Micromechanical modelling of near-ideal polymer networks

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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 architected materials

Mechanics of Li-ion batteries

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

This figure examines the effects of structural relaxation parameter $q_0$ on the stress and disorder. In the early stages of deformation all stress-strain and disorder-strain curves overlap for different $q_0$. In the strain-softening stage larger $q_0$ leads to smaller strain-softening which correspond to smaller step value in disorder. In addition, larger $q_0$, larger relaxation of disorder, causes faster access to steady-state and smaller/larger steady-state value of disorder/stress.

Fig. 4 is plotted for uniaxial tension with $10^{-1}$ applied strain rate and shows the evolution of stress, disorder and the ratio of plastic volume for different degrees of material yield dependency on pressure (different values of $b$). Regarding Fig. 4a, the maximum and steady-state value of stress decreases with increasing $b$ ($b<0.15$). After that, the maximum value of stress decreases while the steady-state value of stress increases. Furthermore, when the yield criterion has a weak dependency on pressure (smaller $b$), material experience larger maximum stress at a larger strain. Based on Eq. (31) the creation of disorder is proportional to $b$. Thus, more disorder and plastic dilatation are expected for larger value of $b$ (Fig. 4b, 4c).

Mean-field homogenisation for transient diffusion problems

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

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

\[ = \frac{1}{V} \int_{\omega} \mu \dot{c} \, dV - \frac{1}{V} \int_{\omega} j \cdot \nabla \mu \, dV \]

Hydrogels in everyday life

Hydrogels are crosslinked polymer networks swollen in water
Network design for strength and toughness

Example: Double-network gels

$\Gamma = 1000 \text{ J/m}^2$

Network design for strength and toughness

Example: hybrid ionic-covalent gels

\[ \lambda = 1 \]

\[ \lambda = 21 \]

\[ \Gamma = 8700 \, \text{J/m}^2 \]

\[ \lambda_{\text{max}} > 20 \]

Continuum modelling

Kinematics:

\[ x = \chi(X, t) \]

\[ F = \nabla \chi \]

\[ \det(F) = 1 + \Omega C \]

Conservation equations:

\[ \nabla \cdot P = 0 \]

\[ \frac{\partial C}{\partial t} = -\nabla \cdot J \]

Constitutive models:

\[ \mu \dot{C} + P : \dot{F} - J \cdot \nabla \mu - \dot{W} \geq 0 \]

\[ W = W^e(F) + W^c(C) \]

+ 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 $b$

\[ w = NkT \left( \frac{\beta}{\tanh \beta} + \log \frac{\beta}{\sinh \beta} \right) \]

\[ \beta = \mathcal{L}^{-1} \left( \frac{r}{Nb} \right) \]

\[ \beta = \frac{3r}{Nb} \]
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

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

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

Input:
- Chain density $v = n/L^3$
- Conversion probability $p$
- average coordination $\bar{Z}$
- Loop fraction $\zeta$

$$x_\alpha = F \cdot X_\alpha$$
$$P = \frac{1}{V} \sum_\alpha (f_\alpha^e \otimes X_\alpha)$$

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:

\[ G = kT \nu \frac{\bar{r}_0^2}{Nb^2} \quad \bar{r}_0^2 = \langle r_0^2 \rangle \]

(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 \( \bar{r}_0 = \sqrt{Nb} \):

\[ G = \nu kT \]

![Graph showing the relationship between \( \bar{r}_0^3 \) and \( \bar{Z}_{\text{eff}} \)]
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

\[
\lambda_{\text{max}} \approx N \nu^{1/3} (\bar{Z}_{\text{eff}} - \bar{Z}_{\text{eff},c})^{-1/3}
\]

\[
\lambda_{\text{max}} = \frac{n^{SP} Nb}{L}
\]
Comparison to analytical models

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

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

Uniaxial extension

\[ \lambda_1 = \lambda_2 \geq 1, \quad \lambda_3 = \frac{1}{\lambda_1^2} \]

Biaxial extension
Chain length distribution: Uniaxial extension

The full-network model well captures the chain length distribution.
Chain length distribution: Biaxial extension

The full-network misses out a fraction of the highly extended chains.
Application to PEG hydrogels

\[
\text{\begin{tikzpicture}
\draw[thick,->] (0,0) -- (0,1);
\draw[thick,->] (0,1) -- (1,1);
\draw[thick,->] (1,1) -- (1,0);
\draw[thick,->] (1,0) -- (0,0);
\draw[thick] (0.5,0.5) circle (0.1);
\draw[thick] (0.5,0.5) circle (0.2);
\end{tikzpicture}}_n
\]

- Kuhn length: \( b = 1.1 \text{ nm} \)
- Contour length:
  \[
  L_c = n_{\text{mon}} \times 0.36 \text{ nm} = Nb
  \]

- Modified FJC to account for non-ideal chain behaviour

\[
\frac{f \bar{b}}{kT} = \mathcal{L}^{-1} \left( \frac{r}{N_b} \right) \quad \bar{b} = \frac{R_F^2}{Nb} \quad \bar{N} = \frac{(Nb)^2}{R_F^2}
\]

\[R_F \approx v^{1/5} b^{3/5} N^{3/5}\]
Quantifying Loops in 4-arm PEG gels

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

Lange et al., Macromol. (2011)
4-arm PEG with tunable connectivity probability


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

Akagi et al., *Macromol.* (2013)
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, 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., *JMP$, 2019