Polymer 43 (2002) 2569–2574

polymer

www.elsevier.com/locate/polymer

Effect of non-Gaussian chains on fluctuations of junctions in bimodal networks

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Received 12 July 2001; accepted 11 November 2001

Abstract

A simple tetrahedron model is used to study the effect of non-Gaussian chains on fluctuations of junctions in bimodal networks. The four chains are assumed to meet at a junction with their other ends being fixed at the vertices of the tetrahedron. It is assumed that the angles between mean end-to-end vectors of all four chains connected at the junction are tetrahedral, but the lengths of edges of the tetrahedron may differ due to the difference in the lengths of the chains. The central junction is free to fluctuate, subject to the constraints imposed by the pendant chains. The long chains are chosen to be Gaussian. The short chains are assumed to be non-Gaussian. Calculations show that the non-Gaussian nature of the short chains imposes severe restrictions on the fluctuations of the central junction. The strength of these restrictions directs attention to the importance of anharmonic modes in networks. © 2002 Published by Elsevier Science Ltd.

Keywords: Non-Gaussian; Bimodal networks; Tetrahedron

1. Introduction

The significant progress in the synthesis of polymeric materials allows for the design of well characterized networks by using various end-linking techniques [1–4]. Of particular importance is the end linking of mixtures of long and very short chains to form bimodal networks [5]. Experimental results on bimodal polydimethylsiloxane networks show [5] that they have highly desirable mechanical and ultimate properties such as increased modulus, strength and ductility depending on the composition, relative lengths of the short and the long chains, spatial heterogeneity, junction functionality, temperature and the degree of swelling. Analysis of experimental data shows that the improvements observed in the ultimate properties depend predominantly on the finite extensibility or the non-Gaussian nature of the short chains reached at high degrees of deformation. The effect of the non-Gaussian chain behavior on bimodal network properties have been studied theoretically by several investigators [6–9]. However, in all of these studies, the junctions have been assumed to be rigidly embedded in the network. This assumption is unrealistic in as much as the junctions exhibit wide ranges of fluctuations. For unimodal Gaussian networks, the extent of fluctuations and their relation to network topology were studied in detail [10–12]. Spin echo neutron scattering experiments [13] on polydimethylsiloxane networks clearly demonstrate that junction fluctuations are substantial, both statically and dynamically. For bimodal Gaussian networks, the extent of fluctuations of junctions has been studied by Higgs and Ball [14] and by Kloczkowski et al. [15]. The theory of molecular orientation in deformed bimodal networks was developed by Bahar et al. [16] Theoretical treatment of trimodal elastomeric networks has been recently proposed by Erman and Mark [17].

The aim of the present paper is to investigate the fluctuations of junctions in bimodal networks when a fraction of the chains are non-Gaussian. A rigorous treatment of the complete bimodal non-Gaussian network tree becomes rather complicated, however. Therefore, we propose a simple model of a tetrahedron, similar to the Flory–Rehner tetrahedron [18], with four fixed vertices as the four junctions and allow only a central junction to fluctuate. Even in this simplified case, several mathematical difficulties are encountered and simplifying assumptions have to be

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0032-3861/02/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0032-3861(01)00797-2

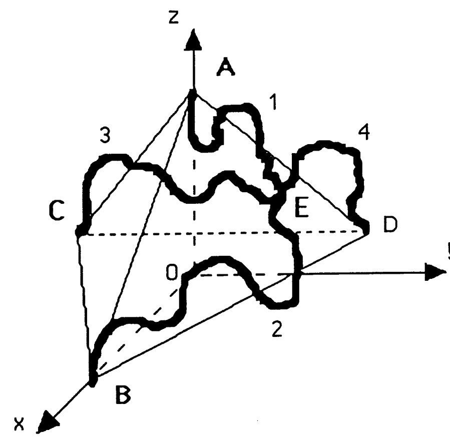

Fig. 1. The modified version of the Flory–Rehner tetrahedron model studied in this paper. The four chains which meet at junction E may have two different lengths.

made. The proposed model may serve as a starting point for the more complicated theories in the future studies of this problem.

2. The model and assumptions

The model is based on a modified version of the Flory–Rehner tetrahedron [18] shown in Fig. 1. Four chains shown by the heavy lines and numbered from one to four in Fig. 1 meet at a central junction E which is assumed to fluctuate. The junctions at the other ends of the chains are at vertices A, B, C and D of the tetrahedron. These points are assumed to be fixed. The coordinate system shown in Fig. 1 is a tetrahedron-based system chosen such that the plane BCD lies in the x–y plane and the z-axis passes through the fourth vertex A. The locations of the vertices are chosen subject to the following two conditions:

(i) the time averaged forces exerted by the chains AE, BE, CE and DE on the junction E is zero, and
(ii) the angles between four lines from A, B, C and D to the average location of the central junction are tetrahedral. The chains are numbered such that the first ϕ_S are short and the rest, $\phi_L = 4 - \phi_S$, are long. The long chains are assumed to be Gaussian and the short ones non-Gaussian. These conditions are described in more detail later.

A similar model of a micro-network was used by Adolf and Curro [19] to study the effect of topological constraints on junction fluctuations in uniaxial extensions.

3. Theory

The distribution function for long chains is given as

$$W(r) = C_1 \exp\left[-\gamma_L r^2\right] \quad (1)$$

and that for the short chains by

$$W(r) = C_2 \exp\left[-\gamma_S r^2 - (\beta r^2)^n\right] \quad (2)$$

where n is an integer with $n \geq 2$, $\gamma_i = 3\langle r_i^2\rangle_0/2$, and the subscripts L and S stand for long and short chains, respectively. In the following formulation, these subscripts will be replaced by indices from one to four. The symbols C_1 and C_2 in Eqs. (1) and (2) are normalization constants and $\langle r_i^2\rangle_0$ is the mean square value of the end-to-end vector of the ith chain in the undeformed state.

The expression given by Eq. (2) is a generalization [9] of the Fixman–Alben distribution function [20]. The Fixman–Alben distribution ($n = 2$) is the simplest and the most natural representation for non-Gaussian chains, because the distribution of the end-to-end vector $\mathbf{r}$ of polymer chains depends only on even powers of r, and the quartic term r^{2n} is the lowest level correction to the Gaussian behavior.

The probability of the four chains of the tetrahedron to meet at the central junction is the product of the probabilities given by Eqs. (1) and (2) for the respective chains. Thus

$$W(\mathbf{R}) = C \exp\left[-\gamma_1(\mathbf{R}_1 - \mathbf{R})^2 - \gamma_2(\mathbf{R}_2 - \mathbf{R})^2 - \gamma_3(\mathbf{R}_3 - \mathbf{R})^2 - \gamma_4(\mathbf{R}_4 - \mathbf{R})^2 - \sum_{i=1}^{\phi_S} \beta^n(\mathbf{R}_i - \mathbf{R})^{2n}\right] \quad (3)$$

where $\mathbf{R}$ is the position vector of the central junction and $\mathbf{R}_1$, $\mathbf{R}_2$, $\mathbf{R}_3$ and $\mathbf{R}_4$ are the position vectors of the vertices of the tetrahedron. The indices also serve as the labels for the four chains, the first ϕ_S of which are short. The normalization constant C in Eq. (3) is a product of constants C_1 and C_2 for long and short chains $C = C_1^{4-\phi_S} C_2^{\phi_S}$ where $4 - \phi_S$ and ϕ_S are the numbers of long and short chains in the tetrahedron. The free energy of the system is obtained as

$$\Delta A = -k_B T \ln W(\mathbf{R}) \quad (4)$$

Minimizing the free energy with respect to $\mathbf{R}$ we find that the mean position $\bar{\mathbf{R}}$ of the fluctuating junction satisfies the following equation

$$2\sum_{i=1}^{4} \gamma_i(\mathbf{R}_i - \bar{\mathbf{R}}_i) + 2n\sum_{i=1}^{\phi_S} \beta^n(\mathbf{R}_i - \bar{\mathbf{R}}_i)^{2n-1} = 0 \quad (5)$$

The distribution function $W(\mathbf{R})$ may be written in terms of the fluctuations $\Delta\mathbf{R}$ of $\mathbf{R}$ from the mean position

$$\mathbf{R} = \bar{\mathbf{R}} + \Delta\mathbf{R} \quad (6)$$

as

$$W(\mathbf{R}) = C \exp\left[-\sum_{i=1}^{4} \gamma_i(\bar{\mathbf{r}}_i - \Delta\mathbf{R})^2 - \sum_{i=1}^{\phi_S} \beta^n(\bar{\mathbf{r}}_i - \Delta\mathbf{R})^{2n}\right] \quad (7)$$

Here,

$$\bar{\mathbf{r}}_i = \mathbf{R}_i - \bar{\mathbf{R}} \tag{8}$$

is the mean end-to-end vector for the ith chain in the tetrahedron. From the assumption that the angles between mean chain vectors are tetrahedral, we have

$$\bar{\mathbf{r}}_i \cdot \bar{\mathbf{r}}_j = -\frac{1}{3}|\bar{\mathbf{r}}_i||\bar{\mathbf{r}}_j| \tag{9}$$

for any $1 \le i, j \le 4$, $i \ne j$.

The expression given by Eq. (7) may be rearranged as

$$W(\mathbf{R}) = C \exp\Bigg\{ -\sum_{i=1}^{4} \gamma_i \Big[\bar{r}_i^2 - 2\bar{\mathbf{r}}_i \cdot \Delta\mathbf{R} + (\Delta R)^2 \Big] - \sum_{i=1}^{\phi_S} \beta^n \sum_{k=1}^{n} \sum_{l}^{k} \binom{n}{k}\binom{k}{l} \bar{r}_i^{2l} (-2\bar{\mathbf{r}}_i \cdot \Delta\mathbf{R})^{k-l} (\Delta R)^{2n-2k} \Bigg\} \tag{10}$$

In order to simplify the derivations in the rest of the paper we take as a first approximation $n = 2$, which means that the non-Gaussian term has a quartic (r^4) form. Eq. (10) then simplifies to

$$W(\mathbf{R}) = C \exp\Bigg\{ -\sum_{i=1}^{4} \gamma_i \Big[\bar{r}_i^2 - 2\bar{\mathbf{r}}_i \cdot \Delta\mathbf{R} + (\Delta R)^2 \Big] - \sum_{i=1}^{\phi_S} \beta^2 \Big[\bar{r}_i^4 + 4(\bar{\mathbf{r}}_i \cdot \Delta\mathbf{R})^2 + (\Delta R)^4 - 4\bar{r}_i^2 (\bar{\mathbf{r}}_i \cdot \Delta\mathbf{R}) + 2\bar{r}_i^2 (\Delta R)^2 - 4(\bar{\mathbf{r}}_i \cdot \Delta\mathbf{R})(\Delta R)^2 \Big] \Bigg\} \tag{11}$$

Terms that do not depend on $\Delta\mathbf{R}$ in Eq. (11) may be incorporated into the new constant as

$$C' = C \exp\Bigg[-\sum_{i=1}^{4} \gamma_i \bar{r}_i^2 - \sum_{i=1}^{\phi_S} \beta^2 \bar{r}_i^4 \Bigg] \tag{12}$$

The minimization of the free energy gives

$$2\sum_{i=1}^{4} \gamma_i (\bar{\mathbf{r}}_i \cdot \Delta\mathbf{R}) + 4\sum_{i=1}^{\phi_S} \beta^2 \bar{r}_i^2 (\bar{\mathbf{r}}_i \cdot \Delta\mathbf{R}) = 0 \tag{13}$$

which leads to the following expression for the fluctuation distribution function

$$W(\Delta\mathbf{R}) = C' \exp\Bigg\{ -(\phi_S \gamma_S + \phi_L \gamma_L)(\Delta R)^2 - \sum_{i=1}^{\phi_S} \beta^2 \times \Big[4(\bar{\mathbf{r}}_i \cdot \Delta\mathbf{R})^2 + 2\bar{r}_i^2 (\Delta R)^2 - 4(\bar{\mathbf{r}}_i \cdot \Delta\mathbf{R})(\Delta R)^2 + (\Delta R)^4 \Big] \Bigg\} \tag{14}$$

The dot product between the mean vectors and the fluctuation vector may be written as

$$\bar{\mathbf{r}}_i \cdot \Delta\mathbf{R} = |\bar{\mathbf{r}}_i||\Delta\mathbf{R}| \cos\theta_{i\mathrm{R}} \tag{15}$$

where $\theta_{i\mathrm{R}}$ is the angle between the direction of the end-to-end vector for ith short chain and the fluctuation vector. We choose the coordinate system of the tetrahedron such that the mean end-to-end vector $\bar{\mathbf{r}}_1$ of the first short chain lies along the z-axis. Designating the polar angles of the four mean vectors by

$$\begin{aligned} &\theta_1 = 0 && \psi_1 = 0 \\ &\theta_2 = \arccos(-1/3) && \psi_2 = 0 \\ &\theta_3 = \arccos(-1/3) && \psi_3 = 2\pi/3 \\ &\theta_4 = \arccos(-1/3) && \psi_4 = 4\pi/3 \end{aligned} \tag{16}$$

and the polar angles of the vector $\Delta\mathbf{R}$ by θ_R by ψ_R, we can write the relations

$$\cos\theta_{1\mathrm{R}} = \cos\theta_\mathrm{R} \tag{17}$$

$$\cos\theta_{2\mathrm{R}} = -\frac{1}{3}\cos\theta_\mathrm{R} + \frac{\sqrt{8}}{3}\sin\theta_\mathrm{R}\cos\psi_\mathrm{R}$$

$$\cos\theta_{3\mathrm{R}} = -\frac{1}{3}\cos\theta_\mathrm{R} + \frac{\sqrt{8}}{3}\sin\theta_\mathrm{R}\cos(\psi_\mathrm{R} - 2\pi/3)$$

$$\cos\theta_{4\mathrm{R}} = -\frac{1}{3}\cos\theta_\mathrm{R} + \frac{\sqrt{8}}{3}\sin\theta_\mathrm{R}\cos(\psi_\mathrm{R} - 4\pi/3)$$

The distribution function for fluctuations $\Delta\mathbf{R}$ may be written as

$$W(\Delta\mathbf{R}) = C' \exp\Big\{ -(\phi_S \gamma_S + \phi_L \gamma_L)(\Delta R)^2 - \phi_S \beta^2 \Big[4\bar{r}_S^2 (\Delta R)^2 F(\phi_S; \theta_\mathrm{R}, \psi_\mathrm{R}) + 2\bar{r}_S^2 (\Delta R)^2 - 4\bar{r}_S (\Delta R)^3 G(\phi_S; \theta_\mathrm{R}, \psi_\mathrm{R}) + (\Delta R)^4 \Big] \Big\} \tag{18}$$

The functions $F(\phi_S; \theta_\mathrm{R}, \psi_\mathrm{R})$ and $G(\phi_S; \theta_\mathrm{R}, \psi_\mathrm{R})$ depend on the number of short chains in the tetrahedron and on the direction of the fluctuation vector $\Delta\mathbf{R}$. The four different types of tetrahedra will be denoted by S_1L_3, S_2L_2, S_3L_1 and S_4 where S_kL_m represents the tetrahedron with k short and m long chains. The functions F and G for different tetrahedra are given by Eqs. (A1)–(A4) in Appendix A.

Eq. (18) contains terms up to the quartic in $\Delta\mathbf{R}$. The cubic and quartic terms may be omitted if the fluctuations are small. With this approximation, it becomes possible to obtain relatively simple expressions for the mean square fluctuations of the central junction. The mean square fluctuation for the central junction is given by the formula

$$\langle(\Delta R)^2\rangle = \frac{\int W(\Delta\mathbf{R})(\Delta R)^2\,\mathrm{d}\Delta\mathbf{R}}{\int W(\Delta\mathbf{R})\mathrm{d}\Delta\mathbf{R}} = \frac{3}{2}\frac{\int_0^{2\pi}\mathrm{d}\psi_\mathrm{R}\int_0^{\pi}\mathrm{d}\theta_\mathrm{R}\sin\theta_\mathrm{R}\left\{\phi_\mathrm{S}\gamma_\mathrm{S}+\phi_\mathrm{L}\gamma_\mathrm{L}+2\beta^2\phi_\mathrm{S}\bar{r}_\mathrm{S}^2[1+2F(\phi_\mathrm{S};\theta_\mathrm{R},\psi_\mathrm{R})]\right\}^{-5/2}}{\int_0^{2\pi}\mathrm{d}\psi_\mathrm{R}\int_0^{\pi}\mathrm{d}\theta_\mathrm{R}\sin\theta_\mathrm{R}\left\{\phi_\mathrm{S}\gamma_\mathrm{S}+\phi_\mathrm{L}\gamma_\mathrm{L}+2\beta^2\phi_\mathrm{S}\bar{r}_\mathrm{S}^2[1+2F(\phi_\mathrm{S};\theta_\mathrm{R},\psi_\mathrm{R})]\right\}^{-3/2}} \tag{19}$$

In Eq. (19) the integration over the variable ΔR have been performed analytically, due to the approximation neglecting the higher (than the quadratic) powers of ΔR. The double integrals in Eq. (19) may be additionally simplified by pre-averaging over the angle ψ_R. With this approximation, the expression for the distribution of fluctuations takes the following form

$$W(\Delta R,\theta_\mathrm{R}) = C'\exp\Big\{-\Big[\phi_\mathrm{S}\gamma_\mathrm{S}+\phi_\mathrm{L}\gamma_\mathrm{L} + 2\beta^2\phi_\mathrm{S}\bar{r}_\mathrm{S}^2(1+2f(\phi_\mathrm{S};\theta_\mathrm{R}))\Big](\Delta R)^2\Big\} \tag{20}$$

where the new function $f(\phi_\mathrm{S};\theta_\mathrm{R})$ for various types of tetrahedra is given by Eqs. (A5)–(A8) in Appendix A.

With this approximation we obtain

$$W(\Delta R,\theta_\mathrm{R}) = C'\exp\Big\{-A[1+B(1+2f(\phi_\mathrm{S},\theta_\mathrm{R}))](\Delta R)^2\Big\} \tag{21}$$

and

$$\langle(\Delta R)^2\rangle = \frac{3}{2A}\frac{\int_0^{\pi}\mathrm{d}\theta_\mathrm{R}\sin\theta_\mathrm{R}[1+B(1+2f(\phi_\mathrm{S};\theta_\mathrm{R}))]^{-5/2}}{\int_0^{\pi}\mathrm{d}\theta_\mathrm{R}\sin\theta_\mathrm{R}[1+B(1+2f(\phi_\mathrm{S};\theta_\mathrm{R}))]^{-3/2}} \tag{22}$$

where

$$A = \phi_\mathrm{S}\gamma_\mathrm{S}+\phi_\mathrm{L}\gamma_\mathrm{L} \tag{23}$$

represents the Gaussian part of the exponent and the ratio of the non-Gaussian contribution to the Gaussian one is

$$B = 2\beta^2\phi_\mathrm{S}\bar{r}_\mathrm{S}^2/A \tag{24}$$

The integration in Eq. (22) may be performed easily to yield

For S_1L_3

$$\langle(\Delta R)^2\rangle_{\mathrm{S_1L_3}} = \Big\langle(\Delta R)_\mathrm{G}^2\Big\rangle_{\mathrm{S_1L_3}}\left[1-\frac{2B}{3(1+3B)}\right]\frac{1}{(1+B)} \tag{25}$$

For S_2L_2

$$\langle(\Delta R)^2\rangle_{\mathrm{S_2L_2}} = \Big\langle(\Delta R)_\mathrm{G}^2\Big\rangle_{\mathrm{S_2L_2}}\left[1-\frac{2B/3}{3(1+19B/9)}\right]\times\frac{1}{(1+13B/9)} \tag{26}$$

For S_3L_1

$$\langle(\Delta R)^2\rangle_{\mathrm{S_3L_1}} = \Big\langle(\Delta R)_\mathrm{G}^2\Big\rangle_{\mathrm{S_3L_1}}\left[1-\frac{2B/27}{3(1+49B/27)}\right]\times\frac{1}{(1+49B/27)} \tag{27}$$

For S_4

$$\langle(\Delta R)^2\rangle_{\mathrm{S_4}} = \Big\langle(\Delta R)_\mathrm{G}^2\Big\rangle_{\mathrm{S_4}}\frac{1}{(1+5B/3)} \tag{28}$$

One should note that the coefficient B depends on the number of short chains in the tetrahedron. Here, $\langle(\Delta R)_\mathrm{G}^2\rangle$ represents fluctuations of junctions in the tetrahedron built up from Gaussian chains, namely

$$\Big\langle(\Delta R)_\mathrm{G}^2\Big\rangle_{\mathrm{S_1L_3}} = \frac{\langle r_\mathrm{S}^2\rangle_0}{1+3\xi} \tag{29}$$

$$\Big\langle(\Delta R)_\mathrm{G}^2\Big\rangle_{\mathrm{S_2L_2}} = \frac{\langle r_\mathrm{S}^2\rangle_0}{2+2\xi} \tag{30}$$

$$\Big\langle(\Delta R)_\mathrm{G}^2\Big\rangle_{\mathrm{S_3L_1}} = \frac{\langle r_\mathrm{S}^2\rangle_0}{3+\xi} \tag{31}$$

$$\Big\langle(\Delta R)_\mathrm{G}^2\Big\rangle_{\mathrm{S_4}} = \langle r_\mathrm{S}^2\rangle_0/4 \tag{32}$$

where ξ is the ratio of the mean square lengths of the short chains to long chains ($0<\xi<1$)

$$\xi = \langle r^2\rangle_\mathrm{S}/\langle r^2\rangle_\mathrm{L} \tag{33}$$

Fig. 2 shows the plots of the ratio $\langle(\Delta R)^2\rangle/\langle(\Delta R)_\mathrm{G}^2\rangle$ for various types of tetrahedra as the function of ξ for two values of the parameter B ($B=0.2$ and $B=1.0$). The

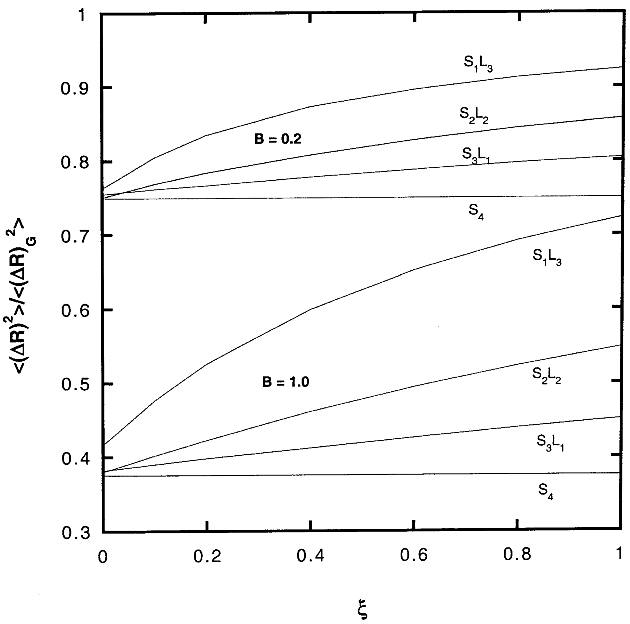

Fig. 2. The plot of the ratio of fluctuations of the junction for the non-Gaussian chains to the Gaussian ones $\langle(\Delta R)^2\rangle/\langle(\Delta R)^2_{\mathrm{G}}\rangle$ as the function of the ratio ξ of mean square length of short chains to long chains for two values of the parameter B ($B = 0.2$ and $B = 1.0$) and for various types of tetrahedra S_kL_m (containing k short and m long chains).

results show that for larger B the ratio $\langle(\Delta R)^2\rangle/\langle(\Delta R)^2_{\mathrm{G}}\rangle$ decreases and non-Gaussian effects play significant role. Also the increase of the number of short chains decrease the ratio $\langle(\Delta R)^2\rangle/\langle(\Delta R)^2_{\mathrm{G}}\rangle$. Additionally, the shorter are the short chains in respect to the long ones (i.e. for small ξ) the smaller is the ratio of fluctuations $\langle(\Delta R)^2\rangle/\langle(\Delta R)^2_{\mathrm{G}}\rangle$. The results presented here show that the non-Gaussian behavior of short chains play an important role for the elastomeric properties of bimodal networks by restricting fluctuations of the central junction. The strength of these restrictions directs attention to the importance of anharmonic modes in such networks. By analyzing experimental data on siloxane oligomers, Sharaf and Mark [21] came to conclusion in that larger than expected elongation moduli of these networks can be explained by assumption that segments between cross-links act as short chains. The application of the Fixman–Alben non-Gaussian distribution to these short chains led to a good reproduction of experimental stress–strain behavior. The theoretical predictions of our model support these conclusions and provide useful tool for the detailed analysis of these effects in the future.

The big advantage of the proposed model is that all these effects could be expressed in relatively simple analytical from. The main simplification of the model is the assumption that the ends of the four chains located at the vertices of the tetrahedron do not fluctuate. This restriction can be removed in the future for the more realistic models of elastomeric networks.

Appendix A

The expressions for functions G and F in Eq. (18) for various types of bimodal networks are shown later. Here, S_kL_m denotes the tetrahedron composed of k short (non-Gaussian) and m long (Gaussian) chains.

For S_1L_3

$$F(1,\theta_R,\psi_R) = \cos^2\theta_R, \qquad G(1,\theta_R,\psi_R) = \cos\theta_R \tag{A1}$$

For S_2L_2

$$F(2,\theta_R,\psi_R) = (1/2)\left[\frac{10}{9}\cos^2\theta_R + \frac{8}{9}\sin^2\theta_R\cos^2\psi_R - \frac{4\sqrt{2}}{9}\sin\theta_R\cos\theta_R\cos\psi_R\right],$$

$$G(2,\theta_R,\psi_R) = (1/2)\left[\frac{2}{3}\cos\theta_R + \frac{2\sqrt{2}}{3}\sin\theta_R\cos\psi_R\right] \tag{A2}$$

For S_3L_1

$$\begin{aligned} F(3,\theta_R,\psi_R) = (1/3)\Bigg\{&\frac{11}{9}\cos^2\theta_R + \frac{8}{9}\sin^2\theta_R \times\left[\cos^2\psi_R + \cos^2\left(\psi_R - \frac{2\pi}{3}\right)\right] \\ &- \frac{4\sqrt{2}}{9}\sin\theta_R\cos\theta_R \times\left[\cos\psi_R + \cos\left(\psi_R - \frac{2\pi}{3}\right)\right]\Bigg\}, \end{aligned} \tag{A3}$$

$$G(3,\theta_R,\psi_R) = (1/3)\left\{\frac{1}{3}\cos\theta_R + \frac{2\sqrt{2}}{3}\sin\theta_R \times\left[\cos\psi_R + \cos\left(\psi_R - \frac{2\pi}{3}\right)\right]\right\}$$

For S_4

$$F(4,\theta_R,\psi_R) = (1/4)\left[\frac{4}{3}\cos^2\theta_R + \frac{8}{3}\sin^2\theta_R\cos^2\psi_R\right],$$

$$G(4,\theta_R,\psi_R) = 0 \tag{A4}$$

By pre-averaging Eq. (19) over the angle ψ_R, the distribution of fluctuations is given by Eq. (20) with a new function $f(\phi_S;\theta_R)$ given by the following expressions:

For S_1L_3

$$f(1,\theta_R) = \cos^2\theta_R \tag{A5}$$

For S_2L_2

$$f(2,\theta_R) = (1/2)\left[\frac{2}{3}\cos^2\theta_R + \frac{4}{9}\right] \tag{A6}$$

For S_3L_1

$$f(3, \theta_R) = (1/9)\left(\cos^2 \theta_R + \frac{8}{3}\right) \tag{A7}$$

For S_4

$$f(4, \theta_R) = 1/3 \tag{A8}$$

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