

# **Thermodynamics of water in concrete**



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# Outline

**The role of chemical potential of water  
in porous system.**



**Transport of water  
in concrete and  
new method to  
determine trans-  
port properties.**

**Equilibrium of  
water in concrete  
and shrinkage,  
AAR expansion  
and frost damage.**

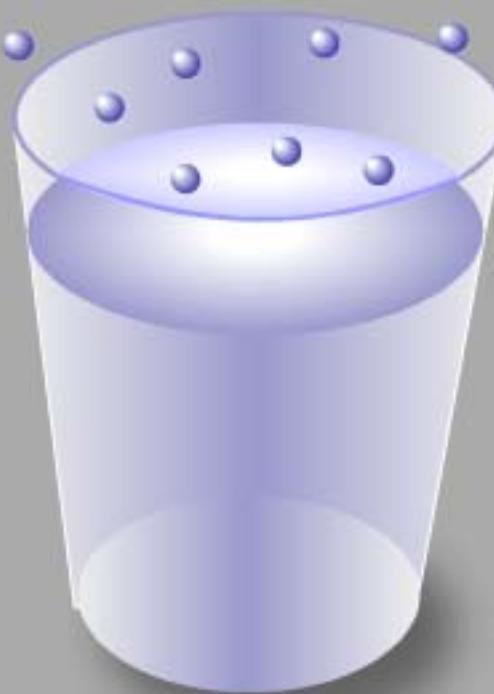
Porous media

## Chemical potential as the driving force of water

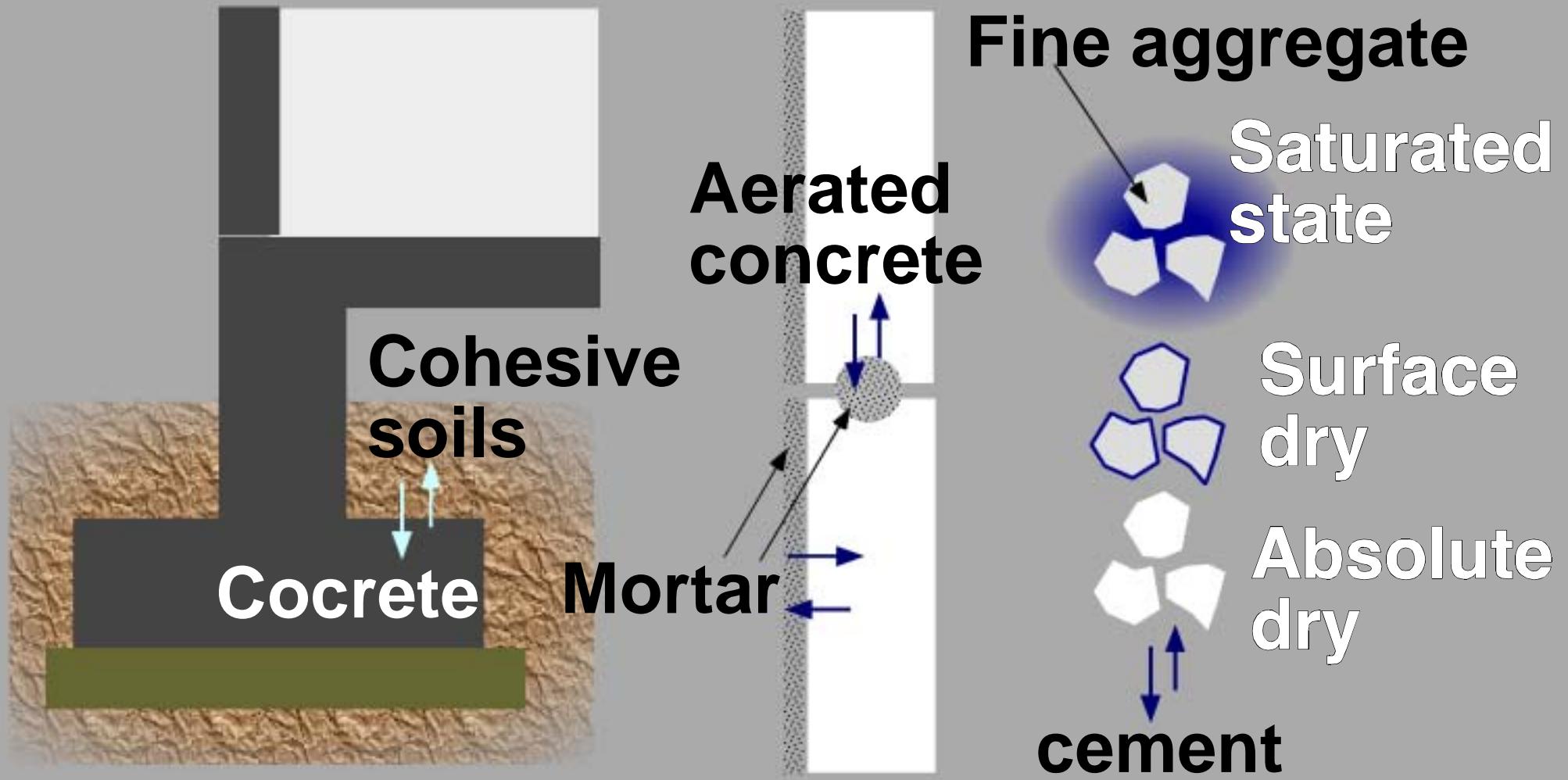
Water in  
porous  
media

$\geq$  Moisture in air  $\geq$  Water in a cup

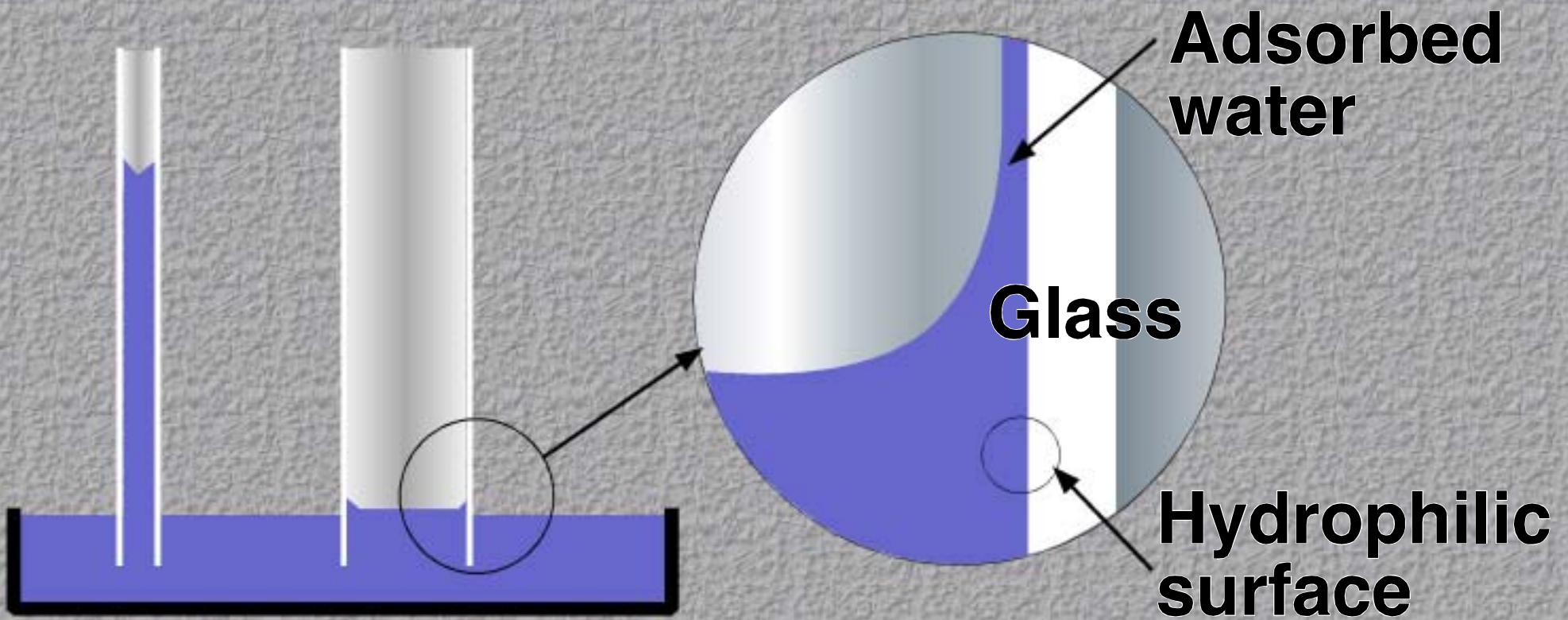
Water  
molecule



# Moisture transport between different materials

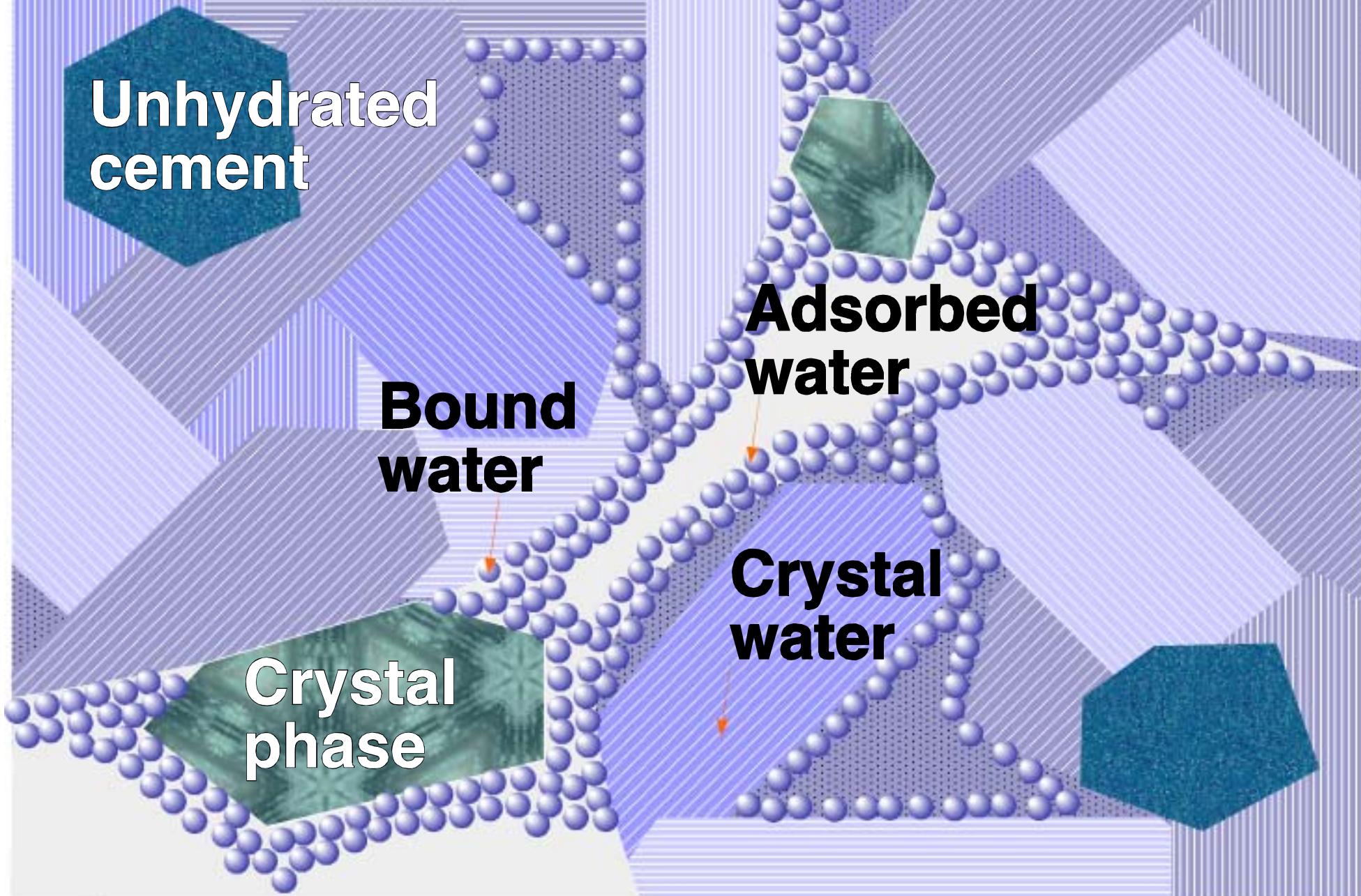


# Origin of the capillary force



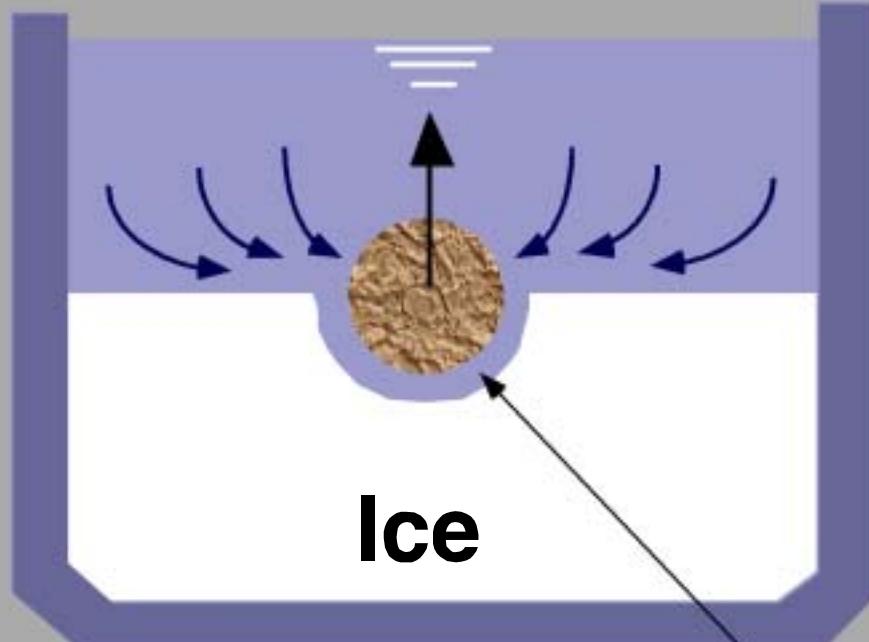
**Capillary force** = Free water rising induced by the adsorbed water

**Crystal water > Bound water > Adsorbed water**

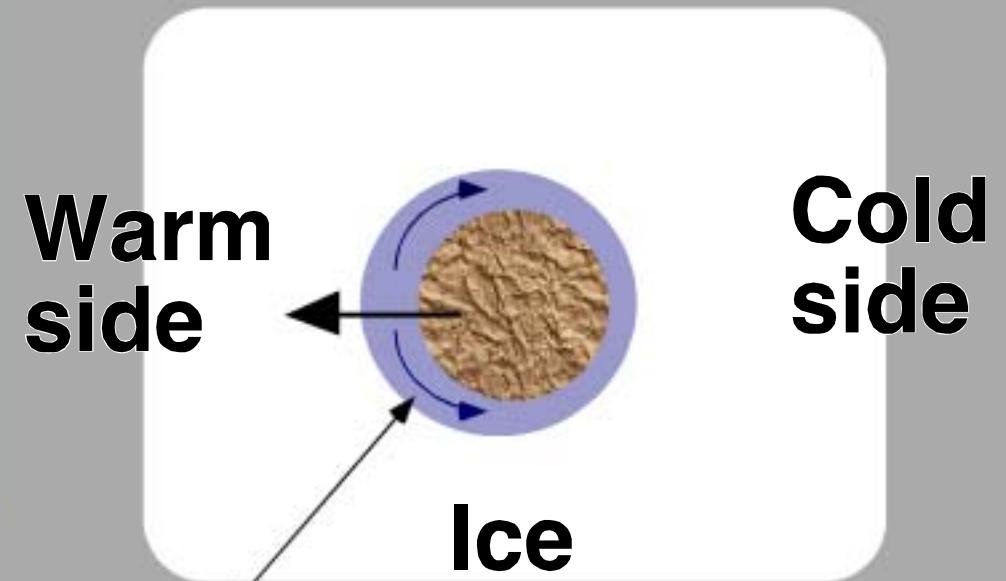


# Adsorbed water transport

Corte 1962



Hoekstra and  
Miller 1967



Unfrozen  
adsorbed film

# Chemical potential

$$W = - \int_P^{P_s} V dp = RT \int_{P_s}^P \frac{dp}{P} = RT \ln(P/P_s)$$

Work

Water vapor pressure

Volume

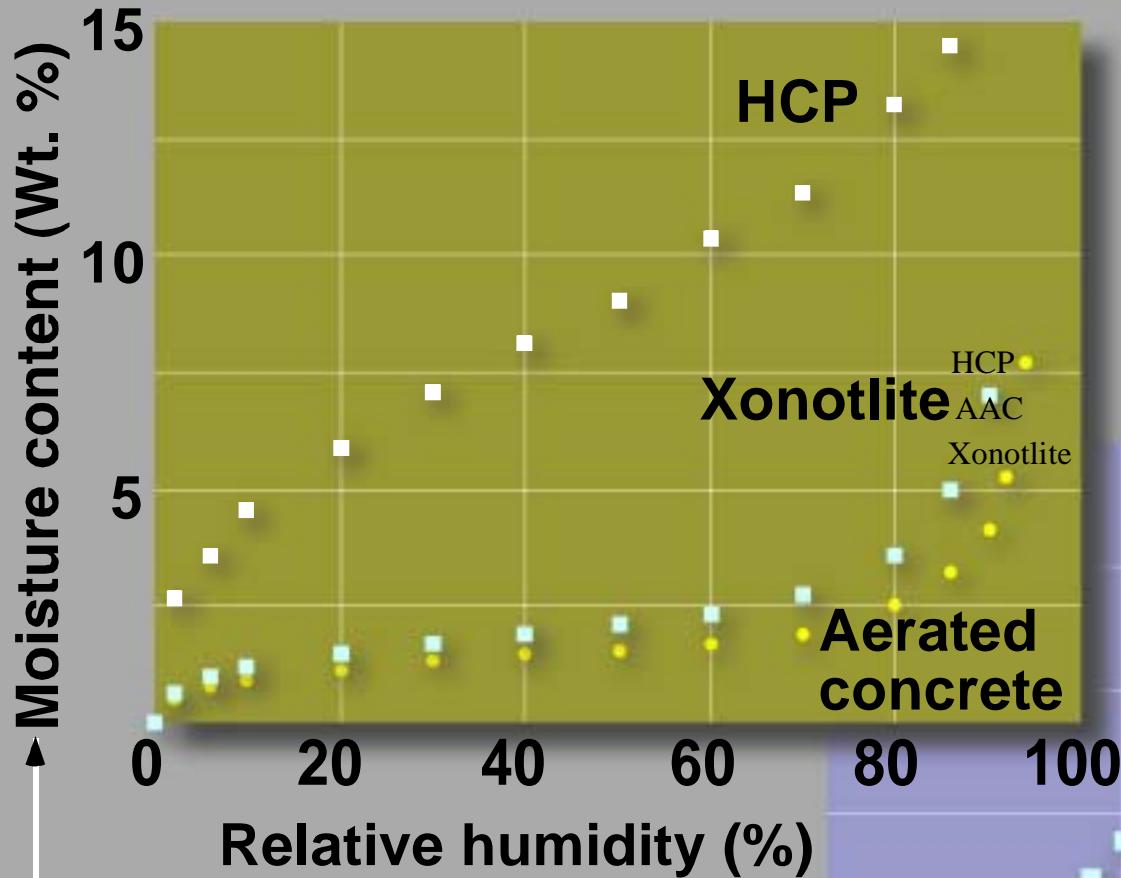
Gas constant

Absolute temperature

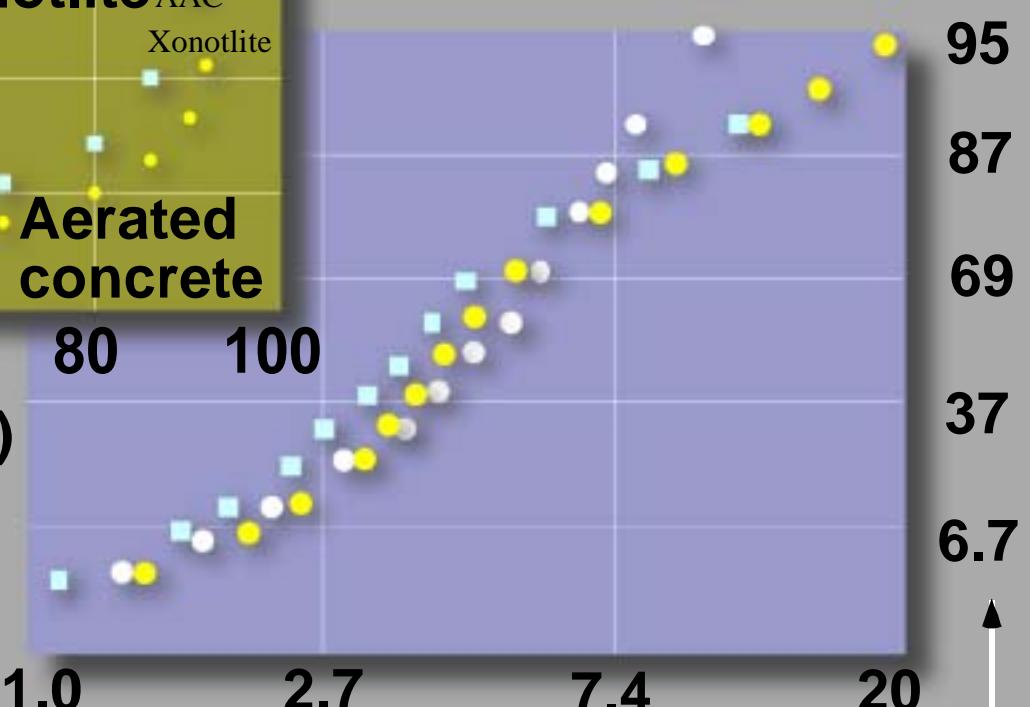
Saturated water vapor pressure

- Fundamental driving force of mass.
- Equal regardless of phase in equilibrium.
- Comparable regardless of medium.

# Sorption isotherm



Relative Humidity (%)



$$\frac{\Phi}{\text{BET surface area}} = \text{Statistical thickness of adsorbed water (\AA)}$$

# Kelvin equation

Pressure due to the difference  
in chemical potential of water

$$\frac{RT \ln(P/P_s)}{\bar{V}} = -\frac{2\Phi}{r}$$

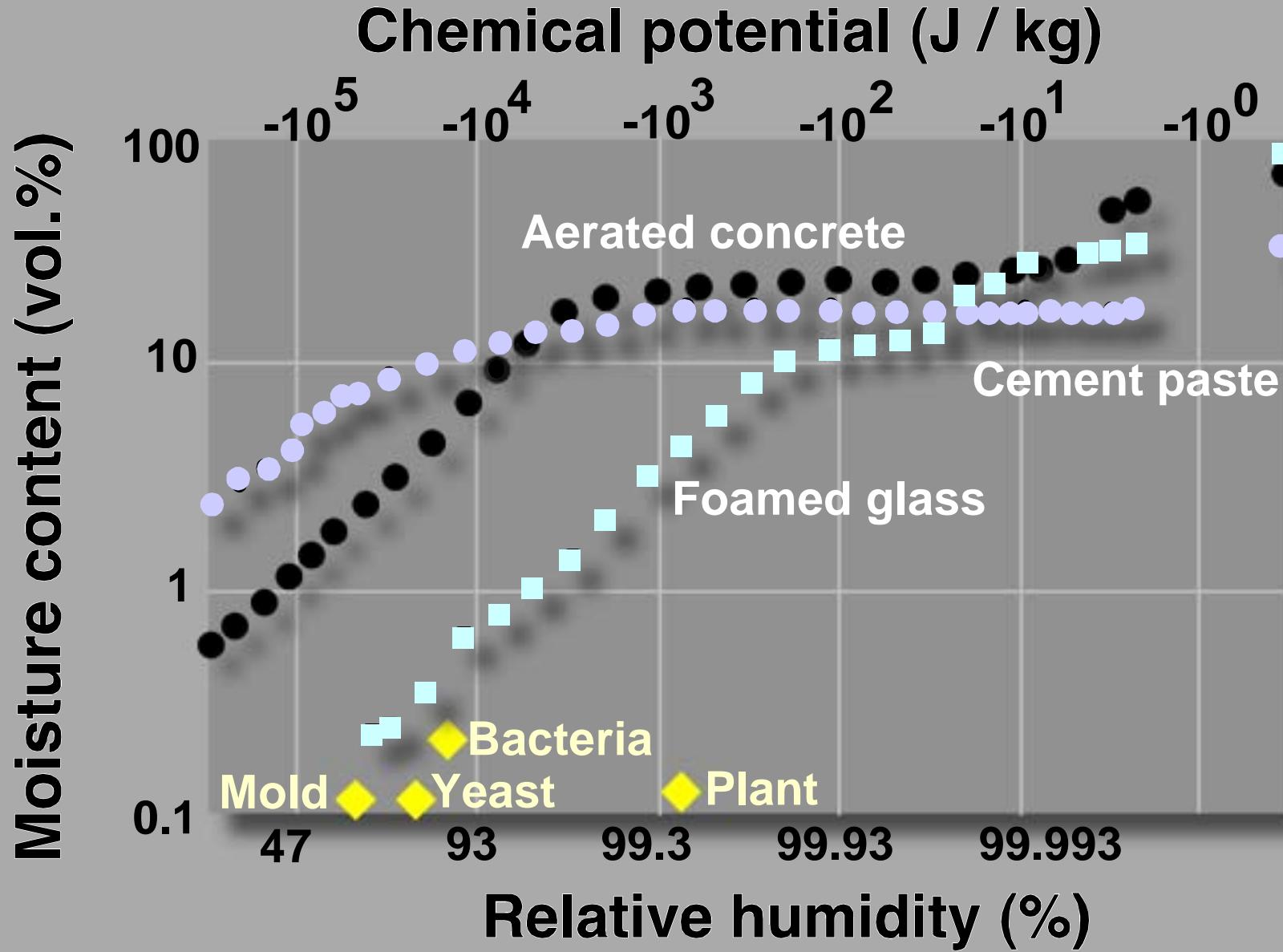
Surface tension of water

Molar volume of water

Radius of curvature  
at liquid-gas interface

- An equation of state at the interface
- Negative pressure due to difference in  $\Delta\mu$
- Osmotic pressure

# Moisture characteristic curve

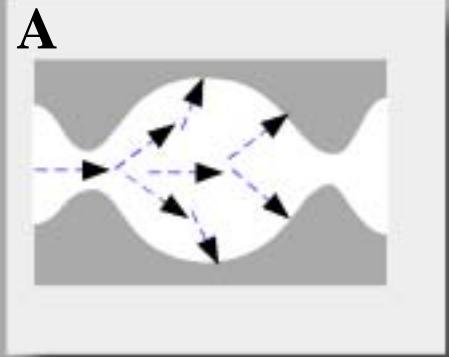


# Flow of water

Fick's diffusion

$$J_v = D_v \nabla p$$

Adsorption

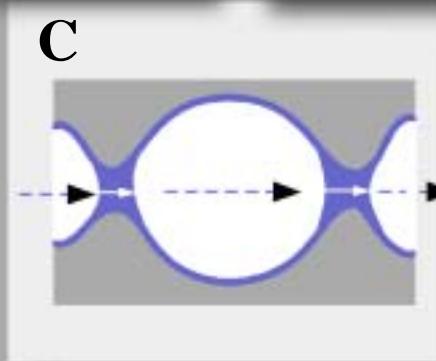
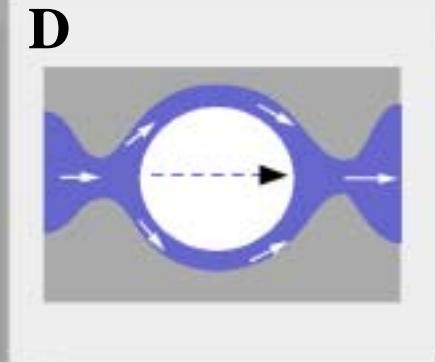
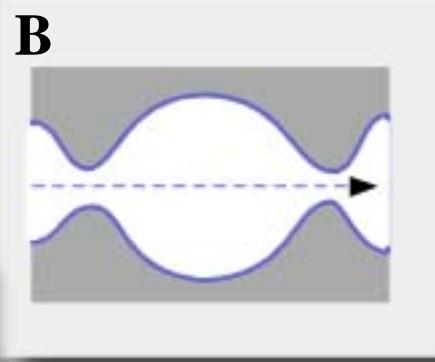


Unsaturated Darcy flow

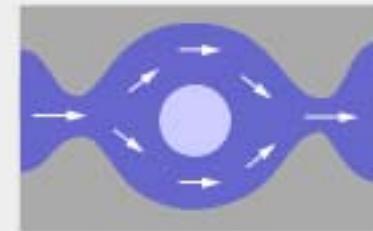
$$J_L = D_\theta \nabla \theta$$

Film flow

$$J_c = D \nabla \Pi$$



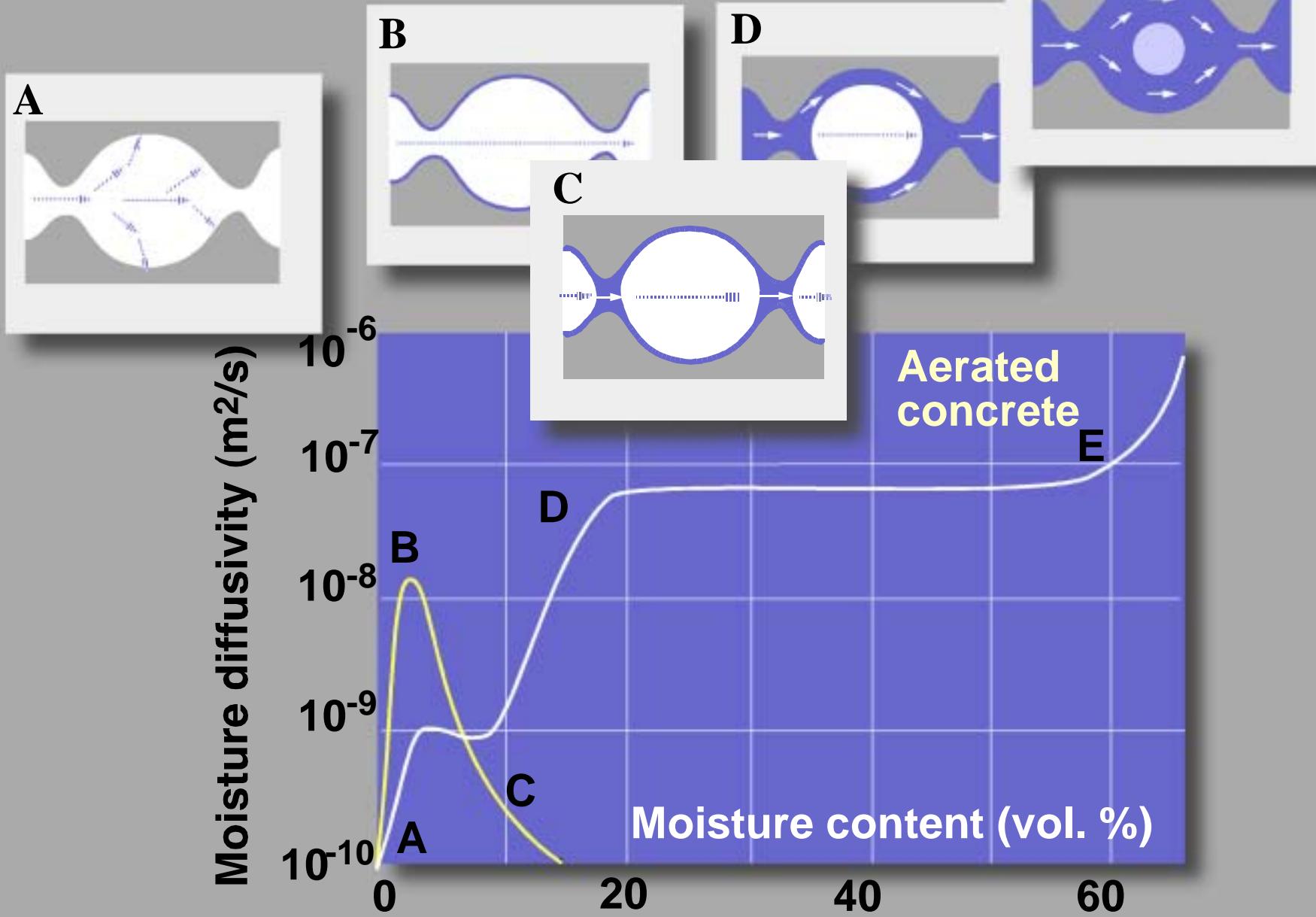
E



Darcy flow

$$J_c = K \nabla P$$

# Flow and pore structure



# Water flux

Fick's diffusion flow      Unsaturated Darcy flow

$$\mathbf{J}_V = -D_V \nabla p_V$$

Water vapor pressure

$$\mathbf{J}_V = -p_{VS} D_V \nabla h$$

Saturated water vapor pressure

$$\mathbf{J}_L = -\frac{K_L}{\mu} \nabla p_C$$

Capillary pressure

$$\mathbf{J}_L = -\frac{K_L}{\mu} \frac{RT}{vh} \nabla h$$

Unsaturated permeability

Gas constant

Dynamic viscosity

Specific volume

Relative pressure

# Moisture content gradient as an apparent driving force

Gradient of sorption isotherm

$$\nabla h = \frac{\partial h}{\partial \theta} \nabla \theta,$$

$$\mathbf{J}_V = -D_{\theta V} \nabla \theta,$$

$$D_{\theta V} = \rho_{VS} \frac{\partial h}{\partial \theta} D_V,$$

Gradient of moisture characteristic curve

$$\nabla p_C = \frac{\partial p_C}{\partial \theta} \nabla \theta$$

$$\mathbf{J}_L = -D_{\theta L} \nabla \theta$$

$$D_{\theta L} = \frac{K_L}{\mu} \frac{\partial p_c}{\partial \theta}$$

# Moisture balance equations

$$\frac{\partial \theta}{\partial t} = \nabla(D_\theta \nabla \theta)$$

$$D_\theta = D_{\theta V} + D_{\theta L}$$

When  $D$  is not a function of  $x$ , one dimensional flow driven by moisture content is

$$\frac{\partial \theta}{\partial t} = D_\theta \frac{\partial^2 \theta}{\partial x^2}$$

# Experimental determination

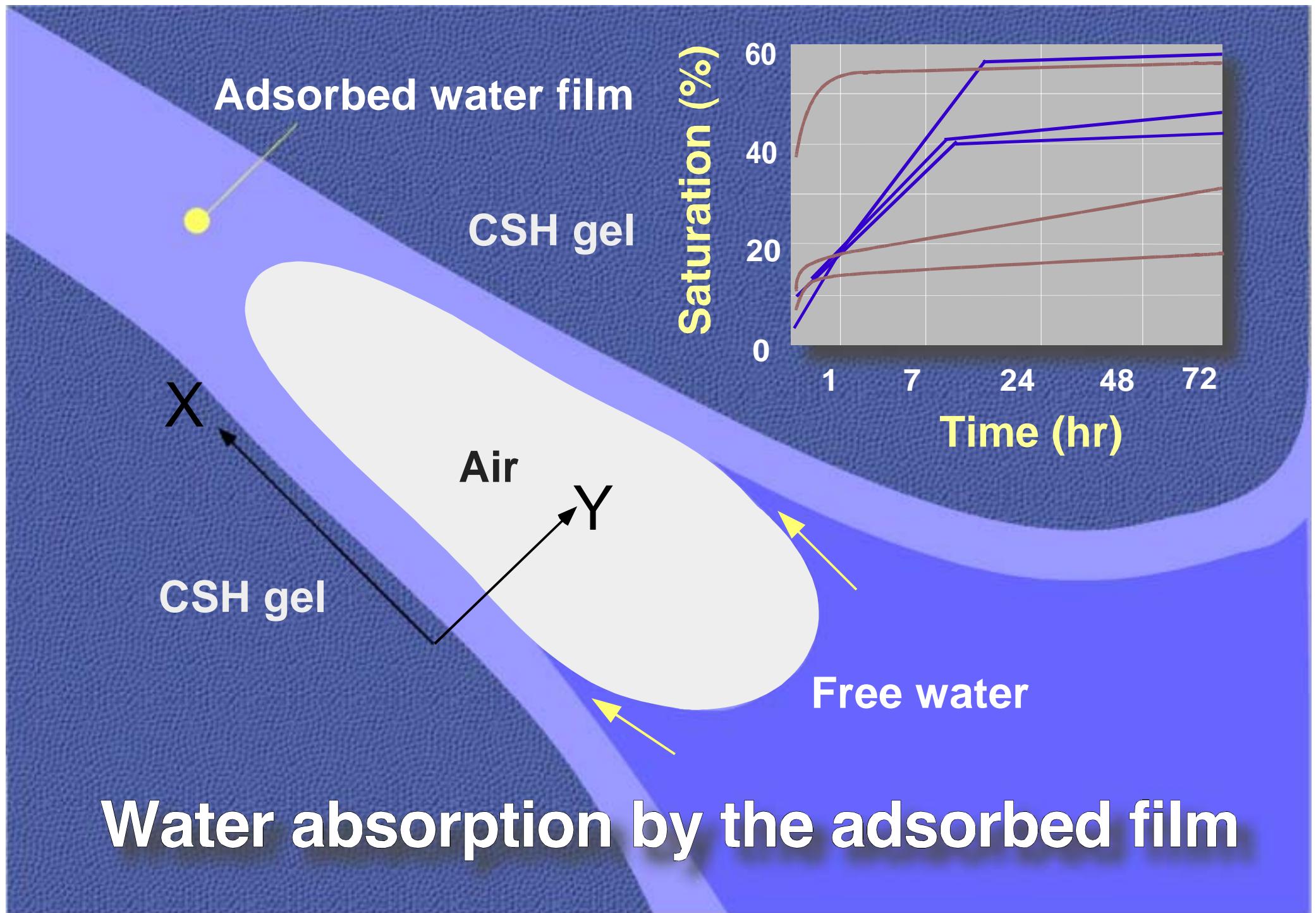
$$J = - \rho_{VS} \frac{\partial h}{\partial \theta} D_V \nabla \theta - \left[ \frac{K_L}{\mu} \frac{\partial p_c}{\partial \theta} \right] \nabla \theta$$

$D_{\theta V} \qquad \qquad \qquad D_{\theta L}$

**Vapor conductivity**

**Sorption isotherm**

**Moisture characteristics**



**Disjoining pressure (Powers)**

**Hindered adsorption region**

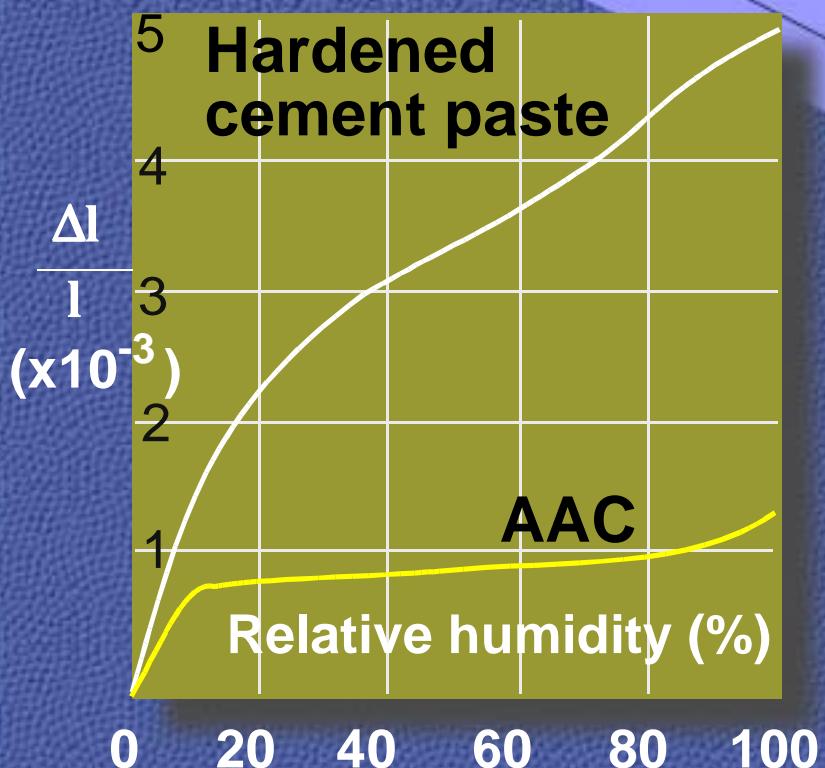
**CSH gel**

**Adsorbed water film**

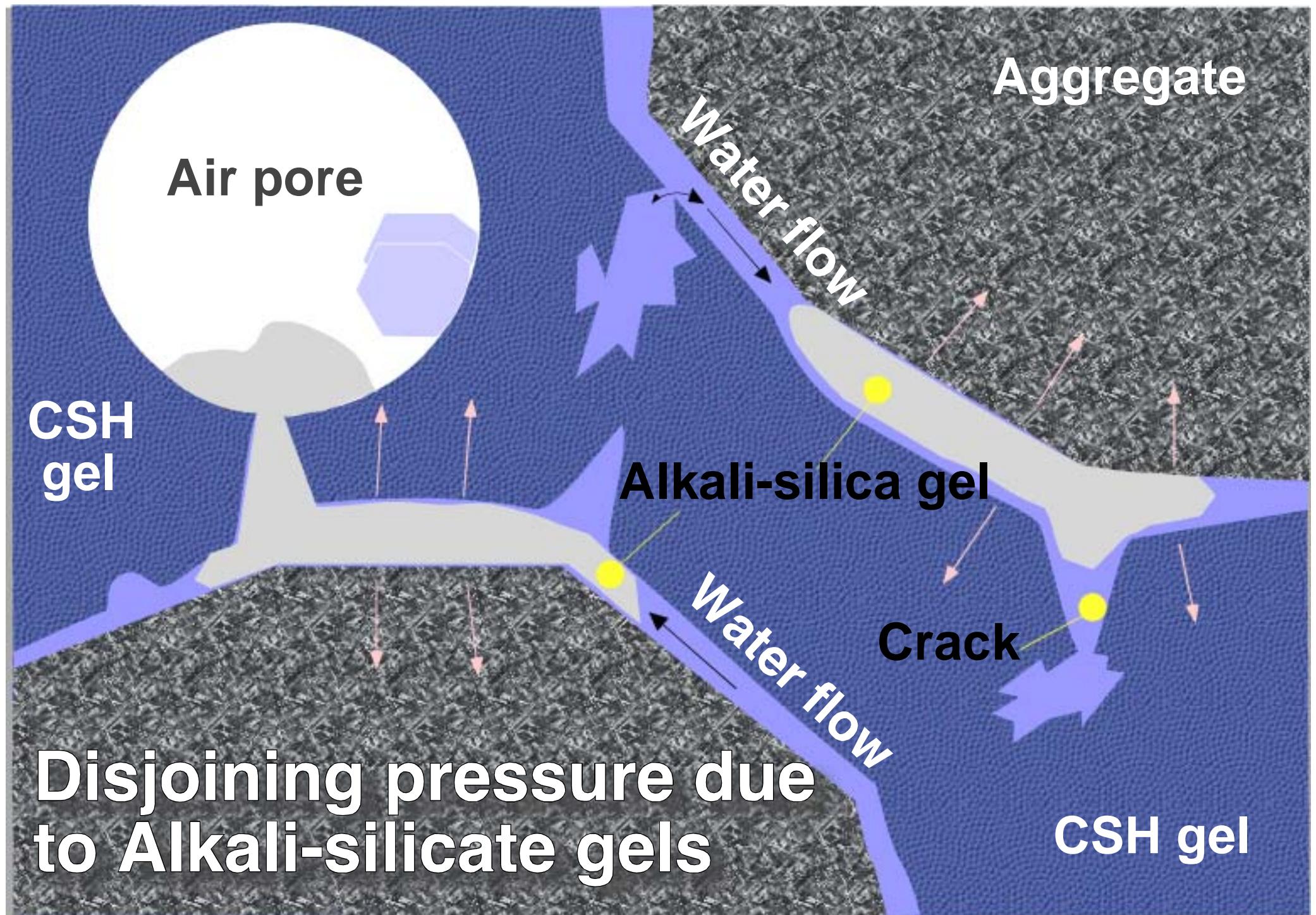
**Air**

**Free adsorption**

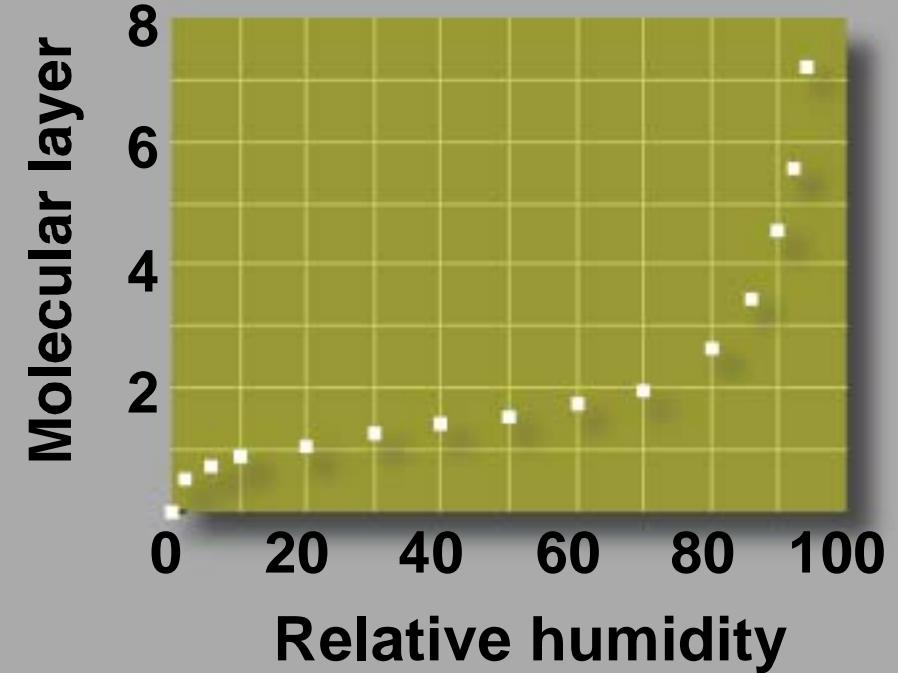
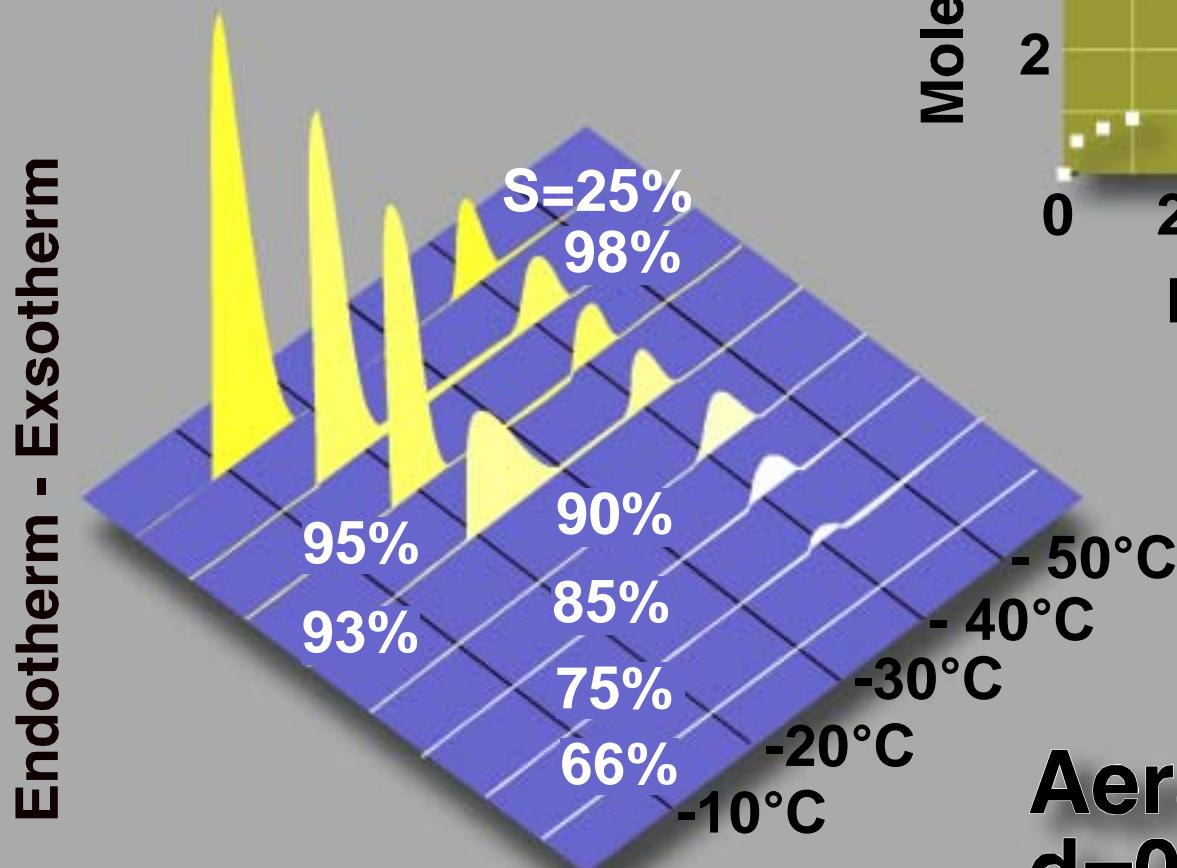
**CSH gel**



**Disjoining pressure between gel particles**

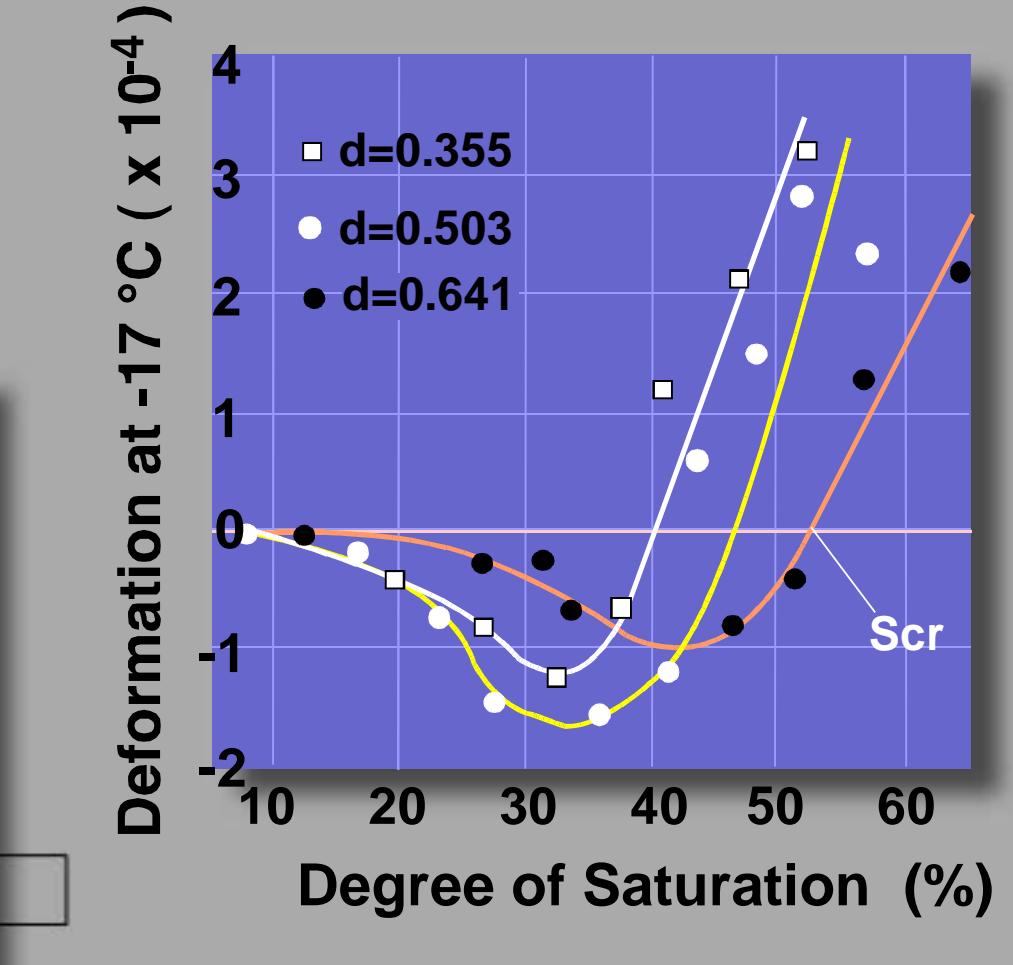
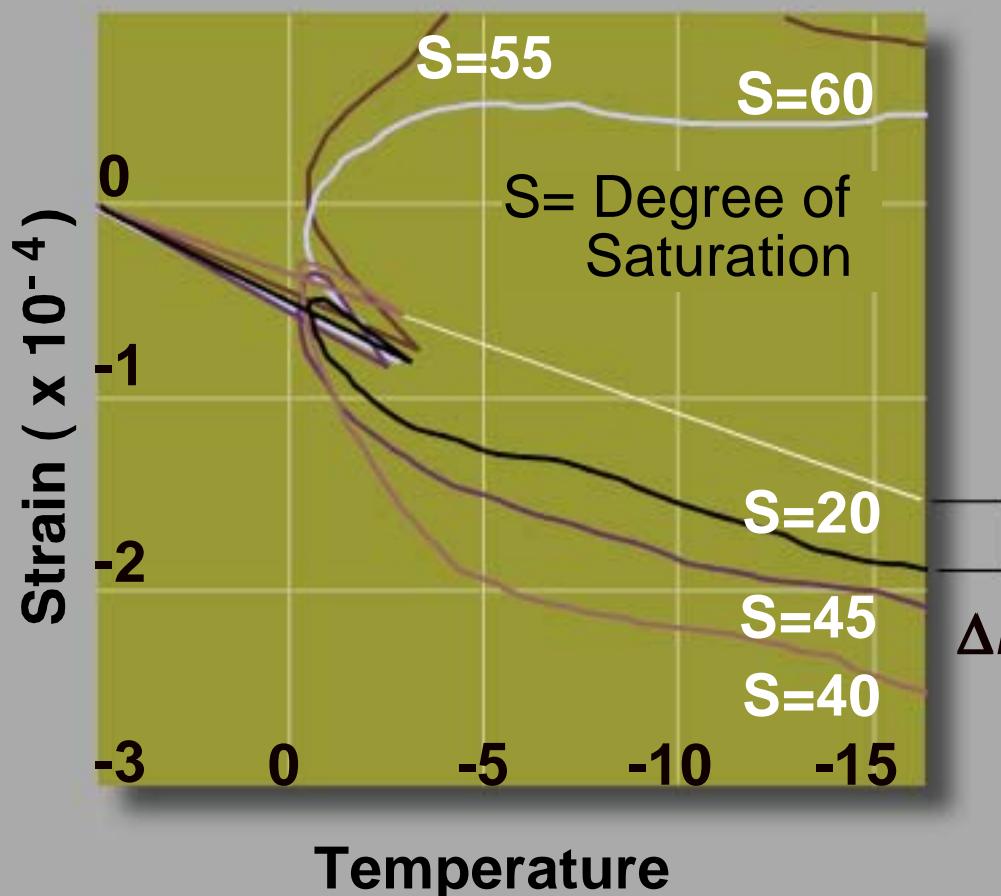


# Unfrozen water film

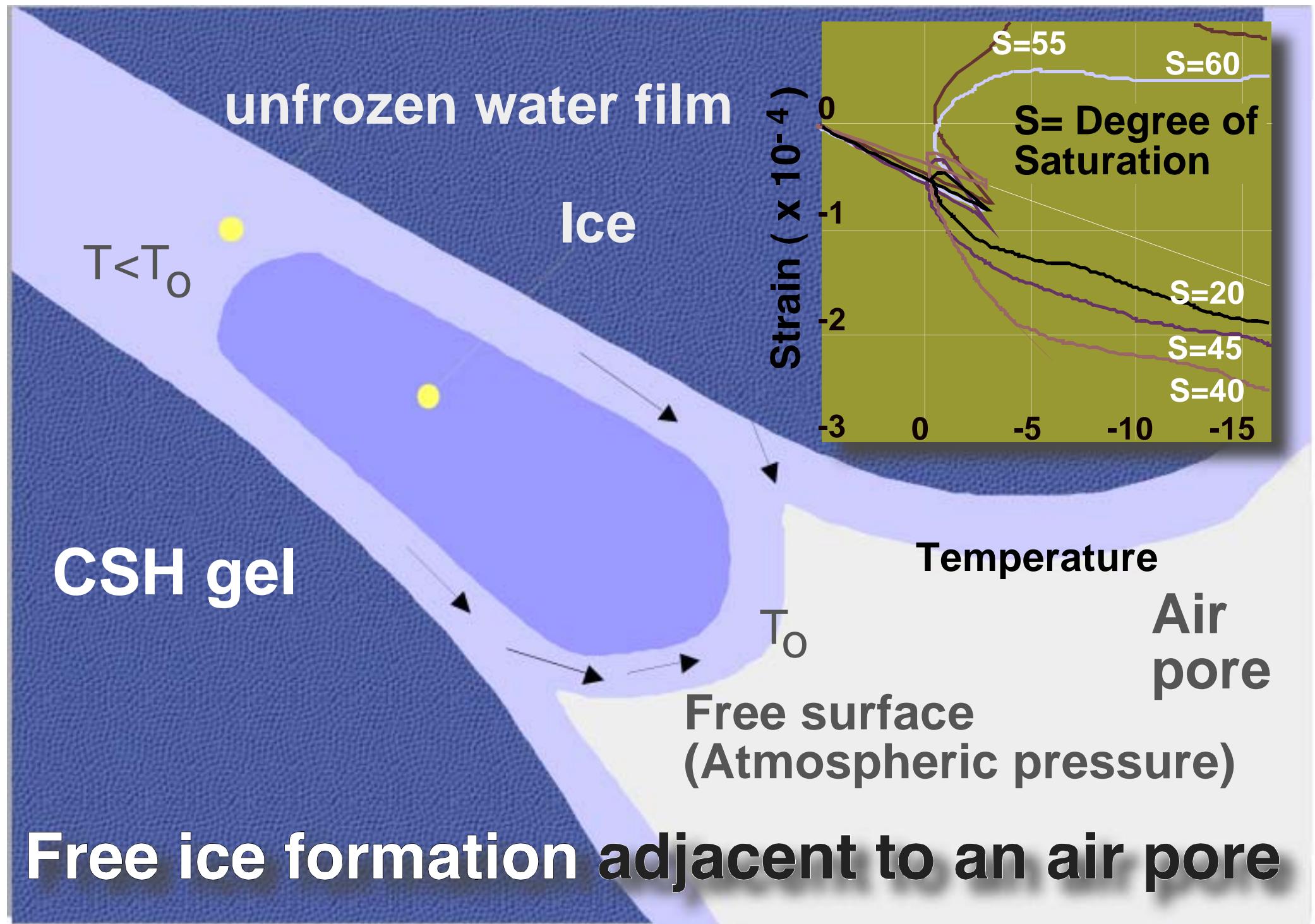


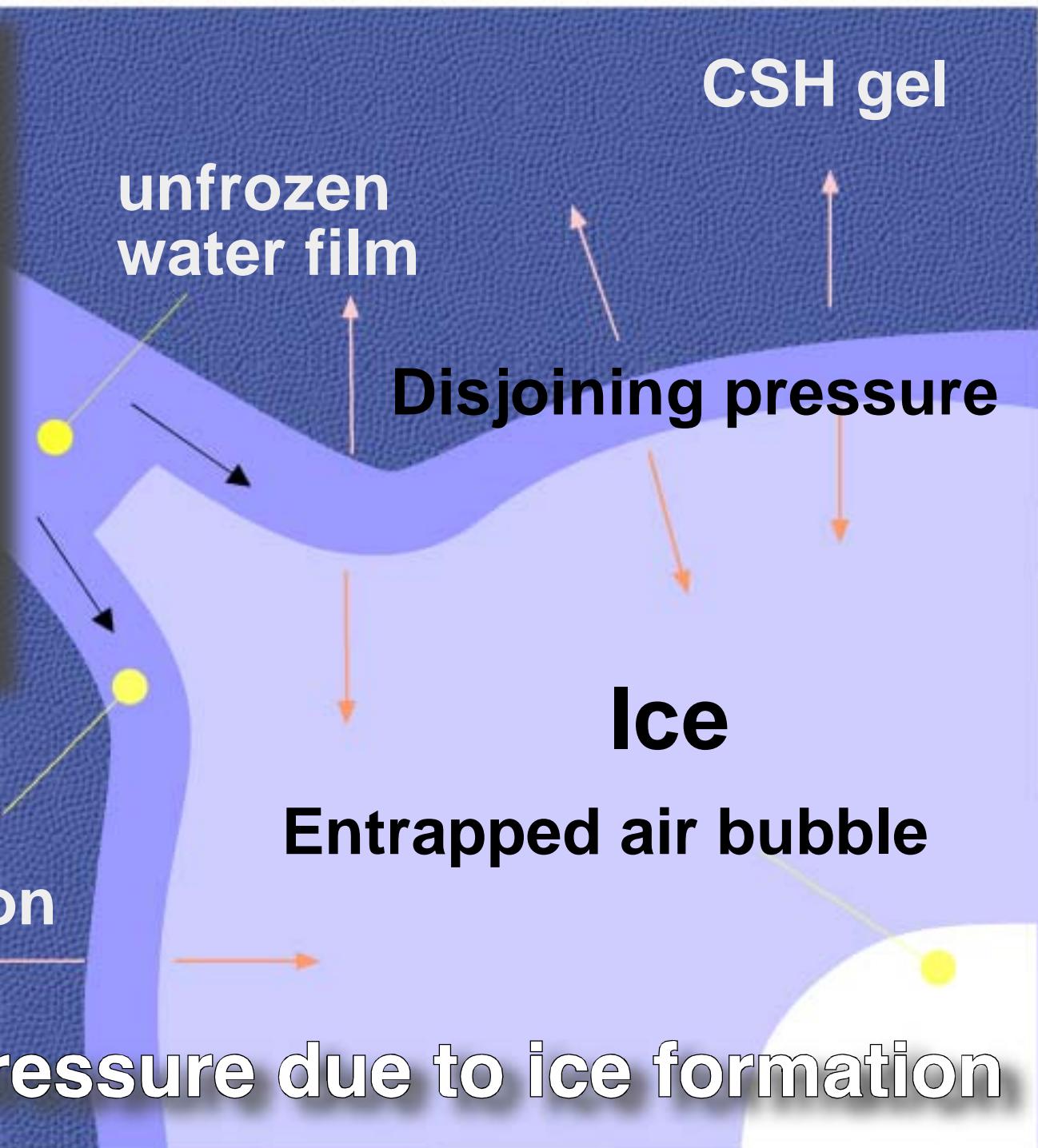
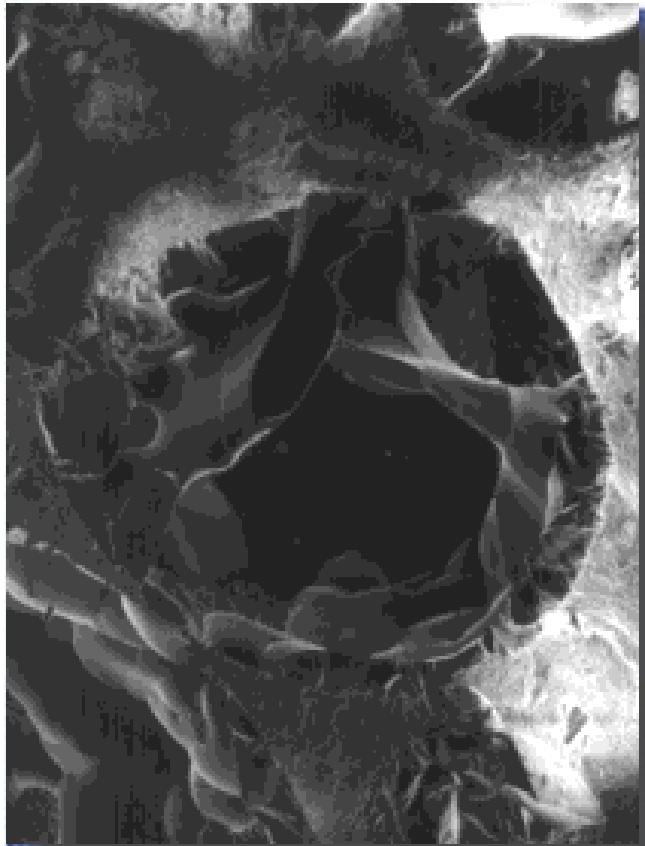
**Aerated concrete**  
 $d=0.503$

# Critical saturation

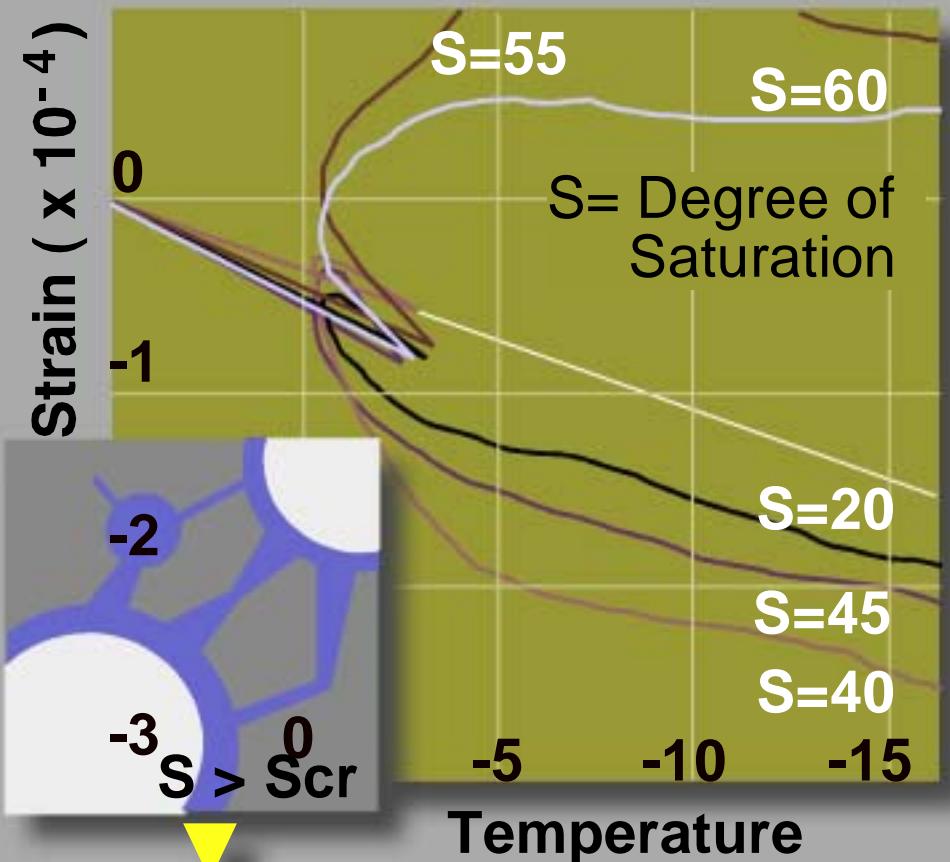
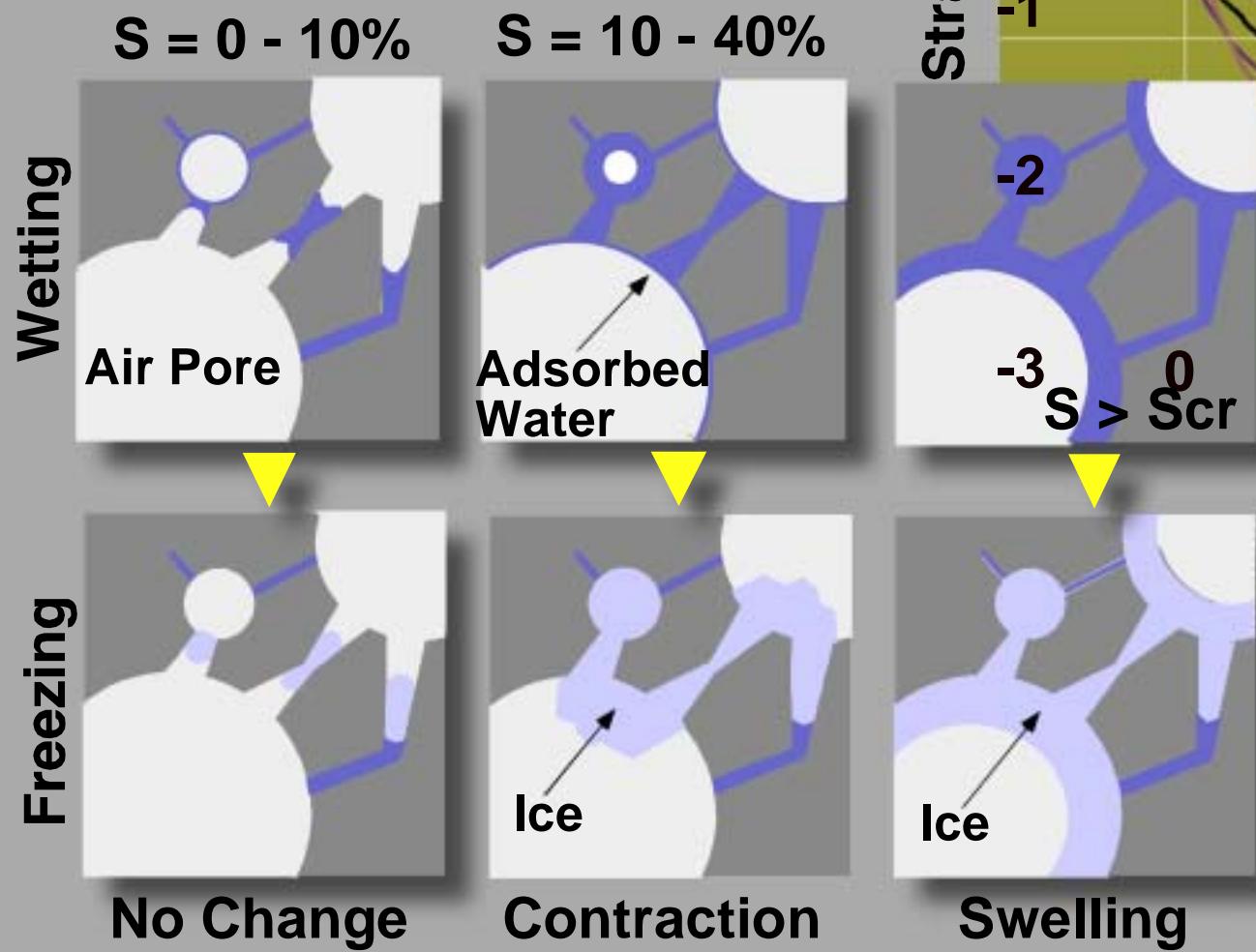


Aerated concrete  
 $d=0.503$





# Mechanism



**Thank you for your attentions**

