Multiscale Mechanical Polymer Modelling: From Macroscopic Hyperelasticity to Strain Induced Crystallisation.

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in collaboration with

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Many applications: tires, seals, absorbers, protections,..

Put to severe regimes: large deformations, time variations, environment.

High performance and reliability requirements.
Many interesting issues:

- Mechanical models: hyperelasticity, evolving anisotropy, viscosity, aging, damage,..
- Structural unstabilities.
- Multiphysics: thermics, magnetorheology, crystallisation, wetting, ...
Basic model: hyperelasticity

- Simplified case where second Piola stress tensor $S(X)$ (the one totally in reference configuration) only function on (full) deformation tensor $C = F^T \cdot F = 2E + 1$ between reference and present configurations

$$S(X) = 2 \frac{\partial \psi(X, C)}{\partial C} = \frac{\partial \psi(X, E)}{\partial E}.$$ 

- Problem: which form for $\psi$, which coefficients to cover large deformation regimes?
Variational Formulation

Equilibrium problem well posed for conservative loads with coercive energy because formally writes

$$\xi \text{ minimizes } I(\mathbf{v}) \text{ on } U$$

with

$$I(\mathbf{v}) = \int_{\Omega} \psi(X, (\mathbf{1} + \nabla \mathbf{v})^T \cdot (\mathbf{1} + \nabla \mathbf{v})) \, dx - \int_{\Omega} F \cdot \mathbf{v} \, dx - \int_{\Gamma_1} g \cdot \mathbf{v}.$$ 

Proof due to J. Ball (1977), based on Weirstrass theorem on weak topology in weakly closed set

$$\{ \mathbf{v} \in \mathcal{W}^{1, s}(\Omega), \text{cof}(\mathbf{1} + \nabla \mathbf{v}) \in L^q(\Omega), J \in L^r(\Omega) \}.$$ 

**Weak lower semi continuity** usually obtained from polyconvexity of free energy.
Nonuniqueness: highly nonlinear problem (in strain $E$ and Jacobian $J$) with presence of buckling at different scales → develop multiscale stability analysis (direct simulation with proper solver or Bloch waves, Lignon-PLT-Triantafyllidis, 2012)
Viscoelasticity

Even after cyclic preloading (for elimination of Mullins effect), polymers show relaxation, creep and dissipation. Can be modelled by dapshots models with additive decomposition of stress

\[ S = S_{ex} + S_{e}(\varepsilon), \]
\[ \dot{\varepsilon} = \dot{\varepsilon}^{e} + \dot{\varepsilon}^{v}, \]
\[ S_{ex} = C_{e}^{e} = \mu \dot{\varepsilon}^{v}, \]

yielding the extra stress constitutive equation

\[ \tau \dot{S}_{ex} + S_{ex} = \alpha S_{e}. \]

Popular (Simo 1992) but numerical evidence of thermodynamic inconsistency in large deformation (Govindjee 2014).
Viscoelastic thermodynamical model

Idea (Sidoroff, PLT-Rahier, Govindjee-Reese): Extend theory of standard materials introducing a multiplicative objective decomposition of strains

\[ \underline{C}_e = \sqrt{\underline{C}_v^{-1}} \cdot \underline{C} \cdot \sqrt{\underline{C}_v^{-1}}, \]

using the macroscopic viscous strain as internal variable \( W = W(\underline{C}, \underline{C}_v) \) and explicitly controlling the dissipation rate

\[ \frac{1}{2} S : d\underline{C} - d\Psi = \underline{\phi}(\dot{\underline{C}}_v) : d\underline{C}_v \geq 0, \quad \forall d\underline{C}_v, \forall d\underline{C}, \]

yielding an evolution law in \( \underline{C}_v \)

\[ \underline{\phi}(\dot{\underline{C}}_v) = -\frac{\partial \Psi(\underline{C}, \underline{C}_v)}{\partial \underline{C}_v}. \]
Thermodynamic viscoelastic extensions: structure

► This is an ODE (per point acting on internal variables) coupled to a global PDE.

► No notion of steady solution: either time periodic or initial data boundary value problem.

► Numerics: hyperelastic problem plus local algebraic elimination of internal variables at each point and time step. Ongoing issue on finding fast solvers for periodic problems (Ustim Kritschenko).

► Natural treatment of thermal coupling (second law + direct access to dissipation) and extension to MagnetoRheologicElastomers (Triantafyllidis and al. 2010) or other multiphysics.

► Many more internal variables can be added, but stays phenomenological.
The purpose of downscaling

- Above definition of macro free energy $\Psi$, of macro internal variable $C_v$ and of dissipation $\phi$ are phenomenological.

- For fillers, fibers, large deformations, damage, reptation, crystallisation, often not good enough.

- Must then relate stresses to local microstructure of material at network level.
Microstructure of an elastomer

Network of entropic (oscillating) chains of monomers connected through chemical bonds.

Typical length $l^0 = \varepsilon \approx 10 \text{ nm}$. 
Network construction

1. Network of chains $IJ$ made of $N$ monomers of length $l_b$ in free rotation
   $\sqrt{N}l_b \approx 10 \text{ nm}$, $N$ from 10 to 1000.

2. Describe network structure from junctions position $x_J$ and monomers orientations $s_i$ with two heuristics simplifications.

3. Time scale splitting assumed between monomers and junctions (very large times compared to atomistic) $\Leftrightarrow$ monomers in thermal equilibrium, links at zero temperature.

4. Excluding volume energy taken as function of junctions only.
Network free energy

Given by

$$\psi(x_J) = \inf_{x_J} \left( H_{vol}(x_J) + \sum_{IJ} \psi_{IJ} \right),$$

$$\psi_{IJ}(x_I - x_J) = \sum_i k_B T \ln \left( \int_{S_i(x_I - x_J)} \exp \left( -\frac{H_i(s_i)}{k_B T} \right) ds_i \right)$$

$$= cnk_B T \left( r\theta(r) + \log \left( \frac{\theta(r)}{\sinh \theta(r)} \right) \right), r = \|x_I - x_J\|/N_l.$$

Get thus macroscopic free energy and deformed positions $x_H$ of junctions by minimizing local free energy on RVE $\Omega_H(X)$ of size $H$ ($L \gg H \gg \varepsilon$) with imposed macroscopic boundary deformation

$$x_H \in V_H = \{x_H, \lim_{Y \to \partial \Omega_H(X)} x_H(Y) - \bar{F} \cdot Y = 0\}.$$
Implementation of network based hyperelasticity

- Full variational: numerical minimization of network energy (Gloria-PLT-Vidrascu (2012)) using random construction of network.

- Approximate minimisation (Treloar (1949), Arruda Boyce (1993), Linder (2012), ...)

Hyperelasticity
Extension to viscoelasticity
Network based hyperelasticity
Microsphere
Strain-induced crystallization
Variational approach

- Choose the sampling size $M = H/\varepsilon$.
- Randomly construct $M^3$ points in $\Omega_H$ (random parking lattice).
- Construct a Delaunay grid on these points.
Numerical network model

A typical randomly generated network
Variational approach

- Choose the sampling size $M = H/\varepsilon$.

- Randomly construct $M^3$ points in $\Omega_H$ (random parking lattice).

- Construct a Delaunay grid on these points.

- Remove some edges to reach proper network functionality.

- Perform energy minimisation of this (finite element like) model.
Properties of the variational approach

- Existence of a limit

\[ \psi_{\text{hom}}(\bar{F}) = \lim_{M \to \infty} \langle \psi \rangle(\bar{F}, M, \omega) \]

when \( M = H/\varepsilon \to \infty \).

- \( \Gamma \) convergence (almost surely) of local solution to limit.

- Variance of reconstructed stress \( P(\bar{F}, M, \omega) \) is in \( O(1/M^3) \).

- Limit solution is hyperelastic, isotropic, weakly lower semi continuous and quasi incompressible.

- Gives access to information on network deformation.
Microstructure prediction of scattering pattern

Neutron scattering patterns

\[ p(q) = \sum_{IJ} \cos \left( q \cdot (x_I - x_J) \right) \]

calculated at an elongation of \( \lambda = 3.63 \), as function of reduced incident wave vector \( q^*_\perp = q_\perp / \sqrt{\lambda} \), \( q^*_// = \lambda q_// \) (total result and difference to affine prediction)
Approximate deformed network of Treloar

- Assumes affine deformation $x_H = \bar{F} \cdot Y$ in network.
- Get analytical form of limit solution if initial statistics $f(R)$ of sides $R$ is given

\[
\psi_T(J, \bar{F}) = \lim_{H \to \infty} \frac{1}{|\Omega_H|} \psi(\bar{F} \cdot Y)
\]

\[
= \psi(J) + \rho n_c \int_R f(R) \psi_c \left( \frac{\sqrt{R \cdot \bar{F}^T \cdot \bar{F} \cdot R}}{N_R l_b} \right) dR.
\]

- Analytical integration can be carried at any order. Standard model is at first order on an isotropic network.
- Always stiffer than variational approach.
Maximal advanced path constraint

Minimization assuming (Linder 2012)

- single type chains (single end to end distance and same free energy for all)
- isotropic dense initial distribution
- two chains with same orientation \((X_J - X_I)\) have same deformation \((x_J - x_I)\)
- affine motions imposed only on maximal advance paths

\[
\rightarrow \frac{1}{V} \sum_{JI} \frac{1}{l^2} (x_J - x_I) \otimes (X_J - X_I) = F.
\]

Convex minimization on unit sphere with global linear constraint.
Consistent answers at moderate deformations. Deviation at large deformations especially on transverse stresses. Key effect of network connectivity.
Microsphere

Idea (Miehe (2004), Merckel-Diani-Roux-Brieu (2011): for better local physics, introduce dissipation and damage at chain level and assume

- no thermal motion of junction points
- single type chains (single end to end distance and same free energy for all)
- isotropic initial distribution
- two chains with same orientation $R = \mathbf{x}_J - \mathbf{x}_I$ have same deformation $(\mathbf{x}_J - \mathbf{x}_I)$ and follow the same dissipation mechanism (same internal variables)
- one set of internal variable $\alpha(R)$ by original direction $R$
- directional elongation $\lambda(R)$ deduced from global motion (usually **affine assumption**)

$$
\lambda(R) = \sqrt{R \cdot \bar{F}^T \cdot \bar{F} \cdot R}.
$$
**Microsphere image**

**The three levels**: macroscopic structure, material point, microsphere network.

Typical microsphere damage law (Diani-Brieu-Vacherand (2006))

\[ n(R) = (1 - d(\lambda_{\text{max}}(R)))n_0, \quad nN = n_0N_0. \]

Applied recently to Mullins effect with fillers (Diani (2015))
Strain induced crystallisation

Microsphere study of strain induced crystallisation (Guilie-PLT-Le (2013, 2014))

Observe branching due to crystallisation in natural rubber.
Objective: model strain-induced crystallisation and study its influence on crack driving force or on global structural response.

Difficulties:
1. reproduce hysteretic behavior,
2. respect entropy production,
3. predict evolutive anisotropy.
Experiments: Hysteresis in isothermal cyclic elongation

OA: Elastic loading
AB: Beginning of crystallization, Relaxation of the amorphous phase due to crystallization
BC: Mixed relaxation and hardening due to morphology/percolation
CE: Unloading and fusion in quasi-equilibrium
Expereiments : Disorientation in synchrotron Xrays diffractions

**Fig. 3.10.** Optical diffraction patterns (bottom row) of small, identical crystallites in varying orientations (top row). When the crystallites are aligned as in (a), the diffraction spots are only slightly broadened. Completely random orientations produce rings (b). Specimens can show preferred orientation of the crystallites resulting in blurred spots (c).

(From Harburn et al. 1975.)

**Blurred spots : local disorientation.**
Thermodynamic modeling of crystallisation

Uses the following steps

1. construct 1D semi-crystalline chain,

2. introduce chain crystallisation as local internal variable \( \lambda_x \),

3. construct chain free energy,

4. control dissipation rate by bonding thermodynamic forces (plastic like) \( \rightarrow \) chain crystallinity evolution laws,

5. 3D extension by Microsphere approach with local directional dependence of crystallisation (one variable per direction).
1D Chain free energy

Standard model of amorphous part (Representative chain with finite extensibility, constrained inside a tube (Miehe’s Model))

with three additional constitutive mechanisms:

1. remove crystallized part of entropic energy $\psi_{IJ}$
   (translate crystallinity in change of elongation $\lambda \to \lambda - \lambda_\chi$)

2. add network hardening energy $\psi_\chi$ due to morphology change

3. add elasticity stiffening due to crystallisation in "tube" energy $\psi_{el}$. 
1D Free energy with network hardening

\[ \psi = \psi_IJ(\lambda - \lambda_\chi) + \psi_\chi(\lambda_\chi) + \psi_{el}(\lambda, \nu) \]

\[ \psi_\chi(\lambda_\chi) = g(\lambda_\chi) + n\lambda_\chi(Ts_f - h_f) \]

g increases with \( \chi \) and forbids crystallinities which are greater than \( \lambda_\chi, sat \) or negative.
Define thermodynamic force $\pi_{\chi}(\lambda_{\chi},..) = -\frac{\partial \psi}{\partial \lambda_{\chi}}$.

Need entropy dissipation to be positive

$D = \pi_{\chi} \frac{d\lambda_{\chi}}{dt} \geq 0$.

For this, set fusion law (equilibrium) $\pi_{\chi} = 0$ for $\frac{d\lambda_{\chi}}{dt} < 0$.

In crystallisation, introduce rate independent «friction» delay $\pi_{\chi} = Y(\lambda_{\chi}) > 0$ for $\frac{d\lambda_{\chi}}{dt} > 0$.

Possible rate dependent extension by viscous regularisation (PLT 2014) $\frac{d\lambda_{\chi}}{dt} = \eta \pi_{\chi}$ if $0 < \pi_{\chi} < Y$. 
Analysis of 1D model

Schematically given by

- Loading in green, unloading in red.
- As in plasticity, forcing force to stay at threshold controls evolution of crystallinity.
- Dissipation positive by construction.
Microsphere 3D extension

- free energy integrated over all directions

\[ \psi = \int_R \left( \psi_{ij}(\lambda - \chi) + \psi_{\chi}(\lambda_{\chi}) \right) dR + \psi_{el}(\bar{C}) + W(J). \]

- affine elongation (maximal path advance in progress)

\[ \lambda(R) = \sqrt{R \cdot \bar{F}^T \cdot \bar{F} \cdot R}. \]

- use the 1D evolution law on each direction \( R \) to control local evolution of \( \lambda_{\chi}(R) \)

One separate history by direction (50 to 300 in practice) → evolutive anisotropy.
Numerical results: Uniaxial traction -1-

Quadratic chain free energy, affine microsphere model, optimized constants.

Stress Stretch Curve
Numerical results: Uniaxial traction -2-

Quadratic chain free energy, affine microsphere model, optimized constants.

Crystallinity Stretch Curve
Numerical results: Uniaxial traction -3-

Quadratic chain free energy, affine microsphere model, optimized constants.

Anisotropy evolution curve: experimental vs numerical
Numerical results: crack in traction -1-

Geometry and side view of 3D deformed mesh of a PS cracked specimen (110 000 d.o.f)
Numerical results: crack in traction -2-

Evolution of crystallisation in time: fast loading.
Evolution of crystallisation in time: cyclic fatigue loading.
Effect of rate dependance on crystallisation at maximal load ("friction" delay case on right).
Comparison between predicted and experimentally observed crystallisation
Accumulation of crystallinity during loading cycles
Numerical results: crack in traction -7-

Upper part of deformed specimen viewed from below, cut just beyond the crack (with its "moustache"). Crystallinity directionality at specific points.
Conclusion

- Industrial maturity has been gained in numerical models at macroscopic scale, with technical issues on
  1. fast and robust nonlinear solver (contact, periodicity)
  2. thermodynamical consistency and coefficients identification when using complex physics

- New exciting developments by upscaling from network models, producing validated results at macro scale with
  1. new insight on (mesoscopic) free energy,
  2. access to microstructure
  3. access to anisotropic damage,
  4. access to local crystallisation.

- Work to come to finely match experiments and models at network level and to better understand carbon black fillers.