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Constitutive equation for polymer networks with phonon fluctuations

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Recent research by Xing *et al.* [Phys. Rev. Lett. **98**, 075502 (2007)] has provided an expression for the Helmholtz free energy related to phonon fluctuations in polymer networks. We extend this result by constructing the corresponding nonlinear constitutive equation, usable for entirely general, volume conserving deformation fields. Constitutive equations for the sliplink model and the tube model are derived and the three models are examined by comparison with each other and with data from Xu and Mark [Rubber Chem. Technol. **63**, 276 (1990)] and Wang and Mark [J. Polym. Sci., Part B: Polym. Phys. **30**, 801 (1992)]. Elastic moduli are derived for the three models and compared with the moduli determined from the chemical stoichiometry. We conclude that the sliplink model and the phonon fluctuation model are relatively consistent with each other and with the data. The tube model seems consistent neither with the other models nor with the data.

I. INTRODUCTION

A polymer gel is a three-dimensional network of polymer chains joined at a certain number of permanent connection sites, called crosslinks. Furthermore, a network usually contains entanglements, which can be regarded as temporary crosslinks. At the microscopic scale it resembles a liquid with a highly amorphous structure, however, it can sustain shear stresses without flowing, and hence behaves as an elastic solid. Since the 1940s, due to work done by Kuhn, Flory, and Treloar among others [4], it has been known that rubber elasticity is associated with a suppression of entropy by the imposed deformation. Kuhn derived the following expression for the elastic (Helmholtz) free energy, up to an additive function of volume and temperature, of a rubber in a homogeneous deformation [5]:

$$A_0 = \frac{3}{2} N_c k_B T \langle |\mathbf{E} \cdot \boldsymbol{u}|^2 \rangle_{\boldsymbol{u}} = \frac{1}{2} N_c k_B T E_{ij}^2, \tag{1}$$

where $\langle \cdots \rangle_{\boldsymbol{u}}$ denotes an average over the orientation of the three-dimensional unit vector $\boldsymbol{u}$, i.e., an isotropic distribution. N_c is the number of chain segments between two neighboring connection sites, called partial chains, k_B the Boltzmann constant, T the absolute temperature, and $E_{ij} \equiv \partial x_i / \partial x_j'$ the deformation gradient tensor, which is constant in a homogeneous deformation by definition. The 3-vectors $\boldsymbol{x}'$ and $\boldsymbol{x}$ denote the position of a material particle before and after, respectively, deformation. This result is based on two main assumptions: (1) The distribution function of the end-to-end vector $\boldsymbol{r}$ of a partial chain is Gaussian. (2) The connection sites r_i move affinely with the macroscopic deformation, i.e., $r_i = E_{ij} r_j'$. We refer to Eq. (1) as the classical model, and to the corresponding network as an *affine network*. It has long been known that the classical model does not work well for large deformations.

As mentioned by Doi [5] the assumption of Gaussian statistics fails for large extensions, where the Langevin dependence of elongation on force becomes important. However, before this finite extensibility effect becomes important, two other neglected effects are dominant. These are the interactions between partial chains, and the fluctuations in the positions of the connection sites. To cope with entanglement interactions between polymer chains, Edwards and de Gennes introduced the tube model. This model implied another expression [5,6] of the elastic free energy given by

$$A_t = \frac{3}{2} N_c k_B T \frac{Z^2 a^2}{N b^2} \langle |\mathbf{E} \cdot \boldsymbol{u}| \rangle_{\boldsymbol{u}}^2 = \frac{3}{2} N_c k_B T Z \langle |\mathbf{E} \cdot \boldsymbol{u}| \rangle_{\boldsymbol{u}}^2. \tag{2}$$

Here a is the tube radius, N the number of Kuhn steps, b the Kuhn step length, and Z the number of elements of length a spanning the central axis of the tube. Since $Z \propto N$, the prefactor increases linearly with N, which is known from experiments to be true. Note that the averaging in Eq. (2) occurs before the square, *not* after the square as in Eq. (1).

Ball *et al.* [7] introduced the concept of sliplinks, where entanglements are allowed to slide along the polymer strands, implying the elastic free energy

$$A_s = A_0 + \Delta A_s = \frac{1}{2} k_B T N_c \sum_i \lambda_i^2$$
$$+ \frac{1}{2} k_B T N_s \sum_i \left[\frac{(1+\eta)\lambda_i^2}{1+\eta\lambda_i^2} + \ln(1+\eta\lambda_i^2) \right]. \tag{3}$$

Here N_c and N_s are the total number of crosslinks and sliplinks, respectively. λ_i are Cartesian extension ratios (strains) and η is a model specific parameter measuring the freedom of a link to slide compared with the freedom of movement of a chain. Ball *et al.* [7] recommended the value $\eta=0.2343$. Note that the second term, i.e., the contribution from the sliplinks, is added to the classical energy term, since the sliplink nature describes entanglements only.

Fluctuations in the positions of the connection sites have historically been a great barrier towards a precise and physi-

cally reasonable model of rubber elasticity, also working for large deformations. Rubinstein and Panyukov [8] have combined the ideas of the confining tube and sliplink models to a slip-tube model. More recent research by Xing *et al.* [1] provides another modification term to the classical model, based on incompressible phonon fluctuations of the polymer network:

$$\Delta A_p = \frac{4\pi}{\xi^3} V k_B T \langle \ln(C_{\alpha\beta} u_\alpha u_\beta) \rangle_{\boldsymbol{u}}.$$ (4)

In this expression ξ is the typical mesh size of the polymer network, V the volume of the material, and $C_{\alpha\beta}$ the Cauchy strain tensor defined below. In addition to deriving this general result, Xing *et al.* carry out the averaging in Eq. (4) for uniaxially and biaxially deformed systems. They also demonstrate a very encouraging comparison between their theory and data for uniaxial and biaxial stretching of crosslinked networks.

II. CONSTITUTIVE EQUATIONS

In this section we derive general expressions for the stress tensor, σ_{ij}, based on the models from Sec. I. We also introduce the elastic moduli as five independent fitting parameters, G_0^s, G_0^p, G_s, G_p, and G_t, for the three considered models. Following Bird *et al.* [9] we have the general expression for the stress in terms of the free energy density f,

$$\sigma_{ij} = E_{in} \frac{\partial f}{\partial E_{jn}}.$$ (5)

The hydrostatic pressure p, specified by some imposed boundary condition, contributes with an isotropic tensor $p\boldsymbol{\delta}$, where $\boldsymbol{\delta}$ is the unit tensor.

When inserting Eq. (1) into Eq. (5) we get the constitutive equation for the classical model,

$$\sigma_{ij}^{classical} = G_0 E_{in} E_{jn}.$$ (6)

The elastic modulus is $G_0 = n_c k_B T$, where we have defined the density of partial chains $n_c \equiv N_c / V$. Since stresses obtained by the sliplink model (Sec. II B) and the phonon fluctuation model (Sec. II C) are added to the classical contribution, we define, respectively, G_0^s and G_0^p.

A. Tube model

The constitutive equation for the tube model is obtained by inserting Eq. (2) into Eq. (5). Following Nielsen *et al.* [10] we get

$$\sigma_{ij}^{tube} = 3 n_c k_B T Z \langle |\mathbf{E} \cdot \boldsymbol{u}| \rangle_{\boldsymbol{u}} \left\langle \frac{E_{im} u_m E_{jn} u_n}{|\mathbf{E} \cdot \boldsymbol{u}|} \right\rangle_{\boldsymbol{u}}$$

$$= \frac{15}{4} G_t \langle |\mathbf{E} \cdot \boldsymbol{u}| \rangle_{\boldsymbol{u}} \left\langle \frac{E_{im} u_m E_{jn} u_n}{|\mathbf{E} \cdot \boldsymbol{u}|} \right\rangle_{\boldsymbol{u}},$$ (7)

where the elastic modulus $G_t = (4/5) n_c k_B T Z$.

B. Sliplink model

The constitutive equation corresponding to the sliplink energy term from Eq. (3) is derived next. First, we remember

that the nonlinear Finger strain tensor B_{ij} and the Cauchy strain tensor $C_{ij} = B_{ij}^{-1}$ are defined as follows:

$$B_{ij} = E_{in} E_{jn},$$ (8)

$$C_{in} B_{nj} = \delta_{ij}.$$ (9)

The Finger strain tensor B_{ij} is in some literature called the *left Cauchy-Green tensor*, but the Cauchy strain tensor C_{ij} is *not* the same as the *right Cauchy-Green tensor*.

We also introduce the two strain invariants

$$I_1 = B_{ii} = \lambda_1^2 + \lambda_2^2 + \lambda_3^2,$$ (10)

$$I_2 = C_{ii} = \lambda_1^{-2} + \lambda_2^{-2} + \lambda_3^{-2},$$ (11)

and the incompressibility condition

$$\lambda_1 \lambda_2 \lambda_3 = 1.$$ (12)

Using the chain rule, we obtain

$$E_{in} \frac{\partial}{\partial E_{jn}} I_1 = 2 B_{ij},$$ (13)

$$E_{in} \frac{\partial}{\partial E_{jn}} I_2 = -2 C_{ij}.$$ (14)

Hence in general for some function $F(I_1, I_2)$ we have

$$E_{in} \frac{\partial}{\partial E_{jn}} F(I_1, I_2) = 2 \frac{\partial F}{\partial I_1} B_{ij} - 2 \frac{\partial F}{\partial I_2} C_{ij}.$$ (15)

Denoting the energy density $\Delta A_s / V$ by f_{slip} and the number density N_s / V by n_s, we have from Eq. (3)

$$\frac{f_{slip}}{k_B T n_s} = \frac{(1+\eta)}{2} \left[\frac{\lambda_1^2}{1+\eta\lambda_1^2} + \frac{\lambda_2^2}{1+\eta\lambda_2^2} + \frac{\lambda_3^2}{1+\eta\lambda_3^2} \right]$$

$$+ \frac{1}{2} \ln[(1+\eta\lambda_1^2)(1+\eta\lambda_2^2)(1+\eta\lambda_3^2)].$$ (16)

Rewriting in terms of strain invariants, we obtain

$$\frac{f_{slip}}{k_B T n_s} = \frac{(1+\eta)}{2} \frac{I_1 + 2\eta I_2 + 3\eta^2}{1+\eta I_1 + \eta^2 I_2 + \eta^3}$$

$$+ \frac{1}{2} \ln(1+\eta I_1 + \eta^2 I_2 + \eta^3).$$ (17)

From Eq. (15) we can write

$$\sigma_{ij}^{slip} = 2 \frac{\partial f_{slip}}{\partial I_1} B_{ij} - 2 \frac{\partial f_{slip}}{\partial I_2} C_{ij}.$$ (18)

By differentiation we obtain

$$\frac{\partial}{\partial I_1} \frac{f_{slip}}{k_B T n_s} = \frac{(1+\eta)}{2} \frac{1 - \eta^2 I_2 - 2\eta^3}{X^2} + \frac{\eta}{2X},$$ (19)

$$\frac{\partial}{\partial I_2} \frac{f_{slip}}{k_B T n_s} = \frac{(1+\eta)}{2} \frac{2\eta + \eta^2 I_1 - \eta^4}{X^2} + \frac{\eta^2}{2X},$$ (20)

where $X \equiv 1 + \eta I_1 + \eta^2 I_2 + \eta^3$.

Specializing to shear deformation of shear magnitude γ, we find

$$\sigma_{xy} = n_s k_B T \gamma \frac{(1+\eta)^2 + \eta^2 \gamma^2}{[(1+\eta)^2 + \eta \gamma^2]^2}, \quad (21)$$

$$N_1 = \sigma_{xx} - \sigma_{yy} = \gamma \sigma_{xy}, \quad (22)$$

$$N_2 = \sigma_{yy} - \sigma_{zz} = -n_s k_B T \gamma^2 \eta \frac{2(1+\eta) + \eta \gamma^2}{[(1+\eta)^2 + \eta \gamma^2]^2}, \quad (23)$$

as obtained by Oberdisse *et al.* [11]. From the zero strain limit of the shear stress expression, we obtain the elastic modulus

$$G_s = \frac{n_s k_B T}{(1+\eta)^2}. \quad (24)$$

C. Phonon fluctuation model

To obtain the general constitutive equation for polymer networks with phonon fluctuations, one must insert the free energy from Eq. (4) into Eq. (5).

$$\sigma_{ij} = 2\pi k_B T \xi^{-3} \left\langle E_{in} \frac{\partial}{\partial E_{jn}} \ln(C_{\alpha\beta} u_\alpha u_\beta) \right\rangle_{\boldsymbol{u}}$$

$$= 2\pi k_B T \xi^{-3} \left\langle E_{in} \frac{\frac{\partial}{\partial E_{jn}} C_{pq} u_p u_q}{C_{\alpha\beta} u_\alpha u_\beta} \right\rangle_{\boldsymbol{u}}. \quad (25)$$

The derivative in the numerator is carried out:

$$E_{in} \frac{\partial}{\partial E_{jn}} C_{pq} = E_{in} \frac{\partial}{\partial E_{jn}} B_{pq}^{-1} = -C_{pj}\delta_{iq} - C_{jq}\delta_{pi}. \quad (26)$$

Hence

$$E_{in} \frac{\partial}{\partial E_{jn}} C_{pq} u_p u_q = -C_{pj}\delta_{iq} u_p u_q - C_{jq}\delta_{pi} u_p u_q$$

$$= -C_{pj} u_p u_i - C_{jq} u_q u_i. \quad (27)$$

The Cauchy strain tensor is symmetric by construction, which implies

$$E_{in} \frac{\partial}{\partial E_{jn}} C_{pq} u_p u_q = -2 C_{ip} u_p u_j = -2\mathbf{C} \cdot \boldsymbol{uu}. \quad (28)$$

Recognizing the denominator inside the brackets in Eq. (25) as the double dot product, we arrive at the central result of the paper; the stress-strain constitutive equation corresponding to incompressible phonon fluctuations.

$$\sigma_{ij} = -4\pi k_B T \xi^{-3} \left\langle \frac{C_{ip} u_p u_j}{C_{\alpha\beta} u_\alpha u_\beta} \right\rangle_{\boldsymbol{u}} = -4\pi k_B T \xi^{-3} \left\langle \frac{\mathbf{C} \cdot \boldsymbol{uu}}{\mathbf{C}:\boldsymbol{uu}} \right\rangle_{\boldsymbol{u}}. \quad (29)$$

This expression is evaluated numerically in simple shear for N_1, N_2, and σ_{xy}, see Fig. 1. To second order in the shear γ, the normal stress ratio $\Psi = N_2/N_1 = -5/7$.
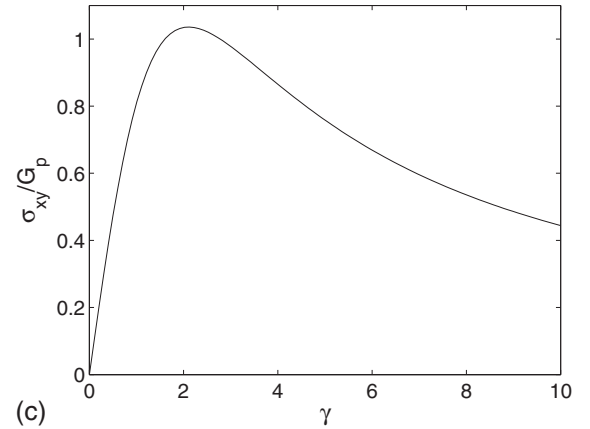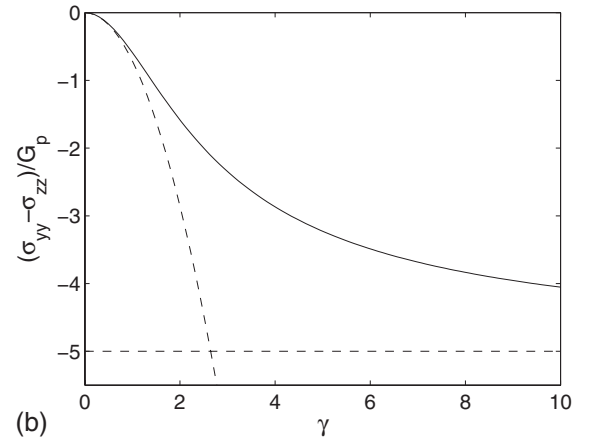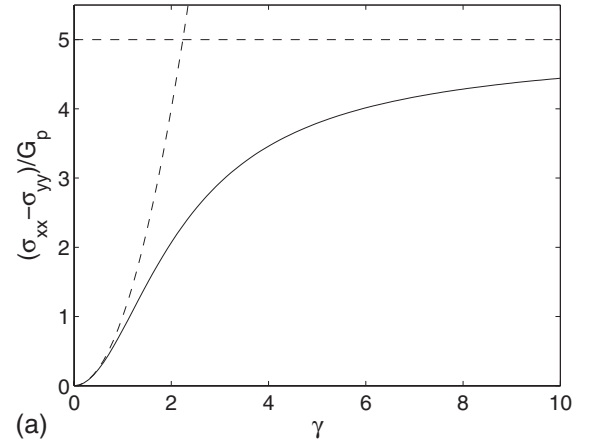

FIG. 1. Dimensionless normal stress differences N_1/G_p and N_2/G_p and shear stress σ_{xy}/G_p from phonon fluctuations in simple shear deformation as a function of the shear magnitude γ. Numerical evaluations of Eq. (29) are plotted along with second order expansions, $N_1/G_p \approx \gamma^2$ and $N_2/G_p \approx -5/7\gamma^2$, and asymptotics, $N_1/G_p 5$ and $N_2/G_p - 5$ (dashed lines).

We now proceed to derive the elastic modulus G_p for the phonon fluctuation model. For infinitesimal shear strain we set

$$C_{mn} = \delta_{mn} - \epsilon_{mn},$$

and expand to first order in ϵ_{mn}:

$$\left\langle \frac{C_{ip}u_p u_j}{C_{\alpha\beta}u_\alpha u_\beta} \right\rangle_{\boldsymbol{u}} = \left\langle \frac{u_i u_j - \epsilon_{ip}u_p u_j}{1 - \epsilon_{\alpha\beta}u_\alpha u_\beta} \right\rangle_{\boldsymbol{u}}$$

$$= \langle u_i u_j + \epsilon_{\alpha\beta}u_\alpha u_\beta u_i u_j - \epsilon_{ip}u_p u_j \rangle_{\boldsymbol{u}} + O(\epsilon_{ij}^2).$$

Using the identities

$$\langle u_\alpha u_\beta \rangle_{\boldsymbol{u}} = \frac{1}{3}\delta_{\alpha\beta},$$

$$\langle u_\alpha u_\beta u_i u_j \rangle_{\boldsymbol{u}} = \frac{1}{15}(\delta_{\alpha\beta}\delta_{ij} + \delta_{\alpha i}\delta_{\beta j} + \delta_{\alpha j}\delta_{\beta i})$$

we get

$$\left\langle \frac{C_{ip}u_p u_j}{C_{\alpha\beta}u_\alpha u_\beta} \right\rangle_{\boldsymbol{u}} = \frac{1}{3}\delta_{ij} - \frac{1}{5}\epsilon_{ij} + O(\epsilon_{ij}^2). \tag{30}$$

Hence the elastic modulus is given by $G_p = 4\pi k_{\mathrm{B}} T \xi^{-3}/5$. Note that G_p and G_0 are not entirely independent, since the mesh size ξ depends on the crosslink density n_c. However, following Xing *et al.* [1], we use both as free fitting parameters.

III. STRESS-STRAIN CURVES AND DATA

Uni- and bi-axial deformation is characterized by the strain λ, where $\lambda > 1$ and $\lambda < 1$ correspond to uni- and bi-axial deformation, respectively. The deformation gradient tensor is given by $\mathbf{E} = \mathrm{diag}(\lambda^{-1/2}, \lambda^{-1/2}, \lambda)$. In uniaxial deformation ($\lambda > 1$) a sphere is deformed into a prolate ellipsoid, while in biaxial deformation ($\lambda < 1$) the sphere is deformed into an oblate ellipsoid.

In simple shear the characterization parameter is γ, and the deformation gradient tensor is given by

$$\mathbf{E} = \begin{pmatrix} 1 & \gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

Planar elongation is characterized by the parameter α, and the deformation gradient tensor is given by $\mathbf{E} = \mathrm{diag}(\alpha, 1, \alpha^{-1})$. The considered material is assumed incompressible in all the considered models, i.e., $\det \mathbf{E} = 1$.

In order to obtain parameters, we make a fit of the three considered models in uni- and bi-axial deformation to data from Xu and Mark [2], in the Mooney-Rivlin plot in Fig. 2 (a). To test the theories, we compare the models with data from the same network [3] in planar elongation, using the same set of parameters, in Fig. 2 (b). It is important to notice that the data has a slight inconsistency in the modulus but the deviation is within experimental uncertainty (5%). In both figures the classical contribution only translates the curves vertically. It is noteworthy how similar the phonon fluctuation model and the sliplink model are. They both contain the essence of the deviation from classical behavior, possibly within experimental error. The tube model is unable to fit the data.

For comparison, we have given also in Table I the value $G_0 = 0.114 \times 10^6$ Pa denoted "chemistry." This value is com-
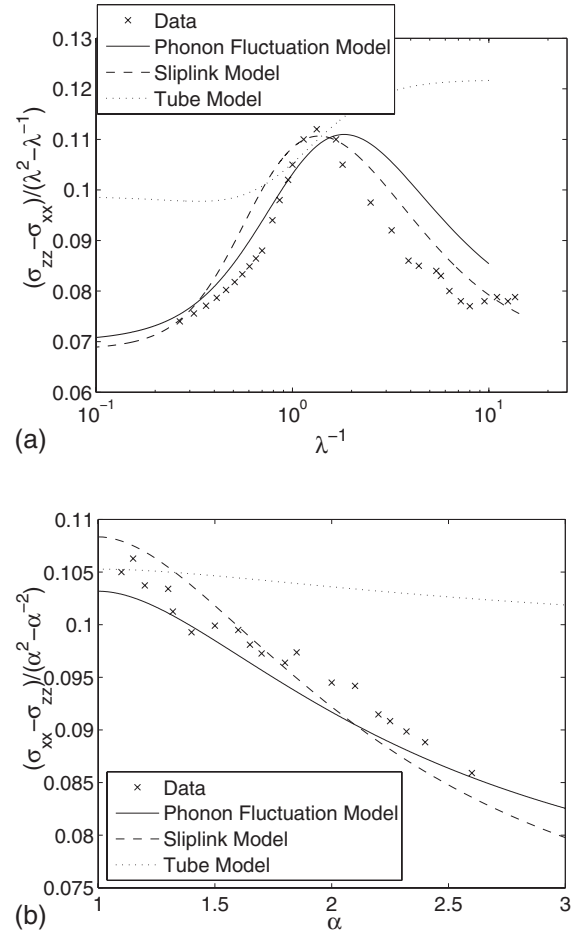

FIG. 2. (a) Fit of the phonon fluctuation model, the sliplink model, and the tube model to data for uni- and bi-axial deformation. The temperature is $T = 298$ K. (b) Comparison of the three models with data from the same network in planar elongation, using the same set of parameters. Data from Xu and Mark [2] and Wang and Mark [3] (unit: 10^6 Pa). In order for the two data sets to predict the same modulus for $\alpha = \lambda = 1$ we have scaled the data for planar elongation with a factor of 0.9545. This corresponds to a temperature variation of approximately 14 K. Parameters are presented in Table I.

puted from the expression $G_0 = n_c k_{\mathrm{B}} T$ with n_c obtained from the stoichiometry given by Xu and Mark [2]. The value closely predicts the total modulus of the network. However, the classical model alone clearly does not describe the nonlinear elasticity of the network. The additional contributions

TABLE I. Parameter values used to fit models to data in Fig. 2 (unit: 10^6 Pa).

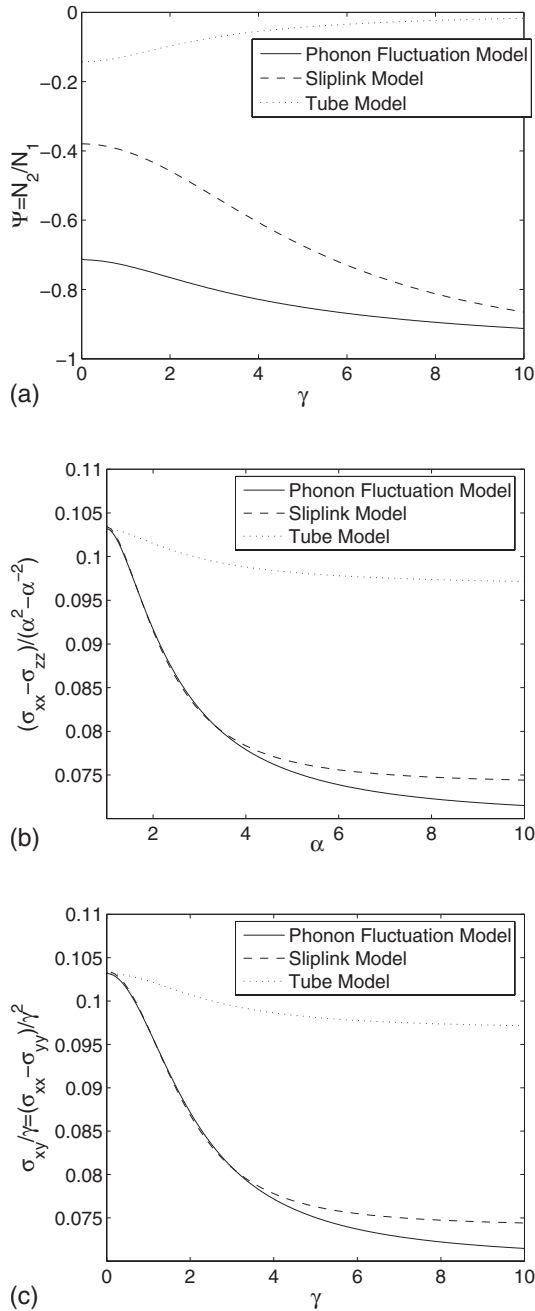| Model	Elastic modulus	Affine (classical)	Additional
Tube	$G_t = 4 n_c k_{\mathrm{B}} T Z/5$		0.1053
Sliplink	$G_s = n_s k_{\mathrm{B}} T/(1+\eta)^2$	0.0683	0.0400
Phonon	$G_p = 4\pi k_{\mathrm{B}} T \xi^{-3}/5$	0.0700	0.0322
Chemistry	$G_0 = 0.114$		

FIG. 3. (a) Normal stress ratio as a function of shear γ. For the classical model $\Psi = 0$. (b-c) Comparison of the phonon fluctuation model, the sliplink model, and the tube model in (planar elongation/simple shear). Parameters for the phonon fluctuation model are taken from the data fit, see Table I, and the two other models are fitted to the phonon fluctuation model.

from either the sliplink model or the phonon fluctuation model greatly improve the nonlinear behavior, whereby almost a perfect fit is obtained. When the additional terms are added it becomes necessary to reduce the classical contribution. The values for G_0^s and G_0^p in Table I are closer to the values predicted by the phantom network model [2], which for the tetrafunctional network is exactly one-half the affine network expression. It seems less obvious how the parameter Z in the tube model can be predicted from the stoichiometry [12,13]. The molar mass between crosslinks is 21 kg/mol, while the entanglement molar mass is 13 kg/mol [14]. This could suggest a number Z in the range 1 to 2, which is in reasonable agreement with Table I. Keep in mind, however, the nonlinear behavior of the tube model is inconsistent with the data.

In closing we compare the three models in large deformations outside the experimentally investigated range. Figure 3 (a) shows the normal stress ratio $\Psi = N_2/N_1$ in simple shear. In (b) we compare the models in planar elongation, fitting the tube model and the sliplink model to the phonon fluctuation model. In (c) we compare the models in simple shear. The sliplink model and the phonon fluctuation model produce very similar results. The tube model deviates markedly from the two other models. The existence of the second normal stress difference is well-documented for polymeric liquids, and the tube model has formed the basis for the pioneering Doi-Edwards model for entangled polymer melts [5,6].

Planar elongation and simple shear differ only by a rotation of coordinates, i.e., the stress components for planar elongation $[\cdots]_p$ and simple shear $[\cdots]_s$ are related by the formula

$$\frac{[\sigma_{xx} - \sigma_{zz}]_p}{\alpha^2 - \alpha^{-2}} = \frac{[\sigma_{xy}]_s}{\gamma} = \frac{[\sigma_{xx} - \sigma_{yy}]_s}{\gamma^2}, \quad (31)$$

provided that the two deformation parameters are related by

$$\alpha^2 = 1 + 1/2\gamma^2 + \gamma\sqrt{1 + 1/4\gamma^2}. \quad (32)$$

This result is obtained by diagonalizing the Finger strain tensor B_{ij} for simple shear.

IV. CONCLUSIONS

The phonon fluctuation model is capable of fitting simultaneously uniaxial, biaxial, and planar extension. At the same time, however, the data may be fitted equally well by the sliplink model, which is based on very different physical ideas. The phonon fluctuation model therefore offers an alternative physical explanation of the deviations from the classical behavior in rubber elasticity. Both models require that the modulus from the classical term, as well as the moduli from the additional terms, are retained as free fitting parameters.

The tube model does provide clear deviations from classical behavior in a Mooney plot. Uniaxial extension and planar elongation are qualitatively correct, while the model fails to give a maximum in biaxial compression.

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