Computational Modeling of Soft Matter Materials

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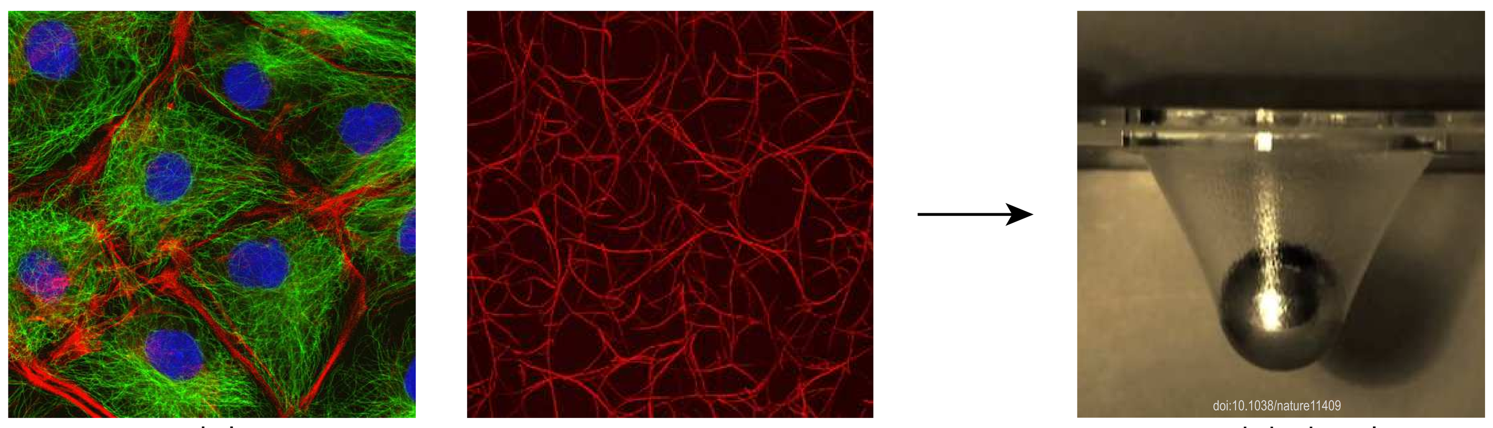
Introduction

New materials are a key driver for the progression of our built environment. An astonishing interplay of microstructural phenomena in biological materials results in macroscopic properties exceeding by far those of our engineered materials. Thus, this project investigates microscopic mechanisms in soft matter materials characterized by their inherent network microstructure.



cytoskeleton actin network tough hydrogel

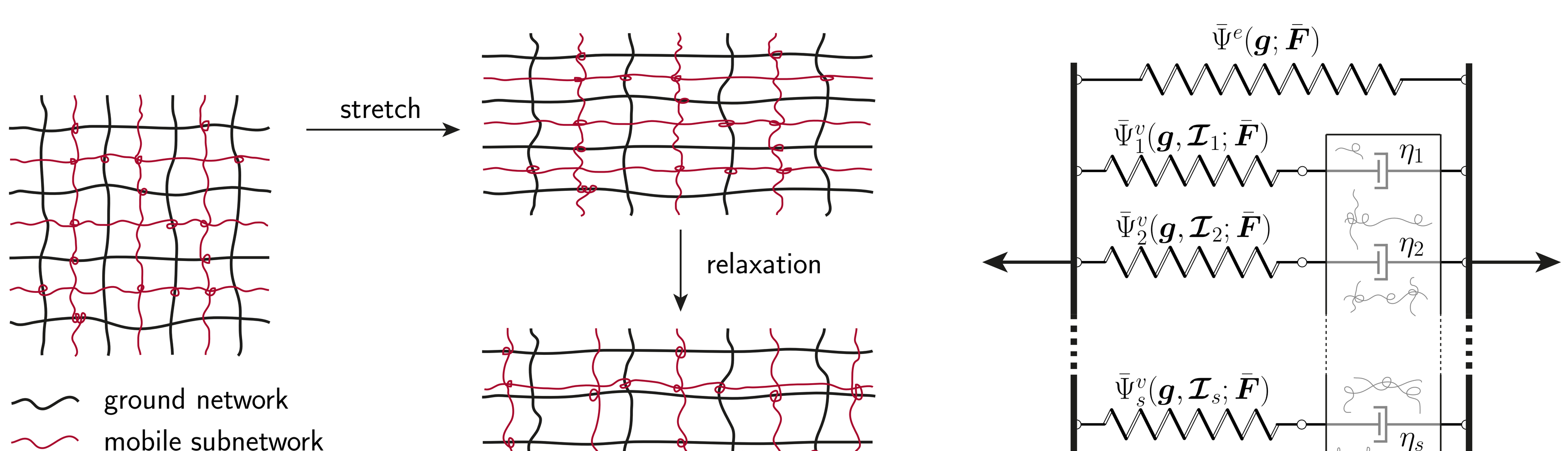
To successfully adapt characteristics from natural to engineered materials, we:

- *identify* characteristic mechanisms in natural soft matter materials;
- *develop* microscopic models to approximate those;
- *transfer* them to scales relevant for engineering applications.

Network representation of soft matter materials

The response of soft matter materials is described by the decomposition into:

- *elastic ground network*, which incorporates the strongly cross-linked macromolecules and produces the macroscopic elastic response;
- *viscous mobile subnetwork*, which is formed by superimposed mobile macromolecules based on entanglement mechanisms. It is transient in nature and responsible for the viscous overstress.



Free energy $\bar{\Psi} = \bar{\Psi}^e(\boldsymbol{g};\bar{\boldsymbol{F}}) + \bar{\Psi}^v(\boldsymbol{g},\boldsymbol{\mathcal{I}};\bar{\boldsymbol{F}})$ with $\bar{\Psi}^v = \sum_{i=1}^s \bar{\Psi}_i^v(\boldsymbol{g},\boldsymbol{\mathcal{I}}_i;\bar{\boldsymbol{F}})$

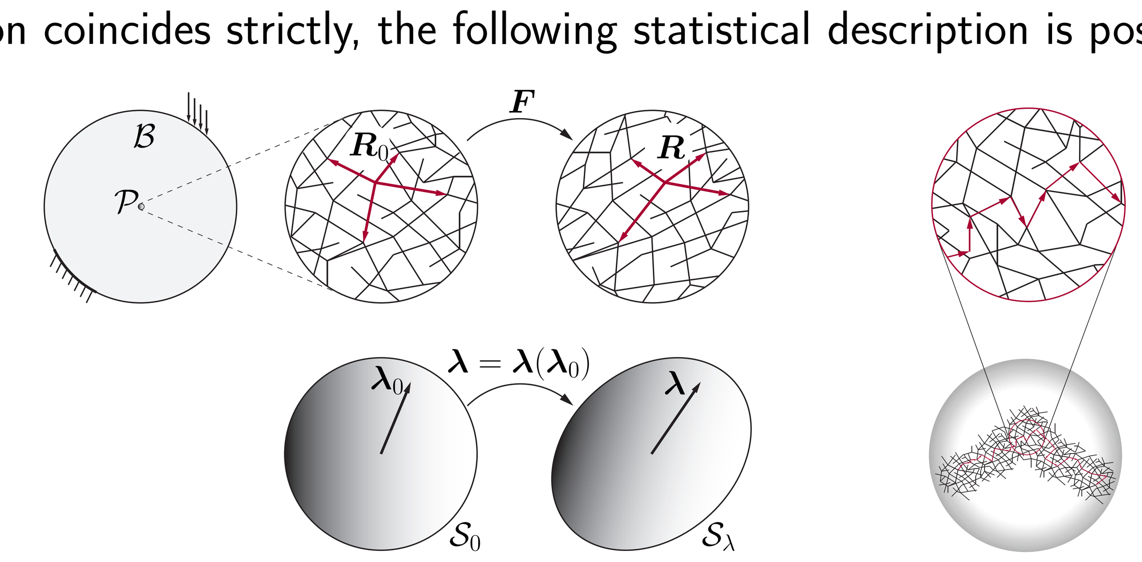
Stress: $\bar{\boldsymbol{\tau}} = \bar{\boldsymbol{\tau}}^e + \bar{\boldsymbol{\tau}}^v$ with $\bar{\boldsymbol{\tau}}^e = 2\partial_{\boldsymbol{g}}\bar{\Psi}^e(\boldsymbol{g};\bar{\boldsymbol{F}})$ and $\bar{\boldsymbol{\tau}}^v = 2\partial_{\boldsymbol{g}}\bar{\Psi}^v(\boldsymbol{g},\boldsymbol{\mathcal{I}};\bar{\boldsymbol{F}})$

Dissipation: $\mathcal{D}_{loc} = -\partial_{\boldsymbol{\mathcal{I}}}\bar{\Psi}\cdot\dot{\boldsymbol{\mathcal{I}}} = \sum_{i=1}^s \mathcal{D}_{loc,i} \geq 0$ with $\mathcal{D}_{loc,i} = -\partial_{\boldsymbol{\mathcal{I}}_i}\bar{\Psi}\cdot\dot{\boldsymbol{\mathcal{I}}}_i$

Elastic mechanisms in soft matter materials

The maximal-advance-path-constraint based microscopic model

Assuming that junction points do not perform any thermal motion, that all fibers in the network are of one single type and uniform properties, that the initial network consists of fibers with the same end-to-end distance oriented isotropically, and that the deformation of fibers with equal initial orientation coincides strictly, the following statistical description is possible:



The maximal advance path constraint can then be derived as

$$\langle\boldsymbol{\lambda}\otimes\boldsymbol{\lambda}_0\rangle = \int_{\mathcal{S}_0}\boldsymbol{\lambda}(\boldsymbol{\lambda}_0)\otimes\boldsymbol{\lambda}_0 d\boldsymbol{\lambda}_0 = \frac{1}{3}\boldsymbol{F}.$$

The homogenized macroscopic response

With the assumption that the network total energy can be expressed in terms of the stretch vector $\boldsymbol{\lambda}$, the constraint variational principle of minimum averaged free energy is given as

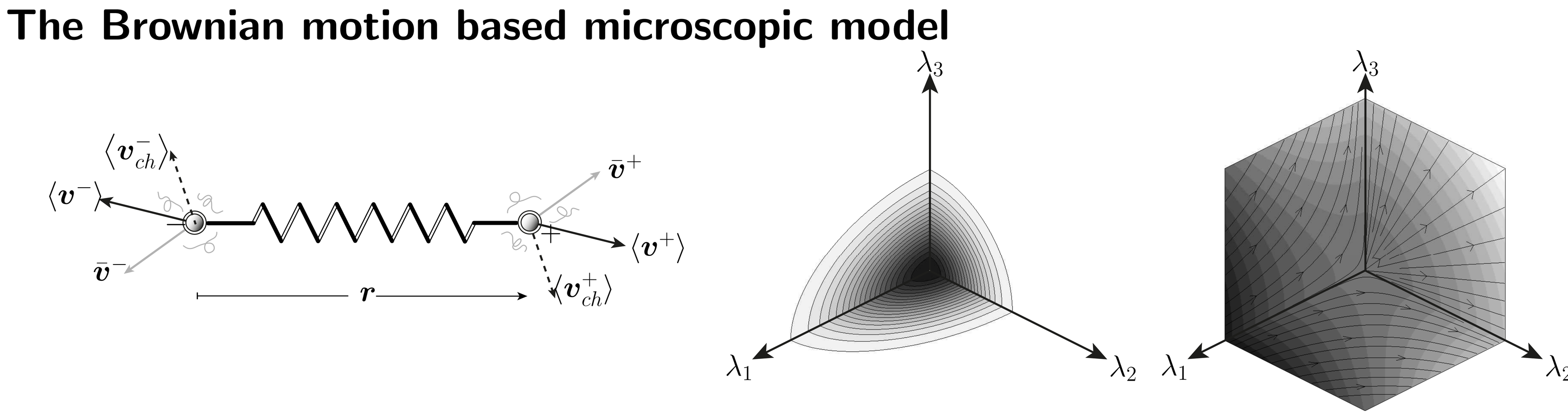
$$\Psi^e[\boldsymbol{\lambda}] \sim \langle\psi_f\rangle = \frac{1}{|\mathcal{S}_0|}\int_{\mathcal{S}_0}\psi_f(|\boldsymbol{\lambda}(\boldsymbol{\lambda}_0)|)\,|d\boldsymbol{\lambda}_0| \underset{\boldsymbol{\lambda}(\boldsymbol{\lambda}_0)}{\longrightarrow} \min$$
$$\langle\boldsymbol{\lambda}\otimes\boldsymbol{\lambda}_0\rangle = \frac{1}{|\mathcal{S}_0|}\int_{\mathcal{S}_0}\boldsymbol{\lambda}(\boldsymbol{\lambda}_0)\otimes\boldsymbol{\lambda}_0\,|d\boldsymbol{\lambda}_0| = \frac{1}{3}\boldsymbol{F},$$

which results in the homogenized equilibrium stress as

$$\boldsymbol{P} = \partial_{\boldsymbol{F}}\Psi^*_{net} = n\langle\partial_{\boldsymbol{F}}\psi_f(|\boldsymbol{\lambda}^*|)\rangle = n\langle\boldsymbol{f}_f(\boldsymbol{\lambda}^*)\otimes\boldsymbol{\lambda}_0\rangle.$$

Inelastic mechanisms in soft matter materials

The Brownian motion based microscopic model



Each macromolecule is modeled based on Gaussian chain statistics as

$$p(\boldsymbol{r}) = \Big(\frac{3}{2\pi r_0^2}\Big)^{\frac{3}{2}}\exp\Big[-\frac{3}{2}\lambda^2\Big],\quad \mathcal{S}(\boldsymbol{r}) = -\frac{3}{2}k_B\lambda^2 \quad\text{and}\quad \mathcal{A}(\boldsymbol{r}) = \frac{3}{2}k_B\theta\lambda^2 \quad\text{with}\quad \boldsymbol{\lambda} = \frac{\boldsymbol{r}}{r_0}.$$

Viscosity is assumed to be concentrated at the chain end points, which move based on

$$\langle\boldsymbol{v}^{\pm}\rangle = \bar{\boldsymbol{v}}^{\pm} + \langle\boldsymbol{v}_{ch}^{\pm}\rangle$$

- where $\bar{\boldsymbol{v}}^{\pm} = \pm\boldsymbol{l}\,\boldsymbol{r}/2$ represents the motion of the surrounding viscous medium, and
- $\langle\boldsymbol{v}_{ch}^{\pm}\rangle = \mp\frac{1}{\eta}\nabla_r U_{ch}(\boldsymbol{r},t)$ is the motion of the thermally active chains.

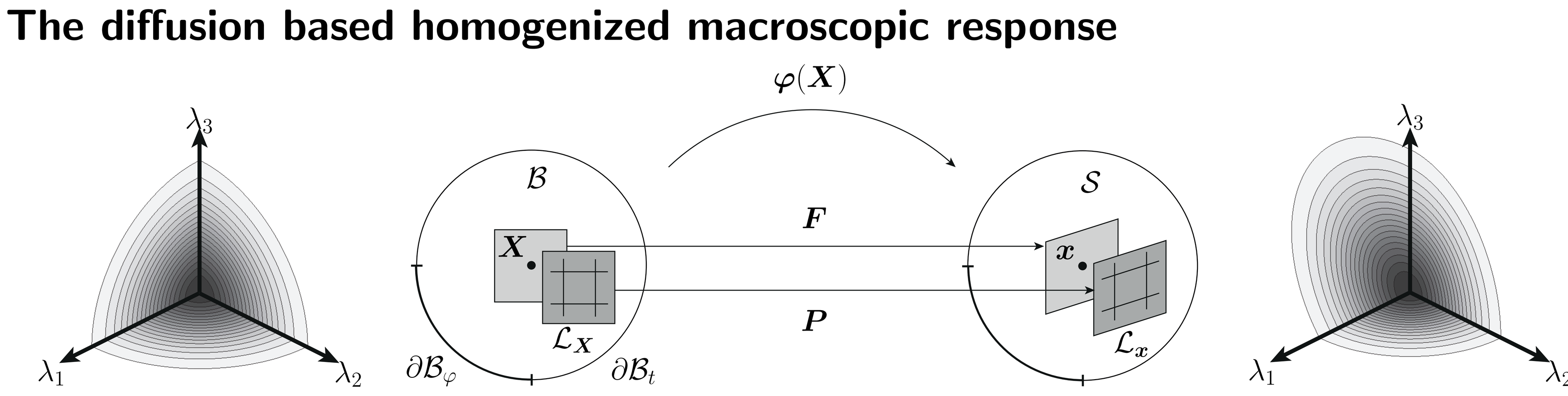
Insertion of $U_{ch}(\boldsymbol{x},t) = k_B\theta\ln p(\boldsymbol{x},t) + U(\boldsymbol{x})$ yields the relative motion of the end points

$$(\langle\boldsymbol{v}^+\rangle - \langle\boldsymbol{v}^-\rangle)/r_0 = \langle\dot{\boldsymbol{\lambda}}\rangle = \boldsymbol{l}\boldsymbol{\lambda} - D^{\lambda}\nabla_{\lambda}\big[\ln p(\boldsymbol{\lambda},t) + \frac{3}{2}\lambda^2\big] \quad\text{with}\quad D^{\lambda} = \frac{2\,k_B\theta}{\eta\,r_0^2}.$$

The re-orientation and re-distribution of the chain is then given by the modified Smoluchowski equation as

$$\partial_t p(\boldsymbol{\lambda},t) = -\mathrm{div}_{\lambda}\big(p(\boldsymbol{\lambda},t)\boldsymbol{l}\boldsymbol{\lambda}\big) + \mathrm{div}_{\lambda}\big(D^{\lambda}p(\boldsymbol{\lambda},t)\nabla_{\lambda}\big[\ln p(\boldsymbol{\lambda},t) + \frac{3}{2}\lambda^2\big]\big).$$

The diffusion based homogenized macroscopic response

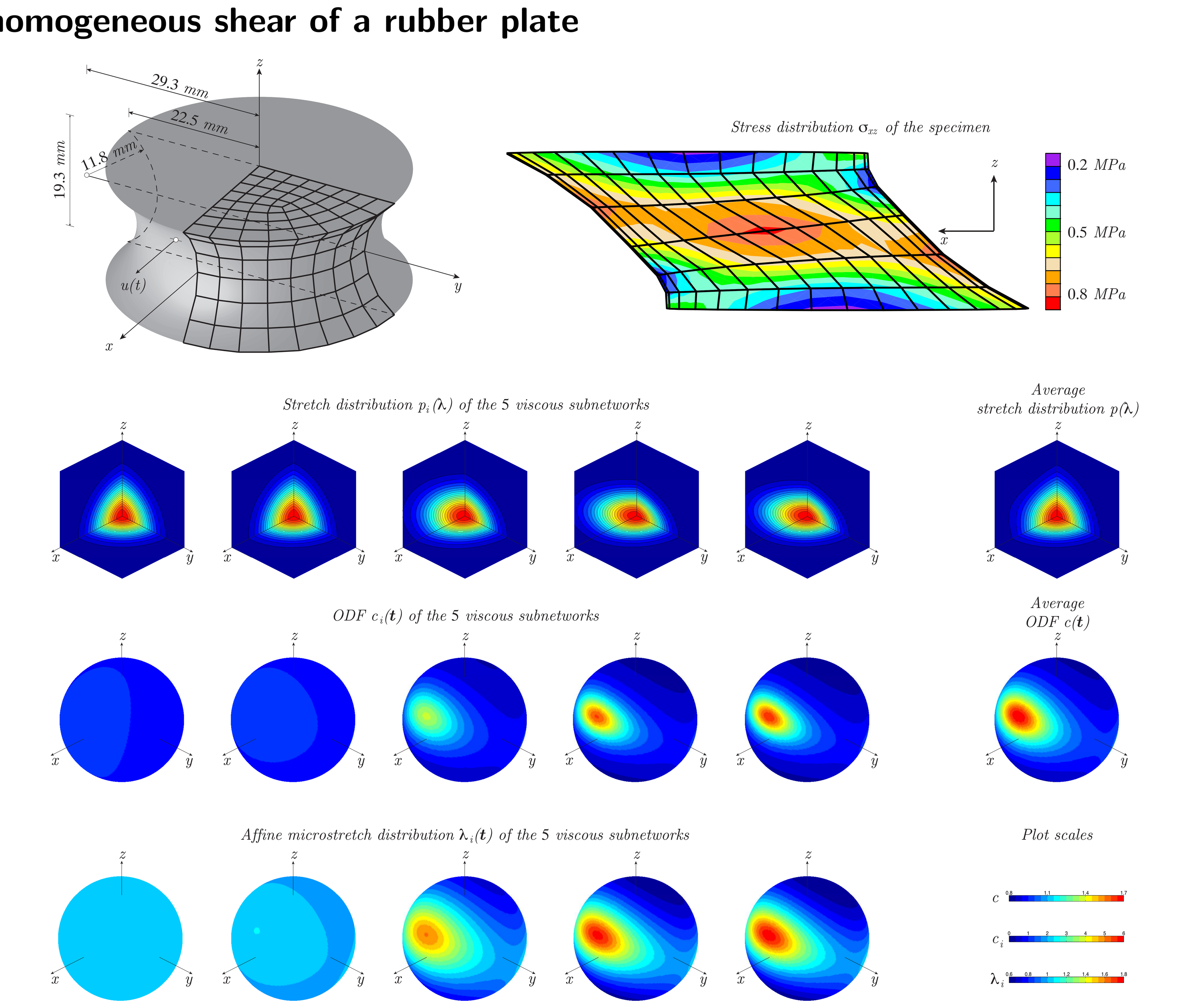


The homogenized viscous response is obtained through an introduced *micro-deformation map* $\boldsymbol{P}$ finally resulting in an evolution equation of the form $\dot{\boldsymbol{A}} = 6\,D^{\lambda}\Big(\bar{\boldsymbol{C}}^{-1} - \boldsymbol{A}\Big)$ and closed form solutions for the energy and overstress as

$$\bar{\Psi}^v = \tfrac{1}{2}\mu^v\Big[\big(\boldsymbol{A}:\bar{\boldsymbol{C}} - 3\big) - \ln\big(\det\boldsymbol{A}\big)\Big] \quad\text{and}\quad \bar{\boldsymbol{\tau}}^v = \mu^v\bar{\boldsymbol{F}}\boldsymbol{A}\bar{\boldsymbol{F}}^T.$$

Homogenized response of engineering applications

Inhomogeneous shear of a rubber plate



References

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