Polymer Bulletin 60, 425–430 (2008)
DOI 10.1007/s00289-007-0860-z

Polymer Bulletin

Non-Gaussian Model for Rubber Elasticity: (I) Finite Chain Extensibility and Tube Concept

Yoshio Hoei (✉)

S&S Japan Company Ltd., 6-1-18, Hamazoe-dori, Nagata-ku, Kobe, Hyogo 653-0024, Japan

Received: 4 October 2007 / Accepted: 27 October 2007
Published online: 9 November 2007 –

Summary

A simple, useful model for an elastic network is developed in terms of finite chain extensibility and entanglement constraints. For the former, each chain that constitutes the network is treated as a specific non-Gaussian one and for the latter is confined within a tube that represents entanglement constraints. The model is built within the framework of the classical phantom network theory. In addition, it considers fluctuations of diameter of the tube. While the extent of suppression of junction fluctuation is also incorporated through the well-known empirical factor h, the tube diameter is assumed to be deformed under a power law including its exponent (γ) that describes the strain-dependence of spatial constraints. Two free energies due to deformations of the network and tube diameter are calculated.

Introduction

There is still a need for the molecular theory of rubber elasticity to explain mechanical behaviors of rubbers under stress over the entire deformation range. In this regard, the aim of this study is to develop a simple such model for uncrystallizable elastomers. This work considers at least that the network is composed of non-Gaussian chains with the effect of "finite extensibility", while they thermally fluctuate together with its chemical junctions under the topological constraints imposed on them. Accordingly, if an ordinary concept of "tube" that represents the effects of interchain entanglements is taken into account, the tube should then fluctuate as well. In this work, we incorporate a certain non-Gaussian statistics for a flexible chain with limited extensibility. Along with this incorporation, we consider trapped entanglement (tube) fluctuations in a simple way as well as (chemical) junction fluctuations.

Theory

Elastic Free Energy

Teramoto [1] has considered that a single polymer chain's segments can not be located outside the largest elliptic space that the contour chain length forms when its chain ends are fixed at the foci of the ellipsoid. He further assumed that N segments of the single chain behave like N perfect gas particles which are confined to the elliptic space. On this assumption, a chain distribution function ${}^{T}p_N(r)$ was derived for the probability

to become zero on the equality of the end-to-end distance r with that for the extended state Nb' (where b' is the statistical segment length). It was originally given in terms of normalized end-to-end distance r/Nb' as r/Nb' as ${}^{T}p_N(r) \sim [1-(r/Nb')^2]^N$. We here convert the segment size b' to $b'=b\sqrt{(2/3)}$ for reasons mentioned below. That is, the Teramoto function can be modified in the form:

$$p_N(r) \sim [1-(3/2)(r/Nb)^2]^N \quad (\mathbf{1})$$

This equation is found to be closely related to the Gaussian statistics as follows: if $r/Nb \ll 1$, eq.1 can turn into the Gaussian distribution by use of the relation $(1-x)^N \cong \exp(-xN)$:

$$p_N(r) \sim \exp[-(2/3)r^2/(Nb^2)] \quad (\mathbf{2})$$

Also, from eq. 1, the mean end-to-end distance of the single chain [1] is given by

$$R_T^2=(2/3)[B(N+1,5/2)/B(N+1,3/2)](Nb)^2 \quad (\mathbf{3})$$

Here the function B is a Beta function. If $r/Nb \ll 1$, eq. 3 reduces to the Gaussian expression

$$R_T^2 \cong Nb^2 = R_G^2 \quad (\mathbf{4})$$

Next, we first give an elastic free energy of a single chain to proceed to calculations for polymer network. If a polymer network consists of ν chains and they have an end-to-end distance $\langle r^2 \rangle$ averaged over the ν chains, the mean elastic free energy of a single chain is easily given, from eq.1 and the Boltzmann equation $S \sim k \ln p_N(r)$, by

$$F_{EL,single}/kT \sim -N\ln[1-(3/2)(1/N)(\langle r^2\rangle/\langle r^2\rangle_0)] \quad (\mathbf{5})$$

where k is the Boltzmann constant and T is the absolute temperature. Since the mean-squared dimensions may be equivalent to be Gaussian in the natural state; i.e., $\langle r^2 \rangle = \langle r^2 \rangle_0 \equiv R_G^2$, the elastic free energy change of the network of ν chains relative to the undeformed state is written

$$\Delta F_{EL,net}/kT=-\nu N_c \ln\{[1-(3/2)(1/N_c)(\langle r^2\rangle/\langle r^2\rangle_0)]/[1-(3/2)(1/N_c)]\} \quad (\mathbf{6})$$

Here N_c is the number of segments of the length b per chain. Now, if this network is assumed to be a perfect one on the phantom network basis [2−4], the $\langle r^2 \rangle/\langle r^2 \rangle_0$ term in eq. 6 can be calculated by going through a very simplified procedure [3]. The phantom theory rests on the premise that only fixed junctions on the surface of the network system can respond to macroscopic deformation but the other majority freely fluctuate over time, so that one can proceed without considering the former. The mean squared chain dimensions before and after macroscopic deformation are then given by

$$\langle r^2\rangle_0=\langle \bar{r}^2\rangle_0+\langle(\Delta r)^2\rangle_0 \quad (\mathbf{7})$$

and

$$\langle r^2\rangle=\langle \bar{r}^2\rangle+\langle(\Delta r)^2\rangle, \quad (\mathbf{8})$$

respectively, where $\bar{r}$ and Δr represent the mean positions of all the fluctuating chains and fluctuations from the mean, respectively. It is assumed that there is no correlation between the mean position and the fluctuation and also the fluctuation statistics is Gaussian. Next, we consider a prismatic test sample subjected to the macroscopic deformation given by the principal extension ratios λ_i (i=1, 2, 3). According to the

phantom network theory [2], the components of the mean positions are deformed affinely with the macroscopic deformation and those of the fluctuations to be unchanged. This gives the following respective relations

$$<\bar{r}_i^2>=\lambda_i{}^2<\bar{r}_i^2>_0 \quad (i=1, 2, 3) \tag{9}$$

and

$$<(\Delta r_i)^2>=<(\Delta r_i)^2>_0 \tag{10}$$

Equations 9 can be expressed by the decomposed form $<r^2> = \sum(<\bar{r}_i^2>+<(\Delta r_i)^2>)$ on the r-component basis. Thus, from eqs. 9 and 10 and by using the condition of isotropy in the natural state $<\bar{r}_i^2>_0=<\bar{r}^2>_0/3$, eq. 8 becomes

$$<r^2>=(<\bar{r}^2>_0/3)\sum_i \lambda_i^2 +<(\Delta r)^2>_0 \tag{11}$$

Now, the earlier mentioned network characteristics ν, μ and f relevant to structural elements of the perfect network topology have the following specific relations [2, 4]

$$\xi = \nu - \mu \quad \text{and} \quad \mu = 2\nu / f \tag{12}$$

where ξ is the so-called "cycle rank", defined as the number of chains that need to be cut to reduce the network topology to a tree-like one with no rings. With these relations, the two quantities $<\bar{r}^2>_0$ and $<(\Delta r)^2>_0$ in eq. 11 can also be given by the following well-proven relations [3]

$$<\overline{r^2}>_0=(\xi/\nu)<r^2>_0 \quad \text{and} \quad <(\Delta r)^2>_0=(\mu/\nu)<r^2>_0, \tag{13}$$

respectively. Therefore, substituting these expressions into eq. 11 leads to the following relation [3] that bridges the deformation of chains with the macroscopic deformation, including the structural characteristics

$$<r^2>/<r^2>_0 = [(\xi/\nu)(1/3)\sum_{i=1,2,3}\lambda_i^2 + (\mu/\nu)] \tag{14}$$

At this point, the completely freely fluctuating system is modified to a practical system that can depend on the degree of thermal fluctuation of crosslinks: this can be simply done by replacing eq. 14 with $\nu - h\mu$ where h is an empirical parameter between zero (complete suppression) and unity (no suppression), as defined previously by Dossin and Grassley [5].Hence, in consideration of the factor h, substitution of eq. 14 into eq. 6 gives the following elastic free energy expression:

$$\Delta F_{EL,net}/kT=-\nu N_c \ln\left\{\frac{1-(3/2)(1/N_c)[(1-h\,\mu/\nu)(1/3)\sum_i \lambda_i^2 + (h\,\mu/\nu)]}{1-(3/2)(1/N_c)}\right\} \tag{15}$$

Equation 15 is found to be reasonable: if expanding its log term with respect to $1/N_c$ on the assumption that N_c is very large and taking only the first term, then eq. 15 reduces to $(1/2)(\nu - h\mu)(\sum\lambda_i^2 - 3)$ Obviously, if h = 1, this equation agrees with the

free energy expression of the classical phantom network model and if h=0, it agrees with that of the classical affine network model.

Confinement Free Energy

The present network system is comprised of non-Gaussian chains that fluctuate depending on the magnitude of the suppression parameter h. Now, since each network chain is confined within its tube that constrains segmental thermal motion [6,7], it must be reasonable to consider more generally that the tube dimensions also fluctuate in the network. We here incorporate also the fluctuations of the tube into the network system as follows: we first recall a confinement free energy expression [8] for a segment confined within a single tube of the diameter D

$$f_{conf,\ single}/kT \cong (\ b\ /D)^{\ 2}, \tag{16}$$

which has been derived from a scaling analysis [9] for a tube containing a Gaussian chain. In the present case, the use of this relation should be allowed since the Teramoto chain is also assumed to be basically gaseous as well as the Gaussian chain. The increment of a confinement free energy of the network of ν chains relative to the undeformed state may then be given by

$$\begin{aligned} \Delta F_{CONF,net}/kT &= -b^{\ 2} N_c \sum_{\nu} (D^{-2} - D_0^{-2}) \\ &= -\nu\ N_c <(b/D)^2>_0 (<D^{-2}>/<D^{-2}>_0 - 1) \end{aligned} \tag{17}$$

Here $<D^{-2}> = \sum_\nu D^{\ -\ 2}/\nu$, $<D^{-2}>_0 = \sum_\nu D_0^{\ -\ 2}/\nu$ and $<(b/D)^2>_0 \equiv b^2/<D_0^2>$. Concerning deformation properties of the mean tube diameter, we assume two approximations of the averaged quantities $<D^{-2}>$ and $<D^{-2}>_0$ to be $<D^2>^{-1}$ and $<D^2>_0^{\ -1}$, respectively. To get the ratio $<D^2>_0/<D^2>$ in terms of the macroscopic deformation, we can then take a similar calculation procedure in calculating the $<r^2>/<r^2>_0$ term, as in the earlier section. That is, a tube containing a network chain in the natural (isotropic) state can be regarded as randomly linked by the central axes of N_c/N_e short tubes of equivalent length D_0 (where N_e is the number of segments between neighboring entanglements) [7]. If considering an analogy with the treatment in the above section, the mean squared tube diameters before and after undergoing macroscopic deformation may then be given as $<D^2>_0 = <\overline{D}^2>_0 + <(\Delta D)^2>_0$ and $<D^2> = <\overline{D}^2> + <(\Delta D)^2>$ ($<(\Delta D)^2>_0 = <(\Delta D)^2>$), respectively. Here, $\overline{D}$ and ΔD represent the mean diameters of all the short tubes and fluctuations from the mean, respectively. It is also assumed that there is no correlation between the mean and the fluctuation and also the fluctuation statistics conforms to the Gaussian.

These considerations can lead to useful relations corresponding to eq. 13: first, if letting the central axes of the short tubes (containing a network chain) correspond to a vector $\boldsymbol{D}_{0\alpha}$ ($= \overline{\boldsymbol{D}}_{0\alpha} + \Delta\boldsymbol{D}_{0\alpha}$), we can have the relation $\boldsymbol{r}_o = \sum \boldsymbol{D}_{0\alpha}$ so that $<r^2>_0 = <(\boldsymbol{r}_0 \cdot \boldsymbol{r}_0)> = \sum_\alpha \sum_\beta <(\boldsymbol{D}_{0\alpha} \cdot \boldsymbol{D}_{0\beta})>$ where α and β take between unity and N_c/N_e. It should also be noted that $|\boldsymbol{D}_{0\alpha}| = D_0$ and $|\Delta\boldsymbol{D}_{0\alpha}| = \Delta D_0$. Since $\boldsymbol{r}_0 = \overline{\boldsymbol{r}}_0 + \Delta\boldsymbol{r}_0$, we further have two relations immediately

$$<\overline{r}^{\ 2}>_0 = \sum_\alpha \sum_\beta <(\overline{\boldsymbol{D}}_{0\alpha} \cdot \overline{\boldsymbol{D}}_{0\beta})> \quad \text{and} \quad <(\Delta r)^2>_0 = \sum_\alpha \sum_\beta <(\Delta\boldsymbol{D}_{0\alpha} \cdot \Delta\boldsymbol{D}_{0\beta})>).$$

Therefore, substituting the above two equations into eq. 13 can lead to

$$<\overline{D}^{\ 2}>_0 = (\xi\ /\nu\ ) <D^{\ 2}>_0 \quad \text{and} \quad <(\Delta D)^{\ 2}>_0 = (\mu/\nu) <D^{\ 2}>_0 \tag{18}$$

We next incorporate another essential assumption that the principal components of $\bar{\boldsymbol{D}}_0$ may deform in a power law, as was hypothesized by Gaylord [8] and Heinrich et al.[6]

$$<\bar{D}_i^{\,2}> = \lambda_i^{\,2\gamma} <\bar{D}_i^{\,2}>_0 \qquad (i=1,2,3) \tag{19}$$

Here, γ is the exponent. The character of this exponent will become clear later in comparing with the Gaylord case [8]. Using eq. 18 and the isotropic condition $<\bar{D}_i^{\,2}>_0 = <\bar{D}^2>_0/3$, we may have the following equation redefining the cycle rank as $\nu - h\mu$

$$<D^2>^{-1} / <D^2>_0^{-1} = [(1 - h\mu/\nu)(1/3) \sum_i \lambda_i^{2\gamma} \; + \; h\mu/\nu \,]^{-1} \tag{20}$$

Hence, substitution of eq. 20 into eq. 17 gives the following free energy change with deformation of the mean tube diameter:

$$F_{CONF,net}/kT = -\nu N_c <(b/D)^2>_0 \left[\frac{1}{(1-h\mu/\nu)(1/3)(\sum_i \lambda_i^{2\gamma} - 3) + 1} - 1 \right] \tag{21}$$

Next , if assuming the $(1 - h\mu/\nu)(1/3)(\sum \lambda_i^{\,2\gamma} - 3)$ term in the dominator of eq. 21 not to be large, it becomes the following approximation

$$\Delta F_{CONF,net}/kT \approx (\nu - h\mu) N_c <(b/D)^2>_0 \, (1/3) \, (\sum_i \lambda^{2\gamma} - 3) \tag{22}$$

This equation will be found to be sufficiently workable in analyzing experimental stress-strain data, as will be seen in the paper (II) [10]. Also, eq. 22 is similar to the corresponding expression of the Gaylord model [8]. However, it should be noted that the sign of the exponent is opposite (negative) unlike the Gaylord case. From eq. 19, the parameter γ is described as follows: if $\gamma = 0$, the tube state remains unchanged in responding to macroscopic deformation, if $0 < \gamma < 1$, the tube state changes in a scaled affine way, and if $\gamma = 1$ the tube state changes completely affinely. Also, if γ takes a value within the range of $0 < \gamma \leqslant 1$, the segmental fluctuations in a deformation direction would increase or decrease depending on a deformation mode. Particularly, Heinrich et al. [6] and Rubinstein et.al.[11] have stressed that the γ should be taken as $\gamma = 1/2$ in their sophisticated tube models. What to remark finally is that, in the limit of $h = 0$ (or $f = \infty$), eq. 22 turns to an equation of scaled affine-tube-deformation without tube fluctuation (i.e., $<(\Delta D)^2> = 0$).

Total Network Free Energy

We have had two equations of free energy changes, eqs. 17 and 22, for finitely extensible network deformation and for a tube deformation, respectively. Hence, the total network free energy change per unit volume is given on the molar basis by:

$$\begin{aligned} \Delta\tilde{F}_{EL,total} / RT &= (\Delta\tilde{F}_{EL,net} + \Delta\tilde{F}_{CONF,net}) / RT \\ &= -\tilde{\nu} N_c \, \ln \left\{ \frac{1 - (3/2)(1/N_c)[(1 - h\tilde{\mu}/\tilde{\nu})(1/3)\sum_i \lambda_i^2 + (h\tilde{\mu}/\tilde{\nu})]}{1 - (3/2)(1/N_c)} \right\} \\ &\quad + (\tilde{\nu} - h\tilde{\mu}) N_c \langle (b/D)^2 \rangle_0 (1/3) \, (\sum_i \lambda^{2\gamma} - 3) \end{aligned} \tag{23}$$

where R is the gas constant and the wavy lines denote quantities divided by the volume of the system. The present model has particularly two advantageous points: one is that it is applicable to polymer networks that show affine, phantom, or the intermediate behavior via the suppression factor h and another is that it will be applicable to both entanglement- and chemical cross-link-dominated networks.

References

1. Teramoto E (1954) Busseiron Kenkyu 76:40
2. James H M, Guth E (1947) J Chem Phys 15:651; (1947) J Chem Phys 15: 669
3. Mark J E, Erman B (1988) Rubberlike Elasticity Molecular Primer, John Wiley, New York
4. Flory P J (1976) Proc R Soc London Ser A 351:351
5. Dossin L M, Graessley W W (1979) Macromolecules 12:123
6. Kaliske M, Heinrich G (1999) Rubber Chem Technol 72:602 ; Heinrich G, Straube E (1983) Acta Polym 34:589
7. Edwards S F (1976) Proc Phys Soc 92:9; Doi M, Edwards S F (1986) The Theory of Polymer Dynamics, Clarendon, Oxford; Doi M (1996) Introduction to Polymer Physics, Clarendon, Oxford
8. Gaylord R J (1979) Polym Eng Sci 19:263; (1982) Polym Bulletin 8:325; Gaylord R J (1983) Polym Bulletin 9:181
9. de Gennes P G (1979) Scaling Concept in Polymer Physics, Cornell, Ithaca, NY
10. Hoei Y (2007) Polym Bulletin, submitted
11. Rubinstein M, Panyukov S (1997) Macromolecules 30:8036; Rubinstein M, Colby R H (2003) Polymer Physics, Oxford