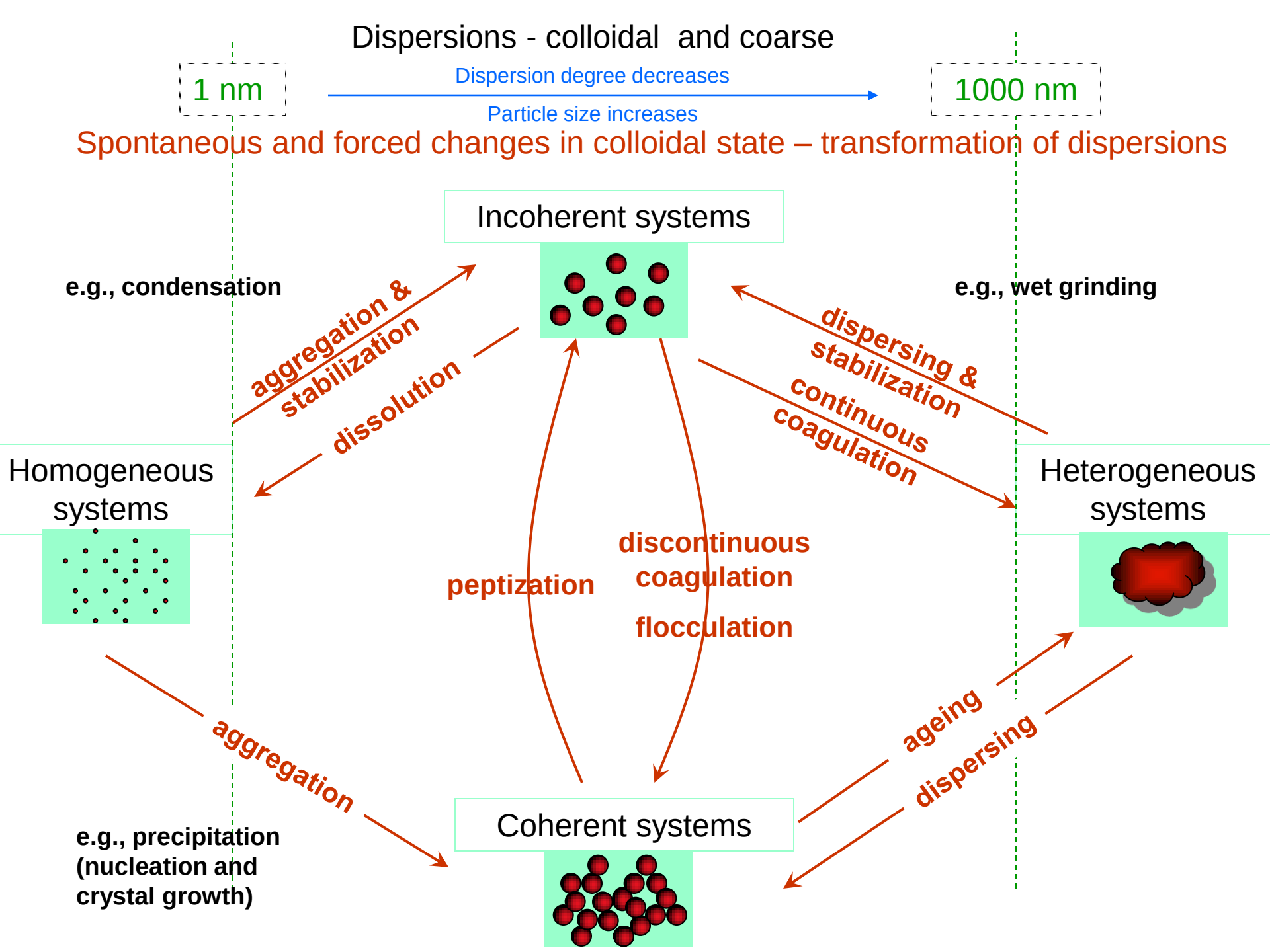
Colloid chemistry for pharmaceutical students 2011/12 year

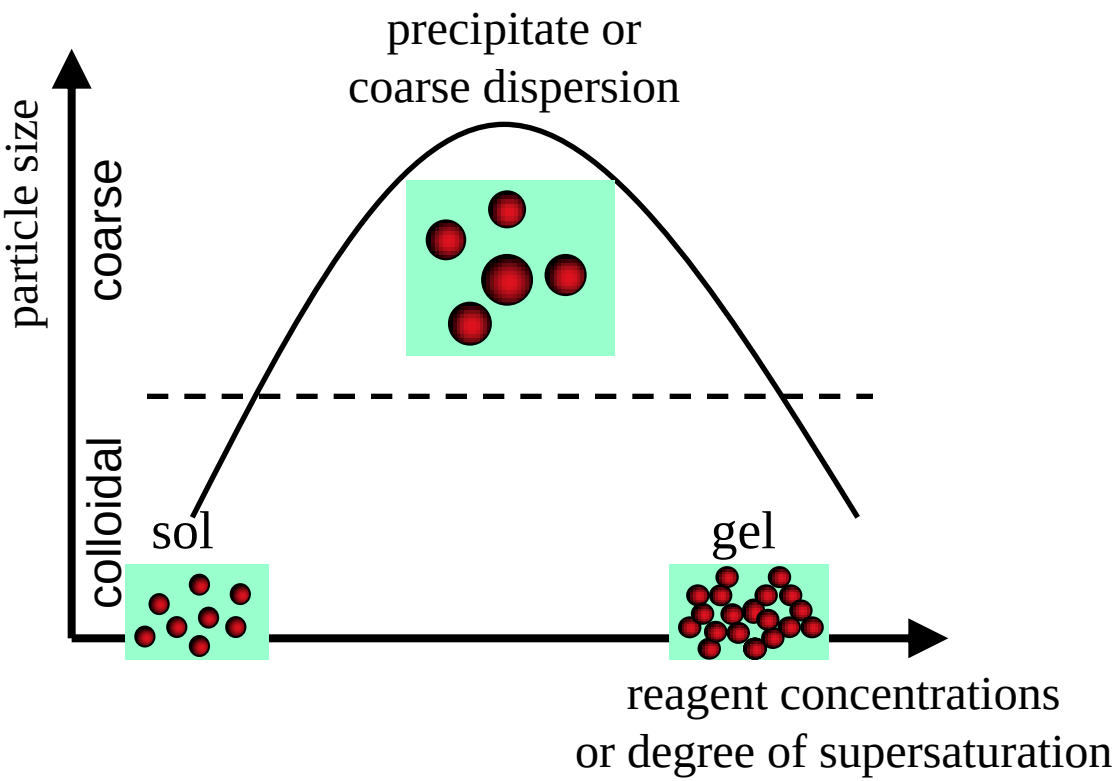
Suspensions and sols

Coherent systems

by Etelka Tombácz


Dispersions - colloidal and coarse
1 nm
Dispersion degree decreases
Particle size increases
1000 nm
Spontaneous and forced changes in colloidal state – transformation of dispersions
Incoherent systems
e.g., condensation
e.g., wet grinding
aggregation & stabilization
dissolution
dispersing & stabilization
continuous coagulation
Homogeneous systems
Heterogeneous systems
peptization
discontinuous coagulation
flocculation
aggregation
ageing
dispersing
Coherent systems
e.g., precipitation (nucleation and crystal growth)

Weimarn's rule



e.g. $Pb(NO_3)_2 + K_2CrO_4 = \underline{PbCrO_4} + 2\ KNO_3$

The more concentrated a solution is, the greater the speed of precipitation. This is known as von Weimarn's rule: *the rate of precipitation can be slowed down by lowering the concentrations of the reactants and raising the solubility of the precipitate.*

Suspensions and sols:

solid particles are dispersed in liquid medium

they are thermodynamically unstable (large surface of separation between the particles and the medium ⇒ high specific surface free energy), but exist during a certain period of time (*kinetic permanency*).

Difference in particle size

relative large particles are in suspensions

small, submicroscopic (< ~1000 nm) particles are in sols

Preparation:

- dispersing bulk solid matter (e.g., grinding, milling)
- precipitation from supersaturated solution
  - change of solvent (e.g., alcoholic solution of sulfur is poured into water)
  - cooling saturated solutions
  - chemical reactions (e.g., hydroxide precipitate formation)

Purification:

suspensions – washing (filtration, centrifugation, etc.)

sols – dialysis (colloidal particles cannot pass through the pores of semi-permeable membrane)

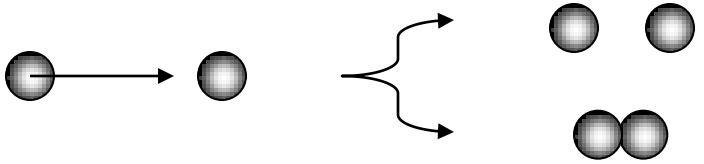
ultrafiltration (pressure applies above membrane, ions/molecules pass through, colloidal particles are retained)

Stabilization due to either electric repulsion or steric hindrance, or even both

preserving individual particles, initial particle size and dispersion degree, protecting against coagulation, flocculation and sedimentation

Colloidal stability and changes of state

Particle interactions (random collision) — Colloidal state



repulsion — sol

attraction — gel

How to hinder adhesion?

coating particles with adsorption layers to prevent close contact (where van der Waals forces act)

How to control adhesion?

bridging particles through macromolecular chains

- **electrostatic stabilization** (DLVO theory)

electric double layer (edl) overlapping in aqueous systems

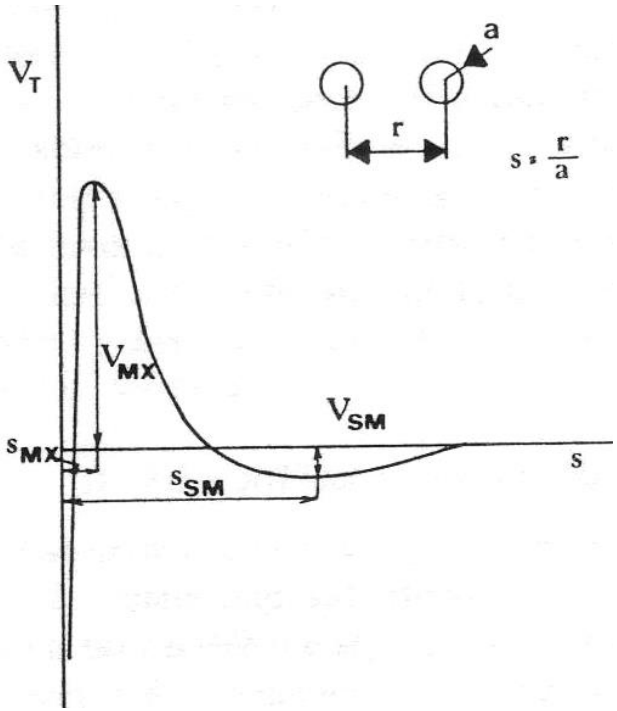
for particles with same sign of charges

diffuse edl (low salt conc.) – stable (repulsion)

compressed (high salt conc.) – coagulated (no repulsion)

for particles with dissimilar charges (opposite sign)

heterocoagulated – attraction (apart from the very dilute region)



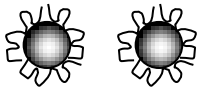
- **steric stabilization** – steric hindrance due to

hydration shell (repulsion)

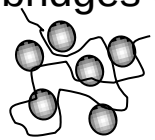
surfactant mono or bilayers (attraction or repulsion)

hydrophobic hydration of alkyl chains in aqueous medium

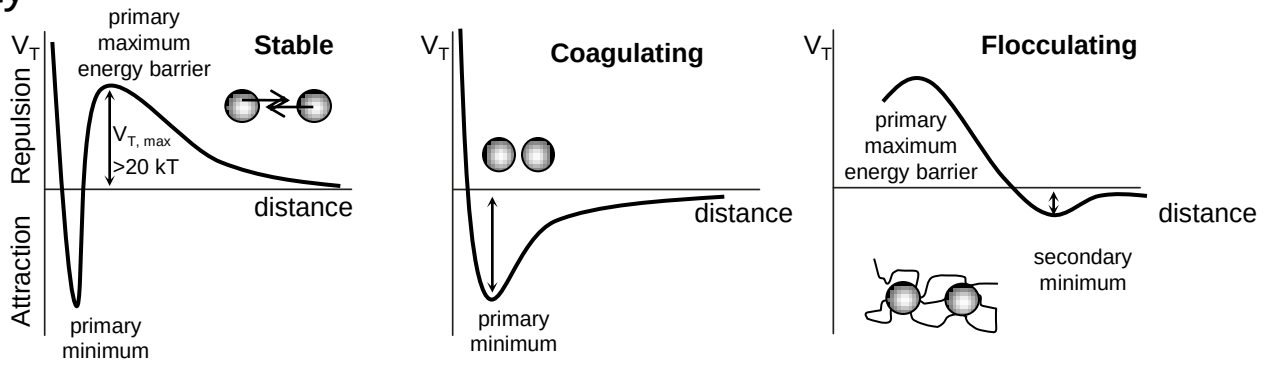
macromolecular layer (repulsion)



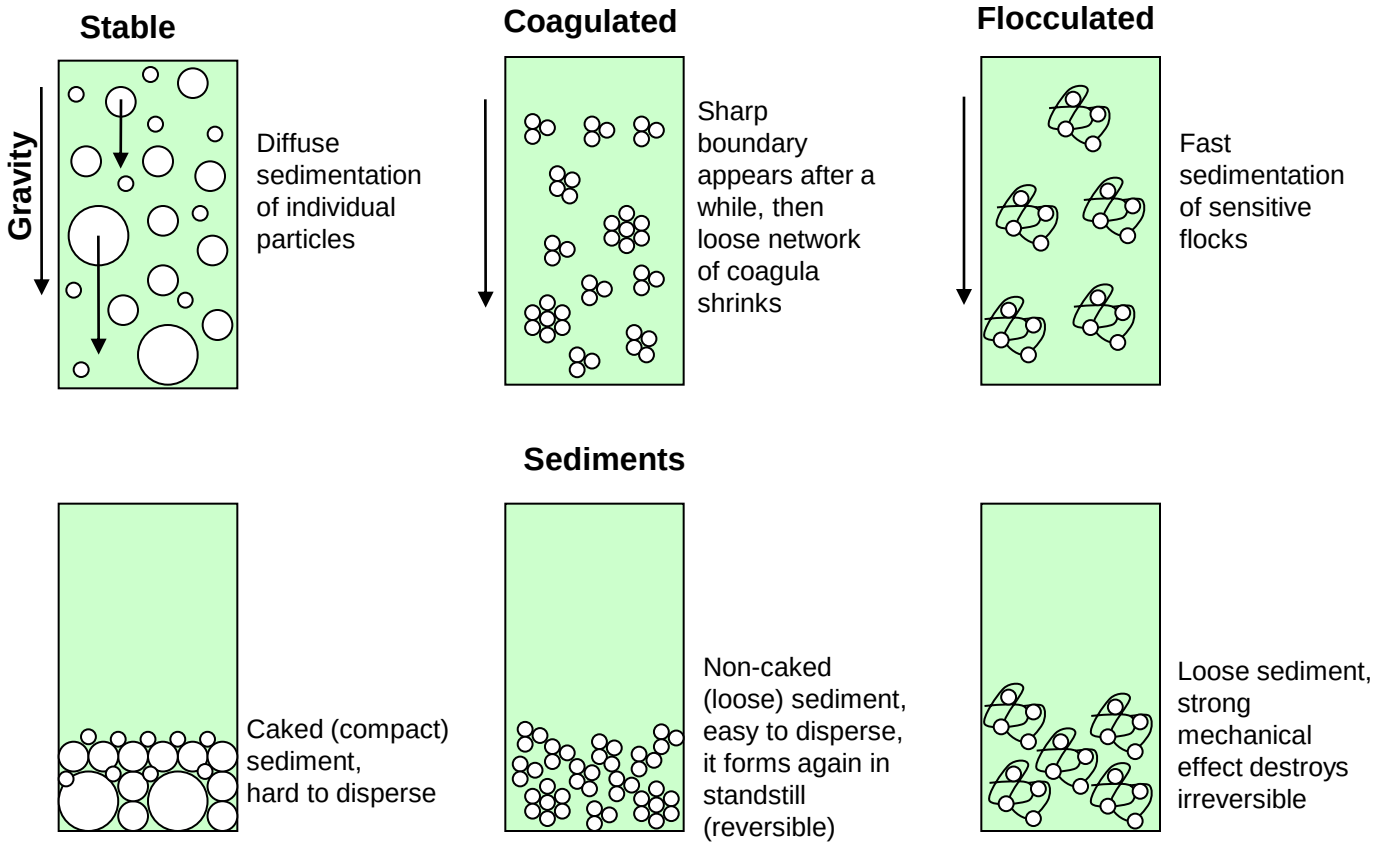
but macromolecular bridges (low concentration and high Mw) - flocculation



Colloidal stability



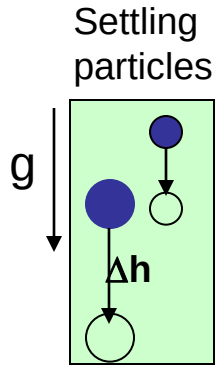
Sedimentation of suspensions under gravity



Sedimentation rate of particles having a radius r

Stokes' equation:

$$v = \frac{\Delta h}{\Delta t} = \frac{2r^2 \pi \Delta \rho g}{9\eta}$$



Deduction

gravitational pull = frictional resistance

$m_{eff}\, g = v\, f$

$m_{eff} = (\rho_S - \rho_L)V = \Delta\, \rho\, (4/3)\, r^3\, \pi$

$f = 6\, \pi\, \eta\, r$

$v = 2\, r^2 \Delta\rho\, g\, /\, 9\, \eta$

It is valid for suspensions.

Particles having radius larger than ~ 2 μm can settle down under gravity.

Smaller, colloidal particles such as particles in sols can diffuse (random, thermal or Brownian motion), therefore cannot settle down. The smaller the particle the faster the diffusion rate.

Methods for inhibition of settling :

- decrease in particle size (wet grinding is the most effective)
- increase in viscosity of dispersion medium (the most frequently used)

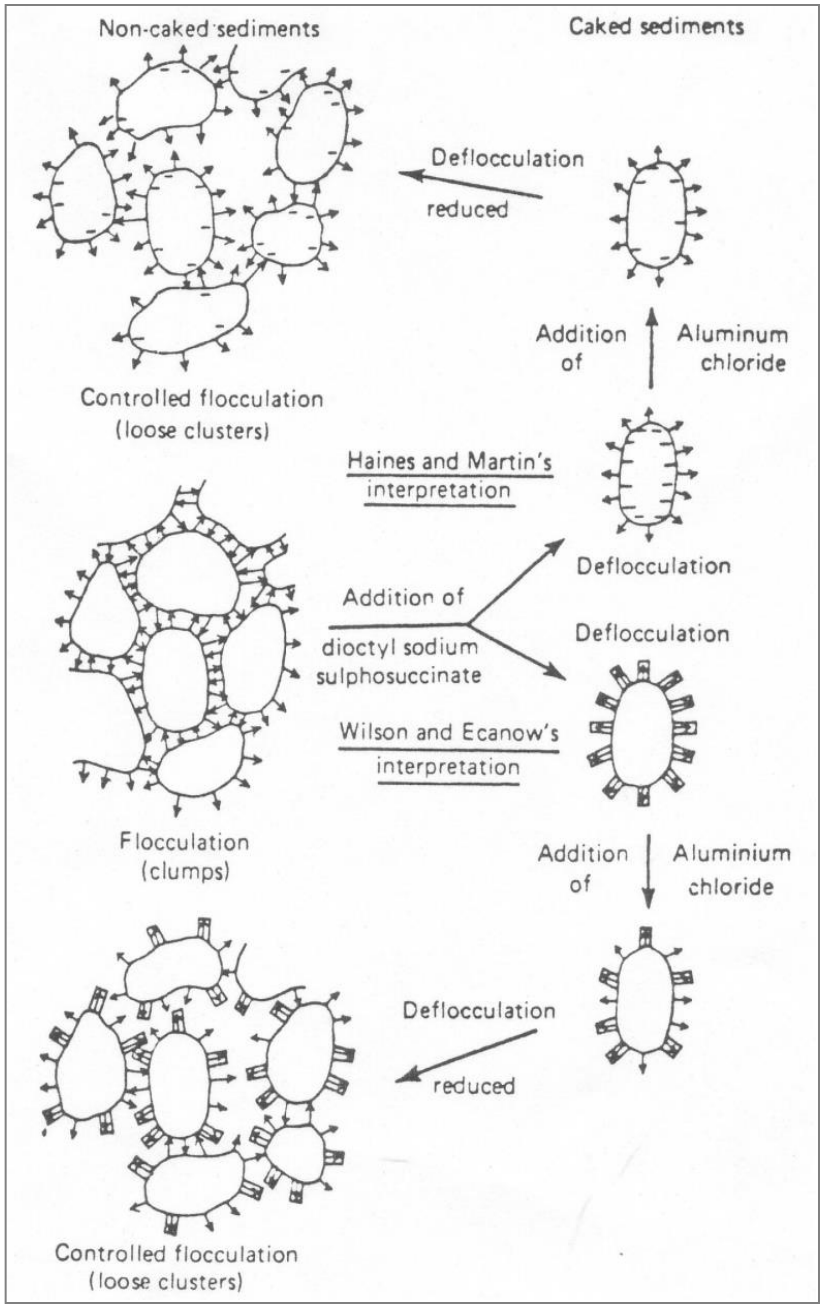
Tuning properties of suspensions

- wetting by adding **surfactant**
  (non-ionic (Tweens, Spans),
  anionic (succinates, oleates),
  polymeric (Pluronics/Poloxamers: PEO-PPO copolymers)
- viscosity by adding **macromolecules**
  (non-ionic hydrophilic polymers (PEO, PEG), in general)
- particle adhesion by adding **surfactants, hydrophilic polymers** and/or **electrolytes**

One example

Sulphamerazine (drug particles) dispersed in aqueous medium
⇒flocculated clumps form

Adding
surfactant (Na-dioctyl sulphosuccinate) and electrolyte ($AlCl_3$)
⇒ controlled flocculated network of particle form



Coherent systems, gels

Particles, molecules or micelles are linked by weak physical or chemical bonds.

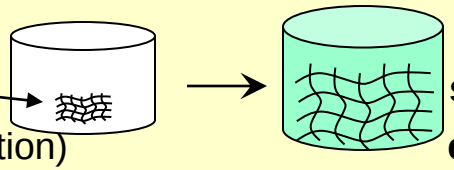
Classification according to

the size of discontinuities	- coarse
	- colloidal (gels)
the nature of material	- dispersed particles
	- macromolecular and
	- micellar systems
the spatial network	- granular
	- reticular
	- sponge

Spatial network is built up from the dispersed part and the dispersion medium is entrapped in.

Formation:

- aggregation of ions/molecules, precipitation at high degree of supersaturation
- discontinuous coagulation
- flocculation
- swelling (mainly macromolecular solids)
- cooling of incoherent systems (sol-gel transformation)



swelled gel

e.g., gelatine in water

Aging of coherent systems: **slow spontaneous processes – desolvation, recrystallization, loose interactions – taking place on standing.**

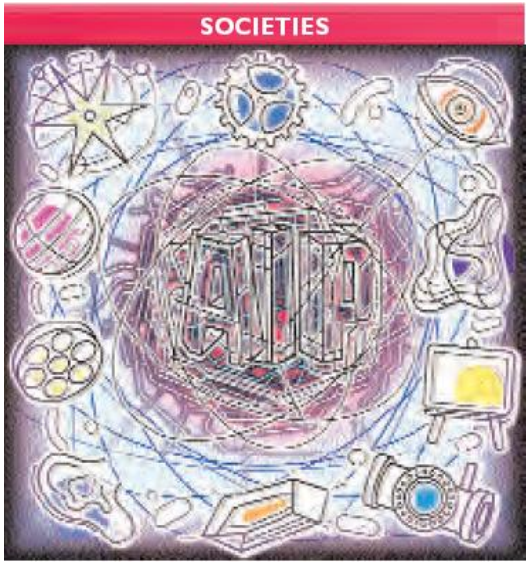
Ageing of jellies results in volume contraction and exuding of liquids. **It is called** syneresis**.**

One of the most often used experimental method for studying coherent systems such as pastes, creams is the **rheology**.

"Rheology is the study of the deformation and flow of matter" (E.C.Bingham)

- Roots in mechanics and hydrodynamics

(American) Society of Rheology was founded in 1929.

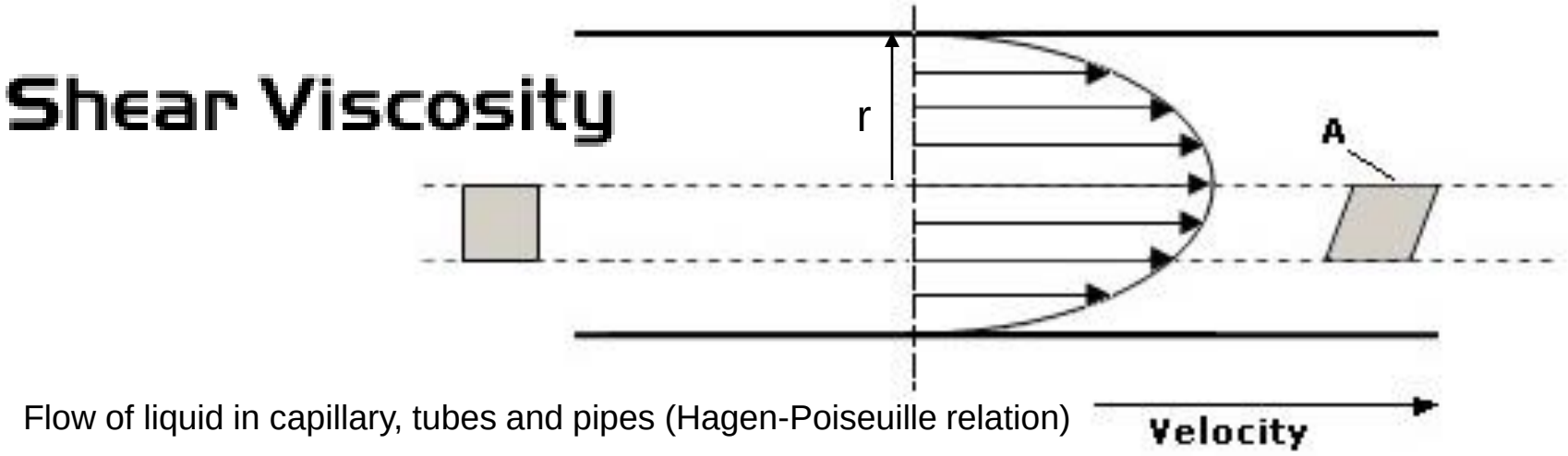


The rheological behavior of dispersions depends mainly on the following factors:

- the viscosity of the dispersion medium,
- the concentration of particles
- the size and shape of particles, and
- the particle-particle and the particle-medium interactions.

Without an understanding of a given material's flow characteristics, viscosity can be simply defined.

Viscosity is basically the ***resistance to flow*** of a material.
As we know, the flow in a river is fastest at the centre and stationary at the bank.
Similar situation exists in tube, pipe, slit, etc.



Flow of liquid in capillary, tubes and pipes (Hagen-Poiseuille relation)

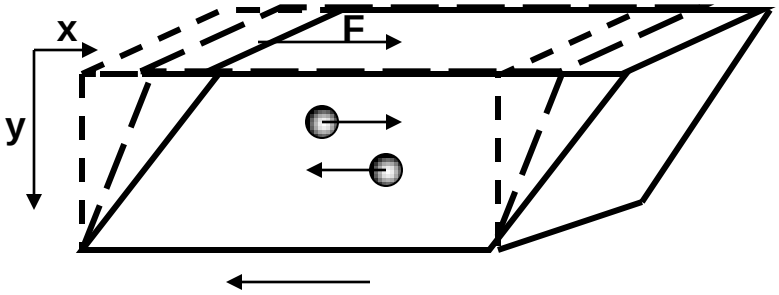
The velocity (v) of the liquid is increasing from the wall of the pipe to the centre line and this causes material to be sheared at the laminar interfaces. The gradient of this increasing velocity is known as the ***shear rate***:

$$d\gamma/dt = dv/dr$$

In flow, the elements of liquids are deformed, and the adjacent points in the liquid are moving related to one another.

deformation change in shape (shear deformation is also called shear strain)

In shear flows shear force (F) acts in parallel



the adjacent particles moving over and past each other.

shear rate (**$d\gamma/dt$**,1/s) is the gradient of the velocity perpendicular to the flow; i.e. **$dv/dy = d\gamma/dt$**,
where deformation: γ**=dx/dy**; flow velocity: **v=dx/dt**

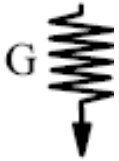
shear stress (τ, $N/m^2 = Pa$) is the **force (F) per unit area** creating by flow

Classification of rheological behavior

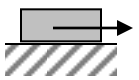
ideal: viscous (liquid), elastic (solid) and plastic

dashpot
viscosity η
$\tau = \eta\, d\gamma/dt$
viscosity

spring
modulus G
$\tau = G\, \gamma$
elastic modulus



friction
element



real: shear-thinning, shear-thickening, pseudoplastic (Bingham)

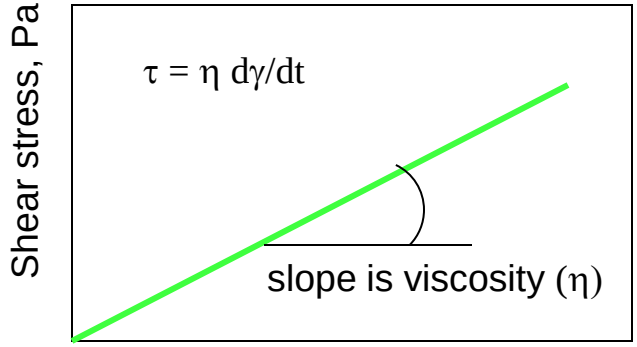
and viscoelastic (liquid-solid and solid-liquid) systems.

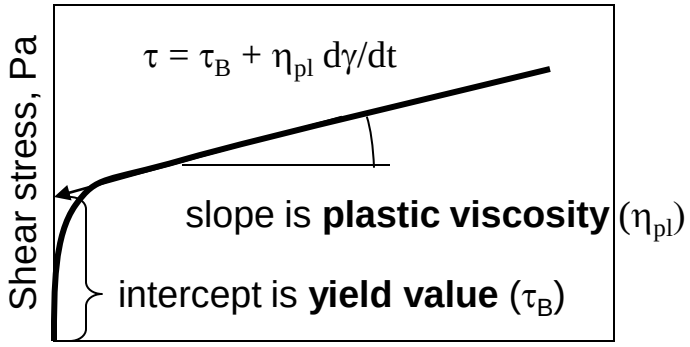
Flow curve: relationship between shear rate ($d\gamma/dt$) and shear stress (τ)

for **Newtonian (viscous)** liquid and for **Bingham (pseudoplastic)** system

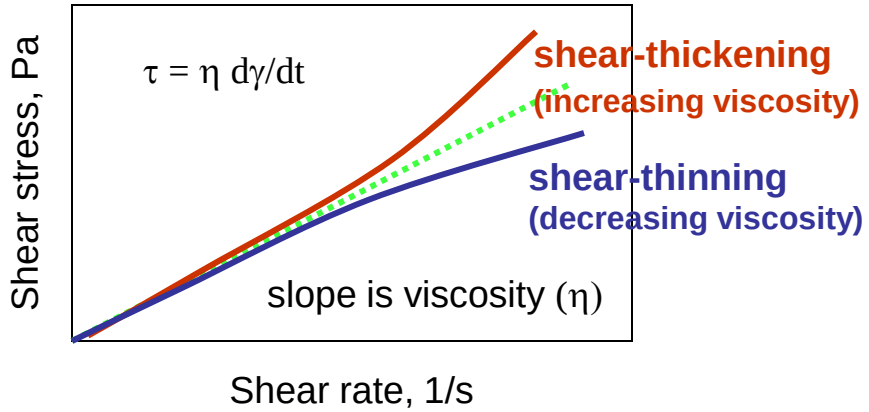
viscosity constant $\eta = \tau / (d\gamma/dt)$

plastic viscosity constant

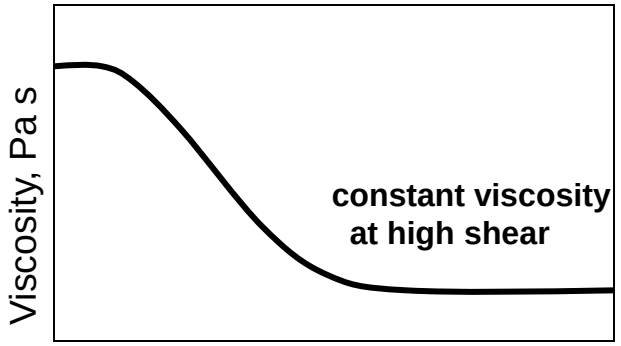




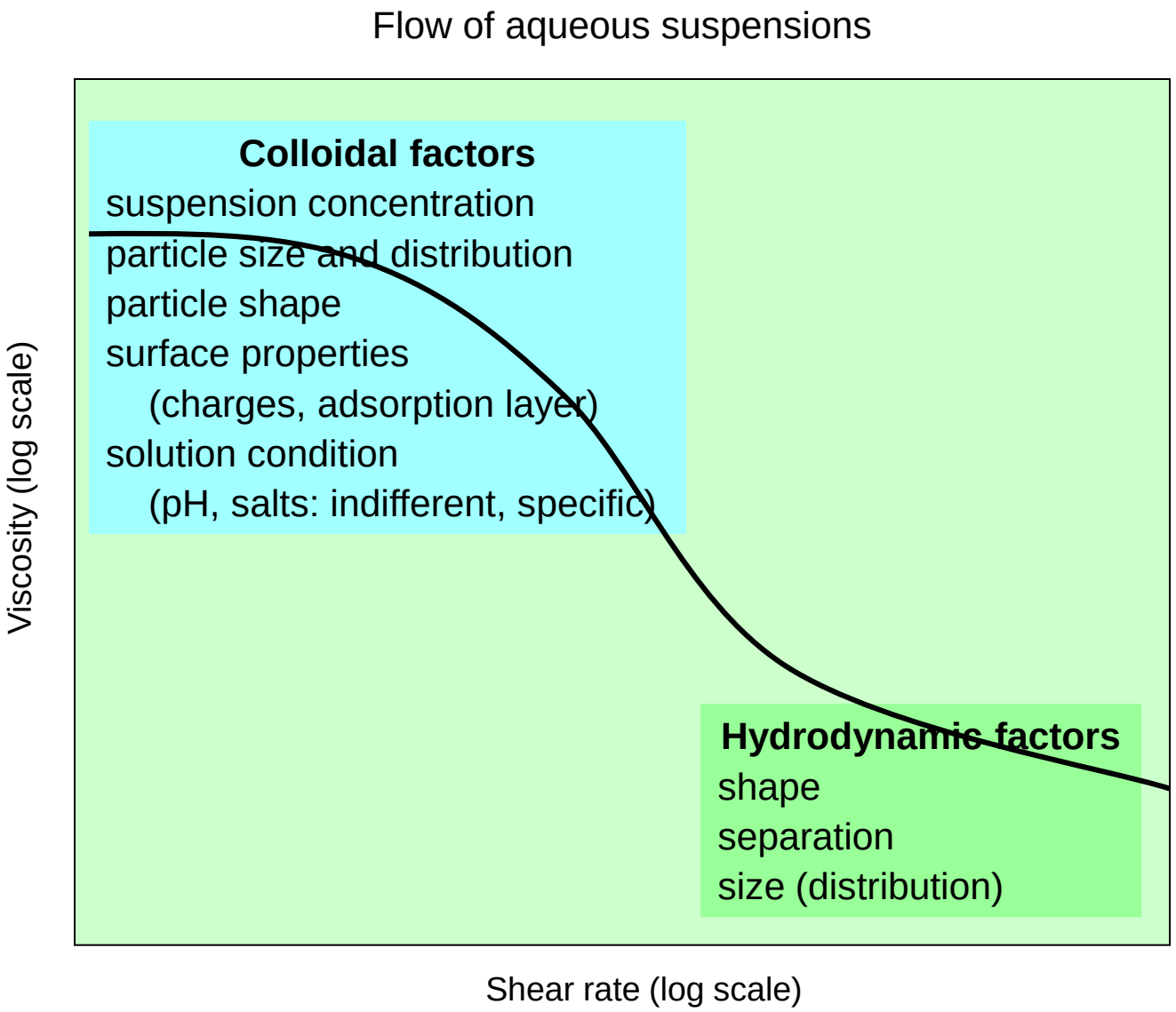
viscosity depends on the shear rate



Viscosity curve – pseudoplastic



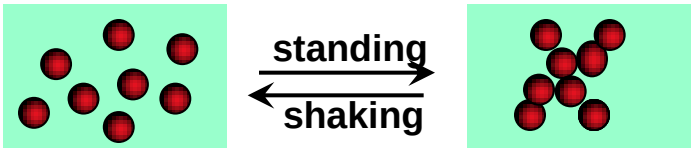
Suspension rheology

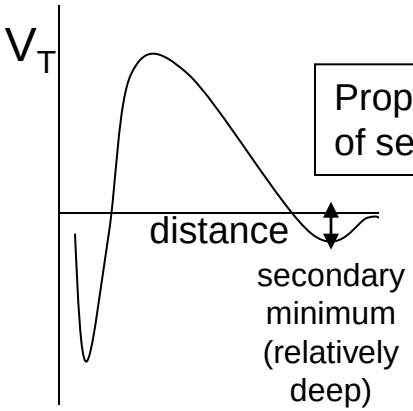


Thixotropy: "change on touching" (Greek)

time dependent flow behavior,

an isotherm reversible sol-gel transformation

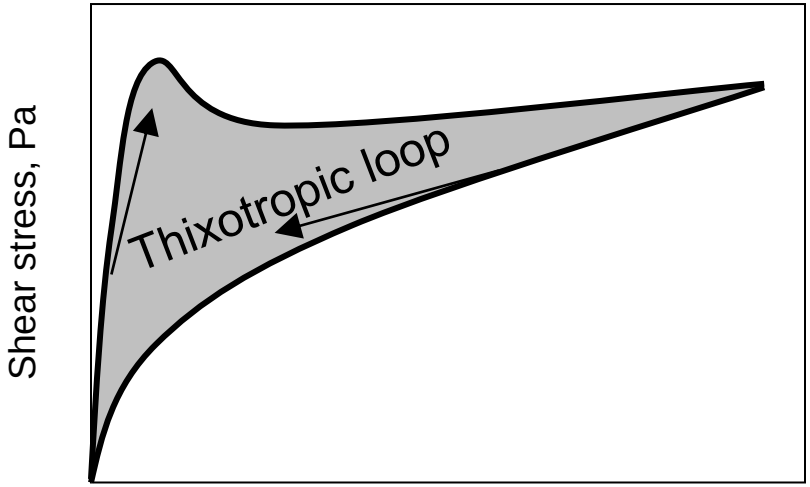




weak attraction between particles

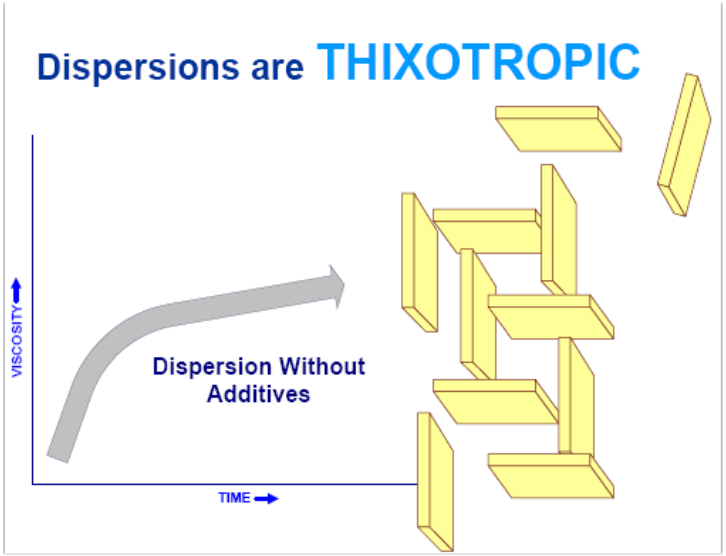
Proportional to the depth of secondary minimum

Loose network does not collapse on the action of thermal motion.

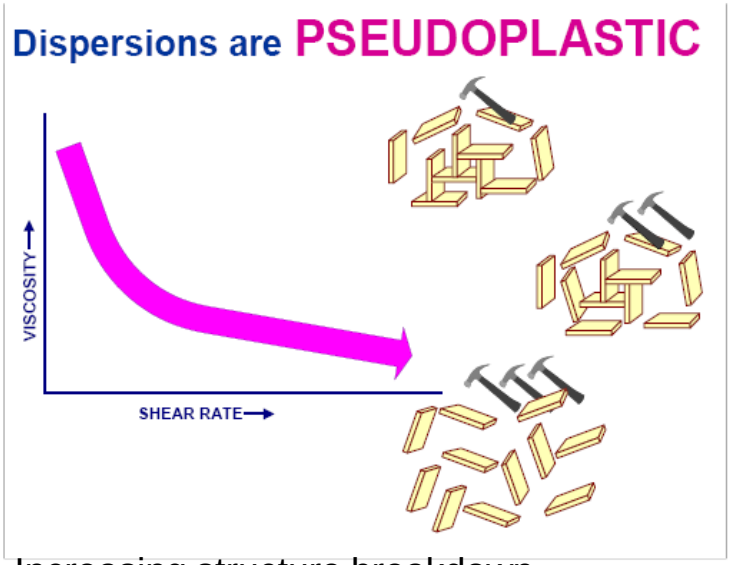


Loop test (increasing shear rate from zero to a maximum and back again): up- and down curves are measured, area between them may be calculated

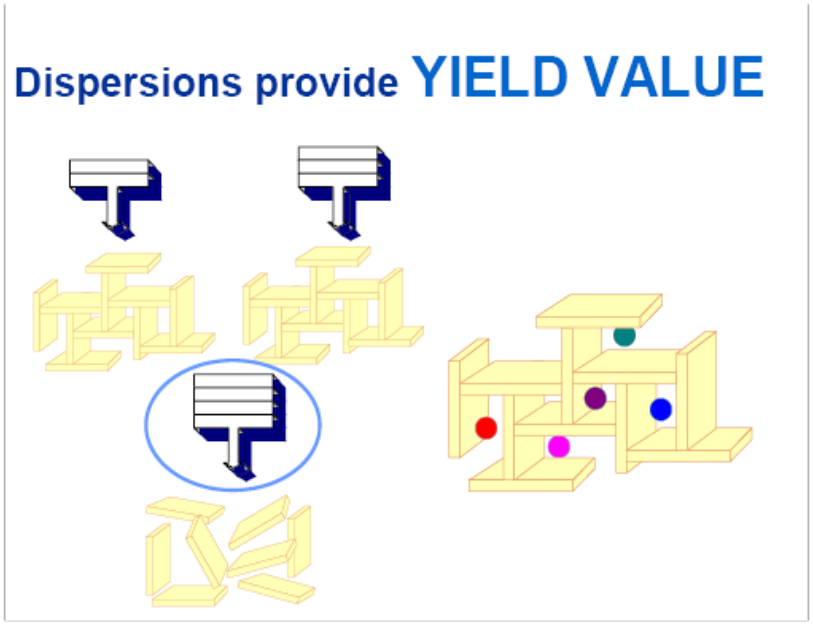
Attractive colloidal forces (weak, coagulation at primary minimum with some 10 kTs depth, flocculation in a shallow – a few kTs - secondary minimum) can act between particles under random collision, however, **any flow will progressively break down the particle network** formed in standstill, when shear rate is greater than a critical value hydrodynamic effects dictate the flow of dispersions; thereafter further rest reform the aggregates under the action of Brownian motion. Thixotropy is a function of time and shear rate, and therefore cannot be properly accounted for in experiments where both these variables are changed simultaneously.



Three dimensional “house of cards” colloidal structure.



Increasing structure breakdown results in decreasing viscosities.



A certain minimum force, the yield value, must be applied to start disrupting the structure.

Water-soluble components modify smectite rheology.

Effect of cations:

Monovalent > Divalent >Trivalent