Theory of Colloid Stability

1. Introduction

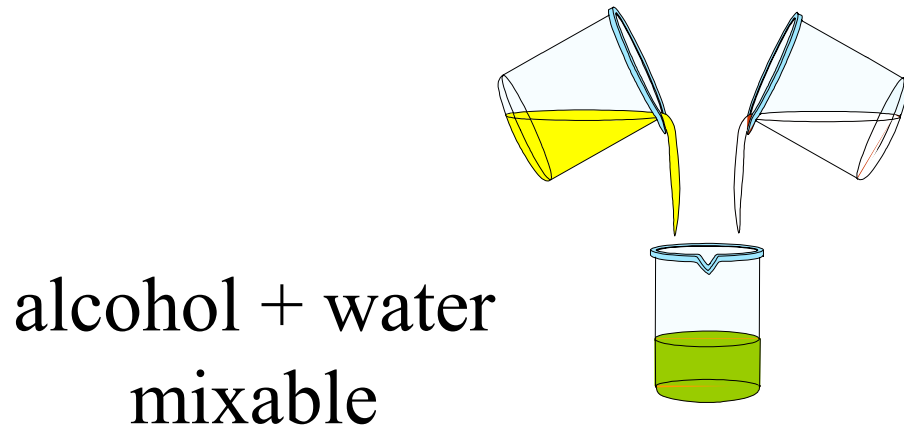### Colloid science in a nutshell

2. Solutions and dispersions

3. Colloid stability

The main cast and DLVO theory

Colloid science

To mix or not to mix, that is the question !
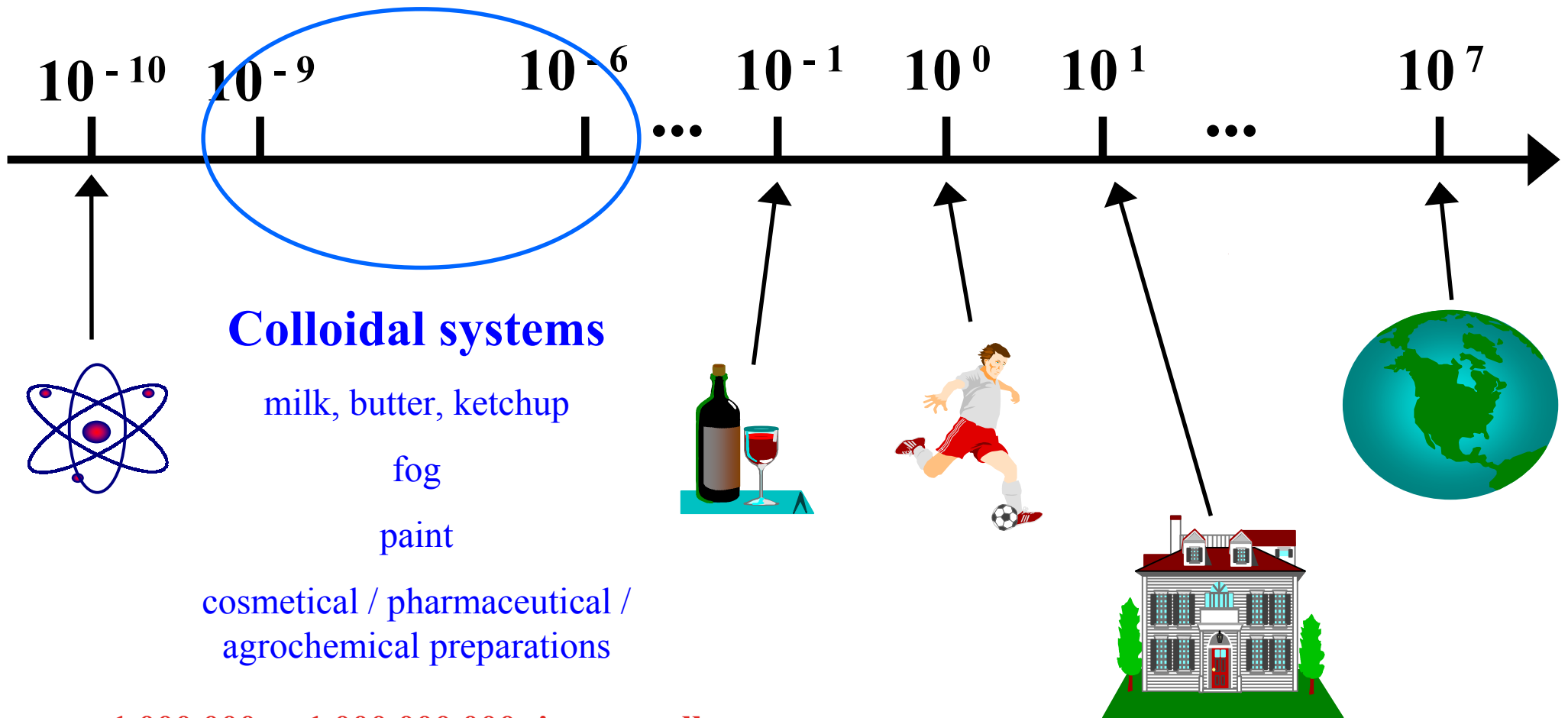

alcohol + water
mixable

oil + water
unmixable

A colloid scientist wants to:

1. mix the unmixable ⟶ colloidal dispersions
2. keep it mixed ⟶ colloid stability

Colloid science … ?

size (meter)

$$10^{-10} \quad 10^{-9} \quad 10^{-6} \quad \ldots \quad 10^{-1} \quad 10^{0} \quad 10^{1} \quad \ldots \quad 10^{7}$$

Colloidal systems

milk, butter, ketchup

fog

paint

cosmetical / pharmaceutical /
agrochemical preparations

**1.000.000 to 1.000.000.000 times smaller
than a person**

Examples of colloidal dispersions

Food industry

- Dairy products
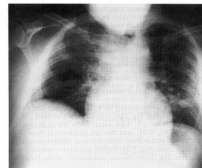- Dressings
- Chocolate
- …

Pharmaceutics and cosmetic

- Water-insoluble pharmaceutics
- All kind of gels, emulsions and cosmetics

Photographic industry

- Photographic emulsions (films)
- X-ray plates and films
- Photocopy materials (paper, ink…)

Electrical an Electronic industry

- Materials for displays:
  - phosphors
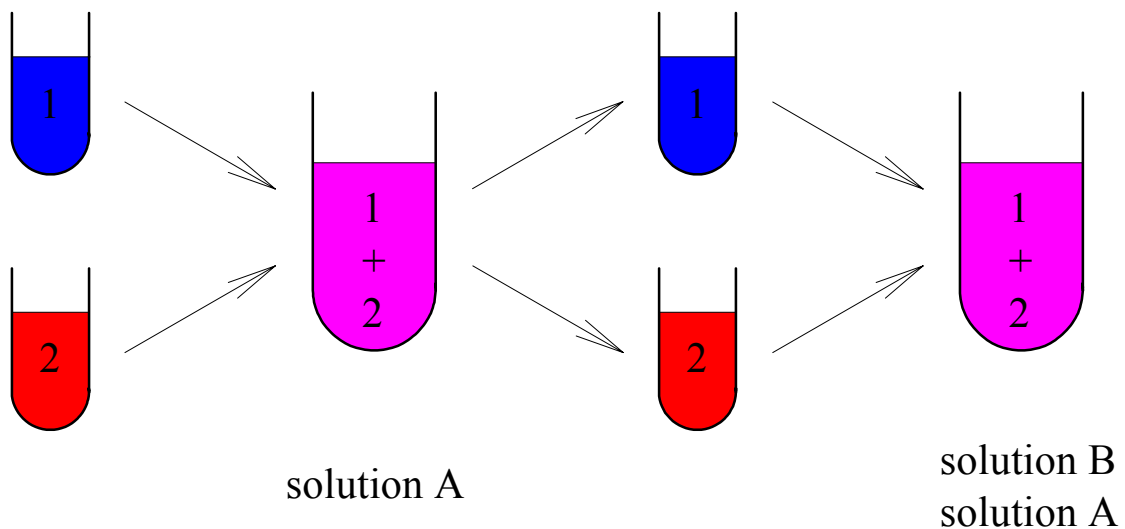 - liquid crystals
  - Isolating materials

Other

- Agrochemicals, paints, dyestuffs, cement, bitumen….

2. To mix or not to mix ?

Solutions

- **Mixing is *SPONTANEOUS***
- **Mixtures are Thermodynamically *STABLE***
- **Inhomogeneities on molecular level**
- **Mixing is *REVERSIBLE***

solution A

solution B
solution A

- **Properties of solution independent on the way it is prepared**

Dispersions

- **Mixing is *NON-SPONTANEOUS* (requires mechanical energy)**

- ***UNSTABLE* (requires stabilizing agents) i.e. unmix spontaneously**

- **Inhomogeneities on length scales large compared to molecular dimensions**

- **Mixing is irreversible**

dispersion A

dispersion B
$\neq$ dispersion A
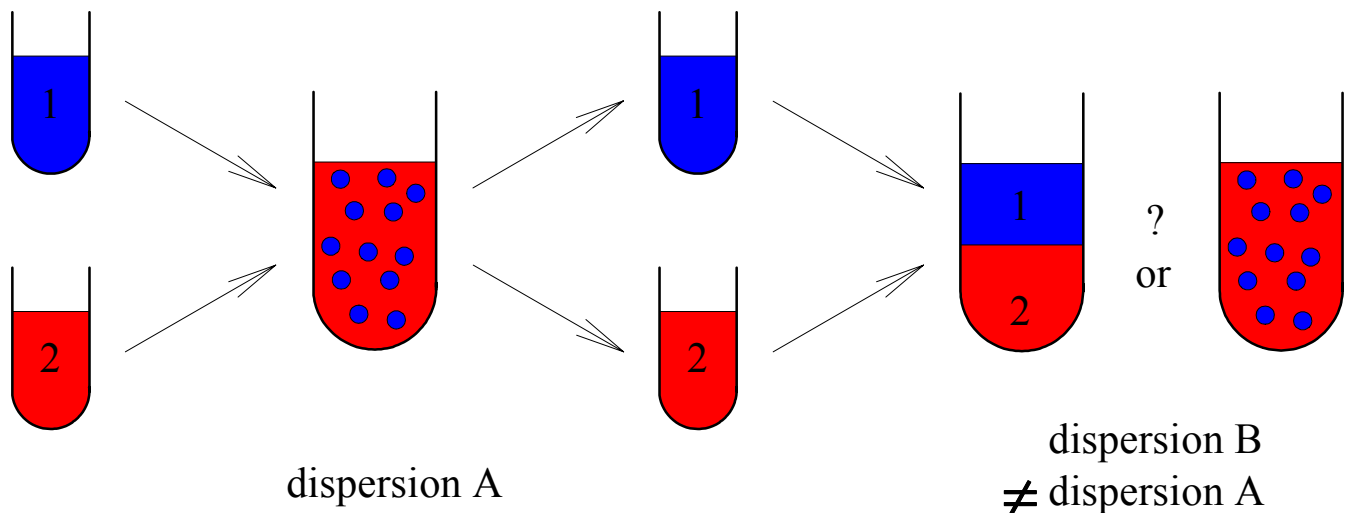
- **Properties are strongly dependent on the way the dispersion is prepared**

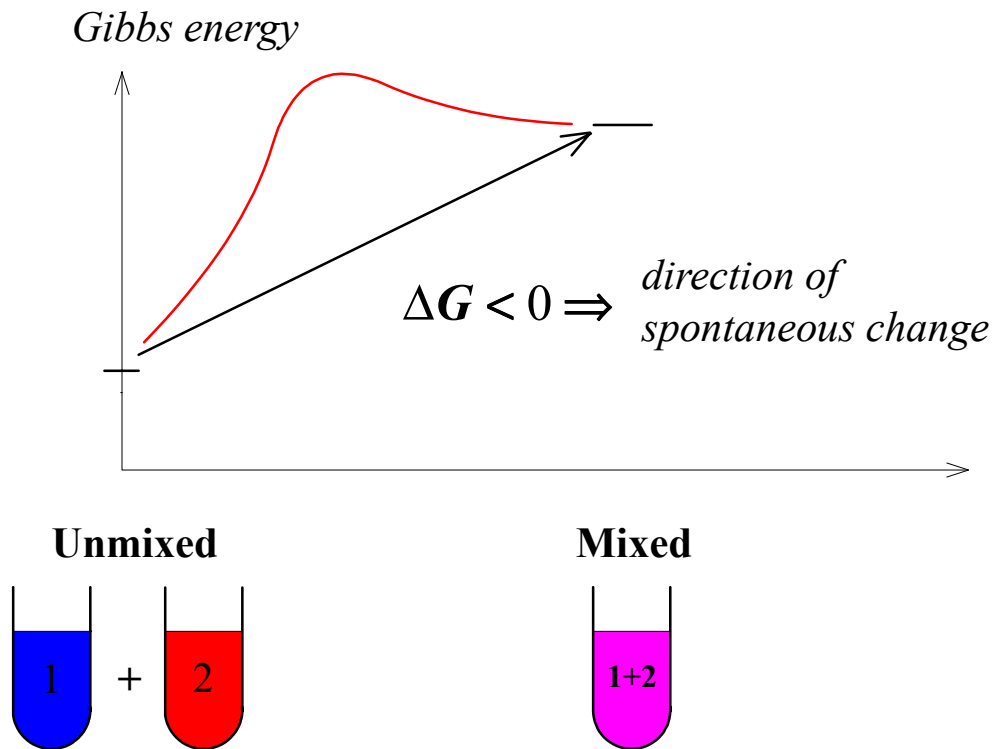⟶ **Empirical preparation procedures**

Equilibrium thermodynamics

(predicts spontaneous changes)

- **Equilibrium state = state with lowest Gibbs energy (at constant T and P)**

- **Spontaneous change toward states with lower Gibbs energy $\Delta G_{T,p} < 0$**

SOLUTIONS

Gibbs energy

$\Delta G < 0 \Rightarrow$ *spontaneous mixing*

Unmixed   **Mixed**

1 + 2   1+2

Dispersions

Gibbs energy

$\Delta G < 0 \Rightarrow$ *direction of spontaneous change*

Unmixed

1 + 2

Mixed

1+2
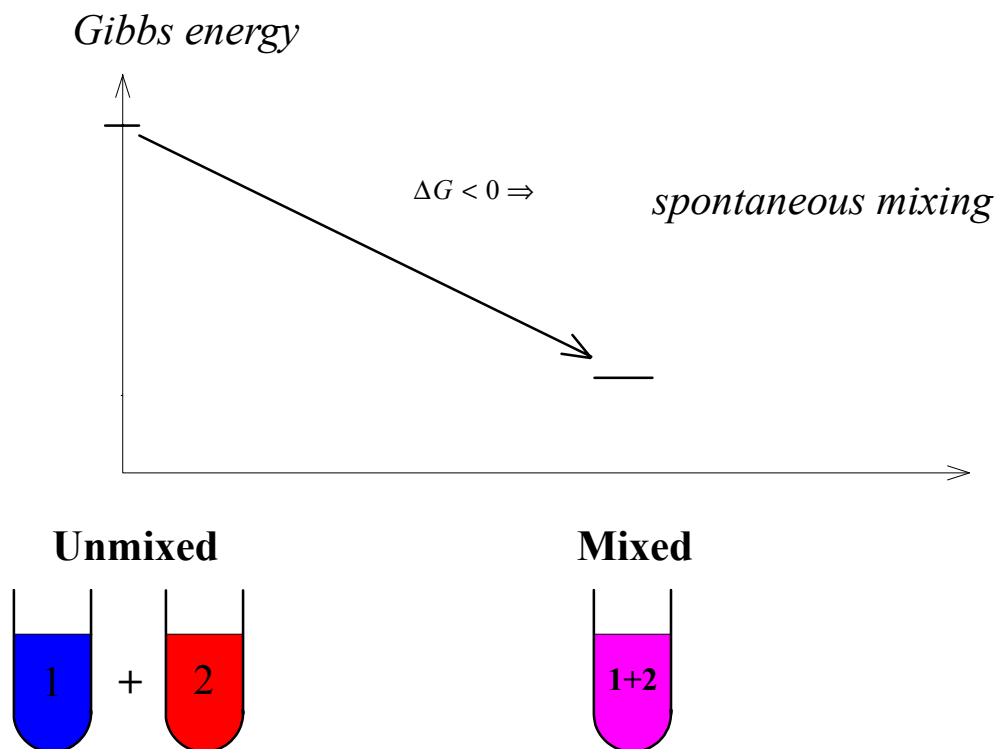
? Kinetics of unmixing ?

if slow enough ⟶   kinetic stable system

Main trick

Protect dispersed particles against aggregation/flocculation and coalescence by

REPULSIVE INTERACTIONS

3. Colloid stability

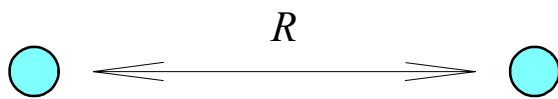## = Balance of attractive and repulsive interactions
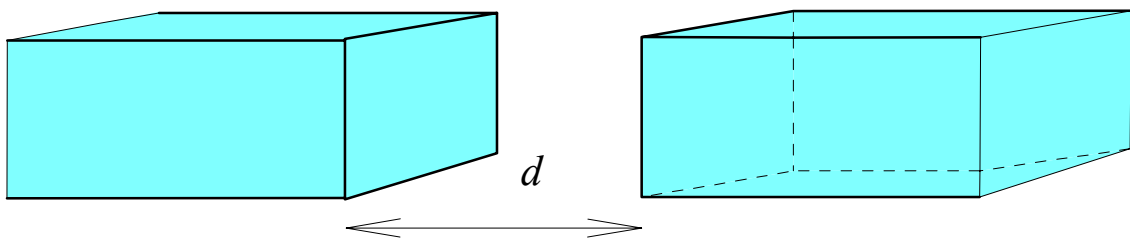
The main cast

London-Van der Waals forces (attractive)
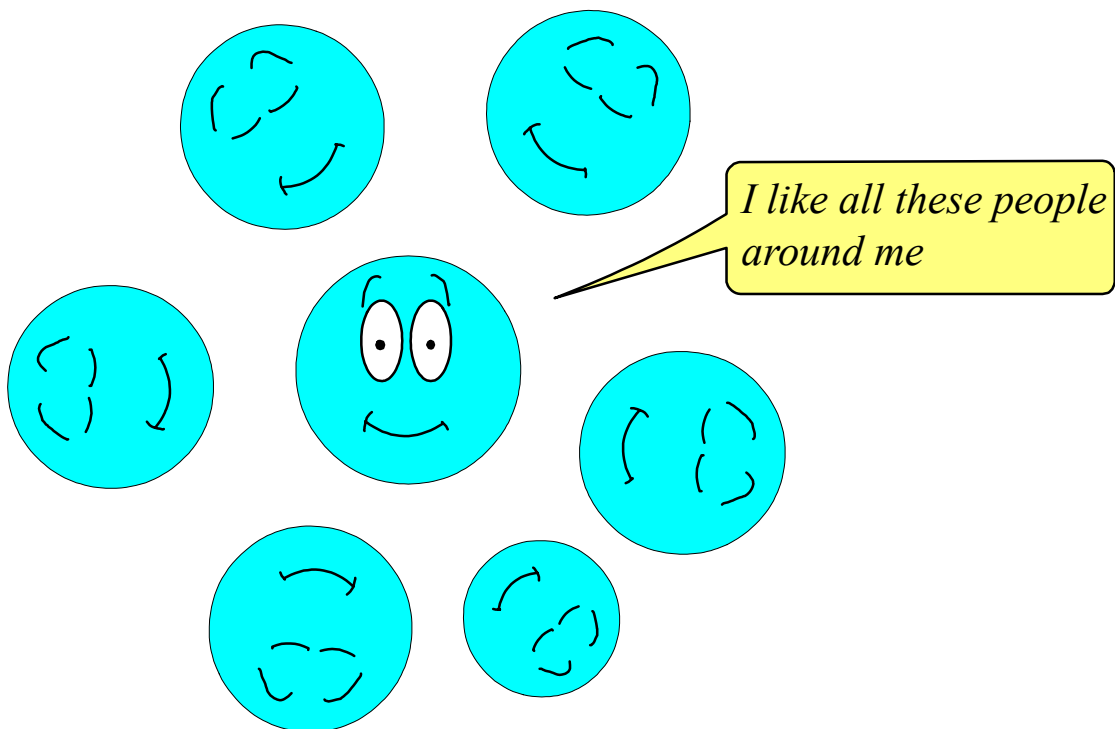
Attraction between atoms/molecules in vacuo

R » molecular dimensions
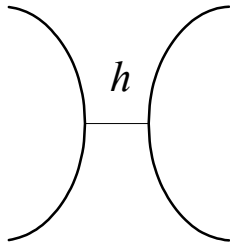
$$V_A(R) \approx -\frac{1}{R^6}$$

Macroscopic bodies (dependent on geometry)

$$V_A(d) \approx -\frac{A}{d^2}$$

Hamaker constant (dependent on material properties: density, polarizability)
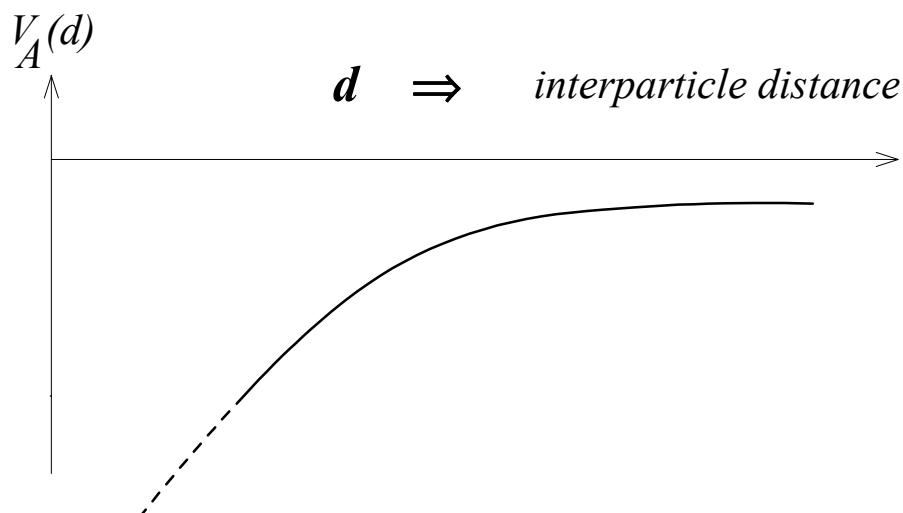
$$V_A(R) \approx -\frac{A}{h}$$

with h the interparticle gap.

Effective Hamaker constant A_{eff} also dependent on dispersion medium

$$A_{eff} = \left(\sqrt{A_{11}} - \sqrt{A_{22}}\right)^2$$

Order of magnitude $10^{-20} - 10^{-21}$ J

$V_A(d)$

$d \Rightarrow$ *interparticle distance*

Electrostatic (repulsive) forces

Charged surface

Solution

Diffuse layer

Plane of zero shear $\Rightarrow$ ζ potential

Surface potential Ψ_o

Potential at Stern layer Ψ_d

Stern layer strong adsorption

Potential

Diffusive layer

Distance from charge surface

Stern plane
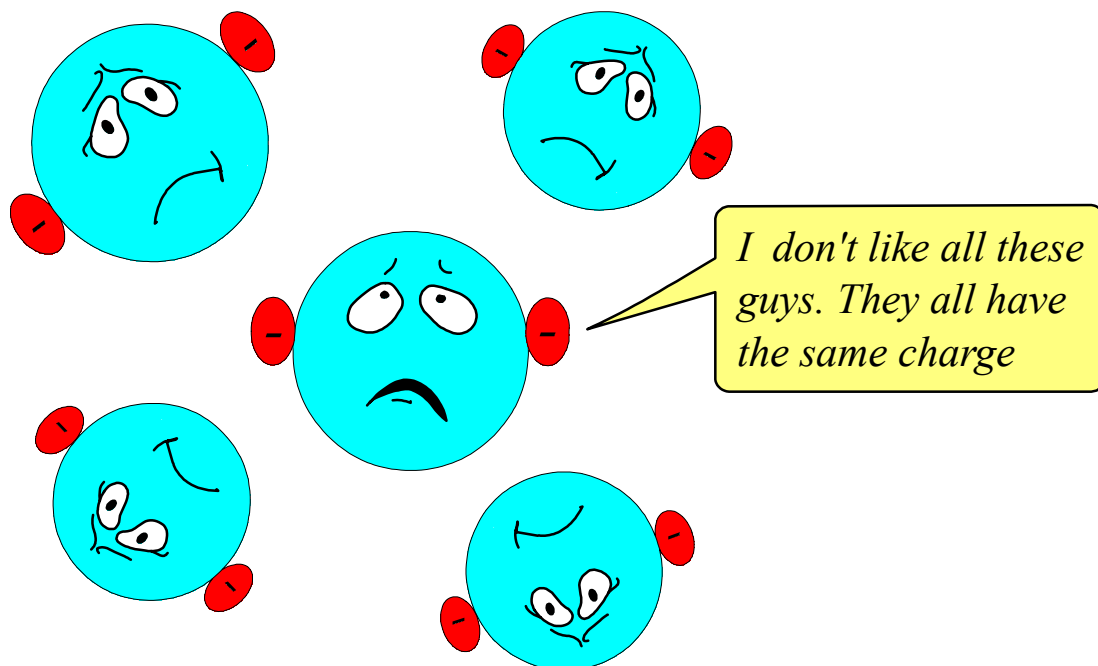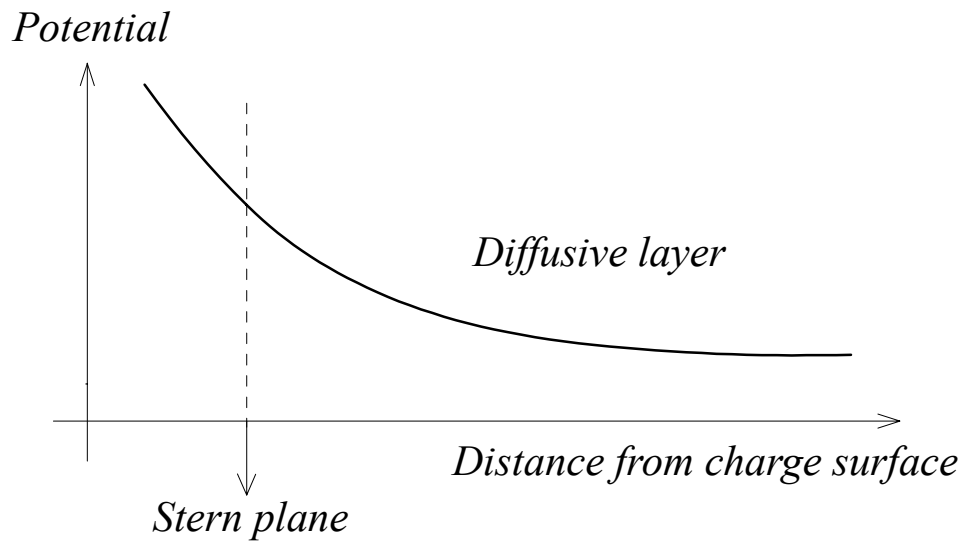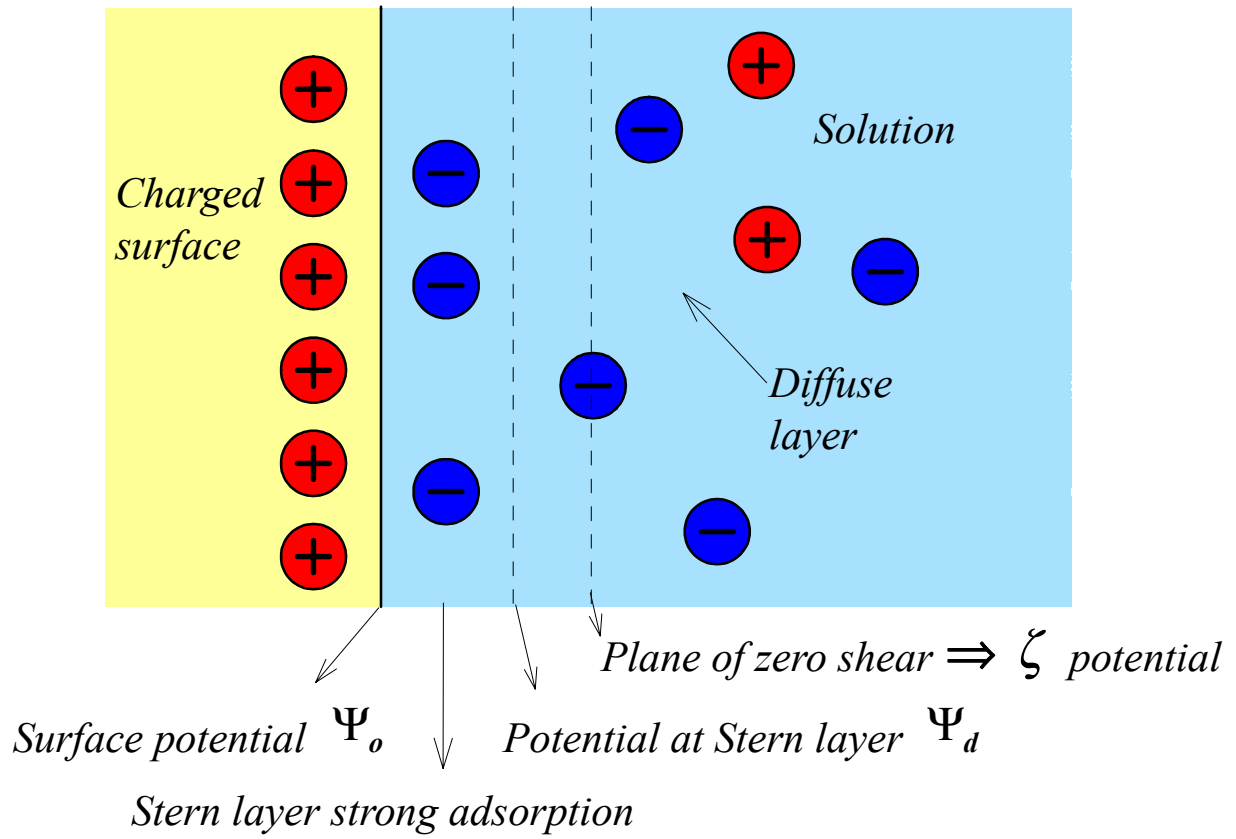
$$\psi = \psi_0 e^{-\kappa X}$$

$$\kappa^{-1} \longrightarrow \text{Debye-Hückel length}$$

$$\kappa^2 = \frac{2e^2}{\varepsilon\, kT} I$$

$$I = \frac{1}{2}\sum_i Z_i^2 n_{i,\infty}$$

ionic charge number

electrolyte concentration

κ^{-1} ↗ with ↘ electrolyte concentration

↘ with ↗ electrolyte concentration

Interaction between overlapping double-layers

d

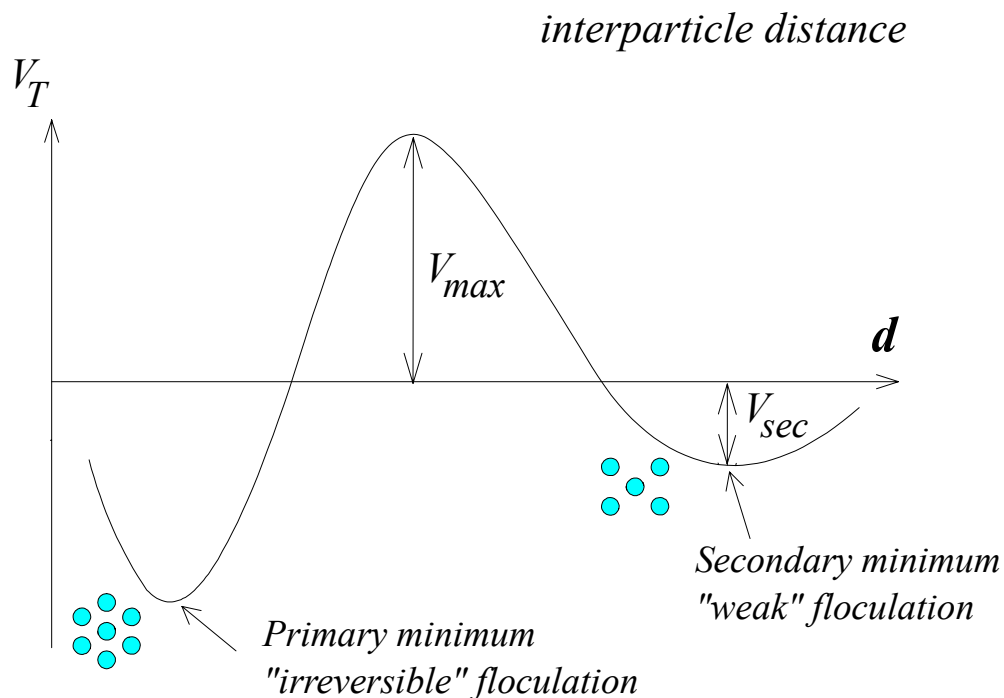## Repulsive force

$$V_R(d) \approx e^{-\kappa d}$$

V_R

d

κ^{-1}

Interparticle distance
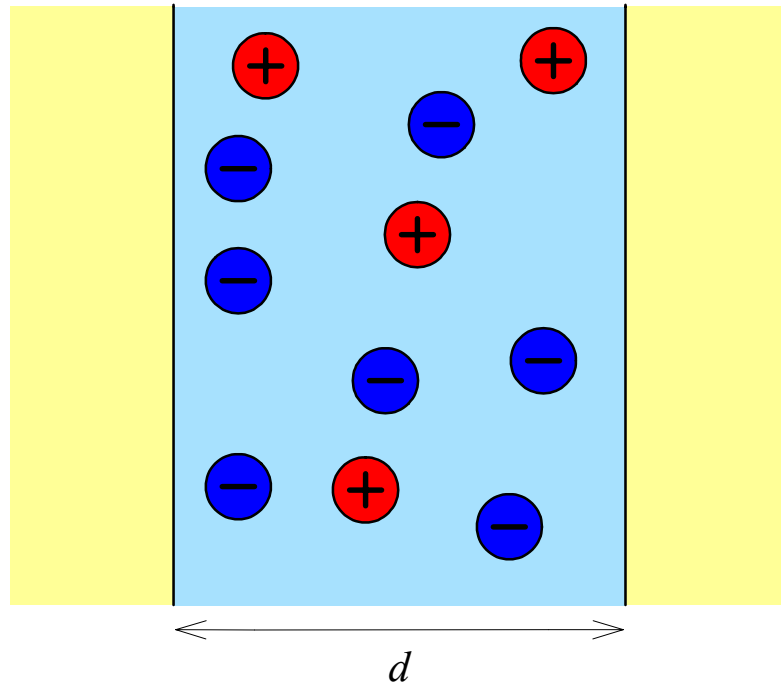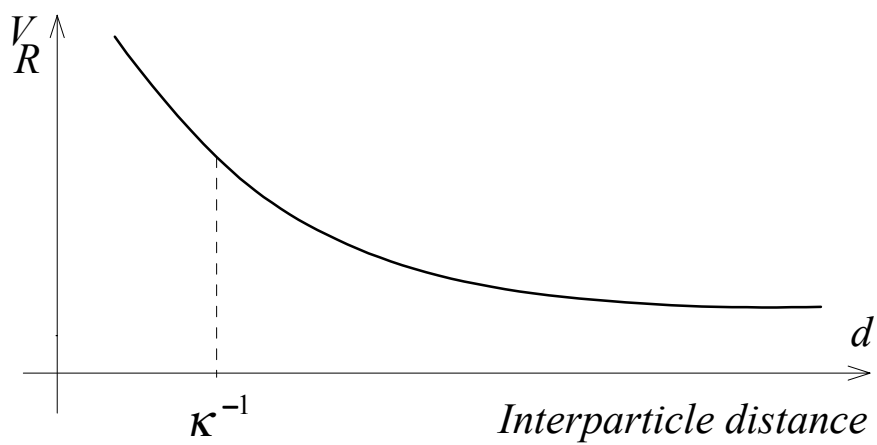
DLVO - theory

Derjaguin-Landau-Verwey-Overbeek

Total interaction = sum of attractive + repulsive interactions

$$V_T(d) = V_A(d) + V_R(d)$$

interparticle distance

V_T

V_{max}

d

V_{sec}

Secondary minimum "weak" floculation

Primary minimum "irreversible" floculation

Stability $V_{max} \gg kT$ kT = thermal kinetic energy

$V_{sec} > kT$ weak flocculation in secondary minimum (reversible)

Factors affecting stability (electrostatic)

- V_{max} ↗ with particle size

- V_{max} ↗ with surface potential

    (in practice ζ potential)

    practical rule $|\zeta| \geq 25$ mV

    ⟶ ± 6 months stable

- Electrolyte (salt) concentration

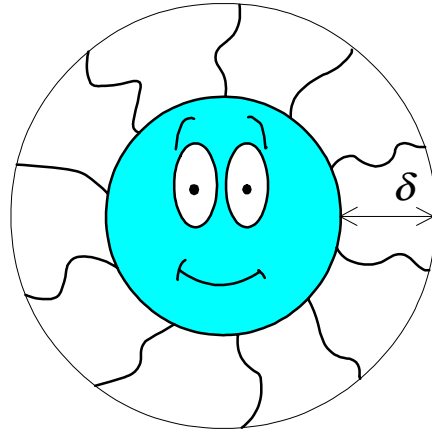   with C_{salt} ↗
    with z (charge number)

    ⟶ death of the dispersion !
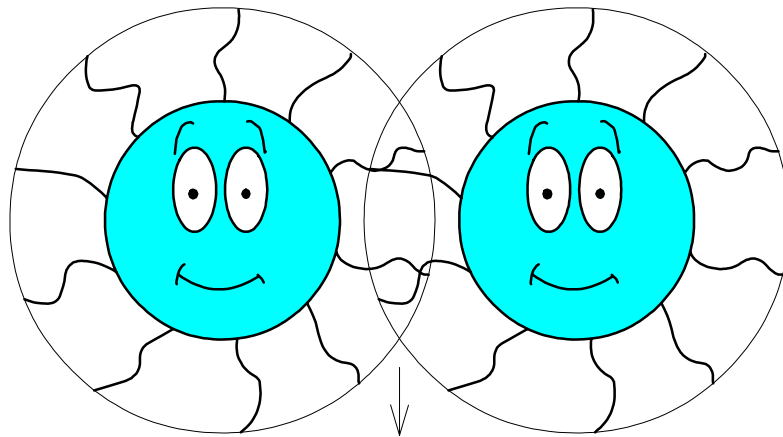   ⟶ desired in water purification

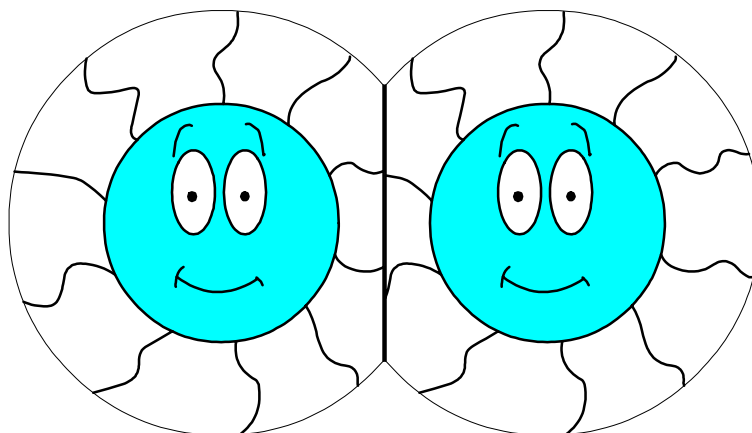# Steric stability

I like the lady but I don't trust the snake

17

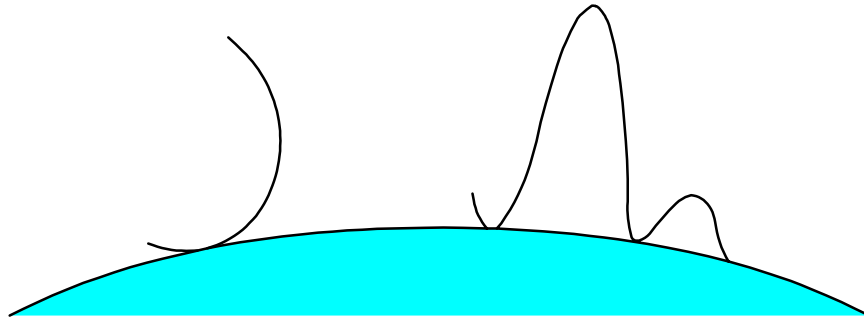# Protective action of adsorbed macromolecules
(natural and synthetic)

Two effects

Interpretation $\Longrightarrow$ *Osmotic repulsion*
Mixing effect

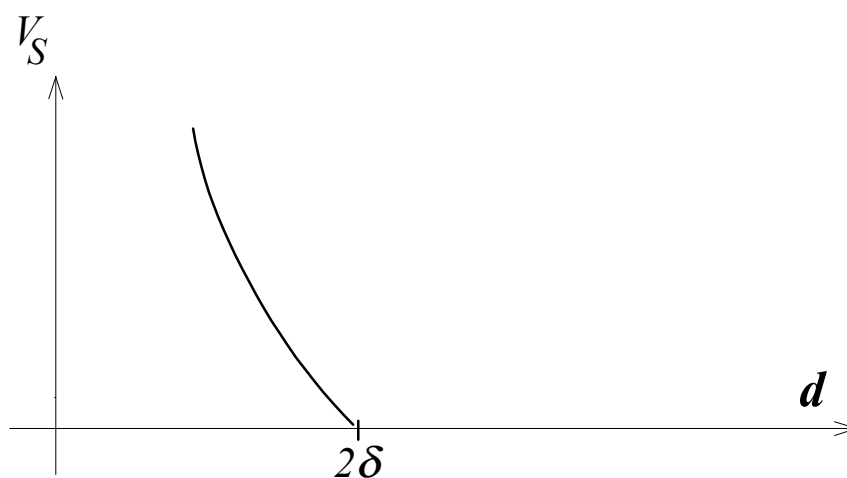*Compression*
(Volume restriction)

$$V_S = V_m + V_{VR}$$

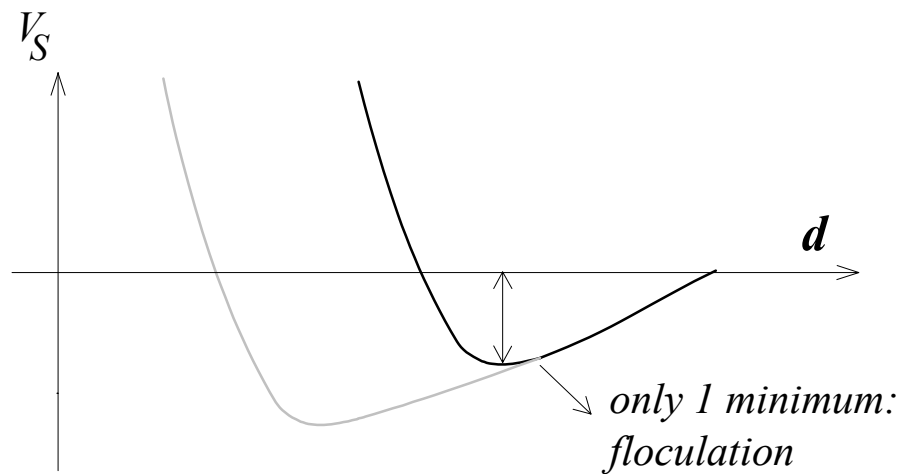**Several possibilities for polymers at interfaces**

Principal factors of steric stabilization

- average loop or tail size
- number of loops or tails per unit area
- polymer-solvent interaction parameter χ
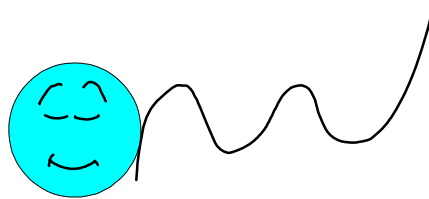- mode of polymer-surface attachment
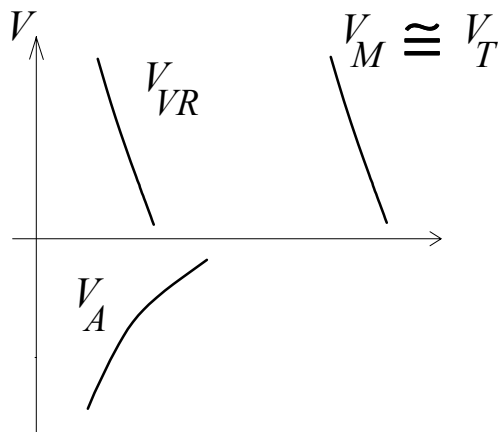
Steric + attractive interactions

only 1 minimum: floculation

How to avoid flocculation ?

- **Full coverage of particles otherwise bridging flocculation**

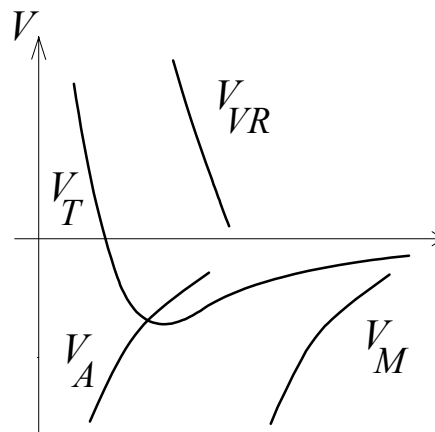- **Firm anchoring of polymer**
  ⟶ AB block co-polymers perform better

- **Sufficiently thick layer d**
  ⟶ small minimum

- **The stabilizing moiety B must be in good solvent environment**

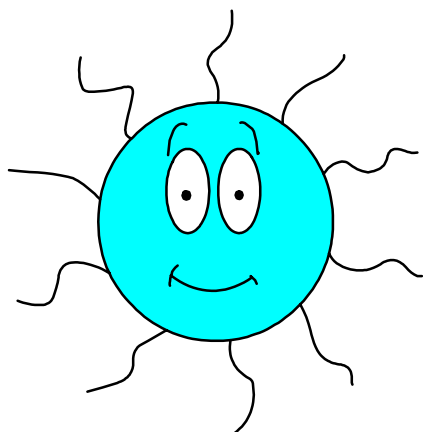$V_M \cong V_T$

Good solvent

*Flory Huggins
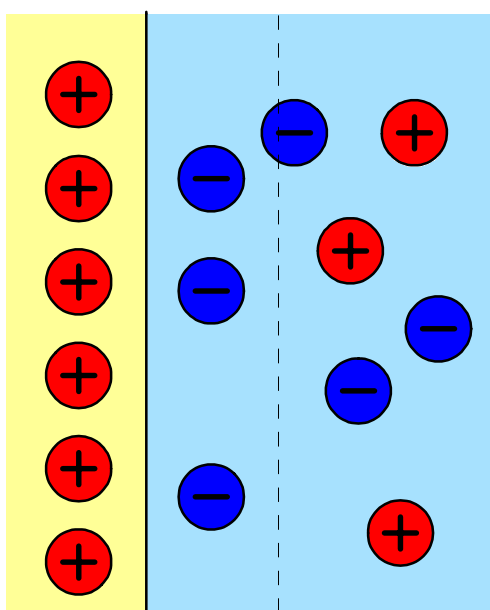Parameter* $\chi < 0.5$

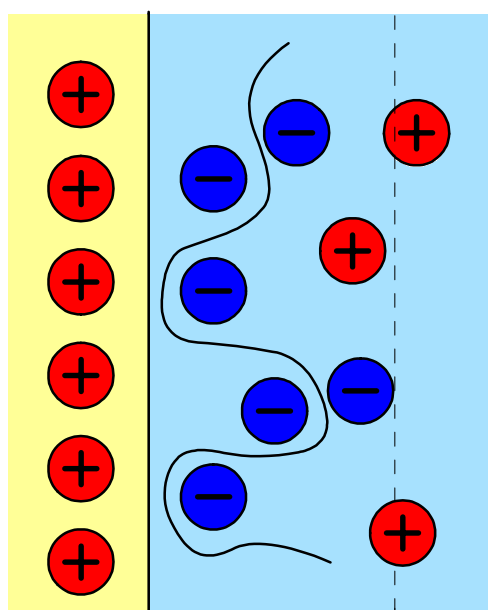*Poor solvent*
$\chi > 0.5$

effect T !

Steric + electrostatic stabilization

Can be achieved by polyelectrolytes (gelatin, proteins, ...) or by charged surfaces + neutral polymers ➡️ caution about ζ potential

Plane of zero shear
$\Rightarrow \zeta$ *potential*

Plane of zero shear
$\Rightarrow \zeta$ *potential*

$V_A + V_S$

$V_A + V_R + V_S$