A Reptation Theory of Rubber Elasticity

Theory of entanglements in isotropic and nematic rubbers

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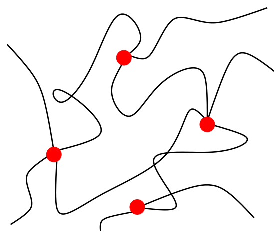
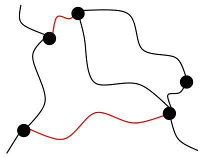
Introduction

Rubbers are highly complex systems. They consist of polymer chains which are crosslinked at their end points.

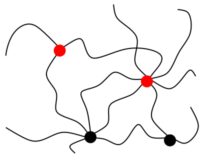


This system can exhibit a great variety of features:

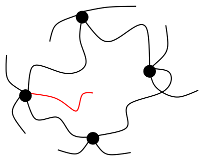
- Strands of differents lengths.



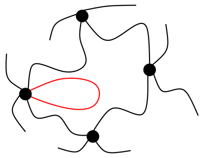
- Crosslinks of different functionality.



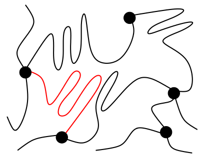
- Dangling ends



- Loops



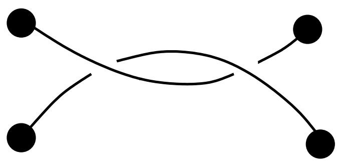
- Liquid crystallinity



Chain entanglements play a key rôle in polymer rheology. In crosslinked systems, one expects an even greater effect on their elastic properties.

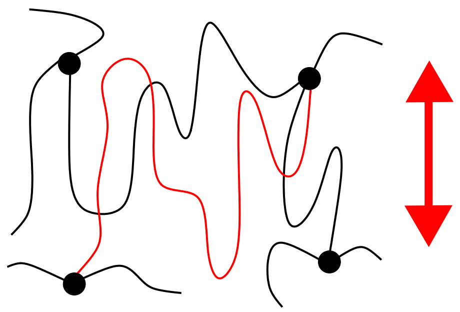
Aim

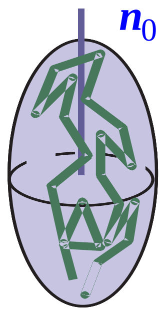
The simplest theory makes the unphysical assumption that the strands do not interact with each other except at the crosslinks: phantom chain network. More sophisticated theories take the entanglements into account: the fact that the strands cannot pass through each other.



Based on existing ideas, we develop the tube model to describe the entanglements in networks and obtain an improved stress–strain relation.

Polymer networks can exhibit a molecular order: liquid crystallinity. In a nematic rubber, the polymer chains orient themselves in a preferred direction $\boldsymbol{n}_0$.





The known theories treat this system on the simplest level (phantom chains), but already find a richer elastic behaviour than in the isotropic case.

We extend our entanglement theory of isotropic rubbers to the case of spontaneously anisotropic nematic rubbers.

Elastic free energy of a network

The entropic free energy of a single polymer chain is:

$$F_{\mathrm{ch}}(\boldsymbol{R}) = -k_{\mathrm{B}}T \ln Z = k_{\mathrm{B}}T \frac{3}{2Nb^2} R^2.$$

Under deformation $\underline{\underline{\lambda}}$, the free energy per chain is changed to $F_{\mathrm{ch}}(\underline{\underline{\lambda}}\boldsymbol{R})$, hence

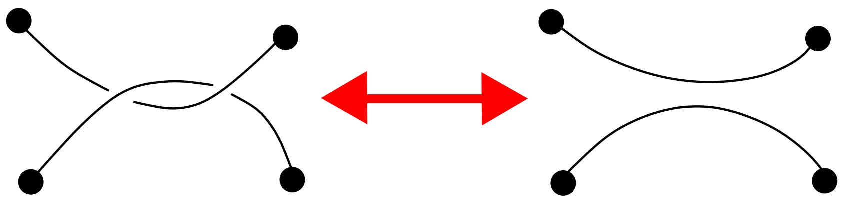
$$F = \left\langle F_{\mathrm{ch}}(\underline{\underline{\lambda}}\boldsymbol{R}) \right\rangle \propto \int \mathrm{d}^3\boldsymbol{R}\; e^{-\frac{3}{2Nb^2}\boldsymbol{R}^2}\; \boldsymbol{R}^{\mathsf{T}} \underline{\underline{\lambda}}^{\mathsf{T}} \underline{\underline{\lambda}} \boldsymbol{R} \propto \mathrm{Tr}(\underline{\underline{\lambda}}^{\mathsf{T}} \underline{\underline{\lambda}})$$

The free energy density or the elastic energy density is then given by:

$$\boxed{F_{\mathrm{elast}} = \tfrac{1}{2} n_{\mathrm{ch}} k_{\mathrm{B}}T \;\mathrm{Tr}(\underline{\underline{\lambda}}^{\mathsf{T}} \underline{\underline{\lambda}}) = \tfrac{1}{2}\mu \;\mathrm{Tr}(\underline{\underline{\lambda}}^{\mathsf{T}} \underline{\underline{\lambda}})}$$

where $\mu = n_{\mathrm{ch}} k_{\mathrm{B}}T$ and n_{ch} is the density of crosslinked strands.

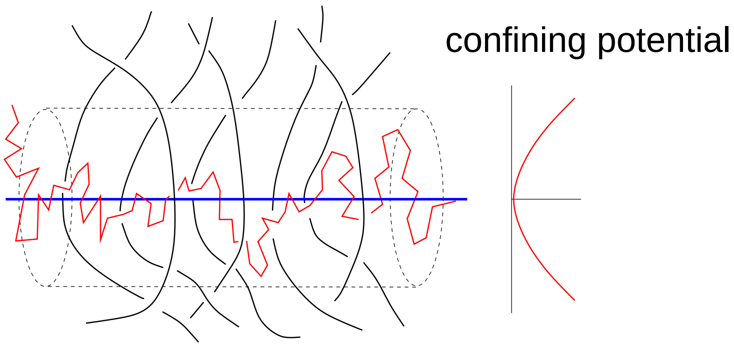
- Assumes unphysical behaviour, e.g.



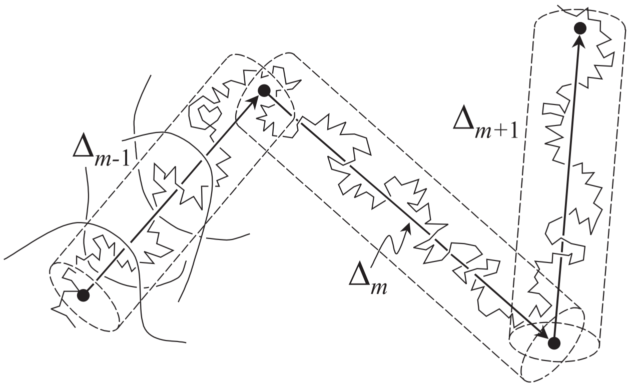
- The scaling behaviour in the long chain limit is incorrect:
  - The elastic energy is proportional to the chain density n_{ch}.
  - The chain density n_{ch} is inversely proportional to the volume of one chain, hence inversely proportional to the length of one chain: $n_{\mathrm{ch}} \propto \frac{1}{N}$
  - Hence, as $N \to \infty$, we find $F_{\mathrm{elast}} \to 0$!

Entanglements

Following the ideas of Edwards [**?**], we assume that one particular network strand is limited in its lateral fluctuations by neighbouring chains. It fluctuates around a mean path: the primitive path. Hence it is confined to an effective tube along the primitive path. We model the tube by a quadratic potential around the axis of the primitive path. The strength of the quadratic potential is $\frac{1}{2}q_0^2 r^2$, where r is the distance from the central axis.



The primitive path itself can be considered as a random walk with M steps $\mathbf{\Delta}_m$, which are much bigger than the monomer steps of length b.



Each tube segment m contains s_m steps, hence $\sum_{m=1,M} s_m = N$.

Under deformation, the tube spans $\mathbf{\Delta}_m$ deform into $\mathbf{\Delta}'_m = \underline{\underline{\lambda}}\mathbf{\Delta}_m$

Confined fluctuations

- In the direction parallel to $\mathbf{\Delta}_m$, the chains are not hindered by neighbouring chains. We have a 1-dimensional random walk with $s_m/3$ steps in this direction, leading to Gaussian statistics.
- In the direction perpendicular to $\mathbf{\Delta}_m$, the chains experience a quadratic potential and are modelled by a 2-dimensional random walk in a quadratic potential with $2/3s_m$ steps. In the limit of $q_0 b s_m \gg 1$ (strong confining potential and large number of monomers in a tube segment), the Green's function is well known [?].

The total number of excursions in segment m:

$$W_m = W_m^{\parallel} W_m^{\perp} \propto \frac{1}{\sqrt{s_m}} \exp\left(-\frac{3}{2b^2 s_m}\mathbf{\Delta}_m^2 - \frac{1}{3} q_0 b s_m\right).$$

The number of configurations of the whole strand becomes:

$$W = \int_0^N ds_1 \cdots \int_0^N ds_M \left(\prod_{m=1}^{M} W_m\right) \delta\left(\sum_{m=1}^{M} s_m - N\right),$$

The number of configurations W of the whole strand, described by the set of vectors $\{\mathbf{\Delta}_m\}$, is proportional to the probability distribution:

$$W(\mathbf{\Delta}_1, \ldots, \mathbf{\Delta}_M) \propto P(\{\mathbf{\Delta}_m\}) \propto \frac{\exp\left(-\frac{3}{2b^2 N}\left(\sum_{m=1}^{M} \Delta_m\right)^2\right)}{\left(\sum_{m=1}^{M} \Delta_m\right)^{M-1}}.$$

This distribution is reminiscent of a Gaussian distribution, but here the exponent takes a slightly different form.

Free energy of deformation

At formation of the network, the strands in the melt obey the distribution P. A deformation $\underline{\underline{\lambda}}$ will transform the segment spans $\mathbf{\Delta}_m$ into $\mathbf{\Delta}'_m = \underline{\underline{\lambda}}\mathbf{\Delta}_m$, hence Δ_m into $\Delta'_m = |\underline{\underline{\lambda}}\mathbf{\Delta}_m|$, and change the free energy $F = -k_{\mathrm{B}}T \ln W(\{\mathbf{\Delta}_m\})$ accordingly.

Therefore, to calculate the free energy of deformation, we have to average $F(\{\underline{\underline{\lambda}}\mathbf{\Delta}_m\})$ with respect to the distribution $P(\{\mathbf{\Delta}_m\})$. The result is the following:

$$\boxed{\begin{aligned} F_{\mathrm{elast}} &= \frac{2}{3}\mu\frac{2M+1}{3M+1}\mathrm{Tr}(\underline{\underline{\lambda}}^{\mathsf{T}}\cdot\underline{\underline{\lambda}}) \\ &+\frac{3}{2}\mu(M-1)\frac{2M+1}{3M+1}(\langle|\underline{\underline{\lambda}}|\rangle)^2 \\ &+\mu(M-1)\langle\ln|\underline{\underline{\lambda}}|\rangle, \end{aligned}}$$

where we have used the following notations

$$\begin{aligned} \langle|\underline{\underline{\lambda}}|\rangle &= \frac{1}{4\pi}\int_{|\boldsymbol{e}|=1} d\Omega\ |\underline{\underline{\lambda}}\ \boldsymbol{e}| \\ \langle\ln|\underline{\underline{\lambda}}|\rangle &= \frac{1}{4\pi}\int_{|\boldsymbol{e}|=1} d\Omega\ \ln|\underline{\underline{\lambda}}\ \boldsymbol{e}|. \end{aligned}$$

For instance, in the case of uniaxial deformation, this can be written in a compact analytical form.

The linear shear modulus of an entangled network is:

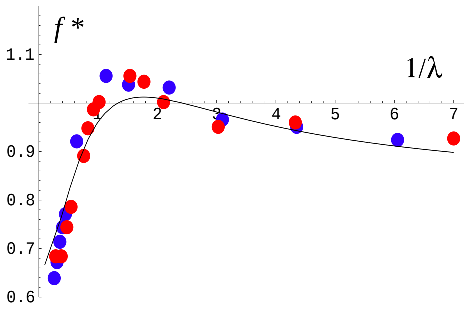
$$G = \mu\left(\frac{4}{3}\cdot\frac{2M+1}{3M+1} + \frac{1}{5}(M-1)\left[\frac{11M+5}{3M+1}\right]\right)$$

Discussion

- Our expression is nearly identical to a result obtained previously by Higgs and Ball [**?**], although their model makes completely different assumptions: the entanglements are thought to make the strands interact with each other at certain points. This is modelled by 3-dimensional random walks which are forced to pass through a number of hoops fixed in space.
- In the case of only one tube segment, $M = 1$, our expression reproduces the phantom chain network result.
- In the limit of many tube segments, $M \to \infty$, we find:

$$F_{\mathrm{elast}} = \mu M \left((\langle |\underline{\lambda}| \rangle)^2 + \langle \ln |\underline{\lambda}| \rangle \right) .$$

  Recall $\mu \propto n_{\mathrm{ch}}$, where n_{ch} is the chain density, and $n_{\mathrm{ch}} \propto \frac{1}{L}$.
  As the polymer strands become longer, $L \to \infty$, we can assume that they experience more entanglements: $M \propto L$.
  Hence as $L \to \infty$, our expression does not vanish in contrast to the unphysical limit of the phantom chain network result!
- The expression (1) fits well to experimental data:

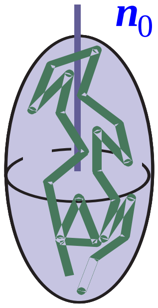


Data from [**?**](●) and [**?**](●) in the Mooney–Rivlin representation.

Nematic rubber

In the isotropic rubber, the monomer steps are oriented isotropically in all directions.

In contrast, in a nematic rubber, i.e. nematic liquid crystal elastomer, the monomer steps acquire one preferred direction along the director $\boldsymbol{n}_0$.



The anisotropy is described by the tensor $\underline{\underline{\ell}}_0$, which appears in the end-to-end distribution function:

$$P(\boldsymbol{R_0}) \propto \exp\left(-\frac{3}{2bN}\boldsymbol{R}_0^{\mathsf{T}} \cdot \underline{\underline{\ell}}_0^{-1} \cdot \boldsymbol{R}_0\right) .$$

In the principal frame, the matrix $\underline{\underline{\ell}}_0$ is has the following form in the nematic case:

$$\underline{\underline{\ell}}_0 = \begin{pmatrix} l_0^{||} & 0 & 0 \\ 0 & l_0^{\perp} & 0 \\ 0 & 0 & l_0^{\perp} \end{pmatrix}$$

$l_0^{||}$ and $l_0^{\perp}$ are the effective step lengths in the parallel and perpendicular directions respectively.

Entanglements in a nematic rubber

As the monomer random walk of each strand is now anisotropic, the tube segments $\mathbf{\Delta}_m$ too orient themselves preferably along $\boldsymbol{n}_0$: the end-to-end distribution of the tube segment spans becomes anisotropic:

$$W_m \propto \frac{1}{\sqrt{s_m/3}} \exp\left(-\frac{3}{2bs_m}\mathbf{\Delta}_m^{\mathsf{T}} \cdot \underline{\underline{\ell}}_0^{-1} \cdot \mathbf{\Delta}_m - \frac{1}{3}q_0 b s_m\right).$$

Under deformation, not only $\mathbf{\Delta}_m$ changes into $\underline{\underline{\lambda}}\mathbf{\Delta}_m$, but the matrix $\underline{\underline{\ell}}_0$ might change to $\underline{\underline{\ell}}_\theta$ with new effective step lengths $l_0^\perp$ and $l_0^\parallel$ in a new, i.e. rotated reference frame.

$$\boxed{\begin{aligned} F_{\text{elast}} \;=\; & \frac{2}{3}\mu\,\frac{2M+1}{3M+1}\mathrm{Tr}(\underline{\underline{\ell}}_0 \cdot \underline{\underline{\lambda}}^{\mathsf{T}} \cdot \underline{\underline{\ell}}_\theta^{-1} \cdot \underline{\underline{\lambda}}) \\ & +\frac{3}{2}\mu(M-1)\frac{2M+1}{3M+1}(\langle|\underline{\underline{\ell}}_\theta^{-1/2} \cdot \underline{\underline{\lambda}} \cdot \underline{\underline{\ell}}_0^{1/2}|\rangle)^2 \\ & +\mu(M-1)\langle \ln |\underline{\underline{\ell}}_\theta^{-1/2} \cdot \underline{\underline{\lambda}} \cdot \underline{\underline{\ell}}_0^{1/2}|\rangle, \end{aligned}}$$

with
$$\begin{aligned} \langle|\underline{\underline{\ell}}_\theta^{-1/2} \cdot \underline{\underline{\lambda}} \cdot \underline{\underline{\ell}}_0^{1/2}|\rangle &= \frac{1}{4\pi}\int\limits_{|\boldsymbol{e}|=1} d\Omega |\underline{\underline{\ell}}_\theta^{-1/2} \cdot \underline{\underline{\lambda}} \cdot \underline{\underline{\ell}}_0^{1/2}\,\boldsymbol{e}| \\ \langle \ln |\underline{\underline{\ell}}_\theta^{-1/2} \cdot \underline{\underline{\lambda}} \cdot \underline{\underline{\ell}}_0^{1/2}|\rangle &= \frac{1}{4\pi}\int\limits_{|\boldsymbol{e}|=1} d\Omega \ln |\underline{\underline{\ell}}_\theta^{-1/2} \cdot \underline{\underline{\lambda}} \cdot \underline{\underline{\ell}}_0^{1/2}\,\boldsymbol{e}|. \end{aligned}$$

This is a first theoretical expression for the elastic free energy of an entangled nematic elastomer.

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