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Finite chain-length effects in rubber elasticity

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Abstract

We present a finite chain-length calculation of the rubber elasticity of an isotropic crosslinked network of freely jointed chains under affine deformation. Whilst this is a classical calculation, the result is derived in its full tensorial structure for the first time, and new predictions of non-Gaussian elasticity for general biaxial deformations are presented. The full tensorial rubber-elasticity derivation allows any deformation regime to be treated, to facilitate validation with experimental data. Even though more complex many-chain effects are neglected, this theory appears to be the only one to offer a physical explanation for negative values of W_2 observed experimentally at small strains.

Keywords: Isotropic crosslinked network; Non-Gaussian elasticity; Rubber elasticity

1. Introduction

Rubber elasticity arises when polymer chains capable of large extensions are crosslinked together to form a network. Such chains can be considered at varying degrees of complexity [1,2]—initially as phantom, Gaussian chains, then accounting for many-chain affects, e.g. entanglements. We reconsider one significant feature of such networks, i.e. the finite length of its constituent chains (i.e. a strand of N monomers cannot extend to a length of more than N times the monomer length), an effect that the very much simplifying and rather successful Gaussian statistical theory does not account for. Gaussian statistics are exact only when the polymer chains they describe are of infinite length. In order to capture the finite chain effect in the network, Kuhn and Grun [3] long ago devised the inverse Langevin approximation within the freely jointed chain model, and obtained the leading correction to Gaussian single chain statistics. More recently, a powerful method based on moment calculations from the characteristic function [4] has been developed to obtain the single end-to-end vector distribution function [5–7], achieving encouraging agreements with Monte Carlo simulations [8].

Under the assumptions of the affine deformation of junction points and the additivity of individual strand entropy, the end-to-end vector distribution function directly leads to the network elasticity through either a finite-chain average or network average [1,9,10]. However, agreement with experiment is incomplete. Alternative theoretical models of rubber elasticity have been proposed to account for interactions between chains. Models range from the constrained junction-fluctuation [11] and primitive path [12,13] to slip-link [14–17] and tube models [18,19]. The relative merits of these approaches in fitting experimental data have been reviewed by Gottlieb and Gaylord [20], who make clear that the only real test of theory is to go beyond uniaxial deformations. The message is somewhat mixed, as none of the eight molecular models available was able to reproduce all of the experimental observations over the entire experimental range. A particularly striking point was that [21] a negative W_2 (the energy density derivative with respect to the second invariant of the deformation tensor) was observed experimentally at small strains, but none of the models could predict it. Computer simulations [22–25] have been helpful, and amongst other things they confirm the negative W_2 seen in experiments [26,27]. A somewhat more generalized method [28] obtained a good fit to experimental stress, but still did not offer any physical origin to the negativity of W_2 found experimentally in the low strain regime.

In this paper, we return to the picture of freely jointed chains cross-linked at junction points deforming under affine conditions. The end-to-end vector distribution function is derived as an expansion in inverse strand length, which ultimately approaches those obtained earlier [5–7]. However, the expansion facilitates the full network average, which follows to give the elastic free energy in a similar expansion. It is assumed that the fluctuation of the junction points will introduce a prefactor [2], but will not

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significantly alter the expansion otherwise. The method we use incorporates the saddle-point integration and Wick's theorem, and the result is obtained in its full tensorial form, which has not been done before [10] for finite chain-length effects. This tensorial expression is then expressed as a function of the two invariants of the deformation tensor. The negative value of W_2 is then found. It appears that finite chain-length is a possible physical origin giving rise to a negative W_2. The results presented here should be applicable to networks with medium to long (for convergence) strand lengths at moderate or low deformations.

An error in the widely used inverse Langevin approximation is examined and corrected. Our motivation is not to surplant models invoking many-chain effects in rubber elasticity, which undoubtedly exist and contribute to rubber elasticity. The purpose of this paper is to: (i) improve a classical model calculation on which much has been based over the years, and give a fully tensorial form for the dependence of free energy on the Cauchy strain λ, since complex deformations are the acid test of theory; (ii) show that this simple physical effect under the simplest assumptions yields $W_2 < 0$, a result inaccessible to more complex models. The last result perhaps suggests that a simple model calculation is indeed instructive—finite chain-length effects in tandem with many-chain effects might be of importance.

2. Single chain statistics

Consider the probability distribution function $P(\mathbf{R})$ of a chain consisting of N freely jointed units of length b, with the end-to-end vector $\mathbf{R}$. By introducing the auxiliary field $\mathbf{k}$, it is rather trivial [29,30] to show:

$$P(\mathbf{R}) \propto \int d\mathbf{k}\, \mathrm{e}^{-i\mathbf{k}.\mathbf{R}} \left(\frac{\sin\, kb}{kb}\right)^N \tag{1}$$

Here, $\left(\frac{\sin kb}{kb}\right)^N$ is the characteristic function for the freely jointed chain. Its successive derivatives with respect to $\mathbf{k}$ give the chain moments, from which the $P(\mathbf{R})$ can be inferred very accurately [5–7]. However, we shall present a perturbative method here for simplicity.

Approximating the characteristic function by $\exp(-Nk^2b^2/6)$ gives rise to the usual Gaussian distribution function, but more accurately, we can write it as a power series expansion in k^2:

$$\left(\frac{\sin\, kb}{kb}\right)^N = \exp\left(-N\left[\frac{k^2b^2}{6}+\frac{k^4b^4}{180}+\frac{k^6b^6}{2835}+,\ldots\right]\right) \tag{2}$$

which gives the probability distribution function in the form of:

$$P(\mathbf{R}) \propto \int d\mathbf{k}\, \exp(-N\, f(\mathbf{k})) \tag{3}$$

with

$$f(\mathbf{k}) = \frac{i}{N}\mathbf{k}.\mathbf{R} + \frac{k^2b^2}{6} + \frac{k^4b^4}{180} + \frac{k^6b^6}{2835} + \ldots \tag{4}$$

This integration can be performed within the saddle-point approximation to give the leading correction to the Gaussian probability. The saddle-point is found to be at:

$$\mathbf{k}_0 = -\frac{3i\mathbf{R}}{Nb^2}\left[1+\frac{3}{5}\left(\frac{R}{Nb}\right)^2+\frac{99}{175}\left(\frac{R}{Nb}\right)^4+\ldots\right] \tag{5}$$

To evaluate the full correction, we write the standard Taylor expansion for $f(\mathbf{k})$ about the saddle-point $\mathbf{k}_0$:

$$f(\mathbf{k}) = f(\mathbf{k}_0) + \sum_{n=2}^{\infty} \frac{(\tilde{\mathbf{k}}.\nabla_k)^n}{n!} f(\mathbf{k})|_{\mathbf{k}_0} \tag{6}$$

where $\tilde{\mathbf{k}} = \mathbf{k} - \mathbf{k}_0$ measures the distance away from the saddle-point, and $|_{\mathbf{k}_0}$ denotes that all derivatives are to be evaluated at the same saddle-point $\mathbf{k}_0$. The leading Gaussian behaviour [1], $R \sim N^{1/2}$ and $k \sim N^{-1/2}$, guides our expansion in orders of $1/N$ throughout this paper. Some details of this expansion are provided in Appendix A. Eq. (3) can be rewritten as:

$$\begin{aligned} P(\mathbf{R}) \propto\ & \exp(-Nf(\mathbf{k}_0)) \int d\tilde{\mathbf{k}}\, \exp\left(-\frac{Nb^2}{6}\tilde{k}^2\right) \\ & \exp\left[\frac{1}{10N}(R^2\tilde{k}^2 + 2R_iR_j\tilde{k}_i\tilde{k}_j)\left(1+\frac{3R^2}{5N^2b^2}\right)\right. \\ & + \frac{b^2 i}{15}R_i\tilde{k}_i\tilde{k}^2 - \frac{N}{180}\tilde{k}^4b^4 \\ & - \frac{3}{35N^3b^2}(R^4\tilde{k}^2 + 4R^2R_iR_j\tilde{k}_i\tilde{k}_j) \\ & \left. + \frac{b^2}{105N}(R^2\tilde{k}^4 + 4R_iR_j\tilde{k}_i\tilde{k}_j\tilde{k}^2) + \ldots\right] \end{aligned} \tag{7}$$

with summations over repeated indices implied here. The first exponential in the integrand describes a Gaussian average which, on its own, gives the prefactor in the saddle-point approximation; the second exponential can be expanded into a power series in k, and the average with respect to the Gaussian distribution is straightforward thanks to Wick's theorem[1]. The resulting probability distribution is an asymtotic series in $R^2(Nb)^{-2} \sim N^{-1}$, which can be written in the following exponential form:

$$\begin{aligned} P(\mathbf{R}) \propto\ & \exp\left(-N\left[\frac{3}{2}\left(\frac{R}{Nb}\right)^2\left(1-\frac{1}{N}+\frac{2}{5N^2}\right)\right.\right. \\ & \left.\left. + \frac{9}{20}\left(\frac{R}{Nb}\right)^4\left(1-\frac{11}{5N}\right) + \frac{99}{350}\left(\frac{R}{Nb}\right)^6\right] + \ldots\right). \end{aligned} \tag{8}$$

[1] Wick's theorem states that the Gaussian average of a product can be evaluated from the average of all possible pairings: $< k_{i_1}k_{i_2}\ldots k_{i_{2p}} > = \sum_{\text{all pairings}} < k_{i_1}k_{i_2} > \ldots < k_{i_{2p-1}}k_{i_{2p}} >$ where $< \ldots >$ indicates a Gaussian average

Note that this probability distribution only depends on the magnitude of **R**, as the system is isotropic. The exponent is a power series in $1/N$, and for large N, should be well approximated by the first few terms, as shown in Eq. (8). For shorter chains, higher-order terms in the expansion will be needed and the process becomes difficult, then the method of Refs [4–7], which in fact is more suited to shorter chains, is more appropriate. Nevertheless, for small corrections to Gaussian statistics due to a finite chain length, Eq. (8) is sufficient. We now compare it with the inverse Langevin approximation of the literature [3], which also deals with this correction to Gaussian statistics due to a finite chain length.

The probability distribution function given by the inverse Langevin approximation is equivalent to taking the saddle point value $\exp[f(\mathbf{k}_0)]$:

$$P_{\mathrm{Lang}}(\mathbf{R}) \propto \exp\left(-N\left[\frac{3}{2}\left(\frac{R}{Nb}\right)^2 + \frac{9}{20}\left(\frac{R}{Nb}\right)^4 + \frac{99}{350}\left(\frac{R}{Nb}\right)^6\right] + \ldots\right), \tag{9}$$

the exponent of which agrees with that of Eq. (8) only partially. In comparison, the multiplicative factors in the exponent, e.g. $(1 - 1/N + 2/5N^2)$, are new and necessary for a self-consistent approximation of the order of $1/N$. Therefore, expanding the inverse Langevin function in a power series, e.g. [26,31], will give an incomplete correction to Gaussian results at order $1/N$. The error in the inverse Langevin approximation comes mainly from the use of Stirling's approximation, which can be viewed as a saddle point approximation of a Gamma function integral.

In Eqs. (8) and (9), we have non-Gaussian probability distributions, which contain the leading order (in $1/N$) corrections due to the finite chain-length. However, the exact expectation values are available (by, e.g. differentiating the characteristic function[4]) for a freely jointed chain: $\langle R^2\rangle = Nb^2$ and $\langle R^4\rangle = (5N^2 - 2N)b^4/3$, etc. which account for the finite chain length effects. These expectation values can be verified with the probability distribution of Eq. (8) by expanding its non-Gaussian parts and utilizing Wick's theorem in the subsequent integrals, but not with that of Eq. (9).

3. Network average

To analyse the mechanical properties of the network, we now consider a general affine deformation $\boldsymbol{\lambda}$, which deforms a span between junction points of the network from $\mathbf{R}_0$ to **R** according to the relation $\mathbf{R} = \boldsymbol{\lambda}.\mathbf{R}_0$. This defines the Cauchy–Green deformation tensor $\boldsymbol{\lambda}$:

$$\lambda_{\alpha\beta} = \partial R_\alpha / \partial R_{0\beta} \tag{10}$$

The elastic free energy per network strand of the distorted state is then given by the quenched average of $\ln P(\mathbf{R})$ over the distribution of strands $P(\mathbf{R}_0)$:

$$F_s(\boldsymbol{\lambda}) = -k_{\mathrm{B}}T\langle \ln P(\mathbf{R})\rangle_0 \tag{11}$$

where $\langle\ldots\rangle_0$ indicates the average with respect to the probability distribution function before deformation, $P(\mathbf{R}_0)$; k_BT is the unit of thermal energy. This implies the following average:

$$\frac{F_s}{k_{\mathrm{B}}T} = const. + \frac{3}{2Nb^2}\left(1 - \frac{1}{N} + \frac{2}{5N^2}\right)\langle R_iR_i\rangle_0 + \frac{9}{20N^3b^4}\left(1 - \frac{11}{5N}\right)\langle R_iR_iR_jR_j\rangle_0 + \frac{99}{350N^5b^6}\langle R_iR_iR_jR_jR_lR_l\rangle_0\ldots \tag{12}$$

However, this average over a non-Gaussian distribution is inconvenient, and we choose to rewrite Eq. (8) for $P(\mathbf{R}_0)$ as:

$$P(\mathbf{R}_0) \propto \exp\left(-\frac{3}{2}\frac{R_0^2}{Nb^2}\left(1 - \frac{1}{N} + \frac{2}{5N^2}\right)\right) \times \left[1 - \frac{9N}{20}\left(\frac{R_0}{Nb}\right)^4\left(1 - \frac{11}{5N}\right) + \frac{81N^2}{800}\left(\frac{R_0}{Nb}\right)^8 - \frac{99}{350}\left(\frac{R_0}{Nb}\right)^6 + \ldots\right] \tag{13}$$

which is a Gaussian distribution with a non-trivial multiplicative factor. Thus, the average in Eq. (12) becomes a Gaussian average of a polynomial in **R**, and Wick's theorem can again be employed after substituting $R_\alpha = \lambda_{\alpha\beta}\, R_{0\beta}$ to give the rubber-elastic contribution to the free energy density $W = n_s\, F_s$:

$$\frac{W}{n_sk_{\mathrm{B}}T} = \frac{1}{2}\left(1 - \frac{1}{N} + \frac{2}{5N^2}\right)\lambda_{ij}\lambda_{ij} + \frac{1}{20N}\left(1 - \frac{13}{5N}\right) \times \left[(\lambda_{ij}\lambda_{ij})^2 + 2\lambda_{ij}\lambda_{lj}\lambda_{lk}\lambda_{ik}\right] + \frac{11}{1050N^2}\left[(\lambda_{ij}\lambda_{ij})^3 + 6\lambda_{ij}\lambda_{ij}\lambda_{lp}\lambda_{lq}\lambda_{mp}\lambda_{mq} + 8\lambda_{ij}\lambda_{iq}\lambda_{lj}\lambda_{lp}\lambda_{mp}\lambda_{mq}\right] + \ldots \tag{14}$$

where we have dropped the irrelevant constant, and n_s is the average number of chain strands per unit volume. Note that the λ^4 terms start at order $1/N$, the λ^6 terms start at order $1/N^2$, etc.

Eq. (14) gives the full tensorial free energy with the finite chain-length effect, and it can be viewed as an extension of the previous work on uniaxial deformations [10]. Our original motivation for such a tensorial formulation is partly that finite chain-length effects are likely to be qualitatively important in nematic elastomers which, being anisotropic, make the tensorial formulation crucial. However, there are also interesting conclusions for isotropic rubber elasticity, as we show below.

The deformation of a homogeneous, isotropic and elastic material is characterised by a symmetric deformation tensor $\boldsymbol{\lambda}$, the diagonalisation of which leaves three principal strains λ_1, λ_2, λ_3 along a set of orthogonal axes. If we further assume incompressibility, which imposes $\lambda_1, \lambda_2, \lambda_3 = 1$, the elastic free energy is then a function of the two

remaining rotational invariants of the deformation tensor [32,33]:

$$I_1 = \sum_{i=1}^{3} \lambda_i^2, \quad I_2 = \sum_{i=1}^{3} \lambda_i^{-2}, \quad W = W(I_1, I_2) \tag{15}$$

Thus, biaxial deformation is the most general deformation, and uniaxial deformation is only a special case. The most strict test of a physical model is therefore only obtained under the former [20]. Rewriting Eq. (14) in terms of I_1 and I_2, we have:

$$\frac{W}{G_0} = \frac{1}{2}\left(1 - \frac{1}{N} + \frac{2}{5N^2}\right) I_1 + \frac{1}{20N}\left(1 - \frac{13}{5N}\right)[3I_1^2 - 4I_2] + \frac{11}{350N^2}[5I_1^3 - 12 I_1 I_2] + \ldots \tag{16}$$

where $G_0 = n_s k_B T$. The derivatives $W_i = \partial W / \partial I_i$ are:

$$\frac{W_1}{G_0} = \frac{1}{2}\left(1 - \frac{1}{N} + \frac{2}{5N^2}\right) + \frac{3}{10N}\left(1 - \frac{13}{5N}\right) I_1 + \frac{11}{350N^2}[15I_1^2 - 12 I_2] + \ldots \tag{17}$$

$$\frac{W_2}{G_0} = -\frac{1}{5N}\left(1 - \frac{13}{5N}\right) - \frac{66 I_1}{175N^2} + \ldots \tag{18}$$

Experimentally, Kawabata and co-workers [21,34,35] have studied the behaviour of rubbers under multiaxial deformation. Special attention was paid to small deformations, at which experimental error was prevalent. While their results can be well fitted by some theoretical models at large strains, no previously available model can explain the negative W_2 observed at low strains [20]. We see from Eq. (18) that the affine assumption with finite chain-length can clearly give rise to a negative W_2 at order $1/N$ and higher. For a typical value of $N = 10$, we would have $W_2 \sim -0.03 G_0$, and for shorter chains we would expect W_2 to be more negative. This is about the same order of magnitude as that measured in Kawabata et al. [21], which gave an average of $\sim -0.1 G_0$ with a rather large uncertainty of more than $0.05 G_0$. The experimental N is difficult to estimate, and the sample is almost certain to have polydisperse N. Qualitatively, the decrease in W_1 with increasing I_2, as predicted in Eq. (17) at order $1/N^2$, can be observed in the data from Gottlieb and Gaylord [20], and Kawabata et al. [21]. The experimental uncertainty prevents a more detailed comparison, and it would therefore be interesting to have more precise data for $W_{1,2}$ at $I_{1,2} \sim 3$ and their variations with N. At large deformations, beyond the region of validity of this model (mainly due to the breakdown of affine deformation assumption), W_2 becomes positive. Comparison with computer simulations [26] is hampered by slight differences in adopted models. In Termonia [26,27], affine deformation was not strictly enforced; the inverse Langevin approximation giving rise to order $1/N$ error in free energy (as discussed earlier) was employed. However, the message of this paper is clear, i.e. that finitely extensible chains, even under the simplest approximation, can account for the negative W_2 observed experimentally. Our theory also predicts that: (i) the absolute value of W_2 increases with increasing crosslink densities or decreasing N and; (ii) for large N, W_2 should approach $G_0/5N$. More complex models, e.g. involving entanglements, may be more successful if they include this physical ingredient.

Finally, we derive an expansion expression for small strains. We write $\lambda_{ij} = \delta_{ij} + \in_{ij}$, and the constant volume condition requires $\mathrm{Det}(\lambda_{ij}) = 1$, which leads to:

$$\in_{ii} = \in_{ij} \in_{ij} /2 + O(\in^3) \tag{19}$$

via the Cayley–Hamilton theorem. Here, in writing Eq. (19), we have assumed the matrix $\in_{ij}$ to be symmetric. It is an assumption without loss of generality since the anti-symmetric part of the matrix gives rise to a net rotation, which leaves the system invariant[2]. Thus, the above elastic energy expression, Eq. (14), can be rewritten as (again dropping the constant term):

$$W(\in) = G_0 \in_{ij} \in_{ij} \left(1 + \frac{2}{5N} + O\left(\frac{1}{N^2}\right)\right) + \ldots \tag{20}$$

This now becomes an expansion in both $\in_{ij}$ and $1/N$. As expected, we indeed see the $1/N$ corrections to the usual Gaussian behaviour $W_{\mathrm{Gau}}(\in) = G_0 \in_{ij} \in_{ij}$. Cubic, quartic and even higher order (in strain) corrections are also present, but are smaller by increasing powers of $1/N$. With N being typically of the order 20 for rubber and possibly less for liquid-crystalline elastomers thus far studied, the correction can be quite significant even at small deformations.

4. Summary

We have presented a perturbation method of deriving the end-to-end vector distribution function of a freely-jointed chain. By performing a network average, we derive a fully tensorial expression for the rubber elasticity of a crosslinked network with finite chain-length effects. The elastic free energy is then obtained as an explicit function of I_1 and I_2, the two invariants of the deformation tensor. The main results of the paper are: (i) the error in the inverse Langevin approximation is examined; (ii) a tensorial form of the finite chain-length effects is derived; and (iii) the finite length of polymer chains can give rise to the negative W_2, observed experimentally. The expansions in the small deformation tensor $\in$ and inverse strand length $1/N$ are performed. The deviation from the usual Gaussian behaviour is obtained. Work in progress generalises the method presented here to nematic networks.

[2] In nematic elastomers there is an elastic-nematic coupling involving the antisymmetric component of $\in$ and we cannot make this simplification

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Appendix A Taylor expanding $f(\mathbf{k})$

By expanding around the saddle point $\mathbf{k}_0$, the first derivative term is absent. Noting:

$$(\tilde{\mathbf{k}}.\nabla_k)^n f(\mathbf{k})|_{\mathbf{k}_0} = \frac{\partial^n f}{\partial k_i \ldots \partial k_j}|_{\mathbf{k}_0} \tilde{k}_i \ldots \tilde{k}_j \tag{A1}$$

we start with the second order term:

$$(\tilde{\mathbf{k}}.\nabla_k)^2 f(\mathbf{k})|_{\mathbf{k}_0} = \frac{\partial^2 f}{\partial k_i \partial k_j}|_{\mathbf{k}_0} \tilde{k}_i \tilde{k}_j = \frac{b^2}{3}\tilde{k}^2 - \frac{1}{5N^2}(R^2\tilde{k}^2 + 2R_iR_j\tilde{k}_i\tilde{k}_j)\left[1 + \frac{6R^2}{5N^2b^2}\right] + \frac{6}{35N^4b^2}(R^4\tilde{k}^2 + 4R^2R_iR_j\tilde{k}_i\tilde{k}_j) + O(N^{-4}) \tag{A2}$$

and then consider higher order terms in the Taylor expansion:

$$(\tilde{\mathbf{k}}.\nabla_k)^3 f(\mathbf{k})|_{\mathbf{k}_0} = -\frac{2b^2 i}{5N}R_i\tilde{k}_i\tilde{k}^2\left[1 + \frac{3R^2}{5N^2b^2}\right] + \frac{8i}{35N^3}[3R^2R_i\tilde{k}_i\tilde{k}^2 + 2(R_i\tilde{k}_i)^3] + O(N^{-4}) \tag{A3}$$

$$(\tilde{\mathbf{k}}.\nabla_k)^4 f(\mathbf{k})|_{\mathbf{k}_0} = \frac{2}{15}\tilde{k}^4 b^4 - \frac{8b^2}{35N^2}(R^2\tilde{k}^4 + 4R_iR_j\tilde{k}_i\tilde{k}_j\tilde{k}^2) + O(N^{-4}) \tag{A4}$$

$$(\tilde{\mathbf{k}}.\nabla_k)^5 f(\mathbf{k})|_{\mathbf{k}_0} = -\frac{16b^4 i}{21N}(R_i\tilde{k}_i\tilde{k}^4) + O(N^{-4}) \tag{A5}$$

$$(\tilde{\mathbf{k}}.\nabla_k)^6 f(\mathbf{k})|_{\mathbf{k}_0} = \frac{16}{63}b^6\tilde{k}^6 + O(N^{-4}) \tag{A6}$$

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