Computational study of the cross-link and the entanglement contributions to the elastic properties of model PDMS networks

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Abstract

We built randomly cross-linked model PDMS networks and used Molecular Dynamics Methods to obtain stress-strain curves. Mooney-Rivlin (MR) analysis was used to estimate the shear moduli. We applied Primitive Path analysis (PPA) and its variation, Phantom Primitive Path analysis (3PA), to estimate the entanglement and the cross-link moduli, respectively. The MR moduli estimates are in good agreement with the sum of the entanglement and the cross-link moduli, and we observe that the stress-strain data collapse to a universal form when reduced with the PPA and 3PA moduli. We studied how the MR parameters $C_1$, $C_2$ vary from cross-link to entanglement dominated networks. For the latter, we observed a 40%, 60% contribution of $2C_1$, $2C_2$ to the shear modulus, respectively. Finally, we fitted several models to the data. While all fits are good, the estimates for
the entanglement and the cross-link moduli vary significantly when compared to our PPA and 3PA benchmarks.

1 Introduction

Polymers are long chain-like molecules consisting of repeating chemical units. Cross-linking a polymer melt leads to the formation of an amorphous solid, an elastomer. Elastomers are unique due to their ability to reversibly sustain large deformations that can be up to several times their undeformed size. Comprehensive knowledge of the mechanical properties of elastomers and deep understanding of their microscopic origin are of great fundamental and practical importance.

Elastomers represent, in essence, a single huge molecule, a polymer network, which consists of topologically entangled polymer chains chemically connected by cross-links. The large number of conformational degrees of freedom of the polymer chains gives rise to the enormous reversible deformability of the elastomers and explains why their stress response is dominated by entropic effects. Cross-links and topological entanglements localize thermal fluctuations. These two effects are qualitatively different. Once two or more monomers are jointed by a cross-link, their relative motion is constrained. Polymer chains can not move through each other, the result is topological entanglements that can slide freely along the chains.

Historically, the affine network model and the phantom network model was the first attempt to describe rubbery materials with a microscopic model. However, numerous experimental results showed significant deviations from the predictions of these models. These deviations were due to additional topological constraints, entanglements, not described by these early models. In polymer melts, entanglements are solely responsible for the transient elastic properties characterized by the melt plateau modulus. In networks, the entanglements are permanently "trapped" by cross-links and hence preserve their contribution to elastic properties, i.e. the tube topology is frozen by cross-links. Numerous microscopic models for elasticity of entangled polymer networks have been proposed, e.g., the non-affine tube model and the slip tube model of Rubinstein and
Panyukov, the extended tube model \cite{23} of Kaliske and Heinrich, the double tube model \cite{24} of Mergell and Everaers, the non-affine network model of Davidson and Goulbourne \cite{25}, and the general constitutive model of Xiang et al.\cite{26}. These have been compared to experiment, see, e.g., Refs.\cite{27,28,31}

The most well-known macroscopic phenomenological approach for the description of the mechanical behaviour of rubbery materials is the Mooney-Rivlin (MR) model \cite{32,33,34,35,36,37}. The MR model is based on an empirical expression, relating the strain energy density and deformation tensor. It was shown that the predictive power of the model was limited, and the model was only able to describe uniaxial stretching.\cite{35} Moreover, the microscopic interpretation of the MR model parameters is not clear\cite{38,39,40} and has been a topic for discussion in the literature for more than 50 years.\cite{41}

Cross-linking is the process, by which a precursor melt is converted into a random network. The result is rubber materials with varying elastic properties. However, their microscopic structure remains largely unknown and uncontrolled. Hence, systematic investigations of structure-property relations are faced with difficulties, since experimentally it is nearly impossible to accurately and independently characterize the network structure of the studied samples. Furthermore, different cross-linking chemistries give rise to different types of network defects such as chain scission and dangling ends that acerbate the complexity of analyzing experimental results.\cite{40}

Computer simulations and in particular Molecular Dynamics (MD) methods offer a useful alternative to experiment for systematic investigations of structure-property relations. The greatest advantages of computer modelling compared to experiments are its ability to "look inside" the material under study, total control over the cross-linking process and the ability to comprehensively characterize the resultant network structure as well as its topological state, for instance, by analyzing its strand length and cross-link functionality distributions. Furthermore, ideal defect free models materials can be made.

Reproducibility of simulation results hinges on the ability to produce well equilibrated precursor melts. A polymer chain has the structure of an extended random walk, and many molecules pervade the volume spanned by a single chain. Hard interactions between chains are required in computational polymer models to prevent chain from moving through each other. The aim
of equilibration is to produce well equilibrated model melts, where the statistics of each chain is consistent with the desired polymer chemistry, and density fluctuations are absent due to the incompressibility of melts. Brute force relaxation of precursor melts of practical interest would require simulations exceeding what is possible with current hardware. However, recent advances in melts equilibration techniques, see Refs. 42–44, make it possible to generate very large, highly entangled well equilibrated model precursor melts for computational studies such as the present one.

We generated well-equilibrated KG model precursor melts, following the approach described in Ref. 42. The Kuhn number of the KG polymer model was chosen to match PDMS. The chain ends were initially linked to neighbouring beads \((f = 3)\) and afterwards random neighbour beads were cross-linked \((f = 4)\) to produce model polymer materials with varying cross-link density. The resulting model networks are defect free in the sense that they do not have dangling ends, but they can contain loops. The resulting model materials were uniaxially stretched. We estimate the elastic moduli of model PDMS networks by two approaches: analysis of the simulation stress-strain curves within the scope of the MR empirical model and static structural Primitive Path methods.

Elastic moduli can be estimated from simulation stress-strain data, however, such simulations are expensive due to the very long relaxation times of polymer materials. We invested in excess of 200 core years of computer time in estimation of the equilibrium stresses. The resulting stress-strain curves were analyzed within the scope of the MR model to estimate the parameters \(C_1\), \(C_2\) and, consequently, to obtain the shear modulus \(G\).

Static analysis methods such as Primitive Path Analysis (PPA) and Phantom Primitive Path Analysis (3PA) allows us to independently estimate the entanglement modulus \(G_E\) of the precursor network and the cross-links moduli \(G_X\) of the networks, respectively.

To provide a microscopic interpretation of the empirical MR coefficients, we made Langley plots of \(C_1\), \(C_2\) and also studied the cross-link and entanglement modulus contributions to the shear modulus. Using the entanglement and the cross-link shear moduli, we were also able to reduce our stress-strain data to a single universal curve. We fitted the non-affine tube model, the slip
tube model, the extended tube model, the double tube model, the non-affine network model of Davidson and Goulbourne, and the general constitutive model of Xiang to the simulation data, and compared obtained the cross-link and the entanglement moduli to those independently obtained by the Primitive Path methods. This provides a computational calibration standard of these parameters, which is useful when interpreting fits to experimental results where the cross-link and the entanglement moduli are not independently available.

The paper is organized as follows. Sect. 2 summarizes theoretical background used for the interpretation and the analysis of our KG model simulation results. In Sect. 3, we explain how we build the model networks, characterize them and set up the MD simulations. Besides, we describe the PPA techniques and estimate the range of validity of Gaussian chain statistics. Results are summarized and discussed in Sect. 4. In Sect. 5, we present our conclusions.

## 2 Theoretical models

The present section contains the necessary theoretical background. We begin with the introduction of the unified Kuhn notation for description of polymers [Sect. 2.1]. Next we present the macroscopic Mooney-Rivlin model of incompressible hyperelastic solids [Sect. 2.2] and continue with microscopic models for polymer elasticity [Sect. 2.3].

### 2.1 Kuhn model

In this section, we summarize the Kuhn approach for the description of polymers. Kuhn’s seminal insight was the idea to map a polymer chain to an equivalent freely jointed chain (FJC), matching the contour length and end-to-end distance.

The static configuration of a single polymer molecule can be characterized by its contour length $L$ and mean-square end-to-end distance $\langle R^2 \rangle$. The equivalent Kuhn model chain consists of $N_K$ Kuhn segments of length $l_K$, which is denoted as the Kuhn length. Values of $N_K$ and $l_K$ are chosen to match the mean-square end-to-end distance and the contour length of the molecule, hence, $L =$
$l_K N_K, \langle R^2 \rangle = l_K^2 N_K$, therefore, one obtains $l_K = \langle R^2 \rangle / L$ for the Kuhn length and $N_K = L^2 / \langle R^2 \rangle$ for the number of Kuhn segments. The molar mass of a Kuhn segment is $M_K = M_c / N_K$ where $M_c$ denotes the molar mass of the polymer molecule.

To describe the static properties of a system of many interpenetrating long polymer molecules, the number density of Kuhn segments $\rho_K = \rho_c N_K$, where $\rho_c$ is the number density of chains, and the volume spanned by a single chain $V = \langle R^2 \rangle^{3/2} = l_K^3 N_K^{3/2}$ are introduced. The degree of chain interpenetration is described by the Flory number, $n_F = \rho_c V$, which estimates the number of neighbor chains a single chain can interact with. The Flory number can be expressed in Kuhn parameters as $n_F = \rho_K l_K^3 N_K^{1/2}$. While the chain length $N_K$ varies from melt to melt, the prefactor $n_K = \rho_K l_K^3$ called the Kuhn number plays the role of dimensionless density and depends only on the specific polymer chemistry.

The characteristic time scales for the dynamics of a single polymer molecule are obtained from the Rouse model. The dynamics of a Kuhn segment can be characterized by a friction coefficient $\zeta_K$ or, equivalently, by the Kuhn time $\tau_K \sim l_K^2 / D_K \sim l_K^2 N_K^{3/2} / (k_B T)$, which is the time it takes a Kuhn segment to diffuse a Kuhn length $l_K$, where $D_K = k_B T / \zeta_K$ is the Kuhn segment diffusion constant, $k_B$ is the Boltzmann constant, and $T$ is temperature. The dynamics of a whole chain can be characterized by the Rouse time $\tau_R \sim \langle R^2 \rangle / D_c \sim l_K^2 N_K^{2} N_K^{1/2} / (k_B T)$, which is the time required for a chain to diffuse its own size, where $D_c = k_B T / (N_K \zeta_K)$ is the chain diffusion coefficient. Consequently, the Rouse and Kuhn times are related as $\tau_R = \tau_K N_K^2$.

The major advantage of the Kuhn description of polymer physics is that the universal properties (dominated by conformational entropy) become apparent. For the present model networks, we expect their properties to depend only on two dimensionless parameters: the Kuhn number $n_K$ and the average strand length $N_{KK}$.

### 2.2 Mooney-Rivlin material model

The empirical Mooney-Rivlin model (MR) for incompressible hyperelastic material is often used for the analysis of the experimental stress-strain data and elastic moduli estimation of rubbery
polymers. The model relates the strain energy density function $W$ stored by an incompressible solid and its deformation as:

$$W(\Phi) = C_1 (I_1(\Phi) - 3) + C_2 (I_2(\Phi) - 3),$$  

where $C_1$, $C_2$ are the material constants, $I_1(\Phi) = \text{Tr} \Phi$, $I_2(\Phi) = \left( (\text{Tr} \Phi)^2 - \text{Tr} (\Phi^2) \right) / 2$ are the 1st and the 2nd invariants of the Finger tensor $\Phi = E \cdot E^T$, respectively, $E = \left( \begin{array}{c} 0 \\ \nabla \vec{R} \end{array} \right)^T$ is the deformation gradient tensor and $\vec{R}$ is a coordinate vector of a material point in the actual configuration. The operator $\nabla_0$ indicates that differentiation is performed with respect to coordinates of a material point in the reference configuration.

The MR parameters $C_1$, $C_2$ are related to the shear modulus $G$ as:

$$G = 2 \left( C_1 + C_2 \right).$$  

Let us consider uniaxial deformation of a solid along $Ox$ axis by a factor $\lambda$, then the normal tension $\sigma_N$ is given by:

$$\sigma_N \equiv \sigma_{xx} - \frac{\sigma_{yy} + \sigma_{zz}}{2} = 2 \left( C_1 + C_2 \lambda^{-1} \right) \left( \lambda^2 - \lambda^{-1} \right).$$  

here $\sigma_{xx}$, $\sigma_{yy}$ and $\sigma_{zz}$ are the diagonal components of the Cauchy stress tensor $\sigma$:

$$\sigma = \frac{\partial W}{\partial \Phi} \cdot \Phi^T - P \mathbf{I},$$

where $P$ is pressure, $\mathbf{I}$ is the unit tensor. For analysis and convenient representation of experimental results, the reduced normal tension $\tilde{\sigma}_N$ is defined as:

$$\tilde{\sigma}_N(\lambda) \equiv \frac{\sigma_N}{\lambda^2 - \lambda^{-1}} = 2 \left( C_1 + C_2 \lambda^{-1} \right),$$

hence, the MR model postulates a linear dependency of $\tilde{\sigma}_N$ on the inverse elongation $\lambda^{-1}$. 
It was shown that the MR model provided a good description of experiments on uniaxial stretching of rubbery materials, whereas it failed to describe other deformation modes nor did it correctly describe the materials stress response at large deformations.\[20\,27\,52\]

### 2.3 Microscopic models of polymer elasticity

The MR model is empirical, hence the model parameters $C_1$, $C_2$ do not \textit{a priori} have a physical interpretation. To identify them, one would have to elucidate their microscopic origin, e.g. relate them to the cross-link and the entanglement moduli $G_X$, $G_E$ of rubber model materials.\[39\,40\]

The first microscopic theories of polymer elasticity incorporated only the contribution from network connectivity. The affine network model\[7\,14\] assumes that all strands are monodisperse and pinned to a deforming background. The model predicts the cross-link modulus as:

$$G_{X}^{\text{aff}} \equiv \frac{\sigma_N}{\lambda^2 - \lambda^{-1}} = \frac{\rho_{K} k_B T}{N_{XK}},$$

where $N_{XK}$ is the number of Kuhn segments per network strand. On the other hand, the phantom network model\[15\,19\] does not constrain rigidly the thermal fluctuations of the network junctions. For the cross-link modulus the following relation was derived:\[19\,53\,54\]

$$G_{X}^{\text{ph}} = (\rho_{S}^{\text{good}} - \rho_{X}^{\text{good}}) k_B T,$$

where $\rho_{S}^{\text{good}}$, $\rho_{X}^{\text{good}}$ are the densities of ”good” strands and cross-links, respectively. During cross-linking, network defects such as dangling ends and loops are created. They do not carry stress upon macroscopic deformation, hence, do not contribute to the elastic properties of the cross-linked material. ”Bad” strands are only connected to the network by one end, and as such can not carry a load. Loops are formed when two monomers belonging to the same polymer chain are cross-linked. Most such loops are short and do not capture entanglements with other chains. During our network analysis, we designate as ”good” strands those, which end on two different cross-links belonging to the good network, and by ”good” cross-links we mean those, which have
at least two "good" strands, emanating from them.

In the case where all the junctions are assumed to have the same functionality $f$ and the network strands are assumed to be monodisperse with the length $N_{XX}$, the phantom network model Eq. (6) reduces to:

$$G_X^{ph} = \left(1 - \frac{2}{f}\right) \rho_k k_B T \frac{N_{XX}}{N_{XX}}. \quad (7)$$

The prefactor $1 - 2/f$ was interpreted as being due to the fact that the strand ends are not directly pinned to the deforming background as in the affine network model, but rather via an infinite Cayley tree of monodisperse strands and $f$-functional junctions. Refinements of this approximation, including the effects of loops, have been recently proposed in Refs. 55-58.

The effect of topological entanglements can be accounted for in multiple ways, and the tube model, introduced in Refs. 3,4, is among the most successful ones. The idea is that thermal fluctuations of the network chains are restricted in space not only by the cross-links, but also by entanglements. Numerous approaches have been proposed, and below we present several models, which contain the cross-link and the entanglement moduli $G_X, G_E$ as parameters. In addition, we point out the relations of $G_X, G_E$ to the MR model parameters $C_1, C_2$. The expressions below for the reduced normal tension $\tilde{\sigma}_N$ correspond to the uniaxial deformation.

In the Warner-Edwards tube model, it is assumed that the tube moves affinely with the imposed deformation, while its diameter is strain independent. The resulting stress-strain relation is the same as in the phantom network model, hence, the Warner-Edwards tube model predicts that both the cross-link and the entanglement moduli $G_X, G_E$ contribute only to $C_1$ MR model parameter, whereas $C_2$ remains equal to zero.

The non-affine tube model of Rubinstein and Panyukov represents the confinement potential due to entanglements as an additional set of harmonic virtual chains, acting along the real network chains. These virtual chains connect the strand ends to the nonfluctuating elastic background. The spring constant of the virtual chains, which determines the strength of the confinement potential, is supposed to be deformation dependent in such a way that the fluctuations of the virtual strands change affinely with the network deformation. The main result of the model is that the diameter of
the confining tube deforms non-affinely as $d_\mu \sim \lambda_\mu^{1/2}$, $\mu = x, y, z$, where $d_\mu$ is the tube diameter along the coordinate axis $\mu$. For the reduced normal tension, the non-affine tube model predicts:

$$\tilde{\sigma}_N(\lambda) = G_X + \frac{G_E}{\lambda - \lambda^{1/2} + 1},$$

(8)

where $G_X$ is related to the cross-links modulus and $G_E$ is related to the entanglement modulus. Expanding Eqs. (8) and (4) at low strains $\varepsilon$, where $\varepsilon = 1 - \lambda$, one obtains the following relations between the MR model parameters $C_1, C_2$ and microscopic moduli $G_X, G_E$:

$$2C_1 = G_X + 0.5G_E, \quad 2C_2 = 0.5G_E.$$  

(9)

The slip tube model\textsuperscript{22} refines the non-affine tube model\textsuperscript{21} of Rubinstein and Panyukov. The attachment junctions between the virtual chains and the network strands are replaced by the slip links, which are allowed to slide along the network chains, but not to pass each other. Consequently, the chain can redistribute its contour length along the tube upon the network deformation. Within the scope of the slip tube model, the reduced normal tension is given by:

$$\tilde{\sigma}_N(\lambda) = G_X + \frac{G_E}{0.74\lambda + 0.61\lambda^{-1/2} - 0.35},$$

(10)

and the MR model parameters are identified as:

$$2C_1 = G_X + 0.565G_E, \quad 2C_2 = 0.435G_E.$$  

(11)

The double tube model\textsuperscript{24} postulates that the ends of the confinement springs of the confinement potentials deform affinely, while the localization strength is assumed to be sub-affine for the entanglement tube and strain-independent for the cross-link tube. The reduced normal tension within
the scope of the double tube model can be expressed as:

\[ \tilde{\sigma}_N(\lambda) = \frac{\lambda^2 - 1}{\lambda^2 - \lambda^{-1}} \frac{G_X^2 + 2 \left( \frac{G_E}{\lambda} \right)^2}{\sqrt{G_X^2 + 4 \left( \frac{G_E}{\lambda} \right)^2}} + \frac{1 - \lambda^{-1}}{\lambda^2 - \lambda^{-1}} \frac{G_X^2 + 2 G_E^2 \lambda}{\sqrt{G_X^2 + 4 G_E^2 \lambda}}, \]  

(12)

and the MR model parameters are related to \( G_X, G_E \) as:

\[ 2C_1 = \frac{G_X^4 + 6 G_X^2 G_E^2 + 4 G_E^4}{(G_X^2 + 4 G_E^2)^{3/2}}, \quad 2C_2 = \frac{4 G_E^4}{(G_X^2 + 4 G_E^2)^{3/2}}, \]  

(13)

and we note that both the cross-link and the entanglement moduli \( G_X, G_E \) contribute to both MR model parameters \( C_1, C_2 \) and that the network modulus is not just a simple sum \( G_X + G_E \).

The models presented above are all based on Gaussian distribution for chain configurations:

\[ P(N_K, R) \propto \exp \left( -\frac{3 R^2}{2 N_K l_K^2} \right), \]  

(14)

where \( R \) is the absolute values of the chain end-to-end vector, \( N_K \) is number of Kuhn segments in the chain, \( l_K \) is the Kuhn length defined in Sect. 2.1. At large deformations, when a polymer molecule is pulled up to its contour length \( (R \sim N_K l_K) \), this approximation is not reliable as it does not capture the finite extensibility of a polymer molecule. The models presented below are based on more realistic approximations, which take finite chain length effects into account.

The extended tube model developed by Kaliske and Heinrich\(^2^3\) is essentially a more detailed version of the non-affine tube model\(^2^1\). The authors modified the Gaussian distribution by introducing a singularity as proposed in Ref.\(^5^9\). The singularity is controlled by the finite extensibility parameter \( \delta \equiv \left\langle (\partial R(s)/\partial s)^2 \right\rangle \), where \( R \) is the end-to-end vector of the network chain, and \( s \) is the contour coordinate. By construction, the choice \( \delta = 0 \) neglects finite extensibility effects. The tube diameter is supposed to depend on strain as \( d_\mu \sim \lambda^{\alpha \beta} \), \( \mu = x, y, z \), where \( \alpha = 1/2 \) as in the non-affine tube model, \( \beta \in (0; 1) \) is taken as an empirical fit parameter, which is interpreted as indicat-
ing the completeness of the cross-linking reaction. The relaxation of the dangling ends is assumed
to affect the effective strain dependency of the tube diameter making it more isotropic ($\beta \to 0$).
The value $\beta \approx 1$ corresponds to a defect free network.\textsuperscript{23} The reduced normal tension was derived as:

$$\bar{\sigma}_N(\lambda) = G_X + G_E \varphi(\lambda),$$

(15)

where

$$\varphi(\lambda) = \frac{2}{\beta} \frac{\lambda^{\beta/2} - \lambda^{-\beta}}{(\lambda^2 - \lambda^{-1}) g(D, \delta)};$$

$$g(D, \delta) = \frac{1 - \delta^2}{(1 - \delta^2 (D - 3))^2} - \frac{\delta^2}{1 - \delta^2 (D - 3)},$$

and $D = \lambda^2 + 2 \lambda^{-1}$. Consequently, the MR model parameters are found as:

$$2C_1 = G_X + G_E \frac{2 - \beta}{4 - 8 \delta^2}, \quad 2C_2 = G_E \frac{2 + \beta}{4 - 8 \delta^2}.$$

(16)

In particular case, when finite extensibility effects are neglected, $\delta = 0$, and $\beta = 0$, Eq. (16) reduce to Eq. (9). On the other hand, if $\beta = 1$, then Eq. (16) reduces to $2C_1 = G_X + 0.25 G_E$, $2C_2 = 0.75 G_E$.

The non-affine network model of Davidson and Goulbourne\textsuperscript{25} generalizes the phantom network model and combines it with the non-affine tube model of Rubinstein and Panyukov.\textsuperscript{21} The authors repeated the derivation of Eq. (7) as in Ref.\textsuperscript{22}, but for statistics of the effective strands they used the exact solution of the freely jointed chain model derived in Ref.\textsuperscript{8}:

$$P(N, R) \propto \exp \left\{-\frac{R}{l_K} \mathcal{L}^{-1} \left( \frac{R}{N_K l_K} \right) - N_K \ln \left[ \frac{\mathcal{L}^{-1} \left( \frac{R}{N_K l_K} \right)}{\sinh \left( \mathcal{L}^{-1} \left( \frac{R}{N_K l_K} \right) \right)} \right] \right\},$$

(17)

and used the Padé approximant\textsuperscript{41} for the inverse Langevin function $\mathcal{L}^{-1}(x) = \coth(x) - 1/x$. For
the reduced normal tension, they obtained:

\[ \tilde{\sigma}_N(\lambda) = G_X \left( \frac{\lambda^2 + 2\lambda^{-1} - 9\lambda_{\text{max}}^2}{3(\lambda^2 + 2\lambda^{-1} - 3\lambda_{\text{max}}^2)} \right) + G_E \frac{\lambda - \lambda^{-1} - \lambda^{-1/2} + \lambda^{1/2}}{\lambda^2 - \lambda^{-1}}, \]  

(18)

where \( \lambda_{\text{max}} = \frac{1}{g} \sqrt{\frac{N_{XX}}{1-2/f}} \) is the maximum stretch. The \( g \) parameter is used to interpolate between phantom \( (g = 1) \) and affine network behaviour \( (g = 1/\sqrt{1-2f^{-1}}) \). The MR model parameters are expressed as:

\[ 2C_1 = G_X \frac{1 - 3\lambda_{\text{max}}^2}{3(1-\lambda_{\text{max}}^2)} + 0.5G_E, \quad 2C_2 = 0.5G_E. \]  

(19)

When finite extensibility of the network chains is not taken into account, Eq. (19) reduces to the non-affine tube model Eq. (9).

Xiang et al.\(^{26}\) combined a generalized version of the affine network model Eq. (5) with the tube deformation hypotheses of Heinrich and Straube\(^{62}\) and the three-chain model\(^{15}\) to derive their generalized constitutive model. Generalization of the affine network model is based on the freely jointed chain distribution (Eq. 17) with an approximation for the inverse Langevin function due to Kröger.\(^{63}\) Within the scope of Xiang et al. model, the reduced normal tension at uniaxial deformation has the following form:

\[ \tilde{\sigma}_N(\lambda) = G_X \left[ \left( 1 - \frac{I_1}{3N_{XX}} \right) \left( 1 + \frac{I_1}{2(1/3N_{XX})} \right) \right]^{-1} + 2G_E \frac{\lambda^{1/2} - \lambda^{-1}}{\lambda^2 - \lambda^{-1}}, \]  

(20)

where \( I_1 = \lambda^2 + 2\lambda^{-1} \) is the 1\textsuperscript{st} invariant of the Finger deformation tensor, \( N_{XX} \) is the network strand length, and the MR coefficients are derived as:

\[ 2C_1 = G_X \frac{2N_{XX}^2}{2N_{XX}^2 - N_{XX} - 1} + \frac{1}{4}G_E, \quad 2C_2 = \frac{3}{4}G_E. \]  

(21)

Here, we redefined the entanglement modulus \( G_E \) by including a prefactor of 2, so that the sum 2\( C_1 + 2C_2 \) gives the full contribution from entanglement effects \( G_X + G_E \). When finite extensibility of the network chains is not taken into account, the expression for the reduced normal
tension (20) reduces to the extended tube model Eq. (15) with $\beta = 1$, $\delta = 0$.

Hence, to summarize, the classical affine and phantom models, which neglect entanglements, correspond to the MR model with $2C_1 = G_X$, $2C_2 = 0$. This also applies to the Warner-Edwards tube model, which has a strain independent tube diameter. The tube models with strain dependent tube diameters put the cross-link modulus entirely into the $C_1$ parameter and split the entanglement effects between $C_1$ and $C_2$. Among all the models, only the slip tube model accounts for the chain contour length redistribution between parallel and perpendicular tube sections upon deformation. The non-affine tube model, the slip tube model, and the double tube model assume Gaussian chain statistics and neglect finite extensibility effects. The extended tube model of Kaliske and Heinrich, the non-affine network model of Davidson and Goulbourne, and the general constitutive model of Xiang et al. take finite extensibility into account using various approaches to describe non-Gaussian chain statistics at the expense of introduction additional model parameters. It is worth noting that the estimates for the shear modulus provided by extended tube model, the non-affine network model and the general constitutive model depend on their finite extensibility parameters. All models except the double tube assume additivity of network connectiviy and the entanglement effects.

3 Methods

In this section, we briefly introduce the Kremer-Grest (KG) polymer model [Sect. 3.1] and mapping relations between the KG model, the Kuhn representation and PDMS [Sect. 3.2], describe our procedure for generating model polymer networks from an equilibrated precursor melt and characterize their microscopic structure [Sect. 3.3], present our protocol for the model networks deformation and describe the results postprocessing [Sect. 3.4]. In Sect. 3.5 Sect. 3.6 we introduce the Primitive Path Analysis (PPA) and the Phantom Primitive Path Analysis (3PA), respectively. In Sect. 3.7 we introduce the concept of finite extensibility of polymer chains and estimate the limits of applicability of elasticity theories, based on the Gaussian chain statistics.
3.1 Kremer-Grest model

To study structure-property relations for PDMS rubbers, we utilize the KG model in combination with an angular potential. Within the scope of the generic Kremer-Grest model (KG)\textsuperscript{64,65} polymers are represented as linear bead-spring chains. Pair interactions between beads are described by the Weeks-Chandler-Anderson (WCA) potential:

\begin{equation}
U_{\text{WCA}}(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} + \frac{1}{4} \right], \quad r < \sigma^{6/\sqrt{2}}, \tag{22}
\end{equation}

and the interactions of bonded beads are described by the FENE potential:

\begin{equation}
U_{\text{FENE}}(r) = -\frac{1}{2} k R_0 \ln \left[ 1 - \left( \frac{r}{R_0} \right)^2 \right], \tag{23}
\end{equation}

where \(\varepsilon\) is energy scale, \(\sigma\) is chosen as the simulation unit of length. The standard choice for the spring constant is \(k = 30 \varepsilon \sigma^{-2}\), \(R_0\) is set to 1.5 \(\sigma\), which leads to average bond length \(l_b = 0.965 \sigma\). The simulation unit of time is defined as \(\tau = \sqrt{m \sigma^2 / \varepsilon}\), where \(m\) denotes the mass of a bead which we choose as our simulation mass scale.

The KG model is a generic polymer model. To adapt it to specific chemical polymer species\textsuperscript{45,66}, we introduce an additional bending interaction:

\begin{equation}
U_{\text{bend}}(\theta) = \kappa \varepsilon \left( 1 - \cos \theta \right), \tag{24}
\end{equation}

where \(\kappa\) is the stiffness constant. The angular potential\textsuperscript{24} was introduced in Ref.\textsuperscript{66}. For a discussion of the choice of the stiffness constant, see Sect. 3.2.

The dynamics of the KG model is governed by the Langevin equation:

\begin{equation}
m \frac{\partial \mathbf{R}_n}{\partial t^2} = -\nabla_{\mathbf{R}_n} U - \Gamma \frac{\partial \mathbf{R}_n}{\partial t} + \xi_n, \tag{25}
\end{equation}

where \(\mathbf{R}_n\) is the position on \(n\)-th bead, \(U\) is interaction potential. The bead friction \(\Gamma\) is set to
0.5\,m\tau^{-1}. The stochastic force terms $\xi_n$ obey statistics $\langle \xi_n \rangle = 0$ and $\langle \xi_m(t) \otimes \xi_n(t') \rangle = 6\,k_B T \Gamma / \Delta t \delta(m - n) \delta(t - t') I$, where $I$ is the unit tensor and $\Delta t$ is the time step. The Langevin equation was integrated with time step $0.01\,\tau$ using the GJ-F Langevin integrator, which is a Verlet-type algorithm implemented in LAMMPS.

3.2 Mapping of units for PDMS

By its nature, the KG model does not correspond to any specific of chemical polymer. The introduction of the bending potential Eq. (24) allows one to tune the Kuhn number $n_K(\kappa)$ of a KG model to match the Kuhn number of any desired polymer. For instance, to match PDMS, which has $n_K = 2.82$, one has to choose the bending constant $\kappa = 0.013$, which is nearly identical to the standard KG model. This particular KG model we denote PDMS-KG model. It has a Kuhn length of $l_K = 1.853\,\sigma$, which is identified with the experimental value $l_K = 11.42\,\text{Å}$.

Hence, $1\,\sigma = 6.17\,\text{Å}$. The PDMS-KG model also has $C_\infty = 1.921$ beads per Kuhn segment, and the mass of a Kuhn segment $M_K = C_\infty m_b$ expressed in KG units is identified with the molar mass $M_K = 309.28\,\text{g/mol}$ of a PDMS Kuhn segment. Consequently, $m_b = M_K / C_\infty = 160.99\,\text{g/mol}$. The entanglement time of PDMS-KG model $\tau_E = 8500\,\tau$ is identified with the experimental entanglement time of PDMS $\tau_E = 0.11\,\mu\text{s}$. Therefore, $1\,\tau = 0.013\,\text{ns}$. Finally, the energy scale $\epsilon$ of the KG model is identified with $k_B T$, where $T$ denotes the temperature at which the experimental reference system is characterized. Therefore, the energy density conversion for PDMS-KG is obtained as $1\,\epsilon\,\sigma^{-3} = 17.6\,\text{MPa}$, which we use to convert stress data to SI units. Following these relations, results expressed in simulation units of the KG model with PDMS stiffness can be converted into PDMS specific SI or Kuhn units.

Note, that it is not necessary to match independently, for instance, the entanglement length of the KG model with the entanglement length of PDMS, as these structural properties emerge automatically as a result of the proper choice of the Kuhn number. According to the packing argument, $N_{EK} = \alpha^2 / n_K^2$, where $\alpha = 19.0 \pm 2$ is the number of entanglement strands in an entanglement volume. Moreover, in dimensionless Kuhn form, one can write $G_E l_K^3 / (k_B T) =$
\( n_K/N_{EK} \). Hence, our PDMS-KG model with Kuhn number \( n_K = 2.82 \) automatically reproduces the entanglement strand length \( N_{EK} = 45.9 \pm 9.6 \) as well as the entanglement modulus \( G_E = 0.18 \pm 0.04 \text{MPa} \) of the target polymer as these quantities depend only on the Kuhn number.

### 3.3 Generation and characterization of model networks

To build model polymer networks, we start from the melt generation procedure of Svaneborg et al.\(^{42}\) The approach allows one to generate large equilibrated polymer melts in a computationally effective way. Briefly, a polymer melt is generated as a random walk on a cubic lattice. As lattice parameter we choose the tube diameter of the polymer. Multiple chains (\( \alpha = 19 \)) are allowed to occupy the same site in the lattice. A Monte-Carlo simulated annealing algorithm is used to minimize large scale density fluctuations. This results in equilibration of melt configuration above the tube scale. Next, the lattice melt conformation is transformed into a bead-spring conformation, and we simulate a Rouse dynamics with a stiffness tuned and WCA force-capped Kremer-Grest force field. This introduces the desired random walk chain structure below the tube scale, while preventing the growth of density fluctuations. Finally, the local bead packing structure is equilibrated via a short simulation with the full KG force field. Following the procedure, we generated an equilibrated KG polymer melt model, comprising of 500 chains with 10000 beads each, corresponding to about \( Z = 85 \) entanglements per chain and systems with 5 million beads. For comparison, recently in Ref.\(^{78}\), Hsu et al. generated systems with a size of 2 million beads.

Earlier, in Sect. 3.2 we presented the PDMS-KG model. Here, we use the results of an earlier numerical analysis of the mapping of PDMS to the KG model, where the bending stiffness was estimated as \( \kappa = 0.206 \). In subsequent refinements of these mapping relations, the bending stiffness estimate changed to \( \kappa = 0.013 \). The corresponding error of the Kuhn number is \( \approx 8\% \), of the Kuhn length is \( \approx 4\% \), of the entanglement length is \( \approx 15\% \) and of the energy density is \( \approx 12\% \).

Cross-linking was initiated by first connecting chain ends to the closest neighbouring beads in the precursor melt to avoid dangling ends. Afterwards, random bead pairs within a distance \( 1.3\sigma \) were chosen and linked if they were not already connected. Following the procedure, we
Figure 1: Microscopic characterization of model networks. [A] Average network strand length $\langle N_{\text{XK}} \rangle$ as a function of the number of cross-links $N_{\text{X}}$ added for 4 different runs of cross-linking procedure. [B] Distribution of network strand lengths. Dashed lines correspond to empirical relation (25) written for each model network. [C] Distribution of cross-link functionalities.

generated set of the PDMS-KG model networks, ranging from weakly to strongly cross-linked, characterized by average network strand length values $\langle N_{\text{XK}} \rangle$ equal to 100, 75, 50, 35, 20, 10 and number of cross-links from 1000 to 130000. For the end-linked network, we expect entanglement effects to dominate over the network connectivity as there are $\langle N_{\text{XK}} \rangle / N_{\text{EK}} = 56$ entanglements per
network strand, where for the present model the entanglement strand length $N_{E K} \approx 33.11$. For the most strongly cross-linked system, $N_{E K} / \langle N_{X K} \rangle = 3.7$, hence, we have approximately 4 cross-links per entanglement strand. The value $\langle N_{X K} \rangle = 35 \approx N_{E K}$ is of special interest as contributions from the network connectivity and the entanglement effect to the shear modulus are expected to be comparable.

In Fig. 1, we present a characterization of the generated networks. Fig. 1A shows how the average strand length $\langle N_{X K} \rangle$ depends on the number of cross-links $N_X$ added to the system. We derived the empirical relation between average network strand length and number of cross-links in the form $\ln N_{X K} = 0.016 \ln^2 N_X - 1.340 \ln N_X + 16.514$. We repeated the cross-linking process several times from different random initial seeds and verified that the systems were large enough to be self-averaging, hence, we expect our results to be reproducible and report results only for one of the networks.

The plot in Fig. 1B indicates the exponential distribution of network strand lengths $N_{X K}$ with pre-defined average length value $\langle N_{X K} \rangle$:

$$P(N_{X K}) = \frac{1}{\langle N_{X K} \rangle} \exp \left( -\frac{N_{X K}}{\langle N_{X K} \rangle} \right).$$

Relative number of strands $N_s(N_{X K})/N_s$, having specific length $N_{X K}$ in Kuhn units, where $N_s$ is the total number of strands, is shown as a function of $N_{X K}$. Average values of network strand lengths $\langle N_{X K} \rangle$, shown in the legend, are calculated basing on the network analysis. The reason why they differ from the nominal values, targetted during cross-linking the precursor melt, is the way how we define a cross-link. The value $\langle N_{X K} \rangle \approx 1850$, obtained for the end-linked melt, differs from the chain length 10,000 beads. This is due to chain ends are connected to a random bead in their neighbourhood, which is most likely an internal bead in another chain.

The bottom plot in Fig. 1C shows the distribution of cross-link functionalities. We observe that the vast majority of cross-links are 4-functional. For the end-linked model network, most of the initial cross-links are three functional since in this case most ends are cross-linked with an internal
bead in a neighboring chain. We emphasize that the model network statistics is observed to be the same for multiple runs of the cross-linking procedure, which is due to the fact that our system sizes are large enough to be effectively self-averaging.

3.4 Network deformation

Deformation simulations of the networks were carried out in two stages. At first, model networks were stretched uniaxially and volume preserving. Subsequently, we simulated the networks at constant strain to relax the stress. During the deformation, the (engineering) strain rate \( \dot{\varepsilon} \) was chosen large enough to save computer time and minimize relaxation effects and, secondly, small enough to avoid bonds reaching the distance \( 1.5 \sigma \), where the FENE potential diverges. We used \( \dot{\varepsilon} = 0.01 \tau^{-1} \) (in LJ units, see Sect. 3.1), which corresponds to the inverse Rouse time for a net-
work strand of ≈ 4 Kuhn segments (≈ 8 beads), occupying a spatial distance ≈ 4σ. Hence, only short strand segments are in quasi-equilibrium upon deformation, whereas for long strand segments affine deformation response is expected. Simulations were terminated, if a bond reached length of 1.4σ. For KG melts and networks in the unstrained state the topological state is preserved since there is a potential barrier of \( \sim 75 k_B T \) for chains to move through each other.\(^{79}\) As bonds are stretched as a result of the network deformation, this potential barrier is progressively reduced. We estimate that the potential barrier has dropped to \( \sim 30 k_B T \) for a bond with length 1.4σ, see Ref.\(^{80}\). Continuing the simulations beyond this point leads to spurious results as we can not be sure that entanglements are preserved.

Relaxation in elastomers has two characteristic time scales. The Rouse time \( \tau_R \sim N_{XK}^2 \) is the time it takes for a network strand of length \( N_{XK} \) to relax. The entanglement time \( \tau_E \sim N_{EK}^2 \) is the time scale, at which the dynamics of a bead starts being affected by entanglements, where \( N_{EK} \) is the distance between neighbour entanglements. We supposed that the relaxation dynamics of highly cross-linked networks, \( N_{XK} < N_{EK} \), was dominated by the Rouse time of short network strands, whereas the dynamics of loosely cross-linked networks, \( N_{XK} > N_{EK} \), is dominated by the entanglement time. Hence, the characteristic relaxation time \( \tau_{rlx} \) of a model network was estimated as the minimum between the entanglement time \( \tau_E \) and the Rouse time \( \tau_R \) for average network strand length. Stress relaxation was sampled for 10–11 \( \tau_{rlx} \).

Fig. 2A shows the relaxation of the reduced stresses \( \tilde{\sigma}_N \) of the model networks plotted versus simulation time \( t \), which is scaled by the relaxation time \( \tau_{rlx} \). As clearly seen, most stress relaxation occurs for \( t < \tau_{rlx} \) [see inset in Fig. 2A] and the subsequent dynamics is very slow. In addition, the relaxation curves in logarithmic representation are parallel and approximately linear over more than a decade. This suggests an initial powerlaw-like decay as expected from the Rouse model. Moreover, relaxation curves corresponding to the networks with \( N_{XK} \geq 35 \) collapse (the inset plot). This justifies our assumption of the network dependence of the characteristic relaxation times. As expected the shear moduli are ordered by the degree of cross-linking.

Fig. 2B shows relaxation of the reduced normal tension of multiple deformed states of the
model network $N_{XK} = 35$ as a function of the inverse time, starting from $t = 3 \tau_{rlx}$. In Fig. 2A, the stresses appear to be in equilibrium. However, Fig. 2B clearly shows that the stresses have not reached equilibrium for any deformation, and slow relaxation process is observed even after $10 \tau_{rlx}$. To estimate the equilibrium reduced normal tension, we extrapolated the relaxation curves towards $t^{-1} \to 0$, i.e. to $t \to \infty$. As a fitting function a linear polynomium $a + bt^{-1}$ was used. Due to the representation of the data as a function of the inverse time, density of the data in the vicinity of $(t/\tau_{rlx})^{-1} = 0$ is much higher than in the vicinity of $(t/\tau_{rlx})^{-1} = 0.33$. Hence, the data was binned as a function of inverse time prior to fitting to correct for this. When fitting, the data within each bin was weighted by the bin variance. We observed that the relative error could be up to 7% too high, if one uses the time averaged stresses for $t > 3 \tau_{rlx}$ as an estimate of the equilibrium stress rather than the present extrapolation.

### 3.5 PPA: Primitive Path Analysis

Tube models for polymer viscoelasticity are based on the idea that thermal fluctuations of chains are localized by entanglement constraints with neighbouring chains. The central axis of the confinement tube is called primitive path. Tube models inspired the so called Primitive Path Analysis (PPA). The analysis allows one to obtain the primitive path mesh, and in particular their average contour length $L_{pp}$. Based on $L_{pp}$, one can easily estimate the average entanglement strand length $N_{EK}$ as $\frac{L_c^2}{L_{pp}^2}$, where $L_c$ is the original chain contour length, and, consequently, obtain the entanglement modulus:

$$G_E = \frac{\rho K k_B T}{N_{EK}}.$$  

(27)

Implementation of the PPA within the scope of the MD simulations is comprehensively described in Refs. Chain ends are pinned in space, intramolecular pair interactions are switched off, intermolecular pair interactions are kept to prevent chains passing through each other, bonds are modelled as FENE springs with an arbitrary spring constant $k$, and melt is cooled down to $T = 0$ to eliminate thermal fluctuations. Visualization of the precursor melt PPA mesh is shown in
Figure 3: Visualization of a thin slab of the precursor melt PPA mesh (A) and corresponding chain conformations of the model network \( \langle N_{XK} \rangle = 35 \) (B). Colors indicate precursor chains and in the network cross-links are represented by black bonds.

Fig. 3A for comparison, we also show a network Fig. 3B to illustrate the real chain structure.

We identify the result of the PPA analysis with the entanglement modulus and not the plateau modulus. The latter is reduced by 20% compared to the former due to the entanglements which are lost due to chain contraction to the equilibrium contour length after the deformation of a melt. In a network no such contraction process occurs, thus making the entanglement modulus the relevant parameter.

3.6 3PA: Phantom Primitive Path Analysis

It would be natural to ask if we can estimate the cross-link contribution to the shear modulus by performing an analysis similar to the PPA, but applied to the model networks. The theoretical
Figure 4: Visualization of slabs of 3PA meshes for networks with \( \langle N_{XX} \rangle = 10 \) (A), \( \langle N_{XX} \rangle = 35 \) (B), and \( \langle N_{XX} \rangle = 100 \) (C). Slabs and chain colors as in Fig. 3.

The rationale for how to formulate such an analysis is provided by the phantom network model. The Phantom Primitive Path Analysis (3PA) allows us to measure the cross-link modulus by deforming phantom meshes.
The 3PA analysis proceeds similar to PPA analysis, except that all pair interactions between beads are switched off. The model network is cooled down to $T = 0$ to eliminate thermal fluctuations, hence, it is converted into the mechanical equilibrium state of the corresponding phantom model – the 3PA mesh. To eliminate finite extensibility effects, we replaced FENE bonds by harmonic bonds. Instead of analyzing the network topology, we measure the stress tensor of the deformed phantom meshes. Since thermal fluctuations in the phantom model are strain independent, they do not contribute to the stress. Hence the stress-strain behaviour of the phantom mesh is sufficient to estimate the cross-link contribution to the network modulus. Since the 3PA force field differs from the KG force field, the 3PA stress has to be converted to an equivalent KG stress value.\(^\text{47}\) Recall the expression for the entropic stress tensor of a single polymer strand (see Eq. (4.129) in Ref.\(^\text{81}\)):

$$
\sigma^{\text{entr}} = \frac{3 k_B T}{N_K l_K^2} \mathbf{R} \mathbf{R},
$$

(28)

where $\mathbf{R}$ is the strand end-to-end vector. Whereas, in the mechanical equilibrium state the same network strand has a virial stress:

$$
\sigma^{\text{3PA}} = -\frac{k^{\text{3PA}}}{N_b} \mathbf{R} \mathbf{R},
$$

(29)

where $k^{\text{3PA}}$ is the spring constant used in 3PA simulations, which was chosen as $k^{\text{3PA}} = 100 \varepsilon \sigma^{-2}$, and $N_b$ is number of beads in the strand. Eliminating tensor $\mathbf{R} \mathbf{R}$ from Eqs. (28), (29) and converting from Kuhn to bead units as $N_K l_K^2 = C_\infty N_b l_b^2$, one obtains:

$$
\sigma^{\text{entr}} = \sigma^{\text{3PA}} \frac{3 k_B T}{k^{\text{3PA}} l_b l_K},
$$

(30)

here $l_b$ is KG bond length, $C_\infty$ is polymer specific characteristic ratio (see Sect.\(^\text{3.2}\)).

Compared to generation of stress-strain data for the full KG networks, the 3PA analysis provides the cross-link moduli with much less computational effort, since the method requires only a single energy minimization. Visualization of some of the resulting 3PA meshes are shown in Fig.\(^\text{4}\). We observe that all strands forms straight lines connecting cross-links, and each cross-link position is determined by the force balance of all connected strands. We observe a more and more
dense mesh as the density of cross-links increase, in particular, we note the qualitative similarity
between the phantom mesh with $N_{XK} = 35$ and the primitive path mesh shown in Fig. 3A.

3.7 Finite extensibility

The vast majority of microscopic models for polymer elasticity is based on the Gaussian statistics
for the description of polymer chains. It is applicable only if chain end-to-end distance is much
less than the chain contour length, $\sqrt{\langle R^2 \rangle} \ll L$. At small deformations a polymer chain can be
still considered as a random walk, whereas even at relatively small strains, short strands of
the network can have end-to-end distances comparable to their contour length. In this case,
the assumption of Gaussian chain statistics vastly overestimate the number of conformations and,
hence, significantly underestimate the entropic forces.

Gaussian theory for a polymer chain statistics provides the following relation between the end-
to-end vector $\mathbf{R}$ of a chain and the acting force $\mathbf{f}$:

$$\mathbf{R} = \frac{N_{K} l_{K}^2}{3 k_{B} T} \mathbf{f},$$

(31)

where $N_{K}$ is number of Kuhn units in chain. In reality, Eq. (31) is only the weak force limit of the
more general expression:

$$\mathbf{R} = N_{K} l_{K} \mathbf{f} \left| \frac{\mathbf{f}}{|\mathbf{f}|} \right| \mathcal{L} \left( \frac{f_{K}}{k_{B} T} \right),$$

(32)

where $\mathcal{L}(x) = \coth(x) - 1/x$ is the Langevin function. Obviously, the stronger force is applied to a
polymer chain, or, in other words, the more chain is stretched, the larger the deviation of the linear
relation (31) is from the realistic behaviour (32).

Given a specified relative deviation $\alpha$ between "true" force and Gaussian response force, one
can obtain the following condition:

$$k_{B} T \left| \frac{3 R(\lambda)}{L} \mathcal{L}^{-1} \left( \frac{R(\lambda)}{L} \right) \right| < \alpha,$$

(33)
where $R(\lambda) = |\mathbf{R}(\lambda)|$ is the modulus of the chain end-to-end vector at elongation $\lambda$, and $L = N_K l_K$ is the chain contour length.

Let us assume a model network is deformed uniaxially along Ox axis by a factor $\lambda$. Under assumptions about affine response of a material and monodispersity of network strands, the average end-to-end vector magnitude can be approximately written as:

$$\langle R(\lambda) \rangle \approx \sqrt[\lambda]{\langle R^2(\lambda) \rangle} = \sqrt{\left( \frac{\lambda^2 + 2}{\lambda} \right) \frac{N_K l_K^2}{3}}. \quad (34)$$

To obtain quantitative estimations for different networks, we substituted Eq. (34) into Eq. (33), used the Padé approximant for the inverse Langevin function$^{61}$ and solved the resulting inequality numerically, assuming the threshold $\alpha = 5\%$. The results are presented in Table 1.

Fig. 1B shows that the strand lengths $N_s$ are distributed exponentially. Recalling Eq. (26), we estimate that roughly 63% of strands have the length smaller or equal to $\langle N_{XK} \rangle$. We note that this estimation is based on the average chain length, and a better estimate could be made taking into account the full strand length distribution as well as the strand-length dependent deformation response.$^{24}$

### 4 Results and discussion

In the present section, we show the results of the analysis of the our stress-strain simulation data within the scope of the MR model [Sect. 4.1]. Next, we show the results of the PPA methods, compare estimations of the shear modulus given by two different methods and discuss the microscopic origin of the MR model parameters [Sect. 4.2]. Finally, we fit microscopic elasticity models to our simulation stress-strain data [Sect. 4.3].
Figure 5: A Mooney-Rivlin plot of the reduced normal tension $\tilde{\sigma}_N$ vs. the inverse elongation $\lambda^{-1}$. Blue filled circles, orange filled squares, green filled diamonds, violet filled triangles, red filled triangles, yellow stars, moss green empty circles on both plots correspond, respectively, to networks $N_K = 10$, $N_K = 20$, $N_K = 35$, $N_K = 50$, $N_K = 75$, $N_K = 100$ and the end-linked precursor melt. Black solid lines denote a linear interpolation of the stress-strain data.

B: Normalized Mooney-Rivlin plot, where the stress data are normalized by the shear modulus estimates. Grey thick dashed lines define the triangle, showing the cross-over from the cross-link to the entanglement dominated stress-strain behaviour in accordance with the MR model.

C: Experimental data for PDMS, shown in the normalized Mooney-Rivlin representation. Blue filled circles and orange filled squares show the data from Ref.[52], green filled diamonds, violet filled triangle show the data from Ref.[84], red filled triangles, yellow stars and moss green empty circles show the data from Ref.[85].
4.1 MR analysis

Fig. 5A shows stress data on uniaxial stretching simulations of our model networks in Mooney-Rivlin representation. The stress response increases with increasing cross-link density. Moreover, a stress upturn is observed for large deformations, where finite extensibility effects play a significant role. We read off the elongations $\lambda_{\max}^{MR}$, where the stress upturn started. The results are summarized in Table 1. We found them to be in good quantitative agreement with our theoretical estimates of range of applicability of Gaussian chain statistics. The only exception is the end-linked network, where the strand lengths are exceedingly long, and finite extensibility effects are controlled by the entanglement strands rather than by network strands.

For the data where the finite extensibility effects are negligible, we observe a linear relation between the reduced normal tension $\tilde{\sigma}_N$ and the inverse elongation $\lambda^{-1}$ as predicted by the MR model (4). This allowed us to perform linear fitting (shown as the black lines) to the stress-strain data. The statistical errors of the measured stress-strain data were accounted for when performing the fits, though the error bars are comparable to or smaller than the symbols. According to Eq. (4), extrapolation of the linear fitting function towards $\lambda^{-1} \rightarrow 1$ provides estimate for the shear modulus $G^{MR}$, whereas extrapolation towards $\lambda^{-1} \rightarrow 0$ gives estimate for the $C_1$ model parameter. The resulting values for $C_1$, $C_2$ and $G^{MR}$ are presented in Table 1.

Fig. 5B shows the simulation data in a reduced Mooney-Rivlin representation, where the data is normalized by the shear moduli estimates obtained via the MR analysis. In this representation, all stress-strain data is enclosed by the triangular domain (0; 0), (0; 1), (1; 1) (shown as the grey dashed line). This allows one to gauge directly the relative importance of the $C_1$, $C_2$ contributions to the shear modulus. Horizontal stress-strain data are dominated by the $C_1$ term, whereas diagonal stress-strain data would be dominated by the $C_2$ term. The middle dashed line corresponds to an even balance between the $C_1$ and $C_2$ terms. It is clearly seen that our the most strongly cross-linked model network with 4 cross-links between each entanglement on average is mostly dominated by the $C_1$ term. The $C_2$ term contribution progressively increases for weaker cross-linked networks. The stress-strain data for the end-linked network is below the middle line, indicating that the $C_2$
term is slightly larger than the $C_1$ term in this case. The end-linked network has 56 entanglements between cross-links on average and is completely dominated by the entanglements effects.

Fig. 5 shows experimental data for PDMS also in the normalized Mooney-Rivlin form. No special attempts to find or select experimental data matching our model networks have been made. Nevertheless, we observe that the experimental data roughly falls into the same triangular region as our simulation data. This suggests that the range of network cross-links density we have used is relevant for comparison to experimental data and the conclusions, which we draw, basing on our model networks, are applicable to the experimental systems. Additionally, the reliability of the MR model for the description of uniaxial stretching of rubbery materials is justified. We note some scatter for small deformations (data of Kawamura et al.\cite{52}). The Mooney-Rivlin representation of the stress-strain data significantly amplifies any experimental error close to the unstrained state, since it is difficult to measure small stresses precisely as well as to determine the length of the sample exactly in the vicinity of the unstrained state. For comparison, elongation of model networks is exactly defined in our simulations, but we have a significantly reduced signal-to-noise ratio for stresses at small deformations.

4.2 PPA and 3PA analysis

| $N_{XX}$ | $\alpha_S^{good}$ | $G^{ph}$ [MPa] | $G_X$ [MPa] | $\lambda_{thr}$ | $\lambda_{max}^{MR}$ | $C_1^{MR}$ [MPa] | $C_2^{MR}$ [MPa] | $G^{MR}$ [MPa] | $G_X + G_E$ [MPa] |
|----------|------------------|----------------|-------------|----------------|------------------|-----------------|----------------|----------------|-----------------|
| 10       | 0.8648           | 0.2980         | 0.3154      | 1.8           | 2.2              | 0.2846          | -0.0007        | 0.5677 ± 0.0209| 0.5418           |
| 20       | 0.8611           | 0.1410         | 0.1443      | 1.8           | 2.2              | 0.1523          | 0.0454         | 0.3953 ± 0.0083| 0.3707           |
| 35       | 0.8582           | 0.0795         | 0.0793      | 2.63          | 3.0              | 0.1073          | 0.0588         | 0.3320 ± 0.0057| 0.3057           |
| 50       | 0.8539           | 0.0549         | 0.0545      | 3.22          | 3.3              | 0.0877          | 0.0689         | 0.3132 ± 0.0036| 0.2809           |
| 75       | 0.8496           | 0.0359         | 0.0344      | 4.0           | 4.0              | 0.0747          | 0.0725         | 0.2944 ± 0.0034| 0.2608           |
| 100      | 0.8485           | 0.0268         | 0.0254      | 4.64          | 4.4              | 0.0683          | 0.0757         | 0.2879 ± 0.0041| 0.2519           |
| EL       | 0.8321           | 0.0013         | 0.0010      | 19.88         | 5.6              | 0.0520          | 0.0838         | 0.2715 ± 0.0028| 0.2275           |

To complement the MR analysis of the simulation stress-strain data, we performed PPA anal-
Figure 6: Mooney-Rivlin plot of the 3PA reduced normal tension $\tilde{\sigma}_N$. Lines are the phantom network model predictions, Eq. (6), with input from analysis of our model networks. Correspondence of markers and colours to the model networks is the same as in Fig. 5A.

Figure 7: Comparison of the shear moduli estimates obtained by the MR model analysis and by the Primitive Path methods. Blue markers show the MR model estimates for the shear modulus $G_{MR}$. Orange markers are for the Primitive Path methods estimates $G_Y + G_E$. Green markers denote the 3PA estimates for the cross-link modulus $G_X$. For the discussion of the green dashed and the blue dot-dashed lines, see the text. Correspondence of the markers to the networks is the same as in Fig. 5A.

ysis of the precursor melt and 3PA analysis of the deformed model networks. PPA analysis of the precursor melt provides an estimate of $N_{EK} \approx 33.1$. Using the mapping from PDMS-KG model to SI units, see Sect. 3.2, we calculate the entanglement modulus $G_E = 0.23$ MPa, which is in a good
Figure 8: Identification of the MR modulus contributions $2C_1$, $2C_2$ in relation to the entanglement modulus $G_E$ as function of the network structure. The inset shows the same data relatively to the MR estimates for the shear modulus $G^{MR}$. Blue markers denote the $C_1$ parameter, orange markers show the $C_2$ parameter. Correspondence of the markers to the networks is the same as in Fig. 5A.

agreement with the literature values of $N_{EK} = 31.08$ and $G_E = 0.25 \text{MPa}^{[72]}$ and the expectation from the packing argument $N_{EK} = 45.9 \pm 9.6$ and $G_E = 0.18 \pm 0.04 \text{MPa}$, see Sect. 3.2. Comparing the MR modulus estimate of the end-linked network to the entanglement modulus, we obtain fairly good agreement $G^{MR}(EL)/G_E \approx 1.2$, which is discussed below.

Fig. 6 shows Mooney-Rivlin representation of the stress-strain data provided by 3PA analysis of the deformed networks. The phantom network model predicts that the reduced stress is independent of elongation, and this is in excellent agreement with the results of the 3PA analysis. From the reduced stress plateaus, one can directly read off the cross-link modulus $G_X$. For comparison, the figure also shows parameter free predictions of $G^{ph}$ (Eq. 6). To evaluate $G^{ph}$, we used the densities of good strands and cross-links obtained from the network analysis, see discussion of Eq. 6. We observe that phantom model estimates are in excellent agreement with the 3PA analysis results. 3PA method implements Hamiltonian of the phantom network model exactly for a given network, hence, the resulting cross-link modulus estimate $G_X$ is completely independent of any assumptions used to derive the phantom network modulus Eqs. (6, 7). Numerical values of the
moduli $G^{bh}$ and $G_X$ are summarized in Table 1.

Having obtained *model independent* estimates of the cross-link moduli of all networks and the entanglement modulus of the precursor melt, one can ask how they are related to the network structure, e.g., to the quantitative relation between entanglement and network strands. Fig. 7 shows a Langley plot of the results of the 3PA analysis as blue symbols. The phantom network model Eq. (7) with functionality $f = 4$ provides $G_X/G_E = 0.5 N_{EK}/N_{XX}$, whereas we observe $G_X/G_E = 0.42 N_{EK}/N_{XX}$ (dashed green line). This is perfectly consistent with the number of good strands we obtained from the network analysis, suggesting a 15% reduction of the cross-link modulus due to the presence of loops. We also show the linear relation $G/G_E = 1.10 + 0.42 N_{EK}/N_{XX}$ (blue dot-dashed line), which is observed to be in excellent agreement with the moduli obtained from MR analysis. The choice of prefactor will be discussed below.

Many theories assume that the effects of entanglements and cross-links are additive, see e.g. Refs. 21–23,25,26. We are not aware of any theoretical arguments, proving this assumption. For instance, the double tube model of Mergell and Everaers 24 produces a non-additive relation for the modulus. The predictions of the double tube model is derived from a constraint mode Hamiltonian, and hence is thermodynamically consistent.

Having *independent* estimates for the network shear modulus as well as the cross-link and the entanglement moduli, we can test the equality between the $G_{MR}$ estimate on one hand and $G_X + G_E$ on the other hand. To our knowledge, this is perhaps the first time the relation has been tested directly. Fig. 7 shows the shear moduli estimates obtained via the MR model analysis as well as the sum of cross-link and entanglement moduli. We observe that the MR modulus estimates are consistent with, but slightly larger than the sum. The deviation is in the range $5 - 20\%$ and is decreasing with increasing density of cross-linking. We note that the statistical error of the MR shear moduli estimates is smaller than 3%. Hence, we attribute this systematic deviation to the capture of entanglements by cross-linking. Langley proposed that the network modulus comprised the cross-link modulus and entanglements contribution multiplied by Langley trapping factor. Our results are consistent with a Langley trapping factor $T_e < 0.2$ essentially *independent* of the
degree of cross-linking.

The discussion of the physical interpretation of the $C_1$, $C_2$ terms has a long history in the literature, see, e.g., Refs.\textsuperscript{38–40,87–89}. Early on, it was recognized that the $C_2$ term goes to zero, when the polymer network is swollen\textsuperscript{20,90,91}, and the breakdown of the neo-Hookean theory (assuming $C_2 = 0$) in the intermediate range of strains was attributed to entanglements.\textsuperscript{19,92,93} Moreover, the tube theories discussed in Sect. 2.3 also suggests that the parameter $C_1$ is related to both cross-links and entanglements, while the parameter $C_2$ is only related to entanglements. The notable exceptions being the Warner-Edwards tube theory\textsuperscript{5,24,60}, which has a strain independent tube diameter and reduces to a phantom-like stress-strain response, and the double tube model\textsuperscript{24}, where the $C_2$ term depends on both the cross-link and the entanglement moduli $G_X$, $G_E$. To our knowledge, the most recent contribution to this long discussion is the paper of Schlögl et al.\textsuperscript{41}. The authors performed NMR experiments on dry and swollen samples to measure critical molecular weights. Swelling is believed to minimize the entanglement effects, allowing the cross-link modulus to be estimated experimentally. Moreover, the correlations between the critical molecular weights and the MR parameters were studied. The analysis showed that $C_1$ was related to cross-links and entanglements, while $C_2$ is related to entanglements only.

It is interesting to ask if there is a relation between the observables measured by NMR and the Primitive Path methods. NMR measures the residual dipolar coupling, which characterize polymer conformations on time scales where the fluctuations are averaged out.\textsuperscript{94,95} Primitive path methods\textsuperscript{46,47} generate meshes, where thermal fluctuations are also removed. Hence, we conjecture that NMR observables of dry and swollen polymer state samples are related to our PPA and 3PA observables, respectively.

Fig. 8 shows the MR model parameters $C_1$, $C_2$ in units of the entanglement modulus. We observe a roughly linear increase of the $C_1$ parameter with a slope of 0.7 and a concomitant decrease of the $C_2$ parameter with increasing cross-link density. The former is expected as the phantom model alone would predict $2C_1/G_E = G_X/G_E = 0.42N_{EK}/N_{XK}$. Our data suggest transfer of the entanglement contributions progressively from $C_2$ to $C_1$ as the network is progressively cross-
linked causing the increase of the slope as observed. This is similar to a Langley trapping factor, but between the two MR parameters. The inset shows the MR model parameters $C_1$, $C_2$ in units of the shear modulus $G^{MR}$ and, hence, how the two terms are balanced as function of network structure. In the entanglement dominated limit $N_{EK}/N_{XX} \to 0$, we observe that the entanglement modulus is distributed 40%, 60% between the $C_1$, $C_2$ parameters, respectively. At the point $N_{EK} = 0.5N_{XX}$, the contributions are approximately equal. Finally, in the limit $N_{EK} \gg N_{XX}$, the $C_2 \approx 0$ and $2C_1 \approx G^{MR}$.

Both models of Rubinstein and Panyukov, the extended tube model of Kaliske and Heinrich, the non-affine network model of Davidson and Goulbourne, and the general constitutive model of Xiang et al., predict that the entanglement modulus $G_E$ is a constant fraction of the $C_2$ parameter, see Eqs. (9, 11, 16, 19, 21), respectively. This is not consistent with the data shown in Fig. 8. We note that the decreasing $C_2$ parameter is predicted by the Double Tube theory, see Eq. (13). However, the model also predicts that both quantities $2C_1$, $2C_2$ converge to the same point in the limit $N_{EK}/N_{XX} \to 0$, which is not in agreement with our data.

### 4.3 Comparison of microscopic models

In Sect. 4.2, we presented our results for the cross-link and entanglement moduli, and qualitatively discussed their relations to the total shear modulus as well as to the MR parameters.

Many theories predict a universal form of the stress-strain relation, when subtracting the cross-link modulus from the reduced normal tension and normalizing by the entanglement modulus. In Sect. 4.3.1, we check this assumption independently of any model.

Another interesting question is whether the microscopic models, where the entanglement and the cross-link model fit parameters are identified with the Primitive Path estimates, are able to predict the simulation stress-strain data. This is the most stringent consistency test possible for the models, since there are no free parameters, and, hence, no way for a fit to hide systematic errors. In 4.3.1 we apply this test to the stress-strain data not affected by finite extensibility effects.

For models failing such a test, one can fit the moduli prefactors and check how accurate the
models are in estimating the shear, the entanglement and the cross-link moduli from the stress-strain data. In Sect. 4.3.2, we apply this test to the models not taking finite extensibility into account, while in Sect. 4.3.3 we perform the analysis for the models accounting for finite extensibility. Moreover, we compare the fitted estimates for the cross-link and the entanglement moduli to the independent benchmarks provided by the Primitive Path methods.

We emphasize that here and below that $G_E$ and $G_X$ refer to the PPA and 3PA estimates, respectively. The model fit parameters are referred to as $G_{E}^{\text{model}}$ and $G_{X}^{\text{model}}$ where necessary to avoid confusion.

### 4.3.1 Universal representation of the stress-strain data

**Figure 9**: Universal representation of the simulation stress-strain data along with the parameter free predictions (gray lines) and fits of the microscopic elasticity models (black lines). Solid, large dashed and dot-dashed lines illustrate the non-affine tube, the slip tube and the extended tube models, respectively. Correspondence of symbols colouring and markers to the model networks is the same as in Fig. 5A, gray symbols denote stress data discarded due to finite extensibility effects.

The non-affine tube model, the slip tube model and the extended tube model predict reduced normal tensions in the form $\tilde{\sigma}_N(\lambda) = G_X + G_E \varphi(\lambda)$, where $\varphi(\lambda)$ is a model specific universal function. Consequently, $\varphi(\lambda)$ can be isolated as:

$$\varphi(\lambda) = \frac{\tilde{\sigma}_N - G_X}{G_E},$$

independently of the network structure.

In Fig. 9 we plot the simulation stress-strain data in this reduced form using the cross-link
and the entanglement moduli provided independently by the Primitive Path methods. We observed an excellent collapse of that range of the data, which is not affected by finite extensibility. The most strongly cross-linked network \( N_K = 10 \) does not fall on the universal curve (hence, these data are not shown), and small deviations are observed for \( N_K = 20 \). We attribute these effects to the onset of glassy dynamics, where entropic elasticity theory is not applicable. For the remaining data range, obviously, no collapse can be expected, since finite extensibility effects depend on the specific chain length distribution of a given network.

To observe universality of experimental data, often, a theory is fitted to stress-strain data and, afterwards, the data are plotted using the fitted cross-link and the entanglement moduli, see, e.g. Ref.\(^{22}\). This essentially forces the data to collapse around the theoretical prediction. Here our aim is to compare the theories to our simulation stress-strain data and not vise versa. We emphasise that the observed collapse is independent of any microscopic elasticity theory.

Having obtained model independent estimates of the cross-link and the entanglement moduli, one can ask whether the microscopic theories can make a parameter free prediction of the simulation stress-strain data. The gray lines show the default, parameter free predictions for the strain dependent entanglement contributions \( \Phi(\lambda) \) of the non-affine tube model, the slip tube model and the extended tube model. These predictions correspond to the naive identification of the model parameters \( G_{\text{model}}^X = G_X \), \( G_{\text{model}}^E = G_E \) and they are observed to be in poor agreement with the simulation data. The models assume additivity of entanglement and cross-link effects, and hence by construction fall \( 5 \text{--} 20\% \) short of predicting the correct shear modulus. Furthermore, the slope of the universal functions is observed to be too large. If the models correctly predicted the shear modulus, we could attempt to fix the models by shifting part of the entanglement modulus into the cross-link modulus to reduce the slope of the universal function, but the plot suggests that we need to adjust both a scaling and a shift parameter.

Since the direct identification of the fit parameters of the microscopic models with the Primitive Path estimates did not work, we approximated the collapsed stress-strain data in the universal representation by two-parameter fits \( \gamma_X + \gamma_E \Phi(\lambda) \), where \( \Phi(\lambda) \) is the model specific func-
tion (shown as the black lines). As a result, we obtained an excellent agreement between the theories and the collapsed data range. Quality of fitting is characterized by the reduced chi-square quantity denoted as $\chi^2_{\nu}$, and we obtained $\chi^2_{\nu}$ values 20.95, 21.13, 24.52 for the non-affine tube, the slip tube and the extended tube models, respectively. As an empirical parameterization of our stress-strain data, we the "recalibrated" non-affine tube model to obtain the universal function $\varphi(\lambda) = 0.38 + 0.73/(\lambda - \lambda^{1/2} + 1)$.

### 4.3.2 Fitting the data not affected by finite extensibility

**Figure 10:** Fits of the microscopic elasticity theories to the simulation stress-strain data not affected by finite extensibility. Panels [A][B][C][D] show fits of the non-affine tube, the slip tube, the double tube and the extended tube models, respectively. Coloured crosses located at the vertical line $\lambda^{-1} = 1$ indicate the MR estimates of the shear modulus. Correspondence of symbols and lines colouring and markers to the model networks is the same as in Fig. 5A.

We fit the microscopic elasticity theories that do not account for finite extensibility effects to the relevant simulation stress-strain data. For the fitting, two parameters $\gamma_K$, $\gamma_E$ were introduced as
Figure 11: Fitting parameters $A \gamma_X$, $B \gamma_E$: Blue, orange, green and purple symbols show the optimal values for the non-affine tube, the slip tube, the double tube and the extended tube models, respectively. Correspondence of markers to the model networks is the same as in Fig. 5A.

multipliers of $G_X$, $G_E$, which were identified, respectively, with the cross-link and the entanglement moduli estimates provided by the Primitive Path methods. Fitted data are illustrated by coloured symbols, whereas gray symbols indicate the data discarded due to significant finite extensibility effects. We chose the non-affine tube model,[21] the slip tube model,[22] and the double tube model,[24] because they do not capture finite extensibility. The extended tube model,[23] has two additional parameters $\beta$, which roughly accounts for network defects, and $\delta$ for finite extensibility. We set $\beta = 1$ as our model networks are defect free in that sense that they do not have dangling ends (see Sect. 2.3), and we set $\delta = 0$, since we are discarding simulation data affected by finite extensibility. The non-affine network model of Davidson and Goulbourne,[25] and the general constitutive model of Xiang et al.[26] were not fitted, since in the long-chain limit where finite extensibility effects
cancel, they reduce to the non-affine tube model and to the extended tube model with $\delta = 0$, respectively.

The model fits are shown in Fig. 10. We observe an excellent agreement with the stress-strain data. The reduced chi-square quantity $\chi^2$ has the values 4.71, 4.97, 3.97 and 3.20 for the non-affine tube, the slip tube, the double tube and the extended tube model fits, respectively, hence, all fits are of comparable quality. Fits provided new estimates for the shear modulus, which is equal to $\gamma_X G_X + \gamma_E G_E$ for the non-affine tube, the slip tube and the extended tube models and 

$$\left(\left(\gamma_X G_X\right)^2 + 2 \left(\gamma_E G_E\right)^2\right) \left(\sqrt{\left(\gamma_X G_X\right)^2 + 4 \left(\gamma_E G_E\right)^2}\right)^{-1/2}$$

for the double tube model. The shear modulus estimates can be seen in Fig. 10 as intersections of the coloured fitting curves with the vertical line $x = 1$. They are observed to be in good agreement with the MR estimates shown as big coloured crosses.

In Fig. 11 optimal values for the fit parameters $\gamma_X$, $\gamma_E$ are shown. All model fits show that $\gamma_X$ decreases with increasing cross-link density and is located within the range 2 – 6 for almost all model networks. The only exception is the end-linked network, for which we observe that $\gamma_X$ has huge values of the order $10^2$. We attribute this to the tiny cross-link modulus $G_X$ of the end-linked model network, which is used for the normalization. Consequently, though the data for the end-linked can be fitted with high accuracy by any microscopic model, none of them provides a reasonable accurate estimate for the cross-link modulus. At the same time, all fits are consistent with $\gamma_E$ ranging 0.5 – 1.4. The double tube model fit shows the growth of $\gamma_E$ with increasing cross-link density, whereas all other model fits demonstrate the opposite trend. Note that the fitting results of the slip tube and the non-affine models are identical. As noted in Sect. 2.3, the slip tube model allows for the chain contour length redistribution between parallel and perpendicular tube sections upon deformation. This is expected to important, especially for the weakly cross-linked networks. Nevertheless, this model feature seems to have no influence on the model fit.

The microscopic models introduce cross-link and entanglement localization effects using different mathematical approximations, hence, one can not expect the corresponding fit parameters to produce exactly the same values. We observe agreement on a scaling level only with a $O(1)$ pref-
actor. By fitting the models to the stress-strain data for completely characterized systems, where the cross-link and entanglement moduli are known independently of any microscopic model, we have in essence performed a calibration of these models to the Primitive Path moduli estimates. Consequently, from the fit parameters, one can attempt to estimate the correct cross-link and the entanglement moduli as $\gamma_X G_X, \gamma_E G_E$.

### 4.3.3 Fitting full range of the data

The KG polymer model includes finite extensibility effects due to the FENE potential used to model the bonds. At large macroscopic deformations, the upturn of the simulation stress-strain data induced by finite extensibility is observed, see Fig. 5A.

In Fig. 12, fits of the extended tube model of Kaliske and Heinrich, the non-affine network model of Davidson and Goulbourne, and the general constitutive model of Xiang et al. to the full range of simulation data are shown. The fitting was performed in a similar way as in Sect. 4.3.2. In addition to the fit parameters $\gamma_X, \gamma_E$, additional model specific parameters responsible for finite extensibility were fitted. These are $\delta, g, N_{XK}$ for Kaliske and Heinrich, Davidson and Goulbourne, Xiang et al. models, respectively. We set $\beta = 1$ for the extended tube model as before. The resulting fits illustrated as coloured lines are observed to be in perfect agreement with the simulation data. The values of the reduced chi-square quantity are 2.95, 7.61 and 3.39 for the extended tube, the non-affine network and the general constitutive models, respectively. While the model fits are able to reproduce the stress upturn at large deformations, they also provide estimates for the shear modulus (intersections of the coloured fitting curves with the vertical line $x = 1$ in Fig. 10), which are in good quantitative agreement with the MR estimates $G^{MR}$ shown as big coloured crosses.

In Fig. 13, optimal values of the fit parameters are shown. Similarly to Sect. 4.3.2, for all model fits, the value of $\gamma_X$ varies within the range 2 – 7, it decreases with increasing cross-link density and has a huge value of the order $10^2$ for the end-linked model network. For the fit parameter $\gamma_E$, the extended tube model fit shows the drastic decrease from 0.5 down to 0.07. At the same time, both the non-affine network model of Davidson and Goulbourne and the general constitutive
Figure 12: Fits of the microscopic elasticity theories to the full range of the simulation stress-strain data. Panels A, B, C show fits of the extended tube model of Kaliske and Heinrich, the non-affine network model of Davidson and Goulbourne and the general constitutive model of Xiang et al., respectively. Coloured crosses located at the vertical line $\lambda^{-1} = 1$ indicate the MR estimates of the shear modulus. Correspondence of symbols and lines colouring and markers to the model networks is the same as in Fig. 5A.

model of Xiang et al. demonstrate almost constant values of $\gamma_E \approx 0.6 - 0.7$. For the extended tube model, we plot $\alpha = \delta \sqrt{N_{EK}}$ instead of $\delta$. In Ref. [23], the parameter $\alpha$ is introduced as a measure of the network chains inextensibility, and it is claimed that $\alpha \in (0; 1)$. However, the model fit
Figure 13: Fitting parameters $A \gamma_X$, $B \gamma_E$, $C$ finite extensibility parameter. Purple, red and yellow symbols show the optimal values of the fitting parameters for the extended tube model of Kaliske and Heinrich, the non-affine network model of Davidson and Goulbourne and the general constitutive model of Xiang et al., respectively. The plot in Panel $C$ shows parameters responsible for the finite extensibility, $\alpha = \delta \sqrt{N_{EK}}$ for the extended tube model, $\lambda_{\text{DG}}^\text{max} / \lambda_{\text{thr}}^\text{max}$ for the Davidson and Goulbourne model, $N_{X_{IA}}^\text{max} / N_{X_K}$ for the model of Xiang et al. Correspondence of markers to the model networks is the same as in Fig. 5.
shows that α rather varies within range 1 – 3.5. For the non-affine network model, we plot the ratio $\lambda_{DG_{\text{max}}}^{\text{max}}/\lambda_{\text{thr}_{\text{max}}}$ instead of the fit parameter $g$, where $\lambda_{DG_{\text{max}}}^{\text{max}} = \frac{1}{g} \sqrt{\langle N_{XX} \rangle} \frac{1 - 2/f}{f}$, $f = 4$ is the network functionality, $\langle N_{XX} \rangle$ is the network specific average strand length and $\lambda_{\text{thr}_{\text{max}}}$ are the elongations, corresponding to the simulation stress-strain data upturns in Mooney-Rivlin representation, see Fig. 5A and Table 1. We observe that $\lambda_{DG_{\text{max}}}^{\text{max}}/\lambda_{\text{thr}_{\text{max}}} \approx 1.3$ for all model networks. For the general constitutive model, instead of the fitting parameter $N_{XK}$ we plot the ratio $N_{XK}^{Xiang}/\langle N_{XX} \rangle$. The value of the ratio appears to be within the range 0.3 – 0.5, except for the end-linked network, where $N_{XK}^{Xiang}/\langle N_{XX} \rangle \approx 0.04$, presumably, due to large value of the average network strand length $\langle N_{XX} \rangle \approx 1850$.

5 Conclusion

In this work, we studied the relation between the macroscopic mechanical properties and microscopic structure of Kremer-Grest (KG) model polymer networks. We used a PDMS-KG polymer model designed to match the Kuhn number of PDMS and, hence, to reproduce, e.g. the packing length, the entanglement length and the shear modulus of PDMS. We generated well equilibrated precursor melts, linked the chain ends and then proceeded to cross-link random bead pairs. The resulting model networks were free of dangling ends, but contained loops mostly due to intramolecular cross-linking. The networks had different number of cross-links, hence, ranging from cross-link to entanglement dominated elastic response. We characterized the networks in terms of strand length and cross-link functionality distributions.

We performed Molecular Dynamics simulations of uniaxial stretching of the model networks and carefully estimated the equilibrium stresses in the deformed states to obtain the stress-strain curves. We invested in excess of 200 core years of computer time on relaxation of the numerous deformed networks states.

We applied Primitive Path methods to estimate the entanglement modulus of the precursor melt and the cross-link moduli of the networks. The entanglement modulus was found to be
in a good agreement with the literature data. A variation of the PPA analysis named Phantom Primitive Path Analysis (3PA) was introduced, and we applied it to the deformed model networks to estimate the cross-link moduli. The results turned out to be in excellent agreement with the phantom network model estimates based on the network analysis.

To estimate the shear moduli, we applied the Mooney-Rivlin (MR) model. Mooney-Rivlin representation of the data clearly demonstrated linear dependency of the reduced normal tension on the inverse elongation that justifies the applicability of the MR model analysis to estimation of the network moduli.

We observed that the balance of the MR model parameters $C_1$, $C_2$ depends on the level of the network cross-linking. The most strongly cross-linked network was accurately described only by the term with the $C_1$ parameter. With increasing average network strand length, the influence of the $C_2$ parameter concomitantly increased, and, at the point $N_{EK} = 0.5N_{XK}$, the contributions of $C_1$, $C_2$ to the shear modulus are approximately equal. Finally, for the end-linked network, which is entanglement dominated, contributions of $C_1$, $C_2$ parameters to the shear modulus we found to be 40%/60%, respectively.

We compared the MR modulus estimates with the sum of the cross-link and entanglement moduli and observed good agreement. The MR moduli were systematically 5 – 20% larger than the sums. This partially supports the assumption often used in microscopic theories of elasticity of polymer networks that the effects of cross-links and entanglements are additive, see e.g. Refs. We attribute this deviation to the entanglement trapping. Langley proposed a trapping factor $T_e$, where a fraction of the entanglement modulus contribute to the total modulus of a polymer network. Our data are consistent with a tiny trapping factor $T_e < 0.2$ independent of network structure.

Plotting the simulation stress-strain data in a universal form, i.e. subtracting the cross-link modulus and normalizing by the entanglement modulus, we observed a collapse of the data to a universal curve. The collapse only occurs for stress data not affected by finite extensibility, which is system specific. This collapse was already anticipated from several microscopic models, see e.g. Refs. We note that the observed collapse is independent of any microscopic model.
assumptions, since the cross-link and entanglement moduli were obtained via the Primitive Path methods and not via the models fitting to the simulation data. Hence, as a calibration standard we obtained an estimate for the universal function of $\varphi(\lambda) = 0.38 + 0.73/\left(\lambda - \lambda^{1/2} + 1\right)$ for PDMS networks.

We tested the quality of parameter free predictions of the non-affine tube model $^{21}$, the slip tube model $^{97}$, and the extended tube model $^{23}$. For this purpose, we identified the model parameters with the entanglement and the cross-link moduli estimates obtained by the Primitive Path methods and compared the resulting predictions to the simulation stress-strain data. All the models failed in description the data. Therefore, we proceeded to fit the models as well as the double tube model $^{24}$ to the simulation data not affected by finite extensibility. We used two-parameter fitting by allowing the prefactors of the entanglement and the cross-link moduli to vary. We observed an excellent agreement between the resulting model fits and the stress-strain data and obtained good estimates of the shear moduli. However, obtained estimates for the cross-link and the entanglement moduli varied significantly when compared to the benchmarks provided by the Primitive Path methods. We did not observe quantitative agreement, but the prefactors agreed within a $O(1)$ scaling.

Finally, we fitted the extended tube model, the non-affine network model $^{25}$ and the general constitutive model $^{26}$ to the full range of the simulation stress-strain data. The model specific parameters, defining the behaviour at large macroscopic deformations, were used as additional fitting parameters. We observed excellent fits including the stress upturns at large deformations due to finite extensibility effects. Moreover, obtained estimates for the shear moduli are in close agreement with the MR estimates. Nevertheless, the model estimates for the cross-link modulus were $1 - 6$ too large compared to the estimates provided by the 3PA analysis. At the same time, the model estimates for the entanglement modulus were within $0.5 - 2$ range of the PPA analysis estimate. The model that provided the best fit was the non-affine network model of Davidson and Goulbourne, it showed the smallest prefactor for the cross-link moduli, a nearly network independent prefactor for the entanglement moduli, and also a network independent scaling factor for the finite extensibility effects. We note that, in essence, we performed a calibration of the model parameters
to an independent standard offered by the results of the Primitive Path analysis methods applied to our model PDMS networks.

From a computational perspective, the Primitive Path methods have the advantage as computationally they are orders of magnitude cheaper than generation of an equilibrated stress-strain data for the MR analysis. For the latter, one needs a large number of well equilibrated deformed states of a model network, where the data is not affected by finite extensibility effects. Moreover, time consuming simulations are required for accurate estimation of the equilibrium stresses due to the slow relaxation dynamics. For instance, the virial stress tensor is a strongly fluctuating quantity for KG melts due to the hard interaction potentials. The good agreement between the MR estimates and the Primitive Path estimates of the shear moduli suggests that the latter provide a computationally effective alternative for the moduli estimation.

The present results are based only on an analysis of PDMS model KG polymer networks, which represents a single data point in terms of entanglement length/modulus. We are currently generating networks for other polymer models and will also be cross-linking networks in the swollen state to generalize the present results to the situation where the entanglement length also is systematically varied. Furthermore, we hope that our simulation data can offer a benchmark as the reference data for future development of the models that attempt to describe both entanglement and cross-link contributions to polymer network elasticity.

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References

(1) Strobl, G. R. *The physics of polymers*, 2nd ed.; Springer-Verlag: Berlin Heidelberg, 1997.

(2) Mark, J. E. *Physical properties of polymers handbook*, 2nd ed.; Springer-Verlag: New York, 2007.

(3) Edwards, S. Statistical mechanics with topological constraints: I. *Proc. Phys. Soc.* **1967**, *91*, 513–519.

(4) Edwards, S. The statistical mechanics of polymerized material. *Proc. Phys. Soc.* **1967**, *92*, 9–16.

(5) Deam, R.; Edwards, S. The theory of rubber elasticity. *Philos. Trans. R. Soc. A* **1976**, *280*, 317–353.

(6) Khokhlov, A.; Nechaev, S. Polymer chain in an array of obstacles. *Phys. Lett. A* **1990**, *12*, 156–160.

(7) Kuhn, W. Beziehungen zwischen Molekülgröße, statistischer Molekülgestalt und elastischen Eigenschaften hochpolymerer Stoffe. *Kolloid-Zeitschrift* **1936**, *76*, 258–271.

(8) Kuhn, V. W.; Grün, F. Beziehungen zwischen elastischen Konstanten und Dehnungsdoppelbrechung hochelastischer Stoffe. *Kolloid-Zeitschrift* **1942**, *3*, 248–271.

(9) Kuhn, W. Dependence of the average transversal on the longitudinal dimensions of statistical coils formed by chain molecules. *J. Polym. Sci.* **1946**, *1*, 380–388.

(10) Wall, F. Statistical thermodynamics of rubber. *J. Chem. Phys.* **1942**, *10*, 132–134.

(11) Wall, F. Statistical thermodynamics of rubber. II. *J. Chem. Phys.* **1942**, *10*, 485–488.

(12) Wall, F. Statistical thermodynamics of rubber. III. *J. Chem. Phys.* **1943**, *11*, 527–530.

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(13) Flory, P.; Rehner, J. Statistical mechanics of cross-linked polymer networks. I. Rubberlike
elasticity. *J. Chem. Phys.* **1943**, *11*, 512–520.

(14) Treloar, L. The elasticity of a network of long-chain molecules. I. *Trans. Faraday Soc.* **1943**, *39*, 36–41.

(15) James, H. M.; Guth, E. Theory of the elastic properties of rubber. *J. Chem. Phys.* **1943**, *11*, 455–481.

(16) James, H. M. Statistical properties of networks of flexible chains. *J. Chem. Phys.* **1947**, *15*, 651–668.

(17) James, H. M.; Guth, E. Theory of the increase in rigidity of rubber during cure. *J. Chem. Phys.* **1947**, *15*, 669–683.

(18) James, H.; Guth, E. Simple presentation of network theory of rubber, with a discussion of
other theories. *J. Polym. Sci.* **1949**, *14*, 153–182.

(19) Flory, P. J.; Gordon, M.; McCrum, N. Statistical thermodynamics of random networks. *Proc. R. Soc. A* **1976**, *351*, 351–380.

(20) Treloar, L. *The physics of rubber elasticity*, 3rd ed.; Clarendon Press: Oxford, 1975.

(21) Rubinstein, M.; Panyukov, S. Nonaffine deformation and elasticity of polymer networks. *Macromolecules* **1997**, *30*, 8036–8044.

(22) Rubinstein, M.; Panyukov, S. Elasticity of polymer networks. *Macromolecules* **2002**, *35*, 6670–6686.

(23) Kaliske, M.; Heinrich, G. An extended tube model for rubber elasticity: Statistical-
mechanical theory and finite element implementation. *Rubber Chem. Technol.* **1999**, *72*, 602–632.
(24) Mergell, B.; Everaers, R. Tube models for rubber-elastic systems. *Macromolecules* **2001**, *34*, 5675–5686.

(25) Davidson, J. D.; Goulbourne, N. A nonaffine network model for elastomers undergoing finite deformations. *J. Mech. Phys. Solids* **2013**, *61*, 1784–1797.

(26) Xiang, Y.; Zhong, P., Danming nad Wang; Mao, G.; Yu, H.; Qu, S. A general constitutive model of soft elastomers. *J. Mech. Phys. Solids* **2018**, *117*, 110–122.

(27) Gottlieb, M.; Gaylord, R. J. Experimental tests of entanglement models of rubber elasticity:
   1. Uniaxial extension-compression. *Polymer* **1983**, *24*, 1644–1646.

(28) Gottlieb, M.; Gaylord, R. J. Experimental tests of entanglement models of rubber elasticity.
   2. Swelling. *Macromolecules* **1984**, *17*, 2024–2030.

(29) Gottlieb, M.; Gaylord, R. J. Experimental tests of entanglement models of rubber elasticity.
   3. Biaxial deformations. *Macromolecules* **1987**, *20*, 130–138.

(30) Higgs, P.; Gaylord, R. J. Slip-links, hoops and tubes: tests of entanglement models of rubber elasticity. *Polymer* **1990**, *31*, 70–74.

(31) Urayama, K.; Kawamura, T.; Kohjiya, S. Multiaxial deformations of end-linked poly (dimethylsiloxane) networks. II. Experimental tests of molecular entanglement models of rubber elasticity. *Macromolecules* **2001**, *34*, 8261–8269.

(32) Mooney, M. A theory of large elastic deformation. *J. Appl. Phys.* **1940**, *11*, 582–592.

(33) Rivlin, R. Large elastic deformations of isotropic materials. I. Fundamental concepts. *Philos. Trans. R. Soc. A* **1948**, *240*, 459–490.

(34) Rivlin, R. Large elastic deformations of isotropic materials. II. Some uniqueness theorems for pure, homogeneous deformation. *Philos. Trans. R. Soc. A* **1948**, *240*, 491–508.
(35) Rivlin, R. Large elastic deformations of isotropic materials. III. Some simple problems in cylindrical polar co-ordinates. *Philos. Trans. R. Soc. A* **1948**, *240*, 509–525.

(36) Rivlin, R. Large elastic deformations of isotropic materials. IV. Further developments of the general theory. *Philos. Trans. R. Soc. A* **1948**, *241*, 379–397.

(37) Rivlin, R.; Saunders, D. Large elastic deformations of isotropic materials. VII. Experiments on the deformation of rubber. *Philos. Trans. R. Soc. A* **1951**, *243*, 251–288.

(38) Mark, J. The constants $2C_1$ and $2C_2$ in phenomenological elasticity theory and their dependence on experimental variables. *Rubber Chem. Technol.* **1975**, *48*, 495–512.

(39) Mark, J.; Sullivan, J. Model networks of end-linked polydimethylsiloxane chains. I. Comparisons between experimental and theoretical values of the elastic modulus and the equilibrium degree of swelling. *J. Chem. Phys.* **1977**, *66*, 1006–1011.

(40) Sharaf, M.; Mark, J. Interpretation of the small-strain moduli of model networks of polydimethylsiloxane. *J. Chem. Phys.* **1994**, *35*, 740–751.

(41) Schlögl, S.; Trutschel, M.-L.; Chassé, W.; Riess, G.; Saalwächter, K. Entanglement effects in elastomers: macroscopic vs microscopic properties. *Macromolecules* **2014**, *47*, 2759–2773.

(42) Svaneborg, C.; Karimi-Varzaneh, H. A.; Hojdis, N.; Fleck, F.; Everaers, R. Multiscale approach to equilibrating model polymer melts. *Phys. Rev. E* **2016**, *94*, 032502.

(43) Zhang, G.; Moreira, L. A.; Stuehn, T.; Daoulas, K. C.; Kremer, K. Equilibration of high molecular weight polymer melts: a hierarchical strategy. *ACS Macro Lett.* **2014**, *3*, 198–203.

(44) Auhl, R.; Everaers, R.; Grest, G. S.; Kremer, K.; Plimpton, S. J. Equilibration of long chain polymer melts in computer simulations. *J. Chem. Phys.* **2003**, *119*, 12718–12728.

(45) Everaers, R.; Karimi-Varzaneh, H. A.; Fleck, F.; Hojdis, N.; Svaneborg, C. Kremer-Grest models for commodity polymer melts: linking theory, experiment and simulation at the Kuhn scale. DOI: 10.1021/acs.macromol.9b02428.
(46) Everaers, R.; Sukumaran, S. K.; Grest, G. S.; Svaneborg, C.; Sivasubramanian, A.; Kremer, K. Rheology and microscopic topology of entangled polymeric liquids. *Science* **2004**, *303*, 823–826.

(47) Svaneborg, C.; Everaers, R.; Grest, G. S.; Curro, J. G. Connectivity and entanglement stress contributions in strained polymer networks. *Macromolecules* **2008**, *41*, 4920–4928.

(48) Kuhn, W. Über die Gestalt fadenförmiger Moleküle in Lösung. *Kolloid-Zeitschrift* **1934**, *68*, 2–15.

(49) Flory, P. J. *Principles of polymer chemistry*, 1st ed.; Cornell University Press: Ithaca, New York, 1953.

(50) Flory, P. J. The configuration of real polymer chains. *J. Chem. Phys.* **1949**, *17*, 303–310.

(51) Prince E. Rouse, J. A theory of the linear viscoelastic properties of dilute solutions of coiling polymers. *J. Chem. Phys.* **1953**, *21*, 1272–1280.

(52) Kawamura, T.; Urayama, K.; Kohjiya, S. Multiaxial deformations of end-linked poly (dimethylsiloxane) networks. I. Phenomenological approach to strain energy density function. *Macromolecules* **2001**, *34*, 8252–8260.

(53) Graessley, W. W. Elasticity and chain dimensions in Gaussian networks. *Macromolecules* **1975**, *8*, 865–868.

(54) Edwards, S.; Viglis, T. The tube model theory of rubber elasticity. *Rep. Prog. Phys.* **1988**, *51*, 243–297.

(55) Zhong, M.; Wang, R.; Kawamoto, K.; Olsen, B. D.; Johnson, J. A. Quantifying the impact of molecular defects on polymer network elasticity. *Science* **2016**, *353*, 1264–1268.

(56) Lang, M. Elasticity of phantom model networks with cyclic defects. *ACS Macro Lett.* **2018**, *7*, 536–539.
(57) Panyukov, S. Loops in polymer networks. *Macromolecules* 2019, 52, 4145–4153.

(58) Lin, T.-S.; Wang, R.; Johnson, J. A.; Olsen, B. D. Revisiting the elasticity theory for real gaussian phantom networks. *Macromolecules* 2019, 52, 1685–1694.

(59) Edwards, S.; Viglis, T. The effect of entanglements in rubber elasticity. *Polymer* 1986, 27, 483–492.

(60) Warner, M.; Edwards, S. Neutron scattering from strained polymer networks. *J. Phys. A* 1978, 11, 1649–1655.

(61) Cohen, A. A Padé approximant to the inverse Langevin function. *Rheol. Acta* 1991, 30, 270–273.

(62) Heinrich, G.; Straube, E. On the strength and deformation dependence of the tube-like topological constraints of polymer networks, melts and concentrated solutions. II. Polymer melts and concentrated solutions. *Acta Polym.* 1984, 35, 115–119.

(63) Kröger, M. Simple, admissible, and accurate approximants of the inverse Langevin and Brillouin functions, relevant for strong polymer deformations and flows. *J. Nonnewton. Fluid Mech.* 2015, 223, 77–87.

(64) Grest, G. S.; Kremer, K. Molecular dynamics simulation for polymers in the presence of a heat bath. *Phys. Rev. A* 1986, 33, 3628–3631.

(65) Kremer, K.; Grest, G. S. Dynamics of entangled linear polymer melts: A molecular-dynamics simulation. *J. Chem. Phys.* 1990, 92, 5057–5086.

(66) Faller, R.; Kolb, A.; Müller-Plathe, F. Local chain ordering in amorphous polymer melts: influence of chain stiffness. *Phys. Chem. Chem. Phys.* 1999, 1, 2071–2076.

(67) Grønbech-Jensen, N.; Farago, O. A simple and effective Verlet-type algorithm for simulating Langevin dynamics. *Mol. Phys.* 2013, 111, 983–991.
(68) Verlet, P. Computer "experiments" on classical fluids. I. Thermodynamical properties of Lennard-Jones molecules. *Phys. Rev.* **1967**, *159*, 98–103.

(69) Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical recipies in C. The art of scientific computing*, 2nd ed.; Cambridge University Press: New York, 1992.

(70) Plimpton, S. Fast parallel algorithms for short-range molecular dynamics. *J. Comput. Phys.* **1995**, *117*, 1–19.

(71) Svaneborg, C.; Everaers, R. Characteristic time and length scales in melts of Kremer-Grest bead-spring polymers with wormlike bending stiffness. DOI: 10.1021/acs.macromol.9b02437.

(72) Fetters, L. J.; Lohse, D. J.; Colby, R. H. In *Physical Properties of Polymers Handbook*; Mark, J. E., Ed.; Springer Science+Business Media, LLC, 2007; Chapter 25, pp 447–454.

(73) Chávez, F. V.; Saalwächter, K. Time-domain NMR observation of entangled polymer dynamics: analytical theory of signal functions. *Macromolecules* **2011**, *44*, 1560–1569.

(74) Lin, Y.-H. Number of entanglement strands per cubed tube diameter, a fundamental aspect of topological universality in polymer viscoelasticity. *Macromolecules* **1987**, *20*, 3080.

(75) Kavassalis, T.; Noolandi, J. New view of entanglements in dense polymer systems. *Phys. Rev. Lett.* **1987**, *59*, 2674.

(76) Rosa, A.; Everaers, R. Ring polymers in melt state: the physics of crumpling. *Phys. Rev. Lett.* **2014**, *112*, 118302.

(77) Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. Connection between polymer molecular weight, density, chain dimensions, and melt viscoelastic properties. *Macromolecules* **1994**, *27*, 4639.

(78) Hsu, H.-P.; Kremer, K. Clustering of entanglement points in highly strained polymer melts. *Macromolecules* **2019**, *52*, 6756–6772.
(79) Sukumaran, S. K.; Grest, G. S.; Kremer, K.; Everaers, R. Identifying the primitive path mesh in entangled polymer liquids. *J. Polym. Sci. B: Polym. Phys.* 2005, 403, 917–933.

(80) Consider the system of 2 FENE bonds, connecting 4 KG beads, located far away from each other in space, so that pair interactions between non-bonded beads are negligibly small. Let the lengths of the bonds vary in accordance with the system configuration and to be determined in such the way to provide the minimum energy. For the two bonds to pass through each other, they have to appear crossing in the same plane, and this configuration is achievable if the energy threshold $\approx 75k_B T$ is overpassed. Further, let’s consider the system of 5000000 beads, which dynamics is simulated for 10000000 time steps, let’s set $\sigma = 1$, $\varepsilon = 1$, $k = 30$, $k_B = 1$, $T = 1$, $R_0 = 1.5$. Let the probability $P$ of finding a single pair of bonds passed through each other to be of the order of $10^{-3} – 10^{-4}$, then the energy threshold to overpass is $\approx 30 – 31$. Finally, let’s consider the system of 2 FENE bonds, connecting 4 KG beads, located far away from each other in space. Let the length of one of the bonds vary in accordance with the system configuration and to be determined in such the way to provide the minimum energy; let the length of the other bond to be constant and to be determined in such the way that the energy threshold to overpass is $\approx 30 – 31$, then the length of the bond with constant length can be found as $\approx 1.4 \sigma$.

(81) Doi, M.; Edwards, S. *The theory of polymer dynamics*; Clarendon Press: Oxford, 1986.

(82) Hoy, R. S.; Robbins, M. O. Strain hardening of polymer glasses: effect of entanglement density, temperature, and rate. *J. Polym. Sci. B: Polym. Phys.* 2006, 44, 3487–3500.

(83) Boyce, M. C.; Arruda, E. M. Constitutive models of rubber elasticity: A review. *Rubber Chem. Technol.* 2000, 73, 504–523.

(84) Pak, H.; Flory, P. J. Relationship of stress to uniaxial strain in crosslinked poly(dimethylsiloxane) over the full range from large compressions to high elongations. *J. Polym. Sci.: Polymer Physics Edition* 1979, 17, 1845–1854.
(85) Xu, P.; Mark, J. Biaxial extension studies using inflation of sheets of unimodal model networks. *Rubber Chem. Technol.* **1990**, 63, 276–284.

(86) Langley, N. R. Elastically effective strand density in polymer networks. *Macromolecules* **1968**, *1*, 348–352.

(87) Treloar, L. The elasticity and related properties of rubbers. *Rep. Prog. Phys.* **1973**, 36, 755–826.

(88) Treloar, L. The elasticity and related properties of rubbers. *Rubber Chem. Technol.* **1974**, 47, 625–696.

(89) Treloar, L. R. The mechanics of rubber elasticity. *J. Polym. Sci.: Polymer Symposia* **1974**, 48, 107–123.

(90) Gumbrell, S.; Mullins, L.; Rivlin, R. Departures of the elastic behaviour of rubbers in simple extension from the kinetic theory. *Trans. Faraday Soc.* **1953**, 49, 1495–1505.

(91) Han, W. H.; Horka, F.; McKenna, G. B. Mechanical and swelling behaviors of rubber: a comparison of some molecular models with experiment. *Math. Mech. Solids* **1999**, 4, 139–167.

(92) Ronca, G.; Allegra, G. An approach to rubber elasticity with internal constraints. *J. Chem. Phys.* **1975**, 63, 4990–4997.

(93) Boyer, R. F.; Miller, R. L. Correlations involving the Mooney-Rivlin $C_2$ constant and the number of chain atoms between physical entanglements, $N_c$. *Polymer* **1987**, 28, 399–407.

(94) Saleesung, T.; Reichert, D.; Saalwächter, K.; Sirisinha, C. Correlation of crosslink densities using solid state NMR and conventional techniques in peroxide-crosslinked EPDM rubber. *Polymer* **2015**, 56, 309–317.

(95) Saalwächter, K.; Seiffert, S. Dynamics-based assessment of nanoscopic polymer-network mesh structures and their defects. *Soft Matter* **2018**, 14, 1976–1991.
(96) Klüppel, M. Trapped engtanglements in polymer networks and their influence on the stress-strain behaviour up to large extensions. *Progr. Colloid Polym. Sci.* **1992**, *90*, 137–143.

(97) Rubinstein, M.; Colby, R. H. *Polymer physics*; Oxford University Press: New York, 2003.