A Constitutive Tube Model of Rubber Elasticity: The Path from Polymer Network to the Rubber Component

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Innovations in Rubber Design
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London, UK
Acknowledgement:

The Institute of Materials, Minerals and Mining

and

Prof. James Busfield
Introduction:
Some Basic Rubber Properties

\[ F(\{\lambda_i\}) = \sum_{\text{Top}} w_{\text{Top}} F_{\text{Top}}(\{\lambda_i\}) \]

\[ \sigma_{ij} = f(\varepsilon_{lm}) \]
Mechanical Properties of Different Materials

Stress-strain behaviour of polymer and non-polymeric materials

Elastomers:
\[ \varepsilon \approx 1000\% \]

Mechanical properties under uniaxial loading (tensile test)
Tensile Properties of NR and SBR

**BR**

-CH$_2$-CH=CH-CH$_2$-CH$_2$-CH=CH-CH$_2$-CH$_2$-CH=CH-CH$_2$-

**NR**

-CH$_2$-C=CH-CH$_2$-CH$_2$-C=CH-CH$_2$-CH$_2$-C=CH-CH$_2$-

**SBR**

-CH$_2$-CH=CH-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH=CH-CH$_2$-CH$_2$-CH=CH-CH$_2$-

By courtesy of Prof. S. Toki (Stony Brook, NY)
Thermo-elastic Properties

Metal

Rubber

Gas

"Entropy Elasticity"
Augensumme zweier idealer Würfel

<table>
<thead>
<tr>
<th>Augensumme</th>
<th>Augenpaare</th>
<th>günst. Fälle</th>
<th>Wahrscheinlichkeiten</th>
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<tr>
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<td>Summen</td>
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The **entropy** $S$ is proportional to the *log of the number of the microscopic states* ($\rightarrow$ the probability), i.e. the entropy comes from the number of possible conformations:

$$S = k_B \cdot \ln p_N(\vec{R}) = \text{const.} - k_B \cdot \frac{3}{2N \cdot a^2} \cdot \vec{R}^2$$

Thus a polymer chain behaves like a (entropic) spring

The restoring force $f$ (derivation of free energy $F$) comes from the entropy rather than the internal energy.

$$F(\vec{R}) = U - T \cdot S(\vec{R})$$

$$= U - \text{const.} + k_B \cdot T \cdot \frac{3}{2N \cdot a^2} \cdot \vec{R}^2$$

$k_B = 1.38 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1}$

$$f = \left( \frac{\partial F(\vec{R})}{\partial \vec{R}} \right)_T = \frac{3 k_B \cdot T}{N \cdot a^2} \cdot \vec{R}$$
Force-temperature measurements on sulphur-vulcanized natural rubber at constant pressure and length

positive temperature coefficient:
typical of entropy-driven elasticity

Heinrich, G.: Lecture Series „Physik Polymerer Netzwerke“:
https://www.ipfdd.de/de/organisation-und-leute/personal-homepages/prof-dr-gert-heinrich/publikationen/?no_cache=1
Classical network models

Shear modulus:

\[ \sigma(\lambda) = \frac{d}{d\lambda} \left( \frac{\Delta F_{el}}{V} \right) = G_c \left( \lambda - \lambda^{-2} \right) \]

\[ G_c = \frac{E}{3} = \frac{N_{chains}}{V} A kT = \frac{\rho RT}{M_c} \]

\[ M_c = \text{mol. Mass of the network chains [g/mol]} \]

Uniaxial tension

\[ \lambda_1 = \lambda = \frac{L}{L_0} \]

\[ \prod_{i=1}^{3} \lambda_i = 1 \quad \text{(Incompressibility)} \]
Connectivities involve simple lattice structures

James/Guth model:
- surface crosslinks are fixed
- internal crosslinks are free to move (phantoms)
- non-affine deformation of crosslinks

Kuhn, Hermans/ Flory/ Wall model:
- internal crosslinks fixed within the medium
- affine deformation of crosslinks

Elastic free (Helmholtz) energy change of deformation:  

$$\Delta F_{el} = \frac{1}{2} N_{chains} \kappa T \left( \sum_{i=1}^{3} \lambda_i^2 - 3 \right)$$

quantitative factor  

affine network: $A=1$
phantom network: $A=(f-2)/f$

$\xi$ - cycle rank (Zyklisierungsrang)

P.J. Flory 1976
Euler-Poincaré:
\[ \chi = V - E + F \]
\[ \chi = \xi \]

\[ \xi - \text{cycle rank (graph theory)} \]

\[ \xi = v - \mu + 1 = 1 \]

v – network chains
\mu - crosslinks

Euler characteristic:
\[ V - E + F = 2 \]

Tetrahedron
Rubber – a weakly crosslinked Polymer Network

- **a** dangling ends
- **b** temporary entanglements
- **c** trapped entanglements
- **d, e** closed loops
Structures in filled rubbers

Disorder on different length scales!

- Crosslinks & Crosslink Heterogeneities
- Entanglements
- Filler
- Blend-Phases & Interphases

Fillers in Technical Elastomers

Challenges for rigorous constitutive model of rubber elasticity

MD snapshots of two slabs of b-cristobalite (100) covered with a compatibilizer

“Molecular Modeling Approach to the Prediction of Mechanical Properties of Silica-Reinforced Rubbers”
Reinhard Hentschke et al., JAPS 2016
Do we live in a Volterra World?

Flocculation of Filler Clusters

EPDM & Aerosil

- regulation in complex systems?

tempered at 160 °C

Do we live in a Volterra World?

Segregation Model in Social Science of Thomas Schelling
(Noble Price of Economics 2005 for game-theory analysis)

Example of racial segregation in northamerican cities: The simple wish, not to live alone in racial different neighbourhood leads to macroscopic segregation structures.

Flocculation of Filler Cluster

regulation in complex systems:

[M. Peschel, W. Mende: The Predator-Prey Model: Do We Live in a Volterra World?, Akademie-Verlag, 1986]

Emergence discussion!

„What we are seeing is transformation of worldview in which the objective of understanding nature by breaking it down into ever smaller parts is supplanted by the objective of understanding how nature organizes itself.“

Robert B. Laughlin, A Different Universe – Reinventing Physics from the Bottom Down, 2005
Polymer Networks:
The path from polymer networks to a constitutive material law
You must do research in Polymer Theory!

Statistical mechanics with topological constraints: II

S. F. EDWARDS

Department of Theoretical Physics, University of Manchester

MS. Revised 1st October 1947

3. The specification of loops

To have been at all, that is configurations of a curve lying in a certain class which cannot be transformed into other classes (i.e., different loops, including no loop), one must have infinite or similar loops. To state the theorem consider two unknown distinct curves. Two possible configurations are:

\[ \int \frac{d\phi}{\sin \phi} = \int \frac{d\psi}{\sin \psi} \]

which, using Stokes' theorem,

\[ \int \delta_{\text{circ}} \cdot d\phi = \int \delta_{\text{circ}} \cdot d\psi \]

Use curl and grad 

\[ \int \delta_{\text{circ}} \cdot d\phi = 0 \]

whence

\[ \int \delta_{\text{circ}} \cdot d\phi = -\int \delta_{\text{circ}} \cdot d\psi \]

Now

\[ \int \delta_{\text{circ}} \cdot d\phi = \int \delta_{\text{circ}} \cdot d\psi \]

Therefore

\[ \int \frac{d\phi}{\sin \phi} = \int \frac{d\psi}{\sin \psi} \]
A reminder: **Gibbs statistics of gases** (canonical distribution)

- no exchange of particles
- exchange of heat energy

is a non-isolated but closed system!

**Gibbsian canonical distribution function of microstates:**

\[
\rho(\{q\}, \{p\}) = Z^{-1} \ e^{-\frac{H(\{q\}, \{p\})}{kT}}
\]

**State Integral:**

\[
Z = \frac{1}{N!h^{3N}} \int ... \int e^{-\frac{H(\{q\}, \{p\})}{kT}} \ dq \ dp
\]

**Helmholtz Free Energy:**

\[
F(T, V, N) = -kT \log Z
\]
Why non-Gibbs statistics for rubber networks?

A reminder: **Gibbs statistics of gases** (canonical distribution) contn.

**Ideal gas**

\[
H = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + U_N(q_1, \ldots, q_N) \quad ; \quad U_N = 0
\]

\[
Z = \left(\frac{2\pi mkT}{\hbar^2}\right)^{\frac{3N}{2}} \frac{Q_N}{N!} \quad Q_N = V^N
\]

**Free Energy:**

\[
F(T, V, N) = -kT \ln Z = -kT \ln \left(\frac{V^N}{N!}\right) + 3NkT \ln \lambda_{dB}
\]

\[
\lambda_{dB} = \frac{h}{\sqrt{2\pi mkT}} \quad \text{(thermal) de Broglie length}
\]

**Thermal equation of state:**

\[
p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{NkT}{V}
\]
Network Formation and "Percolation":

"Sol-Gel Transition as Phase Transition of 2\textsuperscript{nd} Order"

Percolation
Network formation and the art of cooking tasty eggs

**Separated egg white**

**Egg yolk in rheometer**

Aus: Das Molekül-Menü (Thomas Vilgis, 2011), S. 269
Conversations about Sol-Gel-Transitions in Kitchens and in Tire Plants: Similarities, Differences and Consequences

Prof. Dr. Gert Heinrich
Leibniz Institut für Polymerforschung, Dresden, Germany
TU Dresden, Institut für Werkstoffwissenschaft, Germany
Averaging over frozen disorder

(Helmholtz)

Free Energy of Deformation:

\[
F\left(\{\lambda_i\}\right) = \sum_{\text{Top}} w_{\text{Top}} \cdot F_{\text{Top}}\left(\{\lambda_i\}\right)
\]

\begin{itemize}
  \item Macroscopic observable Free Energy
  \item \textit{a priori} probability of the topology "\textbf{Top}"
  \item Free Energy of a network with the topology "\textbf{Top}"
\end{itemize}

Exactly where the crosslinks come and how they are spaced along the chains is beyond the control of processor!

\textbf{Brout-Fixman-Edwards (BFE) Averaging}
Entanglements and tube-like constraints

Chains A, B uncrosslinked

Chains A, B are cross-linked in such a way that their topological relationship with each other cannot change.

Schematic representation of a network chain in a tube. The tube diameter is given by the mean spacing of the topological constraint centers, i.e., cross-links and entanglements, indicated as crosses.

\[ d = d_0 \cdot f(\text{deformation}) \]
Helmholtz free energy change

\[ \Delta F(R_0; \lambda) = kT \frac{R_0^2}{\xi^2(\lambda)} \]

\( \xi(\lambda) = \lambda \cdot \xi \) (stretched contour between two entanglements)

Polymer chain model with entropic tube constraints

Gaussian coil
\( b = \text{(Kuhn's) statistical segments length} \)
\( N_s = \text{segments} \)

Hamiltonian:
\[
\frac{H}{kT} = \frac{3}{2b} \int_0^L ds \left( \frac{\partial \mathbf{r}^2(s)}{\partial s} \right)^2 + \sum_{i=x,y,z} \int_0^L ds \, \Omega_i^2 \left( r_i(s) - R_i(s) \right)^2
\]

Gaussian nature of the polymers

harmonic (tube-like) constraints of conformation \( r(s) \)

"classical path"
(Euler-Lagrange eq.; Hamilton canonical eq.)

polymers \( \ll \) paths of quantum particles (R. Feynman)
arc length \( s \ll i \cdot t \), \( i = \sqrt{-1} \); \( t = \text{time} \)
step length \( b \ll \frac{6}{m} \); \( m = \text{mass} \)
Tube deformation in rubber networks

\[ d_\mu^2 = \xi_\mu b \quad \mu = 1, 2, 3 \]

Tube deformation law:

\[ d_\mu = d_0 \lambda_\mu^{1/2} \]

G. Heinrich, E. Straube:

G. Heinrich, E. Straube:
Polymer Bulletin 17, 247–253 (1987)

G. Heinrich, E. Straube, G. Helmis:
Rubber Elasticity of Polymer Networks: Theories
Advances in Polymer Science 85, 33–87 (1988)
First direct observation of non-affine tube deformation in strained polymer networks

W. Pyckhout-Hintzen\textsuperscript{1}, S. Westermann\textsuperscript{1}, A. Wischnewski\textsuperscript{1}, M. Monkenbusch\textsuperscript{1}, D. Richter\textsuperscript{1}  
\textit{Jülich Centre for Neutron Science (JNCS) \& Institute for Complex Systems (ICS)}, 
Forschungszentrum Jülich, D-52428 Jülich, Germany

E. Straube\textsuperscript{2}  
\textit{FB Physik, University of Halle/Saale, D-06099 Halle, Germany}

B. Farago\textsuperscript{3}, P. Lindner\textsuperscript{3}  
\textit{Institute Laue-Langevin (ILL), Grenoble Cedex 1, France}

(Dated: January 17, 2013)

We present a one-to-one comparison of polymer segmental fluctuations, as measured by small angle neutron scattering (SANS) in a network under deformation with those obtained by neutron spin echo (NSE) spectroscopy. This allows an independent proof of the strain dependence of the chain entanglement length. The experimentally observed non-affine square-root dependence of the tube channel on strain is in excellent agreement with theoretical predictions and allows to exclude an often invoked non-deformed as well as affinely deformed tube.

PACS numbers: 29.30.Hs;83.10.Kn;83.80.Va;81.65.Lg

\[ d_{||,\perp} = d_0 \sqrt{\lambda_{||,\perp}} \]

FIG. 3: Comparison of the measured and predicted dynamic structure factors \( S(q,t)/S(q,0) \) for both directions parallel and perpendicular to the strain. Solid lines are the best fit with the de Gollaux model whereas the dashed lines correspond to the affine predictions with the same model.
Polymer-Filler Interaction: a naive approach

G. Heinrich, T. Vilgis:
*Contribution of Entanglements to the Mechanical Properties of Filled Polymer Networks*

T. Vilgis at MPI Mainz (G)
Observable Free Energy of a Filled Polymer Network

\( F = -k_B T \lim_{n \to 0} \frac{d}{dn} \log Z(n) \)

\[ Z(n) = \int \prod_{\alpha=0}^n \delta R^{(\alpha \alpha)}(s) \frac{1}{2\pi i} \int_{\mu_c} \frac{d\mu}{\mu_c^M !} \frac{d\mu_f}{\mu_f^M !} \]

\[ \exp \left\{ -\frac{3}{2n} \sum_{\alpha=0}^n \int ds \left( \frac{\partial R^\alpha(s)}{\partial s} \right)^2 + Q^* \right\} \]

\[ Q^* = \mu_c \int_{0}^{L} ds_1 \int_{0}^{L} ds_2 \prod_{\alpha=0}^n \delta \left( R^{(\alpha \alpha)}(s_1) - R^{(\alpha \alpha)}(s_2) \right) \]

\[ + \mu_f \int_{0}^{L} ds_k \prod_{\alpha=0}^n \int_{V^{(\alpha \alpha)}} dR^{(\epsilon \epsilon)}_c \]

\[ \prod_{i=1}^{n} g_i^{(\alpha \alpha)} \left( R^{(\alpha \alpha)}_i(s_i) - R^{(\alpha \alpha)}_c \right) \]

\[ g_i(R_i(s_i) - R_c) = \prod_{\mu=x,y,z} \left( \frac{2}{\pi \varepsilon_\mu} \right)^2 \]

\[ \exp \left\{ -\frac{2}{\pi \varepsilon^2_\mu} \left( R_{i\mu}(s_i) - R_{c\mu} \right) \right\} \]

average size of filler particles
Network tube model and elastic free energy

\[
W_{el} = \frac{G_C}{2} \left\{ \left( \sum_{\mu=1}^{3} \lambda_{\mu}^2 \right)^{\frac{3}{2}} \left( 1 - \frac{T_e}{n_e} \right) \left( 1 - \frac{T_e}{n_e} \right) \right\} + \ln \left( 1 - \frac{T_e}{n_e} \right) \left( \sum_{\mu=1}^{3} \lambda_{\mu}^2 - 3 \right) + 2G_e \left( \sum_{\mu=1}^{3} \lambda_{\mu}^{-1} - 3 \right)
\]

Limited chain extensibility

Cross-link modulus:

\[ G_c = \frac{1}{2} u_c k_B T = \frac{u_s l_s^2 k_B T}{2 < R_0^2 >} \]

Topological constraint modulus:

\[ G_e = \frac{u_s l_s^2 k_B T}{4 \sqrt{6} d_0^2} \]

Trapping factor: \( T_e (0 < T_e < 1) \)

\[ v_c = \left( 3 T_e^{1/2} w_g - T_e \right) \mu_c \]

(Scanlan 1960)

- E-SBR / 60 phr N339 (prestrain 200 %)
- Edwards-Vilgis upturn
- inverse Langevin upturn

= extented tube model of rubber elasticity
**Example of "Molecular Fitting"**

**Input**
- \( T = 300 \text{ K} \); \( r = 1 \text{ g/cm}^3 \);
- \( M_n \) (primary chain) \( \approx 10^5 \text{ g/mol} \); \( f = 4 \);
- \( M_{\text{stat}} = 60 \text{ g/mol} \);
- \( b = 0.6 \text{ nm} \);
- \( \alpha \) (start value) = 0.3 (limited chain extensibility)

**Results**
- \( G_c = 0.577 \text{ MPa} \)
- \( G = G_c + G_e \)
- \( G_e = 0.583 \text{ MPa} \)
- network chains per volume: \( 0.17 \text{ nm}^{-3} \)
- cross-links per volume: \( 0.10 \text{ nm}^{-3} \)
- \( M_c = 3448 \text{ g/mol} \)
- front factor \( A \approx 0.77 \)

- tube diameter \( d_0 \): \( d_0/R_c \approx 0.35 \)
- nw. chain size: \( R_c \approx 4.55 \text{ nm} \)
- constraint release: \( \beta \approx 1 \)
Rubber Chemistry and Technology 72, 602–632 (1999)

Prof. Michael Kaliske (University Hannover (G), Continental AG Hannover, now TU Dresden (G), Institute for Structural Analysis.)
Non-affine tube model

\[ G_c = 0.43 \text{ MPa} \]
\[ G_e = 0.2 \text{ MPa} \]
\[ n_e / T_e = 68 \]

Mooney-Rivlin

\[ C_1 = 0.25 \text{ MPa} \]
\[ C_2 = 0.05 \text{ MPa} \]
Plausibility Test of Hyperelastic Models

Non-affine tube model

\[ G_c = 0.43 \text{ MPa} \]
\[ G_e = 0.2 \text{ MPa} \]
\[ n_e / T_e = 68 \]

Mooney-Rivlin

\[ C_1 = 0.25 \text{ MPa} \]
\[ C_2 = 0.05 \text{ MPa} \]

M. Klüppel (DIK Hannover)
"World Cup" of Hyperelastic Models:

Table 1

<table>
<thead>
<tr>
<th>Model</th>
<th>Year</th>
<th>N.m.p</th>
<th>Parameters</th>
<th>Eqs.</th>
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<td>Mooney</td>
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<td>Neo-Hookean</td>
<td>1943</td>
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<td>3-chain</td>
<td>1943</td>
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<td>Ishihara</td>
<td>1951</td>
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<td>Biderman</td>
<td>1958</td>
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<td>$C_{10}, C_{01}, C_{20}, C_{30}$</td>
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<td>Gent and Thomas</td>
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<td>$C_1, C_2$</td>
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<td>Hart-Smith</td>
<td>1966</td>
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<td>$G, k_1, k_2$</td>
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<td>Valanis and Landel</td>
<td>1967</td>
<td>1</td>
<td>$\mu$</td>
<td>(34)</td>
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<tr>
<td>Ogden</td>
<td>1972</td>
<td>6</td>
<td>$(\mu, \alpha i)_{i=13}$</td>
<td>(25)</td>
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<td>Haines-Wilson</td>
<td>1975</td>
<td>6</td>
<td>$C_{10, C_{01}, \ldots, C_{30}}$</td>
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<td>Slip-link</td>
<td>1981</td>
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<td>$N, k N, N, k T, \eta$</td>
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<td>Constrained junctions</td>
<td>1982</td>
<td>3</td>
<td>$C_{10}, k T \mu/2, \kappa$</td>
<td>(44)</td>
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<td>van der Waals</td>
<td>1986</td>
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<td>8-chain</td>
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<tr>
<td>Yeoh and Fleming</td>
<td>1997</td>
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<td>$A, B, C_{10}, I_{m}$</td>
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<td>Tube</td>
<td>1997</td>
<td>3</td>
<td>$G_c, G_e, \beta$</td>
<td>(46)</td>
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<td>Extended-tube</td>
<td>1999</td>
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<td>$G_c, G_e, \beta, \delta$</td>
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<td>Shariff</td>
<td>2000</td>
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<td>$\mu, (\alpha_i)_{i=1,4}$</td>
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<td>Micro-sphere</td>
<td>2004</td>
<td>5</td>
<td>$\mu, N, p, U, q$</td>
<td>(49), (51)</td>
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CONCLUSION

This ranking leads to some remarks. First, only four models are revealed able to fit all experimental data considered here: the extended-tube,\textsuperscript{54} Shariff,\textsuperscript{31} micro-sphere\textsuperscript{55} and Ogden\textsuperscript{19} models. Among them, only the first three ones admit the same material parameters for both data sets. These three models are recent and they are not widely used in industrial context. The best model is the extended-tube model because it involves only four parameters and its derivation is physically-motivated. The Ogden model is older and is classically used for finite element database simulations. It is quite efficient but its six material parameters necessitate a large experimental database to be fitted.

\textit{G. Marckmann, E. Verron,}  
\textit{Rubber Chemistry \& Technology} 79, 835 (2006)
Dynamic Flocculation Model
of Stress Softening and Hysteresis
(M. Klüppel)

The MH-model
(Merseburg-Hannover)
\[
W(\varepsilon_\mu) = (1 - \Phi_{\text{eff}}) W_R(\varepsilon_\mu) + \Phi_{\text{eff}} W_F(\varepsilon_\mu)
\]

\[
W_R(\varepsilon_\mu) = \frac{G_c}{2} \left\{ \frac{\sum_{\mu=1}^{3} \lambda_\mu^{-3} (1 - \frac{T_e}{n_e})}{1 - \frac{T_e}{n_e} \left( \sum_{\mu=1}^{3} \lambda_\mu^{-3} \right)} + \ln \left[ 1 - \frac{T_e}{n_e} \left( \sum_{\mu=1}^{3} \lambda_\mu^{-3} \right) \right] \right\} + 2G_c \left( \sum_{\mu=1}^{3} \lambda_\mu^{-1} - 3 \right)
\]

**Polymer Network**
(tube model)

\[
W_F(\varepsilon_\mu) = \sum_{\mu} \frac{1}{2d} \int_{\xi_{\mu_{\text{min}}}^{\mu}}^{\xi_{\mu}^{(\varepsilon_\mu)}} G_A(\varepsilon_\mu') \varepsilon_\mu^{2} A_{\mu}(\varepsilon_\mu',\varepsilon_\mu) \varphi(\varepsilon_\mu') \, d\varepsilon_\mu'
\]

and

**Filler Cluster** (M. Klüppel)

*M. Klüppel*, Advances in Polymer Science, 2003, 164, 1
Applications in Rubber Engineering

\[ F(\{\lambda_i\}) = \sum_{Top} w_{Top} F_{Top}(\{\lambda_i\}) \]

\[ \sigma_{ij} = f(\varepsilon_{lm}) \]
\[ \sigma_{ij} = f(\varepsilon_{lm}) \]

G. Heinrich, M. Kaliske  
*Theoretical and Numerical Formulation of a Molecular Based Constitutive Tube-Model of Rubber Elasticity*  

M. Kaliske, G. Heinrich  
*An Extended Tube-Model for Rubber Elasticity: Statistical-Mechanical Theory and Finite Element Implementation*  
Rubber Chemistry and Technology 72, 602–632 (1999)
Dynamic Filler Flocculation Model (M. Klüppel et al.)

- fitting on tension tests (with OPTIMA)

**material parameters**

- $G_c = 0.27 \text{ MPa}$
- $G_e = 1.38 \text{ MPa}$
- $n = 10$
- $s_d = 4.75 \text{ MPa}$
- $s_v = 30 \text{ MPa}$
- $x_0 = 5.56$
- $\Phi_{eff} = 0.39$

⇒ only applicable as one-dimensional model

see papers from Klüppel, Schramm, Lorenz, Juhre:

Dynamic Flocculation Model of Stress Softening and Hysteresis
Stress and strain field near crack tips

SEN tensile specimen, CB-filled EPDM:
(a) photograph of prepared specimen, strains are evaluated along the indicated paths;
(b) stress softening expressed by the averaged amplification factor for a nominal tensile strain $\varepsilon_y = 0.5$

Lorenz, H.; Klüppel, M.; Heinrich, G.:
*Microstructure-based modelling and FE implementation of filler-induced stress softening and hysteresis of reinforced rubbers*
Self-healing Rubber with lower crack growth rate

Das et al., ACS Appl. Mater. Interfaces 2015, 7, 20623–20630
Requirements and Functions of Tires

The "Magic Triangle of Conflicts"
Configuration of the biaxial tester

old system

- limited displacement of the clamp-rails
- system not extendable
- asymmetric load on the clamps
- different geometry of the clamps
- heavy steel components

new system

- extended displacement on the rails \( \rightarrow \) it enables 150% strain without collision
- system is extendable
- upper and lower support of the clamps
- same geometry of the individual clamps
- low weight construction by CRP
Imaging System of the Coesfeld Biaxial Tester

- DIC – Digital Image Correlation
- DIE – Digital Image Evaluation
Tear Fatigue Analysis and J-integral

\[ J = \int \left( W \cdot \nabla u - \sigma \cdot \nabla \cdot \sigma \right) ds \]

- It holds for any geometry (also for squared samples)
- It holds for any loading conditions (even multi-axial)
- It is path independent

G. Heinrich, K. Schneider, R. Calabrò, R. Lombardi, C. Kipscholl, T. Horst, A. Schulze, S. Gorelova
Fracture behaviour of elastomers under dynamic biaxial loading conditions
Tire Technology International, Annual Review 2014, 30–32
Set-up of Constitutive Viscoelastic Model

\[
\bar{S} = \bar{S}_{eq} + \bar{S}_{ov}(t)
\]

Equilibrium stress
\[
\psi = \frac{\bar{S}}{\bar{S}_{eq}}
\]

Non equilibrium relax.
\[
\bar{S}_{ov}(t, y)
\]

Constitutive Hypothesis
- Incompressible material
- No damaging
- Additive split of stress in eq. and non-eq. part

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\[^{1}\text{Kaliske, M., & Heinrich, G., Rubber Chemistry and Technology: September 1999, Vol. 72, No. 4, pp. 602-632}\]

Simulation of multi-axial (2d) dynamic tests: effect of boundary conditions

\[ \bar{S}(t, \bar{C}(t)) = 2 \int_{0}^{t} \frac{d}{ds} \frac{d \psi_{eq}(\bar{C}(s))}{d\bar{C}(s)} \left\{ 1 + \sum_{i} \beta_i \exp \left[ -\frac{(t-s)}{\tau_i} \right] \right\} ds \]

GOOD AGREEMENT WITH EXPERIMENTAL DATA

R. Lombardi et al.:
*Experimental investigation and constitutive modeling of a filled rubber under dynamic multi-axial loading conditions*
Proceedings Rubber Con 2014
“Advanced Engineering & Materials Developments”,
Manchester (UK), 14-15 May 2014
Simulation of Tires (Rolling Resistance)

Prof. Michael Kaliske / TU Dresden

**load and speed variation**

![Image of tire test](image)

- $d_{\text{drum}} = 2$ m
- $p = 1.9$ bar
- camber angle $-3^\circ$
- tire $T_0 = 25^\circ$C
- converged value of rolling resistance for heated tire after 1800 s
- **high speed rolling** with viscous stresses included

R. Behnke, M. Kaliske, *The Extended Non-affine Tube Model for Crosslinked Polymer Networks: Physical Basics, Implementation, and Application to Thermomechanical Finite Element Analyses*; in: *From Theory to Applications*, *Advances in Polymer Science*, vol. 275, 2017 (online 2016)
Conclusions

1. Obviously, the M³H model is the most powerful constitutive and physically motivated material law for hyperelasticity of rubbers. It consequently follows the path from polymer network physics to industrial materials design.

2. **Application** of M³H model in industrial context follows the well established iDdc.

\[ M^3H = \text{Manchester-Merseburg-Mainz-Hannover} \]
\[ \text{iDdc} = \text{in Dresden developed concept} \]

Manchester
Merseburg
Mainz
Hannover
Every day each one of us trusts on rubber

Some days more than others...

Thank you for your kind attention!