

2019-01-30

“Cellulosa-vatten växelverkan” - Ekmandagarna 2019
**The Thermodynamics of the Water-retaining
Properties of Cellulose-based Networks**

A photograph showing two water droplets of different sizes on a dark, reflective surface. The larger droplet on the right is more spherical and shows a clear reflection on the surface below it. The smaller droplet on the left is also spherical but smaller. The background is a dark, slightly textured surface.

Pernilla Karlsson

WWSC is a joint research center at KTH and Chalmers

Acknowledgement

Supervisors and co-authors

Professor Per Tomas Larsson,
RISE Bio economy-Sweden/KTH

Professor Per Hansson,
Uppsala University

Professor Lars Wågberg,
KTH Royal Institute of Technology-Sweden



Contact info

E-mail: pernkar@kth.se

Why?

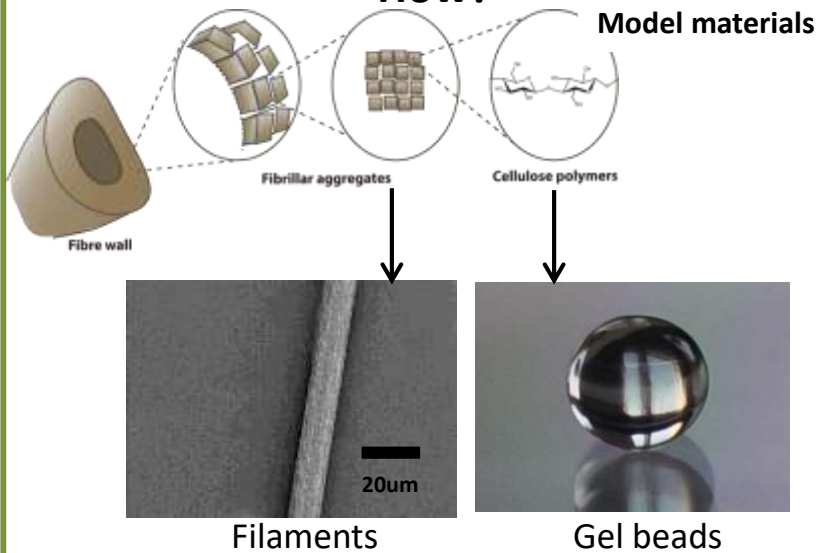
Pulp fibres takes up its own weight in water

Drying stand for a large part of the energy consumption

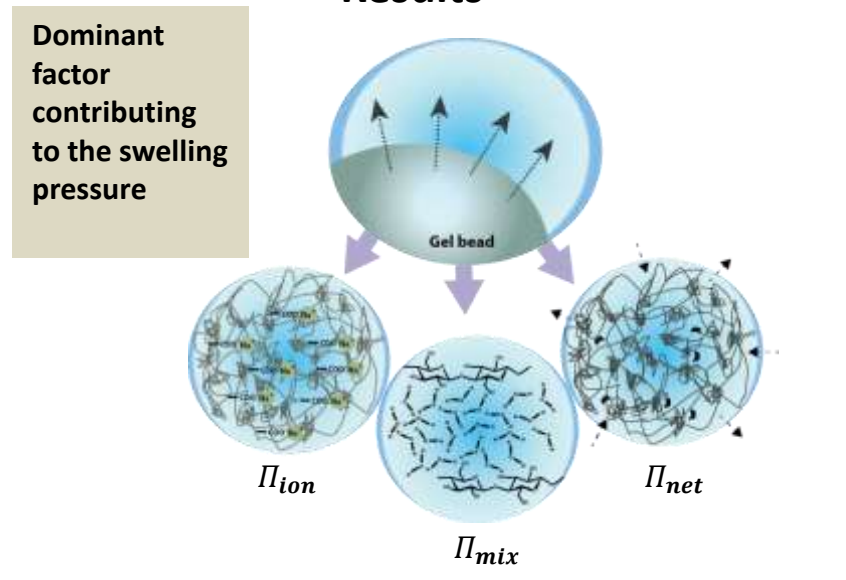
Predict/reduce/enhance the water uptake in cellulosic materials

$$\Delta G_{ion} + \Delta G_{mix} + \Delta G_{net} = \Delta G_{swell}$$

How?



Results



Why?

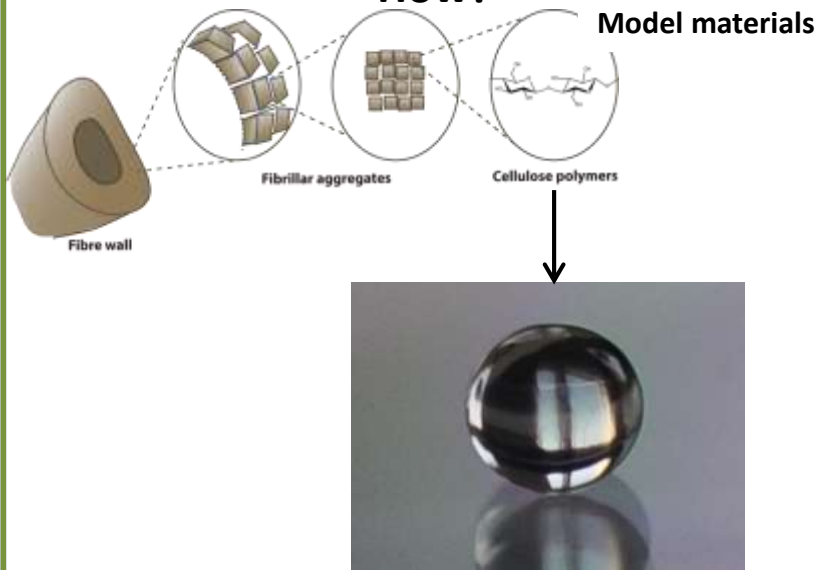
Pulp fibres takes up its own weight in water

Drying stand for a large part of the energy consumption

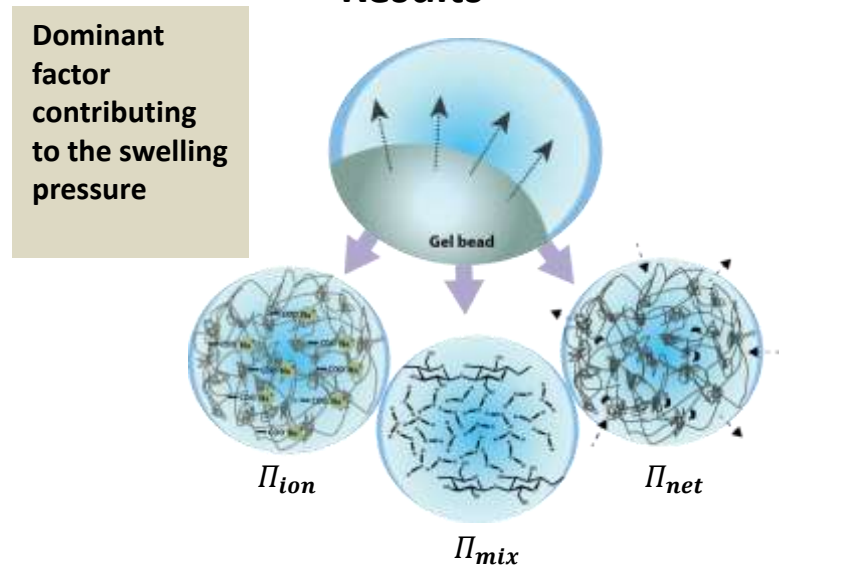
Predict/reduce/enhance the water uptake in cellulosic materials

$$\Delta G_{ion} + \Delta G_{mix} + \Delta G_{net} = \Delta G_{swell}$$

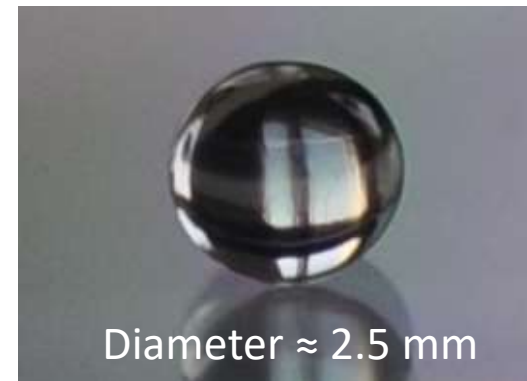
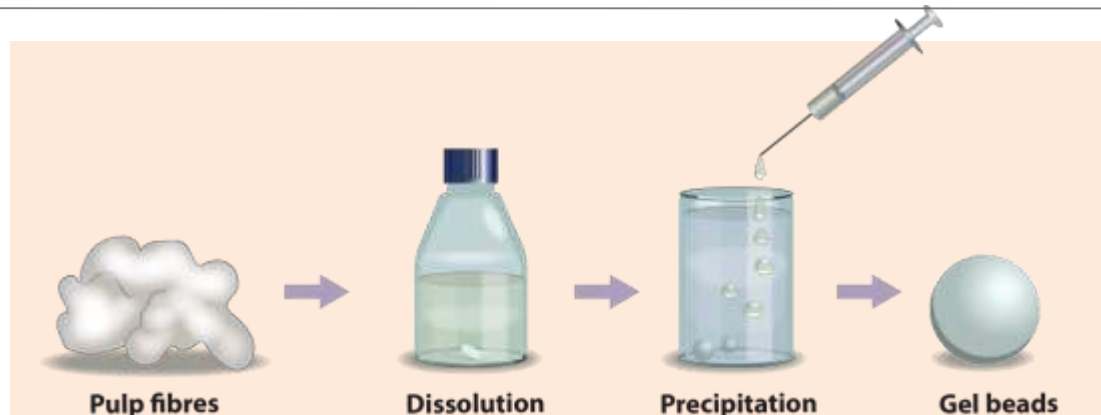
How?



Results



Gel bead preparation and characteristics



Charge content:

30 $\mu\text{eq/g}$
 Carboxymethylation
 300 $\mu\text{eq/g}$
 600 $\mu\text{eq/g}$

Structural features:

Non-crystalline
 Entities of approx. 25nm
 More stretched as charge increases

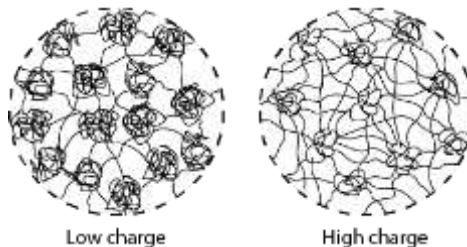
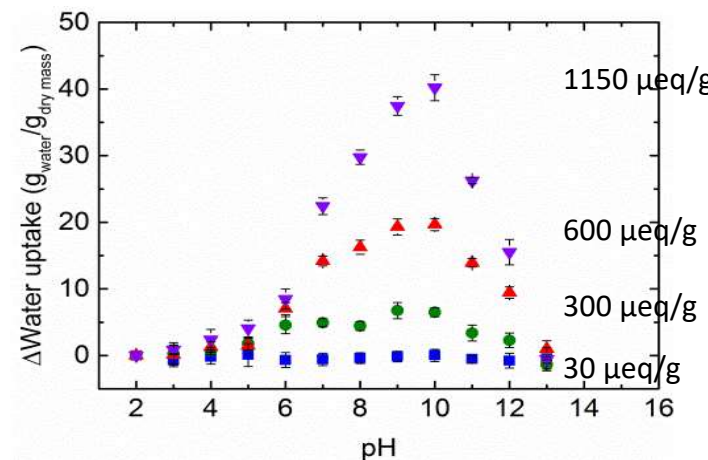


Illustration of interpretation of SAXS-data

pH and water uptake



Our definition of swelling

The expansion of a material caused by a spontaneous flow of liquid into the material network due to a difference in the chemical potential inside and outside the network

The expansion can be translated into an increase in pressure i.e. the osmotic pressure

What is Osmotic Pressure?

Osmotic pressure, Π

$$\Pi = - \left(\frac{\partial \Delta G}{\partial n_s} \right) \frac{1}{V_{m,s}}$$

Osmotic pressure is positive as ΔG is negative, i.e. a spontaneous reaction.

Change in free energy:

$$\Delta G(T, p) = \Delta H - T\Delta S$$

ΔH - change in enthalpy
 ΔS - change in entropy

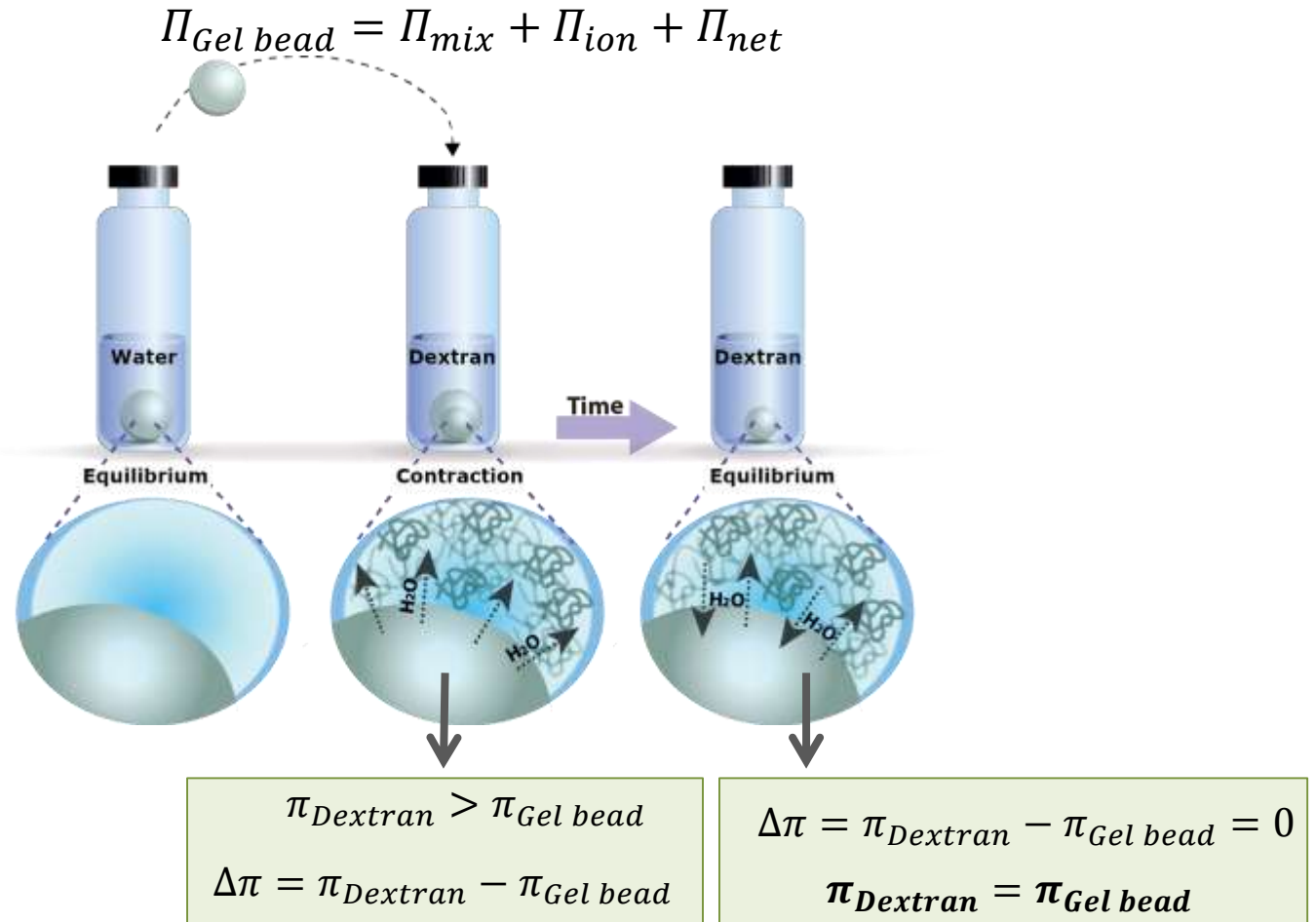
Polyelectrolyte gel swelling:

$$\Delta G_{tot} = \Delta G_{mix} + \Delta G_{ion} + \Delta G_{net}$$

Or

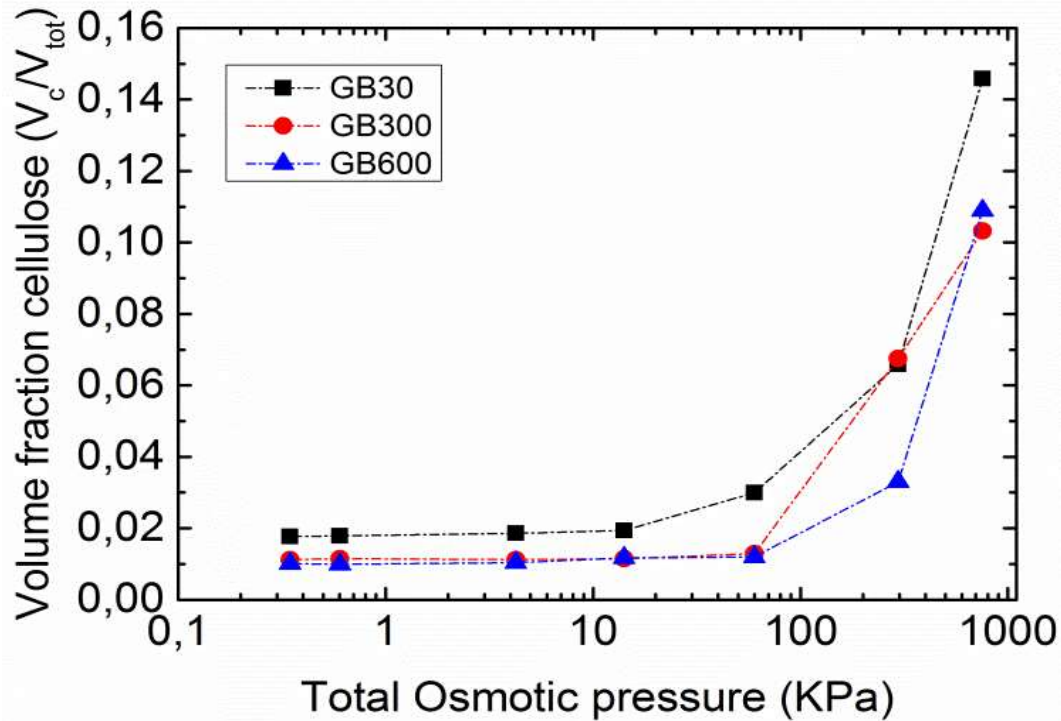
$$\Pi_{tot} = \Pi_{mix} + \Pi_{ion} + \Pi_{net}$$

Total Osmotic Pressure in Gel beads using Dextran



Volume fraction cellulose vs. Osmotic pressure

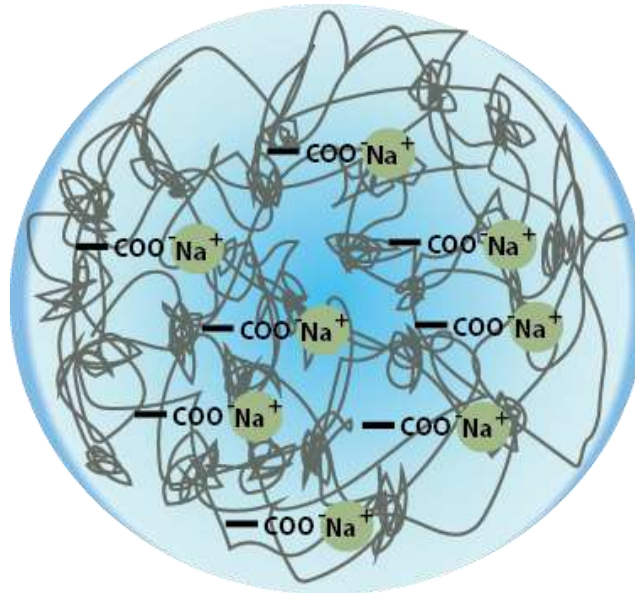
Volume fraction of cellulose in equilibrium with dextran solutions



Ionic contribution, Π_{ion} in Gel beads

- Carboxyl groups
-fully dissociated
- Immobile
- No added salt

Gel bead



$$\text{Van't Hoff} \\ \Pi_{ion} = RT \sum_{j=1}^N C_j^{gel} - C_j^{sol}$$

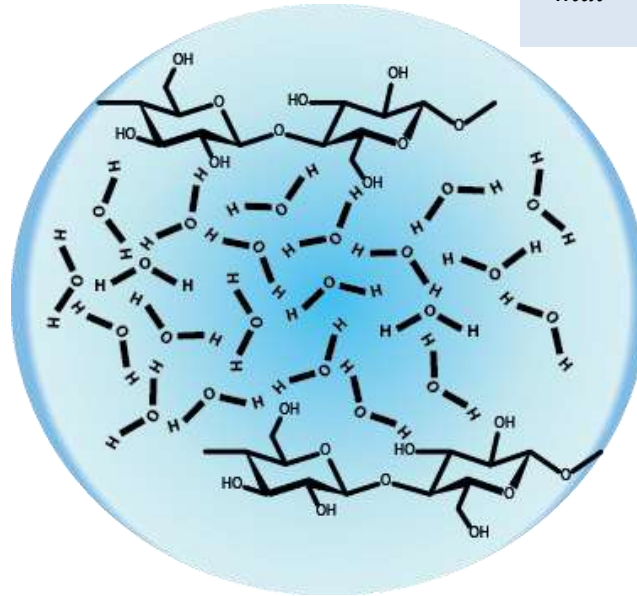
C_j^{gel} - ion conc in gel
 C_j^{sol} - ion conc in solution
R – gas constant
T- temperature

Π_{ion}

Polymer-solvent mixing, Π_{mix} in Gel bead

- Cellulose water in-soluble
 $\chi > 0.50$
- $M \rightarrow \infty$
(network)

Gel bead



Π_{mix}

Flory-Huggins

$$\Pi_{mix} = -\frac{RT}{V_m} [\ln(1 - \varphi) + (1 - M^{-1})\varphi + \chi\varphi^2]$$

φ - vol frac polymer
 M - molar mass polymer
 χ -interaction parameter

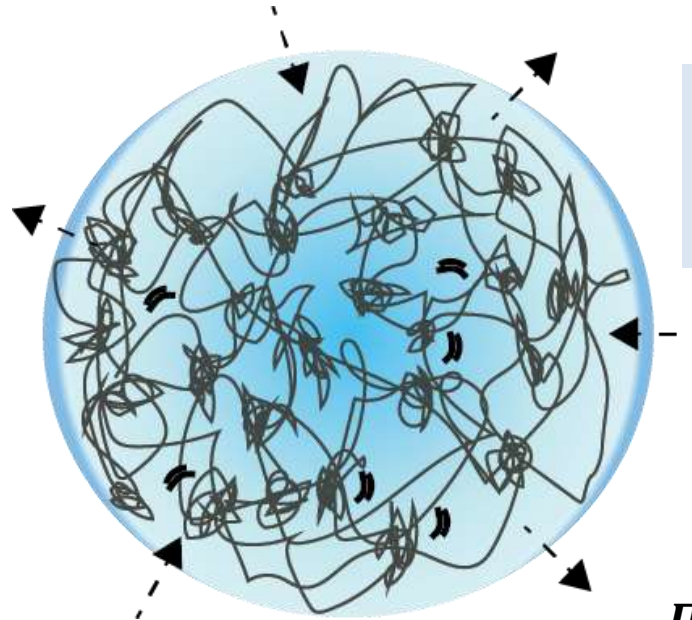
Entropy - number of possible state dependent on the concentration, φ and size, M of the polymers.

Enthalpy - i.e. the willingness of the polymer to mix with the solvent (interaction parameter, χ)

Network deformation, Π_{net}

$$\Pi_{Gel\ bead} - \Pi_{mix} - \Pi_{ion} = \Pi_{net}$$

Gel bead



Π_{net}

- Stiff polymer
- Dilute system

Wall model

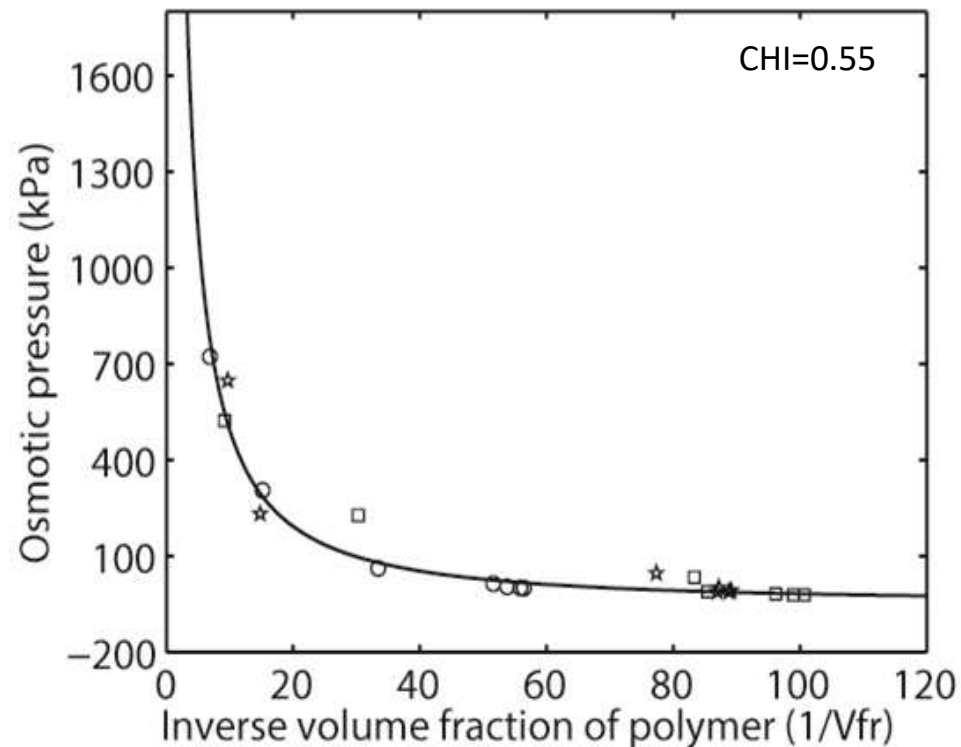
$$\Pi_{net} = \frac{RT\phi}{V_m 2P} \left(1 - \left(\frac{\phi_0}{\phi} \right)^{\frac{2}{3}} \right)$$

ϕ - vol frac polymer
 ϕ_0 - initial vol frac of polymer
 P - length of polymer segments between cross-links

$\Pi_{net} > 0$ - favors swelling
 $\Pi_{net} < 0$ - restricts swelling

Network pressure and Wall-model

$$\Pi_{Gel\ bead} - \Pi_{mix} - \Pi_{ion} = \Pi_{net}$$

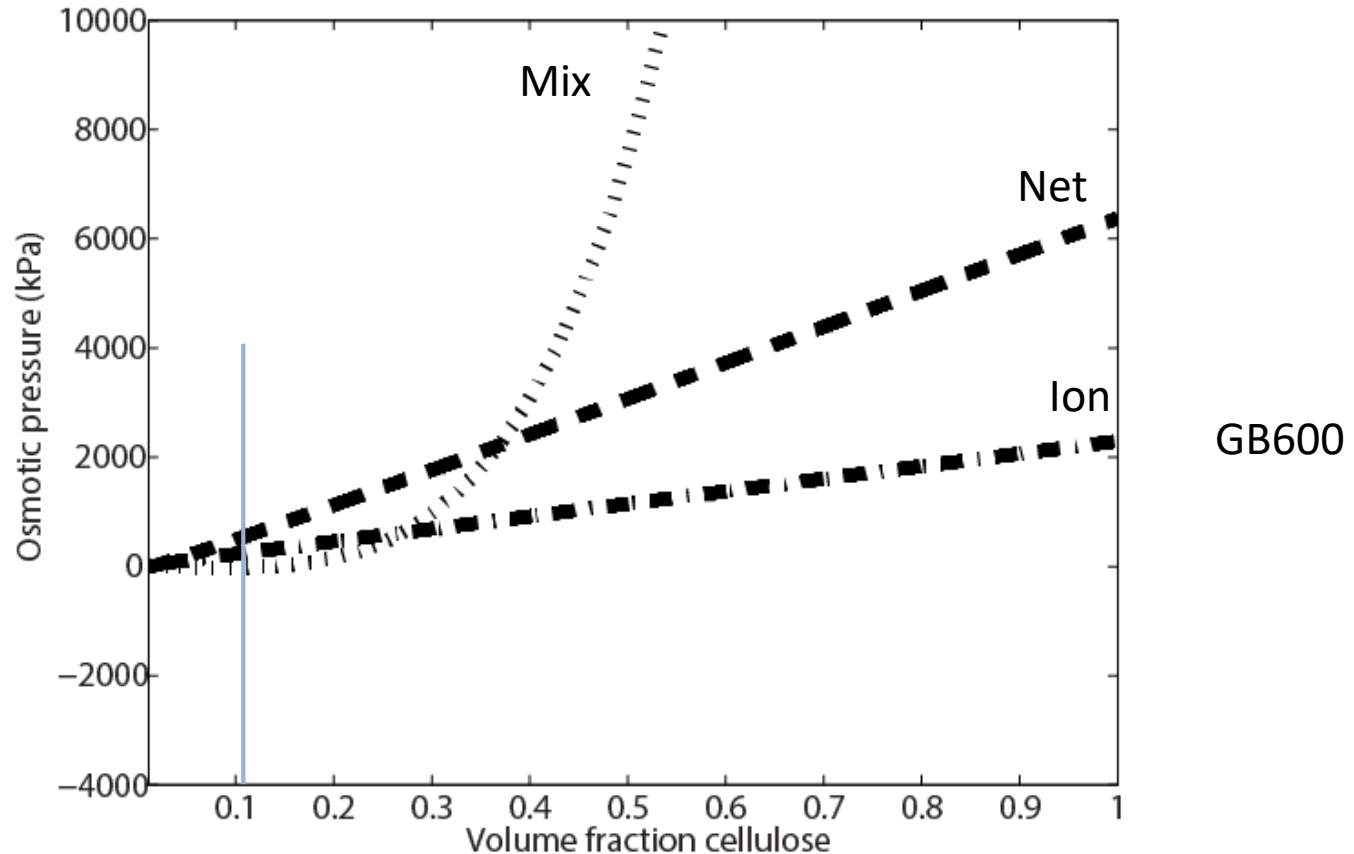


Quantification of swelling factors

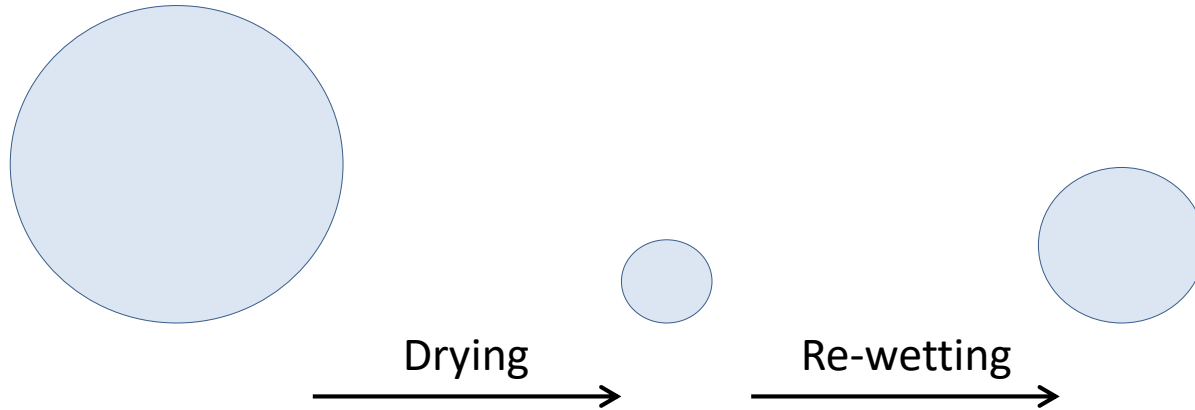
-an example (Chi=0.55)

30 $\mu\text{eq/g}$							
Vol %	1.8	1.8	1.9	1.9	3.0	6.6	14.6
Π_{ion} (kPa)	2,0	2,0	2,1	2,2	3,4	6,5	18,6
Π_{Mix} (kPa)	-1,9	-1,9	-2,0	-2,2	-4,8	-15,8	13,3
Π_{Net} (kPa)	0,2	0,5	4,2	14,2	61,4	304,9	722,4
300 $\mu\text{eq/g}$							
Vol %	1.1	1.2	1.1	1.2	1.3	6.8	10.3
Π_{ion} (kPa)	12,5	12,8	12,4	12,7	14,3	79,6	124,7
Π_{Mix} (kPa)	-0,79	-0,83	-0,79	-0,82	-1,00	-16,2	-18,3
Π_{Net} (kPa)	-11,4	-11,3	-7,39	2,20	46,7	232,3	647,9
600 $\mu\text{eq/g}$							
Vol %	1.0	1.0	1.0	1.2	1.2	3.3	10.9
Π_{ion} (kPa)	22,6	22,0	22,9	26,0	26,6	73,8	249,2
Π_{Mix} (kPa)	-0,64	-0,62	-0,68	-0,85	-0,90	-5,71	-16,8
Π_{Net} (kPa)	-21,5	-20,8	-18,0	-11,0	34,2	227,5	521,9

Extrapolation of volume fraction



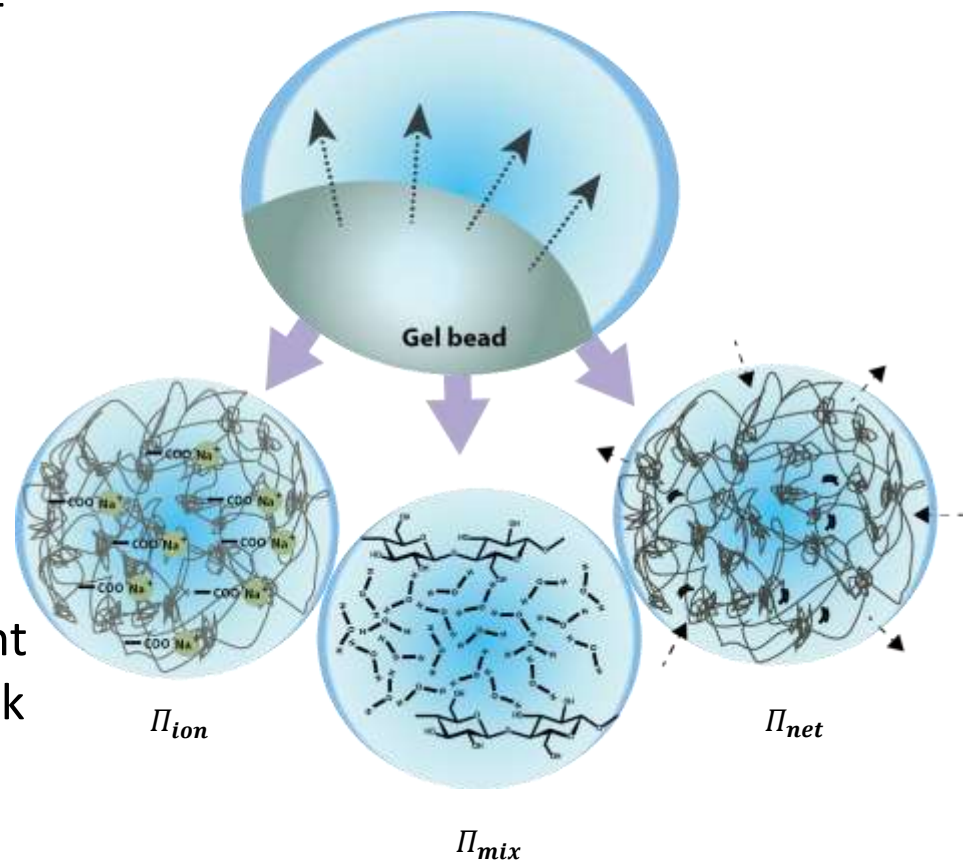
Changing the network structure



	Π_{tot} (kPa)	Vol frac	Π_{ion} (kPa)	Π_{mix} (kPa)	Π_{net} (kPa)
Rew30	296	0.289	49	800	-550
Rew300	296	0.186	240	100	-50
Rew600	296	0.116	293	-14	20

Conclusion

- Separation and quantification of swelling factors shows that the dominating factor shifts with volume fraction of cellulose.
- Possible that the mixing term starts to dominate at higher cellulose fractions.
- The method is system dependent and is valid for a specific network structure.



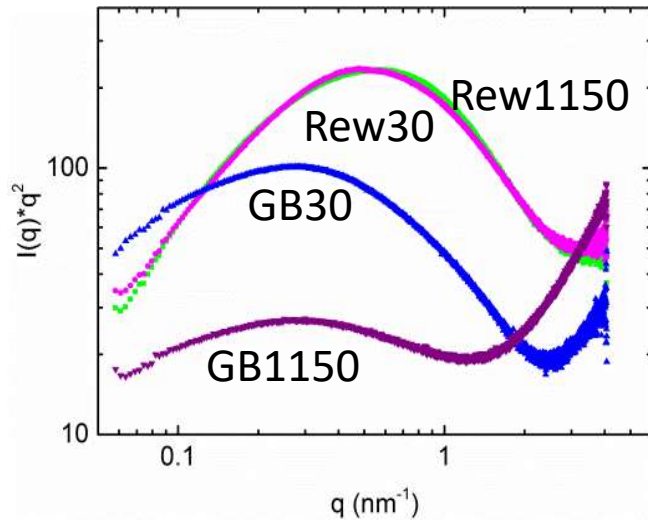
Tack!

“Swelling of Cellulose Fibrillar Matrices and Gels”*

Disputation 24 maj kl. 14.00 sal F3, KTH

pernkar@kth.se

* preliminär titel



Sample	CNF340
Charge ($\mu\text{eq/g}$)	340
Volume fraction (%)	49.0
Π_{ion} (kPa)	1500
Π_{mix} (kPa)	6900
Π_{def} (kPa)	-8100
Π_{tot} (kPa)	296