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A non-Gaussian network model for rubber elasticity

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Abstract

A simple constitutive model based on the non-Gaussian, Kuhn–Grün probability distribution function is derived. It is assumed that the actual macromolecular structure of a rubber-like material can be replaced by idealized equilateral tetrahedra cells that are not mutually exclusive so far as occupancy of the space is concerned. The three chains are assumed to meet at a junction point located at the centroid of the cell with their other ends being fixed at the vertices of the equilateral tetrahedron. The centroid junction point is free to fluctuate, subject to the constraint imposed by the equilibrium of chain forces. Stress–stretch constitutive equations are then derived to study homogeneous deformations of isotropic, incompressible hyperelastic rubber like materials. The accuracy of the derived constitutive equations is demonstrated by using uniaxial, equibiaxial, pure shear, and plane strain experimental data provided in the literature.

Keywords: Rubber elasticity; Non-Gaussian chain statistics; Rubber molecular network models

1. Introduction

A major objective of this work is to develop a constitutive material network model to predict the state of deformation of incompressible rubber-like materials under different types of deformation states. This model is based on the statistical theory of networks of non-Gaussian flexible chains and it is assumed that the actual macromolecular structure of a rubber material can be replaced by idealized equilateral tetrahedra in which all the chains are of the same contour length and are connected at junction points which in rubber-like materials are provided by the chemical cross-links between macromolecules. The concept of idealized regular tetrahedra cells as a representative unit of the actual network structure was introduced by Flory and Rehner on their treatment of cross-linked polymer networks [1,2]. There, they assumed that the properties of the material network can be computed from those of a tetrahedron cell and that the most probable position of the four nearest neighbor cross-linkages lie at the corners of the tetrahedron. Wang and Guth [3] based on James–Guth non-Gaussian theory found that the tetrahedron network is not isotropic for all orientation of the axes.

Arruda and Boyce developed a non-Gaussian constitutive model that is highly accurate in predicting experimental results [4]. This model is based on a network of eight chains which possesses the cubic symmetry of principal stretch space as it averages eight orientations of that space in determining the network response. However, Yeoh and Fleming [5] noted that Arruda–Boyce and Flory–Rehner models yield identical expressions for the strain energy function since the former may be envisioned to consist basically of two tetrahedral cells as illustrated in Fig. 1. Hence, the Flory–Rehner and the Arruda–Boyce models possess the same features although they differ in their topology.

Others non-Gaussian network models proposed by several researchers to predict the mechanical response of rubber-like materials can be found in the literature. See Flory and Rehner [1], Wang and Guth [3], Arruda and Boyce [4], Treloar [6], Wu and van Der Giessen [7], and Dorfmann and Muhr [8] for an overview of the main features of these network models. Very recently, Beatty determined the squared chain stretch of an arbitrarily directed chain averaged over a unit sphere surrounding all chains radiating from a cross-link junction as its center by using an average-stretch, full-network approximation [9]. He used this result to obtain from the Kuhn–Grün probability distribution function an approximate total strain energy function for a uniform full-network model that led to the same constitutive equations for the Flory–Rehner and Arruda–Boyce models in which no specific chain cell morphology is required.

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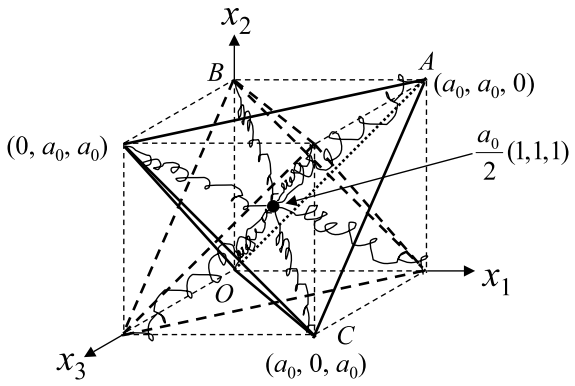

Fig. 1. Regular tetrahedral cells and the eight-chain network model.

Here, the formulation of a new constitutive model based on non-Gaussian statistical theory is investigated by assuming that the actual macromolecular structure of a rubber material can be replaced by idealized equilateral tetrahedra cells that are not mutually exclusive so far as occupancy of the space is concerned [1,2]. We introduce a network whose junction point is located at the centroid of an equilateral tetrahedron that is allowed to take up all possible positions and then we derive its stress–stretch constitutive equations for different deformation states.

We shall begin with a brief review of the non-Gaussian work of deformation of perfectly flexible jointed chains.

2. Non-Gaussian work of deformation

It is well-known that the non-Gaussian theory leads to a more realistic molecular distribution function valid over the whole range of r-values up to the ultimate, or fully extended length [3,10,11]. In this theory, the maximum chain extensibility is taken to be proportional to the square root of the number N of random links in a chain of length l. According to Khun and Grün [10], the configurational entropy for the distribution function of a stretch chain of current length r is given by

$$S = k\left[c - N\left[\frac{\beta r}{Nl} + \ln\left(\frac{\beta}{\sinh\beta}\right)\right]\right], \tag{1}$$

where c is a constant, k is Boltzmann's constant, and $\beta = \mathcal{L}^{-1}[r/(Nl)]$ is the inverse Langevin function $\mathcal{L}(\beta)$ defined by

$$\frac{r}{Nl} = \mathcal{L}(\beta) \equiv \coth\beta - \frac{1}{\beta} \tag{2}$$

Some amendments to Eq. (1) were introduced by Jerningan and Flory [12] to account for the uniform distribution of the chain end-to-end vector **r**. Numerical calculations of these modifications on the configurational entropy value for different deformation states and chain number of links N were performed by Jerningan and Flory [12] and Elías-Zúñiga and Beatty [13]. In accordance with kinetic theory, we assume that there is no change of internal energy on deformation, so the Helmholtz free energy per unit volume is given by

$$W = -\Theta S, \tag{3}$$

in which W represents the chain work of deformation or elastically stored free energy per unit volume of the rubber material, and Θ is the absolute temperature. Thus, the work of deformation is given by

$$W = nk\Theta\left[N\left[\frac{\beta r}{Nl} + \ln\left(\frac{\beta}{\sinh\beta}\right)\right] - c^*\right], \tag{4}$$

in which the constant c^* is chosen so that the strain energy vanishes in the undeformed state and n is the chain density. Hence, the principal Cauchy stresses T_i of an incompressible material may be determined from the strain–energy function as

$$T_i = \lambda_i \frac{\partial W}{\partial \lambda_i} - p, \tag{5}$$

where λ_i, are the principal stretches that satisfy the incompressibility constraint $\lambda_1\lambda_2\lambda_3 = 1$, and the pressure p is an arbitrary hydrostatic stress that may be eliminated by forming the difference

$$T_j - T_k = \lambda_j \frac{\partial W}{\partial \lambda_j} - \lambda_k \frac{\partial W}{\partial \lambda_k}, \quad j \neq k = 1,2,3 \text{ (no sum)} \tag{6}$$

Based on the above equations, we next consider the theoretical development of a new non-Gaussian network model.

3. The equilateral tetrahedron model

This model is based on an equilateral tetrahedron cell that is assumed to have three chains initially of the same contour length which is equal to the root-mean-square chain length $r_0 = l\sqrt{N_F}$, where N_F defines the number of links in a chain of length l. These chains occupy average positions at the corners A, B, and C of an undeformed base triangle with edge lengths a_0 that bounds the trihedral angle and that could initially meet, as shown in Fig. 2, at the point G, the centroid of the tetrahedron base located at $a_0(1/3,1/3,1/3)$ which is allowed to take up all possible positions [3].

Note, that our proposed model differs from that of the four-chain average tetrahedron network model proposed by Flory and Rehner [1] in which four chains extending from the corners of an average tetrahedron network meet at its central junction point that is allowed to take up all possible positions or from

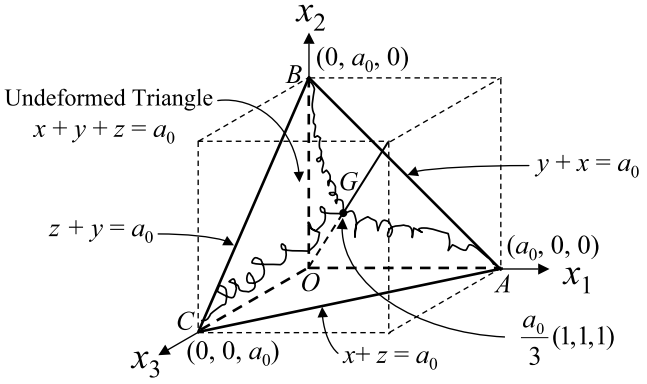

Fig. 2. Undeformed equilateral tetrahedron cell with the junction point located on its centroid.

the simple tetrahedron model proposed by Kloczkowski, Erman and Mark to study the effect of non-Gaussian chains fluctuation of junctions in bimodal networks [14].

We also make the following initial assumptions: (1) the equilateral tetrahedron is inside a regular cube and that its edges remain align with the principal stretch directions, (2) the corners of the equilateral tetrahedron as well as the junction point G are subjected to affine deformation. Thus, from the geometry of the equilateral tetrahedron shown in Fig. 2, the chain end-to-end vector length in its undeformed state is related to the tetrahedron initial dimensions by

$$r_0 = l\sqrt{N_F} = a_0\sqrt{\frac{2}{3}}, \tag{7}$$

and hence,

$$a_0 = l\sqrt{\frac{3N_F}{2}} \tag{8}$$

If the tetrahedron shown in Fig. 2 is stretched by $\lambda_1\mathbf{i}$, $\lambda_2\mathbf{j}$, $\lambda_3\mathbf{k}$ in the principal directions so that its edges measure, respectively, $a_0\lambda_1$, $a_0\lambda_2$, and $a_0\lambda_3$ in the x_1, x_2, and x_3 directions as illustrated in Fig. 3, then G moves to its mean or equilibrium position G' of coordinates $(x_{1c}\lambda_1, x_{2c}\lambda_2, x_{3c}\lambda_3)$, where (x_{1c}, x_{2c}, x_{3c}) represent the position coordinates of the junction point in the tetrahedron. Their values are determined from equilibrium of chain forces at the network junction point G'.

It is seen in Fig. 3, that the chain vectors from the equilibrium point G' to the corners A', B', and C' may be written down, respectively, as

$$\mathbf{r}_{GA'} = a_0[\lambda_1(1-x_{1c})\mathbf{i} - \lambda_2 x_{2c}\mathbf{j} - \lambda_3 x_{3c}\mathbf{k}], \tag{9}$$

$$\mathbf{r}_{GB'} = a_0[-\lambda_1 x_{1c}\mathbf{i} + \lambda_2(1-x_{2c})\mathbf{j} - \lambda_3 x_{3c}\mathbf{k}],$$

$$\mathbf{r}_{GC'} = a_0[-\lambda_1 x_{1c}\mathbf{i} - \lambda_2 x_{2c}\mathbf{j} + \lambda_3(1-x_{3c})\mathbf{k}],$$

Thus, the magnitude of each chain vector is given by

$$r_{GA'} = a_0[\lambda_1^2(1-x_{1c})^2 + \lambda_2^2 x_{2c}^2 + \lambda_3^2 x_{3c}^2]^{1/2}, \tag{10}$$

$$r_{GB'} = a_0[\lambda_1^2 x_{1c}^2 + \lambda_2^2(1-x_{2c})^2 + \lambda_3^2 x_{3c}^2]^{1/2},$$

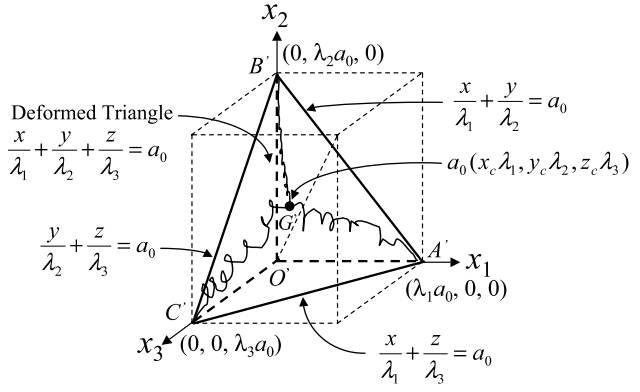

Fig. 3. Deformed equilateral tetrahedral cell with the junction point taking up all possible positions.

$$r_{GC'} = a_0[\lambda_1^2 x_{1c}^2 + \lambda_2^2 x_{2c}^2 + \lambda_3^2(1-x_{3c})^2]^{1/2}.$$

Since the chain stretch is obtained by dividing its current length by its initial length, we obtain upon substitution of Eq. (8) into Eq. (10), the current relative chain stretches:

$$\lambda_{kr} \equiv \frac{\lambda_{k\text{chain}}}{\lambda_l} = \sqrt{\frac{3}{2N_F}}[\lambda_k^2(1-x_{kc})^2 + \lambda_i^2 x_{ic}^2 + \lambda_j^2 x_{jc}^2]^{1/2}, \tag{11}$$

$i \neq j \neq k = 1, 2, 3$ (no sum), where $\lambda_l \equiv \sqrt{N_F}$ denotes the ultimate, fully extended chain stretch. Note that the position coordinates (x_{1c}, x_{2c}, x_{3c}) of G' are to be found by using an iterative numerical scheme for each stretch increment that satisfies the condition of no net forces on the junction point. In the present article, we also have assumed that the corresponding elastic tension force in each non-Gaussian chain may be computed from

$$f_j = \frac{k\Theta}{l}\beta_j, \tag{12}$$

where $\beta_j = \mathcal{L}^{-1}(\lambda_{j\text{chain}}/\sqrt{N_F})$ is the inverse Langevin function defined as $\mathcal{L}(\beta) \equiv \coth\beta - (1/\beta)$ [15]. With the help of Fig. 3, we may write the corresponding equilibrium equations for the junction point G' in the x_1, x_2, and x_3 directions; this gives

$$\sum F_1 = 0: \quad (1-x_{1c})\frac{f_1}{\lambda_{1\text{chain}}} - x_{1c}\frac{f_2}{\lambda_{2\text{chain}}} - x_{1c}\frac{f_3}{\lambda_{3\text{chain}}} + C_1 = 0, \tag{13}$$

$$\sum F_2 = 0: \quad -x_{2c}\frac{f_1}{\lambda_{1\text{chain}}} + (1-x_{2c})\frac{f_2}{\lambda_{2\text{chain}}} - x_{2c}\frac{f_3}{\lambda_{3\text{chain}}} + C_2 = 0 \tag{14}$$

$$\sum F_3 = 0: \quad -x_{3c}\frac{f_1}{\lambda_{1\text{chain}}} - x_{3c}\frac{f_2}{\lambda_{2\text{chain}}} + (1-x_{3c})\frac{f_3}{\lambda_{3\text{chain}}} + C_3 = 0, \tag{15}$$

where C_1, C_2, and C_3 are the rectangular components of the diffusion, friction, internal viscosity and other forces that are acting on the chains [16,17]. To simplify our analysis, we make the assumption that the magnitude of these unknown forces is the same, i.e.

$$C_1 = C_2 = C_3 = C. \tag{16}$$

To eliminate C from the above equations, we subtract Eq. (14) from Eq. (13), Eq. (15) from Eq. (13), and (15) from Eq. (14) to obtain the following equilibrium equations

$$(1-x_{1c}+x_{2c})\frac{f_1}{\lambda_{1\text{chain}}} - (1+x_{1c}-x_{2c})\frac{f_2}{\lambda_{2\text{chain}}} + (x_{2c}-x_{1c})\frac{f_3}{\lambda_{3\text{chain}}} = 0, \tag{17}$$

$$(1-x_{1c}+x_{3c})\frac{f_1}{\lambda_{1chain}}-(x_{1c}-x_3)\frac{f_2}{\lambda_{2chain}} -(1+x_{1c}-x_{3c})\frac{f_3}{\lambda_{3chain}}=0, \tag{18}$$

$$f-(x_{2c}-x_{3c})\frac{f_1}{\lambda_{1chain}}+(1-x_{2c}+x_{3c})\frac{f_2}{\lambda_{2chain}} -(1+x_{2c}-x_{3c})\frac{f_3}{\lambda_{3chain}}=0 \tag{19}$$

The coordinates of the equilibrium position of the central junction point G' can be found by solving numerically Eqs. (17)–(19). Once the values of (x_{1c},x_{2c},x_{3c}) are known, then the network work of deformation of the equilateral tetrahedron cell may be determined by adding the corresponding entropy contribution of each chain. Therefore, substitution of Eq. (11) into Eq. (4) yields the strain energy function per unit volume in the principal reference system:

$$W(\lambda_1,\lambda_2,\lambda_3)=\frac{nk\Theta}{3}N_F\sum_{k=1}^{3}\left(\beta_k\lambda_{kr}+\ln\frac{\beta_k}{\sinh\beta_k}\right)-c^* \tag{20}$$

where $\beta_k=\mathcal{L}^{-1}(\lambda_{kr})$, for $k=1, 2, 3$ and c^* is a constant chosen so that $W(1,1,1)=0$. For convenience, we write again Eq. (6) to recall that the principal values of Cauchy stresses are given by

$$T_k=-p+\lambda_k\frac{\partial W}{\partial\lambda_k},\quad k=1,2,3 \text{ (no sum)} \tag{21}$$

Use of Eq. (20) in Eq. (21) yields the following stress components:

$$T_k=-p+\mu_0\lambda_k^2 f_k(\lambda_{1r},\lambda_{2r},\lambda_{3r}),\quad k=1,2,3 \text{ (no sum)} \tag{22}$$

wherein, by definition,

$$f_k(\lambda_{1r},\lambda_{2r},\lambda_{3r})\equiv\frac{\sqrt{N_F}}{2}\left(\frac{\beta_k}{\lambda_{kr}}(1-x_{kc})^2+\left(\frac{\beta_i}{\lambda_{ir}}+\frac{\beta_j}{\lambda_{jr}}\right)x_{kc}^2\right) \tag{23}$$

$i\neq j\neq k=1, 2, 3$ (no sum), and the relative stretches are defined in Eq. (11). Eliminating the pressure from Eq. (22), yields

$$T_j-T_k=\mu_0(\lambda_j^2 f_j(\lambda_{1r},\lambda_{2r},\lambda_{3r})-\lambda_k^2 f_k(\lambda_{1r},\lambda_{2r},\lambda_{3r})) \tag{24}$$

where, in general, $j\neq k=1, 2, 3$ (no sum) and $\mu_0=nk\Theta$ is the material shear modulus in the undeformed state. Finally, with the aid of (11) and using Eq. (23) in Eq. (24) delivers the virgin material stress difference for our equilateral tetrahedron network model:

$$T_1-T_2=\frac{\mu_0\sqrt{N_F}}{2}\left[\frac{\beta_1}{\lambda_{1r}}(\lambda_1^2(1-x_{1c})^2-\lambda_2^2x_{2c}^2) +\frac{\beta_2}{\lambda_{2r}}(\lambda_1^2x_{1c}^2-\lambda_2^2(1-x_{2c})^2)+\frac{\beta_3}{\lambda_{3r}}(\lambda_1^2x_{1c}^2-\lambda_2^2x_{2c}^2)\right] \tag{25}$$

4. An average-stretch non-Gaussian full-network model

To assess stress–stretch responses from our derived network model described by Eq. (24), we shall compare predicted results with the Arruda–Boyce constitutive equation for an average stretch, full-network of arbitrarily oriented molecular chains since this model is the most accurate of the non-Gaussian network models in fitting experimental data for different deformation states [4].

4.1. The Arruda–Boyce model

In this section, we briefly review the Arruda–Boyce model that is described by an average-stretch, full-network model for homogeneous non-Gaussian networks of randomly oriented molecular chains. According to Beatty [9], the constitutive Cauchy stress–stretch equation for the Arruda–Boyce material model is given by

$$\mathbf{T}=-p\mathbf{I}+\aleph(I_1)\mathbf{B} \tag{26}$$

where $\mathbf{B}=\mathrm{diag}[\lambda_1^2,\lambda_2^2,\lambda_3^2]$ in the principal reference system of the deformed state and the material response function $\aleph(I_1)$ is defined by:

$$\aleph(I_1)\equiv\frac{\mu_0\beta_8}{3\lambda_r} \tag{27}$$

where $\beta_8=\mathcal{L}^{-1}(\lambda_r)$ and λ_r is given by

$$\lambda_r=\frac{\lambda_{ch}}{\lambda_L}=\sqrt{\frac{I_1}{3N_8}} \tag{28}$$

where $\lambda_L=\sqrt{N_8}$ represents the fully extended chain-stretch and N_8 is the eight-chain number of links. We can also obtained from Eq. (26) the following general relation for the difference of principal Cauchy stresses as a functions of the principal stretches for the Arruda–Boyce non-Gaussian network model:

$$T_j-T_k=\aleph(I_1)(\lambda_j^2-\lambda_k^2),\quad j\neq k=1,2,3 \tag{29}$$

Note that for an incompressible material, the engineering stress $\boldsymbol{\sigma}$ is related to the Cauchy stress by

$$\boldsymbol{\sigma}=\mathbf{T}\mathbf{F}^{-1} \tag{30}$$

5. Homogeneous deformations

Here, we first recall some basic definitions of homogeneous deformations and then we provide the corresponding stress–stretch relations for simple extension and compression, equibiaxial extension, pure shear and plain strain compression by using Eqs. (24) and (29) in conjunction with Eq. (30).

5.1. Basic definitions

Let us consider a material particle at the place $\mathbf{X}$ in an initially undeformed reference configuration of a body. The particle at $\mathbf{X}$ when subjected to a prescribed deformation, has a new position $\mathbf{x}$ in the resulting deformed configuration of the body. Then, a pure homogeneous deformation is described by

$$x_1=\lambda_1X_1,\quad x_2=\lambda_2X_2,\quad x_3=\lambda_3X_3 \tag{31}$$

in which λ_k are the constant principal stretches and x_k and X_k are the respective coordinates of $\mathbf{x}$ and $\mathbf{X}$ in a common rectangular Cartesian frame $\varphi=\{O;\ \mathbf{e}_k\}$ with origin O and orthonormal basis $\mathbf{e}_k$. For a volume preserving deformation, we require that

$$\det \mathbf{F} = \lambda_1\lambda_2\lambda_3 = 1 \tag{32}$$

for all deformations, with the deformation gradient tensor given by $\mathbf{F}=\partial\mathbf{x}/\partial\mathbf{X}$. In the undistorted state $\mathbf{F}=\mathbf{I}$, the identity tensor.

5.2. Simple extension and compression

For a simple extension in the $\mathbf{e}_1$ direction, we take the principal stretches as $\lambda_1=\lambda$, $\lambda_2=\lambda_3=\lambda^{1/2}$. The corresponding uniaxial stress is $T_1=T$. In this case $T_2=T_3=0$.

Recalling Eq. (11) for the current relative chain-stretch components, we thus find from Eq. (24) the following uniaxial engineering stress–stretch relation for the equilateral tetrahedron network model:

$$\sigma_{\mathrm{F}} = \frac{\mu_0\sqrt{N_{\mathrm{F}}}}{2}\left[\frac{\beta_1}{\lambda_{1\mathrm{r}}}\left(\lambda(1-x_{1\mathrm{c}})^2-\frac{1}{\lambda^2}x_{2\mathrm{c}}^2\right) + \frac{\beta_2}{\lambda_{2\mathrm{r}}}\left(\lambda x_{1\mathrm{c}}^2-\frac{1}{\lambda^2}(1-x_{2\mathrm{c}})^2\right)+\frac{\beta_3}{\lambda_{3\mathrm{r}}}\left(\lambda x_{1\mathrm{c}}^2-\frac{1}{\lambda^2}x_{2\mathrm{c}}^2\right)\right] \tag{33}$$

wherein $\beta_k=\mathcal{L}^{-1}(\lambda_{k\mathrm{r}})$, for $k=1, 2, 3$.

For the Arruda–Boyce material network model, we can obtain by using Eq. (29) together with Eqs. (27) and (28) the uniaxial engineering stress–stretch relation:

$$(\sigma)_{8-\mathrm{ch}} = \frac{\mu_0\beta(\lambda-\lambda^{-2})}{3\lambda_{\mathrm{r}}} \tag{34}$$

in which $\beta=\mathcal{L}^{-1}(\lambda_{\mathrm{r}})$ and

$$\lambda_{\mathrm{r}} = \sqrt{\frac{1}{3N_8}\left(\lambda^2+\frac{2}{\lambda}\right)} \tag{35}$$

5.3. Equibiaxial extension and balloon inflation

For an equibiaxial homogeneous deformation, we know that $\lambda_1=\lambda_2=\lambda$, and $\lambda_3=\lambda^{-2}$ satisfies Eq. (32). Then, the principal engineering stress components are given by $\sigma_1=\sigma_2=\sigma=T/\lambda$ and $\sigma_3=0$. Thus, the equibiaxial engineering stress for our derived equilateral tetrahedron network model is described by

$$\sigma_{\mathrm{F}} = \frac{\mu_0\sqrt{N_{\mathrm{F}}}}{2}\left[\frac{\beta_1}{\lambda_{1\mathrm{r}}}\left(\lambda(1-x_{1\mathrm{c}})^2-\lambda^{-5}x_{3\mathrm{c}}^2\right) + \frac{\beta_3}{\lambda_{3\mathrm{r}}}(\lambda x_{1\mathrm{c}}^2-\lambda^{-5}(1-x_{3\mathrm{c}})^2)\right)+\frac{\beta_2}{\lambda_{2\mathrm{r}}}(\lambda x_{1\mathrm{c}}^2-\lambda^{-5}x_{3\mathrm{c}}^2)] \tag{36}$$

where $\beta_k=\mathcal{L}^{-1}(\lambda_{k\mathrm{r}})$, for $k=1, 2, 3$.

The equibiaxial engineering stress for the Arruda–Boyce model can be readily shown to be given by

$$(\sigma)_{8-\mathrm{ch}} = \frac{\mu_0\beta}{3\lambda_{\mathrm{r}}}(\lambda-\lambda^{-5}) \tag{37}$$

Here $\beta=\mathcal{L}^{-1}(\lambda_{\mathrm{r}})$ and the relative stretch is

$$\lambda_{\mathrm{r}} = \sqrt{\frac{1}{3N_8}\left(2\lambda^2+\frac{1}{\lambda^4}\right)} \tag{38}$$

5.4. Pure shear or plane strain compression

This homogeneous isochoric deformation is described by Eq. (31) with $\lambda_1=\lambda$, $\lambda_2=1$, $\lambda_3=\lambda^{-1}$. Here, the tensile or compressive engineering stress is $\sigma_1=T_1/\lambda$, the restraining stress is $\sigma_2=T_2$, and the free surface stress is $\sigma_3=0$. Then, the compressive engineering stress in a pure shear of the equilateral tetrahedron model is given by the following equation

$$\sigma_{\mathrm{F}} = \frac{\mu_0\sqrt{N_{\mathrm{F}}}}{2}\left[\frac{\beta_1}{\lambda_{1\mathrm{r}}}(\lambda(1-x_{1\mathrm{c}})^2-\lambda^{-3}x_{3\mathrm{c}}^2) + \frac{\beta_3}{\lambda_{3\mathrm{r}}}(\lambda x_{1\mathrm{c}}^2-\lambda^{-3}(1-x_{3\mathrm{c}})^2)+\frac{\beta_2}{\lambda_{2\mathrm{r}}}(\lambda x_{1\mathrm{c}}^2-\lambda^{-3}x_{3\mathrm{c}}^2)\right] \tag{39}$$

where $\beta_k=\mathcal{L}^{-1}(\lambda_{k\mathrm{r}})$, for $k=1, 2, 3$. The corresponding constitutive compressive engineering stress equation for the Arruda–Boyce network material model may be obtained by using Eq. (29) in conjunction with a pure shear or plane strain compression homogeneous deformation, this yields

$$\sigma_{8-\mathrm{ch}} = \frac{\mu_0\beta}{3\lambda_{\mathrm{r}}}(\lambda-\lambda^{-3}) \tag{40}$$

where $\beta=\mathcal{L}^{-1}(\lambda_{\mathrm{r}})$ and the relative stretch Eq. (28) is given by

$$\lambda_{\mathrm{r}} = \sqrt{\frac{1}{3N_8}(\lambda^2+\lambda^{-2}+1)} \tag{41}$$

It is important to emphasize that in all the above equations the inverse Langevin functions $\beta=\mathcal{L}^{-1}(\lambda_{\mathrm{r}})$ and $\beta_k=\mathcal{L}^{-1}(\lambda_{k\mathrm{r}})$ can be replaced by the empirical estimates

$$\beta = \mathcal{L}^{-1}(\lambda_{\mathrm{r}}) \approx \frac{3\lambda_{\mathrm{r}}}{1-\lambda_{\mathrm{r}}^3};\quad \beta_k = \mathcal{L}^{-1}(\lambda_{k\mathrm{r}}) \approx \frac{3\lambda_{k\mathrm{r}}}{1-\lambda_{k\mathrm{r}}^3} \tag{42}$$

that exhibits very good graphical comparisons [18].

6. Numerical results

Our objective from here onward is to assess the accuracy of our equilateral tetrahedron model described by Eq. (24) when compared to the Arruda–Boyce constitutive Eq. (26) for different deformation states. Also, we shall compare some predicted results with experimental data by Treloar [15], Kawabata and Kawai [19], James, Green and Simpson [20], and Arruda and Boyce [4]. Fig. 4 illustrates the theoretical predictions of the equilateral tetrahedron and Arruda–Boyce network models as well as the engineering stress–stretch data for simple extension, pure shear, and equibiaxial extension obtained by Treloar [15,21]. Here, we chose to fit Treloar's

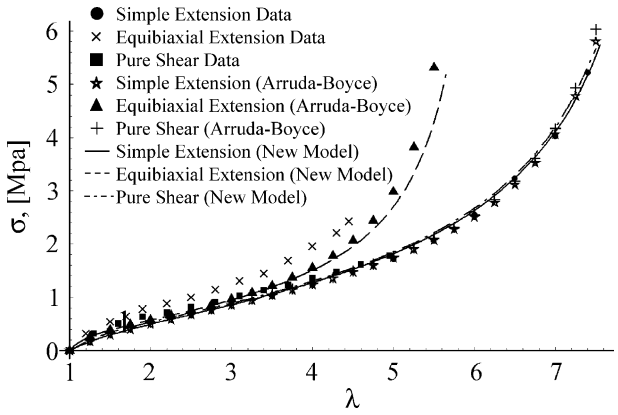

Fig. 4. Stress–stretch behavior for simple extension, equibiaxial extension, and pure shear. Experimental data is taken from Treloar for which the material parameter values are: $nk\Theta = 0.27$ MPa, $N_8 = 25.12$, and $N_F = 30.25$.

simple extension data with the following parameter values: $nk\Theta = 0.27$ MPa, $N_8 = 25.12$, and $N_F = 30.25$. It is seen in Fig. 4 that numerical results obtained from the Arruda–Boyce and the equilateral tetrahedron model are strikingly identical, although the former is stiffer in equibiaxial extension at large stretch values. We have plotted in Fig. 5 for each deformation state the displacement of the equilibrium position of G' measured from the origin O' of the coordinate system shown in Fig. 3. The coordinates that describe the equilibrium position of G' were obtained from Eqs. (17)–(19) by using a numerical algorithm provided by the Mathematica symbolic package. During the application of this algorithm, we have used the following starting coordinate values $(x_{1c}, x_{2c}, x_{3c}) = (1/3,1/3,1/3)$. If different starting values are used in the Mathematica numerical algorithm solution, we may obtain other roots for (x_{1c},x_{2c},x_{3c})

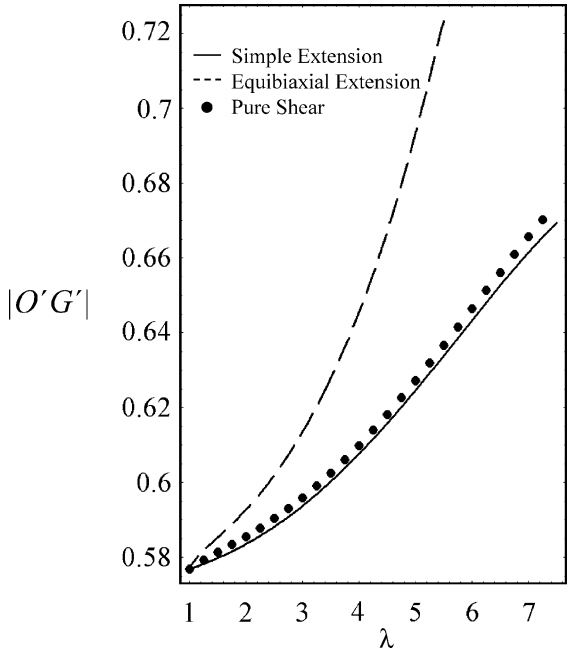

Fig. 5. Displacement of the equilibrium position of G' measured from the origin O' for simple extension, equibiaxial extension, and pure shear. The material parameter values are: $nk\Theta = 0.27$ MPa and $N_F = 30.25$.

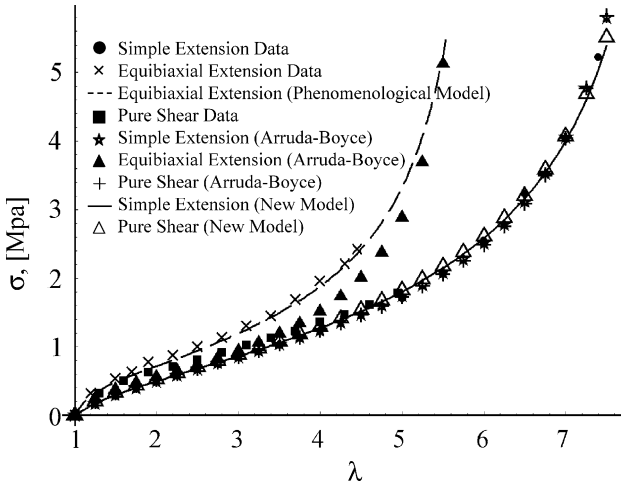

Fig. 6. Stress–stretch behavior for equibiaxial extension of our phenomenological model. Experimental data is taken from Treloar for which the material parameter values are: $nk\Theta = 0.27$ MPa, $N_8 = 25.12$, and $N_F = 30.25$.

that satisfy the equilibrium Eqs. (17)–(19). For instance, if we take the starting values of $(x_{1c}, x_{2c}, x_{3c}) = (1/\sqrt{3}, 1/\sqrt{3}, 1/\sqrt{3})$ for the equibiaxial deformation state, while keeping constant the material parameter values, the engineering stress–stretch values obtained by our equilateral tetrahedron model are almost identical to Treloar's experimental data as shown in Fig. 6. From the results of our numerical simulations it appears unrealistic to have relative chain stretch values determined from Eq. (11) that are different for equibiaxial and simple extension deformation states when $\lambda = 1$ however, it is commonly known that rubber-like material response depends on the direction of stretching [21–23]. In spite of this, the assumption that G' is initially located at the point $(x_{1c}, x_{2c}, x_{3c}) = (1/\sqrt{3}, 1/\sqrt{3}, 1/\sqrt{3})$ is inconsistent with our desire that G' should be initially located at the centroid of the equilateral tetrahedron base. Therefore, when we look at the quantitative equibiaxial extension behavior of our proposed model by considering that the initial equilibrium position of the mean point G' is not at the centroid of the tetrahedron base, we may regard it as a phenomenological model. In the comparison of theoretical results and experimental data that follows, we will show that this phenomenological model also fits well equibiaxial experimental data by Kawabata and Kawai and experimental results obtained by James, Green and Simpson. Notice that stress–stretch numerical results for deformation states that are different from the equibiaxial state have been computed by considering the starting coordinate values of $(x_{1c},x_{2c},x_{3c}) = (1/3,1/3,1/3)$.

Fig. 7 illustrates the behavior of the equilateral tetrahedron and Arruda–Boyce models compared to experimental data provided by Kawabata and Kawai [19]. The material parameters are determined by fitting simple extension data. This gives $nk\Theta = 0.3$ MPa, $N_8 = 100.11$, and $N_F = 180.25$. We observe in Fig. 7 that theoretical results obtained from both the Arruda–Boyce and the equilateral tetrahedron models almost coincide. Furthermore, both models predict well simple extension data but underestimate pure shear and equibiaxial deformations. It is also seen in Fig. 7 that our

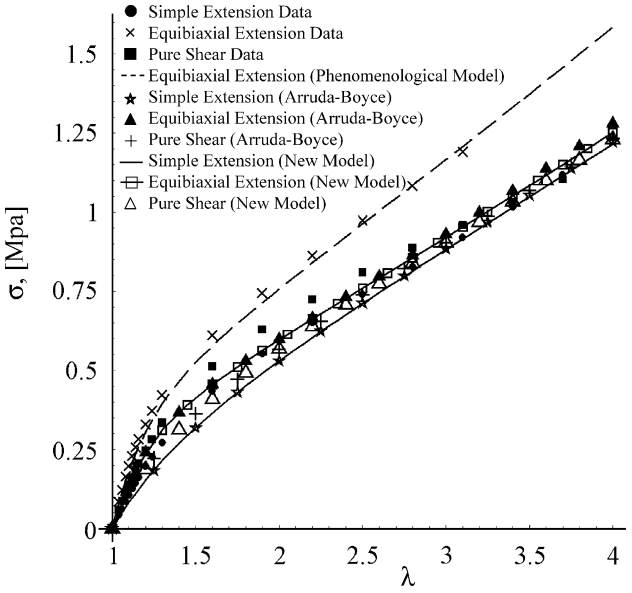

Fig. 7. Stress–stretch behavior for simple extension, equibiaxial extension, and pure shear. Experimental data is taken from Kawabata and Kawai for which the material parameter values are: $nk\Theta = 0.3$ MPa, $N_8 = 100.11$, and $N_F = 180.25$.

phenomenological model predicts satisfactorily equibiaxial extension data.

We now compare our theoretical results with experimental data obtained by James et al. [20]. Here, we fit simple extension data with the following material parameter values: $nk\Theta = 0.375$ MPa, $N_8 = 23.14$, and $N_F = 30.5$. As we may see in Fig. 8, both models predict well simple extension data but diverge from equibiaxial experimental data. Notice however, that results obtained from our phenomenological equilateral model compare well with equibiaxial experimental data. In Fig. 9, we now plot experimental results for silicone rubber recorded by Arruda and Boyce [4] for simple and plane strain compression

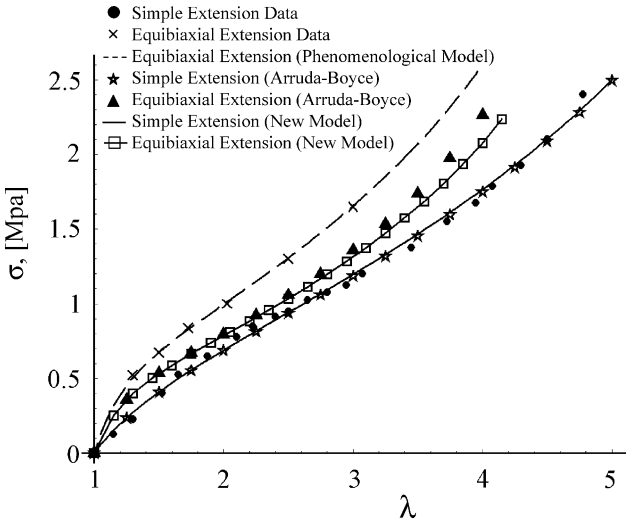

Fig. 8. Stress–stretch behavior for simple extension, equibiaxial extension, and pure shear. Experimental data is taken from James et al. for which the material parameter values are: $nk\Theta = 0.375$ MPa, $N_8 = 23.14$, and $N_F = 30.5$.

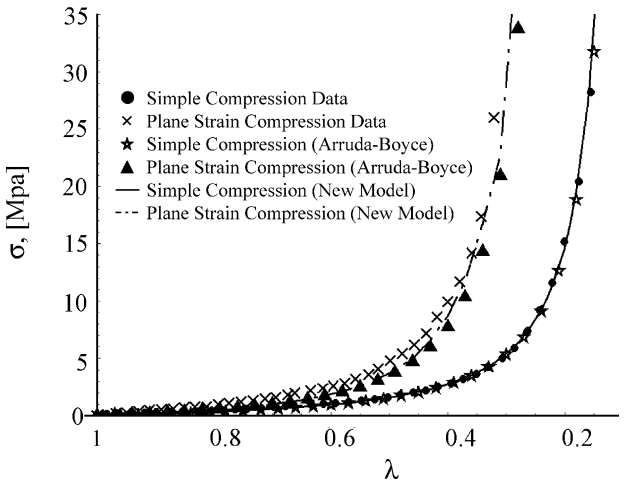

Fig. 9. Stress–stretch behavior for simple compression and plane strain compression. Experimental data is taken from Arruda–Boyce for which the material parameter values are: $nk\Theta = 0.4$ MPa, $N_8 = 7.83$, and $N_F = 8.7$.

homogeneous deformations. We chose to fit Arruda–Boyce simple compression data with the following parameter values: $nk\Theta = 0.4$ MPa, $N_8 = 7.83$, and $N_F = 8.7$. We note from Fig. 9, that both models compare well with experimental results but now the equilateral tetrahedron model predicts a stiffer response at larger stretches and it virtually coincides with experimental data.

7. Conclusions

A constitutive equilateral tetrahedron network model based on non-Gaussian statistical theory has been proposed in an attempt to predict available experimental data. The equilateral tetrahedron model described by the simple constitutive relations (24) can be easily used to predict with good accuracy the physical response of incompressible rubber-like materials for different deformation states since it successfully accounts for the state of deformation dependence by only using two materials parameters, the shear modulus $nk\Theta$, and the model specific molecular chain number of links N_F. This model when compare with the Arruda–Boyce model tends to underestimate at large stretch values the stiffness of the network in equibiaxial deformation but in the case of plane strain compression, it virtually matches experimental data. We believe that the improvement achieved in this deformation state lies in the location of the junction point during deformation which is determined from equilibrium of chain forces that must satisfied the equilibrium condition of no net forces.

We have also shown that theoretical results obtained from our proposed phenomenological equilateral tetrahedron model agree well with equibiaxial experimental data by assuming that in this deformation state the equilibrium position of G' is initially located at the point $(x_{1c}, x_{2c}, x_{3c}) = (1/\sqrt{3}, 1/\sqrt{3}, 1/\sqrt{3})$.

Finally, our proposed model can be used to derive stress–stretch constitutive equations by considering the effect of non-Gaussian chains on fluctuations of junctions in bimodal networks by following a procedure similar to the one describe

in [14]. The results of this new work will be reported in a subsequent paper elsewhere.

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References

[1] Flory PJ, Rehner Jr J. J Chem Phys 1943;11:512–20.
[2] Flory PJ. Chem Rev 1944;35:51–75.
[3] Wang MC, Guth EJ. Chem Phys 1952;20:1144–57.
[4] Arruda EM, Boyce MC. J Mech Phys Solids 1993;41:389–412.
[5] Yeoh OH, Fleming PD. J Polym Sci 1997;35:1919–31.
[6] Treloar LRG, Riding G. Proc R Soc London 1979;A369:261–80.
[7] Wu PD, Van Der Giessen EJ. Mech Phys Solids 1993;41(3):427–56.
[8] Dorfmann A, Muhr A. Constitutive models for rubber. Rotterdam: A.A. Balkema; 1999 p. 189–93.
[9] Beatty MF. J Elasticity 2003;70:65–86.
[10] Kuhn W, Grüm F. Kolloid-Z 1942;101:248–71.
[11] James HM, Guth EJ. Chem Phys 1943;10:455–81.
[12] Jerningan RL, Flory PJ. J Chem Phys 1969;50:4185–200.
[13] Elias-Zuniga A, Beatty MF. Int J Eng Sci 2002;40:2265–94.
[14] Kloczkowski A, Erman B, Mark JE. Polymer 2002;43:2569–74.
[15] Treloar LRG. The physics of rubber elasticity. 3rd ed. Oxford: Clarendon Press; 1975.
[16] Takserman-Krozer R, Ziabicki A. J Polym Sci 1970;8:321–32.
[17] Gao J, Weiner JH. Macromolecules 1991;24:5179–91.
[18] Puso MA. Mechanistic constitutive models for rubber elasticity and viscoelasticity. Doctoral dissertation, University of California, Davis; 1994.
[19] Kawabata S, Kawai H. Adv Polym Sci 1977;24:89–123.
[20] James AG, Green A, Simpson GMJ. Appl Polym Sci 1975;19:2033–58.
[21] Treloar LRG. Trans Faraday Soc 1944;40:59–70.
[22] Lu J, Papadopoulus P. Z Angew Math Phys 2000;51:204–17.
[23] Diani J, Brieu M, Vacherand JM, Rezgui A. Mech Matls 2004;36: 313–21.