Critical fouling conditions induced by colloidal surface interaction : from causes to consequences

Causes :
property of concentrated colloidal suspension

From causes to consequences :
a way to depict consequences of these properties on filtration

Consequences :
critical filtered volume in dead end filtration
critical Pe number in cross flow filtration
structure and kinetics of deposit formation

Critical flux : chronological account

Before the critical flux birth

1986

- Colloid flux paradox (Cohen and Probstein 1986)
- Effect of colloid interaction of UF (McDonogh et al. 1989)
- In the review of Belfort, Davis and Zydney (1994)
  still exist a need to develop *“quantitative understanding of the possible interaction that can occur between particles in a complex process streams”*

Critical flux : first definition

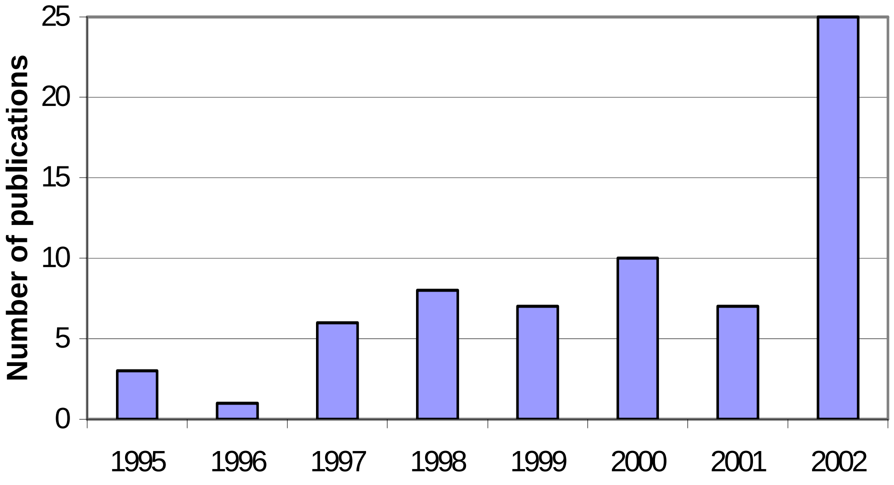
1995

- Theoretical demonstration and definition of critical flux (Bacchin 1994, 1995)
  “*flux required to overcome surface interaction and leads to coagulation at the membrane*”
- First experimental highlight (Field et al. 1995 and Howell 1995)
  Definition of “*sub critical flux operation*”

Critical flux : evolution and importance of the concept

- In 2002, critical flux is used in around 10 % of publication dealing with membrane fouling (around 250 in a year)

2002



Surface interaction and concentration **control structure** of concentrated colloidal suspension

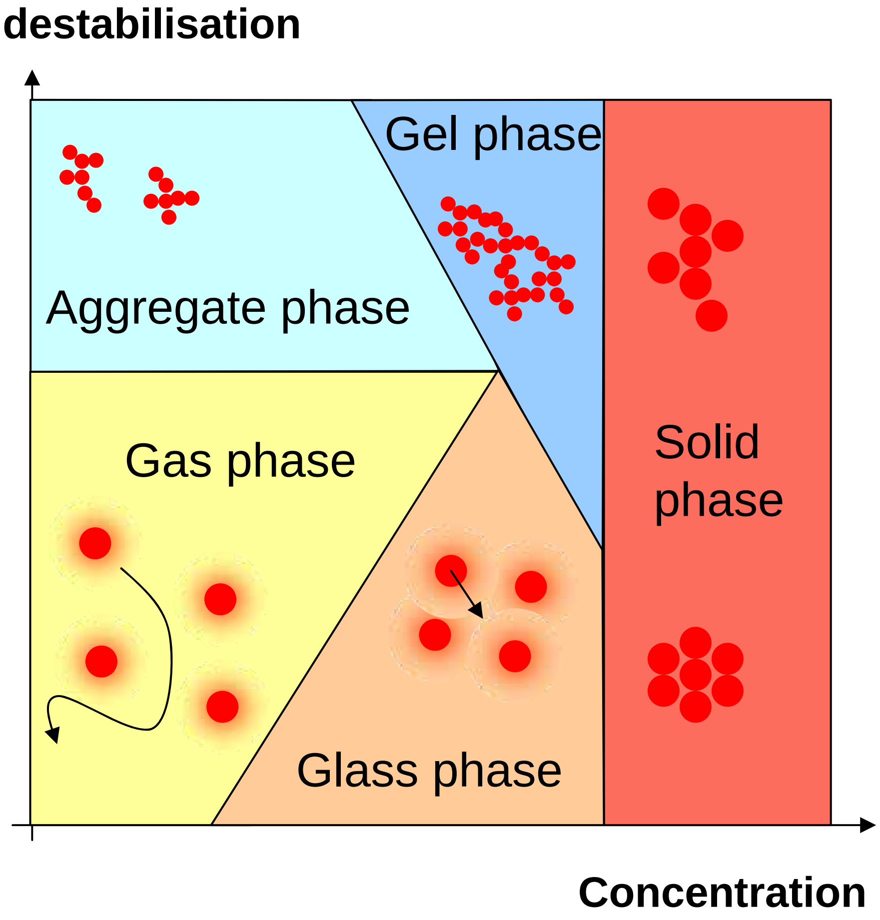
Gas phase : free and random move of particles in the solvent

Aggregate phase : free and random Move of aggregates in the solvent

Glass phase : network of ordered repulsive particles (move from and towards equilibrium position)

Gel phase : network of elastic attractive particles

Solid phase : network of Particles in contact



Surface interaction and concentration **control phase transitions** in concentrated colloidal suspension

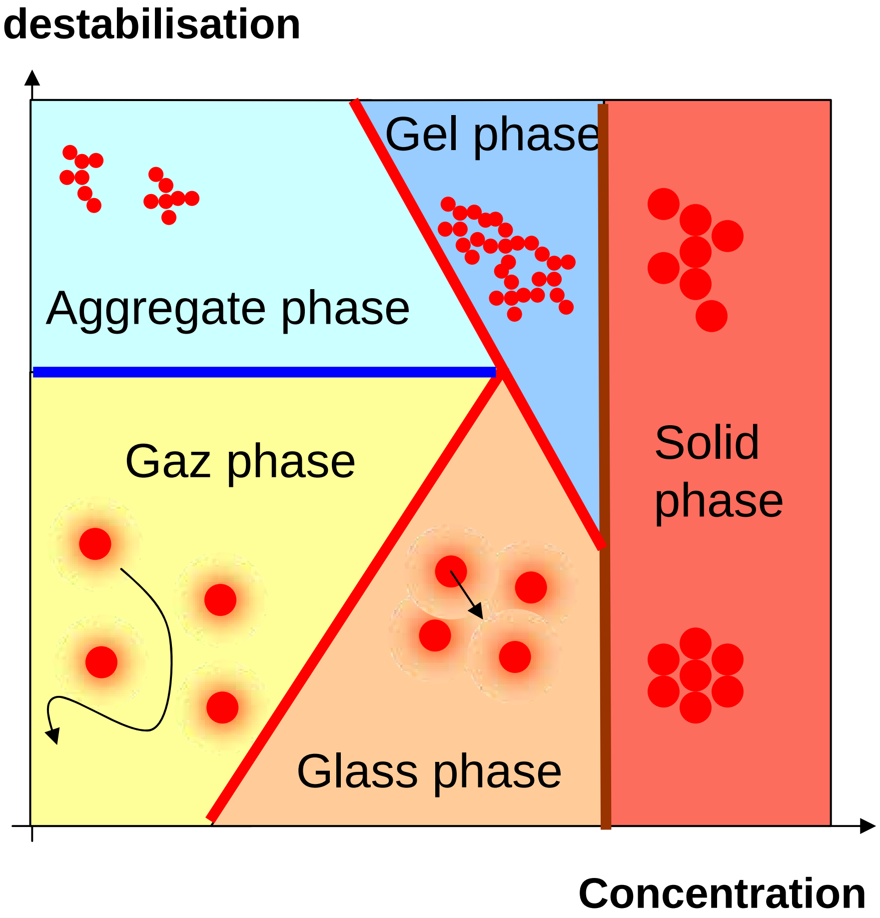
Aggregation :
formation of aggregate

Percolation of attraction or repulsion : formation of a network

Spinodal decomposition :
irreversible solid formation

↓

critical phenomena in term of transition reversibility



Which properties can describe this complexity ?

Osmotic pressure, π :

- relative to the resistance to the local over concentration of the suspension

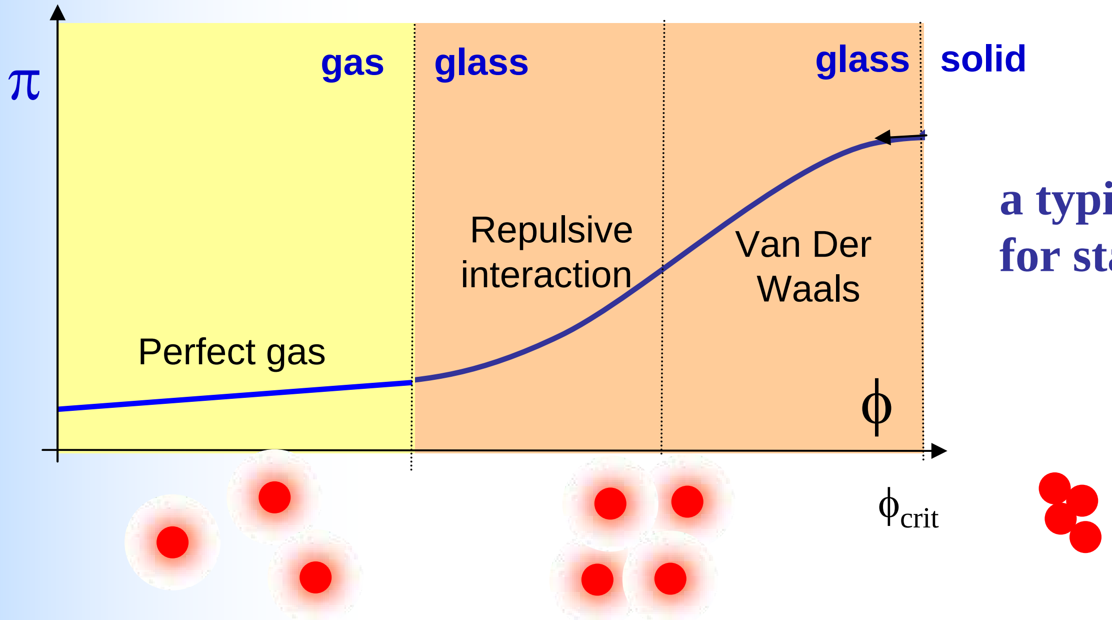
- macroscopic property experimentally accessible

- relative to the equilibrium of the dispersed phase in the solvent sensitive to multi-body surface interaction and depicting phase transitions

relevant to filtration

measurable for complex fluid

adapted to describe the complexity responsible of fouling



a typical π curve for stable colloid

Osmotic pressure : a key property for filtration process

Osmosis

$$J = \frac{\Delta P - \pi_i}{\mu(R_m + R_c)}$$

Diffusion

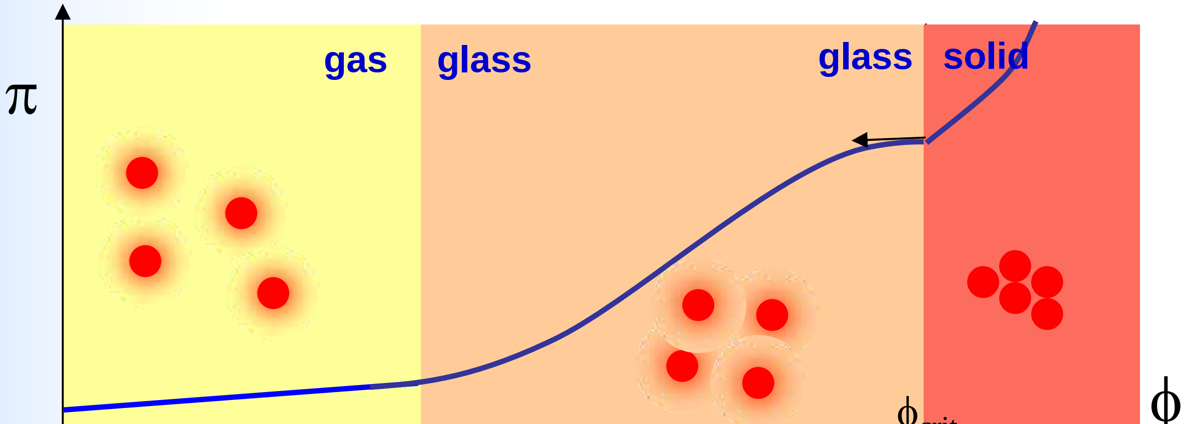
$$D(\phi) = \frac{K(\phi)}{6\pi\mu a}\frac{d\pi}{d\phi}V_p$$

+

Compression yield : resistance to the applied pressure in a deposit

= **« Solid » pressure**

equation of state for the divided matter in water
which describe continuously properties of colloidal suspension
when concentrated from bulk to deposit



Analogy between diffusion in a polarised layer and permeation in a deposit using solid pressure

Mass balance in a polarised layer

$$J\phi - D(\phi)\frac{d\phi}{dx} = 0$$

Permeation in a deposit

$$J = -\frac{k}{\mu}\frac{dp}{dx}$$

Einstein [1] relation
for diffusion coefficient

$$k = \frac{2a^2}{9}\frac{K(\phi)}{\phi}$$ [2]

$$\frac{d(p+\pi)}{dx} = 0$$ [3]

A single equation to link
accumulation to operating
conditions and fluid properties

$$\boxed{\phi dx = \frac{D_b}{J}K(\phi)d\pi^*}$$

with $$\pi^* = \pi\frac{V_p}{k_B T}$$

[2] A.A. Zick and G.M. Homsy, Stokes flow through periodic arrays of spheres, Journal of fluid mechanics, 115 (1982) 13-26.

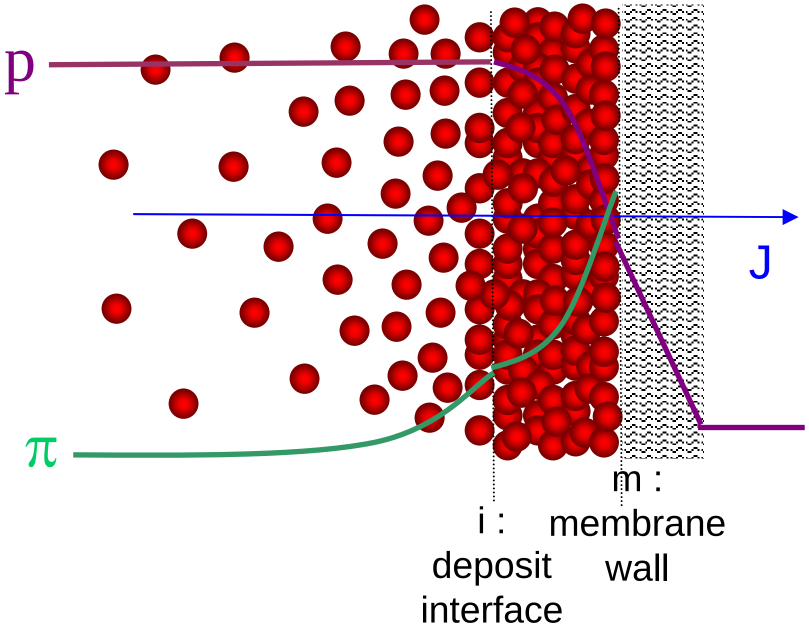
[3] J.D. Sherwood, Initial and final stages of compressible filtercake compaction, AIChE J., 43 (1997) 1488-1493.

Solvent transfer $$J=\frac{\Delta P-\pi_i}{\mu(R_m+R_c)}$$

- $$\frac{d(p+\pi)}{dx}=0$$
- $$J=\frac{p_i-p_m}{\mu R_c}$$

in the deposit

$$\pi_m=\pi_{crit}+J\mu R_c$$



Equation linking permeate flux to accumulation

$$\boxed{\frac{J}{J_0}=1-\frac{\pi_m^*}{A}}$$

with $A=\frac{\Delta P V_p}{kT}$

- $\pi_m < \pi_{crit}$ polarized layer
- $\pi_m > \pi_{crit}$ polarized layer with $\pi_i = \pi_{crit}$

  and deposit with $R_c=\frac{\pi_m-\pi_{crit}}{J\mu}$

« Solid » pressure can describe in a same equation both osmosis phenomenom and deposit resistance

Dead end filtration :

accumulated volume fraction

$$Pe = \frac{JV_a}{D_b} = \int_{\pi_b^*}^{\pi_m^*} K(\phi)\,d\pi^*$$

$$V_a = \int_0^\infty \phi\,dx$$

volume accumulated per area

Pe number = dissipated friction energy on whole particles accumulated / Brownian energy

integration of

$$\phi dx = \frac{D_b}{J} K(\phi)\,d\pi^*$$

Cross flow filtration :

accumulation in a given boundary layer thickness

$$Pe = \frac{J\delta}{D_b} = \int_{\pi_b^*}^{\pi_m^*} \frac{K(\phi)}{\phi}\,d\pi^*$$

$$\delta = \int_0^\delta dx$$

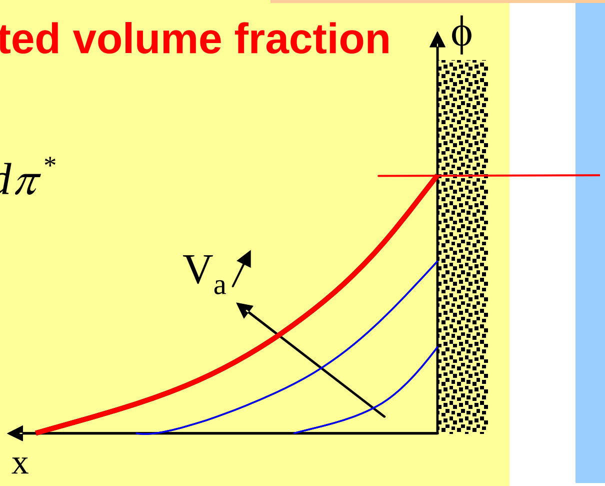
length of mass boundary layer

Pe number = dissipated friction energy on a particle across BL / Brownian energy

Critical fouling conditions

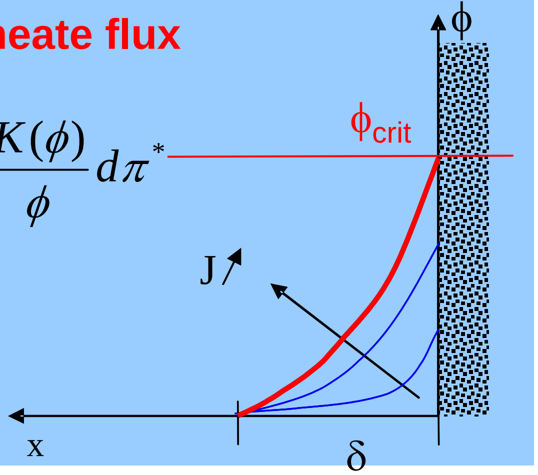
Critical accumulated volume fraction

$$V_{a\ \mathrm{crit}} = \frac{D_b}{J} \int_{\pi_b^*}^{\pi_{crit}^*} K(\phi)\,d\pi^*$$



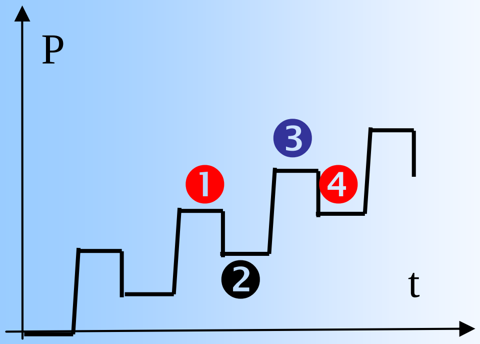
Critical permeate flux

$$J_{crit} = \frac{D_b}{\delta} \int_{\pi_b^*}^{\pi_{crit}^*} \frac{K(\phi)}{\phi}\,d\pi^*$$



Experimental determination of critical flux

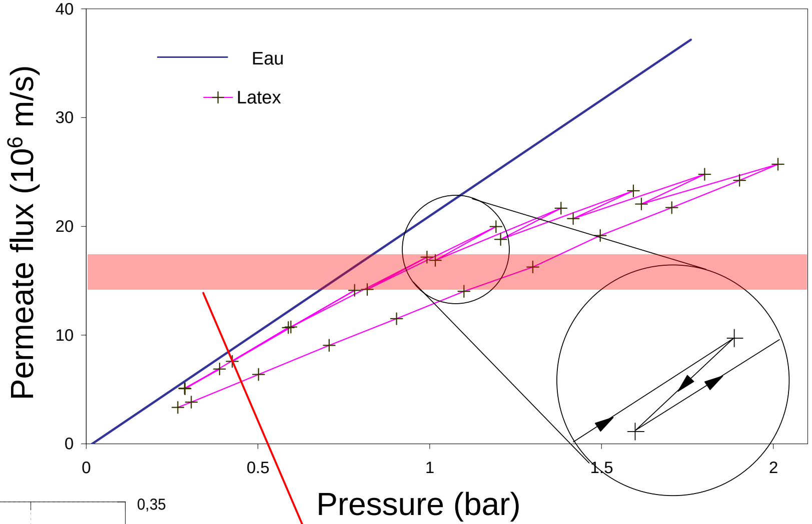
Principles

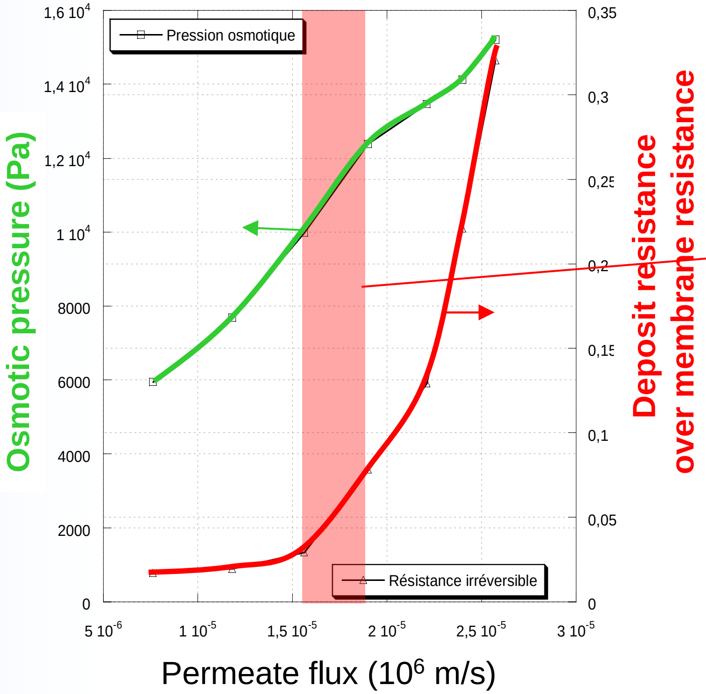


Fouling comparaison in pressure step ❶ and ❹ allows determining the irreversibility degree of fouling in step ❸

Espinasse et al. 2002

Results





critical flux

J_{crit}= f(colloidal interaction, hydrodynamics)

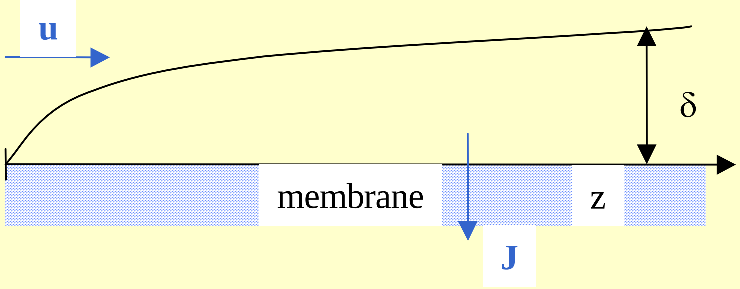
Consequences of a critical Peclet number

u : cross flow velocity
z : axial position

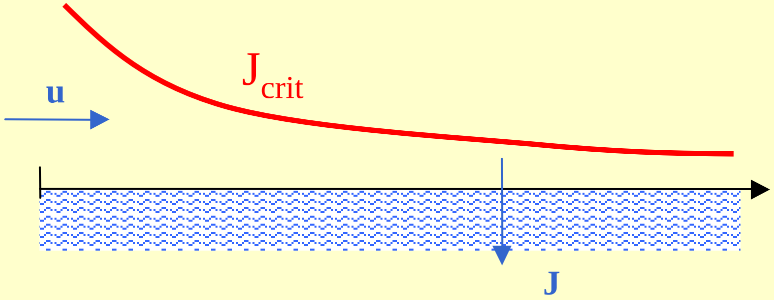
$$Pe_{crit} = \frac{J_{crit}\,\delta}{D} = \int_{\pi_b^*}^{\pi_{crit}^*} \frac{K(\phi)}{\phi}\, d\pi^*$$

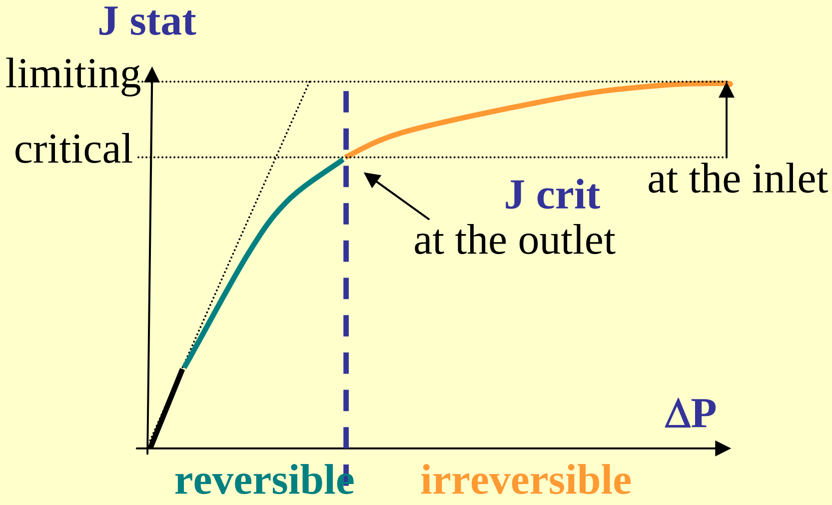
colloidal interaction

δ : mass boundary layer thickness



Critical flux distribution $J_{crit} = cste/\delta$

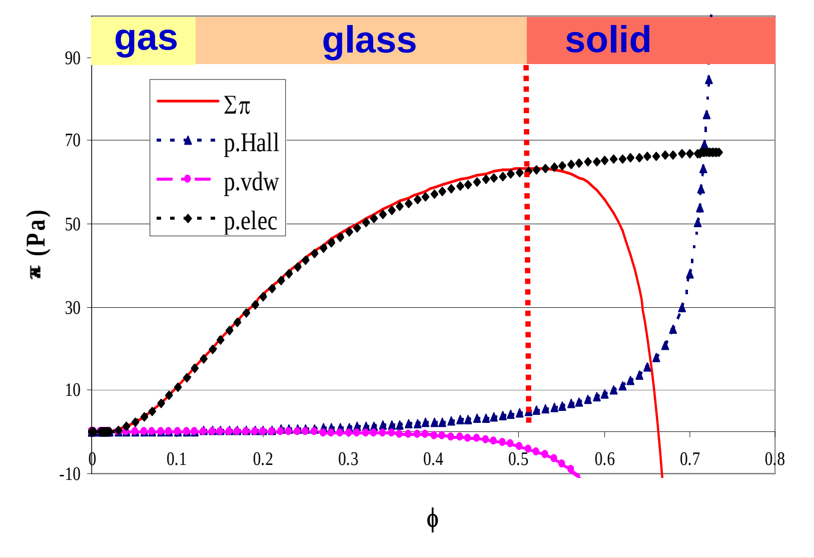




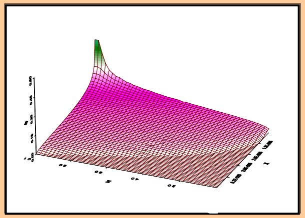
Bacchin (to be published)

Consequences of π behavior on fouling layer formation and structure

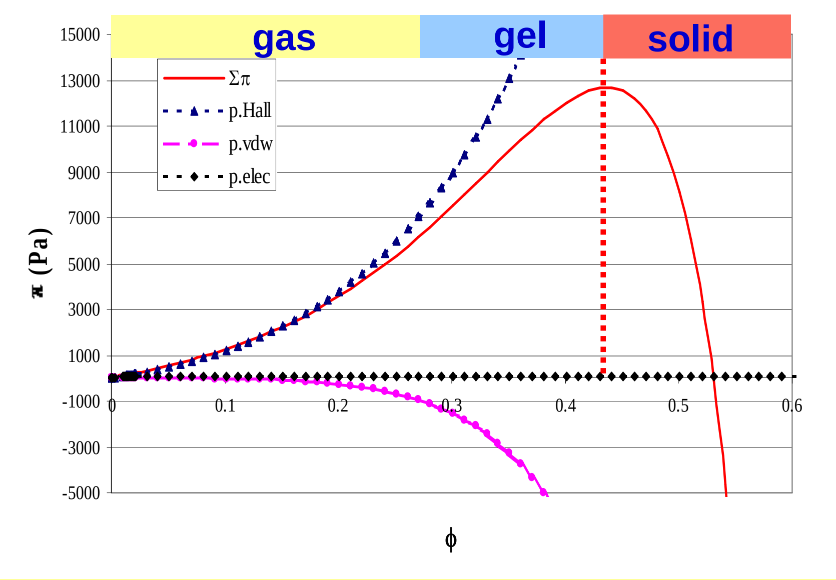
Simulation of **deposit layer** formation with particles



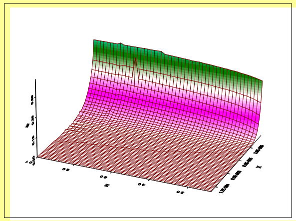
deposit layer : stiff formation with progressive development along the membrane



Simulation of **gel layer** formation with macromolecules

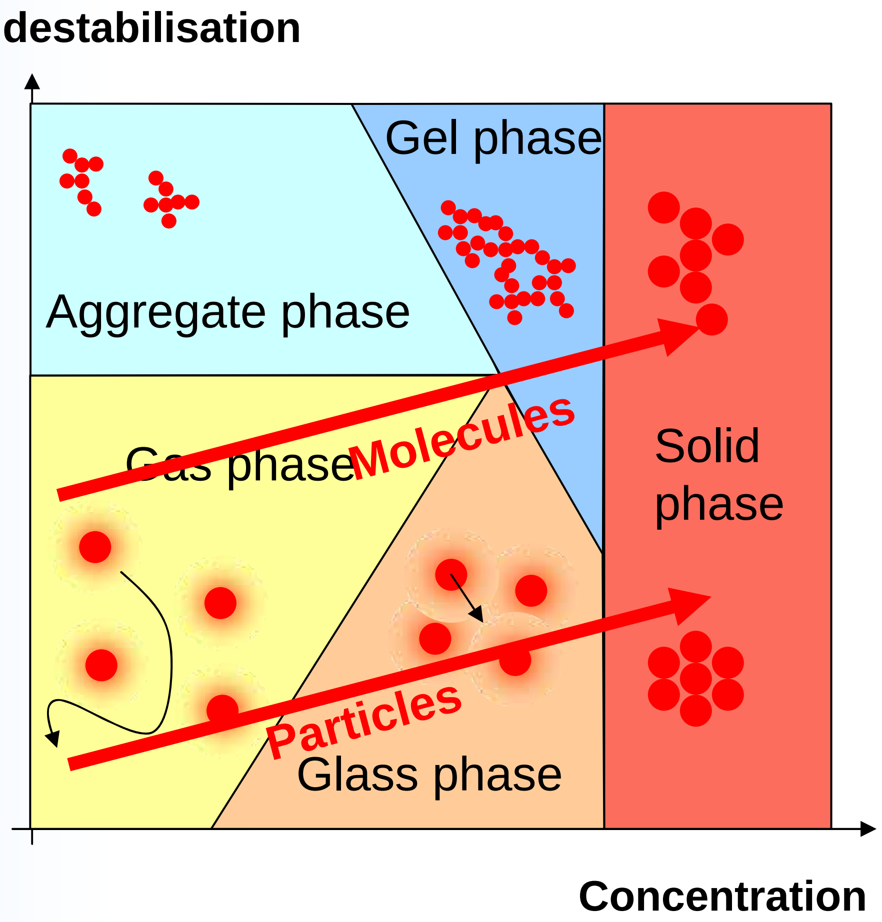


gel layer : slow formation with rapid development along the membrane



Bacchin et al. 2002

Phase diagram and fouling layer formation and structure



destabilisation

Aggregate phase

Gel phase

Solid phase

Gas phase

Glass phase

Molecules

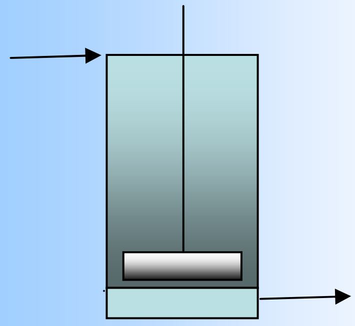
Particles

Concentration

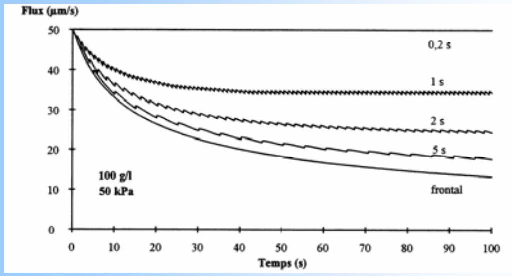
Experimental highlight of critical accumulated volume fraction

Principles

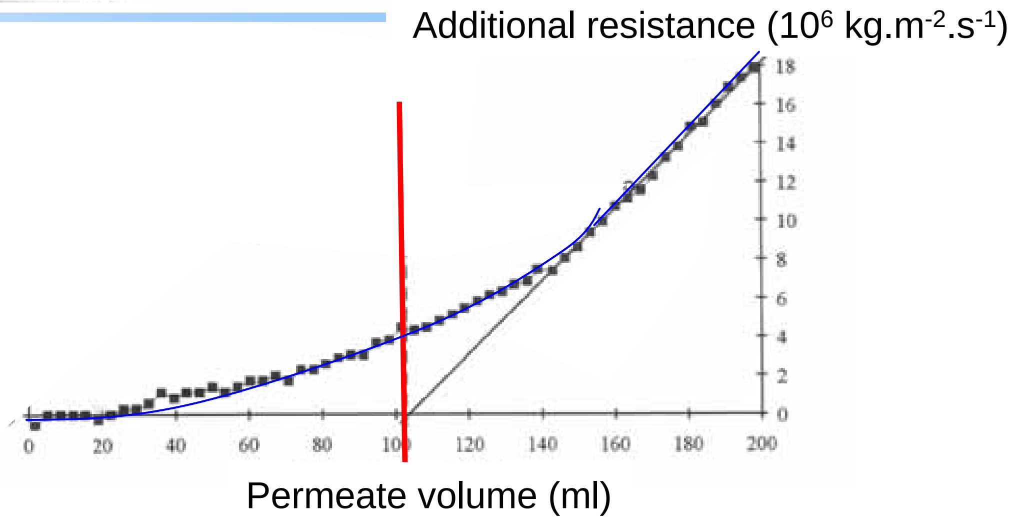
Dead end

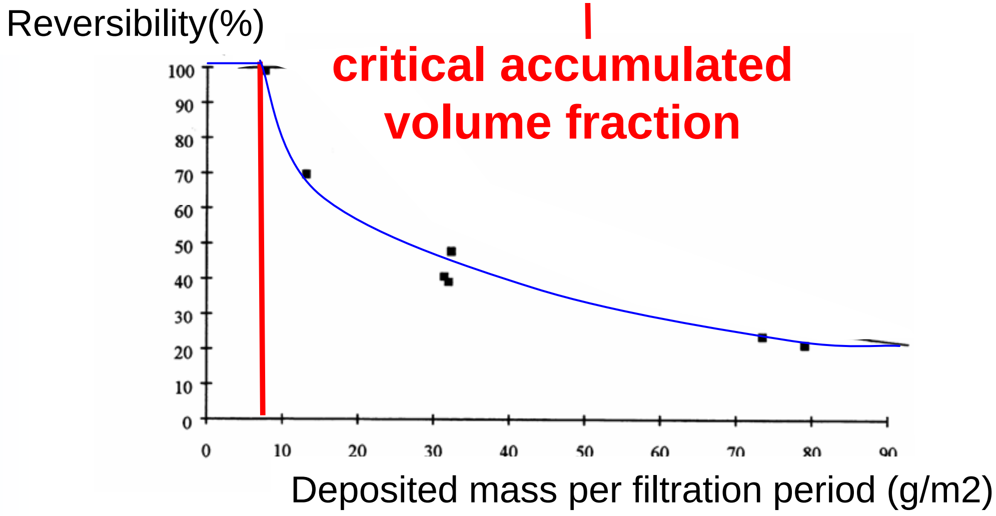


Sequential dead end filtration



Results



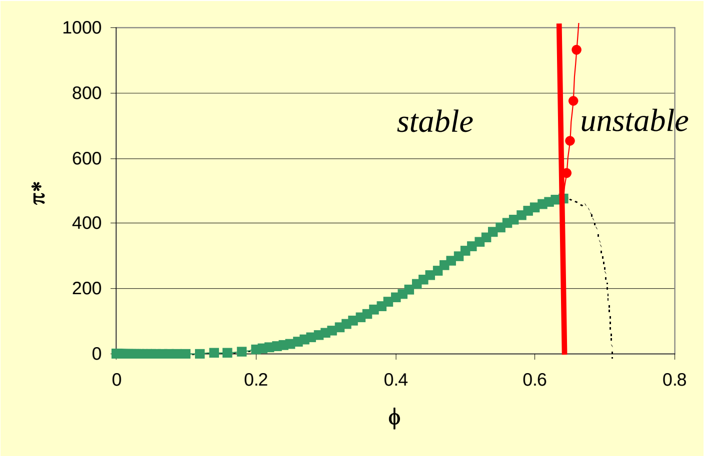


critical accumulated volume fraction

Harmant 1996

Modeling of dead end filtration mode

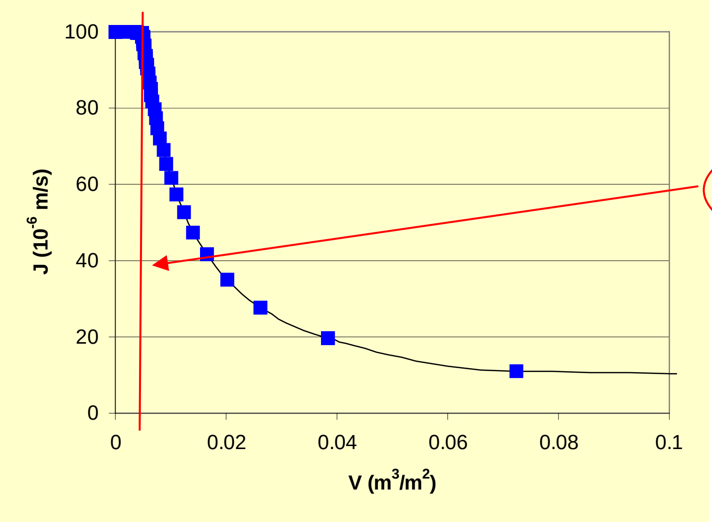
Solid pressure



a=100 nm, ζ=30 mV, I=10^{-4} M

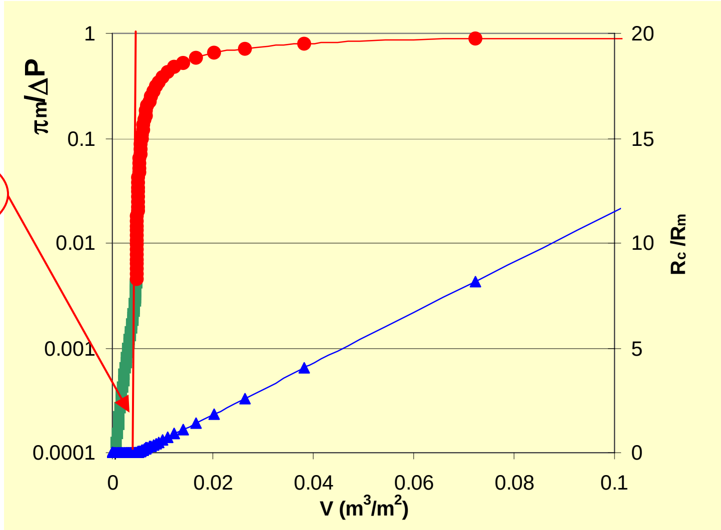
Critical accumulated volume fraction

$$V_{a\ \mathrm{crit}} = \frac{D_b}{J}\int_{\pi_b^*}^{\pi_{crit}^*} K(\phi)\, d\pi^*$$



critical filtered volume

leading to deposit formation on the surface

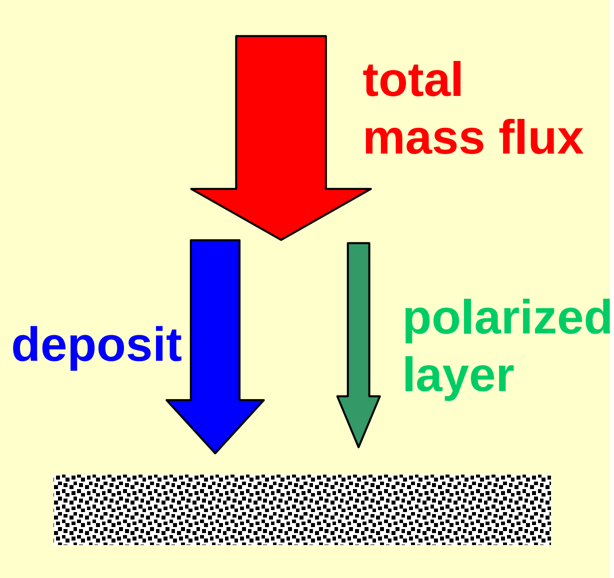


Bacchin et al. 2002

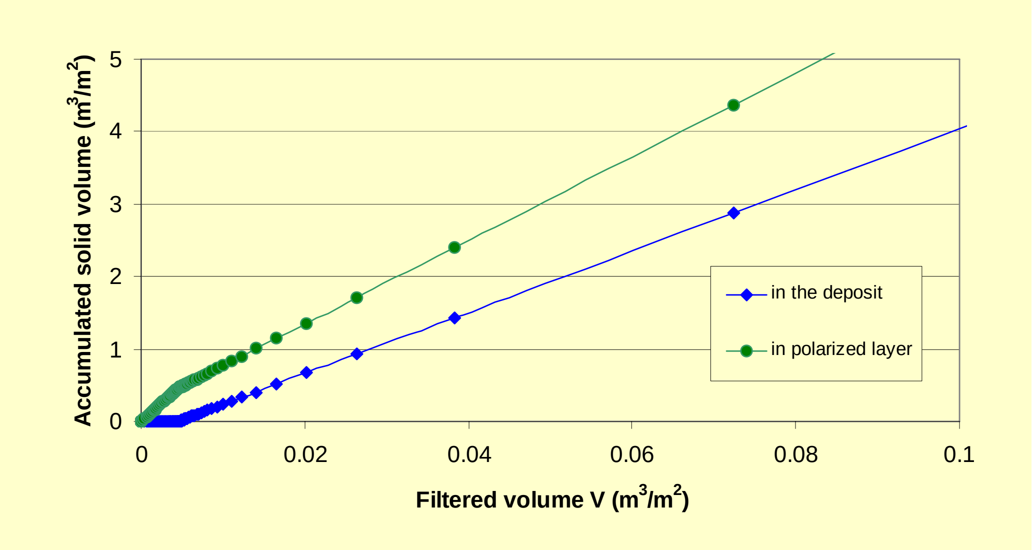
Critical accumulated volume fraction is inversely proportionnal to permeate flux

at given pressure :

critical accumulated volume ↗
when
permeate flux (and then time) ↘



Actual mass of particles irreversibly transfer to deposit can be very different from the mass transferred by permeation from the solution



For constant pressure operating mode, specific resistance may not be accurately determined with classical relationship t/V versus V for stable suspension

Conclusions

critical fouling conditions

Causes : spinodal decomposition

From causes to consequences : π-based modeling

Consequences :

critical flux (or more accurately critical Pe number) in cross flow
critical accumulated volume fraction in dead end
formation kinetics and structure of gel or deposit layer

Questions

- is critical flux a concept for real world membrane processes ?
- is there several critical flux ? i.e. one considering interaction between particles and membrane and another one for particles/particles interactions
- how critical flux has to be experimentally determined ?
- What suspension property can be directly linked to the critical flux (or Peclet number) ?
- Is this concept have future to scale up membrane process ?

References

[1] A. Einstein, Investigation on the theory of the Brownian movement, ed. R. Furth, New York : Dover Publications, 1956.

[2] A.A. Zick and G.M. Homsy, Stokes flow through periodic arrays of spheres, Journal of fluid mechanics, 115 (1982) 13-26.

[3] J.D. Sherwood, Initial and final stages of compressible filtercake compaction, AIChE J., 43 (1997) 1488-1493.

[4] P. Bacchin, M. Meireles and P. Aimar, Modelling of filtration: From the polarised layer to deposit formation and compaction, Desalination, 145 (2002), 139-146.

[5] P. Bacchin, D. Si-Hassen, V. Starov, M.J. Clifton and P. Aimar, A unifying model for concentration polarization gel-layer formation and particle deposition in cross-flow membrane filtration of colloidal suspensions, Chem. Eng. Sci., 75 (2002) 77-91

[6] P. Harmant, Contrôle de la structure de dépôts de particules colloidales en filtration frontale et tangentielle, Thèse de l'Université Paul Sabatier, 2505 (1996)

[7] P. Bacchin, Formation et résistance au transfert d'un dépôt de colloïdes sur une membrane d'ultrafiltration" Thèse de l'Université Paul Sabatier, Toulouse III, (1994)

[8] ESPINASSE P., P. BACCHIN, P. AIMAR, Accurate measures of critical flux, a new tool to manage operating conditions in ultrafiltration processes., Desalination, 146, 91-97 (2002)

[9] BACCHIN P. A possible link between critical and limiting flux by consideration of a critical deposit formation along a membrane, to be published on Journal of Membrane Science

Settling coefficient :

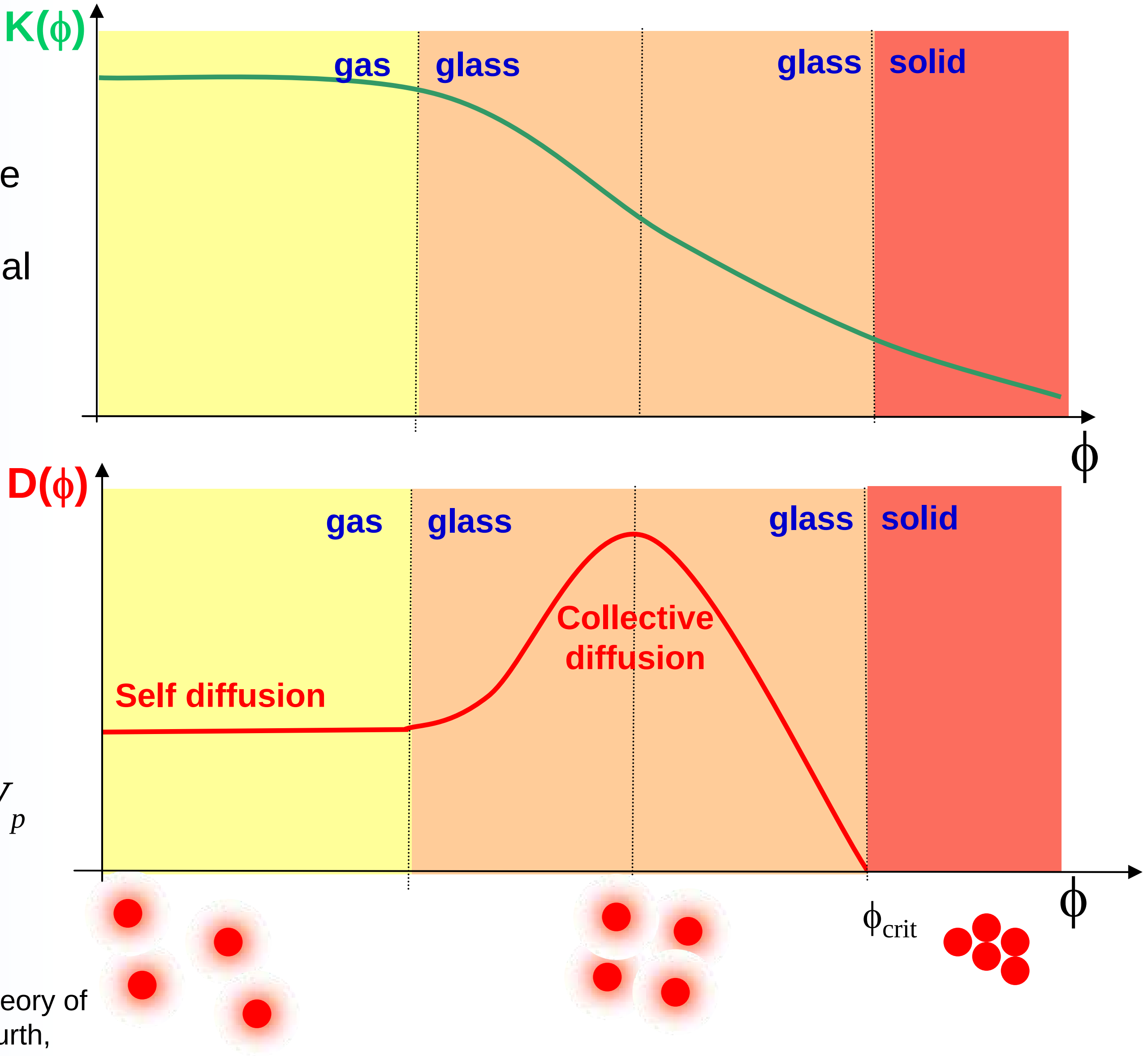
$K(\phi)=U(\phi)/U_0$

a dynamic property relative to the resulting velocity particle/water at an external force field

Diffusion :

a transfer property relative to particles transport in a concentration gradient

$$D(\phi) = \frac{K(\phi)}{6\pi\mu a}\frac{d\pi}{d\phi}V_p$$



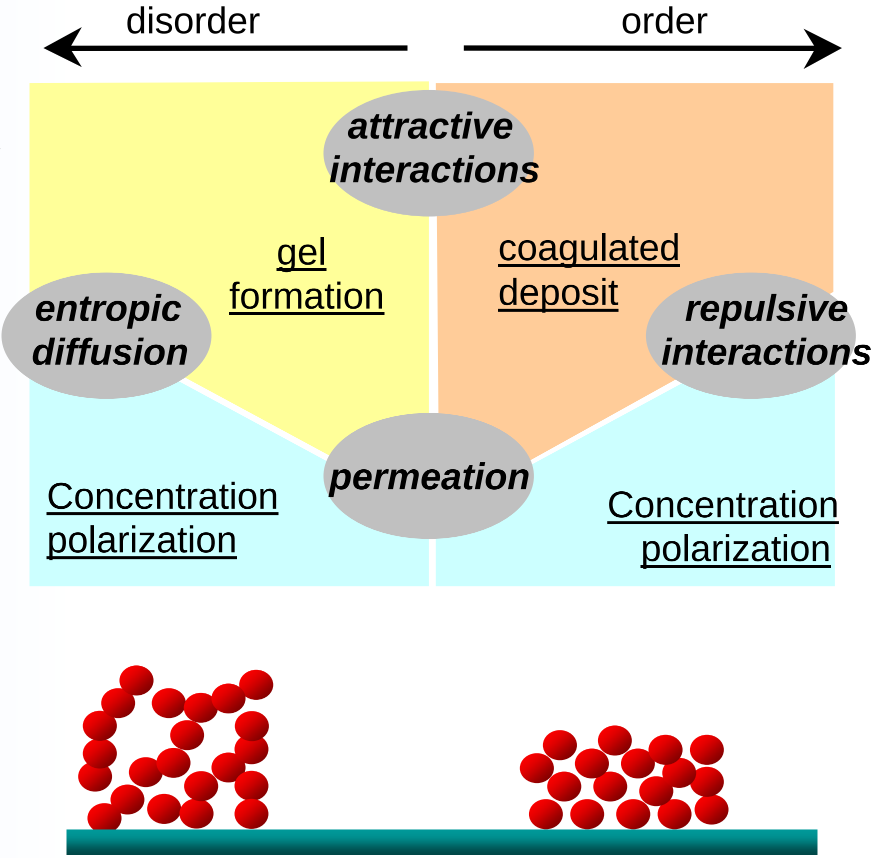
[1] A. Einstein, Investigation on the theory of the Brownian movement, ed. R. Furth, New York : Dover Publications, 1956.

Osmotic pressure and fouling mechanisms

Irreversible phenomena
reaction

Regulating phenomena
mixing force

Driving phenomena
separation force



disorder

order

attractive interactions

<u>gel formation</u>

<u>coagulated deposit</u>

entropic diffusion

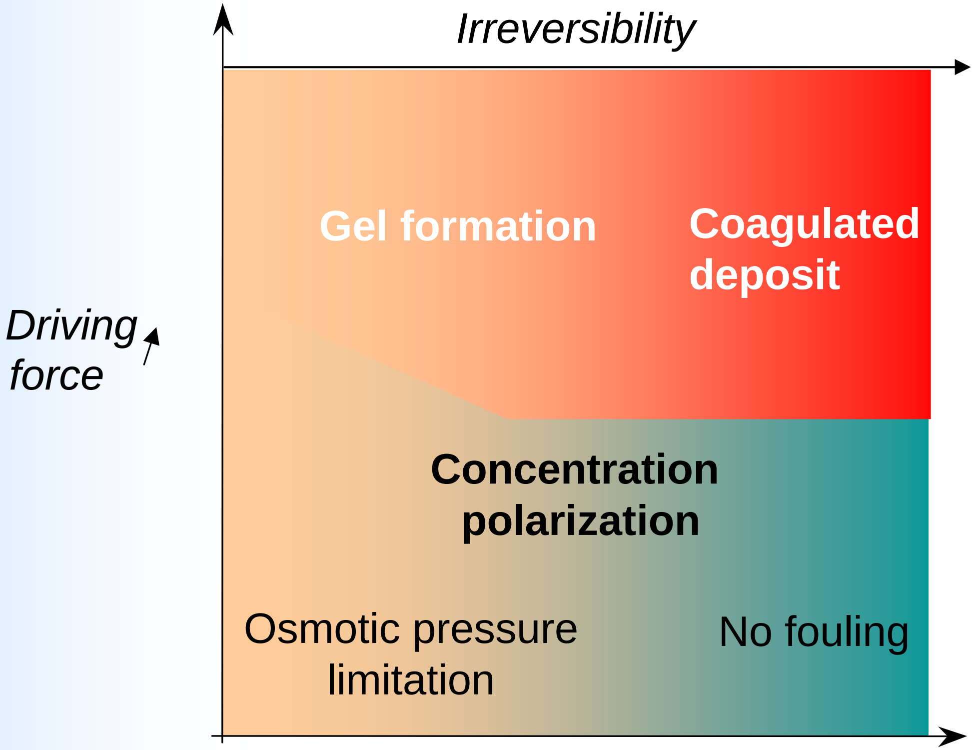
repulsive interactions

permeation

<u>Concentration polarization</u>

<u>Concentration polarization</u>

Fouling mechanisms and operating conditions



Irreversibility

Driving force ↑

Gel formation

Coagulated deposit

Concentration polarization

Osmotic pressure limitation

No fouling

$$\text{ratio for regulating phenomena} = \frac{\text{repulsive interaction}}{\text{entropic diffusion}} \uparrow$$

% size and surface charge

Conclusions

Osmotic pressure of colloidal suspension is an accessible property depicting the **resistance of the suspension to the local over concentration**

Osmotic pressure use in theoretical modeling leads to interesting simplification and allows to develop **continuous modeling integrating both gel, deposit or polarization mechanisms**

Explanations with π-based modeling are given for :

-**critical fouling conditions** : critical flux in cross flow filtration
critical accumulated mass in dead end

-**the effect of physico-chemical properties on fouling layer formation**

Osmotic pressure and settling coefficient form
an indispensable data set to characterize suspension
in regard to filtration experiments (or simulation)

But in which conditions is it sufficient ?