# Is the free energy of hydrogel the sum of an elastic energy and ionic energy?

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## Introduction

Ionised porous media are profusely present in biology as well as in geology. Numerical techniques have been developed to handle these materials. The constitutive laws used in these models are satisfactory in relatively stiff materials, such as bone, shale or cartilage. But for high deformable materials ($E < 1MPa$) they don't satisfy, both in robustness as in their ability to fit experiments.

## Objective

The development of a constitutive law for flexible gels, suitable for numerical implementation.

## Methods

### Swelling and compression experiment

We have conducted 1D swelling and compression experiments on samples of acrylic acid acrylamid copolymer gel [2] (see fig. 1). In these experiments, the swelling and compression was achieved by varying ionic concentration and applied load as a function of time (see fig. 2a). The resulting variation of sample height is measured (see fig. 2b).

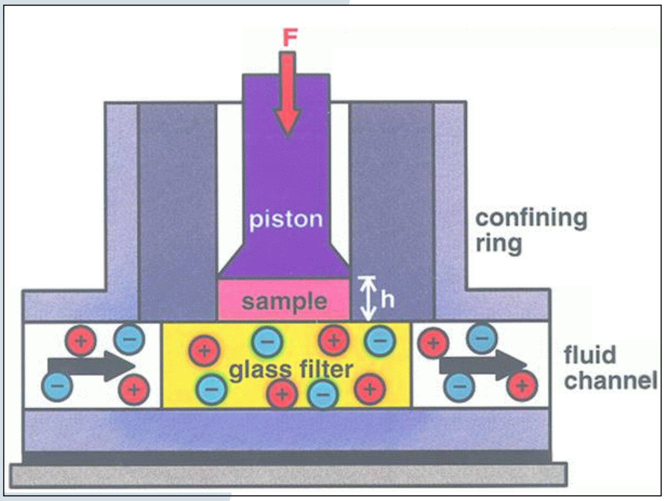


**Figure 1:** *Schematic set-up of the experiment.*

The applied load in hydrogel can be divided in liquid pressure $p$, and effective stress - $\sigma_{eff}$:

$$\sigma = \sigma_{eff} - p \tag{1}$$

In figure 2c, this effective stress is shown as a function of strain.

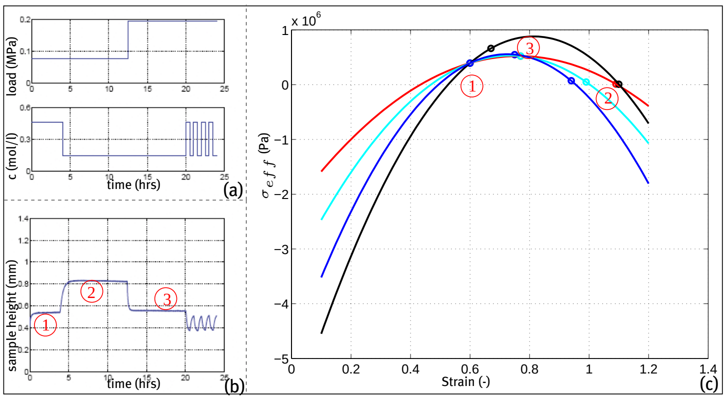


**Figure 2:** *The load and concentration are varied in time (a). This leads to 1D swelling and compression behaviour (b). The effective stress is displayed versus strain at 3 swell stages for several measurements.*

## Interpretation

Figure 2c, displays consistently strain softening; e.g. a negative derivative of effective stress to strain. In stable ('*real*') materials, this can only be true when the stiffness is influenced by another quantity: *ionic concentration*.

## Free energy

Equilibrium behaviour of hydrogel can be derived form the free energy function $W$ which depends on both ionic concentration and strain. In common macroscopic analysis [3] the free energy is written as the sum of an elastic energy dependent on strain and a Donnan ionic energy dependent on fixed charge density and ionic concentration. The results of 1D swelling and compression experiments suggest that we should add an extra term which depends both on strain and ionic concentration.

$$W = H\epsilon^2 + b\epsilon c^+ + d + f(c^+), \tag{2}$$

where $\epsilon$ is strain (-), $c^+$ is the cation concentration in the hydrogel ($\mathrm{mol/m^3}$), $H$ is the stiffness (Pa), $b$ and $d$ are extra parameters which should be fitted with the experiments ($\mathrm{J/m^3}$), and $f(c^+)$ is the Donnan ionic energy ($\mathrm{J/m^3}$).

## Acknowledgment

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