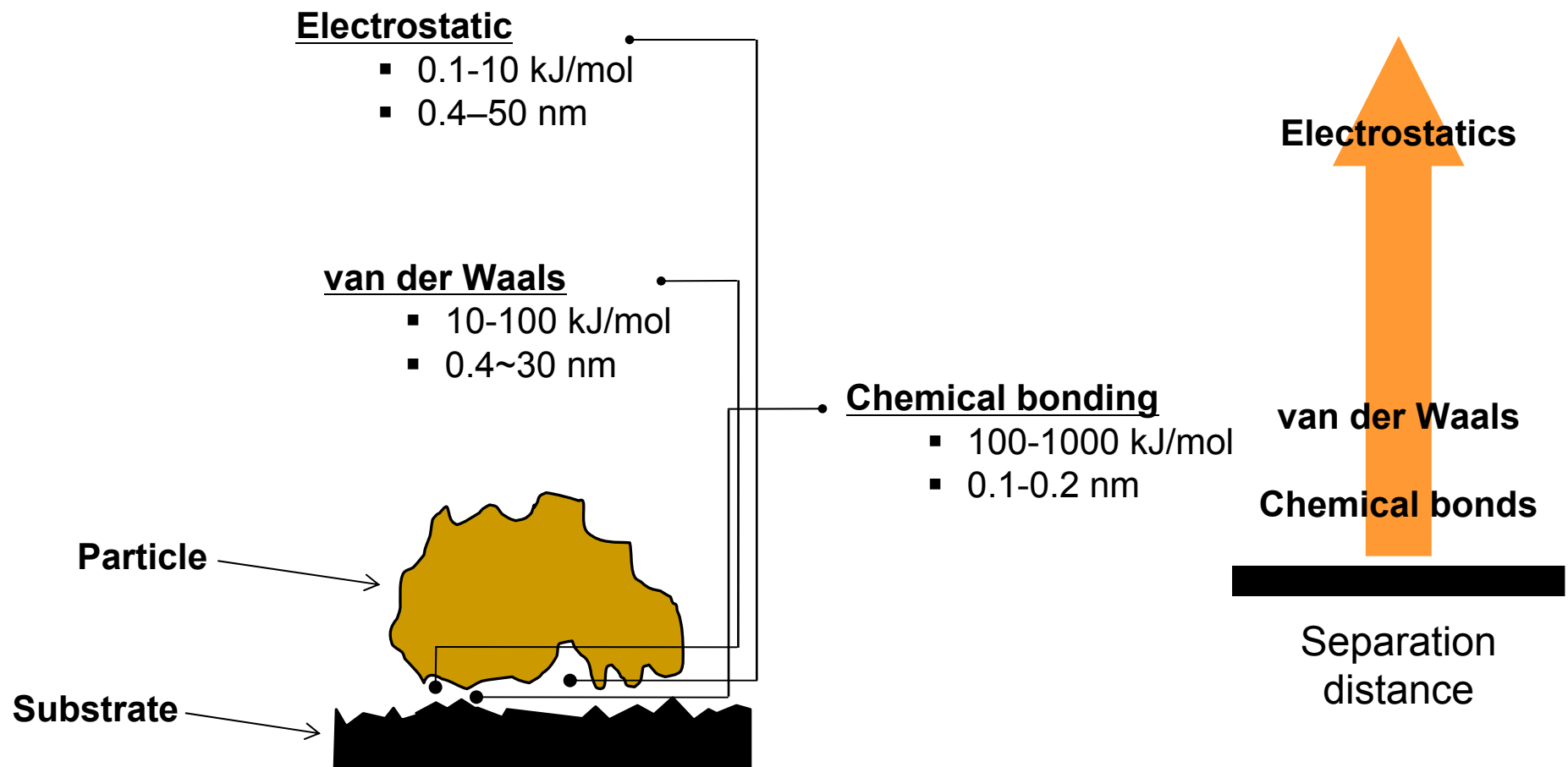
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# Forces of Adhesion: Dry Systems

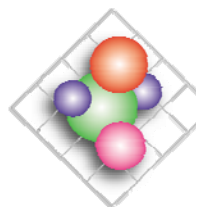
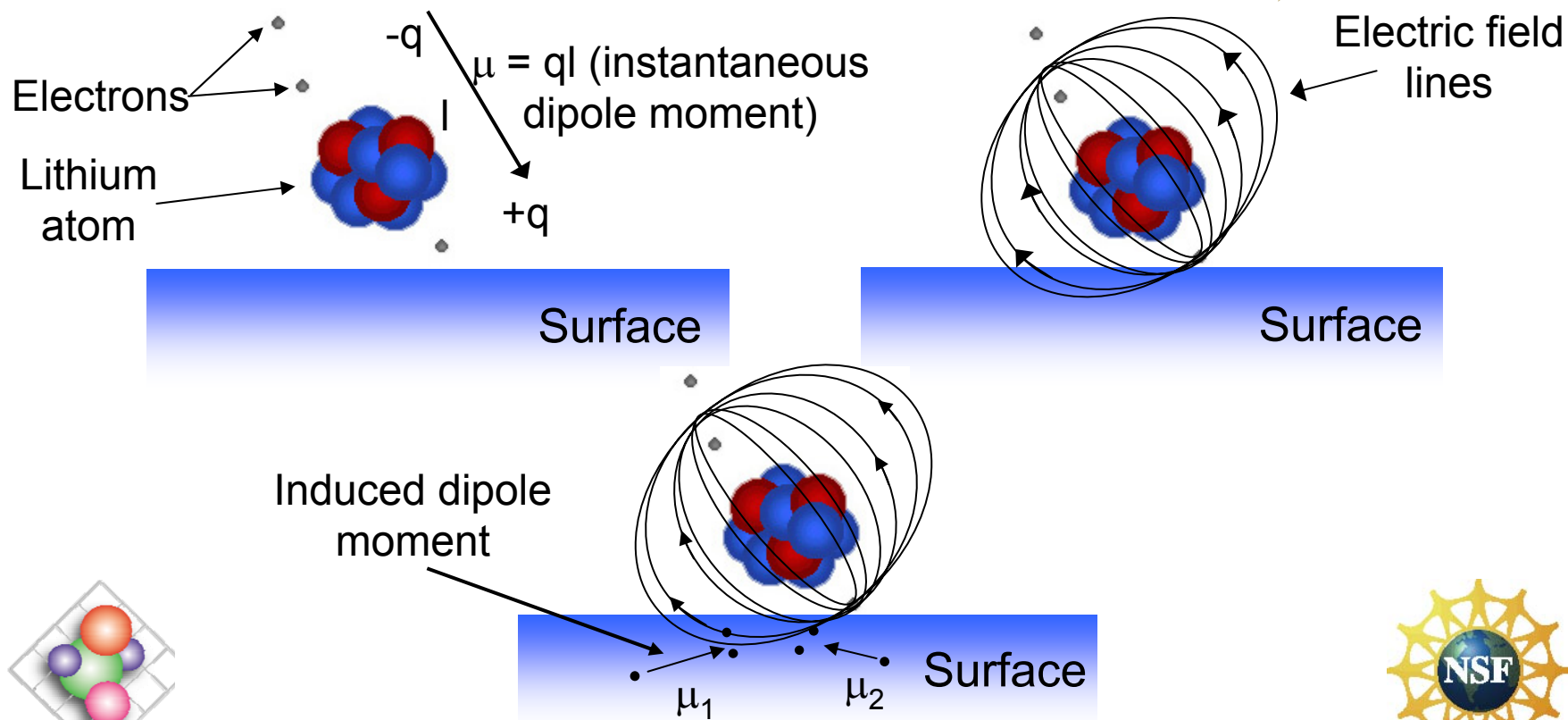
Understanding particle adhesion depends on understanding dominant forces as a function of system parameters



# van der Waals (vdW) Force

$$F_{\text{vdW}} = F_{\text{Keesom}} + F_{\text{Debye}} + F_{\text{London}}$$

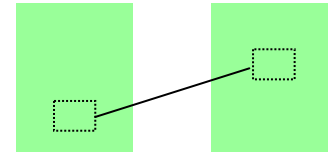
induced-permanent   
 permanent-permanent   
 induced-induced



# Describing vdW Forces

## Engineering Approach

Point-by-point additivity  
(molecule to molecule or atom to atom)

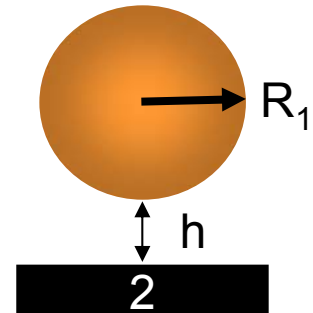


$$dU_{12} = - \frac{C_{12} \rho_1 \rho_2 dV_1 dV_2}{\left\{ (x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2 \right\}^{\frac{3}{2}}}$$

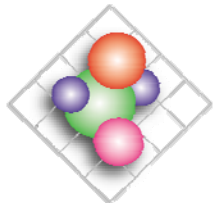
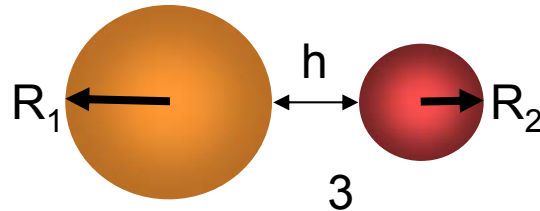
Hamaker Constant,  $A_{12}$

## Approximate Force Solutions

$$F = \frac{-A_{12} R_1}{6h^2}$$



$$F = \frac{-A_{12}}{6h} \frac{R_1 R_2}{R_1 + R_2}$$



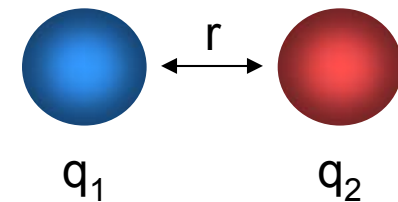
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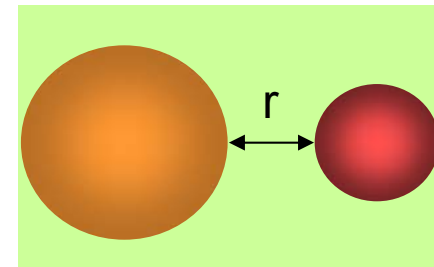
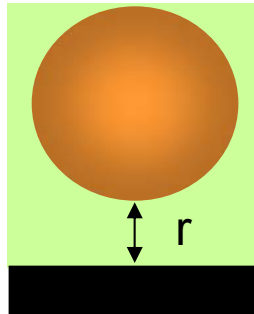


# Electrostatic (ES) Forces

In air or a vacuum or an ion-free liquid if the particle other surface with which the particle is interacting are not moving



$$F = \frac{q_1 q_2}{4\pi\epsilon\epsilon_0 r^2}$$



Must integrate over all point charges in both objects -> More later



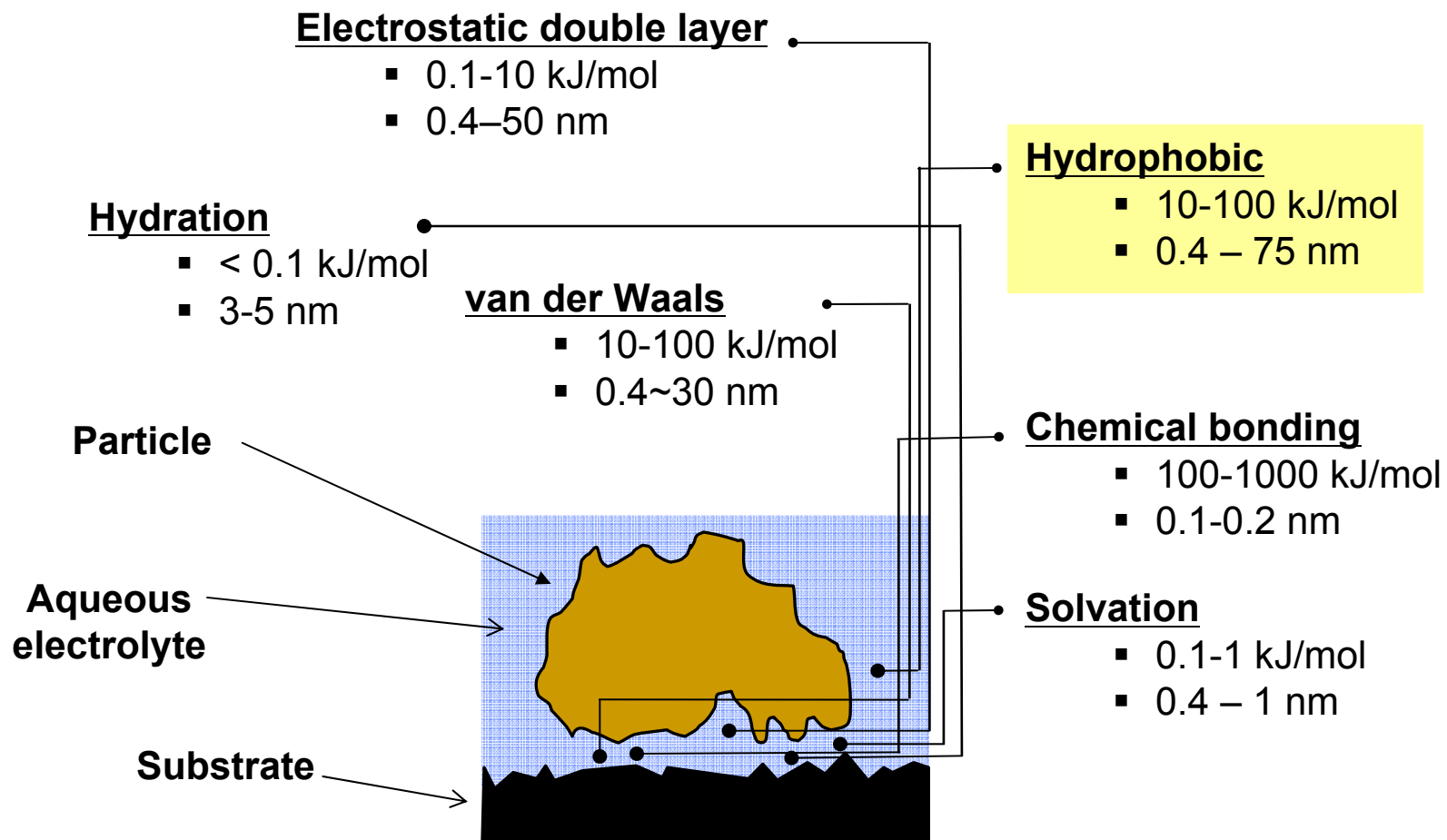
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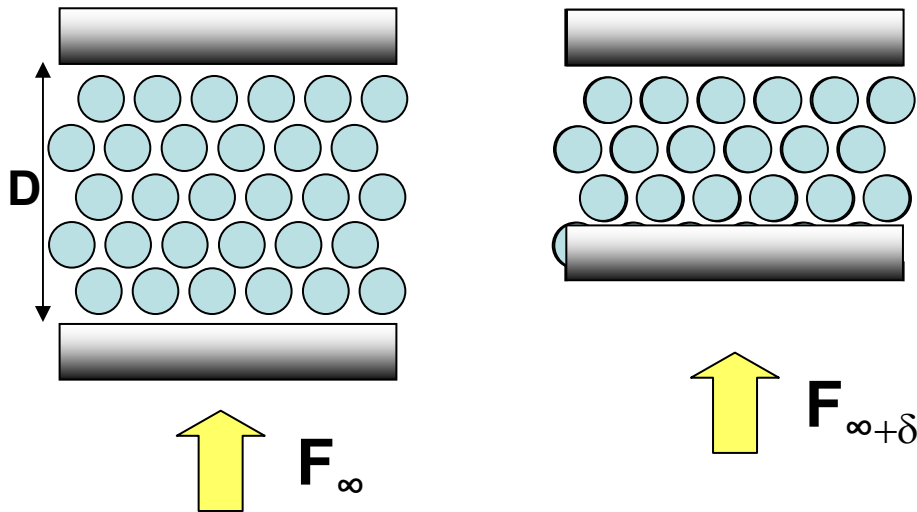


# Forces of Interest: Aqueous Systems

Understanding particle adhesion depends on understanding dominant forces as a function of system parameters



# Solvation Forces



$D \Rightarrow \infty$

- Liquid behaves as bulk
- Pressure change required to decrease  $D$  is predictable

- As  $D \Rightarrow 0$
- New forces arise when liquid molecules orient into discrete layers between solid surfaces
  - May involve liquid-solid and liquid-liquid interactions
  - May involve geometry only
- Oscillatory character
  - One layer at a time is removed

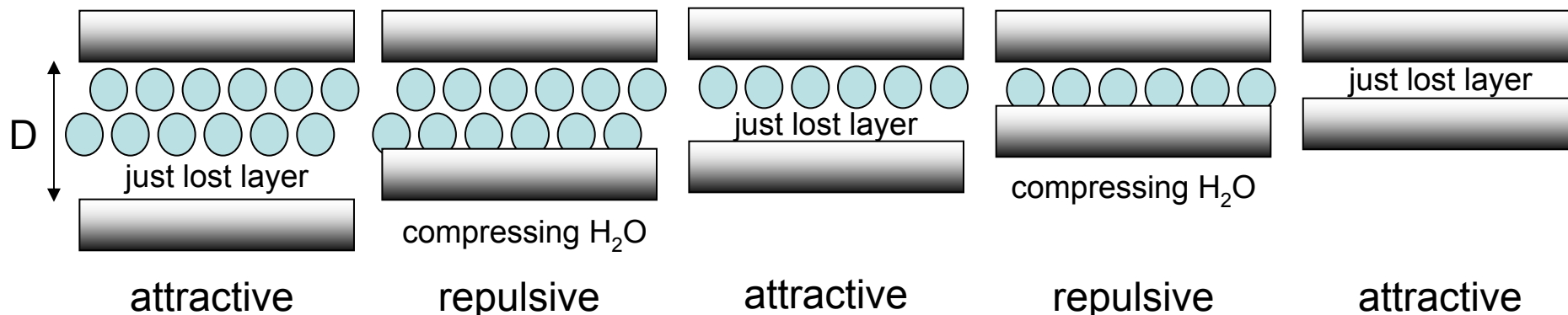


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# Solvation Force



Consider differential pressure between that required to reduce  $D$  in the bulk ( $D \Rightarrow \infty$ ) and that required to reduce  $D$  as  $D \Rightarrow 0$

$$P_s^D = k_B T \left( \rho_s^D(0) - \rho_s^\infty \right)$$

$$\lim_{D \rightarrow 0} (P) = -k_B T \rho_s^\infty \Rightarrow \text{force is attractive}$$



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# Hydration Force

- Controversial
  - Origin and magnitude not known
  - May be on order of measurement error in adhesion force

May be a specific case of solvation

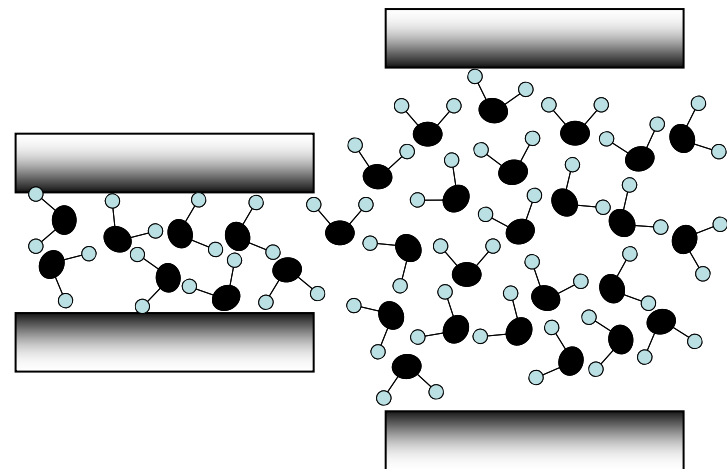
$$F_{hyd} = \eta R e^{-\tau D}$$

$\eta$  = viscosity

$R$  = solvent molecular radius

$\tau$  = decay length (= 0.41nm for pure water)

$D$  = separation distance



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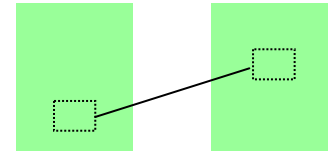
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# Describing vdW Forces

## Engineering Approach

Point-by-point additivity  
(molecule to molecule or atom to atom)

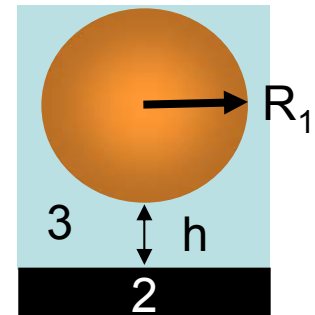


$$dU_{12} = - \frac{C_{12} \rho_1 \rho_2 dV_1 dV_2}{\left\{ (x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2 \right\}^{\frac{3}{2}}}$$

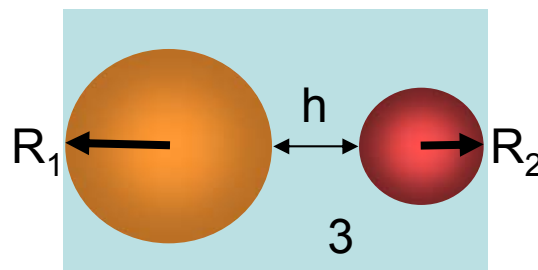
Hamaker Constant,  $A_{12}$

## Approximate Force Solutions

$$F = \frac{-A_{132} R_1}{6h^2}$$



$$F = \frac{-A_{132}}{6h} \frac{R_1 R_2}{R_1 + R_2}$$



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# Hydrophobic Interactions

- **Controversial**

- Require particles and surfaces to be somewhat/highly hydrophobic
- Physical idea
  - Particles and surfaces are hydrophobic
  - Bringing particles and surfaces together in aqueous solution reduces contact area of hydrophobic surface and water
- Quantitative models very complex

- **Most cited approach**

$$\gamma_A = \gamma_{vdW} + \gamma_{AB} + \gamma_E$$

- Surface tension of object in solution broken into van der Waals (vdW), electrostatic (E), and acid-base (AB) terms
  - AB is origin of hydrophobic effect



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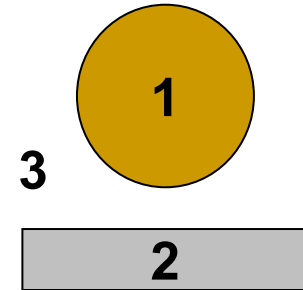


# Hydrophobic Interactions, cont'd

- Each surface tension component for vdW and AB force rewritten based on combining rules and free energy (Dupré)

$$\Delta G_{123}^{vdW} = \gamma_{12}^{vdW} - \gamma_{13}^{vdW} - \gamma_{23}^{vdW}$$

*for materials in medium 3*



- Then one rewrites the mixed vdW interfacial tensions using more combining rules
  - Goal: write free energies in terms of surface tensions of individual species

$$\gamma_{12}^{vdW} = \gamma_1^{vdW} + \gamma_2^{vdW} - 2\sqrt{\gamma_1^{vdW} \gamma_2^{vdW}}$$



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# Hydrophobic Interactions, cont'd

- Final relation

1 = particle, 2 = substrate, 3 = liquid

$$\Delta\Delta G_{\lambda}^{TOT} = \left( \Delta G_{\lambda}^{TOT} - \Delta G_{\lambda}^{TOT} \right) + \left( \Delta G_{131,\lambda_0}^{EL} - \Delta G_{232,\lambda_0}^{EL} \right)$$



$$\left( \Delta G_{\lambda}^{TOT} - \Delta G_{\lambda}^{TOT} \right) \exp \left[ \frac{h_o - h}{\lambda} \right]$$

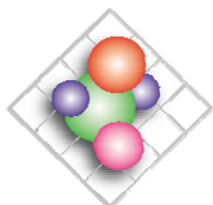
$$\left[ \frac{h_o - h}{\lambda} \right]$$

- Difficulties

- Many en
- Predictio
- Predictio

sical basis

S

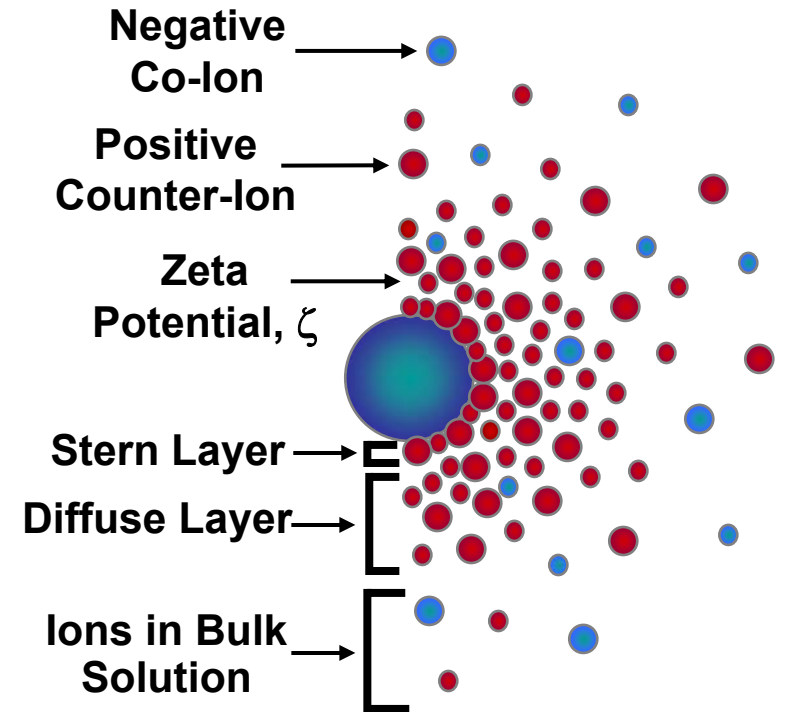
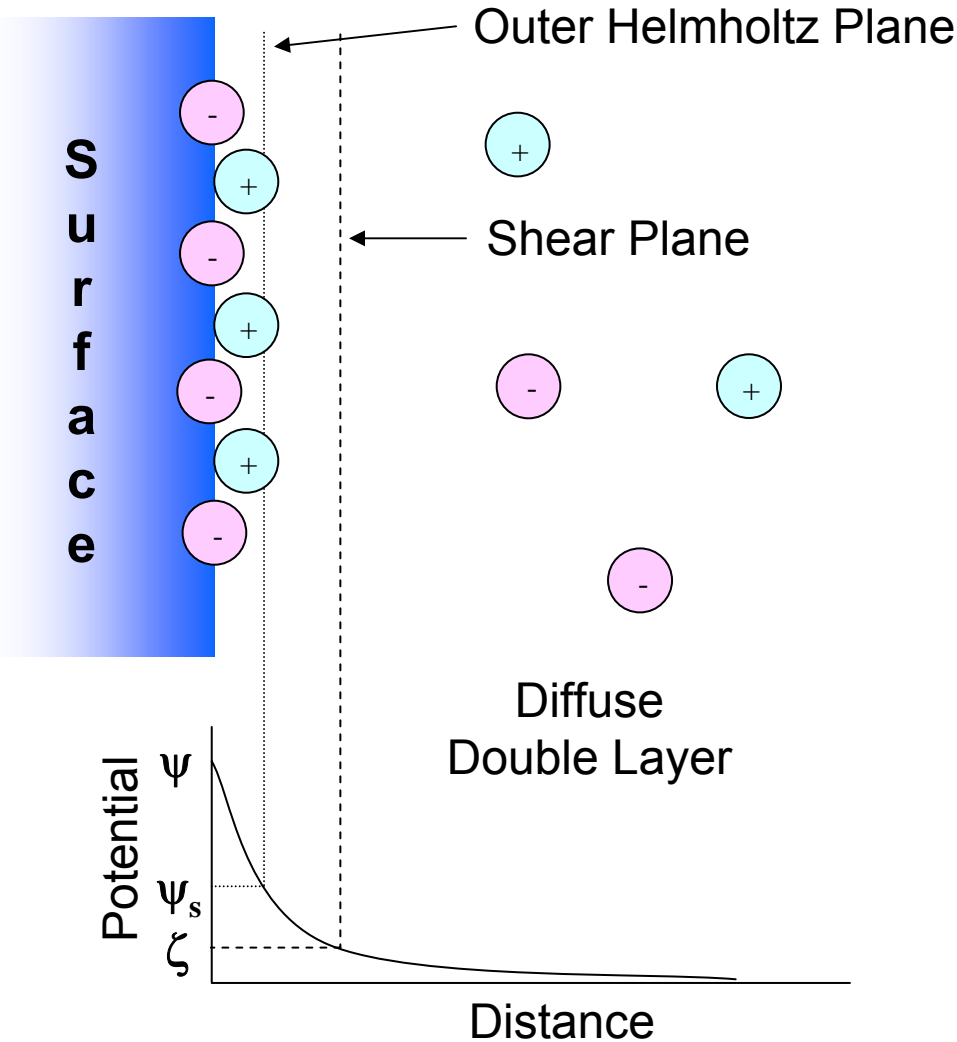


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# Electrostatic Double Layer (EDL) Force



$\psi$  usually approximated by  $\zeta$

# Electrostatic (ES) Forces

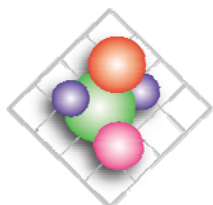
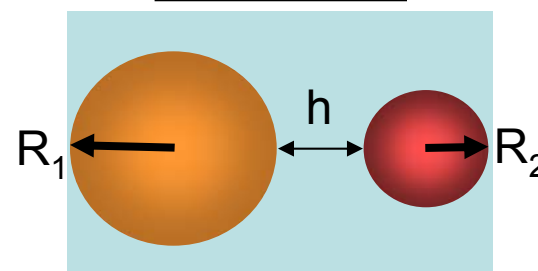
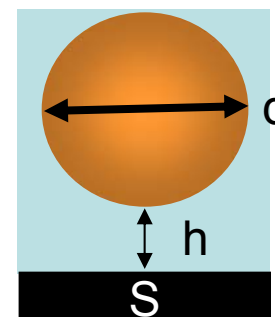
In aqueous solution,  
approximate solution (low  
potentials on surfaces)

$$\nabla^2 \psi = \kappa^2 \psi \quad \kappa = \sqrt{\frac{e^2 \sum_i z_i^2 n_{i0}}{\epsilon_0 \epsilon_r k_B T}}$$

Linearized Poisson-Boltzmann equation

$$F = \frac{\epsilon \epsilon_0 d \kappa e^{-\kappa h} (\psi_p^2 + \psi_s^2)}{4 (1 - e^{-2\kappa h})} \left( \frac{2\psi_p \psi_s}{(\psi_p^2 + \psi_s^2)} + e^{-\kappa h} \right)$$

$$F = \frac{\kappa^2 \epsilon_0 \epsilon_r}{2 \sinh^2(\kappa h)} (2\psi_1 \psi_2 \cosh(\kappa h) - \psi_1^2 - \psi_2^2)$$



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# Summary

1. Have reviewed forces that dominate interactions between particles and surfaces in various environments
2. Engineering equations exist for most cases, in relatively simple form for idealized systems
  1. Well-defined geometries
  2. Well-behaved solutions



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