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An expansion approach in rubber elasticity

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Abstract

We introduce an expansion approach to obtain the elastic free energy density in rubber elasticity. This new approach presents fast convergence for whole range of deformation. We apply this method to the freely jointed model and get an analytical form for the free elastic energy density in terms of the strain invariants. We use this expression to fit experimental data for PMDS network.

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1. Introduction

The most important physical characteristic of the rubber is the high degree of deformability from the action of stress. The typical behavior of the stress–strain curve presents a non-linear relation, in which Hooke's law is applied only in region of small deformation. This aspect can be explained using the classical rubber elasticity theory [1–3] based on the entropic distribution of two connected crosslinks. In this framework, the elastic resorting force of the polymer network results from the entropy change in a set of independent chains. The free energy per strand is $F_s(\mathbf{R}) = -k_B T \ln P(\mathbf{R})$, where $P(\mathbf{R})$ is the end-to-end probability distribution, k_B is the Boltzmann constant and T is the temperature. In this case, when the end-to-end distance of a polymeric chain is lengthened, its configurational freedom is lowered, the entropy decreases and the free energy increases.

In this context, the network elastic free energy density to deformed body is obtained by averaging the free energy per strand over their initial distribution (quenched average) and multiplying by the total number of network strand per unit of volume, n_s,

$$F = n_s \langle F_s(\mathbf{R}) \rangle_0 = n_s \int F_s(\mathbf{R}) P(\mathbf{R}_0) \mathrm{d}^3\mathbf{R}_0. \tag{1.1}$$

Here we consider the assumptions of perfect rubber elasticity, i.e., the assumptions of incompressibility in bulk, isotropy in the undeformed state, and reversible stress–strain relations. When we consider some kinds of materials, like c^* gels [4], where the multi-chain effects such as screening or entanglements may not come into play, the application of the classical rubber theory seems to be justified. On the other hand, when compared with a more complete scenario, where only tube models taking entanglement and finite extensibility contributions into account are able to describe the stress–strain behavior with physically reasonable parameters [5], the approach based on Eq. (1.1) does not lead to a general treatment but it may be useful as a source of motivation for some advances. In this case, constraints like entanglement or junction fluctuations, which are essential for a good agreement with experimental data, may be incorporated by the addition of phenomenological terms such as the Mooney–Rivlin one [1].

For non-trivial distribution the above average can be cumbersome. For example, by considering a chain composed by N freely jointed monomers of length b, with all directions having the same probability, $P(\mathbf{R})$ is given by [6]

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$$P(\mathbf{R}) = \frac{1}{(2\pi)^3}\int \mathrm{e}^{i\,\mathbf{k}\cdot\mathbf{R}}\left[\frac{\sin(kb)}{kb}\right]^N \mathrm{d}^3\overrightarrow{k}, \tag{1.2}$$

which depends only on the modulus of the end-to-end vector $\mathbf{R}$ and can be obtained in a close form only in terms of a series. The simplest approximation for this freely jointed model is given by the Gaussian end-to-end approximation,

$$P(\mathbf{R}) = \left(\frac{3}{2\pi \mathbf{L}b}\right)^{3/2}\exp\left[-\frac{3}{2}\frac{\mathbf{R}^2}{\mathbf{L}b}\right], \tag{1.3}$$

where $\mathbf{L} = Nb$ is the chain arc length. However, it is well known that Gaussian approximation is valid only for N sufficiently large and end-to-end distances R small compared to the maximum chain length Nb. Natural rubber values of N (for the chains in a normal cross-linked network) are likely to lie in the range 50–100 and the use of the Gaussian approximation may not be sufficiently exact. Another weakness of the Gaussian distribution is that it predicts zero probability only in the limit $R \to \infty$, which is directly related to Hooke's law for unlimited deformation.

Unfortunately the attempt to replace the Gaussian statistical theory by a more exact treatment involves a considerable sacrifice of both simplicity and generality. For instance, an explicit way to take the finite length effect into account is given by the inverse Langevin approximation [7]

$$P_{\mathrm{L}}(\mathbf{R}) \propto \exp\left[-N\int_0^{R/Nb} L(x)\mathrm{d}x\right], \tag{1.4}$$

where $L(x)$ is the inverse Langevin function. However, in this case and for other more realistic distribution, the quenched average, Eq. (1.1), becomes very difficult to be performed in an exact way. The usual approach employed is to expand $F_{\mathrm{s}}(\mathbf{R})$ in a Taylor series for $R/(Nb) < 1$ and to perform the average term-by-term [8,9]. One inconvenience of the series expansion for $R/(Nb) < 1$ is that it does not present good accuracy for large deformation (slowly convergence for $R/(Nb) > 1/2$), so that in this case, it is necessary to take a high number of terms into account with increasing complexity [1]. This difficulty principally arises by the necessity of calculation of $\langle R_i R_j \ldots R_m\rangle$, which is a hard task depending on the form of the distribution, what in general is possible only by numerical calculation.

In order to circumvent this difficulty, in the next section, we consider an expansion approach which avoids the previous problem. In this context, the main advances of our approach are: (i) a mathematically convenient way to solve the junction affine model of rubber elasticity for arbitrary chain end-to-end distance distributions, (ii) relevant expressions for the elastic free energy in invariant form, and (iii) fast convergence expression for the whole range of deformation when compared with the usual Taylor expansion. In Section 3, we apply the approach developed in Section 2 to obtain the analytical free energy density for the freely jointed model. In the last section, we present our conclusions and final remarks.

2. Expansion approach

Firstly note that considering the affine deformation $\mathbf{R} = \boldsymbol{\lambda}\mathbf{R}_0$, with the strain matrix $\boldsymbol{\lambda}$ being written in terms of the principal axis, $\boldsymbol{\lambda} = \mathrm{Diag}(\lambda_1, \lambda_2, \lambda_3)$, we can write, in spherical coordinates,

$$\mathbf{R}^2 = \lambda^2(\theta,\varphi)R_0^2, \tag{2.1}$$

where

$$\lambda^2(\theta,\varphi) = \lambda_1^2\cos^2(\varphi)\sin^2(\theta) + \lambda_2^2\sin^2(\theta)\sin^2(\varphi) + \lambda_3^2\cos^2(\theta). \tag{2.2}$$

In this way, considering that F_{s} depends on the modulus of the end-to-end vector $\mathbf{R}$, the elastic free energy density Eq. (1.1) becomes

$$F = n_{\mathrm{s}}\int F_{\mathrm{s}}\left(\lambda^2, R_0^2\right)P\left(R^0\right)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi\,R_0^2\,\mathrm{d}R_0. \tag{2.3}$$

Now, for this F, we can make a series expansion around $\langle\lambda^2\rangle$ and $\langle R_0^2\rangle$ leading to

$$F = n_{\mathrm{s}}\sum_{i,j=1}^{\infty} C_{ij}\left\langle\left(\lambda^2 - \langle\lambda^2\rangle\right)^i\right\rangle\left\langle\left(R_0^2 - \langle R_0^2\rangle\right)^j\right\rangle, \tag{2.4}$$

with the coefficients C_{ij} given by

$$C_{ij} = \frac{1}{i!j!}\frac{\partial}{\partial\left(\lambda^2\right)^i}\frac{\partial}{\partial\left(R_0^2\right)^j}F_{\mathrm{s}}(\lambda^2, R_0^2)\Big|_{\lambda^2=\langle\lambda^2\rangle, R_0^2=\langle R_0^2\rangle}, \tag{2.5}$$

and the mean values given by

$$\left\langle\left(\lambda^2 - \langle\lambda^2\rangle\right)^i\right\rangle = \int_0^{2\pi}\int_0^{\pi}\left(\lambda^2 - \langle\lambda^2\rangle\right)^i\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi \tag{2.6}$$

and

$$\left\langle\left(R_0^2 - \langle R_0^2\rangle\right)^j\right\rangle = \int_0^{Nb}\left(R_0^2 - \langle R_0^2\rangle\right)^j P(R_0)R_0^2\mathrm{d}\,R_0. \tag{2.7}$$

By construction, the mean values $\langle(R_0^2 - \langle R_0^2\rangle)\rangle$ and $\langle(\lambda^2 - \langle\lambda^2\rangle)\rangle$ vanish. Note that the angular integration can be performed independently of the distribution leading, for example, to

$$\begin{aligned}
\left\langle\left(\lambda^2 - \langle\lambda^2\rangle\right)^2\right\rangle &= \frac{4}{45}\left(I_1^2 - 3I_2\right)\\
\left\langle\left(\lambda^2 - \langle\lambda^2\rangle\right)^3\right\rangle &= \frac{8}{945}\left(2I_1^3 - 9I_1I_2 + 27I_3\right)\\
\left\langle\left(\lambda^2 - \langle\lambda^2\rangle\right)^4\right\rangle &= \frac{16}{945}\left(I_1^2 - 3I_2\right)^2,
\end{aligned} \tag{2.8}$$

with I_1, I_2 and I_3 being the three strain invariants, $I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$, $I_2 = (\lambda_1\lambda_2)^2 + (\lambda_2\lambda_3)^2 + (\lambda_3\lambda_1)^2$ and $I_3 = (\lambda_1\lambda_2\lambda_3)^2$. On the other hand, the coefficients C_{ij} and the radial integration depend on the form of the end-to-end distribution. For homogeneous networks' approximation, where every

network chain has the same initial end-to-end distance, $\sqrt{N}b$, the above expansion reduces to the Puso approach [10].

As pointed in Section 1, to incorporate finite length effects, the Taylor series for $R/(Nb) < 1$, which presents slow convergence for $R/(Nb) > 1/2$, is usually employed [8,9]. On the other hand, our approach circumvents this difficulty by introducing an expansion which presents fast convergence for the whole range of deformation. Moreover, we observe that in the non-Gaussian region, the treatment in a rigorous manner presents enormous mathematical difficulties. These difficulties can be reduced by the introduction of assumptions which are not strictly valid such as the affine approximation.

3. Application

Let us now show that the above approach leads to rapidly convergent series, so that we can consider only few terms for the integer range of deformation. To do this, let us take a generalization of the Fixman and Alben distribution introduced by Erman and Mark [11],

$$P(\mathbf{R}) = P_0 \exp\left[-\frac{3\mathbf{R}^2}{2Nb^2} - c\left(\mathbf{R}^2\right)^{\xi}\right], \tag{3.1}$$

where P_0 is a normalization constant, c and ξ are adjustable parameters. We chose this distribution because of its simplicity and the facility of getting the exact numerical results. For this end-to-end distribution, the elastic free energy per strand to deformed body, in spherical coordinates, becomes

$$F_s\left(\lambda^2, R_0^2\right) = -k_B T\left(\frac{3\lambda^2 R_0^2}{2Nb^2} + c\left(\lambda^2 R_0^2\right)^{\xi}\right). \tag{3.2}$$

We omitted a constant that arises from the normalization term in Eq. (3.1). Fig. 1 shows the results of applying our expansion

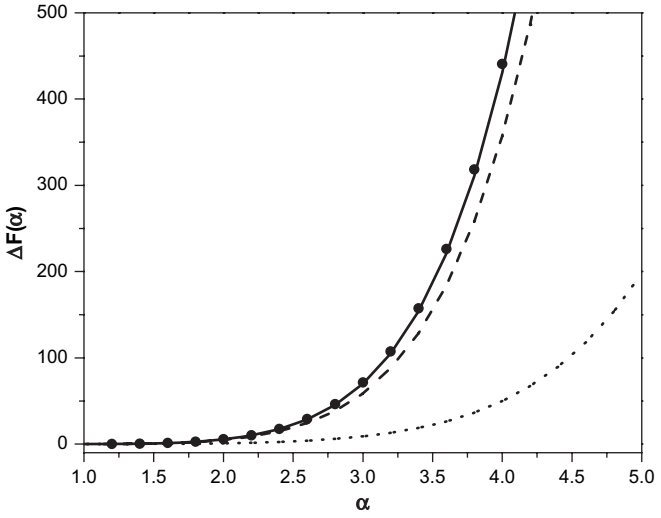

Fig. 1. Free elastic energy graphic for Erman and Mark's model: exact result (dot), the new expansion up to zero order (dotted line), second order (dashed line) and third order (solid line). The parameters used were $N = 50$, $b = 1$, $c = 0.02$, $\mu = n_s k_B T = 1$, and $\xi = 3.2$. For other sets of parameters we got similar results.

approach (uniaxial tension, $\lambda_1 = \alpha$ and $\lambda_2 = \lambda_3 = \alpha^{-1/2}$) to this distribution by taking zero $(i,j = 0)$, second $(i,j = 0,2)$ and third $(i,j = 0,2,3)$ order in the expansion and also the exact result directly obtained from Eq. (2.3). As we can see, the third order gives good agreement with the exact result for the integer range of deformation.

Now, let us consider the end-to-end distribution $P(\mathbf{R})$ obtained by considering a chain composed by N freely jointed monomers of length b, with all directions having the same probability. This distribution is given by Eq. (1.2). Although the distribution is cumbersome, we can get all exact $\langle R^{2p}\rangle$ values by considering the relation

$$\left\langle R^{2p}\right\rangle = \lim_{k\to 0}(-1)^p(2p+1)\partial_k^{2p} c(k), \tag{3.3}$$

where $c(k) = [\sin(kb)/(kb)]^N$ is the characteristic function. It leads to

$$\begin{aligned}
\left\langle R_0^2\right\rangle &= Nb^2 \\
\left\langle R_0^4\right\rangle &= \frac{1}{3}Nb^4(5N-2) \\
\left\langle R_0^6\right\rangle &= \frac{1}{9}Nb^6\left(35N^2 - 42N + 16\right) \\
&\vdots
\end{aligned} \tag{3.4}$$

These results can be used to get the $\langle(R_0^2 - \langle R_0^2\rangle)^j\rangle$ values.

We can also obtain an approximate analytical expression for the coefficients C_{ij} by using the inverse Langevin approximation together with the Pade representation [12],

$$P(\mathbf{R}) = P_0\left(1 - \frac{\mathbf{R}^2}{N^2b^2}\right)^N \exp\left[-\frac{\mathbf{R}^2}{2Nb^2}\right], \tag{3.5}$$

which gives

$$F_s\left(\lambda^2, R_0^2\right) = N\ln\left(1 - \frac{\lambda^2 R_0^2}{N^2b^2}\right) + \frac{\lambda^2 R_0^2}{2Nb^2}. \tag{3.6}$$

Using the above chain free energy in Eq. (2.5), we obtain

$$\begin{aligned}
C_{00} &= \mu\left[\frac{I_1}{6} - N\ln\left(1 - \frac{I_1}{3N}\right)\right] \\
C_{02} &= \frac{\mu I_1^2}{18N^3b^4}\left(1 - \frac{I_1}{3N}\right)^{-2} \\
C_{20} &= \frac{\mu}{2N}\left(1 - \frac{I_1}{3N}\right)^{-2} \\
C_{22} &= \frac{\mu}{2N^3b^4}\left(1 + \frac{2I_1}{3N}\right)\left(1 - \frac{I_1}{3N}\right)^{-4} \\
&\vdots
\end{aligned} \tag{3.7}$$

Numerical calculation for the above coefficients obtained by using the Pade representation and the exact distribution shows no significant difference.

The results obtained from Eqs. (2.8), (3.4) and (3.7) allow us to get an analytical expression for the free energy density in terms of two strain invariants, I_1 and I_2. For convenience, let us write just the second order $(i,j = 0,1,2)$,

$$F=\mu\left\{\left[\frac{I_1}{6}-N\ln\left(1-\frac{I_1}{3N}\right)\right]+\frac{2}{45N}\frac{I_1^2-3I_2}{\left(1-\frac{I_1}{3N}\right)^2}+\frac{(N-1)}{27N^2}\frac{I_1^2}{\left(1-\frac{I_1}{3N}\right)^2}+\frac{4}{135}\frac{(N-1)}{N^2}\frac{\left(I_1^2-3I_2\right)\left(1+\frac{2I_1}{3N}\right)}{\left(1-\frac{I_1}{3N}\right)^4}+\ldots\right\}, \tag{3.8}$$

where $\mu = n_s k_B T$. Notice that this expression presents a fast convergence to large strain region. For instance, we can see that the maximum limit extension is preserved even though we consider just the zero order term in the expansion, $\ln[1 - I_1/(3N)]$.

Despite the fact that it is necessary to consider several modes of deformation to check a given theory, we use the simple extension just as an example of application of our approach since it is the simplest one possible. Applying the above result to the uniaxial tension, $\lambda_1 = \alpha$ and $\lambda_2 = \lambda_3 = \alpha^{-1/2}$, the nominal stress (the force per unit unstrained area) is directly obtained from [1]

$$\sigma = 2\left(\alpha-\alpha^{-2}\right)\left[\frac{\partial F}{\partial I_1}+\frac{1}{\alpha}\frac{\partial F}{\partial I_2}\right]. \tag{3.9}$$

Fig. 2 shows the fit of experimental data for unswollen bimodal PDMS network [13] consisting of relatively long chains and very short chains using the nominal stress from the Gaussian theory and the corresponding adjustment with the expression from Eq. (3.8), up to third order ($i,j = 0,1,2,3$). As we can see, the Gaussian result is able to adjust the data only in the small deformation region. On the other hand, the upturn to high extension is an effect of the finite extensibility of the chains, and our results from Eq. (3.8) can incorporate this behavior, leading to a satisfactory agreement with the data for the whole range of deformation. Note that our model does not incorporate other intermolecular effects like entanglement or junction fluctuation. To take these effects into account, at least in part, we may write the total elastic free energy density as a sum of the elastic energy density from the quenched average and the elastic contribution that arises from the other constrains [13]. For instance, it is well known, from the Mooney–Rivlin plot, that in the small and intermediary regions of strain an additional deviation appears that is not connected to the finite chain length effects [1]. We may, in a phenomenological way, add the Mooney–Rivlin term, $C_2 I_2$, to the elastic free energy, with the C_2 coefficient being adjusted to fit the experimental data in these regions.

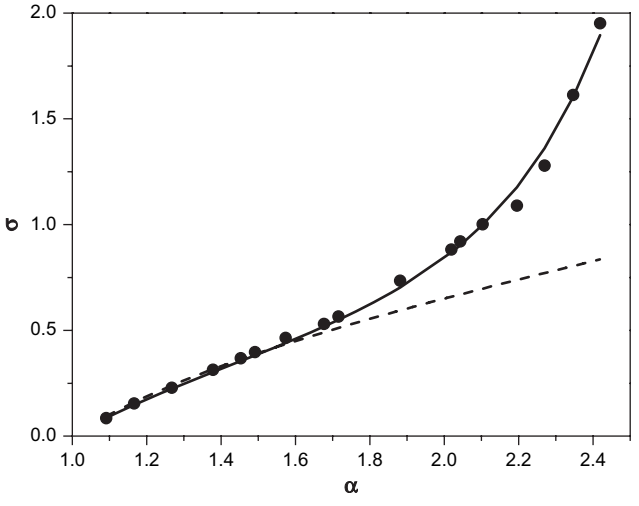

Fig. 2. Stress × strain data for unswollen bimodal PDMS network consisting of relatively long chains and very short chains [13] (black dot) and the corresponding adjustment with the new expansion, Eq. (3.9) (black line). The parameters used were $\mu = 0.28$ and $N = 11.54$. The dashed line represents the same data but adjusted with the Gaussian model with $\mu = 0.37$.

4. Discussion

Here, we introduced a new expansion approach to obtain the elastic free energy. This procedure presents a fast convergence at strain approaching the limiting extension of the network. Using a generalization of Fixman and Alben distribution, we showed the convergence of our approach. We also applied the method to get an analytical expression for the elastic free energy density to the freely jointed model. This model is able to fit in a very satisfactory way the experimental data for bimodal PDMS network over the whole range of extension. These results indicate that this method may be useful in the study of elastic deformation, specially concerning in the case of large deformation or short polymer chain where the Gaussian theory does not give satisfactory result.

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