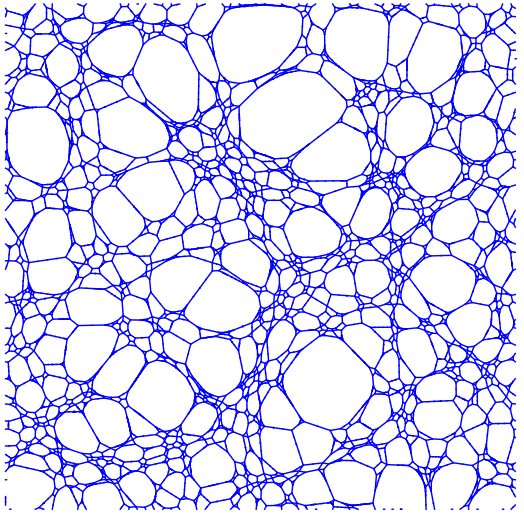
Department of Engineering Science

UNIVERSITY OF OXFORD

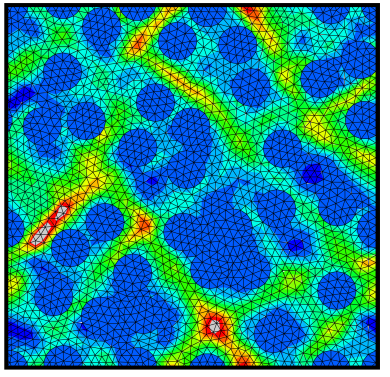
Micromechanical modelling of near-ideal polymer networks

Laurence Brassart

18 May 2020



Research interests



- Continuum mechanics
- Constitutive modelling
- Micromechanics, scale transition methods
- Chemo-mechanical couplings in materials

Materials:

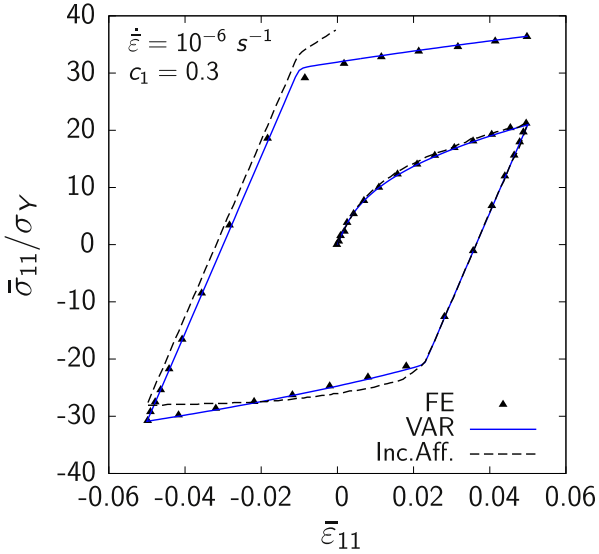
Composite materials; Polymers; Energy materials; Soft materials; Biomaterials

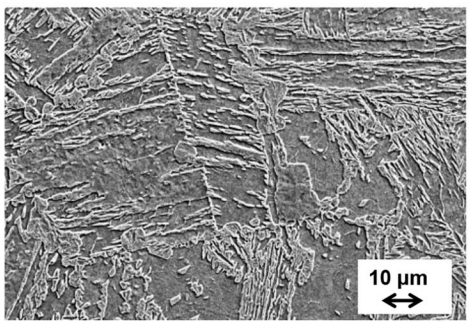
Collaborations:

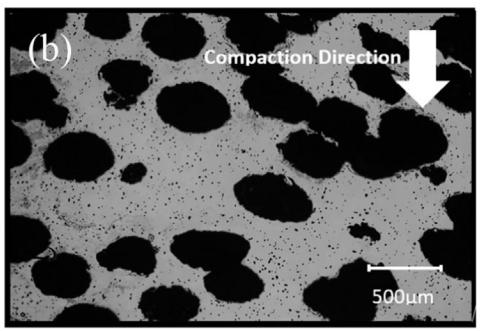
Université catholique de Louvain, Harvard University, Monash University, Ecole Centrale de Nantes

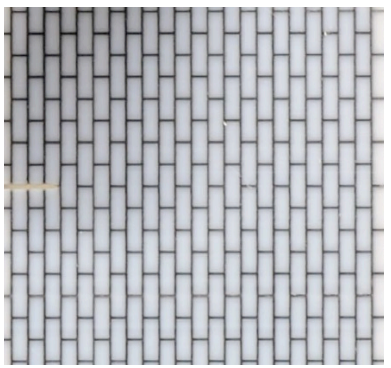
Micromechanics of composites

- Mean-field modelling in elasto-viscoplasticity
- FEA at micro and macro scales
- Applications to fibre-reinforced composites, dual-phase steels, porous materials, 3D-printed architectured materials





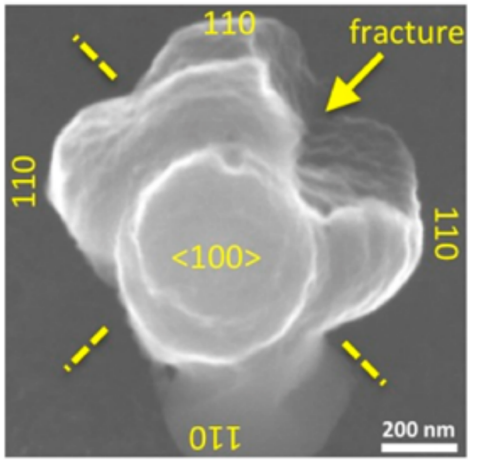


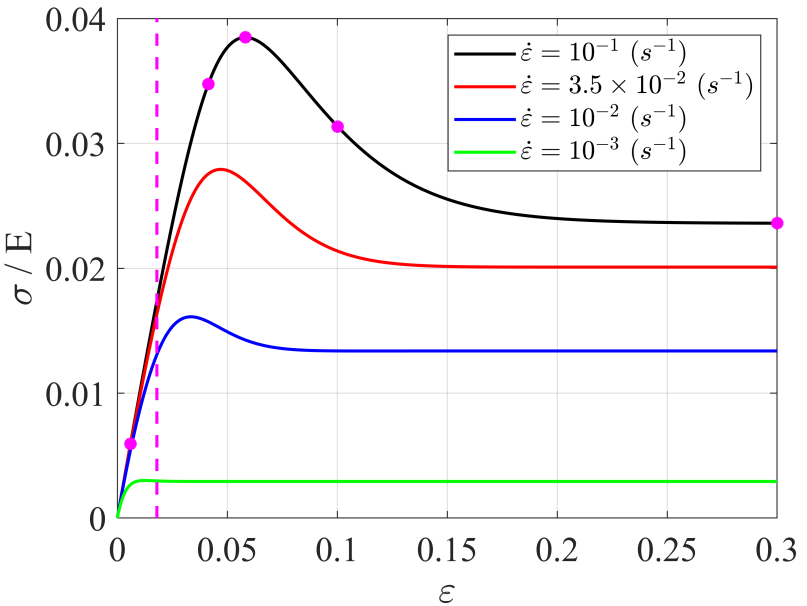


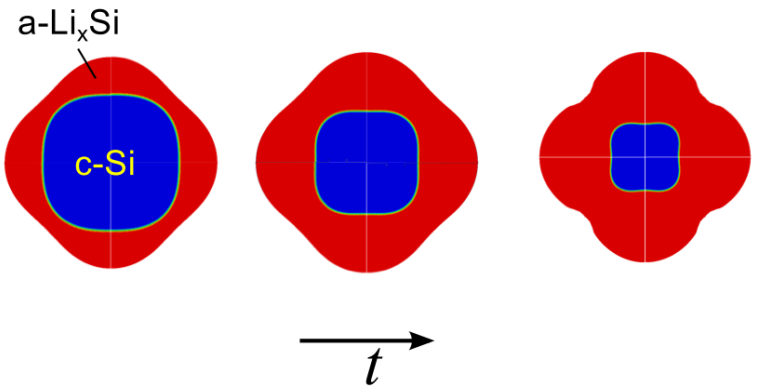
Brassart et al., *IJP* (2012); Pierman et al, *Acta Mat*, (2014); Soro et al., *Mater. Sci. Eng. A* (2018), Ismail et al, *IJP* (2019);

Mechanics of Li-ion batteries

- Constitutive modelling of a-LiSi
- Coupled diffusion-plasticity analysis
- Anisotropic swelling and fracture in c-Si



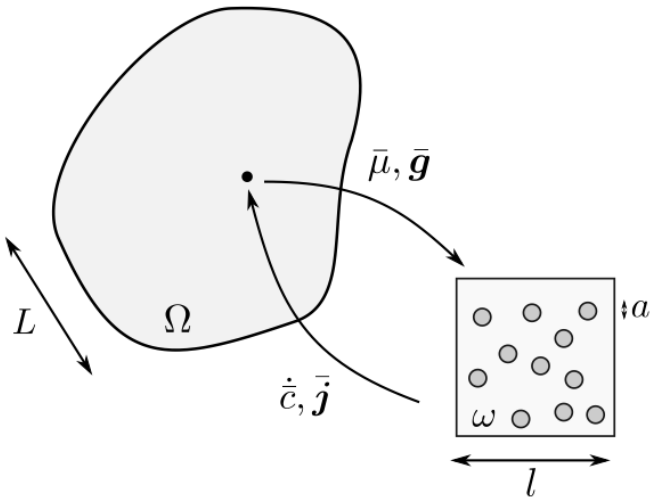




Brassart and Suo, *JMPS* (2013); Brassart et al., *IJSS* (2013); Sandu et al., *ACS Nano*, (2014); Bagheri and Brassart, *in preparation*.

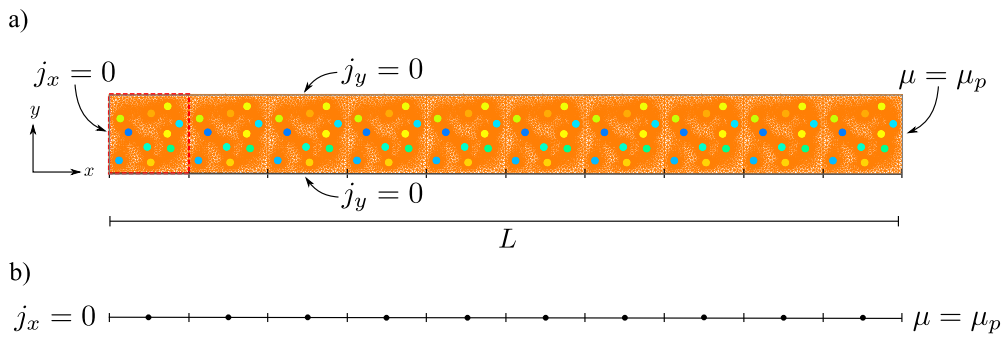
Mean-field homogenisation for transient diffusion problems

- Diffusion in heterogeneous media with high diffusivity contrast
- Non-classical effective behaviour



$$\bar{\mu}\dot{\bar{c}} - \bar{\boldsymbol{j}} \cdot \bar{\boldsymbol{g}} = -\frac{1}{V}\int_{\partial\omega} \mu \boldsymbol{j} \cdot \boldsymbol{n} dS$$

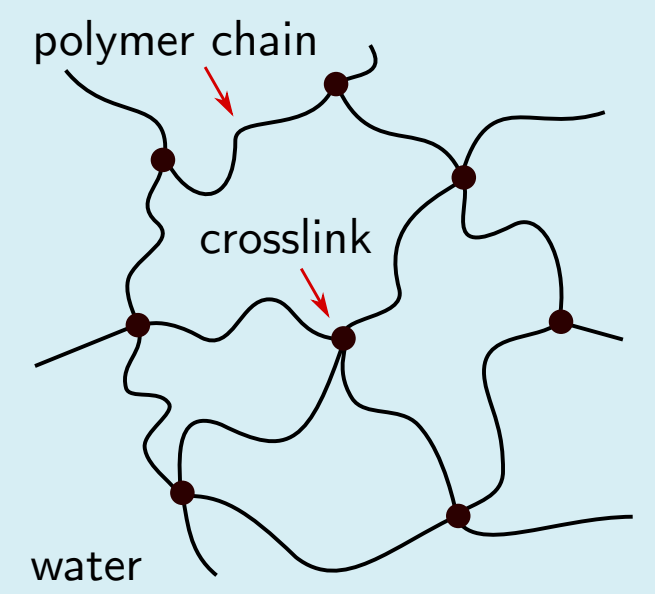
$$= \frac{1}{V}\int_{\omega} \mu \dot{c}\ dV - \frac{1}{V}\int_{\omega} \boldsymbol{j} \cdot \nabla \mu\ dV$$

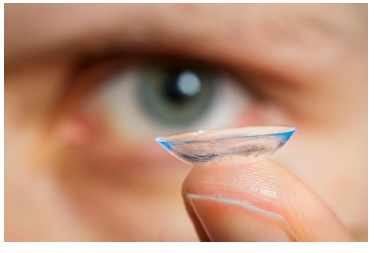


Brassart et al, *JMPS* (2018); Brassart and Stainier, *JMPS* (2019)

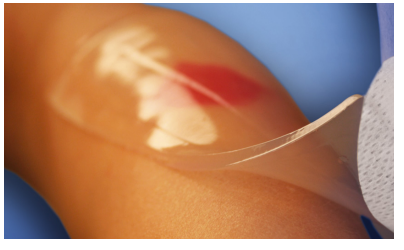
Hydrogels in everyday life

Hydrogels are crosslinked polymer networks swollen in water





Contact lenses



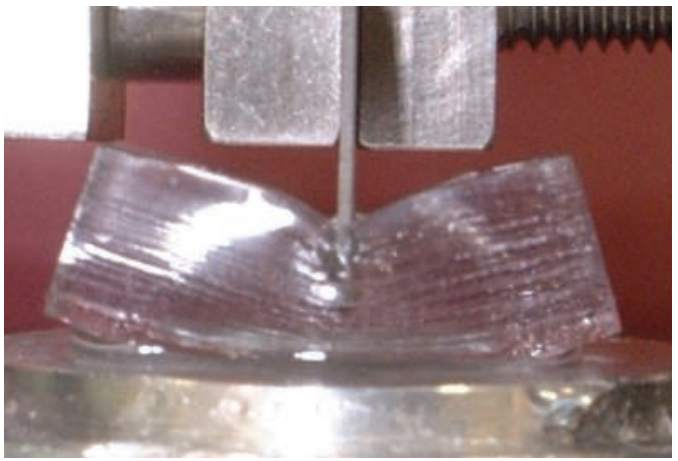
Wound dressing

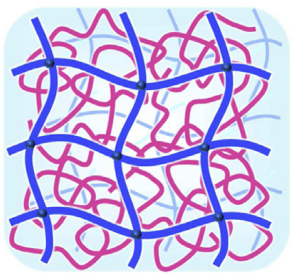
Superabsorbent diapers

Water beads

Network design for strength and toughness

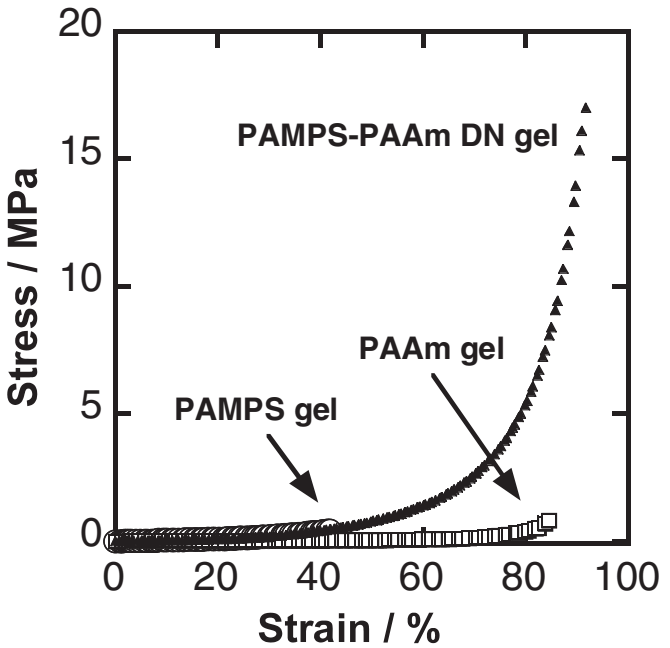
Example: Double-network gels





1st network:
Rigid skeleton, dilute,
short chains

2nd network:
Flexible matrix,
concentrated, long chains

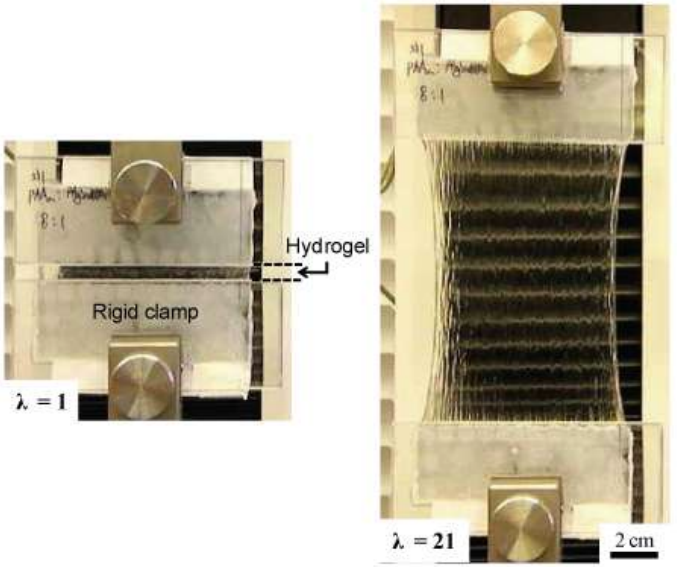


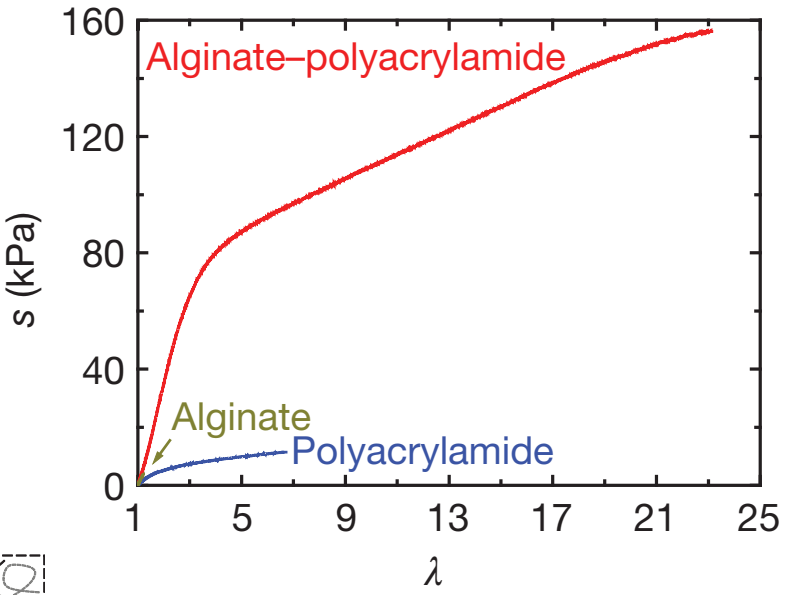
Γ=1000 J/m^2

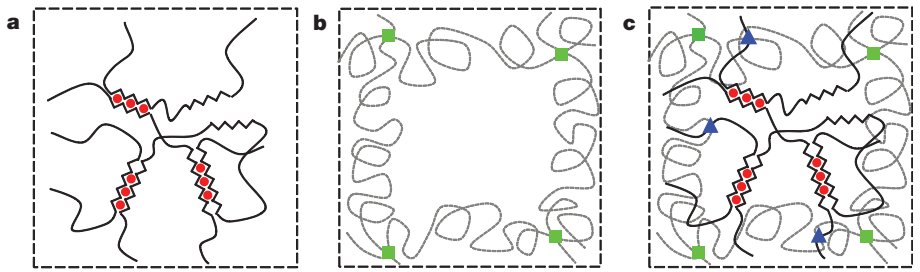
Gong et al., *Adv. Mater.* (2003) > 2000 citations

Network design for strength and toughness

Example: hybrid ionic-covalent gels







Γ=8700 J/m^2

λ_{max}>20

Sun, Zhao, ... Vlassak, Suo, *Nature* (2012) > 2000 citations

Continuum modelling

Kinematics:

$$\boldsymbol{x} = \boldsymbol{\chi}(\boldsymbol{X}, t)$$
$$\boldsymbol{F} = \boldsymbol{\nabla}\boldsymbol{\chi}$$
$$\det(\boldsymbol{F}) = 1 + \Omega C$$

Conservation equations:

$$\boldsymbol{\nabla} \cdot \boldsymbol{P} = \boldsymbol{0}$$
$$\frac{\partial C}{\partial t} = -\boldsymbol{\nabla} \cdot \boldsymbol{J}$$

Constitutive models:

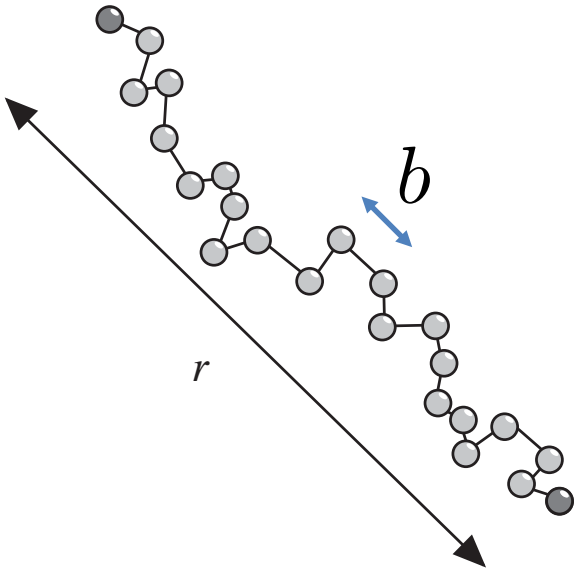
$$\mu \dot{C} + \boldsymbol{P} : \dot{\boldsymbol{F}} - \boldsymbol{J} \cdot \boldsymbol{\nabla}\mu - \dot{W} \geq 0$$
$$W = W^e(\boldsymbol{F}) + W^c(C)$$
$+$ kinetic relations

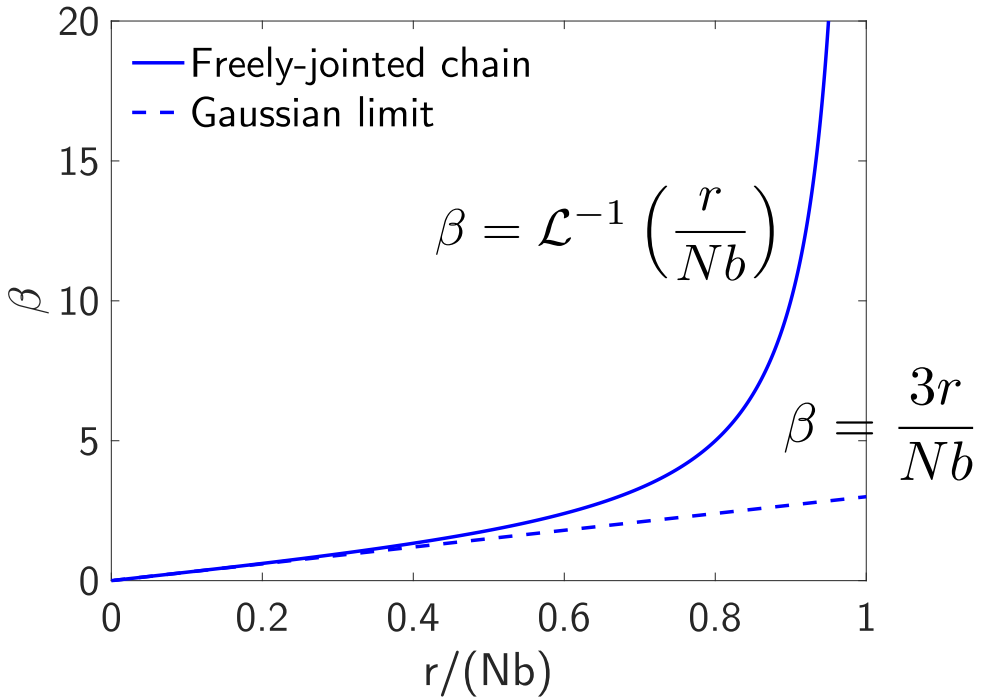
← Micromechanical modelling

e.g. Hong et al., *JMPS* (2008); Chester and Anand, *JMPS* (2010).

Single chain behaviour

Freely-jointed chain with N Kuhn segments of length b



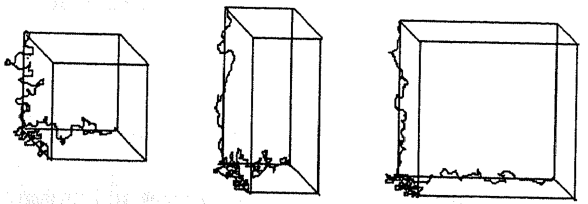


$$w = NkT\left(\frac{\beta}{\tanh\beta} + \log\frac{\beta}{\sinh\beta}\right) \qquad \beta = \frac{fb}{kT}$$

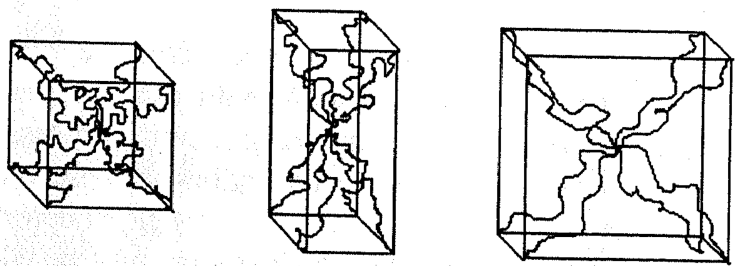
Network models

Assembly of representative chains deforming affinely with the macroscopic strain

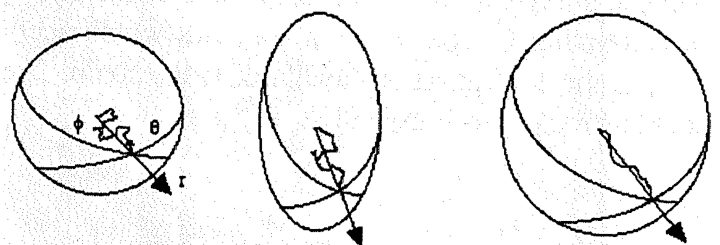
- 3-chain model



- 8-chain model



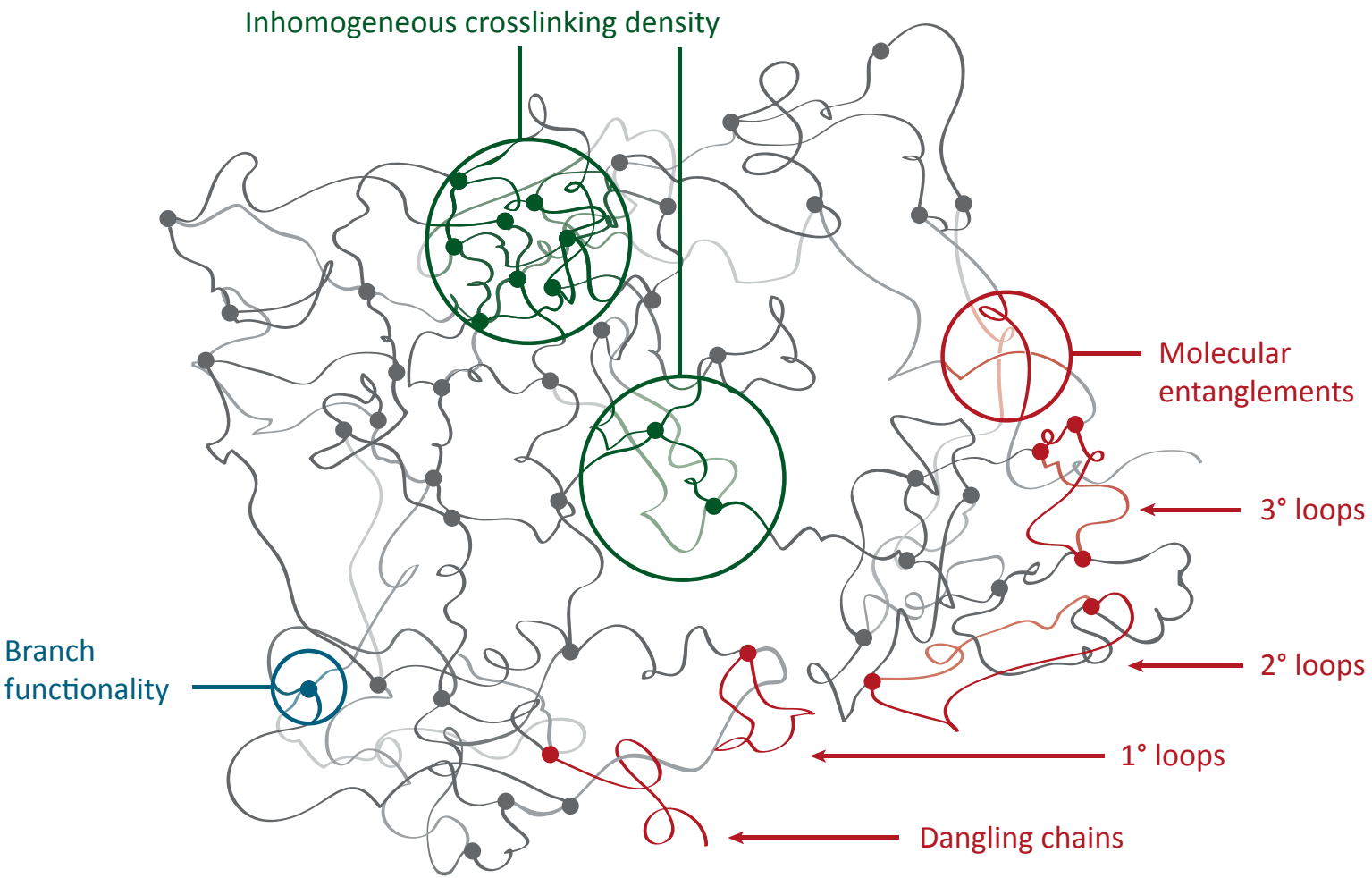
- Full-network model



$$W^e = \frac{1}{V}\sum_n w$$

Wang and Guth (1952); Treloar (1975); Arruda and Boyce (1993); Wu and Van Der Giessen (1993)

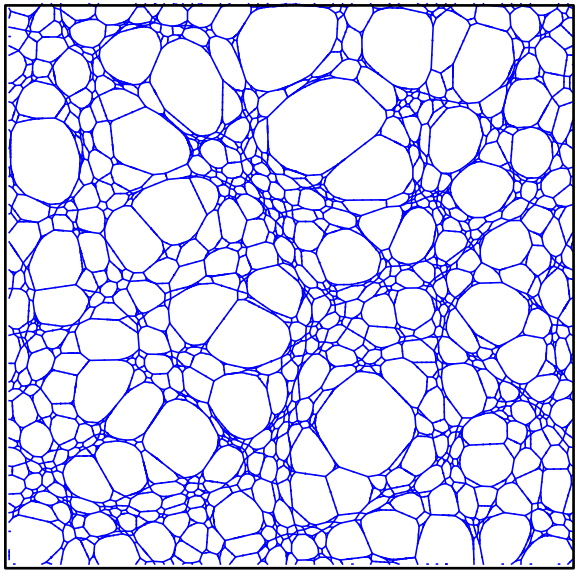
Real networks are imperfect



Gu et al., *Trends Chem.* (2019)

Micromechanical modelling

- Random assembly of springs (polymer chains) connecting at junction points (crosslinks)
- Spring behaviour described by entropic force-extension relation
- Includes topological defects



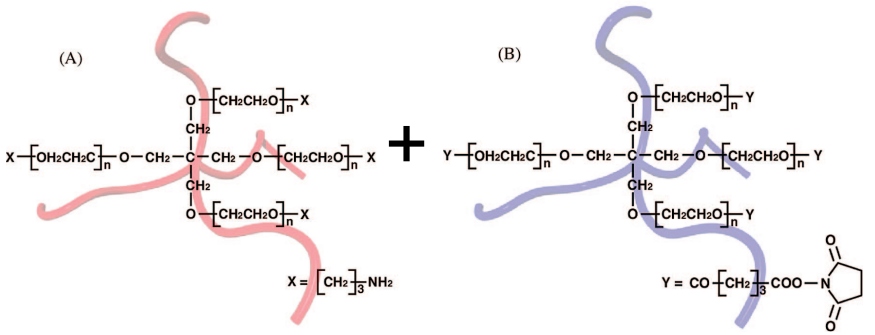
Objectives

- Understand the relative contributions of network parameters to mechanical properties
- Generate reference results to validate constitutive models

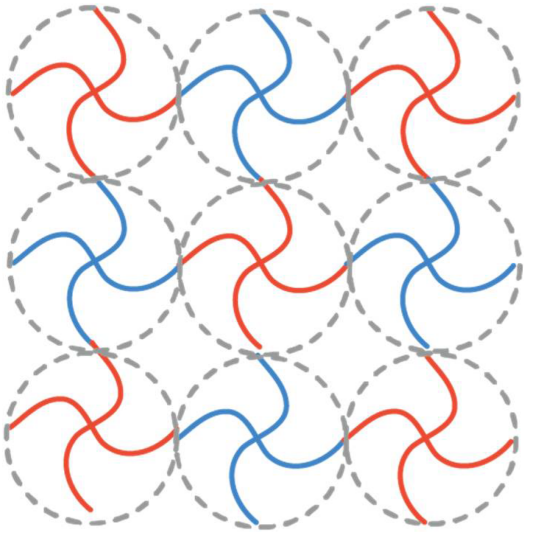
Model system: near-ideal networks

4-arm PEG hydrogels

Polymer precursors



Gelation in solution



Ideal-network gel

- Controlled arm length
- High conversion rate
- No first-order loops
- Few entanglements

Sakai et al., *Macromol.* (2008) > 700 citations

Network structures

Input:

- Chain density $\nu = n/L^3$
- Conversion probability p

→ average coordination $\bar{Z}$

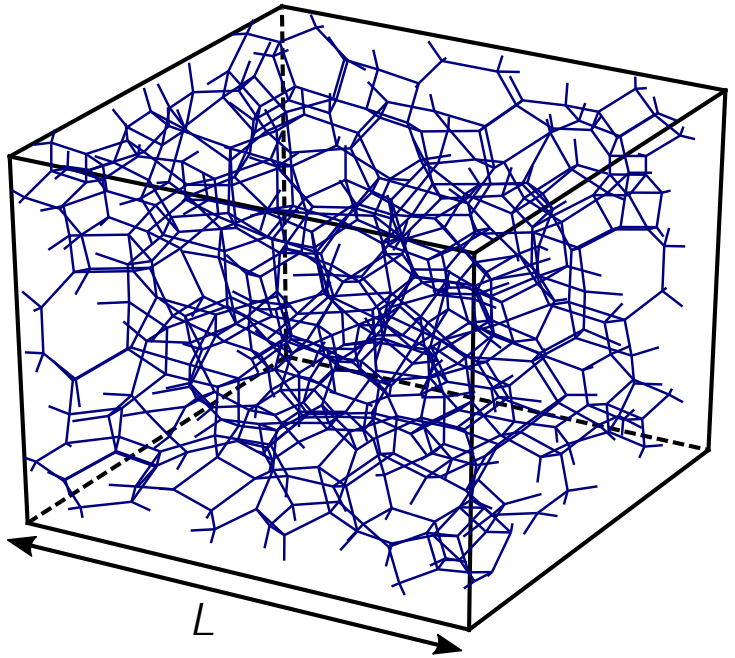
- Loop fraction ζ

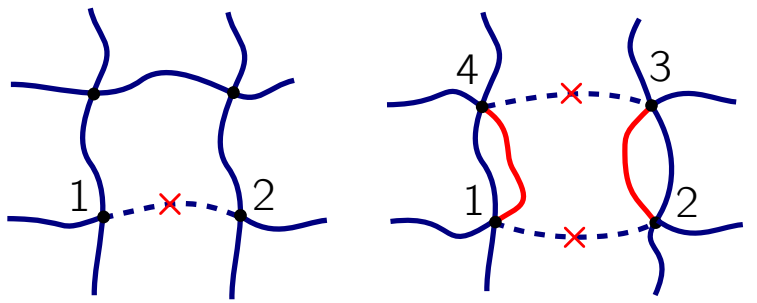
$$\boldsymbol{x}_\alpha = \boldsymbol{F} \cdot \boldsymbol{X}_\alpha$$

$$\boldsymbol{P} = \frac{1}{V} \sum_\alpha (\boldsymbol{f}_\alpha^e \otimes \boldsymbol{X}_\alpha)$$

Output:

- Stress-strain curves
- Chain length and orientation distribution



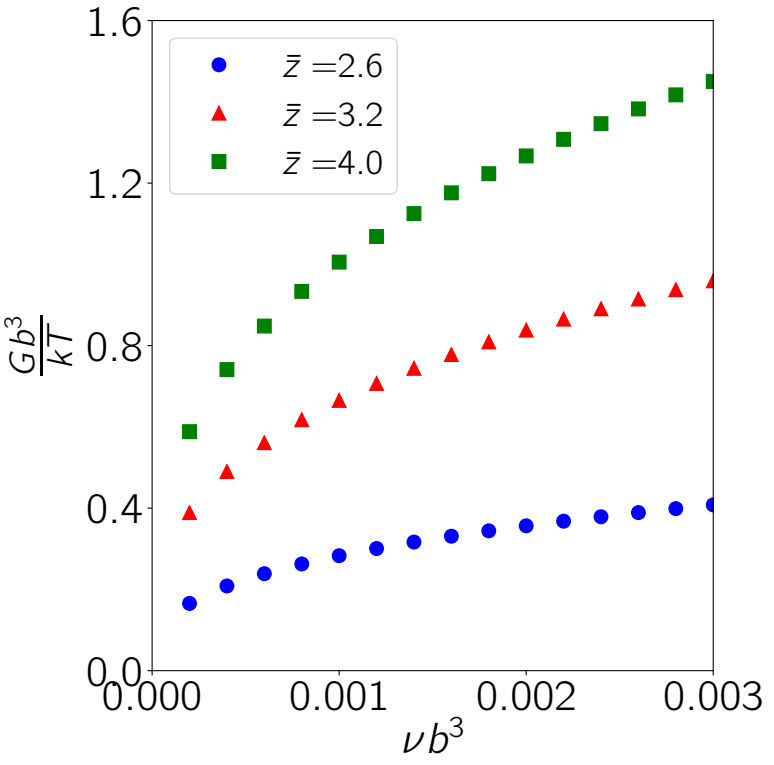


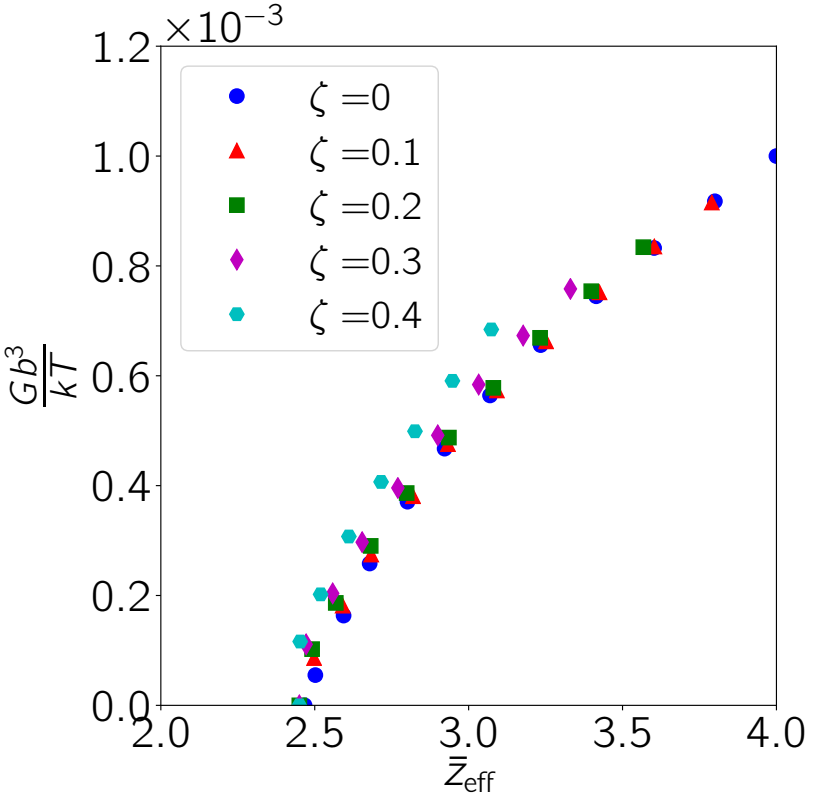
Energy minimisation (LAMMPS)

$$\bar{Z}_{\text{eff}} \approx \bar{Z}(1 - \frac{\zeta}{2})$$

Scaling of the shear modulus

$$G \sim \frac{1}{N}\nu^{1/3}(\bar{Z}_{\text{eff}} - \bar{Z}_{\text{eff},c})^{2/3}$$





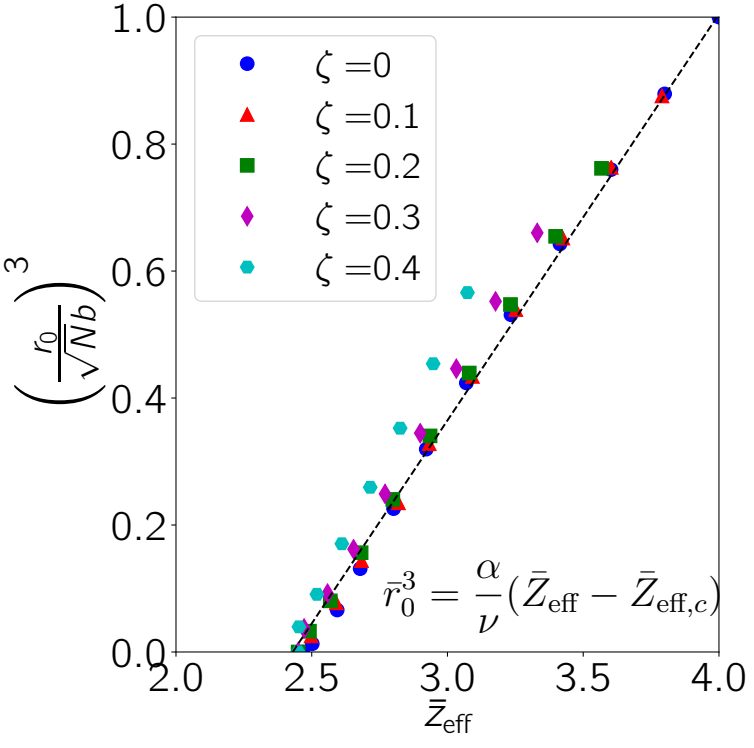
Interpretation based on chain pre-stretch

Elastic modulus of a network of Gaussian chains:

$$G = kT\nu\frac{\bar{r}_0^2}{Nb^2} \qquad \bar{r}_0^2 = \langle r_0^2 \rangle \qquad \text{(exact result)}$$

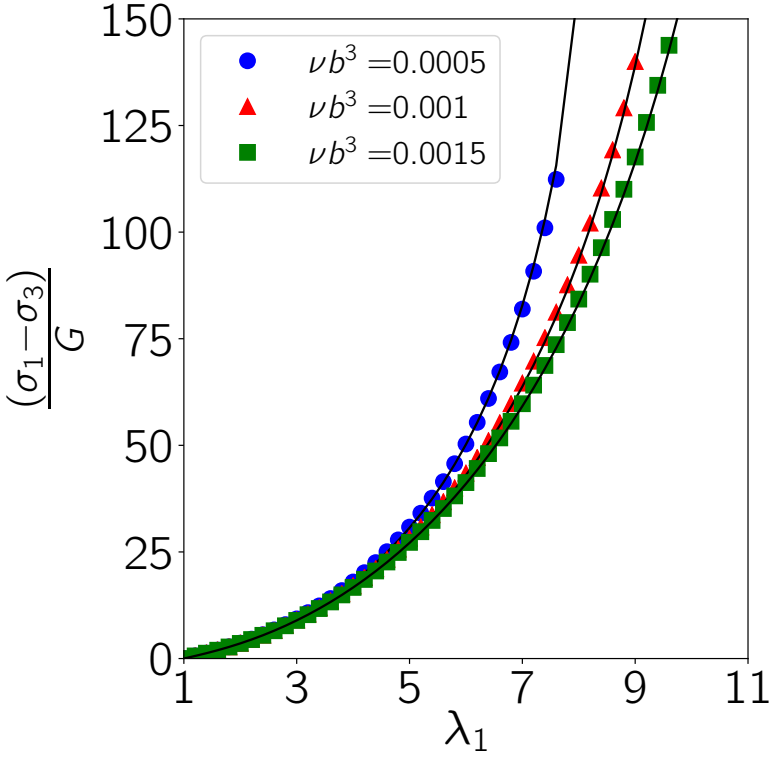
- Topology impacts the modulus via the chain pre-stretch
- Scaling of chain pre-stretch with topology largely explained by geometric arguments
- Coincides with the classical affine estimate only when $\bar{r}_0 = \sqrt{N}b$:

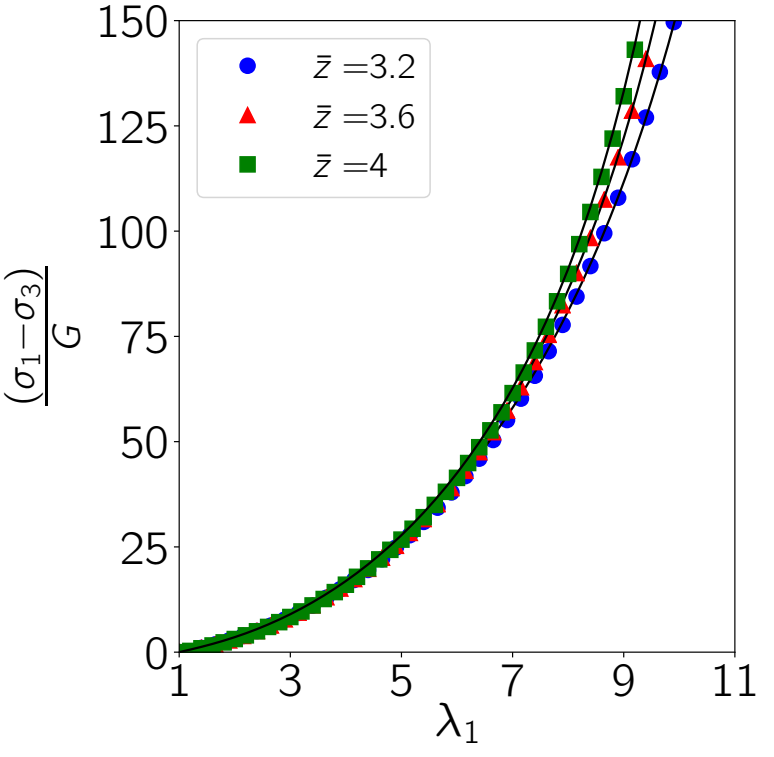
$$G = \nu kT$$



Large-deformation behaviour

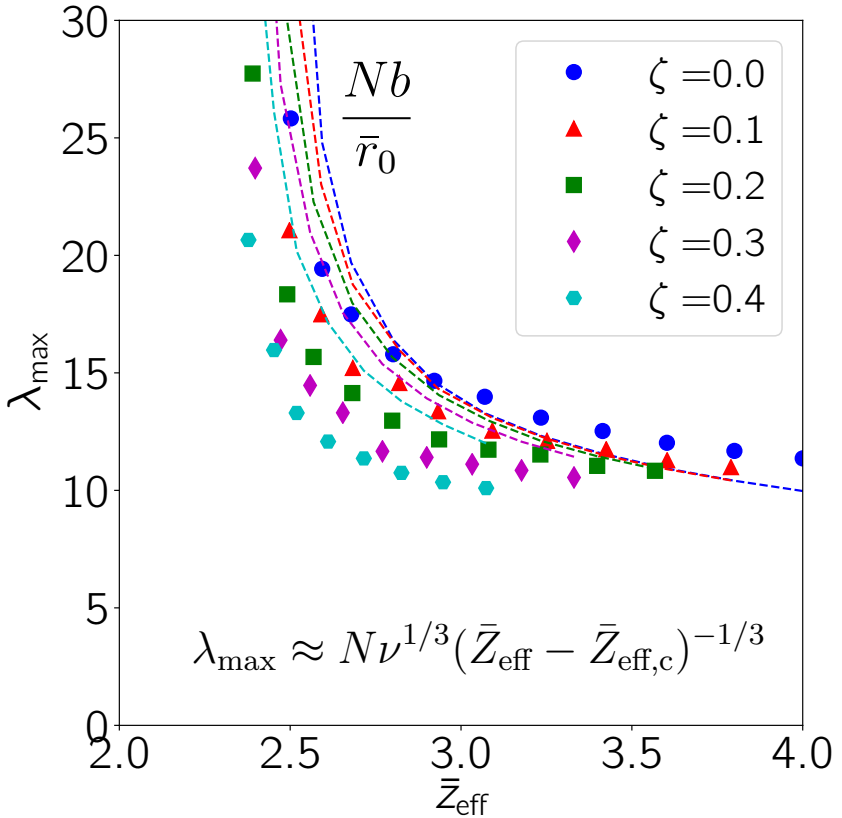
Stiffening rate depends on density and topology via the pre-stretch

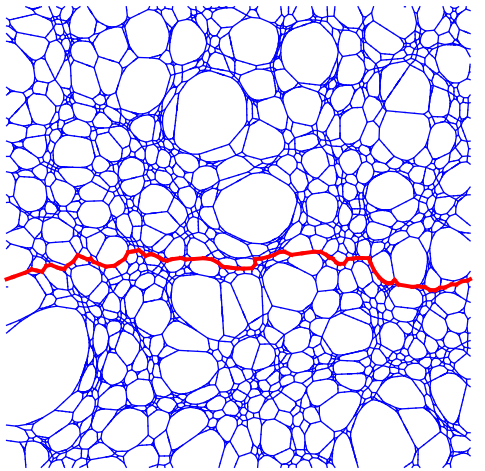




Limit extensibility

- Limit extensibility partly explained by the pre-stretch
- Loops reduce the shortest chain path

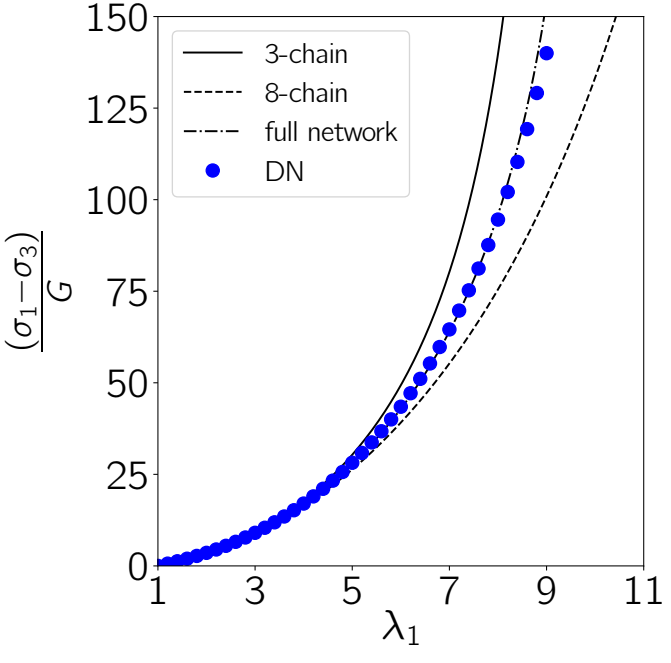




$$\lambda_{max} = \frac{n^{SP} Nb}{L}$$

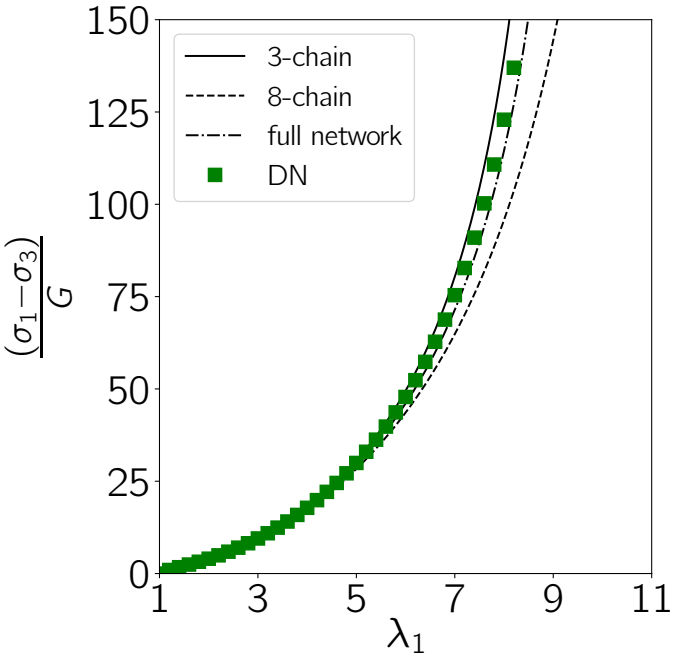
Comparison to analytical models

- Overall, the full-network is the most accurate
- The 8-chain model consistently underestimates the response



Uniaxial extension

$\lambda_1 \geq 1 \quad \lambda_2 = \lambda_3 = \frac{1}{\sqrt{\lambda_1}}$



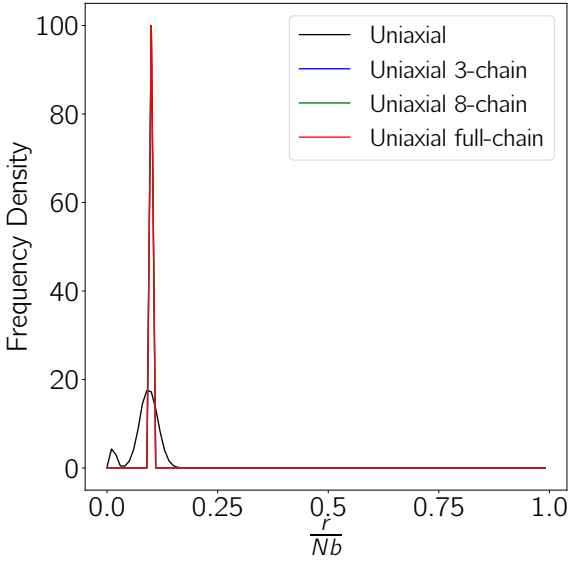
Biaxial extension

$\lambda_1 = \lambda_2 \geq 1, \; \lambda_3 = \frac{1}{\lambda_1^2}$

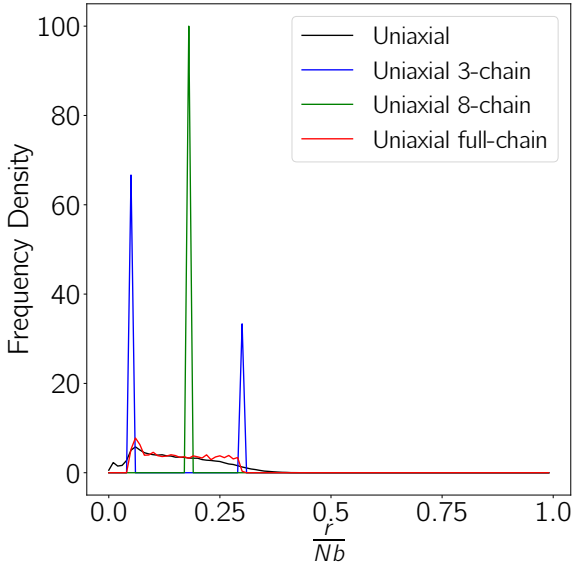
Chain length distribution: Uniaxial extension

The full-network model well captures the chain length distribution

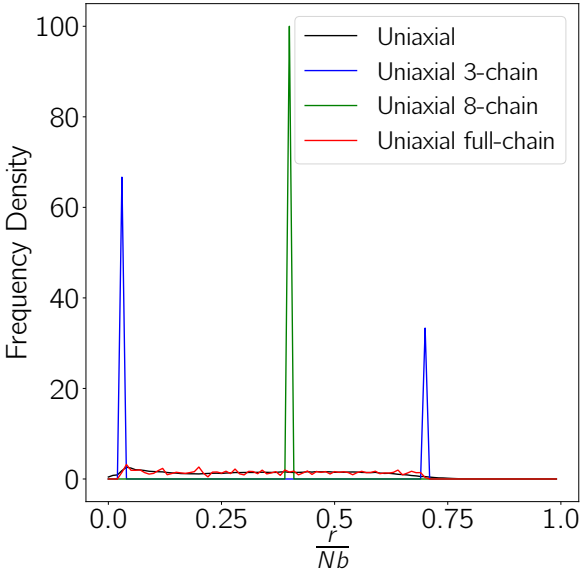
$\lambda_1 = 1$



$\lambda_1 = 3$

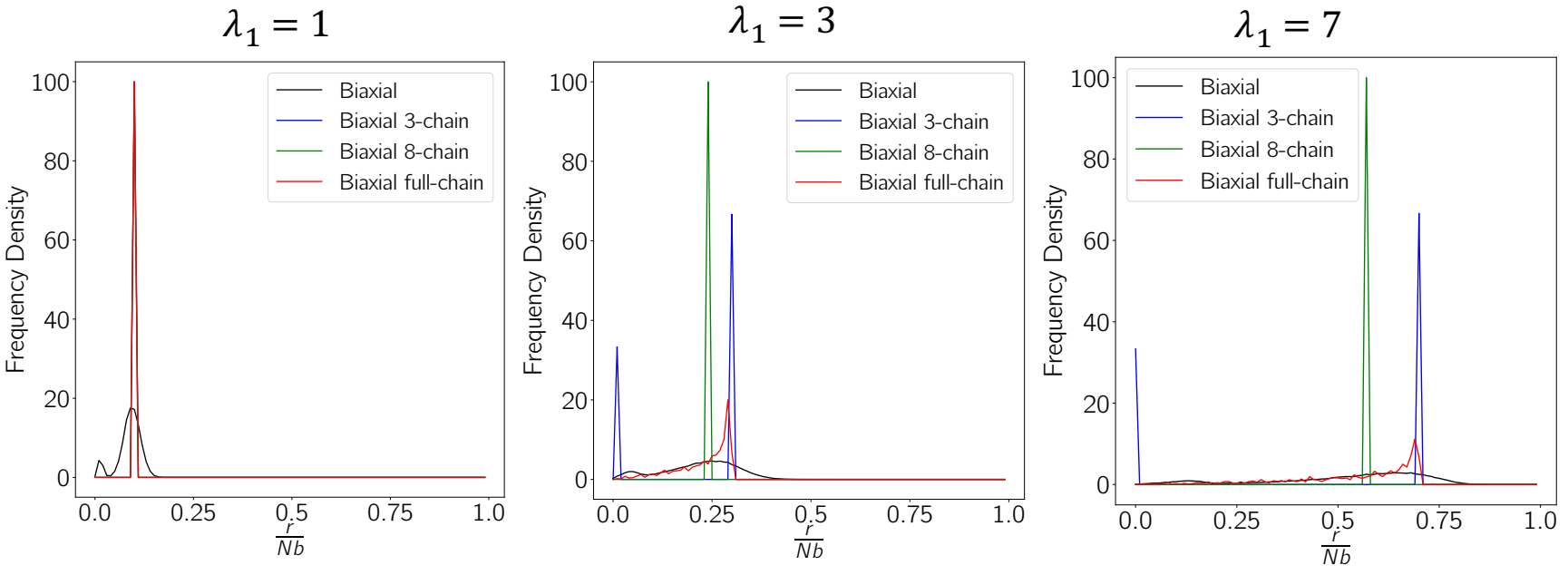


$\lambda_1 = 7$

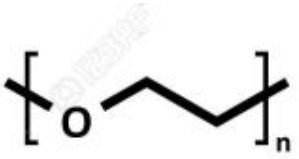


Chain length distribution: Biaxial extension

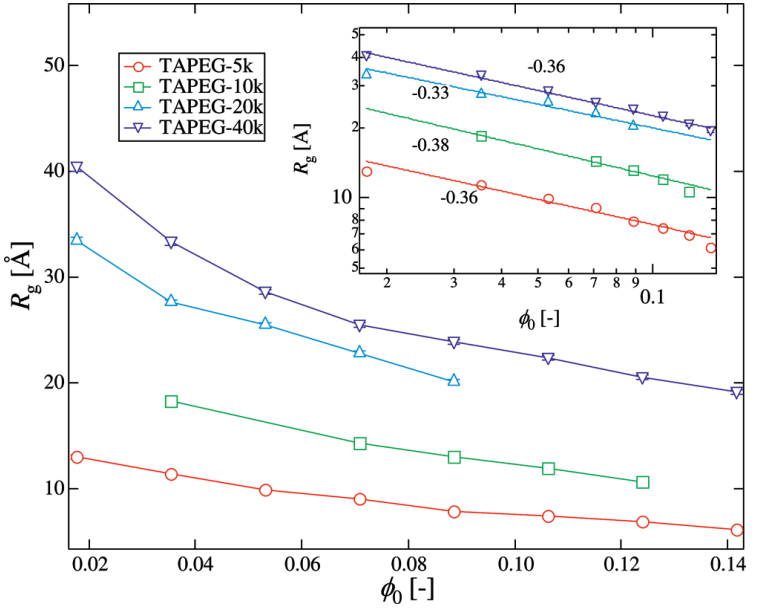
The full-network misses out a fraction of the highly extended chains.



Application to PEG hydrogels



Matsunaga et al., *Macromol.* (2009)



- Kuhn length: $b = 1.1$ nm
- Contour length:

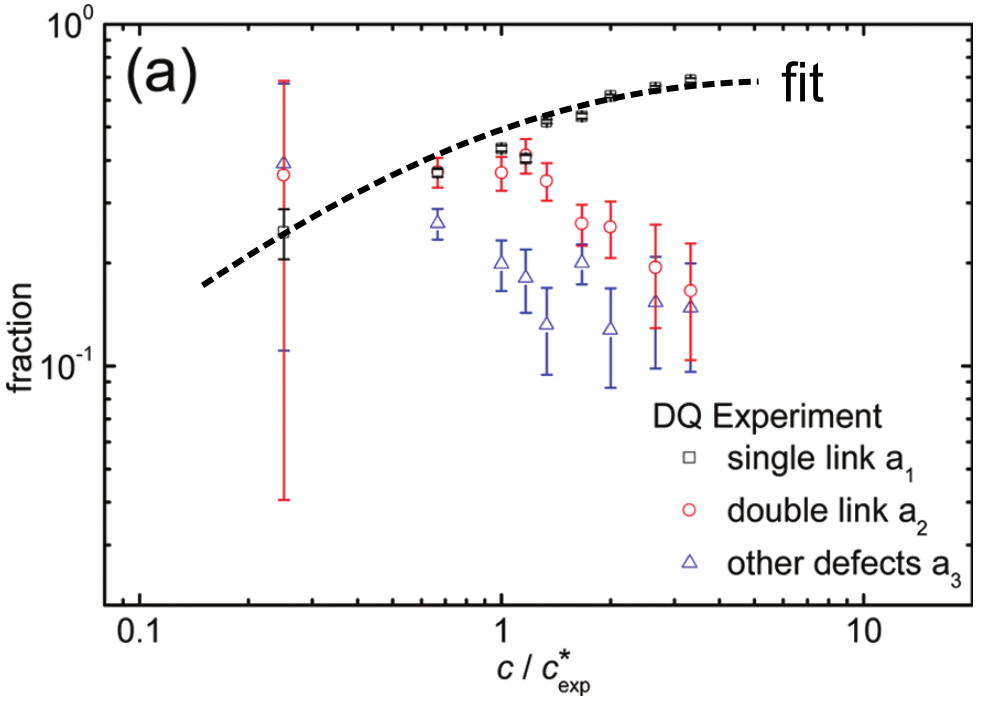
$$L_c = n_{mon} \times 0.36\, nm = Nb$$

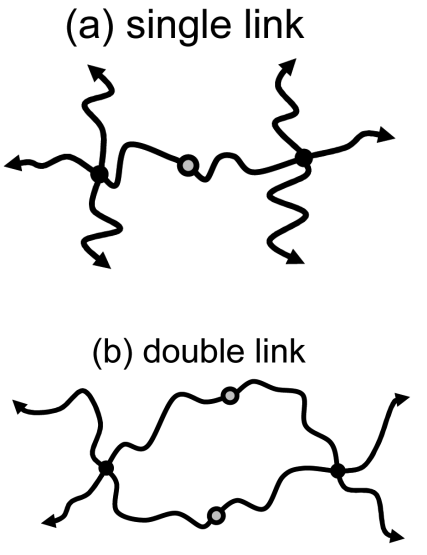
- Modified FJC to account for **non-ideal chain behaviour**

$$R_F \approx v^{1/5} b^{3/5} N^{3/5}$$

$$\frac{f\bar{b}}{kT} = \mathcal{L}^{-1}\left(\frac{r}{\bar{N}\bar{b}}\right) \qquad \bar{b} = \frac{R_F^2}{Nb} \qquad \bar{N} = \frac{(Nb)^2}{R_F^2}$$

Quantifying Loops in 4-arm PEG gels

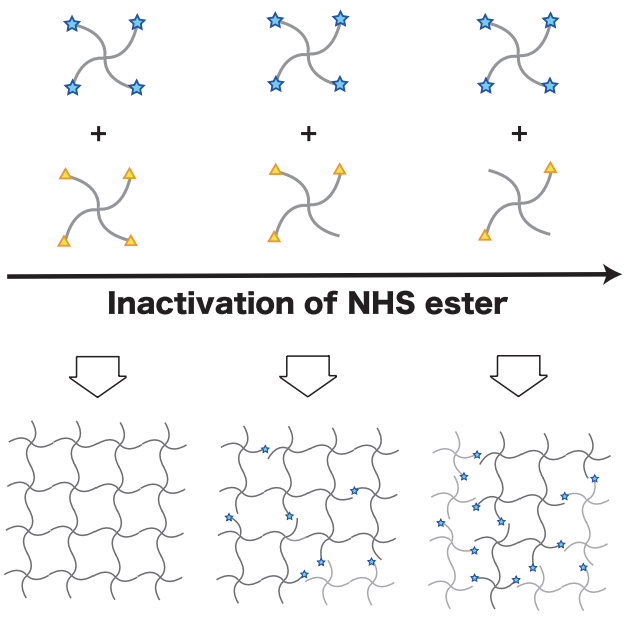




Lange et al., *Macromol.* (2011)

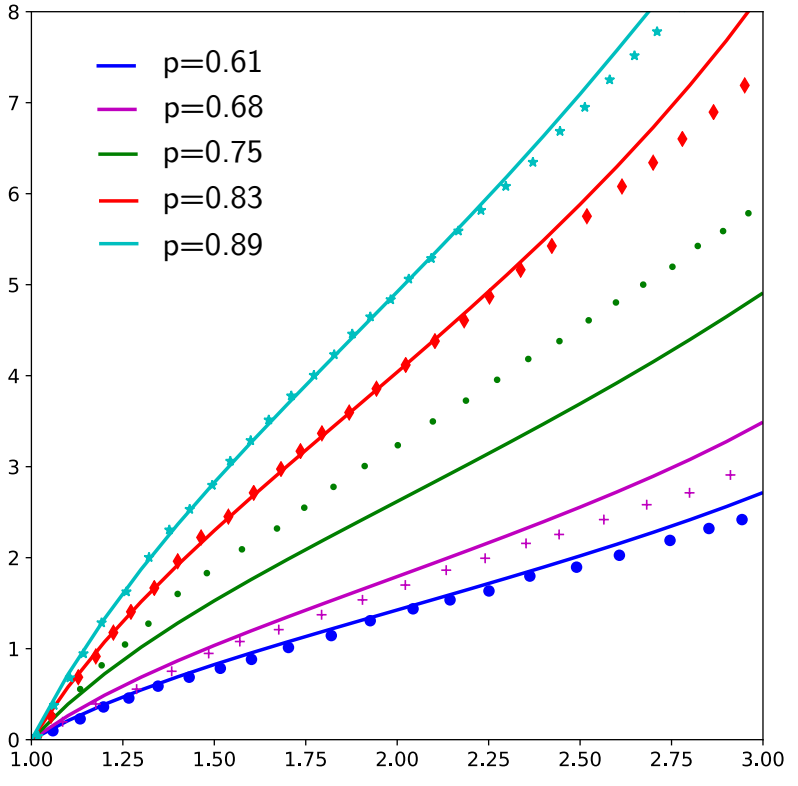
The fraction of loops increases as the pre-polymer volume fraction decreases

4-arm PEG with tunable connectivity probability



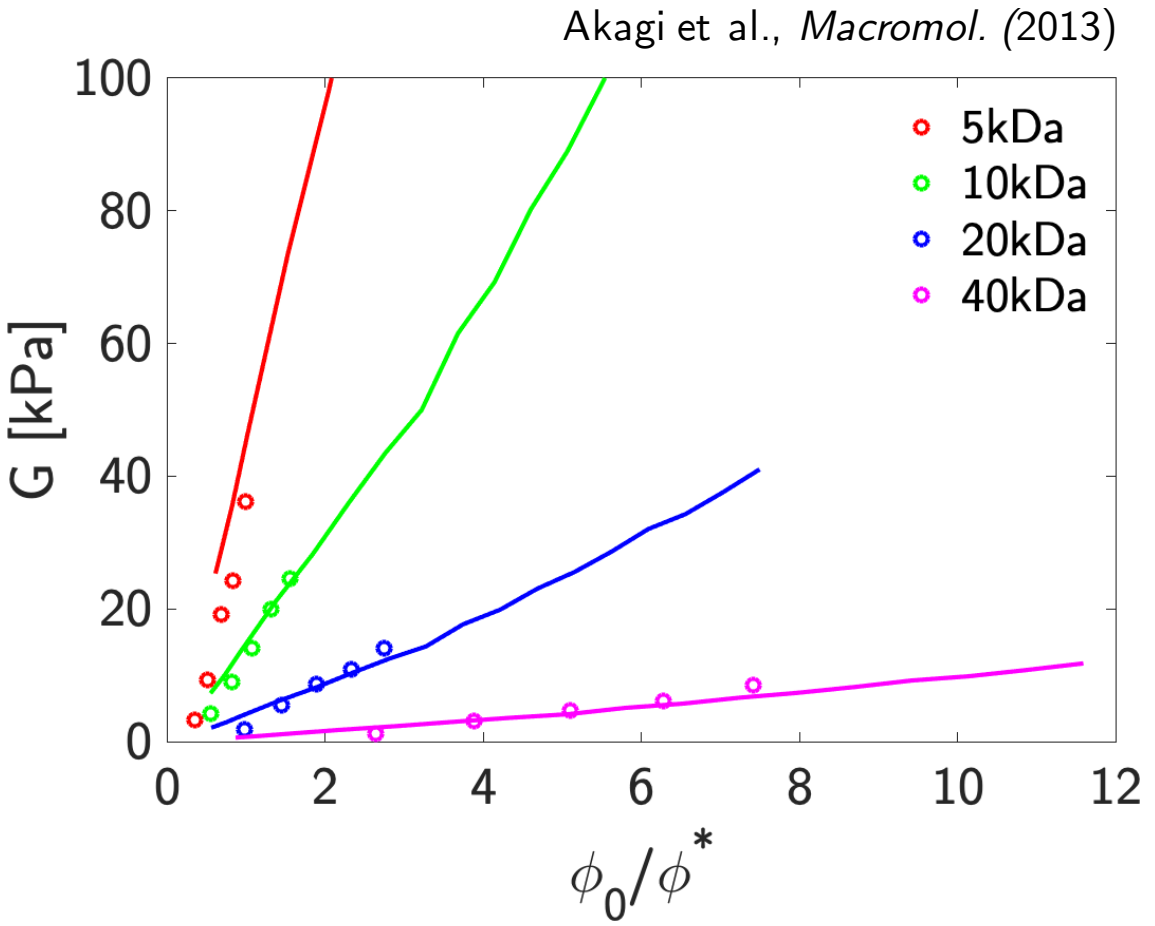
Nishi et al., *J. Chem. Phys.* (2012)

Akagi et al., *RSC Adv.* (2013)



Good prediction with only one fitting parameter v^*

Dependence of modulus on concentration



Modulus dependence on molecular weight results primarily from the non-ideality of chain behaviour

Summary

- Discrete network models as a tool to investigate the role of network parameters on the mechanical response of hydrogels
- Network defects (dangling ends, loops) have a significant impact on mechanical properties
- Coupling between strain pre-stretch and topology gives scaling relations different from classical theories
- The model can explain experimental trends by considering non-ideal chain behaviour and the presence of network defects

References:

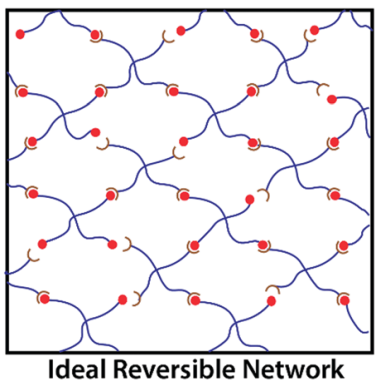
G. Alamé and L. Brassart, Soft Matter 15, 5703 (2019)

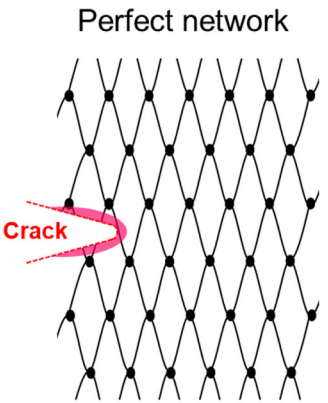
G. Alamé and L. Brassart, *About to be submitted*.

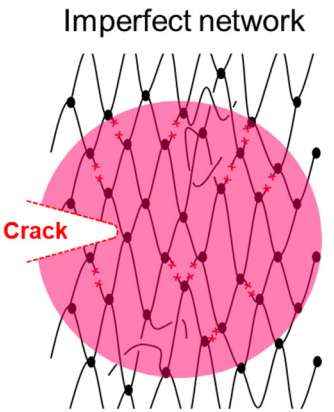
Future work

Extend the computational framework to describe:

- Chain scission
- Crosslink breaking and reforming
- Distribution of chain length
- Interpenetrating networks







Parada and Zhao, *Soft Matter*, 2018

Yang et al., *JMPS*, 2019