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MODEL CALCULATIONS BASED ON A NEW THEORY OF RUBBER ELASTICITY*

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A new theory is presented for elastic deformations of linear polymer chains and phantom polymer networks. It is shown that most of the conclusions of the classical theory of rubber elasticity either are incorrect or inaccurate. Appropriate modifications of the theory are proposed. In particular, we show that for a Gaussian chain network it is the internal energy and not the entropy that is the thermodynamic function mostly responsible for the elasticity of rubbers. Furthermore, an attractive part of the segmental bond potential is essential to account for the thermoelastic inversion and for the basic features of Mooney plots. Simple models of ideal polymer chains and networks are analyzed.

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1. Introduction

The theoretical predictions of the traditional molecular theory of elasticity of polymer chains and networks do, in some cases, deviate markedly from experimental observations.

In an attempt to improve this situation, Altenberger and Dahler (Refs [1] and [2]) have recently developed a new theory which shows, among other things, that there are energetic as well as entropic contributions to the thermoelastic properties of elastomeric networks.

The main purpose of the present work is to produce theoretical predictions by applying the theory developed by Altenberger and Dahler to simple mechanical models.

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A brief historical background is given in Section 2. In Section 3 the basic assumptions of the traditional model are presented and in Section 4 experimental results as well as the difficulties of the traditional theory are pointed out. Section 5 is dedicated to a short presentation of the new theory. In Section 6 three simple mechanical models are used and theoretical predictions are obtained and illustrated by proper plots. The conclusions are reserved to the last section.

2. Historical background

Hevea Brasiliensis is the name of the tree from which the original material of commerce known as rubber is obtained in the form of latex. The word rubber comes from the property of this material to remove marks from paper. Nowadays the term rubber is applied to any material exhibiting mechanical properties analogous to those of natural rubber. The term elastomer is now much used in connection with synthetic materials with rubber-like properties. Throughout this work the word rubber will apply to any rubber-like material, regardless of its chemical constitution.

There are two main properties that characterize rubbers, the capability of large deformations without rapture, and the capacity to recover spontaneously very nearly to its initial dimensions after the agent causing the deformation is removed. The large deformation capability is illustrated by the typical stress-strain isotherm shown in Fig. 1 (Ref. [3], p.15).

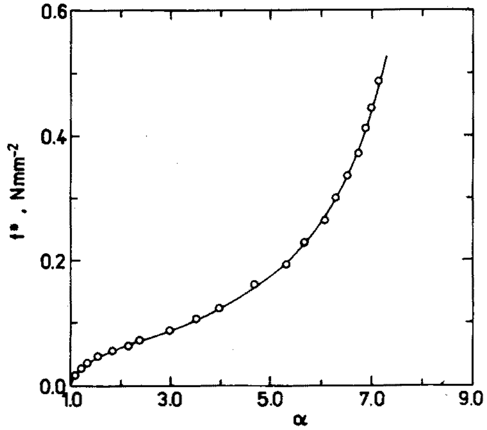


Fig. 1. Stress-strain curve for natural rubber in the vicinity of room temperature.

The earliest experiments on rubber elasticity were performed in 1805 by John Gough. He interpreted the results as evidence of the then prevailing caloric fluid theory of heat. His observations on thermoelastic effects can be summarized as follows:

1) rubber held under a constant load (stretched state) contracts (reversibly) on heating; and
2) when stretched, rubber gives off heat (reversibly).

With the discovery of vulcanization in 1839 by Goodyear and Hyward, experimental investigations were facilitated and in 1859, Joule, working with vulcanized rubber, confirmed Gough's observations. The two thermoelastic effects referred to above are known as the Gough–Joule effects and their full significance could be better appreciated after the formulation of the second law of thermodynamics by Kelvin and Clausius in the early 1850's.

Another important experimental result observed by several workers was that deformations (other than swelling) of rubbers occurred essentially at constant volume, without the occurrence of crystallization.

Early attempts to relate rubber mechanical properties to classical concepts of molecular structure encountered great difficulties. Some hydrocarbons with apparently the same chemical constitution as natural rubber (the only type of rubber then available) were invariably ordinary liquids or solids. Also, the classical model, which pictured a solid as an array of atoms (or molecules) maintained in fixed relative positions by well-defined interatomic forces, was incapable of supporting extensions of magnitude greater than about ten per cent. It was unable to serve as a basis for interpreting the deformations of one hundred times this magnitude, which occurs for rubbers. This major difficulty could in some sense be avoided by postulating a sort of open network structure. The "two-phase" theories were examples of this approach. Another way to circumvent this problem was to postulate a helical or coil-spring type of molecule. In both ways large total deformations could be obtained without introducing large strains of the elastic elements of the structure.

The above theories (and others that were similar) tried to explain rubber's large-extension elasticity at a time when natural rubber was the only elastomer available. Their explanations of rubber's mechanical properties were not convincing and they completely failed to account for rubber's thermoelastic properties.

An important step toward the understanding of rubber elasticity was the recognition that natural rubber was intimately related (in both structure and properties) to other materials (gelatin, muscle fibres, silk, etc.) generally known as colloids, but with very distinct chemical constitution.

As improved methods and technology allowed better measurements of very high molecular weight compounds and with the recognition of the existence of new and remarkable entities called *polymers* (with molecular weights in the range 100 000–1 000 000), it became evident that this kind of molecule could not be considered as a rigid structure constrained by static internal forces. There should be flexibility, internal vibrations and rotations, due to thermal fluctuations.

In 1932, Meyer, vonSusich, and Valko developed a theory of rubber elasticity in which the thermal energy of the atoms in a long chain molecule was assumed to induce greater amplitudes of vibration in directions perpendicular to the chain than in the direction of the chain itself. This was the first insight into the now generally accepted theory of rubber elasticity, which was mainly developed by Frederich T. Wall, Paul J. Flory and L.R.G. Treloar.

3. Standard model assumptions

The basic assumptions that constitute the basis of the now generally accepted theory of rubber elasticity are:

a) The intermolecular interactions that occur in rubbers are independent of configuration, so that each molecule contributes separately to the thermodynamic and mechanical properties of the sample (the "ideal gas" model).

b) The junction points of the chain are assumed to be embedded in the network constituted by the other chains, which are responsible for the transmission of deformations of the macroscopic sample into deformations of the single chain (affine deformation). Figure 2 shows a sample in the unstrained and strained states and equations (3.1) come from the affine deformation.

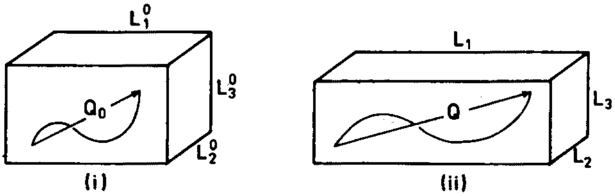


Fig. 2. Unstrained *(i)* and strained *(ii)* states of a sample.

c) The chains (if sufficiently long) will exhibit Gaussian statistics, *i.e.*, the probability distribution function for the end-to-end vector Q is given by

$$\Psi_G = \frac{1}{\alpha_1\alpha_2\alpha_3}\left(\frac{3}{2\pi b^2}\right)^{3/2}\exp\left(\frac{-3}{2b^2}\sum_{i=1}^{3}(q_i/\alpha_i)^2\right), \qquad (3.2)$$

where

$$b^2 = \langle q^2\rangle_0 \qquad (3.3)$$

is the mean square of the end-to-end vector of the undeformed chain ($\alpha_i = 1$). Here

$$\alpha_i = \frac{L_i}{L_i^0} \mathrel{\overset{\rightarrow}{-}} \sqrt{\frac{\langle q^2 \rangle}{\langle \mathbf{q}^2 \rangle_0}} \tag{3.4}$$

is the deformation ratio (or strain) in the i direction.

d) The connection with thermodynamics is made through the expression

$$\delta S = -k \int dq \Psi(q) \ln \frac{\Psi(q)}{\Psi_0(\mathbf{q})} \tag{3.5}$$

for the entropy of deformation. In the case of a Gaussian chain, this becomes

$$\delta S = \frac{-k}{2}\left(\alpha_1^2 + \alpha_2^2 + \alpha_3^2 - 3\right). \tag{3.6}$$

Because the deformation change of internal energy was assumed to be of negligible magnitude, the free energy of deformation is given by

$$\delta F = -T \delta S. \tag{3.7}$$

e) By applying proper constraints, the nominal stress (ratio of force to the initial area on which this force acts) can be evaluated from δF. The constraint appropriate to an isochoric deformation is

$$\alpha_1 \alpha_2 \alpha_3 = 1 \tag{3.8}$$

and, in the case of uniaxial extension along the 1 axis

$$\alpha_2 = \alpha_3 . \tag{3.9}$$

Therefore, for uniaxial extension in the 1 direction,

$$\alpha_2^2 = \alpha_3^2 = \frac{1}{\alpha_1} \tag{3.10}$$

and the nominal stress per chain is

$$f_1 = \frac{\partial \delta F}{\partial \alpha_1} = \frac{-2kT}{\Omega}\left(\alpha_1 - \frac{1}{\alpha_1^2}\right) \tag{3.11}$$

with Ω denoting the volume of the sample.

4. Experimental results and difficulties

The early experiments of Meyer and Ferri (1935) showed that, for a given state of strain (change due to force in the size or shape of a body relative to its original size or shape), the stretching force is proportional to the absolute temperature. This was valid for sufficiently large extensions (Fig. 3), the behaviour appearing anomalous for lower strains with the force increasing less rapidly or even decreasing with rising temperature (Fig. 4). These observations have been confirmed by many others. The reversal in slope of the stress-temperature plots is called the thermoelastic inversion and cannot be predicted from the formula for δS of the previously described standard model.

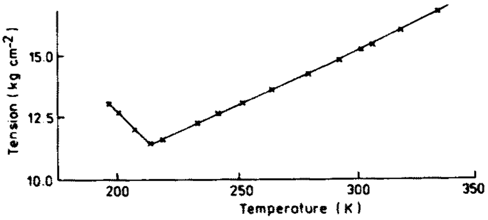


Fig. 3. Force at constant length as function of absolute temperature. Extension 350 per cent. (After Treloar, Ref. [4], p. 25.)

The stress-strain curves predicted by the Gaussian chain standard model are in rather poor agreement with experimental results (Fig. 5). However, according to Treloar [4] this theory is valid only for moderate extensions. When the extensions are very large, non-Gaussian corrections must be introduced. However, even with these corrections, large discrepancies between theory and experiment persist for intermediate values of the strain.

Experimental data often are represented in terms of the reduced stress $[f_1]$ defined as

$$[f_1] \equiv \frac{f_1}{2c(\alpha_1 - \alpha_1^{-2})} . \tag{4.1}$$

Here the subscript 1 refers to the direction of the uniaxial deformation and c is a coefficient that depends on the model to be used. The so called Mooney plots are of $[f]$ *versus* the inverse deformation ratio α^{-1}. For rubber, the Mooney plot illustrates the previously described (Fig. 1) large and rather abrupt increase in the stress that occurs at high elongation. The disagreement between theoretical and experimental results is apparent from Fig. 6.

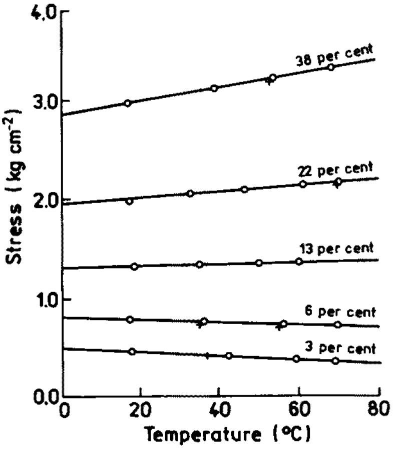


Fig. 4. Force at constant length as function of temperature. Elongation as indicated.(After Treloar, Ref. [4], p. 25.)

There also is a difficulty with the formula for the entropy of deformation,

$$\delta S = -k \int dq \Psi(q) \ln \frac{\Psi(q)}{\Psi(q_0)} \tag{4.2}$$

which is inconsistent with the accepted formula for entropy that comes from statistical mechanics and information theory, namely,

$$S(\Psi) = -k \int dq \Psi(q) \ln \Psi(q) . \tag{4.3}$$

Thus, according to this statistical mechanical formula for entropy, the entropy of deformation should be given by expression

$$\delta S = S(\Psi) - S(\Psi_0) \tag{4.4}$$

and not by (4.2).

When (4.3) is applied to the Gaussian chain, the results are

$$S(\Psi_G) = k\left(\ln \alpha_1\alpha_2\alpha_3 + 3\ln\frac{2\pi b^2}{3}\right) + \frac{3}{2} \tag{4.5}$$

and

$$\delta S = k \ln \alpha_1\alpha_2\alpha_3 . \tag{4.6}$$

From this we conclude that the entropy of deformation vanishes for isochoric deformations of a Gaussian chain!

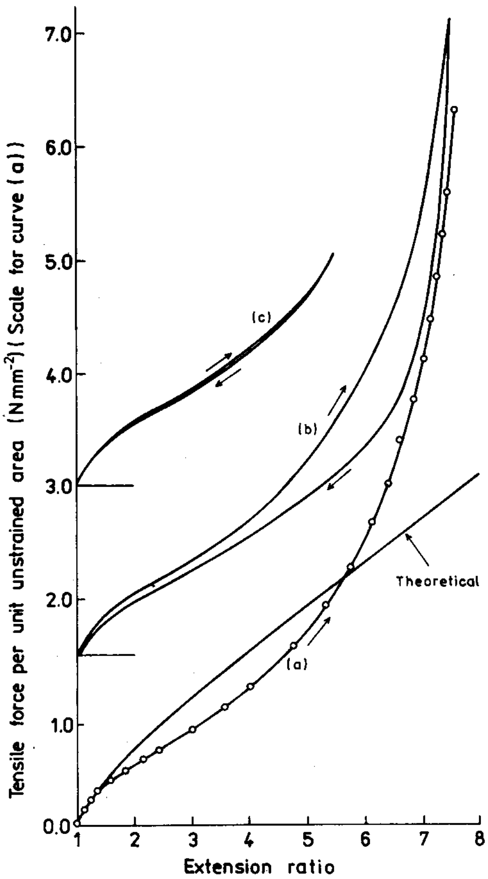


Fig. 5. Simple extension. Comparison of experimental curve with theoretical form. (After Treloar, Ref. [4], p. 87.)

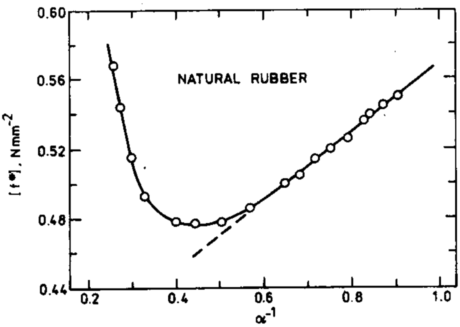


Fig. 6. Stress-strain isotherm for an unfilled rubber network in the vicinity of room temperature. (After Mark, Ref. [3], p. 92.)

5. New approach

5.1 Assumptions

Altenberger and Dahler [1, 2] have recently developed a new theory which is based on assumptions that are somewhat similar to those previously discussed, namely:

a) The "ideal polymer gas" model (the intermolecular interactions are independent of configuration).

b) The model adopted is the relatively simple and widely used beads-and-springs model of a polymeric chain, illustrated by Fig. 7.

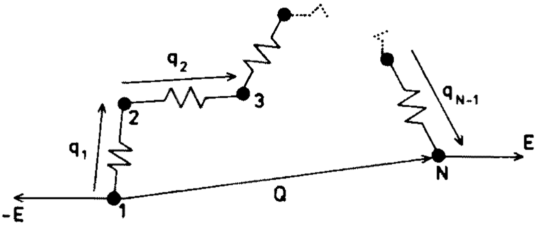


Fig. 7. The beads-and-springs model. (N beads) $\boldsymbol{Q}$ is the end-to-end vector $\boldsymbol{q}_i$ is the i-th segment vector, and $\boldsymbol{E}$ and $-\boldsymbol{E}$ are the forces applied to the ends of chain.

c) The heat and work related to an infinitesimal, quasistatic chain deformation are given, respectively, by

$$dQ_{\text{def}} = T\, d\delta S \tag{5.1}$$

and

$$dW_{\text{def}} = \overline{\boldsymbol{R}} \cdot d\boldsymbol{E} \tag{5.2}$$

with $\overline{\boldsymbol{R}}$ denoting the mean end-to-end vector of chain.

5.2 The theory

The polymer is treated as a three-dimensional curve with its mass evenly distributed along the contour. The curve is divided into small segments, each with a center of mass which is treated as a material point or "bead". The potential energy necessary to hold the "beads" together is identified with the energy of the connecting bonds or "springs". Fig. 7 shows a representation of this model, with the forces $\boldsymbol{E}$ and $-\boldsymbol{E}$ applied to the ends of the chain.

The Hamiltonian of the chain is

$$H = \sum_{i=1}^{N} (m/2)\dot{\boldsymbol{r}}^2 + \sum_{i=1}^{N-1} V(|\boldsymbol{r}_{i+1} - \boldsymbol{r}_i|) + \boldsymbol{E} \cdot (\boldsymbol{r}_N - \boldsymbol{r}_1) \tag{5.3}$$

with m the segment mass and N the number of segments. $\boldsymbol{r}_i$ and $\dot{\boldsymbol{r}}_i$, respectively, denote the position and velocity of the i-th segment and $V(|\boldsymbol{q}_{i+1}|)$ is the bond potential ($\boldsymbol{q}_{i+1} = \boldsymbol{r}_{i+1} - \boldsymbol{r}_i$ being the $(i+1)$-th segment vector).

The Gibbs canonical distribution function for the stretched chain is given by

$$\rho(\dot{\boldsymbol{r}}^N, \boldsymbol{r}^N; \boldsymbol{E}) = \frac{\mathrm{e}^{-\beta H}}{N!\, h^{3N} Q(\beta, \boldsymbol{E})} . \tag{5.4}$$

The quantity $Q(\beta, \boldsymbol{E})$ appearing here is the chain partition function

$$Q(\beta, \boldsymbol{E}) = \frac{1}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3/2N} Z(\beta, \boldsymbol{E}) \tag{5.5}$$

and

$$Z(\beta, \boldsymbol{E}) = \int d\boldsymbol{r}^N \exp(-\beta U)(\boldsymbol{r}^N; \boldsymbol{E})) \tag{5.6}$$

is the configuration integral with $U(\boldsymbol{r}^N; \boldsymbol{E})$ representing the potential energy (second and third of the Hamiltonian, Eq. (5.3)).

The segmental configuration integral is

$$z(\beta, \boldsymbol{E}) = \int d\boldsymbol{q} \exp(-\beta[V(|\boldsymbol{q}|) + \boldsymbol{E} \cdot \boldsymbol{q}]) \tag{5.7}$$

and the segmental probability distribution function is

$$\Psi(\boldsymbol{q}, \boldsymbol{E}) = \frac{\exp(-\beta[V(|\boldsymbol{q}|) + \boldsymbol{q} \cdot \boldsymbol{E}])}{z(\beta, \boldsymbol{E})} . \tag{5.8}$$

From statistical thermodynamics, the thermodynamic functions (free energy, internal energy and entropy) of deformation are, respectively

$$\delta F(\beta, \boldsymbol{E}) = -\beta^{-1}(N-1) \ln \frac{z(\beta, \boldsymbol{E})}{z(\beta, 0)} , \tag{5.9}$$

$$\delta U(\beta, \boldsymbol{E}) = -\beta^{-1}(N-1) \frac{\partial}{\partial \beta} \ln \frac{z\beta, \boldsymbol{E})}{z(\beta, 0)} , \tag{5.10}$$

$$\delta S(\beta, \boldsymbol{E}) = \tfrac{1}{T}(\delta U(\beta, \boldsymbol{E}) - \delta F(\beta, \boldsymbol{E})) . \tag{5.11}$$

The deformation ratios for the segment are

$$\alpha^2_{\|\mathrm{seg}}(\beta, \boldsymbol{E}) = \frac{\overline{q^2_\|}(\beta, \boldsymbol{E})}{\overline{q^2_\|}(\beta, 0)} = \frac{\frac{\partial^2 \ln z}{\partial \boldsymbol{E}^2} + \left(\frac{\partial \ln z}{\partial \boldsymbol{E}}\right)^2}{\left[\frac{\partial^2 \ln z}{\partial \boldsymbol{E}^2} + \left(\frac{\partial \ln z}{\partial \boldsymbol{E}}\right)^2\right]_{\boldsymbol{E}=0}},$$

$$\alpha^2_{\perp\mathrm{seg}}(\beta, \boldsymbol{E}) = \frac{\overline{q^2_\perp}(\beta, \boldsymbol{E})}{\overline{q^2_\perp}(\beta, 0)} = \frac{\frac{\partial \ln z}{\boldsymbol{E}\partial \boldsymbol{E}}}{\left(\frac{\partial \ln z}{\boldsymbol{E}\partial \boldsymbol{E}}\right)_{\boldsymbol{E}=0}} \tag{5.12}$$

and for the chain

$$\alpha^2_\|(\beta, \boldsymbol{E}) = \frac{\overline{\boldsymbol{R}^2_\|}(\beta, \boldsymbol{E})}{\overline{\boldsymbol{R}^2_\|}(\beta, 0)} = \alpha^2_{\|\mathrm{seg}} + (N-2)\frac{\overline{q^2_\|}(\beta, \boldsymbol{E})}{\overline{q^2_\|}(\beta, 0)},$$

$$\alpha^2_\perp(\beta, \boldsymbol{E}) = \alpha^2_{\perp\mathrm{seg}}(\beta, \boldsymbol{E})\,. \tag{5.13}$$

Here

$$\overline{\boldsymbol{R}}(\beta, \boldsymbol{E}) = -\beta^{-1}(N-1)\frac{\partial \ln z(\beta, \boldsymbol{E})}{\partial \boldsymbol{E}} = (N-1)\overline{q}(\beta, \boldsymbol{E}) \tag{5.14}$$

is the mean end-to-end distance vector and $q_\|(\beta, \boldsymbol{E})$ and $q_\perp(\beta, \boldsymbol{E})$, respectively, are the components of q parallel and perpendicular to the direction of the applied force.

6. Simple mechanical models

We now study the elastic properties of systems with three different segmental binding potentials.

6.1 Finitely extendible, infinitely flexible dumbbell chain

According to this model the beads are connected by flexible strings that cannot exceed a finite extension q_0. The binding potential has the square-well form

$$\begin{aligned} V(q) &= 0\,;\ q < q_0 \\ &\infty\,;\ q > q_0 \end{aligned} \tag{6.1}$$

and the segmental configuration integral is given by the formula

$$z(\beta, \boldsymbol{E}) = z(\beta, 0)W(\beta \boldsymbol{E} q_0)\,, \tag{6.2}$$

where

$$W(x) = \frac{3}{x^2}\left(\cosh x - \frac{\sinh x}{x}\right). \tag{6.3}$$

The thermodynamic functions of deformation are

$$\frac{\beta\delta U(\beta, E)}{N-1} = 3\left[1 - \frac{w(X_0)}{W(X_0)}\right], \tag{6.4}$$

$$\frac{\beta\delta F(\beta, E)}{N-1} = -\ln W(X_0), \tag{6.5}$$

$$\frac{\beta\delta S(\beta, E)}{k(N-1)} = \frac{\beta}{N-1}(\delta U - \delta F), \tag{6.6}$$

with

$$X_0 = \beta E q_0 \tag{6.7}$$

and

$$w(x) = \frac{\sinh x}{x}. \tag{6.8}$$

We want to express these thermodynamic functions in terms of the uniaxial deformation ratio α_1. To accomplish this a relationship must be established between X_0 and α_1. For this purpose we use the relationships (Ref. [1])

$$P(\underset{\sim}{\alpha}) = \underset{\sim}{\alpha}^2 - 3 \tag{6.9}$$

and

$$\underset{\sim}{\alpha}^2 = \underset{\sim}{\alpha}_{\|}^2 + 2\underset{\sim}{\alpha}_{\perp}^2. \tag{6.10}$$

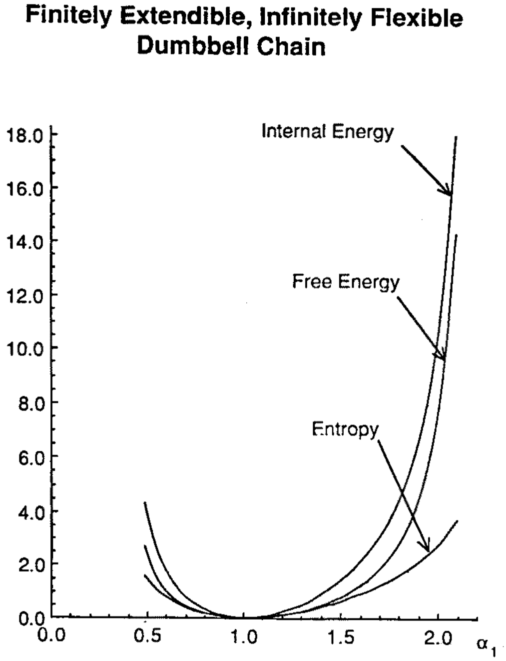
Then, by expressing $\underset{\sim}{\alpha}_{\|}^2$ and $\underset{\sim}{\alpha}_{\perp}^2$ in terms of X_0, we find that

$$P(X_0) = 2 + \frac{30}{X_0^2}\left[1 - \frac{w(X_0)}{W(X_0)}\right] + (N-2)\left\{\frac{3}{X_0}\left[1 - \frac{w(X_0)}{W(X_0)}\right]\right\}^2. \tag{6.11}$$

Finally, by invoking the two constraints (3.8) and (3.9) we can write (6.9) in the form

$$P(\alpha_1) = \alpha_1^2 + \frac{2}{\alpha_1} - 3 \tag{6.12}$$

and also, with the help of (6.11), express X_0 in terms of α_1. This allows us to express the thermodynamic functions in terms of the uniaxial deformation ratio α_1. This procedure produces the results presented in Fig. 8, where the internal energy, free energy and entropy of deformation are plotted *versus* the uniaxial deformation ratio α_1. In Fig. 9 the nominal stress is plotted



Finitely Extendible, Infinitely Flexible Dumbbell Chain

Fig. 8. Internal energy, free energy and entropy of deformation *vs* the uniaxial deformation ratio.

versus the uniaxial deformation ratio and Fig. 10 is a Mooney plot on which the reduced force is plotted *versus* the inverse of the deformation ratio α_1^{-1}.

6.2 The model of a randomly jointed chain

In this model the chain consists of rigid rod segments. The binding potential can be written as

$$\begin{aligned} V(q) = \infty\,;\; & q < q_0 \\ 0\,;\; & q_0 < q_0 < q_0 + \delta q_0 \\ \infty\,;\; & q_0 + \delta q_0 < q\,. \end{aligned} \tag{6.13}$$

The segmental configuration integral then becomes

$$z(\beta,\, \boldsymbol{E}) = \frac{4\pi}{3}\{(q + \delta q_0)^3 W[\beta E(q_0 + \delta q_0)] - q_0^3 W(\beta E q_0)\} \tag{6.14}$$

with $W(x)$ defined by (6.3).

The thermodynamic functions of deformation are given by the formulas

$$\frac{\beta \delta U(\beta,\, \boldsymbol{E})}{N - 1} = 1 - X_0 \coth X_0\,, \tag{6.15}$$

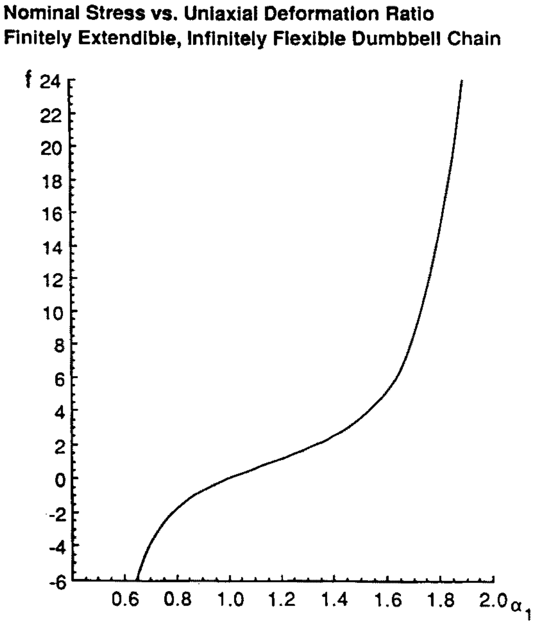


Fig. 9. Nominal stress *vs* uniaxial deformation ratio.

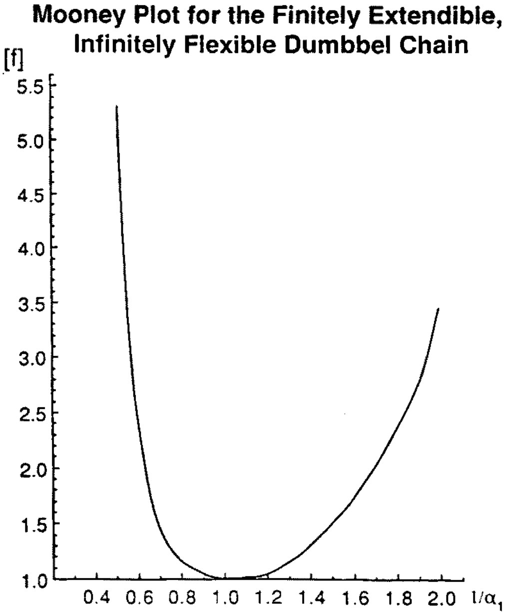


Fig. 10. Reduced force *vs* the inverse of deformation ratio.

$$\frac{\beta\delta F(\beta, \boldsymbol{E})}{N-1} = -\ln w(X_0)\,, \tag{6.16}$$

$$\frac{\delta S(\beta, \boldsymbol{E})}{k(N-1)} = \frac{\beta}{N-1}(\delta U - \delta F)\,. \tag{6.17}$$

The same procedure as before is used to express the function $P(X_0)$ in the form

$$P(X_0) = 3(N-2)\frac{1}{X_0^2}(1 - X_0 \coth X_0)^2\,. \tag{6.18}$$

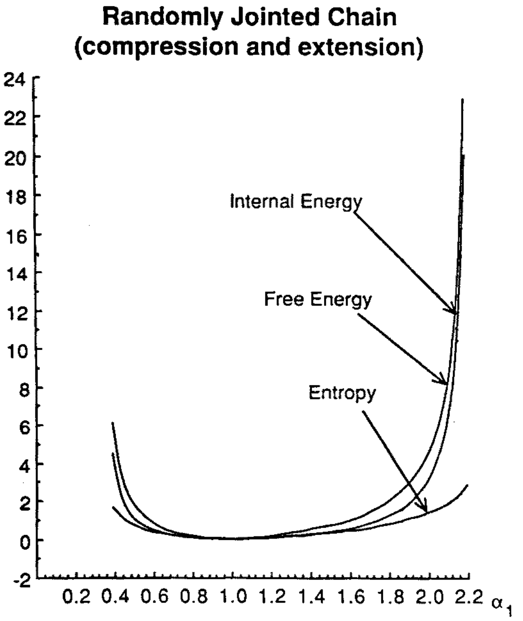


Fig. 11. Internal energy, free energy and entropy of deformation *vs* the uniaxial deformation ratio.

The results are presented in Figs 11, 12 and 13. In Fig. 11 the thermodynamic functions are plotted *versus* the uniaxial deformation ratio. Fig. 12 shows the nominal stress plotted *versus* the uniaxial deformation ratio, and Fig. 13 is the Mooney plot.

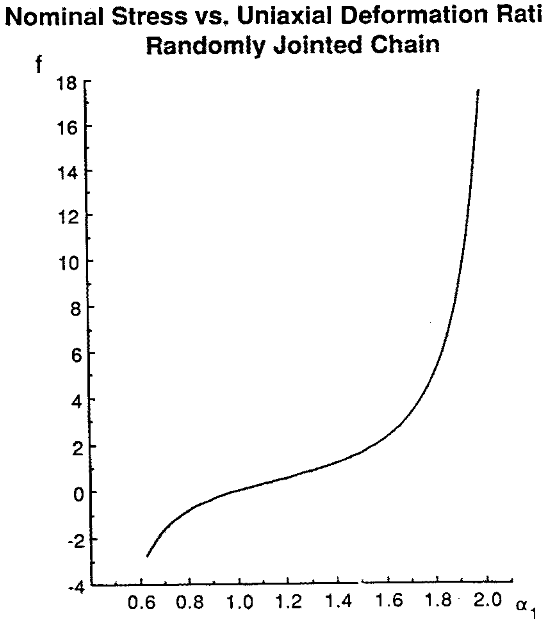

Nominal Stress vs. Uniaxial Deformation Ratio
Randomly Jointed Chain

Fig. 12. Nominal stress *vs* uniaxial deformation ratio.

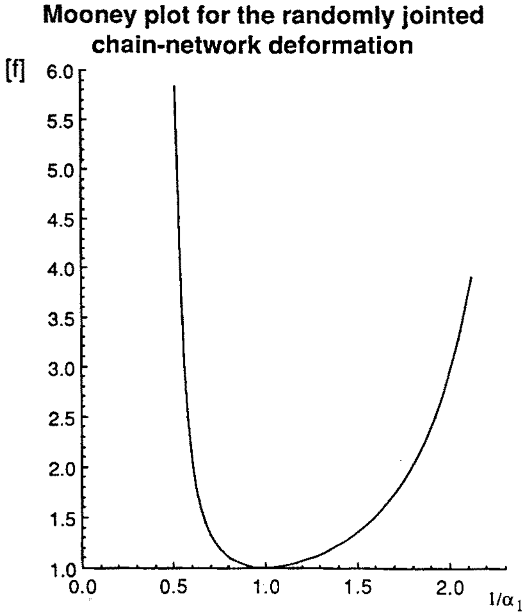

Mooney plot for the randomly jointed
chain-network deformation

Fig. 13. Reduced force *vs* the inverse of the uniaxial deformation ratio (Mooney plot).

6.3 The two-level square-well bonded chain

We now incorporate attractive interactions between neighboring beads. The studies performed by Altenberger and Dahler on the rubber elasticity problem [1, 2] showed that in order to obtain a qualitatively correct description of the deformed rubber, attractive contributions to the interaction potential were essential.

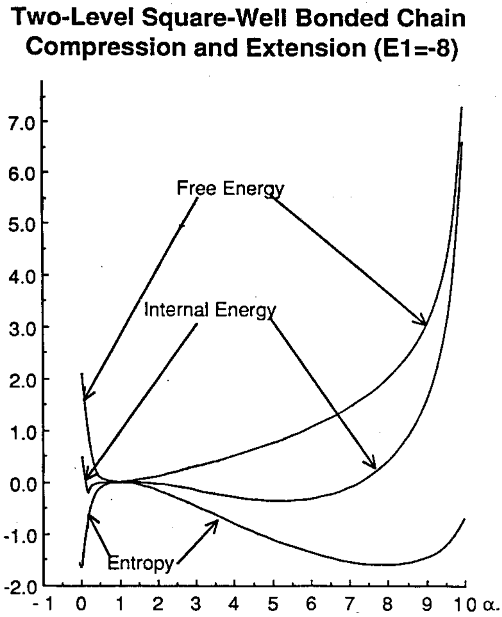


Fig. 14. Internal energy, free energy and entropy of deformation *vs* uniaxial deformation ratio.

The two-level square-well potential can be expressed as follows:

$$\begin{aligned} V(q) = {} & \infty\,;\ q < \sigma_0\,, \\ & V_1\,;\ \sigma_0 \le q \le \sigma_1\,, \\ & V_2\,;\ \sigma_1 < q \le \sigma_2\,, \\ & \infty\,;\ \sigma_2 < q\,. \end{aligned} \tag{6.19}$$

The segmental configuration integral corresponding to this potential is given by the formula

$$z(\beta, E) = \frac{4\pi}{3} e^{-\beta V_1} \left[\sigma_1^3 W(\beta E \sigma_1) - \sigma_0^3 W(\beta E \sigma_0)\right]$$

$$+\frac{4\pi}{3}\mathrm{e}^{-\beta V_2}\left[\sigma_2^3 W(\beta E\sigma_2)-\sigma_1^3 W(\beta E\sigma_1)\right]. \qquad (6.20)$$

The depth of the attractive well, V_1, is chosen to be negative and V_2 is set equal to zero. The three characteristic length parameters $\sigma_i (i = 0, 1, 2)$ can be expressed in units of an arbitrary length a. Calculations were performed for $\sigma_0 = 0.1\,a$, $\sigma_1 = 0.5\,a$ and $\sigma_2 = 2\,a$. The reduced external force $X = \beta E a$ was used as an argument and calculations were performed for the reduced depth $E_1 = \beta V_1 = -8$ (of the attractive well). The same procedure described in the two previous subsections, 6.1 and 6.2, was followed here. This produced expressions for the thermodynamic functions of deformation and the function $P(X_0)$ that were similar to those obtained in preceding subsections. Actually, in the present case we get expressions that are algebraically more complicated. Plots of these are shown in Figs. 14, 15 and 16. From Fig. 14 we see that the behaviour of the free energy is qualitatively the same as before. However, this is not true for the entropy and internal energy. The energy of deformation becomes positive for ranges of α_1, both in extension and compression. Furthermore, the thermoelastic inversion occurs both in extension and compression.

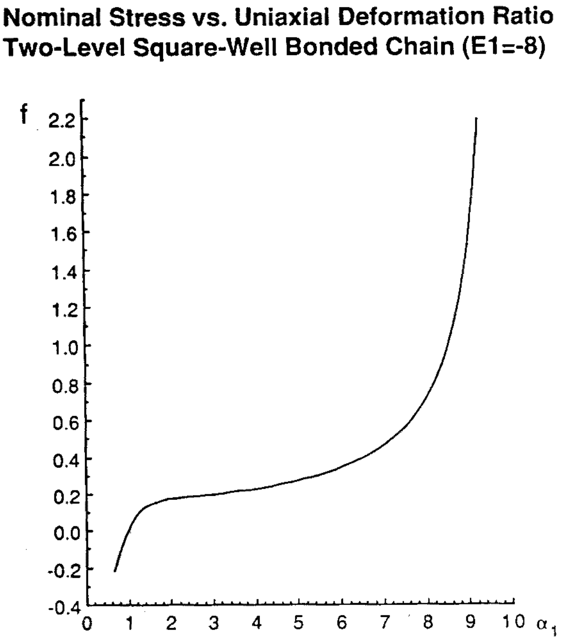


Fig. 15. Nominal stress *vs* uniaxial deformation ratio.

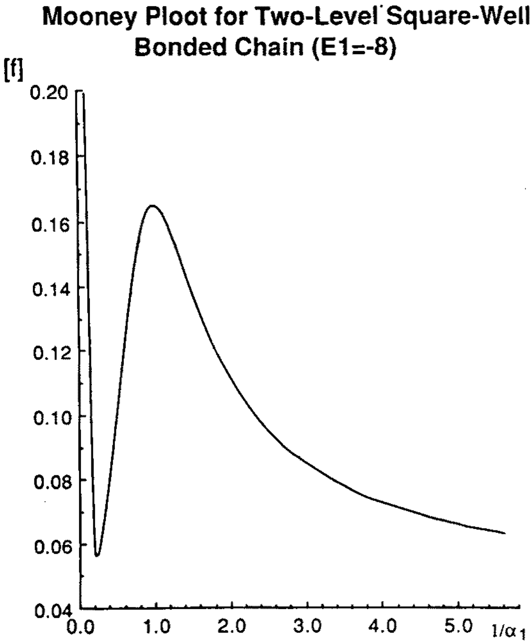


Fig. 16. Reduced force *vs* the inverse of uniaxial deformation ratio (Mooney plot).

7. Conclusions

For equilibrium elastic deformations of rubber-like materials, the new theory developed by Altenberger and Dahler provides results that are consistent with experimental data. In this new theory, based on a well known mechanical model of polymer chains, the thermodynamic and mechanical properties of elastomers are defined very explicitly. As a consequence, it is possible to explain some unclear points of the standard theory.

The results obtained in the present work show that the type of bonds that hold the segments (or beads) together play an essential role with respect to the elastic behaviour of the chain. This can be observed from the differences appearing in the plots of subsection 6.3 in comparison with the plots of subsection 6.1 and 6.2. The introduction of attractive interactions between neighboring beads plays a crucial role in explaining the very unusual behaviour of rubbers, for instance, the thermoelastic inversion and the extensional dependence of the reduced force.

As previously pointed out, the results so far obtained are in very good qualitative agreement with experimental data. Much more could be done to apply and even extend Altenberger and Dahler's theory, but that would be beyond the purpose of this work.

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