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Protein-stabilised emulsions

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Emulsion - definition

- An emulsion consists of two immiscible liquids (generally oil and water) with one liquid forming the continueous phase while the other the dispersed phase.
  - Oil-in-water (O/W)
  - Water-in-oil (W/O)
  - Water-in-oil-in-water (double emulsion, W/O/W)
  - Oil-in-water-in-oil (double emulsion, O/W/O)

Examples

- O/W – milk, cream, mayonnaise, soups and sauces
- W/O – butter and margarine

Oil-in-water emulsions

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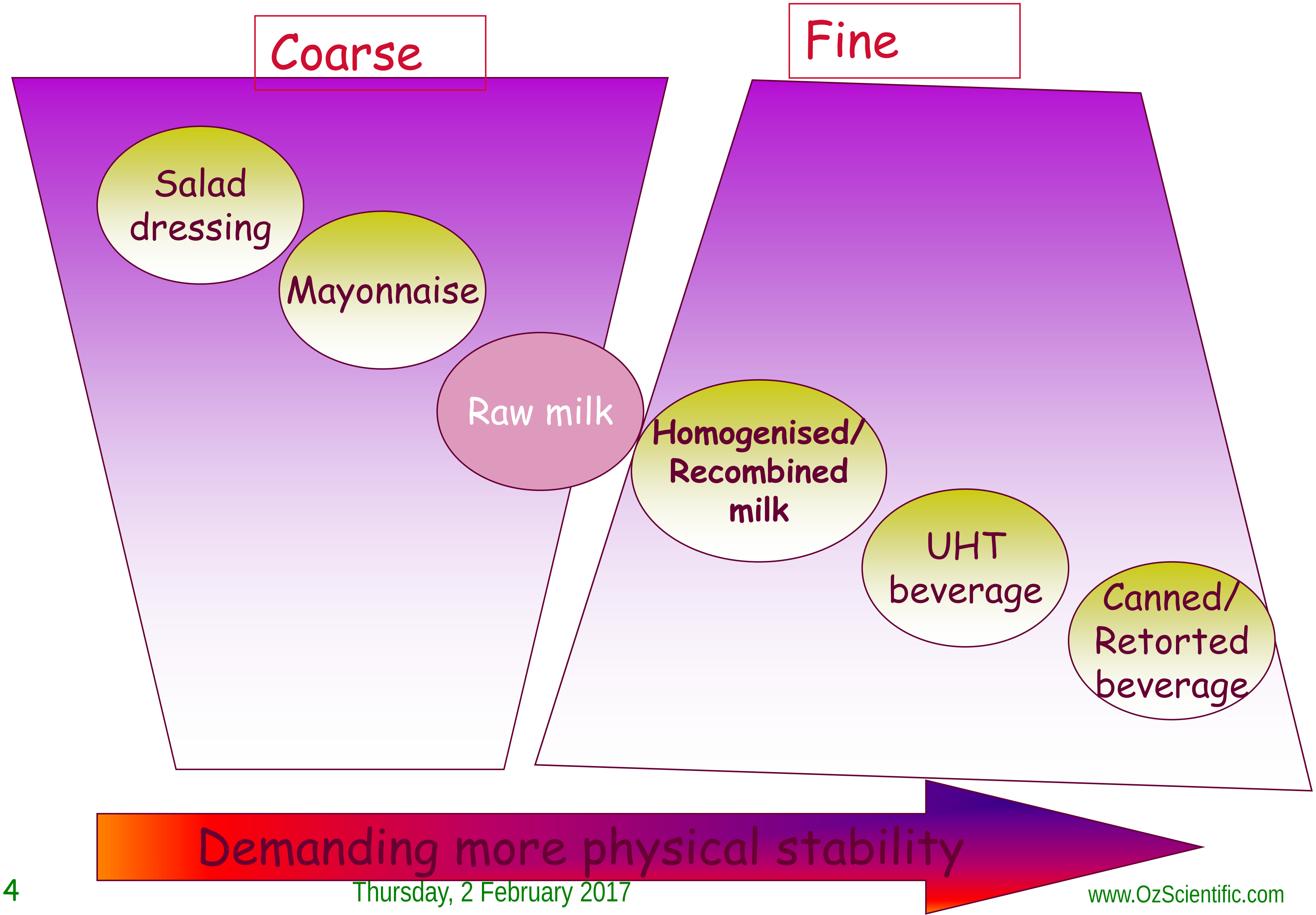
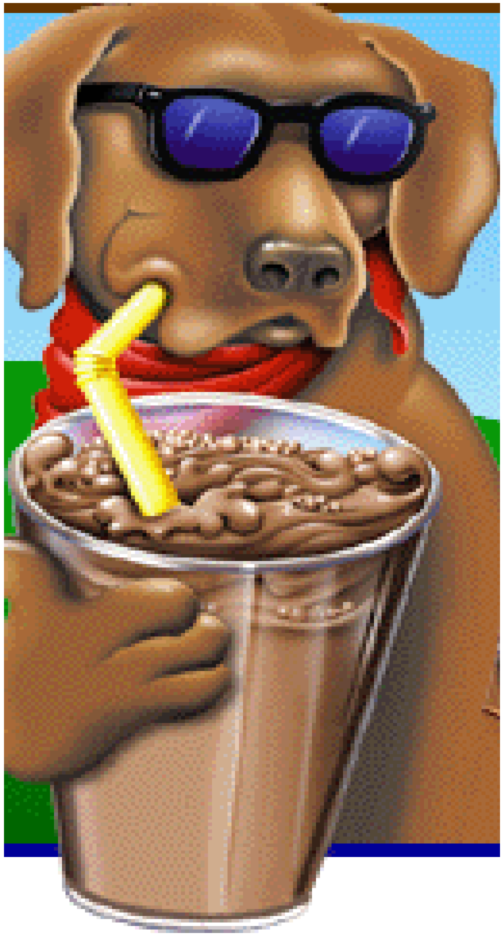


O/W - Chocolate milk and infant formulae



O/W - Complete nutritional formula

O/W - Mayonnaise

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W/O – butter and margarine

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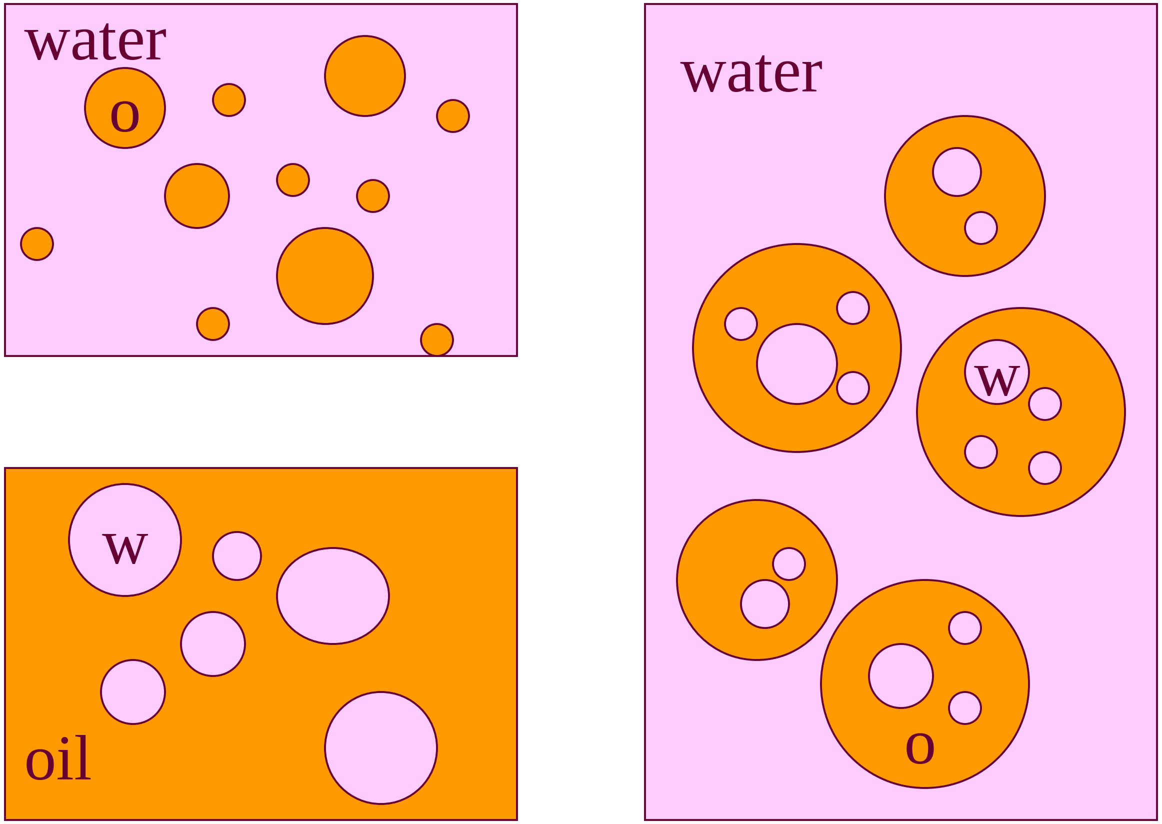
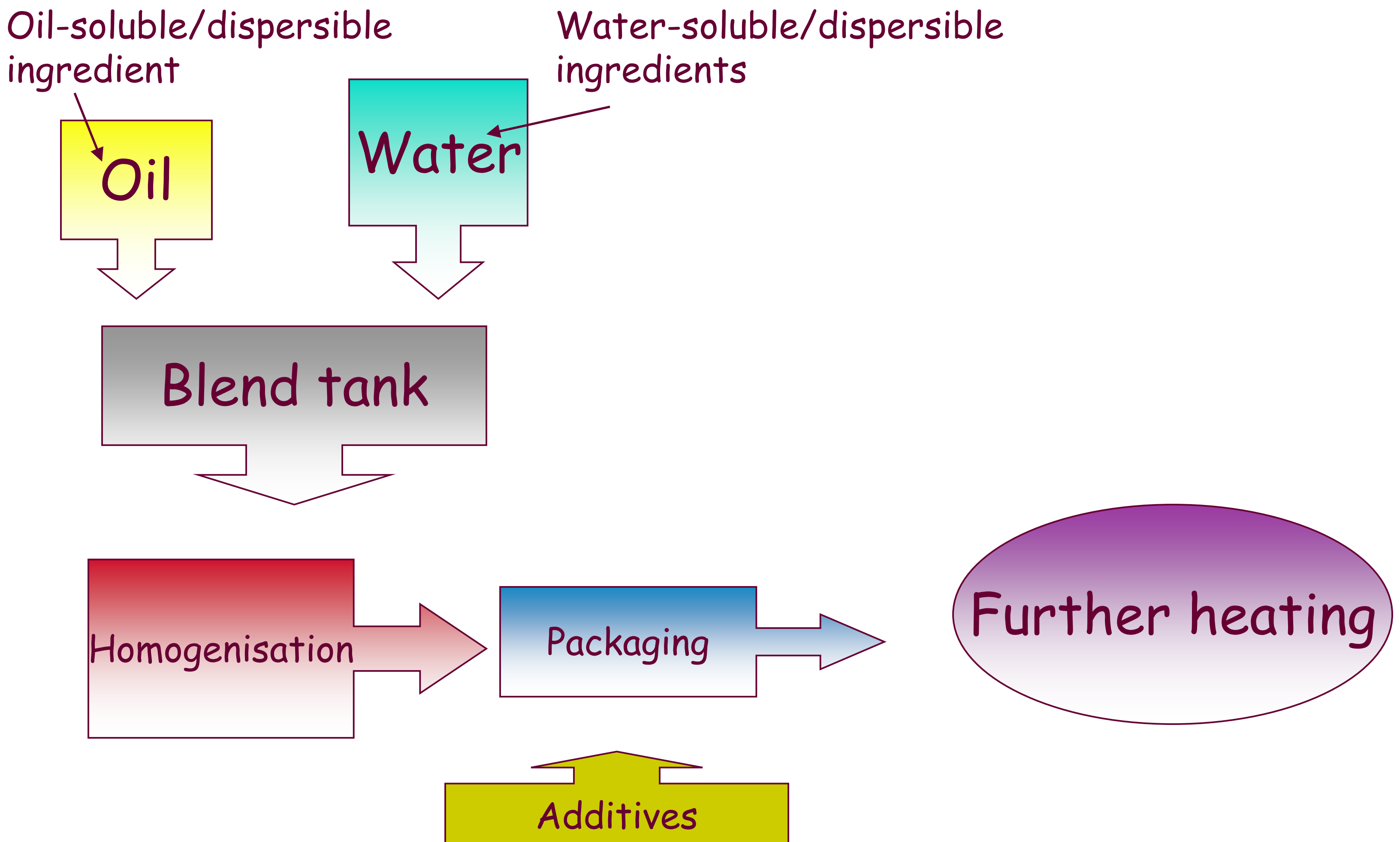
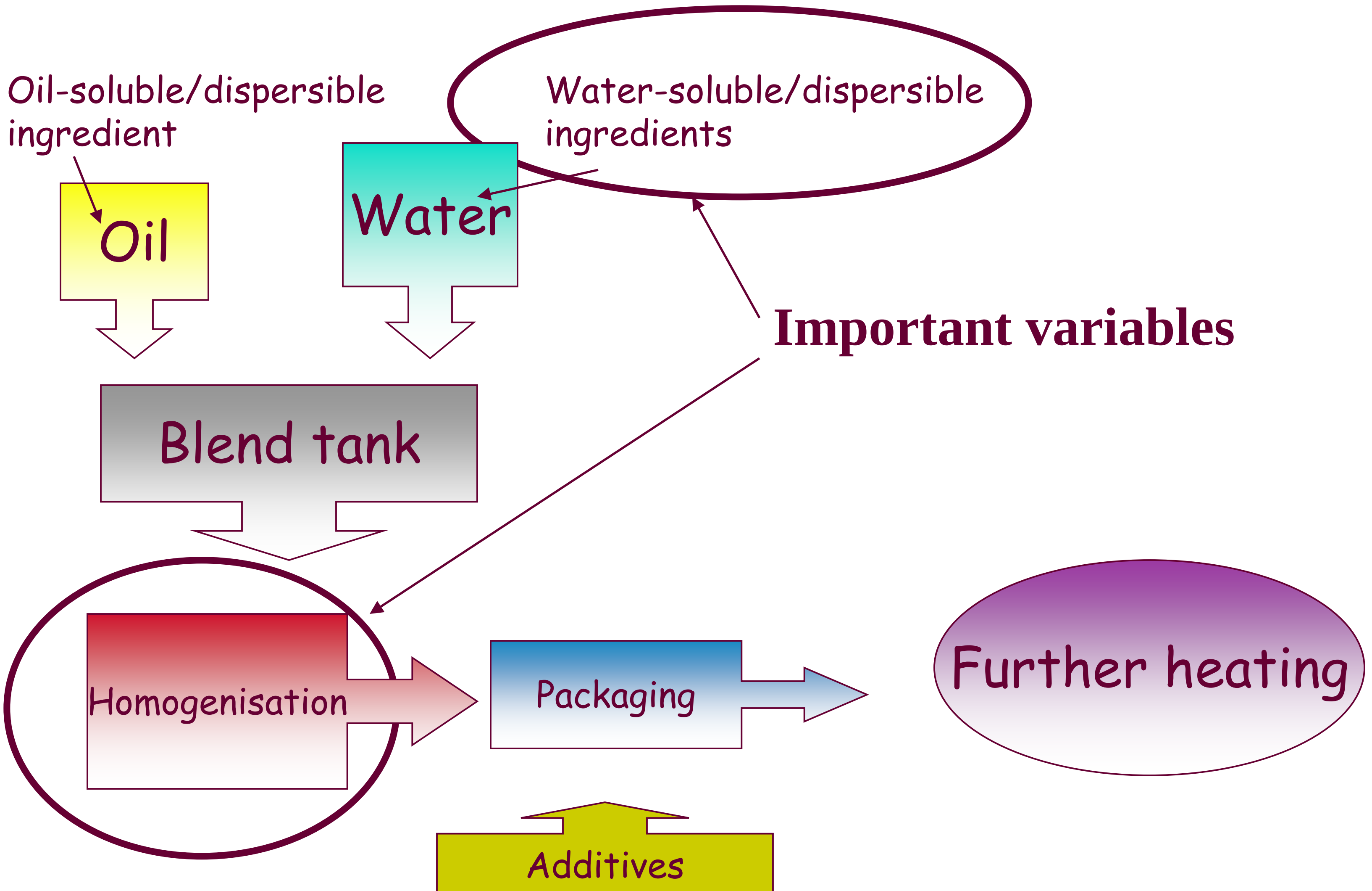
Two & three-phase emulsions



Emulsion formation



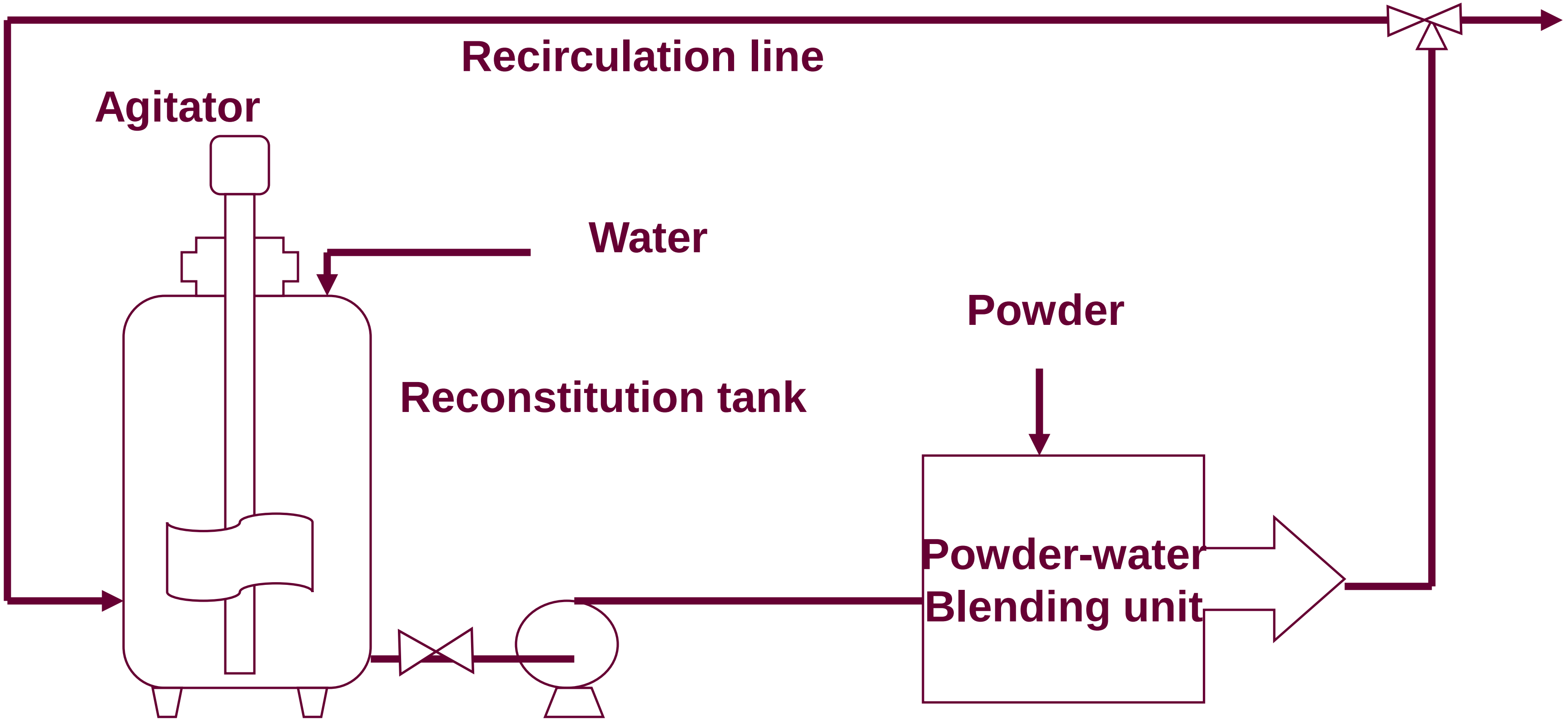
Emulsion formation



Sequence of events

- During homogenisation, fat globules with sub-micron size are formed
- Milk proteins migrate to the newly formed fat globule surfaces
- Capability to form a stable emulsion is determined by the ability of the protein to unfold at the fat-water interface
- Protein load affects the stability of emulsion towards heating and storage

Setup for reconstitution of protein ingredient



Homogenising devices

- High-speed blender
- Colloid mills
- High-pressure valve homogeniser
- Ultrasonic homogeniser
- Microfludiser
- Membrane-based homogeniser

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Homogenisation efficiency

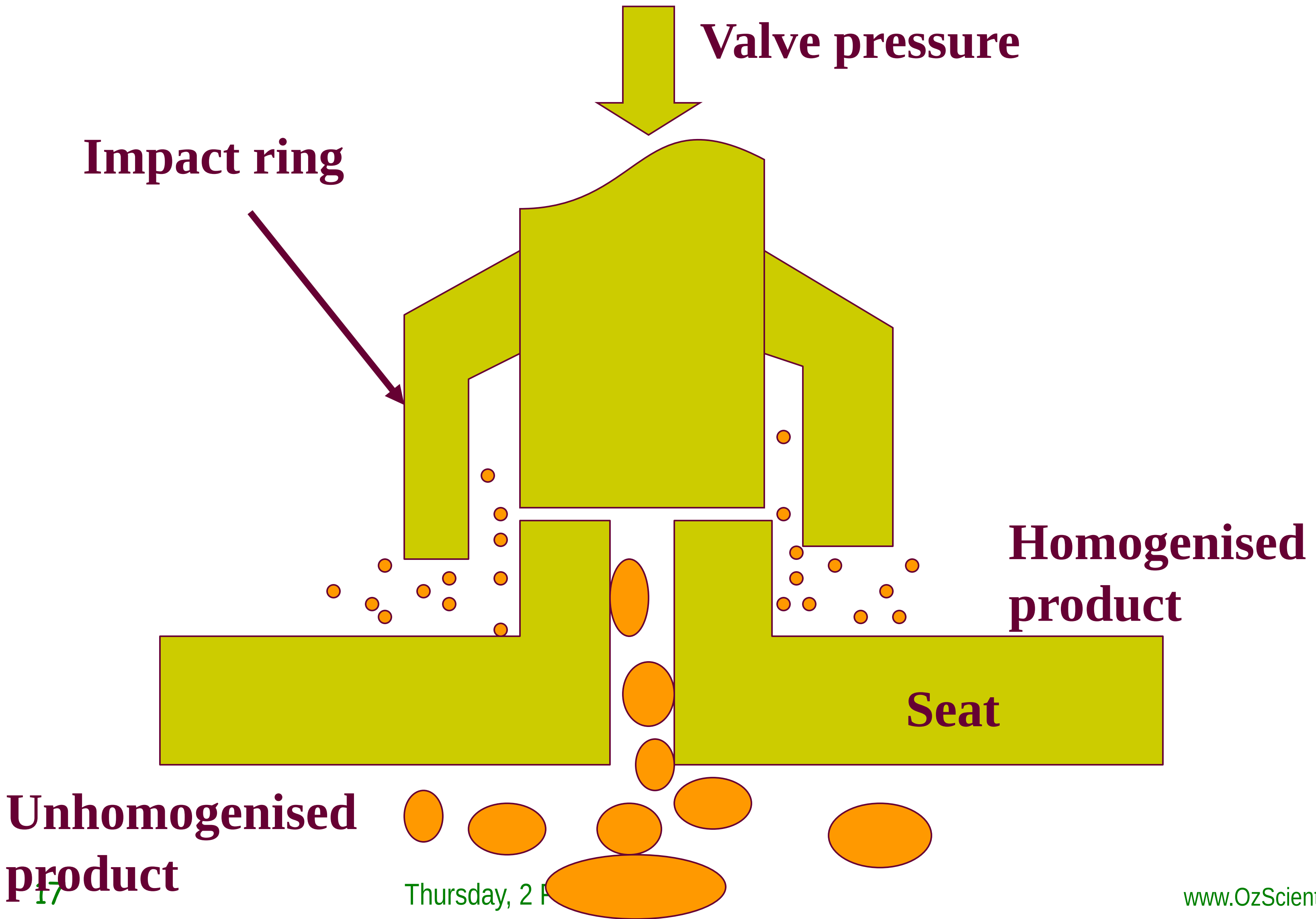
$$E_H = \frac{\Delta E_{min}}{\Delta E_{total}} \times 100$$

E_H – homogenisation efficiency

ΔE_{min} – Minimum amount of energy theoretically required to form emulsion = $\Delta A\gamma$ (interfacial area and interfacial tension)

ΔE_{total} – Actual amount of enegy expended during homogenisation

Homogenising valve



Two-stage homogeniser

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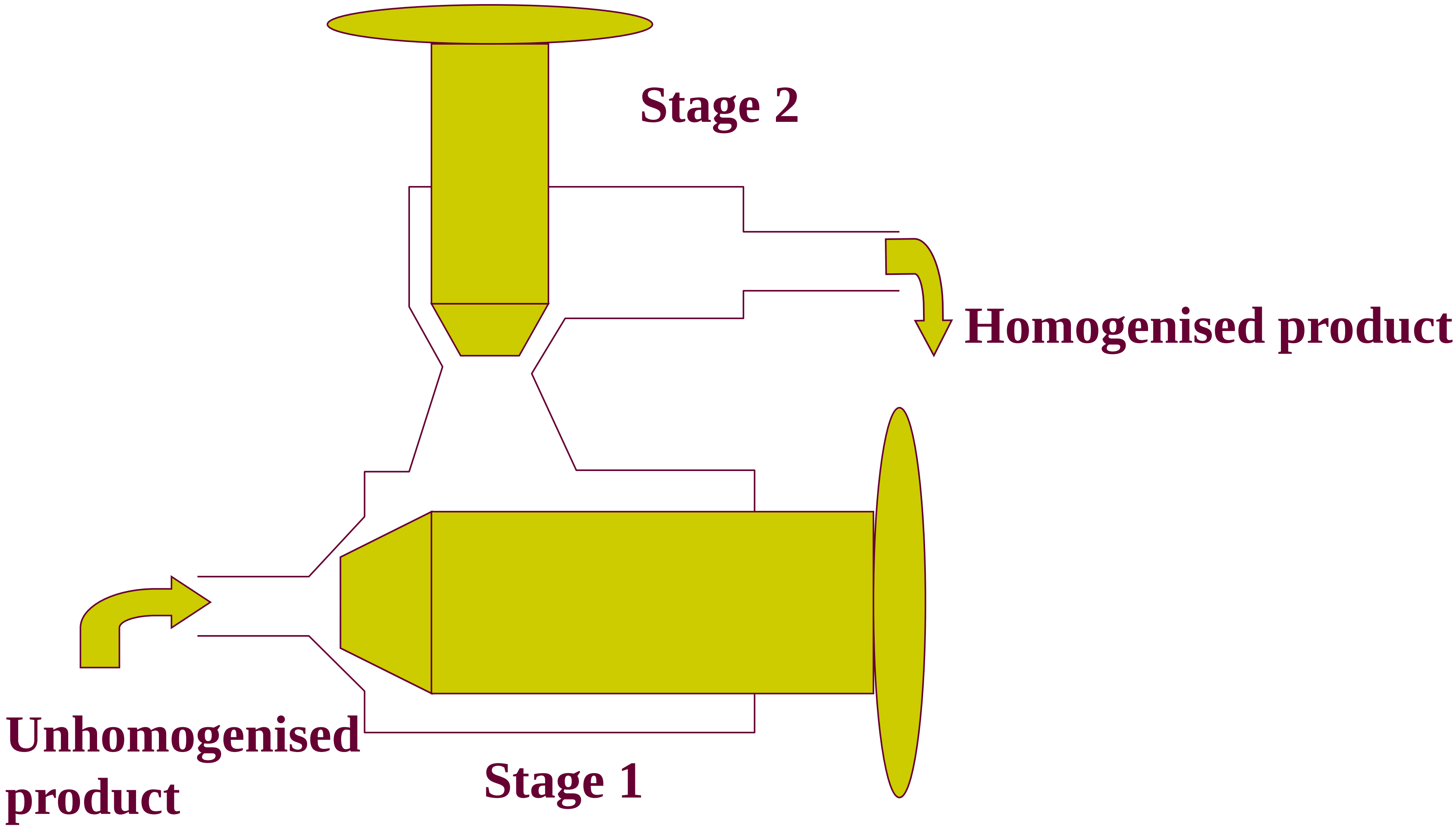
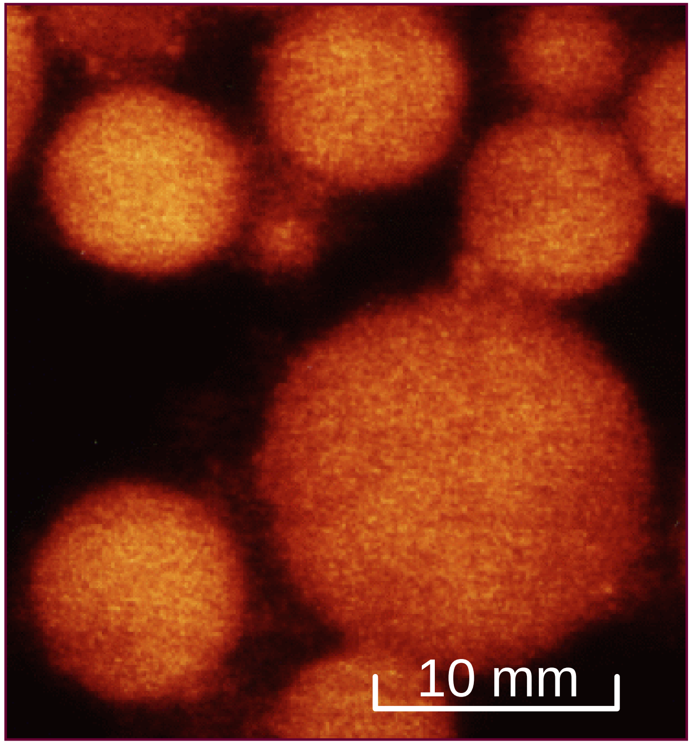
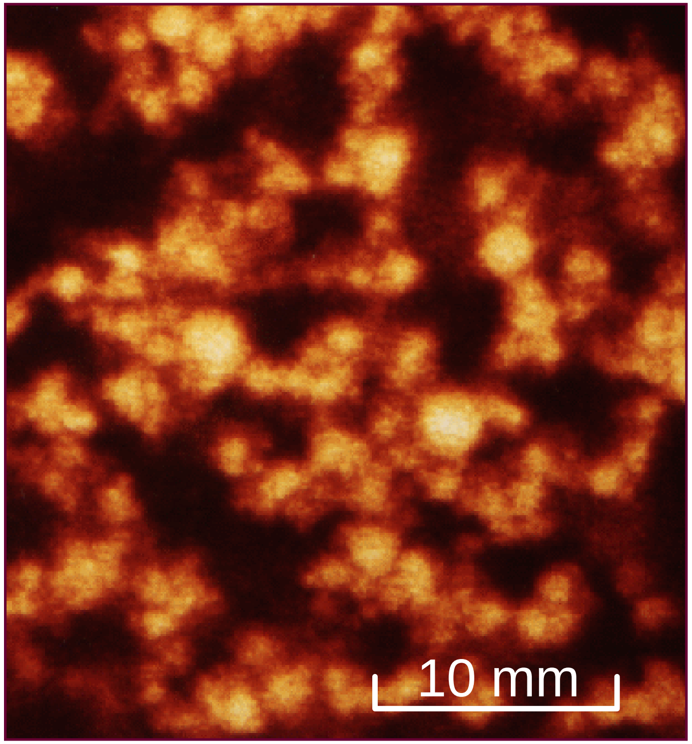


Effect of homogenisation on fat globules in milk

Natural milk



Homogenized milk



Casein micelles and whey proteins at oil-water interface

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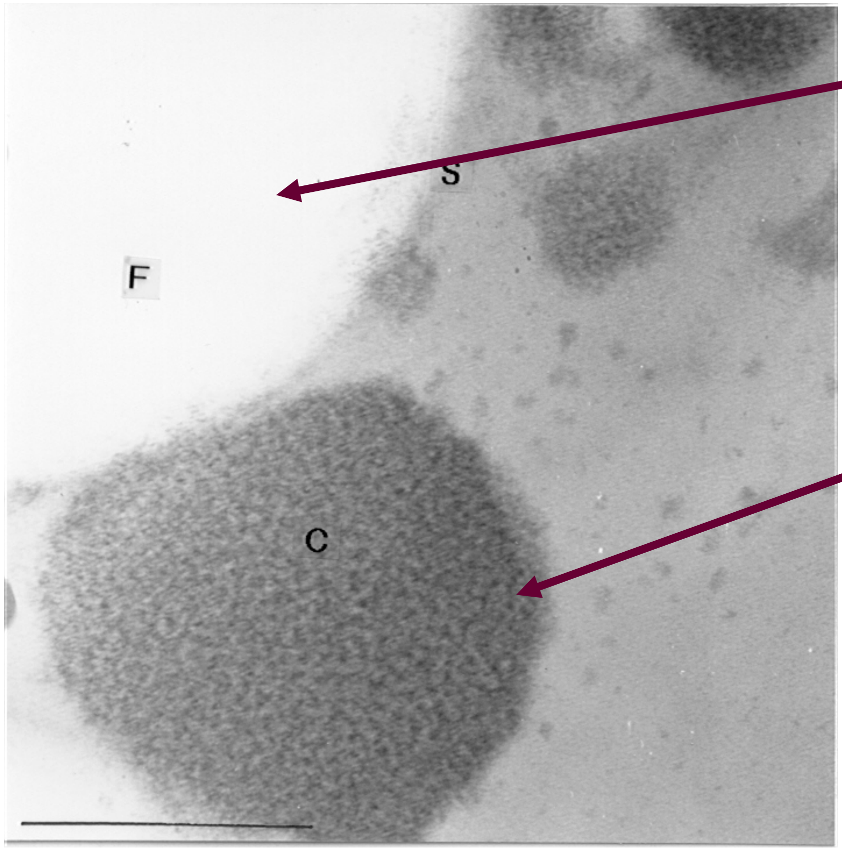


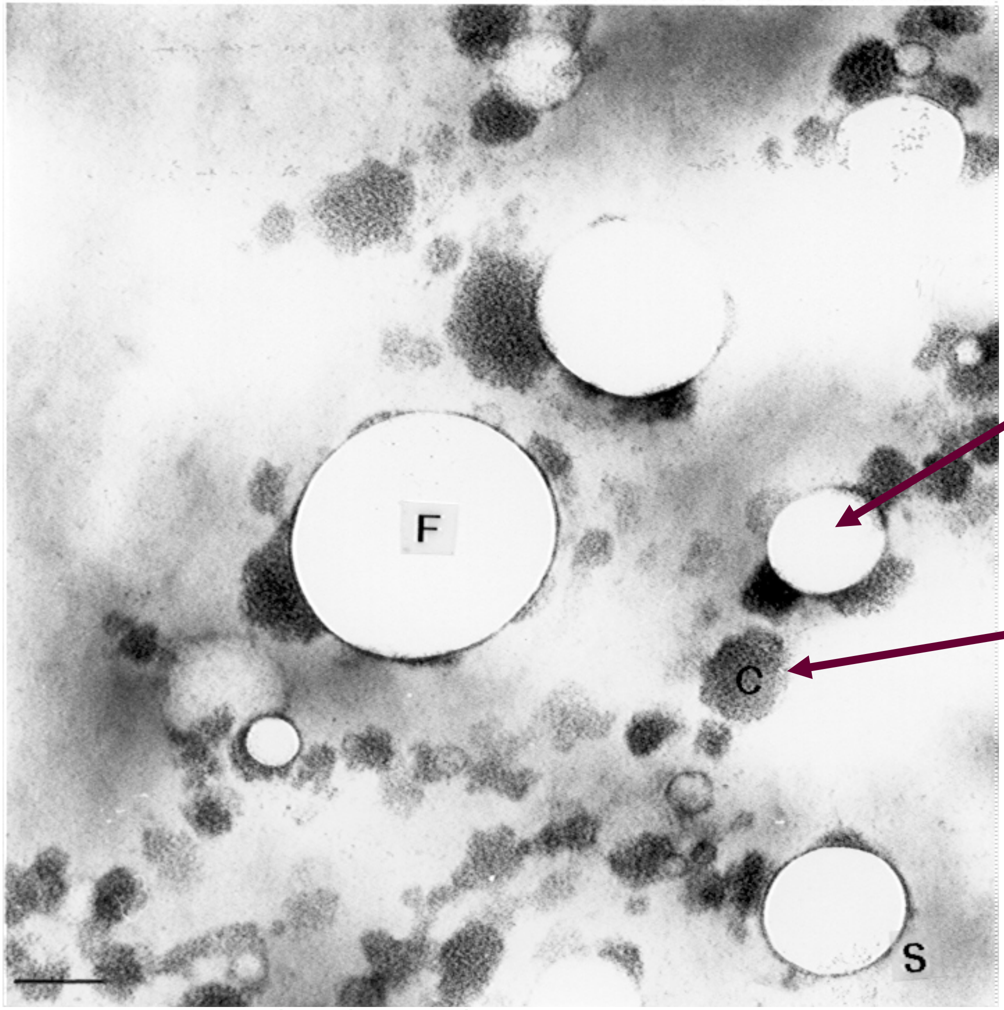
Fat globule

Casein micelle

Sharma (1993)

200 nm

TEM of an oil-water emulsion



Fat globule

Casein micelle

Sharma (1993)

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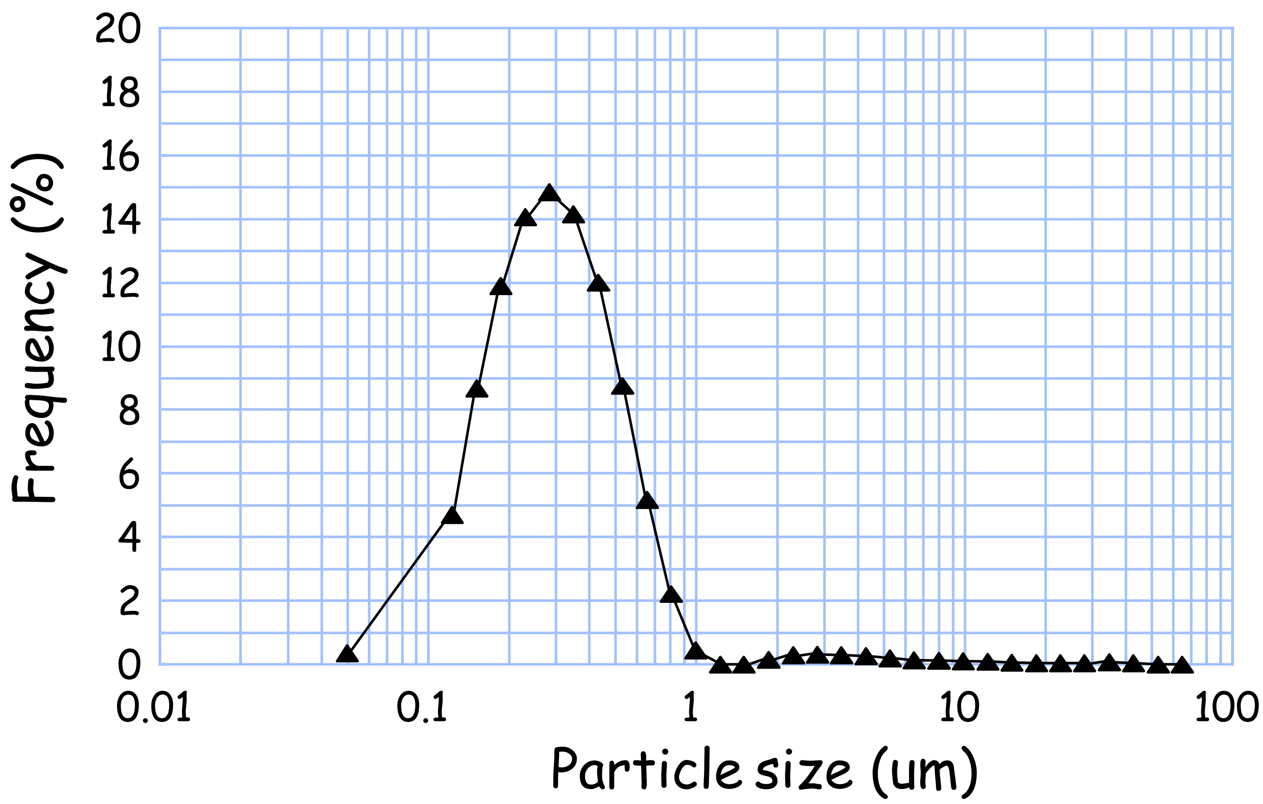
Particle size distribution – A stable emulsion



Particle size distribution – unstable emulsion

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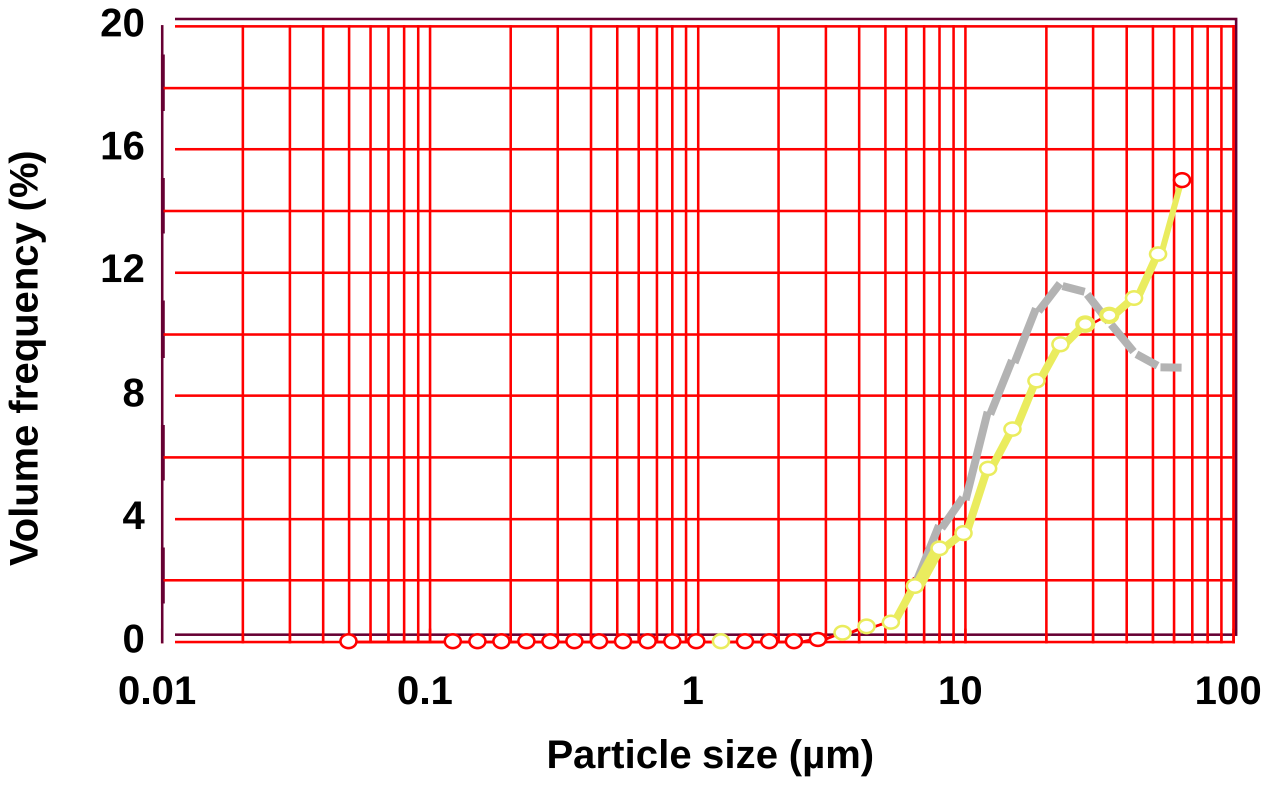
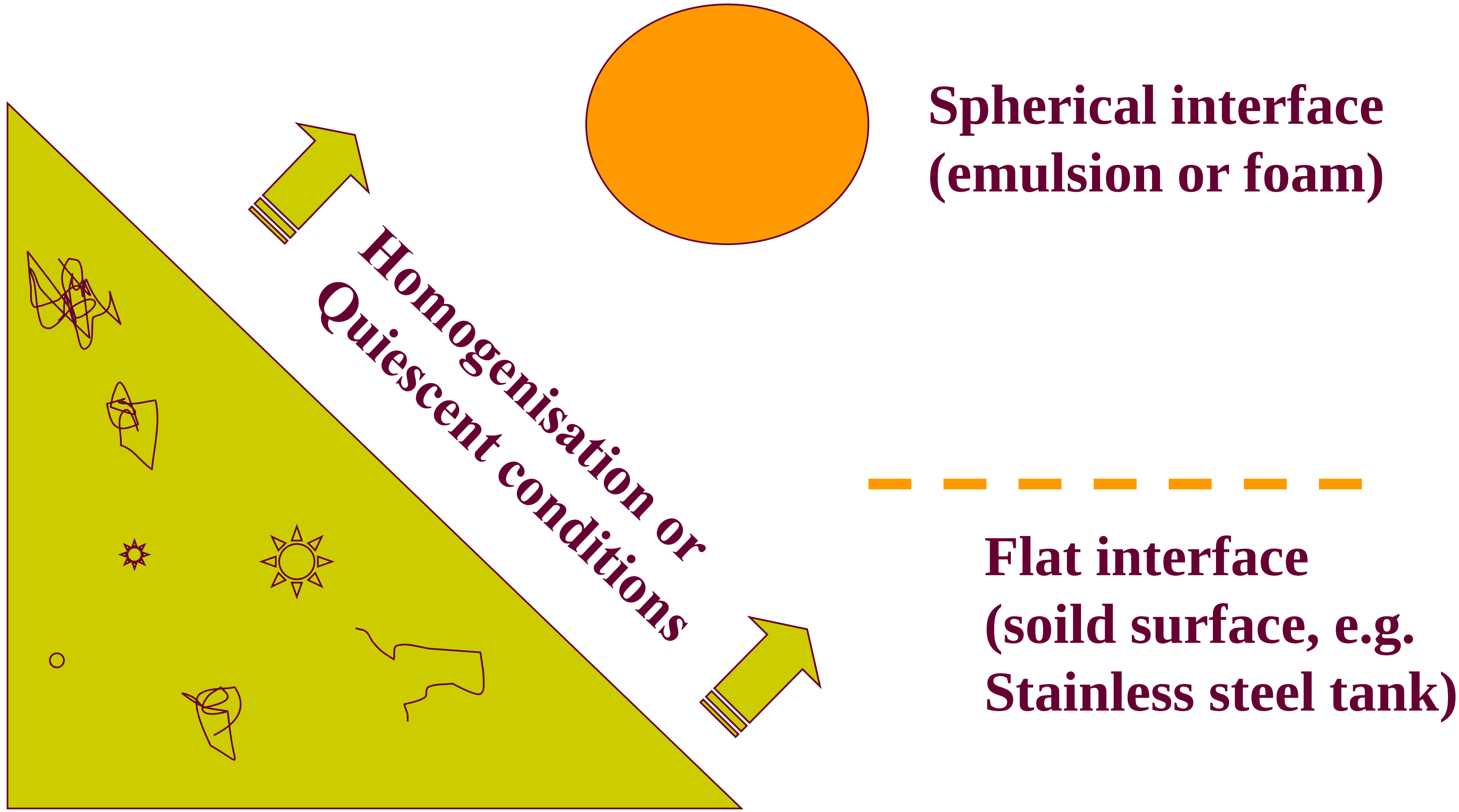


Protein adsorption



PHYSICO-CHEMICAL PROPERTIES OF MILK PROTEINS

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CASEIN	WHEY PROTEIN
•Strong hydrophobic regions •Low cysteine •High ester phosphates •Little or no secondary structure •Unstable in acidic conditions •Micelles in native form •Random coil in dissociated form	•Balance in hydrophobic and hydrophilic residues •Contains cysteine and cystine •Globular, much helical •No ester phosphate •Easily heat denatured •Stable in mild acidic conditions •Present as soluble aggregates (<10 nm)

Selective Chemical Composition and Physico-Chemical Attributes of Milk Protein Products

Attribute	Milk protein concentrate	Sodium caseinate	Whey protein concentrate
Moisture (%)	4.0	4.0	4.0
Total protein (N*6.38, %)	82.5	92	83.5
Casein (%)	66.0	92.0	0
Whey protein (%)	16.5	0	83.5
Calcium (%)	2.20	0.01	0.06
Potassium (%)	0.01	0.005	0.05
Phosphorus (%)	1.40	0.80	0.18
Protein state	Casein micelles, soluble whey protein	Soluble aggregates of casein	Soluble whey proteins

Kinetics of protein adsorption

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Diffusion-controlled (Ward & Tordai, 1946)

$$\frac{d\Gamma}{dt} = C_0 \, (D/\Pi t)^{1/2}$$

Γ – surface protein concentration, t – time
D – diffusion coefficient

Kinetics of protein adsorption

Diffusion-controlled (Ward & Tordai, 1946)

Total adsorbed protein

$$\Gamma = 2C_0(Dt/\Pi)^{1/2}$$

Kinetics of protein adsorption

Convection-controlled (Walstra, 1983)

$$\Gamma(t) = K C_0 d_g \, t \, (1+d_p/d_g)^3$$

C_0 is the bulk protein concentration, d_g and d_p are the fat-globule and protein-particle sizes, respectively, and K is a constant

Protein load

$$\Gamma = \frac{\text{Protein at the oil droplet surface (mg)}}{\text{Total droplet surface area } (m^2)}$$

Protein load at oil-water interface

Protein	Protein load (mg/m^2)
α_s-Casein	3-4.2
β-Casein	1-1.75
κ-Casein	4.2
Casein micelle	20
Sodium caseinate	2.2-2.6
Skim milk powder	10-23
β-Lactoglobulin	1.7

Factors affecting protein load

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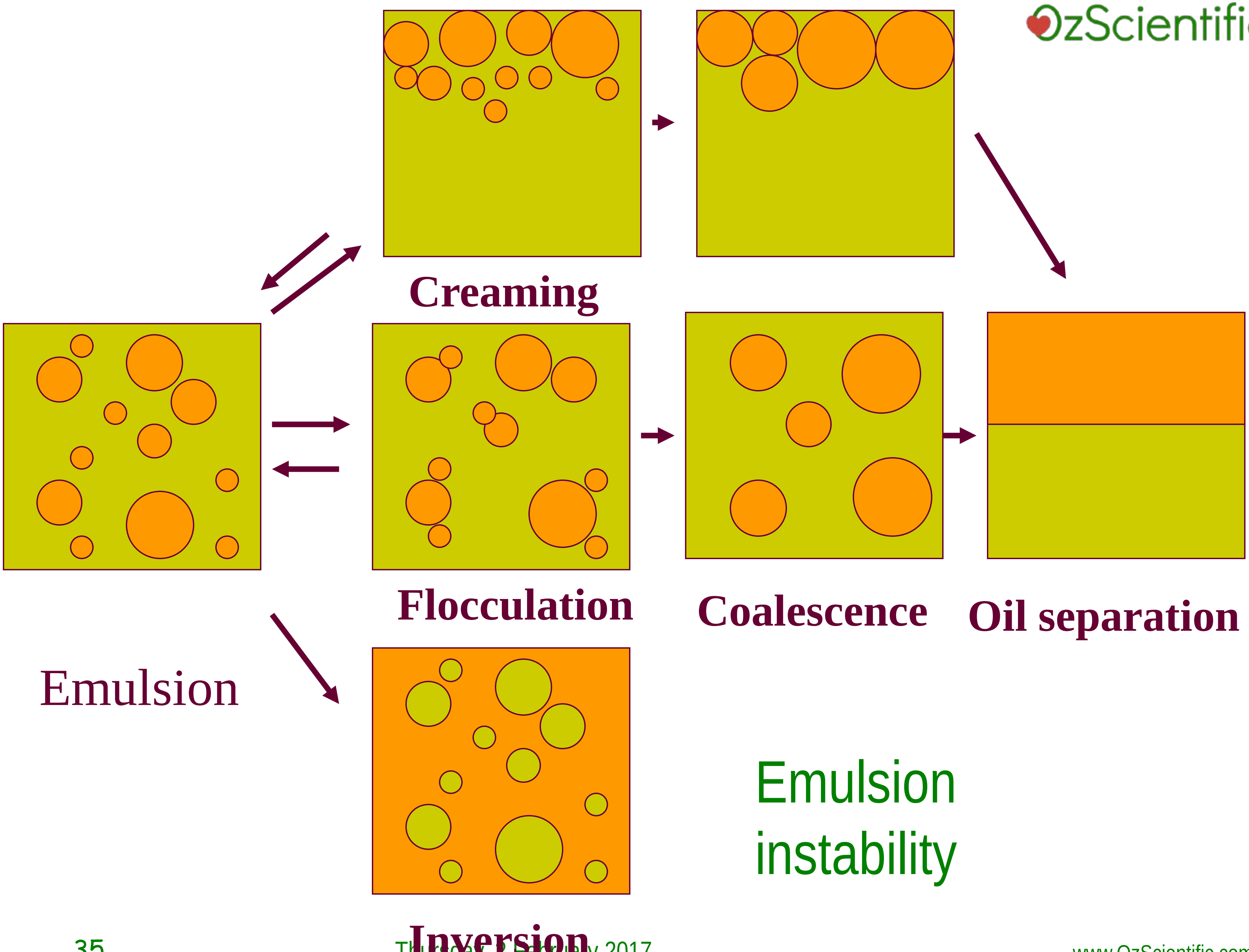
- Volume of oil
- Protein concentration
- Homogenisation temperature
- Homogenisation pressure
- Aggregation state of protein
- Pre-treatment of protein, i.e. Hydrolysis or cross-linking

Types of protein adsorption

- Reversible and irreversible adsorption
- Competitive adsorption

Basic emulsion characteristics

- Thermodynamically unstable
- Possible to make kinetically stable

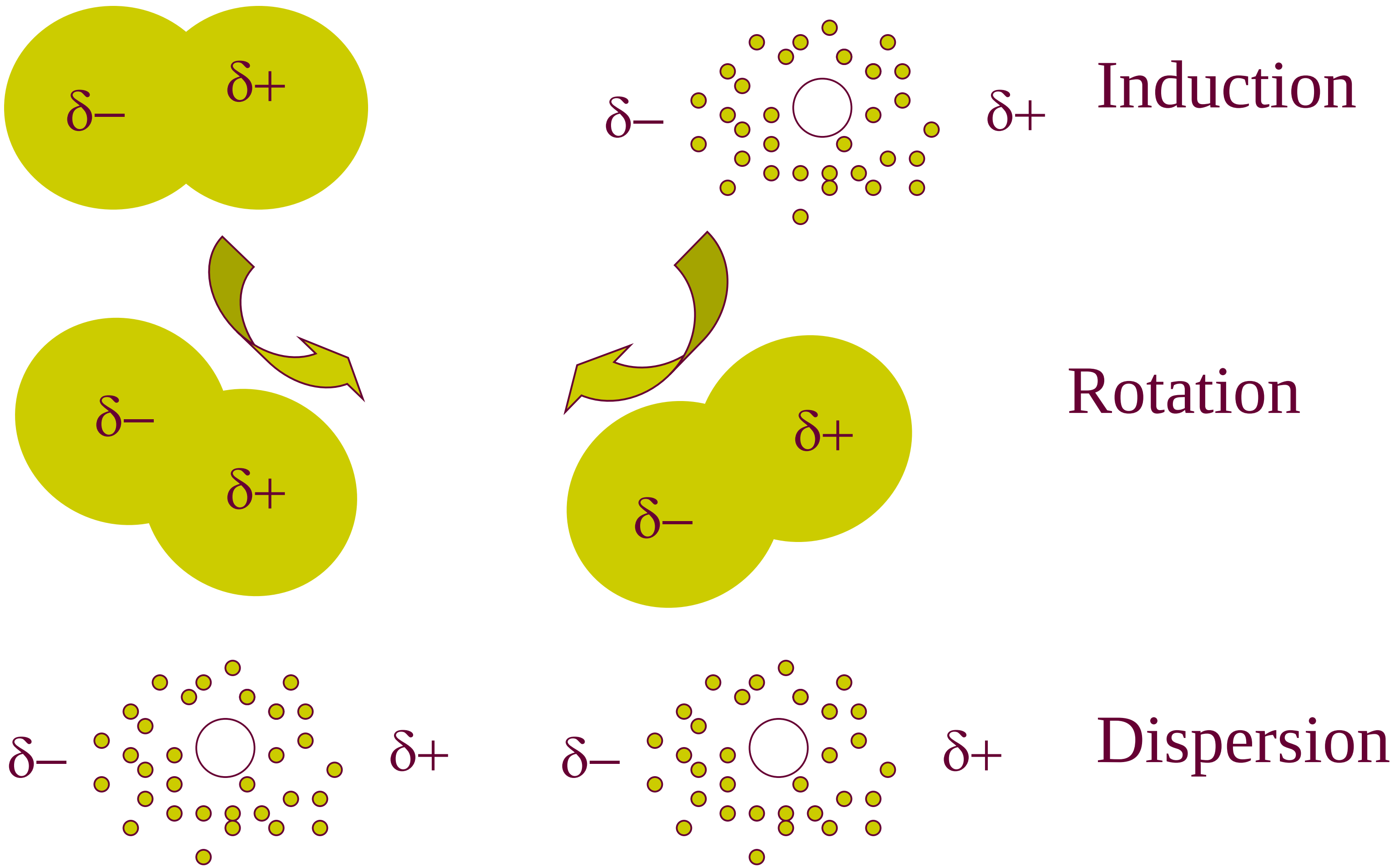


Emulsion instability

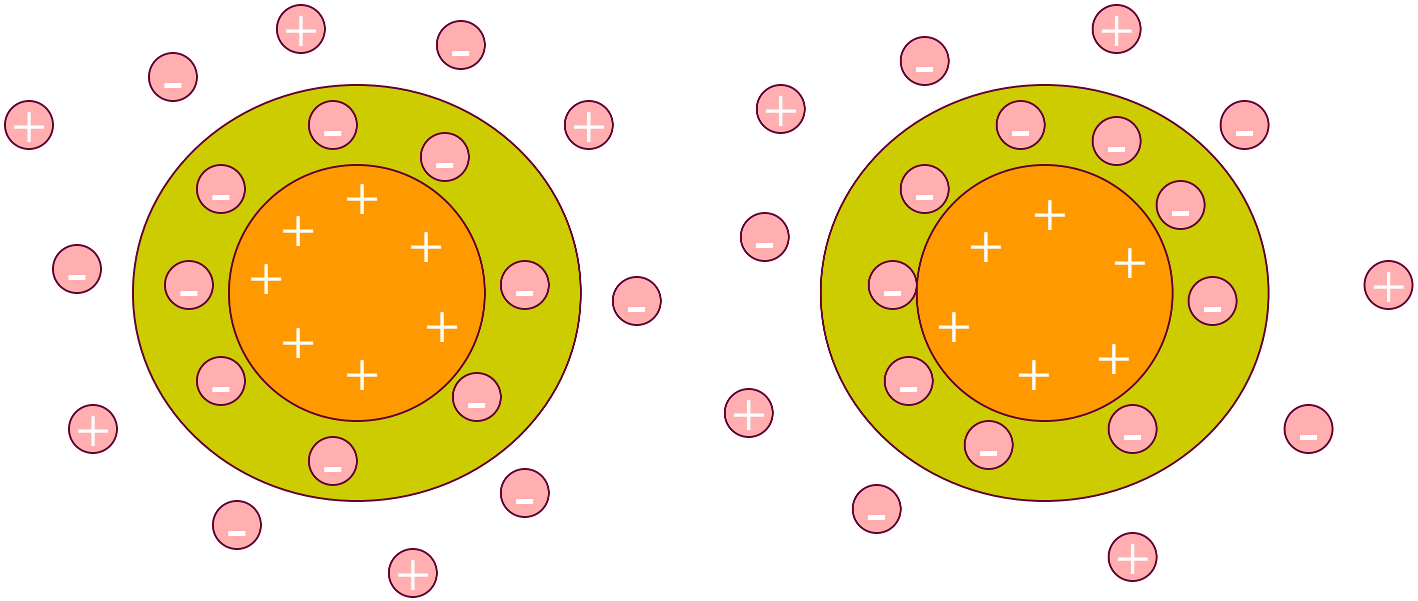
Colloidal interactions

- Van der Waals Interactions
- Electrostatic interactions
- Polymeric steric interactions
- Depletion interactions
- Hydrophobic interactions
- Hydration intrations
- Thermal fluctuation interactions
- Total interaction potential

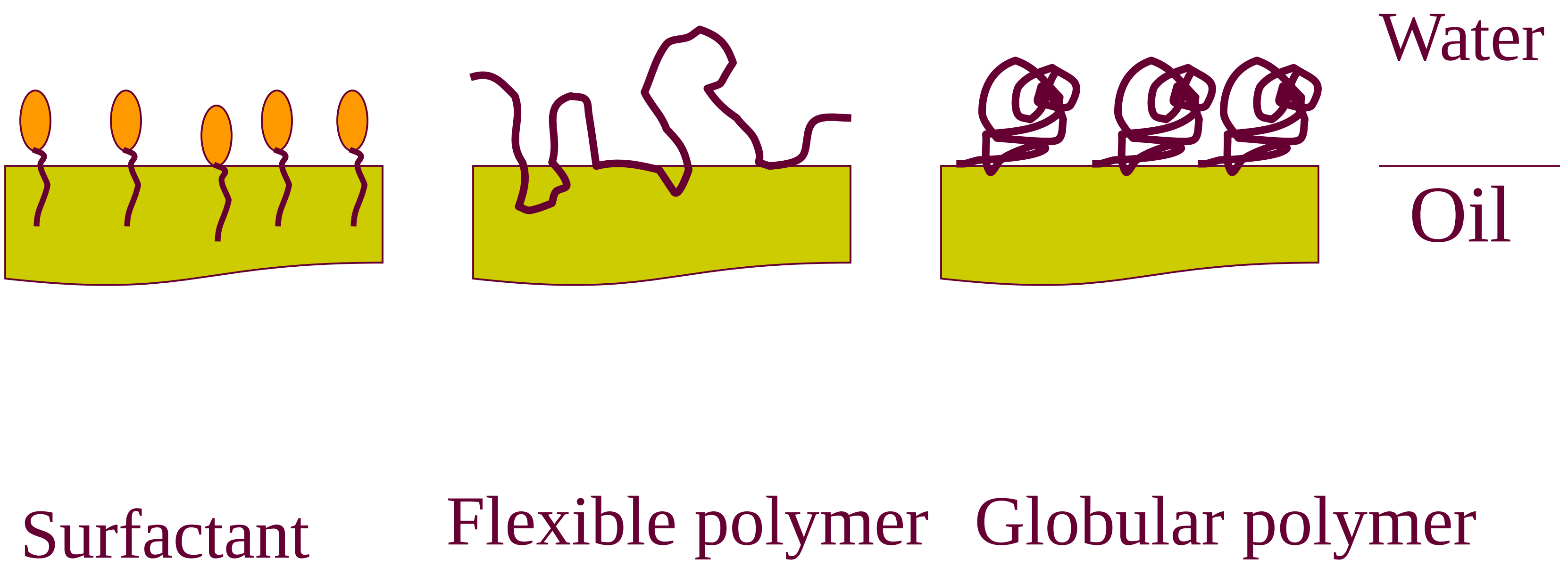
van der Waals interactions



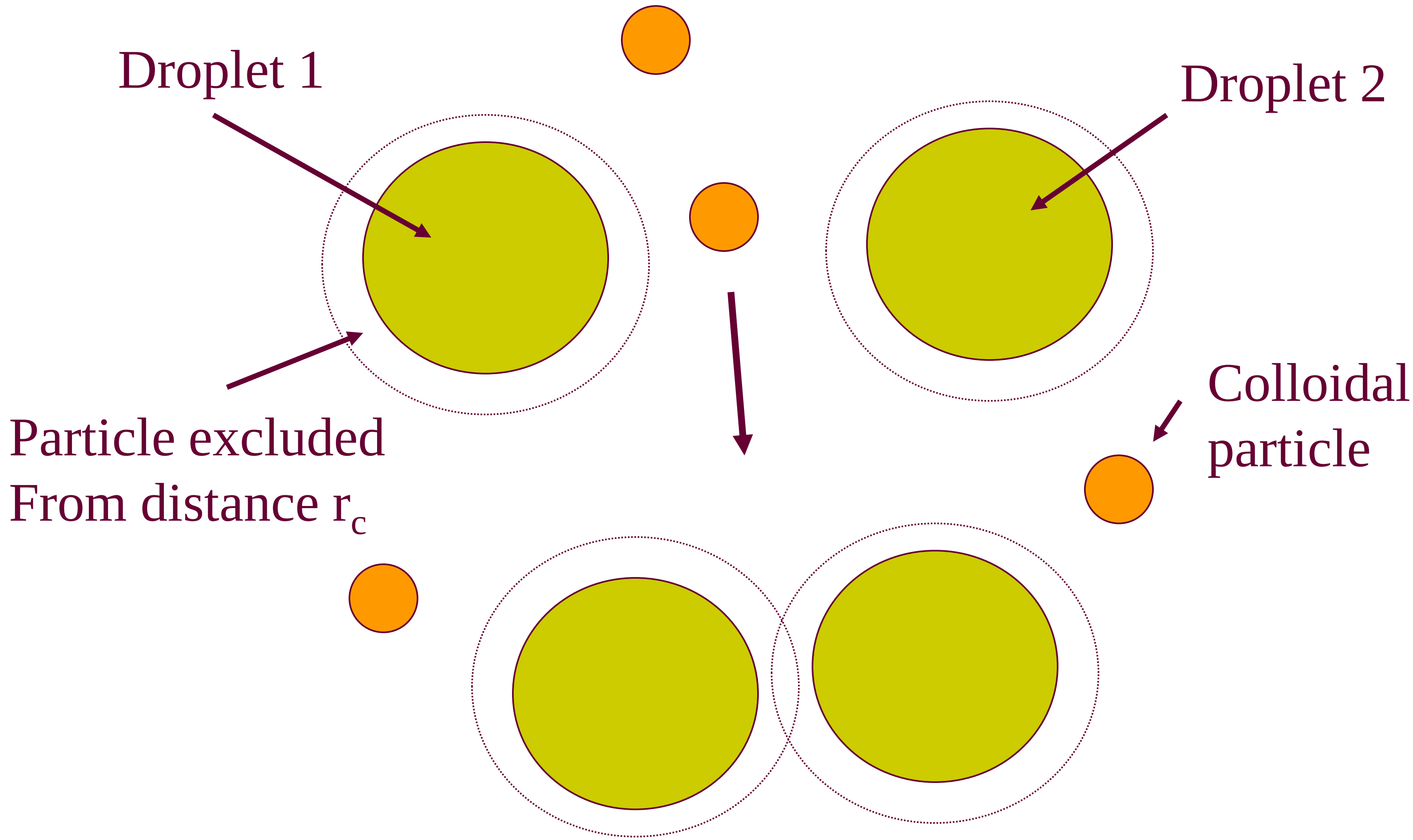
Electrostatic double-layer forces



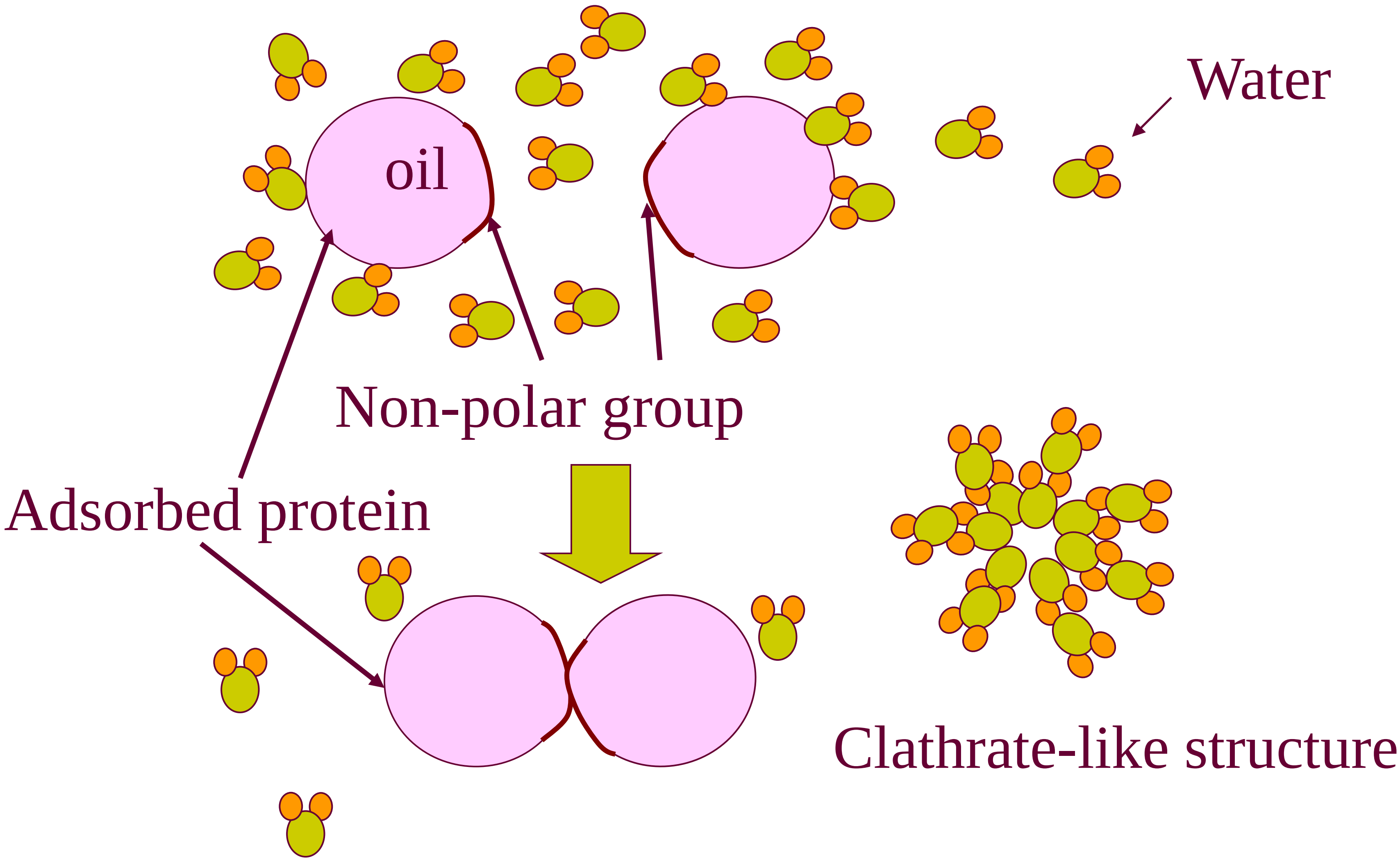
Polymeric steric interactions



Depletion interactions



Hydrophobic interactions



Other interactions

- Hydration interactions
- Thermal fluctuation interaction
- Bridging flocculation
- Hydrodynamic interactions

DLVO Theory for colloidal stability

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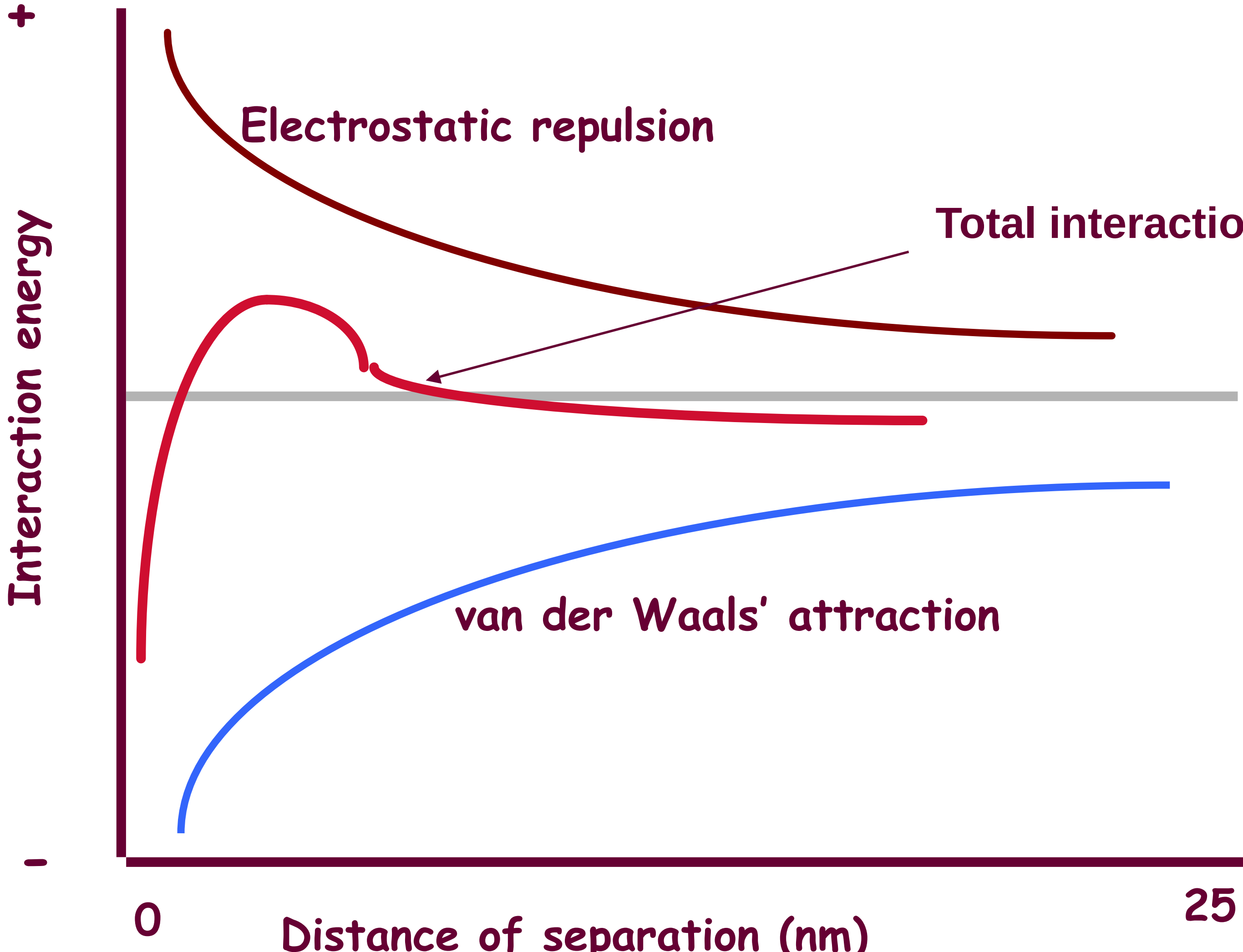


Colloidal forces important for emulsion stability

Type of force	Character	Origin	Influenced by
van der Waals	Attraction	Permanent & fluctuating dipoles	Refractive index Dielectric constant
Electrostatic	Repulsion	Surface charge	Ionic strength, pH
Steric	Repulsion	Adsorbed polymers	Polymer coverage & solubility
Bridging	Attraction	Adsorbed polymers	Polymer coverage
Depletion	Attraction	Non-adsorbed polymers Micelles	Molecular weight Polymer polydispersity
Polyelectrolytes	Repulsion or attraction	Adsorbed polyelectrolytes	Ionic strength, polyelectrolyte coverage

Colloidal forces important for emulsion stability

Type of force	Character	Origin	Influenced by
Hydrophobic	Attraction	Water-water affinity	Solvent properties, surface hydrophobicity
Hydration	Repulsion	Dehydration of polar group	Emulsifier head group, crystallinity
Protrusion	Repulsion	Reduction in movement of emulsifiers normal to the interface	Fluidity of the layer, head-group size, Oil/water interfacial tension

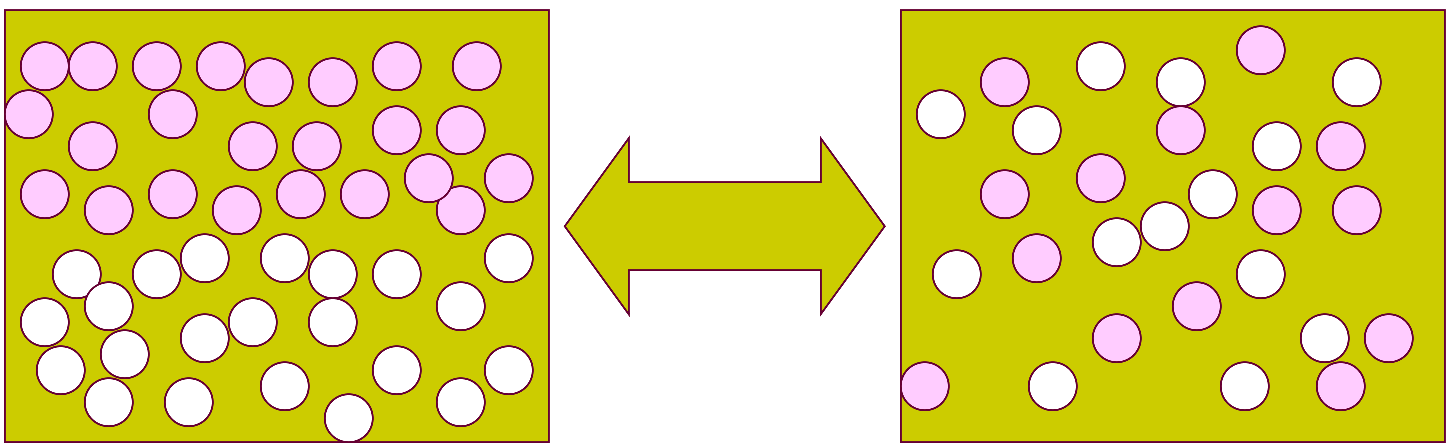
Bergenstahl A & Claesson PM (1997) Surface forces in emulsion. In Food Emulsions (Friberg S & Larsson K, eds), pp 57-109, Marcel Dekker, NY

Structural organisation of molecules in liquids

- Thermodynamics of mixing
- Potential energy change on mixing
- Entropy change on mixing
- Free energy change on mixing

Structural organisation of molecules in liquids

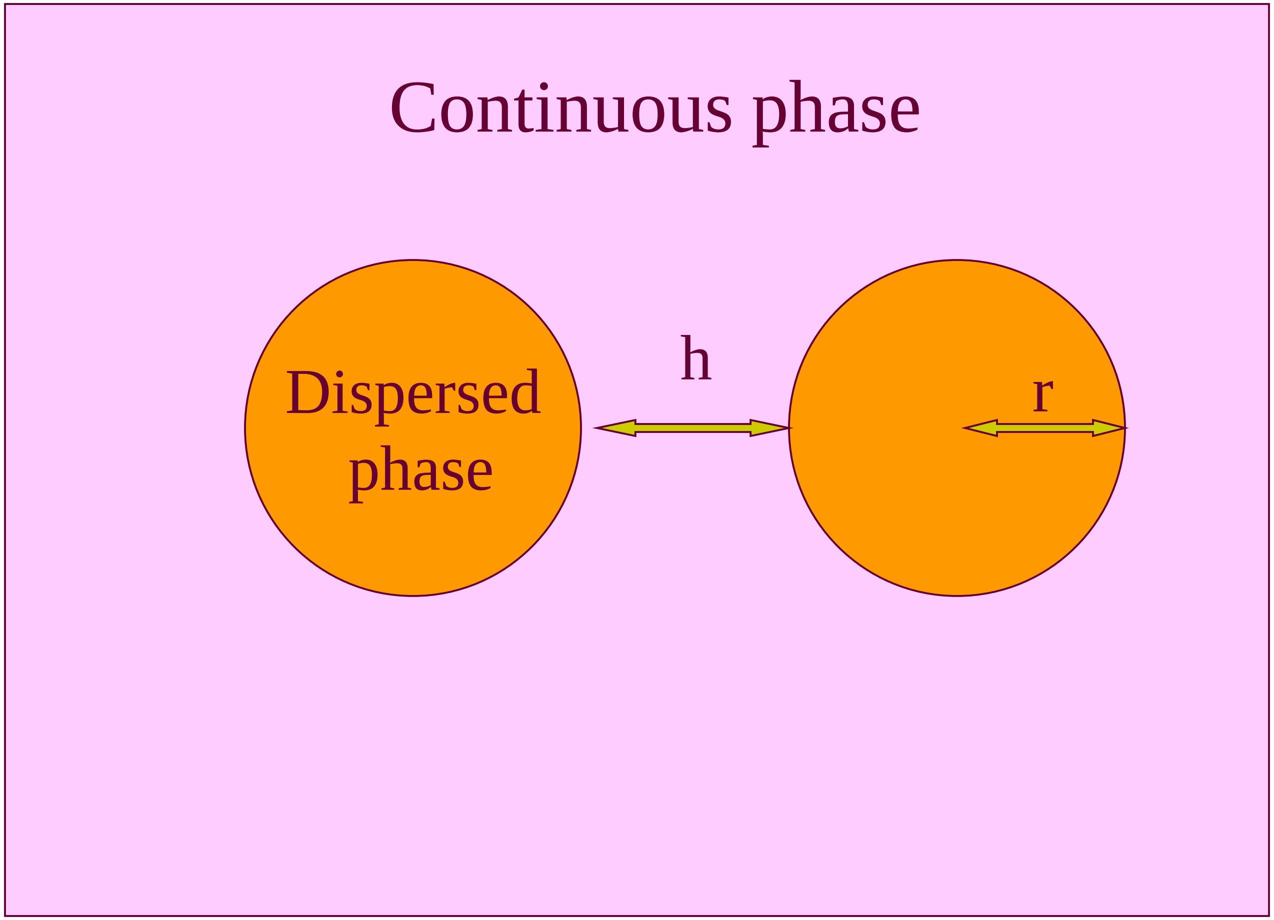
- Thermodynamics of mixing



Immiscible liquid

Miscible liquid

Overall interactions



Overall interaction

- Attractive interactions dominate at all separations
- Repulsive interactions dominate at all separations
- Attractive interactions dominate at larger separations, but repulsive interactions dominate at short separations
- Repulsive interactions dominate at large separations, but attractive interactions dominate at short separation

Inter-particle pair potential

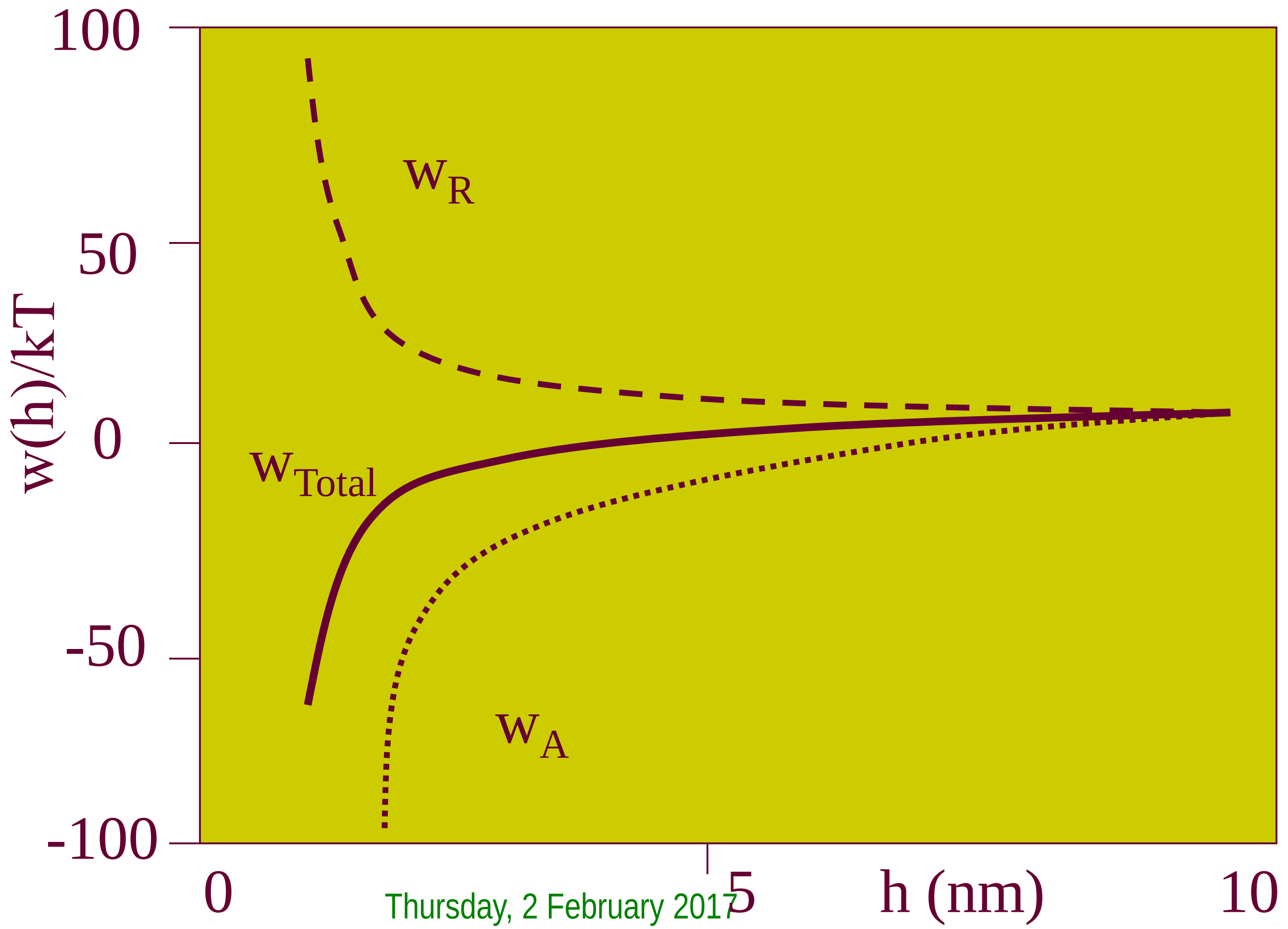
Energy required to bring two emulsion droplets from an infinite distance apart

$$w(h) = w_{attractive}(h) + w_{repulsive}(h)$$

Inter-particle pair potential

- Energy required to bring two emulsion droplets from an infinite distance apart to a surface-to-surface separation of ’h’

Attractive interactions dominate at all separations



Repulsive interactions dominate at all separations

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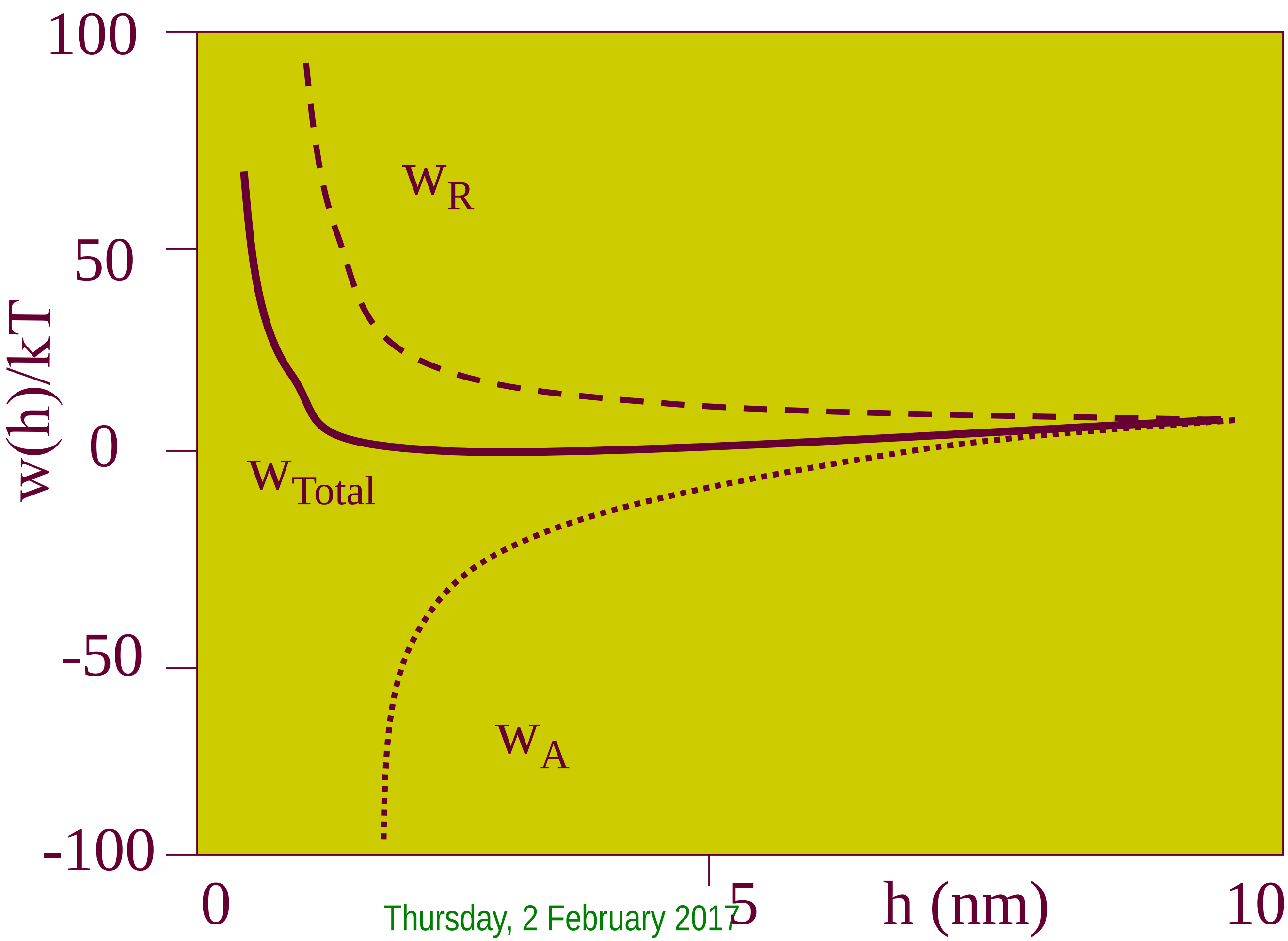
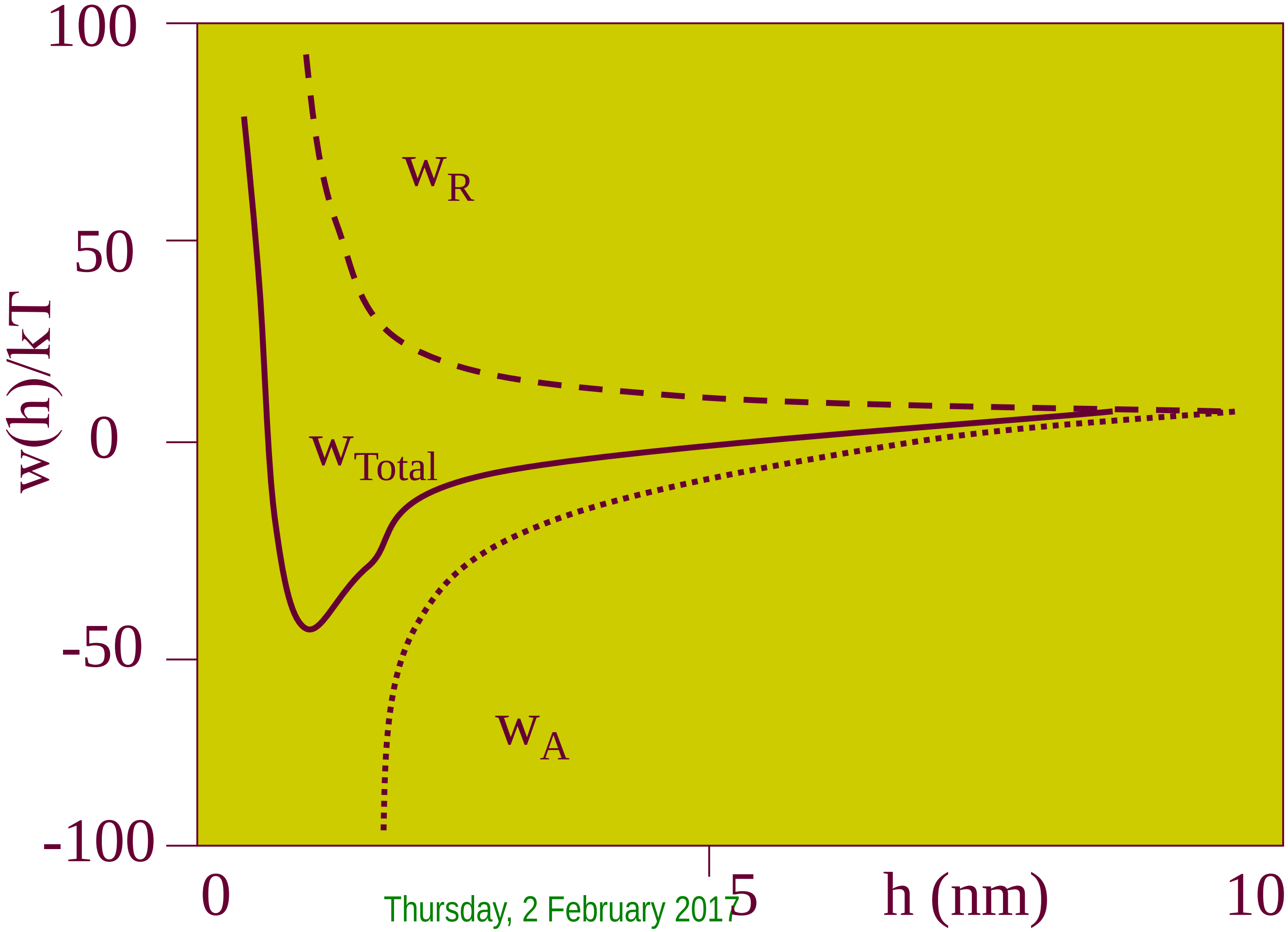
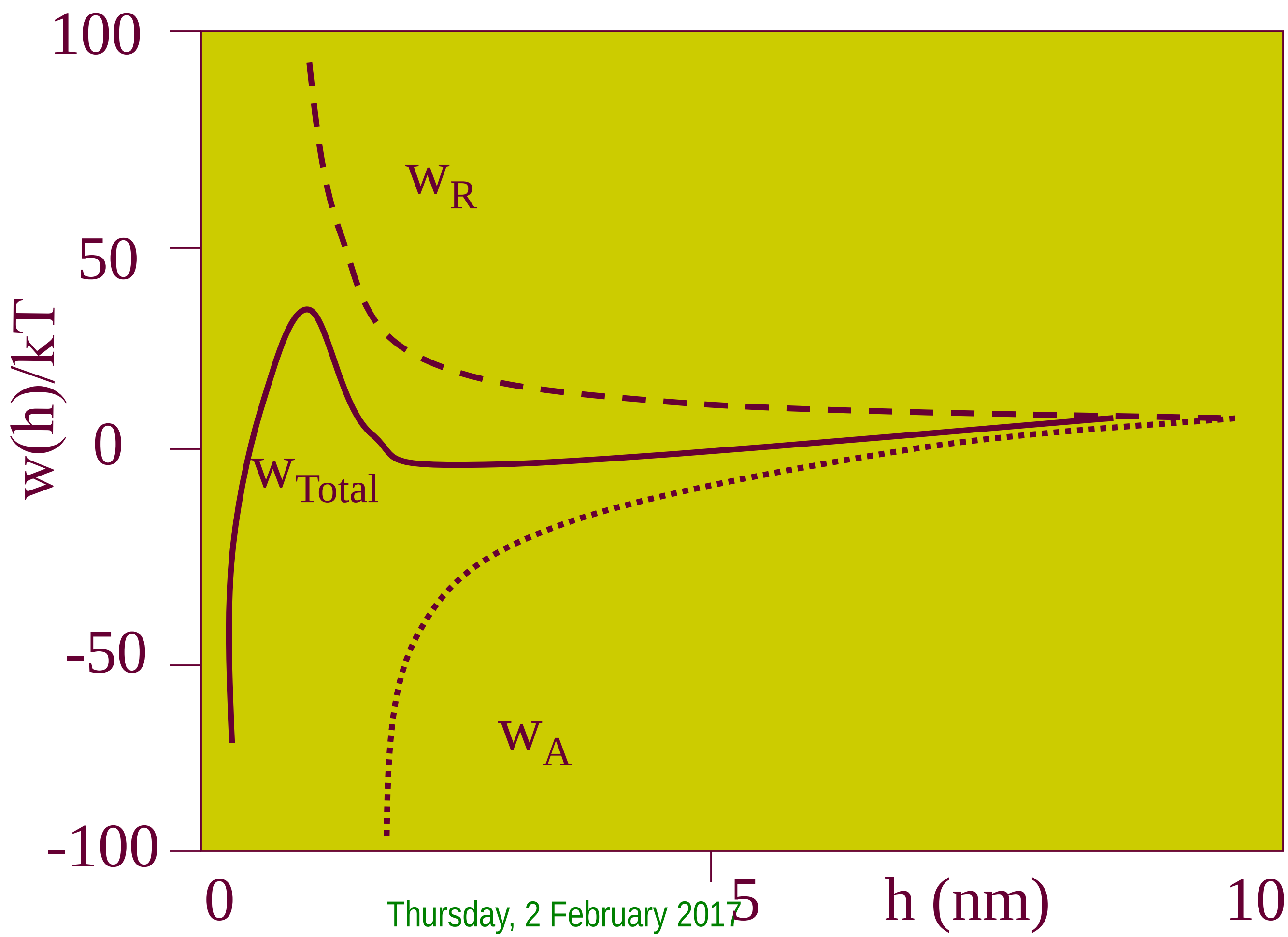


Attractive interactions dominate at large separations, but repulsive interactions dominate at short separations



Repulsive interactions dominate at large separations, but attractive interactions dominate at short separations



Characterisation of emulsions

- Emulsifying properties of proteins
  - Emulsifying activity
  - Emulsion capacity
  - Surface hydrophobicity
- Emulsion stability
  - Emulsion droplet size
  - Protein load
  - Creaming and oil separation
  - Heat stability
- Emulsion rheology
- Emulsion microstructure

Recommeded reading

- Food Emulsions: Principles, practice and techniques by D.J. McClements, CRC Press, Boca Raton, USA, 1999
- Food Emulsions edited by Friberg, S.E. And Larsson, L, Marvel Dekker, Inc, New York, 1997
- Emulsions and Emulsion stability, edited by Sjöblom, J, Marvel Dekker, Inc, New York, 1996