A Micromechanically Based Model for Viscoelasticity of Rubber Polymers

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Abstract

The goal of this work is to apprehend the role of reorientation in the microdynamics of rubber-like materials. Their remarkable mechanical properties are commonly assigned to their complex microstructure. That involves a bog number of long (up to 10000 monomers) macromolecules cross-linked by chemical bonds and thus forming a complicated network. The dynamics of this network is of stochastic nature, since that is a large system with no strict order performing random thermal motion. Those models that take into account this microstructure and capture its response at least on average macroscopic level turn out to have better predictive properties than the alternative purely phenomenological models.

That motivates the development of the proposed model of rubber viscoelasticity based on the evolution of material microstructure. The key aspect in this model is stochastic motion that also includes reorientation of chain segments in the viscoelastic part of the network. It is believed to drive the relaxation mechanisms on the microlevel, in particular the redistribution of stretch of chain segments in the network. The process is seen as a Brownian motion of chain segments and is described by the Smoluchowski equation. The equation governs the change of the distribution of stretch within the subnetwork due to the macrodeformation and internal relaxation of the microstructure.

As a final result an equivalent tensorial formulation of this micromechanically based model is derived. Its thermodynamical consistency comes intrinsically from the micromechanical origin. The performance of the model is illustrated by its fitting capabilities on a broad experimental dataset.
1. Introduction

The present work is focused on the viscoelasticity of rubbery polymers. Polymer materials exhibit incredible properties heavily exploited in numerous applications. One can find them in various aggregate states: they can be liquid or like amorphous dough, they can be solid, either elastic rubber-like or ductile glassy, they can constitute fibers and crystals, the variety of forms they take is really impressive. And, obviously, in all these states polymer materials display different sometimes unique mechanical properties. In particular rubber-like polymers that are considered in this work are not an exception in this respect. Their response to mechanical deformation is generally referred as hyperviscoelastic. First of all it is characterized by large (up to 1000%) deformations rubbery polymers can sustain with small if any residual strains. Furthermore this response is nearly incompressible, i.e. the bulk modulus is much greater than the shear modulus. The latter is usually found to be $10^3 - 10^4$ times lesser than those characteristic of metals. Another distinctive feature is the rate- and history-dependence of the stresses in such materials. Experimental investigations indicate the broad relaxation spectrum and high relaxation ratios of natural and synthetic rubbers.

Hence a substantial effort has been made to develop realistic constitutive models for macroscopic response of these materials. For this purpose two main approaches have been utilized so far: phenomenological and micromechanically based.

1.1. Motivation and state of the Art

This division can be distinctly observed in one of the most developed areas of polymer mechanics, namely, in the elasticity of rubber-like materials. A distinctive feature of elastomers is their ability to undergo large deformations with an almost full recovery of initial shape upon unloading [42]. This hyperelastic response is attributed to the peculiar microstructure of rubber-like materials. It includes a network of highly mobile and flexible polymer chains formed by their three-dimensional cross-linking. It’s nothing else but thermodynamics of this network that is believed to determine the overall macromechanical rubber-like hyperelasticity. That’s why purely phenomenological models fail to predict highly non-linear behaviour at all types of loading in the whole range of deformations ([6],[33]).

More recent micromechanically-based models benefit a lot by accounting for the deformation of the chain network that makes up the macromechanical structural response. The starting point for all these developments is the thermodynamics of a single stretched polymer chain in the network. The corresponding models that are, certainly, idealized to lesser or greater extend are derived by means of statistical mechanics. One can track their development by [27],[26],[22],[15].

There’s the common practice is to consider a polymer molecule as an idealized chain of freely rotating links. This simplest freely joined chain model assumes that a single macromolecule performs a random thermal motion in a medium that does not expose any constraints on it. Thus such a chain consists of $N$ bonds of fixed equal length $l$. The angles between adjacent bonds are considered to be random with equally distributed probability. Therefore bonds orientations do not correlate. Such simplifications result in Gaussian distribution of end-to-end distance $r$ of the chain which is the key kinematic quantity [42]. Usually one introduces the microstretch $\lambda = r/r_0$ ($r_0$ - the mean-square value
of $r$), a dimensionless quantity that is again Gaussianly distributed. One can finally relate the entropy of this Gaussian chain at given stretch $\lambda$ through the Boltzmann’s equation, which constitutes the basis for the so-called entropic elasticity. Really, the internal energy is related to nothing else but the temperature. Therefore the free energy evolution and hence any mechanical response is only due to the change of entropy.

The described above model perfectly illustrates the general framework of most entropic elasticity theories. Nevertheless it is oversimplified and has a limited application area. Particularly, it doesn’t account for the finiteness of chain extensibility and hence is not able to describe elastic response of polymers at high stretches. To overcome this deficiency a big family of non-Gaussian models has been developed.

One of the most widely used non-Gaussian models is derived under the idealized network representation. An isobaric-isothermal ensemble is considered to describe the micromechanical states due to the presence of finite extensibility constraint ([10], [32]).

Introduction of other constraints leads to more advanced chain elasticity models beyond the idealized polymer network setting which assumes no interaction between molecules. According to the type of topological constraints taken into account one can distinguish constrained junction models ([14], [40]) and constrained segment models ([12], [18]). The former formulate the constraints around the cross-links whereas the latter focus on the interaction effects along the chain length. Among the models describing the interaction between chain segments tube model and extended tube model should be mentioned ([11], [12], [23]). They’ve proved themselves to be advantageous for description of area contraction of incompressible rubber-like materials and related macroscopic response ([37], [19]).

Still micromechanical model of polymer network, however precise it were, doesn’t have any value without a relation to macroscopic behavior. Again many approaches serve this purpose. One can refer to several reviews done on this subject ([6], [33]).

The simplest physically based constitutive setting is probably the neo-Hookean model ([42]). The derived free energy expression based on Gaussian statistics is given in terms of first principle invariant of right Cauchy-Green strain tensor $I_1$ and includes linear dependency on the temperature. The model displays good agreement with experiment for all types of loading and deformations lower than 50%.

All the further developments one can divide into affine network models and non-affine network models. The former are presented by the three-chain ([22], [43]) and full-network models ([42], [44]). A distinctive feature of these models is that some set of chains representing the whole network in a material point is assumed to follow affinely the macroscopic strain. In the latter type of models such as four-chain model ([13]), eight-chain model ([2]) and non-affine microsphere model ([37]) affinity of strain is not preserved.

It’s commonly accepted ([33]) that affine network models are not appropriate for describing elastic behaviour at large strains. The point is that the chains oriented in the direction of loading display higher resistance to the stretch when it approaches the limiting value compare to the other chains in the network. Hence the internal structure of polymer becomes heterogenous, which leads to deviation of chain stretches from the macrostrain: the microstructure adjusts in order to minimize the free energy. Remarkably, the non-affine microsphere model incorporates minimization procedure inlined in the homogenization ([37], [16]), hence following the qualitative behaviour of the network.
In a detailed review [33] one can find a ranking of existing micromechanically-based models of polymer elasticity according to their ability to predict true mechanical response of elastomers at different types of loading. A conclusion can be done that the recent models display quite a good performance and, particularly, fit nicely the available experimental data. That should be attributed to the substantial effort made in this field. Moreover the developed approaches are applicable to modeling of non-elastic behaviour of polymers.

The latter is a challenging task and still forms an appealing area of research. A substantial progress in constitutive modeling of irreversible processes in polymers has been done recently. The main topics the researches are focused on are: finite viscoelasticity of rubber-like polymers; deformation-induced softening of rubbery polymers, i.e. Mullins effect ([39]); finite viscoplasticity of glassy polymers; aging of rubber-like polymers to name a few.

Traditionally, non-elastic behaviour of polymers has been investigated from two different viewpoints. The engineering and mechanical community would constitute purely phenomenological models with a strong focus on the numerical modeling. At the same time in physical chemistry and material science the researchers would concentrate on molecular models of these phenomena and their experimental justification by microscopic studies. There was hardly any connection between these two branches of studies. On the one hand material models in continuum mechanics would include non-physical quantities, mainly tensorial, that just can not be measured in reality (take hardening microstress in plasticity as an example). On the other hand atomistic models apply for single molecules (and hence require to reproduce in detail the true material microstructure) and furthermore are quite often statistical but not deterministic.

The stated above division can be illustrated on the example of viscoelasticity of rubber-like materials. The phenomenological approaches exploit largely the formalism of tensorial stress- or strain-like internal variables. One can find recent models based on stress-type variables in the form of convolution integrals in the works [21], [29], [24]. Some other authors use the multiplicative split of deformation gradient into elastic and inelastic parts ([25], [4]) or use viscous metric tensor as internal variable ([38]). As mentioned before the variables that are incorporated into these models are rather mathematical (geometrical) then physical and have no relation to the microstructure.

An alternative to the continuum approaches are the molecular-based theories. These have been developed recently to describe viscous behavior of molten polymers and amorphous rubber-like materials. The bead-spring ([5]), reptation-type tube models ([9], [11]) and transient network model ([17], [41]) are the major results in this area. With rare exception([4], [31]) one will not find any application of these theories to the phenomenological modelling.

It is only the recent progress in micromechanically-based approaches ([2], [37]) what has given space for incorporation of molecular theories of non-elastic phenomena into the macroscopic material models. Currently many researches have appreciated the advantages of micromechanical justification approaches and this research area is now actively developing.

The micro-sphere model ([37]) mentioned above in the context of rubber-like elasticity turned out to be the most appropriate for the extension towards the constitutive modeling of polymers inelasticity. Besides the recent results for the viscoelasticity of rubber-like materials ([35]), this model has been also utilized to predict their aging and damage ([36],
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What is advantageous in this model is the homogenization technique it is based on. It allows to introduce internal variable fields on the microsphere. The output of the homogenization is the macroscopic free energy, macroscopic stresses and moduli. All the history variables remain on the microlevel and no tensoric history variables are introduced. That is really different to the phenomenological modeling described above. Exploiting micro-sphere homogenization on can introduce micromechanical state variables that have physical sense and hence can be related to realistic molecular models.

A particular interest to the current work represents the theory offered in [17]. This extents kinetic theory of rubber elasticity that was developed by many authors ([20],[22],[27],[26],[13]) and is intrinsically molecular-based. The authors offer a relaxation mechanism based on breakage and re-bonding of chains in the network. The most stretched chains are considered to break off from the network and join it again in certain time at a relaxed configuration. The constant amount of chains in the network is introduced by the balance between de-bonding and re-bonding rates. Surprisingly, the approach offered by the authors and their treatment of the relaxation processes in the transient network is not acknowledged by the recent works on the subject. Thus in the paper [30] extending the Green-Tobolsky model its micromechanical origin is nearly neglected, which led to the motivation for this thesis and our work published in [28].

1.2. Scope of the work

The performed literature survey shows that micromechanics has a great influence on the properties of rubbery polymers. Application of molecular theories is an elegant way to obtain robust models of different phenomena. A particular interest is drawn to kinetic theories developed within the framework of statistical mechanics and thermodynamics. In this work we endeavor to follow this approach and to develop a model of rubber viscoelasticity with a micromechanical origin. The key idea of the work is to treat relaxation of the viscoelastic rubber material as a diffusion-based process that results in irreversible changes on the microstructure. These changes are believed to take place in mobile subnetworks that are responsible for the production of the viscous overstress. The process in each subnetwork at a separate material point is described by the polymer chain stretch distribution field that evolves with time.

According to these approach the work is divided in several parts. First in Section 2 the general framework of finite viscoelasticity of a nearly incompressible solid is given. That provides the description of the finite deformation and the basic thermodynamics of continuum. Section 3 contains the micromechanical part of the model. Starting with an entropic spring representation of a single polymer chain that is based on its equilibrium kinetics a model for mobile subnetwork evolution is developed. That is based on the concept of Brownian motion applied to network chains treated as "particles". The final outcome is the flow equation with respect to the stretch probability field that describes the microdeformation of a single subnetwork.

The ultimate goal of the work is attained in Chapter 4. There the macroscopic part of the model is presented. The non-affine microsphere model is utilized for the modeling of the ground elastic response. The main contribution of the work is the viscous overstress model. In this chapter a macroscopic formulation of the viscous subnetwork model is obtained. It turned to be possible to describe the evolution of the microdeformation
by means of a Lagrangian tensorial quantity, which allowed to derive finally a compact three-dimensional formulation for the viscous overstress. The latter has a simple algorithmic representation that concludes the chapter.

Finally, the performance of the model is illustrated in Chapter 5. A parameter fit for the experimental data is performed. It is verified on a set of representative problems for which experimental and numerical data were compared.
2. Basic network mechanisms of finite rubber viscoelasticity

This section briefly summarizes the resulting constitutive equations of finite rubber viscoelasticity under the basic assumption of the polymer microstructure being assembled by several idealized polymer networks.

2.1. Network model of the microscopic response of rubber-like materials

Conceptually in line with the approach in [4], the response of the rubber-like material is considered to be decomposed into a ground network formed by strongly cross-linked macromolecules and a subnetwork consisting of highly mobile and based on temporary entanglement mechanisms linked macromolecules. Whereas the ground network is associated with the elastic response of the material, the subnetwork is responsible for the description of the viscous material properties in the form of the appearance of a viscous overstress. An illustration of the resulting viscoelastic behavior is given in Figure 2.1 displaying a schematic representation of the individual networks under an applied macrodeformation. Based on such deformation, the ground network stretches and drags the mobile subnetwork along with it. After a sufficient amount of time at a constant deformation, the subnetwork relaxes towards a state at which it produces no viscous overstress.

Whereas the elastic ground network can be represented by models such as the 8-chain model developed in [2] or the non-affine network model developed in [37], among many others, the emphasis of this work is to develop a diffusion based micromechanical motivated model for the representation of the viscous mobile subnetwork. In fact, the numerical simulations presented in Section 5 make use of the model developed in [37] for the representation of the elastic ground network but it should be kept in mind that the developed model of the viscous subnetwork does not rely on a particular model choice for the description of the elastic properties.

2.2. Macroscopic representation of finite rubber viscoelasticity

Following the geometric setting of finite inelasticity, the macroscopic finite rubber viscoelastic response is based on a volumetric-isochoric decomposition, where the isochoric part itself is decomposed into an elastic equilibrium and a viscous overstress response, as it is briefly summarized in this section.

To do so, consider a body to be a collection of material points which at time $t \in \mathbb{R}_+$ occupies a spatial configuration $\phi_t(B) \subset \mathbb{R}^{n_{dim}}$ in terms of the space dimension $1 \leq n_{dim} \leq 3$. An individual material point of the body at time $t$ is located at position $x \in \phi_t(B)$. The change of properties of such material point in the body is described relative to a fixed reference configuration $B \subset \mathbb{R}^{n_{dim}}$ which for instance can represent the configuration occupied by the body at the instant time $t_0$ in which the material point is located at position $X \in B$. To avoid any explicit reference to the body itself, the nonlinear deformation map $\phi_t(X): X \mapsto x = \phi_t(X; t)$ is introduced which maps positions $X \in B$ onto positions $x \in \phi_t(B)$. Key kinematic quantities are the local deformation gradient $F = \nabla \phi_t(X; t)$ representing the linear map between tangent vectors in the reference
and the spatial configuration, respectively, where the Jacobian $J = \det F$ has to satisfy $J > 0$, as well as the covariant Cartesian metric tensors $G = \delta_{AB}$ and $g = \delta_{ab}$ of those configurations written in terms of the Kronecker symbol. The boundary value problem of the macroscopic finite viscoelastic problem at hand for the quasi-static case is then governed by the balance of linear momentum

$$\text{Div}\left[\tau F^{-T}\right] + \bar{b} = 0 \quad (2.1)$$

written in terms of the divergence operator Div with respect to the reference position $X$ together with prescribed displacement boundary conditions $\phi_t = \bar{\phi}_t(X; t)$ on $\partial B_x$ and prescribed traction $[\tau F^{-T}]N = \bar{t}(X; t)$ on $\partial B_t$ with outward normal $N$. The usual conditions $\partial B_x \cap \partial B_t = \emptyset$ and $\partial B_x \cup \partial B_t = \partial B$ have to hold in each component of the deformation mapping. In (2.1), the density $\rho_0$ and the prescribed body force field $\bar{b}$ with respect to the unit volume of the reference configuration as well as the Kirchhoff stress tensor $\tau$ are introduced. The latter is assumed to be a function of the local deformation gradient $F$ and some internal variables $I$ responsible for the characterization of the viscous structural changes. The Kirchhoff stress $\tau$ and its associated moduli are given as

$$\tau = 2\partial g \psi(g, I; F) \quad \text{and} \quad C = 4\partial^2_{gg} \psi(g, I; F) \quad (2.2)$$

in terms of the macroscopic free energy per unit volume of the reference configuration stored in a deformed polymer network with the requirement of being material frame invariant in the sense that $\psi(g, I; QF) = \psi(g, I; F)$ for all rotations $Q \in SO(3)$.

The rubber-like material considered in this work is assumed to be nearly incompressible which motivates a decoupled volumetric-isochoric formulation based on the decomposition of the macroscopic free energy as

$$\psi = U(J) + \tilde{\psi}(g, I; \bar{F}) \quad (2.3)$$

in terms of the volumetric and isochoric contributions, respectively. The latter is given in terms of the unimodular part of the deformation gradient defined as $\bar{F} = J^{-1/3}F$ which is assumed to drive the deviatoric part $\bar{\tau} = 2\partial g \tilde{\psi}(g, I; \bar{F})$ of the total stresses decomposed into spherical and deviatoric contribution as

$$\tau = \rho g^{-1} + \mathbb{P} : \bar{\tau} \quad (2.4)$$

\begin{figure}[h]
\centering
\includegraphics[scale=0.5]{network_representation.png}
\caption{Network representation of the microscopic response of rubber-like materials. The schematic response of the material decomposed into a strongly cross-linked ground network (representing the elastic response) and a mobile subnetwork (formed by temporary entanglement mechanisms representing the viscous response) is illustrated under an applied macrodeformation.}
\end{figure}
with \( p = J U'(J) \) and the fourth-order deviatoric projection tensor \( P^{ab}_{cd} = [\delta^a_c \delta^d_b + \delta^a_d \delta^b_c]/2 - \delta^{ab} \delta_{cd}/3 \). This decomposition carries along into the representation of the moduli \( C \) written in terms of the deviatoric part \( \tilde{C} = 4 \partial_{gg} \tilde{\psi}(g, I; \bar{F}) \) as

\[
C = (p + \kappa)g^{-1} \otimes g^{-1} - 2p I + \left[ \tilde{C} + \frac{2}{3}(\bar{\tau} : g) I \right] : P - \frac{2}{3}(P^T : \bar{\tau} \otimes g^{-1} + g^{-1} \otimes \bar{\tau} : P) \quad (2.5)
\]

with \( \kappa = J^2 U''(J) \) and in terms of the fourth-order identity tensor \( I^{abcd} = [\delta^{ac} \delta^{bd} + \delta^{ad} \delta^{bc}]/2 \).

To account for the actual behavior of rubber viscoelasticity, the isochoric part of the above model is further decomposed into elastic and viscous parts in accordance with the representation of the polymer network structure into an elastic ground network and a viscous subnetwork illustrated in Figure 2.1. In case of \( s \) viscous subnetworks which are introduced to obtain a discrete spectrum of relaxation times related to different viscosities \( \{\eta_i\}_{i=1}^s \), the isochoric part \( \tilde{\psi} \) in (2.3) of the free energy can be additively split into

\[
\tilde{\psi} = \tilde{\psi}^e(g; \bar{F}) + \tilde{\psi}^v(g, I; \bar{F}) \quad \text{where} \quad \tilde{\psi}^v(g, I; \bar{F}) = \sum_{i=1}^s \tilde{\psi}^v_i(g, I_i; \bar{F}) \quad (2.6)
\]

is given as a summation over each of the \( s \) viscous subnetworks. The corresponding rheological model for such an isochoric response of the material is illustrated in Figure 2.2. This further yields to the decomposition of the deviatoric part of the stresses into an elastic equilibrium stress response and a viscous overstress response according to

\[
\bar{\tau} = \bar{\tau}^e + \bar{\tau}^v \quad \text{with} \quad \bar{\tau}^e = 2 \partial_g \tilde{\psi}^e(g; \bar{F}) \quad \text{and} \quad \bar{\tau}^v = 2 \partial_g \tilde{\psi}^v(g, I; \bar{F}) \quad (2.7)
\]

Whereas the response of the elastic equilibrium stress is assumed to be isotropic, resulting in the condition \( \tilde{\psi}^e(g, FQ) = \tilde{\psi}^e(g; \bar{F}) \forall Q \in SO(3) \), a deformation induced anisotropy
is provided by the dissipative viscous overstress which is characterized by the evolution of the internal variables $\mathcal{I}$ in time. To obtain a formulation consistent with the second axiom of thermodynamics the local dissipation has to satisfy the inequality

$$D_{\text{loc}} = -\partial_{\mathcal{I}}\bar{\psi} \cdot \dot{\mathcal{I}} = \sum_{i=1}^{s} D_{\text{loc},i} \geq 0 \quad \text{where} \quad D_{\text{loc},i} = -\partial_{\mathcal{I}_i}\bar{\psi} \cdot \dot{\mathcal{I}}_i. \quad (2.8)$$

After presenting a brief overview of the basic network mechanisms of rubber viscoelasticity and its incorporation into standard finite rubber viscoelasticity, the remaining part of the work is concerned with the development of a diffusion based, from a microscopic point of view physically motivated, model resulting in expressions for the viscous part $\bar{\psi}^v$ of the isochoric free energy as well as for the viscous overstress response $\bar{\tau}^v$. Whereas Section 3 will develop the diffusion-based micromechanical polymer model, its incorporation into the macroscopic framework above is achieved in Section 4 and finally evaluated through representative numerical simulations in Section 5.
3. Micromechanical Model

Flexible polymers can take an enormous number of conformations in time by the rotation of chemical bonds. That’s why the statistical methods should be applied for the description of their micromechanical states. In this chapter we will examine the basic behavior of polymer chains both in equilibrium and in dynamics by means of statistical mechanics.

3.1. The Gaussian statistics of a single chain

A single polymer chain statistics is a starting point of the micromechanical model. Here and further on in this work we restrict ourselves to the simplest freely jointed model, which captures the most characteristic properties of polymer chains. Within this model a chain is considered to consist of \( N \) links, each of length \( b \). Their orientations are assumed to be random and independent of each other (see Fig. 3.1). The conformation of such freely jointed chain is determined either by \((N+1)\) position vectors \( \{R_n\}_{n=0}^N \) of the joints (including the two end points) or alternatively by a set of \( N \) bond vectors \( \{r_n\}_{n=1}^N \)

\[
r_n = R_n - R_{n+1}, \quad n = 1..N.
\]

The latter set is more suitable for the description of the state of the chain viewed as a statistical system, since bond vectors \( r_n \) according to the basic assumptions are independent.

Hence the probability of a chain conformation \( \{r_n\}_{n=1}^N \) is nothing else but the product of probabilities

\[
P(\{r_n\}_{n=1}^N) = \prod_{n=1}^N p(r_n).
\]

The isotropic distribution of random bond vectors that have fixed length \( b \) is expressed in terms of a delta-function or rather a single-layer potential in \( \mathbb{R}^3 \)

\[
p(r) = \frac{1}{4\pi b^2} \delta(|r| - b)
\]

normalized according to condition \( \int_{\mathbb{R}^3} p(r) \, dr = 1 \).

The size of a polymer aggregate is then characterized by the end-to-end vector \( R \)
(see Fig. 3.1c) which is also a random quantity

$$ R = R_N - R_0 = \sum_{n=1}^{N} r_n. $$ (3.4)

This vector has a zero mean value but a non-zero mean-square value

$$ \langle R \rangle = \sum_{n=1}^{N} \langle r_n \rangle = 0, $$ (3.5)

$$ R_0^2 := \langle R^2 \rangle = \sum_{n,m=1}^{N} \langle r_n \cdot r_m \rangle = \sum_{n=1}^{N} \langle r_n^2 \rangle + \sum_{n \neq m} \langle r_n \cdot r_m \rangle = Nb^2, $$ (3.6)

since $\langle r_n \rangle = 0$ ($r_n$ are equally distributed in all directions) , $\langle r_n \cdot r_m \rangle = 0$ (for $n \neq m$ bond vectors are independent), $\langle r_n^2 \rangle \equiv b^2$ (lengths of the bond vectors is fixed and equal to $b$). Here we denote by $\langle \bullet \rangle$ the mean value of a random quantity $\bullet$ that is computed as an integral over the probability space $P \ni \{ r_n \}_{n=1}^{N}$:

$$ \langle \bullet \rangle = \int dP(\bullet). $$ (3.7)

The computed mean value does not provide the necessary information about the statistical system. One needs to know the distribution of the end-to-end vector that for this random flight model is expressed as

$$ \mathcal{P}(R) = \mathcal{P} \left\{ r_n \right\}_{n=1}^{N} \mathcal{P}(\{ r_n \}_{n=1}^{N}) \delta \left( R - \sum_{n=1}^{N} r_n \right). $$ (3.8)

Using the identity for the Dirac delta-function

$$ \delta(r) = \frac{1}{(2\pi)^3} \int_{\mathbb{R}^3} dk e^{i \mathbf{k} \cdot \mathbf{r}} $$

one can follow [11] and compute (3.8) as

$$ \mathcal{P}(R) = \frac{1}{(2\pi)^3} \int_{\mathbb{R}^3} dk \exp \left[ i \mathbf{k} \cdot \left( R - \sum_{n=1}^{N} r_n \right) \right] $$

$$ = \frac{1}{(2\pi)^3} \int_{\mathbb{R}^3} dk \exp \{ i \mathbf{k} \cdot \mathbf{R} \} \prod_{n=1}^{N} \int_{\mathbb{R}^3} d\mathbf{r}_n p(r_n) \exp [ i \mathbf{k} \cdot \mathbf{r}_n ] $$

$$ = \frac{1}{(2\pi)^3} \int_{\mathbb{R}^3} dk \exp \{ i \mathbf{k} \cdot \mathbf{R} \} \left( \frac{\sin |\mathbf{k}| b}{|\mathbf{k}| b} \right)^N. $$ (3.9)

For large $N$ one can use an approximation

$$ \left( \frac{\sin |\mathbf{k}| b}{|\mathbf{k}| b} \right)^N \approx \exp \left( -\frac{Nk^2b^2}{6} \right) $$
to derive further the final expression for the distribution of the end-to-end vector of a freely rotating chain

\[ \mathcal{P}(\mathbf{R}) = \frac{1}{(2\pi)^3} \int_{\mathbb{R}^3} d\mathbf{k} \exp\{i \mathbf{k} \cdot \mathbf{R}\} \left( -\frac{Nk^2b^2}{6} \right) \]

\[ = \frac{1}{(2\pi)^3} \prod_{\alpha=1}^{3} \int_{-\infty}^{\infty} dk_{\alpha} \exp\left[ i k_{\alpha} R_{\alpha} - \frac{Nk_{\alpha}^2b^2}{6} \right] \]

\[ = \frac{1}{(2\pi)^3} \prod_{\alpha=1}^{3} \frac{6\pi}{Nb^2} \exp\left[ -\frac{3}{2Nb^2} R_{\alpha} \right] \]

\[ = \left( \frac{3}{2\pi R_0^2} \right)^{3/2} \exp\left[ \frac{3}{2} \frac{R^2}{R_0^2} \right], \quad R = |\mathbf{R}|. \quad (3.10) \]

Hence the distribution of the end-to-end vector \( \mathbf{R} \) is Gaussian. This result given here for the case of a freely jointed chain holds for a much broader class of statistical systems and is generally associated with the central limit theorem.

The obtained distribution (3.10) gives the unrealistic non-zero values for \(|\mathbf{R}|\) greater than \(Nb\) which is the length of a fully extended chain and can not be in principle exceeded. Nevertheless that provides a good estimate for the theories in which highly stretched states of polymers do not play an important role. In this section the Gaussian estimate (3.10) is accepted.

The distribution \( \mathcal{P}(\mathbf{R}) \) provides very important information since it measures the number of conformations of an unconstrained chain. That can be directly linked to the entropy, particularly in the case when some constraints are applied. Thus the simplest constrained state of the chain one can think of is a chain with fixed ends. Restraining of their motion leads to a substantial decrease of the number of conformations chain segments can attain and hence to corresponding a change of entropy that can be computed using Boltzmann’s equation

\[ \Delta \eta = k_B \ln \mathcal{P}(\mathbf{R}), \quad (3.11) \]

where \(k_B\) is the Boltzmann’s constant.

Hence considering a thermodynamic system of a polymer chain with the constrained position of the ends one can postulate the entropy in the form

\[ \eta(\mathbf{R}) = k_B \ln \mathcal{P}(\mathbf{R}) + \text{const} = -\frac{3}{2} k_B \frac{R^2}{R_0^2} + \text{const}. \quad (3.12) \]

Such a system can be viewed as an entropic spring as depicted in Fig. 3.2 with the free energy that can be expressed in case of no internal energy storage by

\[ \Psi(\mathbf{R}) = -\theta \eta(\mathbf{R}) = \frac{3}{2} k_B \theta \frac{R^2}{R_0^2} + \text{const}, \quad (3.13) \]

for the known \(\theta\), the temperature of the polymer.

This viewpoint can be taken to derive the thermodynamic force acting on the fixed ends of the chain

\[ F_R = \frac{\partial \Psi}{\partial R} = 3k_B \theta \frac{R}{R_0^2} \quad (3.14) \]
Figure 3.2: Polymer chain as an entropic spring

which expresses the average response from the thermal motion of the chain segments (see Fig. 3.2).

This simple theory illustrates a more general approach to the polymer mechanics. It postulates that the polymer materials consist of highly mobile thermally activated aggregates. The mechanical response of the thermodynamical systems they form is provided by the internal constraints that introduce some order and hence increase the resistance of the material to the deformation. Hence the microstructure with a permanent order (e.g. constant cross-linking topology) displays the entropic elasticity. The presence of the temporary constraints (bonding and detachments of aggregates, mutual entanglements etc.) leads to the time-dependent phenomena such as viscoelasticity and visco-elastoplasticity frequently related to the constraint release effects.

3.2. Brownian motion of particles

Viscoelasticity is a time-dependent phenomenon related to the dissipation of mechanical work. Hence on the micromechanical level it needs to be treated within the framework of non-equilibrium thermodynamics. In the developed model we treat viscoelastic relaxation of the microstructure as a diffusion-based process and incorporate formalism of Brownian motion.

In this exploration we take a phenomenological approach ([11]) that is more suitable for the derivation of averaged quantities we are interested in. According to this approach the Brownian motion is seen as a stochastic process that is governed by known macroscopic laws (though they are applied to the microscopic objects). Such a treatment is restricted to the time-scales and length-scales larger than those characteristic of the equilibrium thermal oscillations. The resulting phenomenological evolution equation can in one of the possible forms, namely in the form of the Smoluchowski equation, generalizes the diffusion equation and is clearly related to the thermodynamics of the irreversible processes.

In this subsection we focus on the Brownian motion of point particles that possess only the translational degrees of freedom. That allows for clear and illustrative derivation of the Smoluchowski equation which can be later on easier extended on the case of polymer chains diffusion.

Consider a system consisting of a great number of particles submerged in a viscous medium (Fig. 3.3). The discussed phenomenon of diffusion is observed in such a system in the case when the distribution of particles in the medium due to some reasons is not uniform. It shows up in the form of the flux that is proportional to the spatial gradient of the concentration. The microscopic origin of the flux is the random thermal motion of the particles. In the case of nonuniform concentration the number of particles that happen to flow from the region of higher concentration to the region of lower concentration is
larger than the number of particles flowing in the opposite direction (see Fig. 3.3). This imbalance is what ultimately produces the macroscopic flux.

To describe this process consider the probability function \( p(x,t) \) which expresses the probability of finding a particle at a position(state) \( x \) at certain time \( t \). That can be simply viewed as the concentration \( c(x,t) \) scaled to the total number of particles \( n \): \( c(x,t) = \frac{n}{D^2} p(x,t) \). This distribution evolves due to the flux \( h(x,t) \), which is governed by the flow equation

\[
\frac{\partial p(x,t)}{\partial t} = -\nabla_x h(x,t)
\]  

(3.15)

that simply expresses the balance of mass (particles). This flux has several components that are to be determined.

First part of the flux comes from the thermal motion of particles in the presence of inhomogeneity of concentration as mentioned above. That produces a probability flux

\[
h_{df} = -D \nabla_x p(x,t)
\]  

(3.16)
in the direction opposite to the gradient of the probability and proportional to the diffusion constant \( D \). The Einstein relation gives an expression

\[
D = \frac{k_B \theta}{\eta}
\]  

(3.17)
in terms of viscosity \( \eta \) of the surrounding medium.

Another part of the flux will appear in case when external forces are acting on the particles. Consider a stationary potential field \( U(x) \) and the force field

\[
F(x) = -\nabla_x U(x)
\]  

(3.18)
determined for each point \( x \) of the medium. One can relate it then to an additional non-vanishing average velocity

\[
\langle v(x) \rangle = \frac{1}{\eta} F(x) = -\frac{1}{\eta} \nabla_x U(x).
\]  

(3.19)

The average is taken over all the particles that happen to occur in point \( x \) at time \( t \). Multiplying this average velocity on the current concentration of the particles at this point yields the expression for the additional fluxed induced by the potential \( U(x) \)

\[
h_{pot} = -\frac{p(x,t)}{\eta} \nabla_x U(x).
\]  

(3.20)
The resulting from the superposition of these two components flux

\[ h = h_{\text{dif}} + h_{\text{pot}} = -\frac{k_B \theta}{\eta} \nabla_x p(x,t) - \frac{1}{\eta} \nabla_x U(x) \]  

(3.21)
can be further expressed in terms of a chemical potential

\[ U_{\text{ch}}(x,t) = k_B \theta \ln p(x,t) + U(x) \]  

(3.22)as

\[ h_{\text{rel}} = -p(x,t) \frac{1}{\eta} \nabla_x U_{\text{ch}}. \]  

(3.23)

This dynamic potential expresses the energy per particle at the state \( x \) so that the whole process can be seen as the motion of particles from the states with higher energy to the states with lower energy. This motion is driven by a chemical force

\[ \mathbf{F}_{\text{ch}} = -\nabla_x U_{\text{ch}} \]  

(3.24)

that determines the average velocity of particles relative to the viscous surrounding as

\[ \langle v_{\text{rel}} \rangle = \frac{1}{\eta} \mathbf{F}_{\text{ch}}. \]  

(3.25)

With the expression (3.25) at hand one can further consider the macroscopic motion of the medium that obviously influences the flow of particles. Thus one should also include the contribution of the macroscopic velocity field \( \mathbf{\bar{v}}(x,t) \) to the total average velocity and flux:

\[ \mathbf{v} = \mathbf{\bar{v}} + \langle v_{\text{rel}} \rangle \Rightarrow \mathbf{h} = p \mathbf{\bar{v}} + \mathbf{h}_{\text{rel}}, \]  

(3.26)

which leads to the final formulation of the Smoluchowski equation for the Brownian motion of particles subjected to an external potential force field in a moving viscous medium

\[ \partial_t p = - \text{div}_x \left[ p \left( \mathbf{\bar{v}} - \frac{1}{\eta} \nabla_x U_{\text{ch}} \right) \right] \]  

(3.27)

\[ = - \text{div}_x \left[ p \mathbf{\bar{v}} + \frac{1}{\eta} \nabla_x \left( k_B \theta \ln p + U(x) \right) \right]. \]

The Smoluchowski equation has a very important property, namely it is dissipative. To show that consider a functional

\[ \mathcal{A}(p) = \pi \int p(x,t) U_{\text{ch}} \, |dx| \]  

(3.28)
of current distribution \( p(x,t) \) that summates the potential \( U_{\text{ch}} \) over all the particles in the system (note that the number of particles \( \pi \) comes into the expression). The time change of \( \mathcal{A} \) provided there’s no macroscopic motion and no change in temperature is computed as

\[ \left( \frac{d \mathcal{A}}{dt} \right)_{\pi, \theta} = \frac{1}{\pi} \int p(x,t) \left[ k_B \theta \ln p(x,t) + U(x) \right] \, |dx| = \pi \int \left[ k_B \theta \ln p + U \right] \partial_t p \, |dx| \]

\[ = \pi \int \left[ k_B \theta \ln p + U \right] \left\{ \frac{1}{\eta} \nabla_x \cdot \left[ p \nabla_x \left( k_B \theta \ln p + U(x) \right) \right] \right\} \, |dx| \]

\[ = -\pi \int \frac{1}{p} \left[ p \nabla_x \left( k_B \theta \ln p + U(x) \right) \right] \cdot \frac{1}{\eta} \left[ p \nabla_x \left( k_B \theta \ln p + U(x) \right) \right] \, |dx| \]

\[ = -\pi \int \frac{\eta}{p} \mathbf{h}_{\text{rel}} \cdot \mathbf{h}_{\text{rel}} \, |dx| \leq 0 \]  

(3.29)
for $p(x,t) \geq 0$. The functional (3.28) is actually the dynamic free energy of the thermodynamical system of Brownian particles. The inequality (3.29) hence displays that natural fact that diffusion drives the relaxation of this system towards the equilibrium state. That is attained in the absence of the macroscopic flow for the vanishing diffusion flux:

$$\partial_t p = 0 \sim h_{rel} = 0 \Rightarrow \nabla_x U_{ch} = \nabla_x (k_B \theta \ln p + U(x)) = 0$$

\[ \downarrow \]

$$p_{eq} = \exp \left[ -\frac{U}{k_B \theta} \right] / \int \exp \left[ -\frac{U}{k_B \theta} \right] |dx|$$

which is a well known Boltzmann’s distribution. Another notice should be made about the dissipation. One can see from (3.29) that it is fully produced by the dissipative flow $h_{rel}$.

### 3.3. Brownian motion of polymer chains

In this section we proceed with the extension of the presented mathematical description of the Brownian motion onto the dynamics of flexible polymers. Here we consider mobile polymer chains immersed into a viscous medium representing effectively the surrounding network (Fig. 3.4). On the contrary to the previous chapter we do not focus on their translational motion. The state of a single polymer chain is only considered in terms of the end-to-end vector $r$ or further in terms of the stretch vector $\lambda = r/r_0$ and hence we consider only its rotation and stretch. The state of the thermodynamic system consisting of a big number of such chains in a vicinity of a material point is given by the distribution $p(r,t)$ or equivalently $p(\lambda, t)$ in $\mathbb{R}^3$ and hence the diffusion process under consideration is nothing else but reorientation and redistribution of stretch of the chains.

By a certain analogy to the bead spring we assume that each polymer chain is an entropic spring with the energy

$$U(\lambda) = \frac{3}{2} k_B \theta \lambda^2$$

coming from (3.13) and viscosity concentrated in its ends. Hence the dynamics of this chain follows similarly to (3.26) the equation

$$\frac{\langle v \rangle}{2} = \frac{\bar{v}}{2} + \frac{1}{\eta} F_{ch.r}$$

Figure 3.4: Brownian motion of polymer chains in the surrounding network
where \( \langle \mathbf{v} \rangle = \langle \mathbf{r} \rangle \) — average rate of change of the end-to-end vector of the chain and
\[
\pm \frac{\langle \mathbf{v} \rangle}{2} = \text{are the average relative velocities of the beads,}
\]
\[
\mathbf{\bar{v}} = \mathbf{l} \cdot \mathbf{r} = \text{is the translation-free macrovelocity with } \mathbf{l} \text{ being the deformation gradient } \mathbf{l} = \dot{\mathbf{F}} \mathbf{F}^{-1},
\]
\[
\pm \mathbf{F}_{ch,r} = \frac{\partial U_{ch}}{\partial \mathbf{r}} = \text{forces acting on the beads.}
\]

The chemical potential of the thermally active polymer chains driving the evolution of their network
\[
U_{ch} = k_B \theta \ln p(\mathbf{r}, t) + \frac{3}{2} k_B \theta r^2
\]
(3.33)

In terms of the stretch vector this yields the average rate
\[
\langle \mathbf{v} \rangle_\lambda = \dot{\mathbf{v}} + \frac{2}{\eta r_0^2} \mathbf{F}_{ch,\lambda}
\]
(3.34)

where
\[
\langle \mathbf{v}_\lambda \rangle = \langle \dot{\lambda} \rangle = \text{average rate of change of the stretch vector,}
\]
\[
\mathbf{\dot{v}}_\lambda = \mathbf{l} \cdot \dot{\lambda} = \text{macroscopic stretch change rate,}
\]
\[
\mathbf{F}_{ch,\lambda} = -\frac{\partial U_{ch}}{\partial \lambda} = \text{potential force field conjugate to the stretch.}
\]

One can see here that the mean-square length of the chain \( r_0 = \sqrt{N} b \) or equivalently its length length \( L = N b \) influences the diffusion. The shorter is the chain the higher is its mobility. Omitting the subscript \( \lambda \) one the subscript \( \lambda \) for the further derivations we finally derive the equation of motion
\[
\langle \mathbf{v} \rangle = \mathbf{l} \cdot \dot{\lambda} - D^\lambda \nabla \lambda \left[ \ln p(\lambda, t) + \frac{3}{2} \lambda^2 \right], \quad D^\lambda = \frac{2k_B \theta}{\eta r_0^2}
\]
(3.35)

That in a way provides the Lagrangian description of the microscopic diffusional motion since that follows the motion of the average chain. The Eulerian setting on the other hand is retrieved by the Smoluchowski equation. It concerns the time-change of the probability of a certain state \( \lambda \) and hence follows the spacial description:
\[
\partial_t p(\lambda, t) = -\text{div} \left[ p \langle \mathbf{v} \rangle \right]
\]
\[
= -\text{div} \left[ p \mathbf{l} \cdot \dot{\lambda} \right] + D^\lambda \nabla \lambda \cdot \left\{ p \nabla \lambda \left[ \ln p + \frac{3}{2} \lambda^2 \right] \right\}
\]
\[
= -\left( \text{div} \left[ \mathbf{h}_{rev} \right] + \text{div} \left[ \mathbf{h}_{dis} \right] \right).
\]
(3.36)

One can see both a reversible and the dissipative parts of the evolution of the probability distribution. That viewpoint comes from the corresponding split of the flux onto the reversible part due to the motion “together” with the macromedium and the dissipative one due to the diffusion and stretch relaxation.

The dynamic free energy of this evolving thermodynamic system can be again be derived
as an integral of the chemical potential (3.31) over all the possible states $\lambda$ from the stretch space $\Lambda = \mathbb{R}^3$:

$$\mathcal{A} = \int_{\Lambda} p(\lambda, t) U_{ch} |d\lambda| = \frac{nk_B\theta}{\Lambda} \int_{\Lambda} p \left[ \ln p(\lambda, t) + \frac{3}{2}\lambda^2 \right] |d\lambda|$$  \hspace{1cm} (3.37)

Again as in the general setting in the previous setting the dynamic free energy at constant deformation ($l = 0$) and temperature ($\theta = \text{const}$) is decreasing with time and the thermodynamic system of mobile polymer chains relaxes towards the equilibrium state characterized by the distribution

$$p_{eq}(\lambda) = \exp \left[ -\frac{3}{2}\lambda^2 \right] / \int_{\mathbb{R}^3} \exp \left[ -\frac{3}{2}\lambda^2 \right] |d\lambda| = \left( \frac{3}{2\pi} \right)^{3/2} \exp \left[ -\frac{3}{2}\lambda^2 \right].$$  \hspace{1cm} (3.38)

This is a Gaussian bell-shaped distribution for which the diffusion flow $h_{\text{dis}}$ vanishes. This can be seen as a natural unperturbed state of the considered mobile polymer network.

The mechanism of the viscoelasticity can be explained then in the following way. The macroscopic motion of the medium (macrodeformation) pulls the system out of the equilibrium and deforms the initial distribution (3.38) (microdeformation) as depicted on Fig. 3.5a. That entails the change of the chemical potential so that it becomes inhomogeneous. As a result the stress is produced and according to (3.32) the diffusion is initiated by the flow. If the deformation will freeze at some constant value this diffusion will return the system to the unperturbed state in a sufficient amount of time. During this process some part of the mechanical work will be dissipated by the diffusion flow. Thus as can be seen the developed here model can be naturally taken as a micromechanical basis of the viscoelasticity of rubber-like materials.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.5.png}
\caption{Mechanism for the viscoelastic response of the mobile network: perturbation of the probability distribution $p(\lambda, t)$ due to the instantaneous macroscopic deformation (a); the inhomogeneity of the chemical potential field $U_{ch}(\lambda, t)$ and the resulting flow (b)}
\end{figure}
4. Macromechanical model

Viscoelasticity of rubber-like polymers is a general notion that applies to the macromechanical behavior of an extremely broad class of polymeric materials. More commonly the inelastic phenomena observed in rubbery polymers can be characterized as finite elasto-visco-plasticity with deformation induced softening and thus are more complicated. The particular character of the the macromechanical response can be concluded for instance from a cyclic uniaxial test. At this experiment the equilibrium hysteresis is either observed (elasto-visco-plasticity) or not (viscoelasticity). In the latter case the relaxation process converges to an equilibrium curve, i.e. after a sufficiently long holding period the same stress value will be attained for the same stretch value, no matter what was the history of the deformation. The experimental studies ([4],[34]) report that pre-conditioned materials display this kind of behavior and show no equilibrium hysteresis. The mentioned above pre-conditioning is performed to exclude damage effects generally referred as Mulling type effects in the tested materials. That is characterized by the softening of rubbery polymers due to the partial breakdown of the microstructure during the loading.

4.1. Model description

In the present work we focus on the pure viscoelasticity of rubber-like polymers excluding thus the plastic effects and the damage. That seems not to be a strong limitation according to the discussed above experimental evidences. Phenomenologically a broad set of rubbery materials can be treated as viscoelastic.

**Scope of the model.** More particularly the goal of this work is to develop a micromechanically based model capable to present

- **highly non-linear stress response for different types of deformation:** it is known that even the equilibrium response of elastomers is quite complex and differs for the various types of deformation (uniaxial, biaxial, shear, ...);

- **time-dependent behavior:** rubbers display a noticeable dissipative hysteresis within a broad spectrum of loading rates, which has to be captured by the model;

- **hysteresis profile:** the shape of the hysteresis curves is quite particular, the developed model has to reproduce it both in compression and tension;

- **isothermal behavior of rubbery polymers:** the macroscopic response of rubbers is to a great extend purely entropic and thus is strongly coupled with the temperature, we limit ourselves to the isothermal case when all the dissipated heat is taken out from the system and its temperature is kept constant.

**Micromechanical justification.** For the developed model we take the following viewpoint onto the micromechanical foundation of viscoelasticity of rubbery polymers. Following [4] we consider the microstructure as an assembly of several networks as described in Fig. 2.1. The one ground network is formed by the strongly cross-linked macromolecules and has a rigid topology. The other is formed by superimposed mobile macromolecules by means of entanglement mechanisms and is transient by the nature. We associate the ground network with the macroscopic elastic response whereas the superimposed subnetwork is responsible for the production of the viscous overstress.
The ideal ground network can be naturally described by the non-affine microsphere model [37]. The macrodeformation causes elongation or contraction of chain segments of the network according to their spacious orientation. That entails the change of the overall entropy and results in the production of the entropic stress as described in Section 4.2. In the developed model the interaction between the ground network and the superimposed macromolecules is seen as interaction between an effective viscous macromedium that follows the macrodeformation of the material and a system of Brownian particles submerged into this medium. Thus in the description of the viscous subnetwork we follow the theory given in the Section 3.

Altogether the micromechanical mechanism of the viscoelastic behavior is described on the Fig. 2.1. During the displayed stretch of the body the ground network follows the macrodeformation. Simultaneously it drags the viscous subnetwork so that it also takes definite deformation. Provided the sufficient amount of time at the constant stretch the subnetwork relaxes towards an unperturbed state at which it produces no viscous over-stress.

**Model setup.** Schematically the model can be depicted in a material box (Fig.2.2). That includes ground network and several viscous subnetworks in a parallel configuration that excludes direct interaction between them. The ground network as noticed above follows exactly the macrodeformation whereas the subnetworks are deformed due to the interaction with an effective viscous medium. The subnetworks are assigned different viscosity and thus posses a discrete spectrum of relaxation times. Introduction of this division into $s$ Maxwellian branches serves the phenomenological representation of the real relaxation spectrum of the viscoelastic rubbery polymers. According to this parallel structure of the rheologic model on the Fig. 2.2 the constitution of the model, derivation of the stresses and moduli and the enforcement of the thermodynamic consistency follows the Section 2.3.

### 4.2. Non-Affine Microsphere Model for the Elastic Ground Network

As mentioned before we incorporate the recently developed non-affine network model ([37]) to describe the equilibrium response of the rubber-like polymer materials. The model extends both the full network model and the eight-chain model ([6]) and display substantially improved performance. The micromechanical part of the model focuses on the response of a single polymer chain in a constrained environment. It is described in terms of two micro-kinematic variables: the stretch $\lambda$ of the chain and the contraction $\nu$ of the cross-section of the microtube that constrains the motion of the chain segment. The macroscopic response is attained via the non-affine micro-macro transition. It homogenizes microstate variables over the microsphere of space orientations and linkes them to the macroscopic deformation represented by the line-stretch $\lambda$ and the area-stretch $\nu$. This homogenization procedure allows for efficient numerical implementation based on the discretization of the microstate variables and quadrature integration on the microsphere. These characteristic features of the approach are outlined by its name: the non-affine microsphere model.

**Micro-kinematic variables for the chain.** A single chain, which is a part of a long macromolecule between the junctions is treated by means of statistical mechanics. It is assumed to consist of $N$ segments of equal constant length $l$ (called Kuhn segment
length) linked consecutively and freely rotating one relatively to each other at the junction points. As outlined in the Section 3 the primary kinematic variable of such chain is the current end-to-end distance $r$ (see Fig. 4.1). Being related to the root-mean-square value $r_0 = \sqrt{Nb}$ it gives the dimensionless deformation measure

$$\lambda := \frac{r}{r_0},$$

(4.1)

which is the stretch of the chain.

![Figure 4.1: Response of the single chain to the stretch](image)

As previously mentioned the value of stretch determines the free energy of a chain fixed ends. The Gaussian statistics gave us the estimate 3.13. Provided this expression for the free energy one ends up with the representation of a single chain as a linear entropic spring. This model accepted for the treatment of the chain dynamics in Section 3 is only valid in the range of moderate stretches. At large stretches when end-to-end distance get close to the contour length $L = Nl$ the finite extensibility of the chain needs to be taken into account. That is done by the non-Gaussian statistics ([26]) that leads to the following expression for the free energy

$$\psi_f = Nk_B\theta \left( \lambda_r L^{-1}(\lambda_r) + \ln \frac{L^{-1}(\lambda_r)}{\sinh L^{-1}(\lambda_r)} \right) + \text{const}$$

(4.2)

in terms of a relative stretch $\lambda_r = \lambda/\sqrt{N} \in [0, 1)$. Here $L(\beta) = \coth \beta - 1/\beta$ is the well-known Langevin function the inverse of which can be approximated as

$$L^{-1}(\lambda_r) = \lambda_r \frac{3 - \lambda_r^2}{1 - \lambda_r^2}.$$

The dual force to the micro-kinematic variable $\lambda$ is computed as

$$F_\lambda = \frac{\partial \psi_f}{\partial \lambda} = k_B\theta \sqrt{N}L^{-1}(\lambda_r) \approx k_B\theta \lambda \frac{3N - \lambda^2}{N - \lambda^2},$$

(4.3)

is related to the real thermodynamical force acting on the junction points through a relation

$$F_r = \frac{\partial \psi_f}{\partial r} = \frac{\partial \psi_f}{\partial \lambda} \frac{\partial \lambda}{\partial r} = \frac{1}{r_0} F_\lambda$$

and thus has a physical interpretation.

As one can see on the Fig. 4.1 this force gets infinite as the end-to-end distance approaches
the contour length, which is absolutely different to what Gaussian statistics predicts.

The stiffness of this non-Gaussian entropic spring increases with the increasing stress:

$$c_\lambda = \frac{\partial^2 \psi_f}{\partial \lambda^2} \approx k_B \theta \lambda \frac{\lambda^4 + 3N^2}{(N - \lambda^2)^2}$$  \hspace{1cm} (4.4)

So far no interaction between chains in the network except for the junction points was considered. In the real network the motion of the chains is always hindered by the surrounding. Concepts of polymer mechanics that incorporate this effect are called constant segment theories. In the non-affine microsphere model of rubber elasticity one of those, namely the so-called tube model ([8],[12]), is used. This theory characterizes the constraints imposed by the surrounding onto a chain as a tube of certain diameter (see Fig. 4.2). The chain is assumed to perform constrained motion in this tube, which certainly reduces the the number of conformations chain segments can take. The entropic change due to this confinement and thus the corresponding contribution to the free energy are expressed in terms of a dimensionless micro-kinematic variable

$$\nu = \left(\frac{d_0}{d}\right)^2,$$  \hspace{1cm} (4.5)

which is the tube area contraction factor. Here $d_0$ is the reference (initial) tube diameter, $d$ - its current value.

$\textbf{Figure 4.2:}$ Response of the single chain to the tube-like constraints

According to [11] the free energy due to the tube constraint is computed as

$$\psi_c = \alpha k_B \theta N \left(\frac{l}{d_0}\right)^2 \nu + \text{const}$$  \hspace{1cm} (4.6)

($\alpha$ is a factor depending on the geometry of the tube cross-section), which corresponds to a constant dual force

$$F_\nu = \frac{\partial \psi_c}{\partial \nu} = \alpha k_B \theta N \left(\frac{l}{d_0}\right)^2.$$  \hspace{1cm} (4.7)

The force associated with the tube diameter $d$ is shown on the Fig. 4.2 and is always negative, since the tube constraint energy is minimal when $d$ is infinite. In that case there’s merely no lateral constraint.

The introduced two micro-kinematic variables determine fully the equilibrium state of the chain with the free energy which is simply the sum of the stretch and tube constraint parts:

$$\psi(\lambda, \nu) = \psi_f(\lambda) + \psi_c(\nu).$$  \hspace{1cm} (4.8)
The non-affine microsphere model. The transition from the free energy of a single chain to the macroscopic free energy is performed within the framework of the non-affine microsphere model in two steps. First, the micro-variables $\lambda$ and $\nu$ have to be linked to the suitably defined macro-variables $\bar{\lambda}$ and $\bar{\nu}$ that represent the macrodeformation. Secondly, the contributions of all the chains in the network have to be summed up via a homogenisation of the state variables over a unit microsphere that represents the orientation space. Within this approach all the chains of the networks are referred by their initial orientation in the reference configuration. Considering a unit vector $T$ in the reference configuration one should think of all the chains at the material point oriented in this direction, as if they were taken out from the network scaled down by the reference length $r_0$ and put inside the microsphere of unit radius. It would be natural to assume that the chains with equal orientation will be deformed similarly, i.e. that the micro-kinematic variables $\lambda$ and $\nu$ are defined as state variable fields on the microsphere. Within the framework of this approach it would be natural to link their values to the macroscopic line-stretch

$$\bar{\lambda} = |t|g = \sqrt{t \cdot gt} = \sqrt{T \cdot CT} = |T|c, \quad t = \bar{F}T$$

and area-stretch

$$\bar{\nu} = |n|g = \sqrt{n \cdot g^{-1}n} = \sqrt{N \cdot C^{-1}N} = |N|_{c^{-1}}, \quad n = g^{-1}n$$

that are also defined on the microsphere for unit tangent $T$ and unit normal $N$ according to their deformations. That is the first step.

The second step as outlined before is the homogenization. Provided that the chain orientations of the undeformed network are isotropic and thus are equally distributed over the microsphere the stretch and tube constrained parts of the free energy can be summarized over the network by the continuous averaging:

$$\bar{\Psi} = \langle n\psi(\lambda, \nu) \rangle = \bar{\Psi}_f + \bar{\Psi}_c,$$  \hspace{1cm} (4.11)

$$\bar{\Psi}_f = \langle n\psi_f(\lambda) \rangle,$$  \hspace{1cm} (4.12)

$$\bar{\Psi}_c = \langle n\psi_c(\nu) \rangle.$$  \hspace{1cm} (4.13)

Here

$$\langle v \rangle = \frac{1}{|S|} \int_S v(A)dA$$

is a mean square operator, $n$ - number of chains in the network per unit volume in the undeformed configuration.

The non-affine stretch part. To the contrary to the affine full network model which assumes that the microstretch perfectly follows the macrostretch, i.e. $\lambda = \bar{\lambda}$, in the non-affine microsphere model this relation does not hold. A fluctuation of the microstretch around the macrostretch is instead introduced:

$$\lambda = \bar{\lambda}.$$  \hspace{1cm} (4.14)
This fluctuation represents the redistribution of the stretch that is believed to take place in the real networks. This fluctuation is constrained by a condition

\[ \langle \lambda \rangle_p = \langle \bar{\lambda} \rangle_p \]  

where

\[ \langle v \rangle = \left( \frac{1}{|S|} \int v^p(A)dA \right)^{1/p} \]

is a \( p \)-average of a scalar positive variable \( v \) over the referential orientation space.

The exact expression for the fluctuation field comes from the principle of minimum averaged free energy

\[ f = \arg \min \langle n\psi_f(\lambda) \rangle \]  

The solution of the constrained optimisation problem (4.16),(4.15) defines the non-affine microstretch to be constant over the microsphere

\[ \lambda = \langle \bar{\lambda} \rangle_p, \]  

which being inserted into (4.12) yields the homogenized stretch energy:

\[ \bar{\Psi}_f = \langle n\psi_f(\lambda) \rangle = n\psi_f(\langle \bar{\lambda} \rangle_p). \]  

It can be seen that ultimately the macroscopic free energy is a uniquely defined function of the deformation, particularly of the right Cauchy-Green tensor. That follows from (4.9) that defines macrostretch \( \bar{\lambda} = |T|_C \) on the microsphere for given \( C \). It should be also noted that the stretch part of the non-affine microsphere model given by (4.18) in a special case of \( p = 2 \) reproduces the well-known eight-chain model ([33]):

\[ \lambda = \langle \bar{\lambda} \rangle_2 = \sqrt{I_C/3}, \quad I_C = \text{tr}[C]. \]  

Having the expression of the stretch related part of the macroscopic free energy as a function of the deformation measure \( C \) one can derive the corresponding part of the macrostresses and the moduli either in the Lagrangian:

\[ \bar{S}_f = 2\partial_c \bar{\Psi}_f, \quad \bar{C}_f = 2\partial_c \bar{S}_f \]  

or alternatively in the Eulerian setting

\[ \bar{\tau}_f = 2\partial_g \bar{\Psi}_f, \quad \bar{\epsilon}_f = 2\partial_g \bar{\tau}_f. \]  

In the subsequent model setting the latter formulation is preferred. According to this choice the derivative of the micro-kinetic variable in the current metric is needed:

\[ 2\partial_g \bar{\lambda} = 2\partial_g |t|_g = \bar{\lambda}^{-1}t \otimes t \]  

and

\[ 2\partial_g \lambda = 2\partial_g \langle \bar{\lambda} \rangle_p = \lambda^{1-p} \left( \bar{\lambda}^{p-1}2\partial_g \bar{\lambda} \right) = \lambda^{1-p} \left( \bar{\lambda}^{p-2}t \otimes t \right) =: \lambda^{1-p} h \]
Using that one further derive the concrete expressions

\[
\bar{\tau}_f = n \frac{\partial \psi_f}{\partial \lambda} 2 \partial g \lambda = n F_\lambda \lambda^{1-p} h,
\]

\[
\bar{c}_f = \left[ n \frac{\partial^2 \psi_f}{\partial \lambda^2} \lambda^{2-2p} - (p-1)n \frac{\partial \psi_f}{\partial \lambda} \lambda^{-2p} \right] h \otimes h + n \frac{\partial \psi_f}{\partial \lambda} \lambda^{1-p} \mathbb{H}
\]

where

\[
\mathbb{H} = 2 \partial g h = \langle (p-2) \tilde{\lambda} \tilde{\lambda}^{-4} t \otimes t \otimes t \otimes t \rangle.
\]

The tube constraint part. As to the tube constraint the starting point is a straightforward relation

\[
\nu = (\tilde{\nu})^q
\]

linking the tube contraction factor \( \nu \) to the macroscopic area-stretch \( \tilde{\nu} \) in the direction of chain orientation. According to (4.13) the homogenized free energy associated with the tube constraint is found as a function of \( C \)

\[
\bar{\Psi}_c = \langle n \psi_c(\nu) \rangle = \langle n \psi_c((\tilde{\nu})^q) \rangle
\]

with \( \tilde{\nu} = |\tilde{n}| g \).

Again for the computation of stresses one needs derivatives of the kinematic variables:

\[
2 \partial g \tilde{\nu} = 2 \partial g |\tilde{n}| g = -\tilde{\nu}^{-1} \tilde{n} \otimes \tilde{n}
\]

and

\[
2 \partial g \nu = q \tilde{\nu}^{q-1} 2 \partial g \tilde{\nu}.
\]

With that identities at hand the macroscopic Kirchhoff stress is computed as follows

\[
\bar{\tau}_c = 2 \partial g \bar{\Psi}_c = \left( n \frac{\partial \psi_c}{\partial \nu} 2 \partial g \nu \right) = -n F_\nu \langle q \tilde{\nu}^{q-2} \tilde{n} \otimes \tilde{n} \rangle =: n F_\nu k
\]

for the constant tube force \( F_\nu \) given by (4.7).

The Eulerian moduli appear then in the form

\[
\bar{c}_c = n F_\nu \mathbb{K},
\]

where the fourth order tensor \( \mathbb{K} \) is computed using the notation \( \text{sym}[g^{-1} \otimes (\tilde{n} \otimes \tilde{n})] \) as follows

\[
\mathbb{K} = 2 \partial g k = \langle q(q-2) \tilde{\nu}^{q-4} \tilde{n} \otimes \tilde{n} \otimes \tilde{n} \otimes \tilde{n} + q \tilde{\nu}^{q-2} \text{sym}[g^{-1} \otimes (\tilde{n} \otimes \tilde{n}) + (\tilde{n} \otimes \tilde{n}) \otimes g^{-1}] \rangle.
\]
Macromechanical model

Numerical implementation. In the described above model the efficient macroscopic quantities such as stress and moduli are obtained in the form of the integrals over the unit sphere presenting the orientation space in the reference configuration. It would be natural to proceed with the numerical implementation by discretization of the microsphere by a set of discrete orientations \( \{ r_i \}_{i=1}^m \) and application of some quadrature formula with weight factors \( \{ w_i \}_{i=1}^m \) to compute the averages as

\[
\langle v \rangle = \frac{1}{|S|} \int_S v(A) dA = \sum_{i=1}^m v_i w_i,
\]

(4.33)

where \( v \) is some scalar, vectorial or tensorial field on the unit sphere \( S \) and \( \{ v_i \}_{i=1}^m \) are its values at the discrete orientations \( \{ r_i \}_{i=1}^m \). Following this approach one should put some constraints onto the choice of the discretization. The quadrature formula (4.33) should be exact for the identities

\[
\langle r \rangle = 0, \quad \langle r \otimes r \rangle = \frac{1}{3} \mathbf{1}
\]

in order to preserve the isotropy and stress-free state at the reference configuration. These conditions imply

\[
\sum_{i=1}^m r_i w_i = 0, \quad \sum_{i=1}^m r_i \otimes r_i w_i = \frac{1}{3} \mathbf{1}.
\]

A whole family of such discrete representations of the unit sphere can be found in [3]. That
Table 4.2: Numerical implementation of the non-affine microsphere model

1. **Input** Provided is the unimodular part $\bar{F}$ of the deformation gradient. Set up the discrete orientations $\mathbf{r}^i$ and weights $w^i$ for the quadrature integration.

2. **Macro-kinematic fields** Compute discrete values of deformed tangents $\mathbf{t}^i$ and normals $\tilde{\mathbf{n}}^i$ together with the affine line-stretches $\lambda^i$ and area-stretches $\nu^i$:

$$ \mathbf{t}^i = \bar{F} \mathbf{r}^i, \quad \bar{\lambda}^i = |\mathbf{t}^i|; \quad \tilde{\mathbf{n}}^i = \bar{F}^{-T} \mathbf{r}^i, \quad \bar{\nu}^i = |\tilde{\mathbf{n}}^i|. $$

3. **Non-affine stretch part** Compute the non-affine stretch and its derivatives

$$ \lambda = \langle \bar{\lambda}^i \rangle_p = \left[ \sum_{m=1}^{i=1} (\bar{\lambda}^i)^p w^i \right]^{1/p}, $$

$$ \mathbf{h} = 2 \bar{\partial} g^\lambda = \sum_{m=1}^{i=1} (\bar{\lambda}^i)^{p-2} \mathbf{t}^i \otimes \mathbf{t}^i w^i, $$

$$ \mathbf{H} = 2 \bar{\partial} g \mathbf{h} = (p-2) \sum_{m=1}^{i=1} (\bar{\lambda}^i)^{p-4} \mathbf{t}^i \otimes \mathbf{t}^i \otimes \mathbf{t}^i \otimes \mathbf{t}^i w^i. $$

Calculate the microscopic forces and moduli

$$ \tau_f = n \frac{\partial \psi_f}{\partial \lambda} = n F \lambda = \mu \lambda \frac{3N - \lambda^2}{N - \lambda^2} - \mathbf{c} \mathbf{f} = n \frac{\partial^2 \psi_f}{\partial \lambda^2} = n c_\lambda = \mu \frac{\lambda^4 + 3N^2}{(N - \lambda^2)^2}, \quad \mu = n k_B \theta $$

and conclude with the stretch-related macro-stresses and macro-moduli

$$ \bar{\tau}_f = \tau_f \lambda^{1-p} \mathbf{h}, \quad \bar{c}_f = \left[ c_f \lambda^{2-2p} - (p-1) \tau_f \lambda^{1-2p} \right] \mathbf{h} \otimes \mathbf{h} + \tau_g \lambda^{1-p} \mathbf{H} $$

4. **Non-affine tube constraint part** Compute the derivatives

$$ \mathbf{k} = 2 \bar{\partial} g \nu = - \sum_{m=1}^{i=1} q (\bar{\nu}^i)^{q-2} \tilde{\mathbf{n}}^i \otimes \tilde{\mathbf{n}}^i w^i, $$

$$ \mathbf{K} = 2 \bar{\partial} g \mathbf{k} = \sum_{m=1}^{i=1} \left[ q(q-2) (\bar{\nu}^i)^{q-4} \tilde{\mathbf{n}}^i \otimes \tilde{\mathbf{n}}^i \otimes \tilde{\mathbf{n}}^i \otimes \tilde{\mathbf{n}}^i \right] w^i + (\bar{\nu}^i)^{q-2} \text{sym} \left[ \mathbf{g}^{-1} \otimes (\tilde{\mathbf{n}}^i \otimes \tilde{\mathbf{n}}^i) + (\tilde{\mathbf{n}}^i \otimes \tilde{\mathbf{n}}^i) \otimes \mathbf{g}^{-1} \right] w^i $$

and the macroscopic stresses and moduli

$$ \bar{\tau}_c = \mu N \mathbf{U}, \quad \bar{c}_c = \mu N \mathbf{U} \mathbf{K}. $$

4. **Output** Assemble the contributions from both parts of the model to obtain the superimposed elastic response:

$$ \tau^e = \bar{\tau}_f + \bar{\tau}_c, \quad \bar{c}^e = \bar{c}_f + \bar{c}_c $$

and to conclude with the deviatoric projections.

includes 21- and 37-point discretizations that possess central symmetry. This property is useful for taking the averages of the fields that are even ($v(r) = v(-r)$) on the sphere,
which is the case elsewhere in the non-affine microsphere model. It allows to perform the integration over just one half-sphere assigning this result to the integral over the other half. The set of the integration points and the weight factors for the 21-point scheme is given in the Table 4.1. There \( \{r^i_\alpha\}_{\alpha=1}^3 \) are the components of the discrete orientation vectors \( r^i \) in some orthonormal coordinate system in the reference tangent space.

This approximation of the microsphere brings us to a discrete representation of the kinematic fields \( \lambda \) and \( \nu \) in terms of their nodal values \( \lambda^i \) and \( \nu^i \) as well as to the numerical evaluation of all the sought for quantities. The numerical implementation is summarized in the Table 4.2. It should be noted that the numerical representation of the tangent moduli given there is perfectly consistent with the calculated stresses.

### 4.3. Tensorial formulation for viscoelastic subnetwork model

In the previous section it has been shown that the viscoelastic subnetwork can be treated as a thermodynamic system of Brownian particles. Temporal state of this system is fully described by the probability function, namely by \( p(\lambda) : \Lambda \rightarrow \mathbb{R} \) – probability distribution of the stretch vector \( \lambda \in \Lambda = \mathbb{R}^3 \). The change of this microfield due to the macrodeformation of the continuum and viscous relaxation is governed generally by the Smoluchowski equation. The latter is a parabolic partial differential equation in \( \mathbb{R}^3 \), which can not be solved directly neither analytically nor numerically. This fact motivates further reformulation of the evolution equation to a more convenient form. In this section an equivalent fully tensorial setting for the viscoelastic subnetwork is derived.

![Figure 4.3](image)

**Figure 4.3:** Tensorial representation of the microstructure: a) Deformation of the micromechanical space \( \Lambda \) at a material point of the macrobody b) Equilibrium distribution \( p_0(\Lambda_0) \) subjected to a uniaxial stretch.
The Smoluchowski equation is reduced to an ordinary differential equation in one tensorial unknown. Further on the stresses and moduli are expressed in terms of this tensorial quantity.

**Tensorial representation of probability evolution.** To begin with consider a spacial case when at some material point the distribution function takes the form

\[ p(\lambda) = \frac{1}{\det P} p_0(\lambda_0), \]  

(4.34)

where \( \lambda = P \lambda_0 \), \( p_0(\lambda_0) = \left( \frac{3}{2\pi} \right)^{3/2} \exp \left[ -\frac{3}{2} \lambda_0^2 \right] \). One can see this distribution as a deformation of the equilibrium distribution \( p_0(\lambda_0) \) from the reference micromechanical configuration by a microdeformation map \( P \) as depicted in Fig. 4.3. Thus in compliance to the Eulerian stretch vector space \( \Lambda \) at a point \( x \) a Lagrangean space \( \Lambda_0 \) at the initial position \( X \) is introduced. This spaces contain micromechanical objects such as stretch vectors that by nature are not infinitesimal. Nevertheless these microobjects belong to such a small scale that they can interfere with the objects from the tangent spaces. This property was for instance exploited in the previous section where the relative macrovelocity \( \bar{v} \) were added to the microvelocities \( \langle v \rangle \). Moreover they share the metrics \( G \) and \( g \) of the tangential spaces. One can refer to the Fig. 4.4 for the setup of the microspaces and the tensorial maps of the microobjects.

Consider now the evolution of the subnetwork from the microstate given by (4.34). As noted before the flow of stretch probability is driven by the chemical potential which in this case takes the form

\[ U_{ch} = k_B \theta \left\{ \ln p(\lambda) + \frac{3}{2} \lambda^2 \right\} = k_B \theta \left\{ -\frac{3}{2} \lambda_0^2 - \ln \det P + \frac{3}{2} \lambda^2 \right\} + \text{const}, \]  

(4.35)

with

\[ \lambda = |\lambda|_g = \sqrt{\lambda \cdot g \lambda}, \]

\[ \lambda_0 = |\lambda_0|_G = \sqrt{\lambda_0 \cdot G \lambda_0} = \sqrt{P^{-1} \lambda \cdot GP^{-1} \lambda} = \sqrt{\lambda \cdot P^{-T} GP^{-1} \lambda}. \]
Then the average velocity field can be computed as
\[
\langle v \rangle = \bar{v} - \frac{2}{\eta r_0} g^{-1} \nabla \lambda U_{ch} = l\lambda - D^\lambda g^{-1} \left\{ -3 P^{-T} G P^{-1} \lambda + 3 g \lambda \right\} \quad (4.36)
\]
The obtained expression (4.36) for the velocity is linear on \( \lambda \) which allows to make a conclusion that the affinity of the deformation of the stretch distribution assumed in (4.34) is preserved by the probability flow:
\[
\dot{P} P^{-1} \lambda = \dot{P} \lambda_0 = \langle v \rangle = l\lambda - 3 D^\lambda g^{-1} \left\{ -P^{-T} G P^{-1} \lambda + g \lambda \right\}.
\]
Thus the state of the microstructure at a material point \( X \), which is the probability function, is determined by a tensorial history variable \( P(X, t) \). Its evolution at fixed material point is governed by an ordinary differential equation:
\[
g \dot{F} F^{-1} = g \dot{F} F^{-1} - 3 D^\lambda \left\{ -F^{-T} P_0 G P_0^{-1} F^{-1} + g \right\}.
\]
(4.37)
The structure of the evolution of \( P \) given in (4.37) follows the structure of the probability flow. It includes both a reversible part related to the macrodeformation (it contains the velocity gradient \( l = \dot{F} F^{-1} \)) and a dissipative part due to the existing diffusion (\( D^\lambda \) - coefficient of diffusion). In order to get rid of the first part and thus the dependency on the macrodeformation the microdeformation map tensor \( P \) is split into the product
\[
P = F P_0,
\]
(4.38)
where \( P_0 \) is a new history variable fully independent of the macrodeformation. Its evolution equation is derived as follows:
\[
g \left[ \dot{F} F^{-1} + F \dot{P}_0 P_0^{-1} F^{-1} \right] = g \dot{F} F^{-1} + 3 D^\lambda \left\{ F^{-T} P_0 T G P_0^{-1} F^{-1} - g \right\}
\]
\[
g F \dot{P}_0 P_0^{-1} F^{-1} = 3 D^\lambda \left\{ F^{-T} P_0 T G P_0^{-1} F^{-1} - g \right\}
\]
and finally
\[
\dot{P}_0 = 3 D^\lambda \left\{ F^{-1} g^{-1} F^{-T} P_0 G P_0^{-1} G - P_0 \right\}.
\]
(4.39)
The introduced history variable \( P_0 \) represents a map of Lagrangian microstretch space \( \Lambda_0 \) onto itself and has nine independent components. This ”pre-deformation” includes both ”pre-stretch” and ”pre-rotation”. The latter obviously does not affect the overall free energy and apparently can be excluded from the consideration. This is achieved by introduction of an alternative symmetric tensorial variable:
\[
B = P_0 G^{-1} P_0^T,
\]
(4.40)
that has only six independent components and appears to contain all the necessary information about the microdeformation of the viscoelastic subnetwork. One derives from the differential equation (4.39) the following expression for the time derivative of \( B \)
\[
\dot{B} = \dot{P}_0 G^{-1} P_0^T + P_0 G^{-1} \dot{P}_0^T = 6 D^\lambda \left\{ F^{-1} g^{-1} F^{-T} P_0 G^{-1} P_0^T \right\} = 6 D^\lambda \left\{ C^{-1} - B \right\}
\]
or introducing a new parameter relaxation time \( 1/\tau = 6 D^\lambda \)
\[
\dot{B} = \frac{1}{\tau} \left\{ C^{-1} - B \right\}.
\]
(4.41)
Surprisingly the derived evolution equation has a form which is very close to what one postulates in the geometrical approach to the finite viscoelasticity in terms of viscous metric tensors. Indeed, the introduced tensor $B$ can be interpreted as some intermediate metrics. Moreover its change is driven by its difference to the Lagrangian metrics $C^{-1}$ which is perfectly corresponds to what one finds in the mentioned above geometrical models. The evolution stops when these two metrics’ coincide, i.e. the equilibrium state of a fully relaxed subnetwork is represented by $B^\infty = C^{-1}$.

**Homogenized free energy.** Having the tensorial description of microstructure evolution one can proceed with the derivation of the free energy in terms of the introduced time history variable. That is naturally done by the homogenization in the stretch space $\Lambda$ according to expression for the dynamic free energy of the considered thermodynamic system:

$$
\bar{\Psi}^v = n^v \int_{\Lambda} p(\lambda) U_{ch}(\lambda) \, |d\lambda| = \mu^v \int_{\Lambda_0} p(\lambda_0) \left\{ -\frac{3}{2} \lambda_0^2 + \frac{3}{2} \lambda^2 \right\} \, |d\lambda_0| - \ln \det \, P + \text{const.}
$$

In the above relation integration scope was changed to the Lagrangian stretch space $\Lambda_0$ and the chemical potential was expanded according to (4.35). The integral in the right hand side is computed by separating the integration over the stretch value $\lambda_0 = |\lambda_0|$ and orientation $u_0 = \lambda_0/\lambda_0 \in S_0$:

$$
\int_{\Lambda_0} p(\lambda_0) \left\{ -\frac{3}{2} \lambda_0^2 + \frac{3}{2} \lambda^2 \right\} \, |d\lambda_0| = \frac{3}{2} \int_{0}^{\lambda_0} p(\lambda_0) \lambda_0^4 \, d\lambda_0 \cdot \int_{S_0} [u_0 \cdot P^T gP u_0 - 1] \, |du_0|,
$$

since $\lambda^2 = \lambda \cdot g\lambda = \lambda_0^2 u_0 \cdot P^T gP u_0$ and $|d\lambda_0| = \lambda_0^2 \, d\lambda_0 \, |du_0|$.

Using the identities

$$
\int_{0}^{\infty} p(\lambda_0) \lambda_0^4 \, d\lambda_0 = \int_{0}^{\infty} \left( \frac{3}{2\pi} \right)^{3/2} \exp \left[ -\frac{3}{2} \lambda_0^2 \right] \lambda_0^4 \, d\lambda_0 = \frac{1}{4\pi} = \frac{1}{|S_0|}
$$

and

$$
\frac{1}{|S_0|} \int_{S_0} u_0 \cdot P^T gP u_0 \, |du_0| = \frac{1}{|S_0|} \int_{S_0} u_0 \otimes u_0 \, |du_0| : P^T gP = \frac{1}{3} G^{-1} : P^T gP = \frac{1}{3} G^{-1} : P^T_0 F^T gFP_0 = \frac{1}{3} (P_0 G^{-1} P_0^T) : (F^T gF) = \frac{1}{3} B : C
$$

one finally derives

$$
\bar{\Psi}^v = \bar{\Psi}^v (C, B) = \frac{1}{2} \mu^v [B : C - 1] - \mu^v \ln (\det \, B)^{1/2} + \text{const.} \quad (4.42)
$$

The resulting expression for the free energy is of neo-Hookean type, which is another surprising coincidence. As one could expect neither macroscopic nor microscopic rotations are present in (4.42). Another notice should be done about the dependency on the determinant of $B$. Remarkably, it deviates from 1 though in the initial state as well as at fully relaxed configuration it has unit value: $\det \, B = \det \, 1 = 1$ and $\det \, B = \det \, C^{-1} = 1$, correspondingly. Hence this change of $\det \, B$ should be taken into account when the change of the free energy is considered.
Macromechanical model

Macroscopic viscoelastic stress. From the tensorial expression for the free energy given in (4.42) the viscoelastic stress can be easily derived:

$$\bar{\tau}^v = F \left( 2\partial_v \bar{\Psi}^v(C, B) \right) F^T = \mu^v F BF^T$$  \hspace{1cm} (4.43)$$

4.4. Thermodynamic consistency

Although the derivations in the Section 4.3 had as a staring point the Smoluchowski equation (proved to be dissipative) and were done by equivalent transformations thermodynamic consistency of the proposed tensorial formulation needs to be illustrated. Since the introduced internal variable $B$ is independent of the macrodeformation as it was discussed above one can immediately write the reduced expression for the dissipation:

$$D_{\text{loc}} = -2\partial_B \bar{\Psi}^v : \frac{1}{2} B \geq 0,$$  \hspace{1cm} (4.44)$$

the latter inequality to be proved.

The conjugate thermodynamic force that is present in (4.44) is computed as follows

$$2\partial_B \bar{\Psi}^v = \mu^v C - \mu^v \frac{1}{(\det B)^{1/2}} \partial (\det B)^{1/2} \frac{\partial}{\partial B} = \mu^v (C - B^{-1})$$

Hence for the derived above evolution equation (4.41) the reduced dissipation is computed as follows

$$D_{\text{loc}} = -\frac{\mu^v}{2\tau} (C - B^{-1}) : (C^{-1} - B),$$  \hspace{1cm} (4.45)$$

and it only has to be proved that for arbitrary symmetric positive definite matrices $C$ and $B$ the following inequality holds:

$$(C - B^{-1}) : (C^{-1} - B) \leq 0$$  \hspace{1cm} (4.46)$$

$\Box$

In order to prove this statement consider polar decomposition of these two tensors:

$$C = \sum_i \lambda_i u_i \otimes \tilde{u}_i,$$

$$C^{-1} = \sum_i \lambda_i^{-1} \tilde{u}_i \otimes u_i;$$

$$B = \sum_j \mu_j v_j \otimes \tilde{v}_j,$$

$$B^{-1} = \sum_j \mu_j^{-1} \tilde{v}_j \otimes v_j.$$  

Here $\lambda_i > 0$ and $\mu_j > 0$ are the positive eigenvalues, \{$u_i, \tilde{u}_i$\} and \{$v_j, \tilde{v}_j$\} are the biorthogonal eigenbases of $C$ and $B$, respectively.

Exploiting this decomposition one can compute the considered double contraction as

$$(C - B^{-1}) : (C^{-1} - B) = C : C^{-1} - C : B - B^{-1} : C^{-1} - B^{-1} : C^{-1}$$

$$= 6 - C : B - B^{-1} : C^{-1}$$

$$= 6 - \sum_{i,j} \lambda_i \mu_j (u_i \otimes \tilde{u}_i) : (v_j \otimes \tilde{v}_j) - \sum_{i,j} \lambda_i^{-1} \mu_j^{-1} (\tilde{u}_i \otimes u_i) : (\tilde{v}_j \otimes v_j)$$

$$= 6 - \sum_{i,j} \left[ \lambda_i \mu_j + \lambda_i^{-1} \mu_j^{-1} \right] (u_i \otimes \tilde{u}_i) : (v_j \otimes \tilde{v}_j)$$

$$\leq 6 - 2 \cdot 1 : 1 = 0$$
In the above estimation the inequality transition is based upon several general statements:

- \( \alpha + \alpha^{-1} \geq 2, \alpha > 0 \Rightarrow [\lambda_i \mu_j + \lambda_i^{-1} \mu_j^{-1}] \geq 2; \)
- \( (u_i \otimes \tilde{u}_i) : (v_j \otimes \tilde{v}_j) = (u_i \cdot v_j)(\tilde{u}_i \cdot \tilde{v}_j) = (u_i \cdot v_j)^2 \geq 0; \)
- \( \sum_i u_i \otimes \tilde{u}_i = 1, \)
- \( \sum_j v_j \otimes \tilde{v}_j = 1; \)
- \( 1 : 1 = 3. \)

### 4.5. Algorithmic representation of the over-stress response

Within the standard algorithmic setting one considers a time incremental formulation. At a discrete time step \( \Delta t = t_{n+1} - t_n \) for a typical time interval \( [t_n, t_{n+1}] \) an algorithmic update of the state variables is required. Their starting values at time \( t_n \) are known and henceforth denoted by the lower index \( n \).

One can think of both explicit and implicit schemes to be applied for the integration of the evolution equation (4.41). The simpler forward Euler update follows in the form

\[
\frac{B - B_n}{\Delta t} = \frac{1}{\tau} \left[ \tilde{C}_n^{-1} - B_n \right] \\
B = B_n + \Delta t \frac{1}{\tau} \left[ \tilde{C}_n^{-1} - B_n \right].
\]

(4.47)

Following the backward Euler scheme the evolution equation (4.41) is integrated over the time interval yielding another update for the history variable \( B \):

\[
\frac{B - B_n}{\Delta t} = \frac{1}{\tau} \left[ \tilde{C}^{-1} - B \right] \\
B = B_n + \frac{\Delta t}{\tau} \tilde{C}_n^{-1} + \frac{\Delta t}{\tau} \tilde{C}^{-1}.
\]

(4.48)

One finds both update in a closed form due to the linearity of the initial evolution equation. That means that the computational cost for (4.47) and (4.48) is equal. Consequently for the further algorithmic setting we choose the implicit update (4.48) the advantage of which is that it is unconditionally stable. With the algorithmic representation of the evolution of the history variable \( B \) at the time step one can compute the algorithmic update
of the viscous overstress

\[
\tau_{algo}^v = \mu^v \bar{F} B \bar{F}^T = \mu^v \bar{F} \left\{ \frac{1}{1 + \frac{\Delta t}{\tau}} \left[ B_n + \frac{\Delta t}{\tau} \bar{C}^{-1} \right] \right\} \bar{F}^T
\]

(4.49)

\[
= \frac{\mu^v}{1 + \frac{\Delta t}{\tau}} \bar{F} B_n \bar{F}^T + \mu^v \frac{\tau}{1 + \frac{\Delta t}{\tau}} \bar{F}^T
\]

and to proceed with the algorithmic moduli

\[
\bar{\varepsilon}_{algo}^v = 2\partial g \tau_{algo}^v (g, B(g, B_n; \bar{F}_n, \bar{F}); \bar{F}).
\]

(4.50)

That provides the sensitivity of the overstress update to the variation of the deformation at time \(t_{n+1}\). For the fully Eulerian(spacious) setting we adhere in this work that is computed in terms of the derivative in the Eulerian metric \(g\). The exact expression of the spacial tangent moduli that is consistent with (4.49) is finally derived as follows

\[
\bar{\varepsilon}_{algo}^v = 2\partial g \tau_{algo}^v = \mu^v \frac{\Delta t}{1 + \frac{\Delta t}{\tau}} 2\partial g g^{-1}
\]

(4.51)

\[
= -\mu^v \frac{\tau}{1 + \frac{\Delta t}{\tau}} \left[ (g^{-1} \otimes g^{-1})^{23} + (g^{-1} \otimes g^{-1})^{24}\right]
\]

with the transposition operators defined by \((\bullet_{ijkl}^{23})^T = \bullet_{ikjl}^{23}\) and \((\bullet_{ijkl}^{24})^T = \bullet_{ilkj}^{24}\).

At the concluding point we refer back to the rheological description presented on the Fig. 2.2. First we should note that all elements of the model including the viscoelastic subnetworks are assumed to be subjected to the isochoric part of the deformation given by \(\bar{F}\). Hence in order to retrieve the true stresses and their tangent moduli one needs to apply the corresponding projection transformations (2.4) and (2.5). The second issue: the model contains several non-equilibrium branches. We will denote the parameters and variables related to the \(i^{th}\), \(i = 1.s\) branch by the corresponding subindex. The proposed model of the viscoelastic subnetwork includes two material parameters, which make a total of \(2 \times s = 2s\) for all branches (see Table 4.3). In particular we will consider \(s\) different relaxation times \(\{\tau_i\}_{i=1}^s\) representing the broad dissipative spectrum of the material. The history of each of the branches correspondingly described by a separate variable \(B_i\) according to the theory presented in the Sections 4.3-4.5. Altogether one needs \(6 \times s\) scalar variables for the history storage, since the introduced tensor \(B\) is symmetric.

After these remarks we summarize the complete model of viscoelastic overstress in Table 4.4
Table 4.3: Parameters of the subnetwork model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Name</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu^v_i = n^v_i k_B \theta$</td>
<td>overstress moduli</td>
<td>overstress stiffness (scales up the hysteresis)</td>
</tr>
<tr>
<td>$\tau_i = \frac{1}{6D_i^\lambda}$</td>
<td>relaxation time</td>
<td>relaxation spectrum</td>
</tr>
</tbody>
</table>

Table 4.4: Stress update algorithm for the viscoelastic subnetwork model

1. **Database.** Given are the history variables $\{B_{in}\}_{i=1}^s$ at time $t_n$ and the current isochoric deformation gradient $\bar{F}$.

2. **History update.** Update the state variables $B_i$ for all the subnetworks

$$B_i = \frac{1}{1 + \frac{\Delta t}{\tau_i}} \left[ B_{in} + \frac{\Delta t}{\tau_i} \bar{C}^{-1} \right]$$

3. **Update the over stress and moduli.** Compute the algorithmic stresses and tangent moduli for the obtained state of the subnetworks

$$\bar{\tau}^v_i = \mu^v_i F B_i F^T$$

$$\bar{\delta}^v_i = -\mu^v_i \frac{\tau_i}{1 + \frac{\Delta t}{\tau_i}} \left[ (g^{-1} \otimes g^{-1})^{23} + (g^{-1} \otimes g^{-1})^{24} \right]$$

4. **Output.** Assemble the stresses and tangent moduli from all the branches and apply the projection transformations for the output.

$$\bar{\tau}^v = \sum_{i=1}^s \bar{\tau}^v_i, \quad \bar{\delta}^v = \sum_{i=1}^s \bar{\delta}^v_i.$$
5. Model Evaluation

In this chapter we evaluate the capacity of the proposed model by comparison of the experimental data to the numerical results. Different types of loading and loading histories are considered for the model validation. The essential requirement to the model is its ability to capture specific viscoelastic response of rubbery materials at varying finite strains within a broad range of loading velocities.

We start here with the analysis of the experimental data for a homogeneous uniaxial cyclic test and point out the key features of the hysteresis curves to be reproduced. Then a parametric study of the proposed model for the viscous overstress is performed. This is followed by a parameter identification procedure. The obtained parameter set is used in further representative numerical simulations to make a final evaluation of the model performance.

5.1. Uniaxial cyclic test

Here we use the experimental data for a highly saturated nitrile rubber HNBR50 ([34],[35]) produced by Robert Bosch GmbH. In cyclic uniaxial loading experiments with relaxation period pre-damaged specimens of this material displayed no equilibrium hysteresis (see Fig. 5.1). Whatever is the history of the loading same stress values are attained after the relaxation breaks made at a particular strain. This evidences that essentially the HNBR50 material is purely viscoelastic. Hence the proposed model may be applied to it. For its elastic part which is represented by a non-affine microsphere model one can directly use a parameter fit obtained in [35] for the experimental results depicted on Figure 5.1. With the identified five parameters \( N, \mu, p, U \) and \( q \) the equilibrium response of the nitrile rubber in both uniaxial and equi-biaxial experiments is reproduced very well (see Fig. 5.1).

![Image](image.png)

**Figure 5.1:** Equilibrium response of HNBR50 material in homogeneous uniaxial and equi-biaxial experiments and its fit by the non-affine microsphere model. The data points are retrieved from cyclic tests with relaxation breaks in both loading and unloading ([34]). The parameters of the non-affine elasticity model follow [37] as \( N = 5.18, \mu = 0.139 \) MPa, \( p = 0.166, U = 11.2, q = 0.126 \).

For the viscoelastic part, which is the essential contribution of this work, we refer to
the cyclic uniaxial experiments performed over the same material. These were made at three different absolute loading rates $|\dot{\lambda}_1| = 5 \cdot 10^{-2}$ 1/min, $5 \cdot 10^{-1}$ 1/min and $5$ 1/min. The specimen was stretched between the stretch values $\lambda_1 = 0.75 \ldots 2.0$. The stress-stretch curves for the three tests are depicted on the Figure 5.2. We marked there the most distinctive features of the viscoelastic behavior of the material. The most obvious observation is that the stress response is the stiffer the higher is the loading rate, which is characteristic of the viscoelastic materials. Furthermore the area of the hysteresis that represents the amount of energy dissipated per cycle gets larger as the loading rate increases from $5 \cdot 10^{-2}$ 1/min to $5$ 1/min. One can also observe the difference between the first and the second cycles of the loading which is more distinct for the higher loading velocities. In particular one should notice the change of the viscoelastic modulus after the first cycle of loading.

5.2. Parametric analysis and fit

In order to apprehend whether the proposed model is capable to capture the real viscoelastic response and in particular the outlined above features a parametric analysis was done. A single viscous subnetwork is considered. The only two parameters determine the viscous overstress produced by it at a transient deformation according to the model. The first parameter the viscous modulus $\mu^v$ trivially scales the amount of the overstress. The relaxation time $\tau$ on the contrary has a more peculiar impact. This can be illustrated for the cyclic uniaxial test identical to the described above. Figure 5.3a shows the overstress produced by the considered viscous branch depending on the period of the altering stretch $T = 2(\lambda_1^{max} - \lambda_1^{min})/|\dot{\lambda}_1|$. One can observe that the response differs from the stiff quasi-elastic one for $T/\tau \ll 1$ (very quick loading) to an almost vanishing one for $T/\tau \gg 1$ (slow loading). In the first case there’s no time for any changes to occur in the subnetwork during the loading period whereas in the latter case the loading is so slow that the subnetwork has more then sufficient time to relax fully to an unperturbed stress-free configuration.

The viscous hysteretic is only observed at loading rates for which stretch period $T$ is comparable to the relaxation time $\tau$. This fact is illustrated by a diagram on Fig. 5.3b depicting the dependance of the amount of the energy dissipated at the first cycle on the $T$ to $\tau$ ratio. This curve shows that a single viscous branch with a given relaxation time will produce any viscous hysteresis only within a certain range of loading velocities. Its span can be limited to a change of magnitude of approximately 2 orders.

For the representation of the real relaxation spectrum several viscous branches need to be incorporated. For the parameter fit of the experimental stress-stain curves on Fig. 5.2 a discrete spectrum of five relaxation times $\{\tau_i\}_{i=1}^5 = \{3, 10, 100, 1000, 10^6\}$ s was taken. With the elastic part of the model given in Fig. 5.1 the only unknown parameters to be identified are the moduli $\{\mu_i\}_{i=1}^5$. Their values are determined by a simple procedure exploiting the linear dependence of the total overstress on the viscous moduli. Namely, the viscoelastic stress is computed as

$$\tau(t) = \tau^e(t) + \sum_{i=1}^5 \tau_i^v(t). \quad (5.1)$$

Denoting the cyclic tests on Fig. 5.2 by the indexes test = $a, b, c$ one can compute the
Figure 5.2: Cyclic uniaxial experiments performed at loading rates $|\dot{\lambda}_1| = 5 \cdot 10^{-1}$ 1/min and $5 \cdot 10^{-2}$ 1/min (from the left to the right). Their most important features such as rate-dependent stiffening and hysteresis broadening, as well as deference between the first and the second cycle and the corresponding change of the viscoelastic modulus are marked on the plots.

Figure 5.3: Viscous response produced by a single branch. a) Relative overstress $P_{11}/\mu^\nu$ for loading periods $T$ much lesser, comparable and much greater than the relaxation time $\tau$. b) Dependence of the relative hysteresis area $H/\mu^\nu$ at the first cycle on the ratio between the loading time and the relaxation time.

Figure 5.4: Normalized overstress profiles for the five viscous branches with the relaxation times $\{\tau_i\}_{i=1}^5 = \{3, 10, 100, 1000, 10^6\}$ s at the three considered uniaxial cyclic tests.
Figure 5.5: Compressive cyclic experiments performed for stretch values $\lambda_1 = 1.0 \ldots 0.75$ at three different loading rates $|\dot{\lambda}_1| = 5 \cdot 10^{-2} \text{ 1/min}, 5 \cdot 10^{-1} \text{ 1/min}$ and $5 \text{ 1/min}$ and the numerical simulation results obtained for the parameter fit on Fig. 5.5.
stress history as a mere combination

\[ \tau^{\text{test}}(t) = \tau^{e,\text{test}}(t) + \sum_{i=1}^{s} \mu^v_i \tau^{v,\text{test}}_i(t), \quad \text{test} = a, b, c. \]  

(5.2)

where \( \tau^{v,\text{test}}_i(t), i = 1 \ldots s, \text{test} = a, b, c \) are the normalized overstress profiles that can be computed separately for each of the branches \( i = 1 \ldots s \) with unit moduli assigned as \( \tilde{\mu}^v_i = 1 \) and the loadings corresponding to the tests \( a, b, c \) (see Fig. 5.4).

The sought for moduli \( \mu^v_i \) are then obtained by minimizing the discrepancy of the stress-strain curves computed by (5.2) to the experimental ones. Application of this procedure resulted in the fit for the cyclic uniaxial tension-compression tests depicted on the Fig. 5.5. The discussed above features of the true viscoelastic response were captured reasonable well by this fit, which one might not have expected from a simple linear model as employed here.

5.3. Model performance for homogeneous tests

The validity of the developed model with the presented above fit was further tested on the problems different to the tests involved immediately in the fit. First such example is a purely compressive uniaxial tests performed for the same HNBR50 material ([34],[35]).

Figure 5.6: Compressive cyclic experiments performed for stretch values \( \lambda_1 = 1.0 \ldots 0.75 \) at three different loading rates \( |\dot{\lambda}_1| = 5 \cdot 10^{-2} 1/\text{min}, 5 \cdot 10^{-1} 1/\text{min} \) and \( 5 \ 1/\text{min} \) and the numerical simulation results obtained for the parameter fit on Fig. 5.5.
They were conducted for the stretch values $\lambda_1 = 1.0 \ldots 0.75$ at three different loading rates $|\dot{\lambda}_1| = 5 \cdot 10^{-2}$ 1/min, $5 \cdot 10^{-1}$ 1/min and 5 1/min. For this problem the mentioned above features of the viscoelastic response at cyclic loading such as the rate-dependent stiffening, hysteresis growth and difference of the first cycle to the subsequent ones is captured qualitatively (see Fig. 5.6).

However quantitively these experimental data are not fully reproduced by the simulation. Particularly, it can be seen that the viscoelastic moduli are underestimated and a substantially softer response is predicted by the model with the parameter fit in Fig. 5.5.

![Figure 5.7](image)

**Figure 5.7:** Cyclic tension-compression uniaxial test at absolute loading rate $|\dot{\lambda}_1| = 3$ 1/min with one hour relaxation breaks at stretch values $\lambda_1 = 0.75, 0.875, 1.0, 1.25, 1.5, 1.75, 2.0$.

a) Strain-stress diagram. b) Evolution of the overstress with time

Another homogeneous experiment on HNBR50 available in [34] captures the relaxation during the breaks in tension-compression cyclic tests. The same specimen as in the preceding tests is subsequently loaded and unloaded in a stepwise manner. At each step the stretch changed from one intermediate value to a next one with absolute loading rate $|\dot{\lambda}_1| = 3$ 1/min and then is kept at constant deformation for a one-hour period. The hold stretch values are $\lambda_1 = 0.75, 0.875, 1.0, 1.25, 1.5, 1.75, 2.0$. Altogether the experiment involves twelve relaxation tests, which allows to observe overstress development at different stretch levels and its relaxation in detail.
References


