# From polymer chains to nonlinear elasticity: modeling, analysis, and numerical simulations

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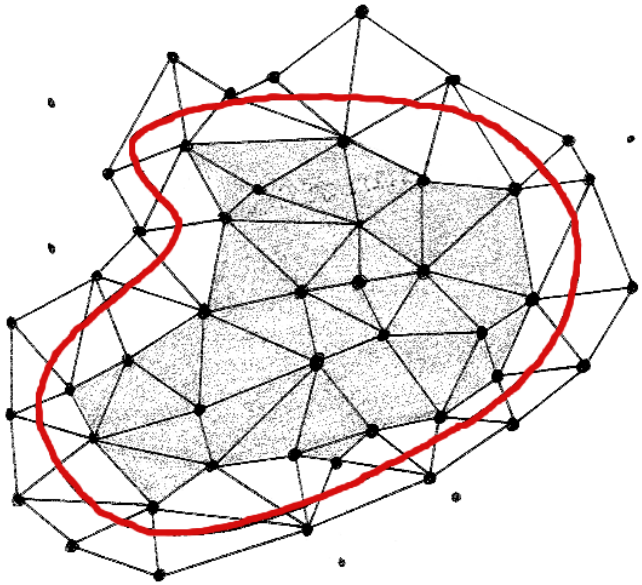
# Aim of study

- Consider a (tractable) microscopic model based on polymer physics
- Make a rigorous derivation of a continuous model (as the typical size of the polymer chains "vanishes")
- Study the mechanical properties of the continuous model
- Design and analyze a numerical method to compute the macroscopic energy density
- Compare the results to mechanical and physical experiments
- Find an analytical formula (that can be used in practice) to approximate this energy density

# Stochastic network of interacting polymer chains



- chain : $u_i$ (end-to-end vector), $s_i$ (monomers)
- Hamiltonian: volumetric term + chains,
- volumetric term stiff (almost isochoric),
- Free energy explicit for a single isolated chain (only depends on $u_i$),
- Network: tetrahedral mesh.

Boltzmann free energy:

$$
\begin{aligned}
F(D,\Lambda) &= -kT \ln \left[ \int_U \int_{\prod s_i(u)} \exp\left( -\frac{H_{\mathrm{vol}}(u,s)}{kT} - \sum_i \frac{H_i(u,s_i)}{kT} \right) du \prod_i ds_i \right] \\
&\simeq \inf_{u\in U} \left\{ H_{\mathrm{vol}}(u) + \sum_i -kT \ln \left[ \int_{s_i(u)} \exp\left( -\frac{H_i(u,s_i)}{kT} \right) ds_i \right] \right\} \\
&= \inf_{u\in U} \left\{ F_{\mathrm{vol}}(u,D) + F_{nn}(u,D) \right\}.
\end{aligned}
$$

# Rescaled free energy

Typical size of a polymer chain: $\varepsilon \ll 1$.

Rescaled energy: Assume the typical size of the network is 1, then energy given for all $u \in L^p_{disc}(D)$ by

$$E_\varepsilon(u, D) = \sum_{x \in \mathcal{L} \cap \frac{D}{\varepsilon}} \varepsilon^d \sum_{y:(x,y) \text{ is a chain in } \frac{D}{\varepsilon}} f\left(x - y, \frac{u(\varepsilon x) - u(\varepsilon y)}{\varepsilon |x - y|}\right) + \int_{D_\varepsilon} W_{\text{vol}}(\nabla u).$$

Then need to take the infimum of $E_\varepsilon(u, D)$ on $u$ to retrieve the free energy.

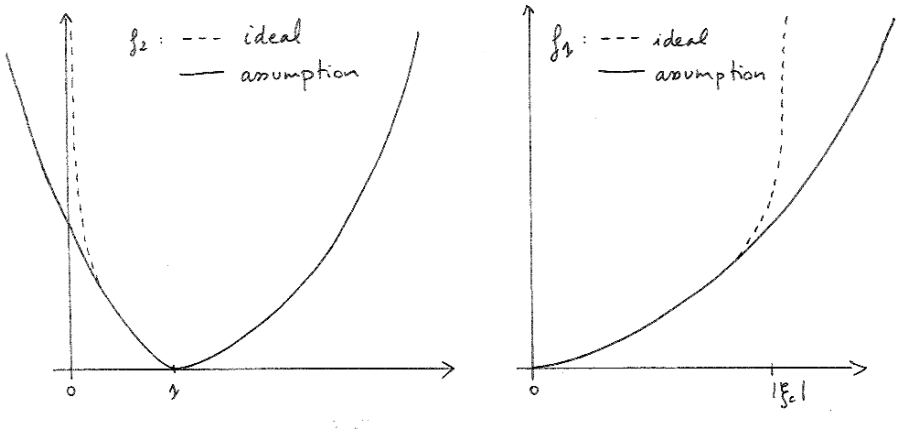
Mathematical insight: let $\varepsilon \to 0$ and get some energy functional $E(u, D)$ at the limit.

Important feature of the derivation: the chosen notion of convergence should be *consistent with minimization* since this is essential in the microscopic model.

# Assumptions on the energy (relation to polymers)

There exist $1 < p < \infty$, and positive constants $c, C$, such that

- $c|\xi|^p - 1 \leq f(\cdot, \xi) \leq C(1 + |\xi|^p)$ (coercivity, continuity)
- $0 \leq W_{\mathrm{vol}}(\Lambda) \leq C|\Lambda|^p$




Example for $f$ and $W_{\mathrm{vol}}$:

- $f(\zeta, \xi) = |\zeta| f_1(|\xi|)$, $f_1(\zeta, 0) = 0$, $f_1$ convex and increasing
- $W_{\mathrm{vol}}(\Lambda) = f_2(\det \Lambda) \geq 0$, $f_2$ convex and $f_2(1) = 0$

There is a competition between $f_1$ (min for $\xi = \Lambda \cdot \zeta = 0$) and $f_2$ (min for $\det \Lambda = 1$).

# Rigorous derivation of a continuous model

## Theorem (Alicandro-Cicalese-G.)

*Let the polymer-chain network be a regular stochastic lattice. Then the rescaled free energy functional*

$$\begin{array}{rcl} E_\varepsilon(\cdot, D) : L^p_{disc}(D) & \to & \mathbb{R} \\ v & \mapsto & E_\varepsilon(v, D) \end{array}$$

*almost surely $\Gamma(L^p)$-converges to*

$$\begin{array}{rcl} E(\cdot, D) : L^p(D) & \to & \mathbb{R} \\ v & \mapsto & \begin{cases} \int_D W(\nabla v(x))dx & \text{if } v \in W^{1,p}(D, \mathbb{R}^d) \\ +\infty & \text{otherwise} \end{cases} . \end{array}$$

*The energy density $W : \mathcal{M}_d(\mathbb{R}) \to \mathbb{R}^+$ is quasiconvex, satisfies standard p-growth conditions and is given by*

$$W(\Lambda) = \lim_{N\to\infty} \frac{1}{N^d} \inf \{E_1(v, Q_N), v(x) = \Lambda \cdot x \text{ for } d(x, \partial Q_N) \leq \mathbf{R}\} .$$

# Mechanical properties

**Hyperelasticity**:

The energy density only depends locally on the gradient of the deformation.

**Frame-invariance**:
The homogenized energy density $W$ is frame-invariant if

- $f(\zeta, \xi) = \tilde{f}(|\zeta|, \xi)$
- $W_{\mathrm{vol}}$ is frame-invariant: $W_{\mathrm{vol}}(\Lambda R) = W_{\mathrm{vol}}(\Lambda)$, for all $\Lambda \in \mathcal{M}_d(\mathbb{R})$ and $R \in SO_d$

**Natural states**

## Theorem (Alicandro-Cicalese-G.)

*If the homogenized energy density $W$ is isotropic, then there is a dilation $\Lambda = \alpha Id$ among its natural states. (Based on a result by Mizel.)*

# Mechanical properties

**Strong ellipticity**

## Theorem (G.)

*In general, $W$ can lose strong ellipticity (cf. continuous homogenization). In the present case (due to specific properties of the polymer chains energies), $W$ is strongly elliptic (at least in a perturbation regime).*

**Isotropy**

## Theorem (Alicandro-Cicalese-G.)

*If the stochastic network is isotropic in the mean, and if*

- $f(\zeta, \xi) = \hat{f}(\zeta, |\xi|)$
- $W_{\mathrm{vol}}$ *is isotropic:* $W_{\mathrm{vol}}(R\Lambda) = W_{\mathrm{vol}}(\Lambda)$, *for all* $\Lambda \in \mathcal{M}_d(\mathbb{R})$ *and* $R \in SO_d$,

*then the homogenized energy density $W$ is isotropic.*

# Existence and approximation of isotropic stochastic lattices

Simplest isotropic stochastic lattice possible: random parking model

- pick uniformly infinitely many unit rigid balls in $Q_R = (-R/2, R/2)^d$,
- accept a ball if it does not overlap with previously accepted balls,
- continue till $Q_R$ is packed,
- let $R \to \infty$.

This procedure rigorously defines a stochastic lattice on $\mathbb{R}^d$ (random parking measure, cf. Penrose '01).

## Theorem (G.-Penrose)

*The random parking measure on $\mathbb{R}^d$ is regular, ergodic, and isotropic. It can be approximated on bounded domains as above, and this approximation is consistent with the homogenization procedure.*

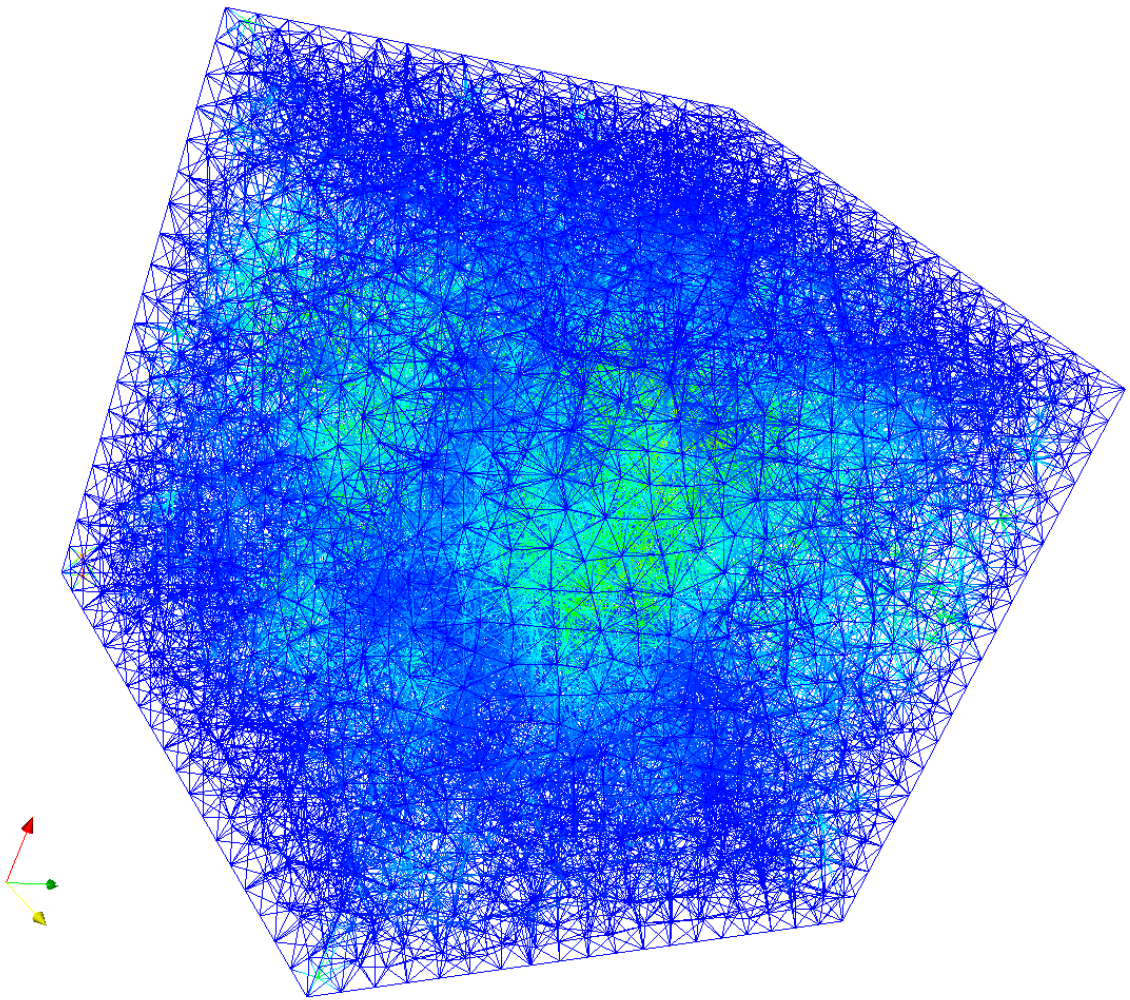
# Numerical approximation of $W$

Procedure:

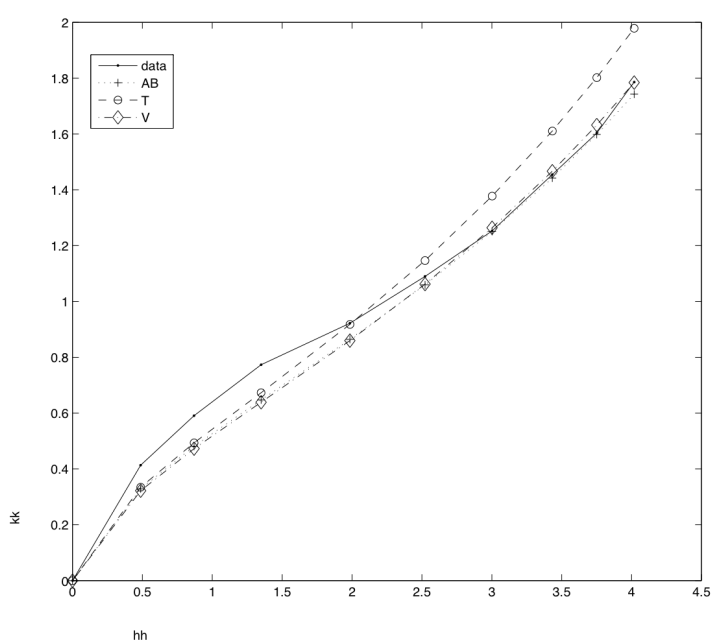
- generate several approximations of the parking measure on $Q_R$,
- construct the associated Delaunay tesselations,
- for any deformation gradient $\Lambda$ and each tesselation, minimize the energy of the network in $Q_R$, the end-to-end points $x$ close to $\partial Q_R$ being deformed as $\Lambda \cdot x$,
- compute the spatial average of the associated stress tensor for each tesselation.
- the empirical average of the stress tensors is the desired approximation of $\frac{\partial W}{\partial \Lambda}(\Lambda)$.

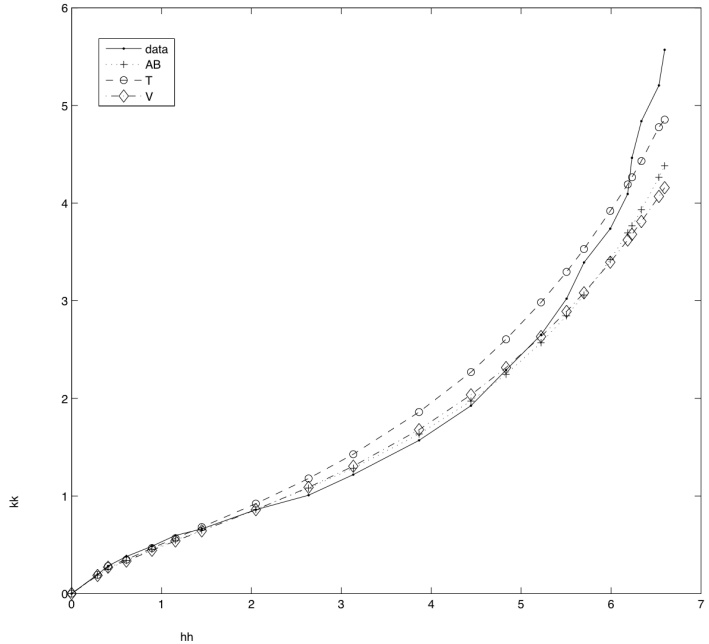
Analysis of the influence of randomness in a simpler case in joint works with F. Otto (MPIMS), J.-C. Mourrat (EPFL), and S. Neukamm (MPIMS).

# Example of random tesselation



# Comparison to Treloar's experiments



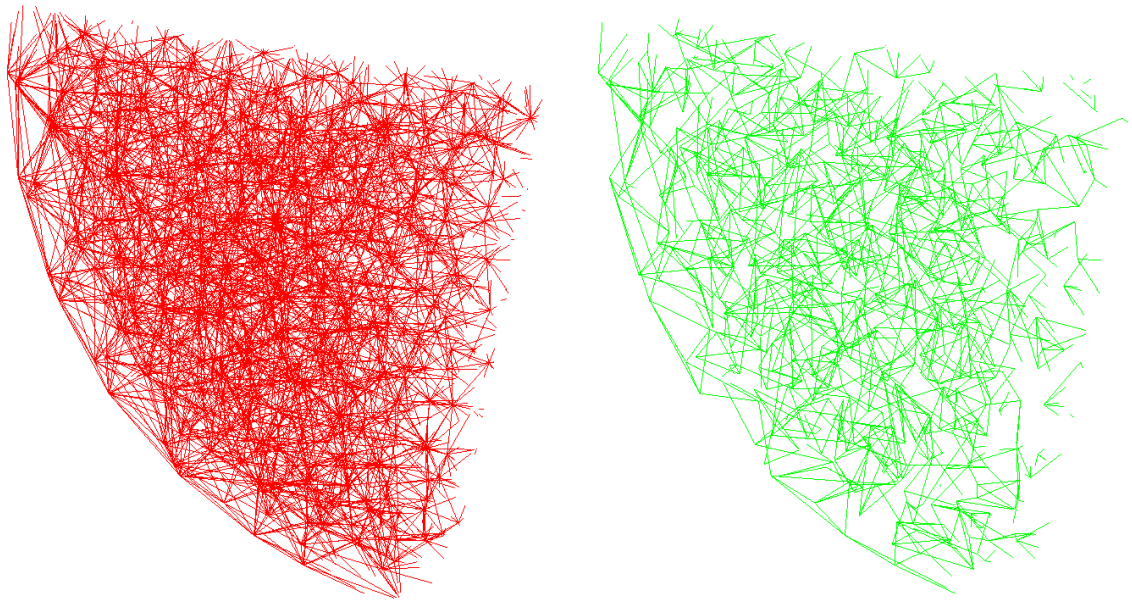




Pure shear, and uniaxial experiments (G., Le Tallec, Vidrascu)

# Comparison to physical experiments

Is the geometry of the model *physically* realistic ?
No: the connectivity of a Delaunay (around 20 in dimension 3) is too high.
In rubber: connectivity between 3 and 4.

$\rightsquigarrow$ modify the network



Numerical difficulties: lose local coercivity.

*In progress* (G., Le Tallec, Lequeux, Vidrascu)

# Analytical approximation for $W$ ?

Our *numerical* approximation of the energy density $W$ is not a practical quantity: for each $\Lambda$, $W(\Lambda)$ is obtained by an expensive numerical computation.

- Idea: find some analytical expression $\tilde{W}$ close to $W$.
- In which class ?

  Use the know how of mechanics ! Take for $\tilde{W}$ an Ogden material.
- Properties: hyperelastic, isotropic, polyconvex, strongly elliptic... as desired.
- Drawback: many parameters to fit.

  However, one can generate as many data as we want, in any mechanical regime ("in silico experiments").

  $\rightsquigarrow$ avoid the issue "number of parameters $>$ number of data".
- Numerical parameter-estimation procedure: genetic algorithm.

*In progress* (de Buhan, G., Le Tallec, Lequeux, Vidrascu)

# Some perspectives

- Compare to physical experiments (cf. talk by François Boué),
- Model Mullins' effect or fatigue phenomena at the discrete level,
- Rigorous derivation of a macroscopic model for Mullins or fatigue ?
- Numerical simulation of the evolution of $W$ ?
- Evolution of $\tilde{W}$ ?

Thanks for your attention !