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The effect of entanglements in rubber elasticity

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This paper presents a theory of rubber elasticity based on the concept of entanglements. It is shown that for small deformation the molecular mechanism of stretching is dominated by the slippage of chains. Hardening of the rubber at a high deformation is due to inextensibility as described by the tube concept. This free energy of deformation agrees well with experiment. The resulting free energy is

$$\frac{F}{k_{\mathrm{B}}T}=\tfrac{1}{2}N_{\mathrm{c}}\left\{\frac{\sum_{i=1}^{3}(1-\alpha^2)\lambda_i^2}{1-\alpha^2\bar{Z}\lambda_i^2}-\log\left(1-\alpha^2\sum_{i=1}^{3}\lambda_i^2\right)\right\}+$$
$$+\tfrac{1}{2}N_{\mathrm{s}}\left[\sum_{i=1}^{3}\left\{\frac{\lambda_i^2(1+\eta)(1-\alpha^2)}{(1+\eta\lambda_i^2)(1-\alpha^2\Sigma\lambda_i^2)}+\log(1+\eta\lambda_i^2)\right\}-\log(1-\alpha^2\Sigma\lambda_i^2)\right]$$

where α is a measure of the inextensibility and η of the slippage, N_{c} is the number of crosslinks and N_{s} the number of slip links.

(Keywords: rubber elasticity; entanglements; slip link; finite extensibility; large deformations; Rouse modes)

INTRODUCTION

This paper attempts to improve the present theories of rubber elasticity by a detailed treatment of the consequences of entanglements. They form further elastic free energy which gives results which are in quite good agreement with experimental observations. Discussion of the various models of rubber elasticity in the literature are concerned with the calculation of the modulus in certain typical situations and models[1]. Most molecular theories produce a typical sum of square of the extension ratios, $F\sim kT\sum_{i=1}^{3}\lambda_i^2$ for the form of the free energy, but in comparison with the experiments this 'sum of squares law' is not good enough to explain the departures from the linear behaviour[2]. For incompressible material $F\sim\lambda^2+2\lambda^{-1}$ and the force like $\lambda-\lambda^{-2}$, and the well known Mooney Rivlin plot, which plots (force)/$(\lambda-\lambda^{-2})$ against $1/\lambda$ gives a straight line while the experiments show a softening in the low deformation regime and a hardening in the high deformation regime. This softening effect is phenomenologically represented by adding the second invariant of the stress tensor to the sum of squares free energy[2], but this procedure has no molecular basis since it does not correspond to any molecular model. In a single chain representation an explanation for the hardening at higher deformation was offered by the early calculation of Kuhn and collaborators[3], who showed that the entropic force becomes singular if the chain is fully stretched. However a simple study of chain extension shows that far too large an extension is required to bring this mechanism into action.

What conditions are given by a real rubber system? Since a real crosslinked system is very dense we are not able to argue as if we had a single chain limit, because every chain is constrained by the other chains in the environment. These constraints may be assumed to be purely entropic in nature, since this is in accordance to experiments[2]. In polymer dynamics the constraints can be successfully modelled by the reptation tube[4] and give quite good results of viscoelastic properties of polymeric melts. In the static theory of rubber elasticity these constraints are given by the slip link picture[5] which gives a correction to the usual expression of the free energy due to the possibility of slipping by the entanglements between two crosslinks. The stretched rubber has more space for slippage than the unstretched, hence the entropy increases; the experimental data in the small deformation regime can be explained by this model as has been shown recently by Thirion and Weil[6].

What about the tube constraint in a crosslinked system? Here we may argue in the same manner as in the case of viscoelasticity. Crosslinking in the melt fixes the topology of the polymer system[7] and so the tube is fixed also. In the equilibrium state, i.e. no deformation, the tube can be established by the primitive path concept[8], and the slip length of this primitive path (which can be understood as the centre of the tube) is given by the fixed number of entanglements between two crosslinks and so by the concentration of material present. The path length of the polymer is clearly larger as the path length of the tube (see *Figure 2*), so that a large amount of the real chain is 'slack'.

If we deform the rubber system the tube will always get longer[9]; we can only deform until all the slack is used up. Thereafter there is no free polymer present, the polymer is taut and no further conformations of the constrained polymer are available. Therefore the number of

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configurations tends to unity and this gives rise to the hardening in the high deformation limit. This happens long before the extension, which would fully extend the polymer between crosslinks, for now only the polymer between entanglements need be fully extended. Both effects have the *same* origin. We should then be able to bring both regimes together in order to calculate a free energy from which we can deduce an equation of state which can be used for experimental analysis of various properties of rubbers.

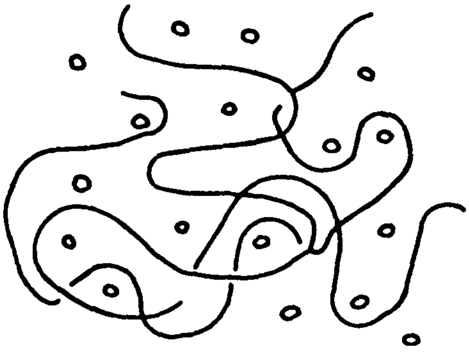
These effects of entanglements will now be discussed in more detail. In the next section we will give a discussion of the slip link model by means of a simple Flory segment argument rather than the replica calculation of Ball *et al.*[5]. In the third section we discuss the tube model for rubbers in order to obtain the high deformation limit and the finite extensibility. Both deformation regimes are connected in section 4 using different scales of the Rouse model to define the tube and the slippage. A brief discussion of the resulting free energy and the resulting force and discussion with experiments will be given in section 5.

THE FLORY SEGMENT ARGUMENT FOR THE SLIP LINK FREE ENERGY

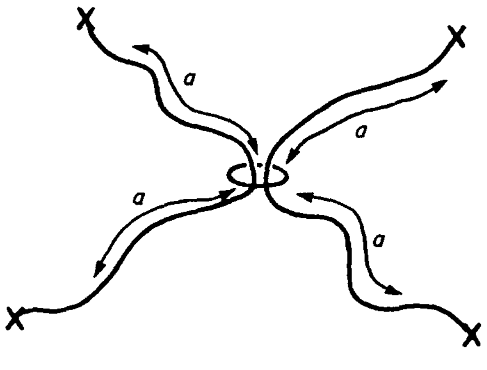
The classical theory of rubber elasticity contains the unrealistic assumption that the chains can pass through each other (i.e. see ref. 2 and references therein). The only constraints are the crosslinks which held the phantom chains together. The classical theories of rubber elasticity also neglect repulsive forces which give rise to the bulk modulus[10].

In this paper the material will also be considered incompressible so we use also a density constraint rather than repulsive forces. We will deal with the pure slip link contribution to the rubber elasticity.

In a recent paper the effect of the slip link was calculated by means of the replica trick (Ball *et al.*[5]). The slip link concept is a simplification of the real entanglement constraint which replaces the 'real' situation



by a simpler situation[4,5,11]



in which the ring can move along the chains by an arc length a.

The total number of slip links (assumed to be given) will occur as a parameter in the theory, which can be estimated from the plateau modulus. This problem can be calculated using the replica trick in order of averaging the free energy according to a number of frozen degrees of the freedom represented by the crosslinks[7].

Assuming that the chains are Gaussian they can be expressed by the Wiener representation:

$$\mathcal{N}\exp\left\{-\frac{3}{2l}\int_0^L R'^2(s)\mathrm{d}s\right\} \tag{2.1}$$

where $\mathcal{N}$ is the normalization and $R(s)$ the locus of a chain in the intrinsic representation. If we have chains $R_i(s_i)$ where s_i labels the ith link the crosslinks are given by

$$\underset{\sim}{R}_i(s_i^j)=\underset{\sim}{R}_j(s_j^i) \tag{2.2}$$

i.e. there is a constraint

$$\prod_{\text{crosslinks}} \delta(\underset{\sim}{R}_i(s_i^j)-\underset{\sim}{R}_j(s_j^i)) \tag{2.3}$$

present in the partition integrals of the problem. If the link slips by an amount a then the constraint has between $s_i^j \pm a$ on chain i and $s_j^i \pm a$ on chain j. The problem is that s_i^j is permanent but the condition is now

$$\frac{1}{4a^2}\int_{-a}^{+a}\mathrm{d}\varepsilon_i\int_{-a}^{+a}\mathrm{d}\varepsilon_j\delta(\underset{\sim}{R}_i(s_i^j+\varepsilon_i)-\underset{\sim}{R}_j(s_j^i+\varepsilon_j)) \tag{2.4}$$

To build in these constraints is a difficult task and the replica method used by Deam and Edwards[7] for crosslinks and Ball *et al.*[5] for slip links offers a clean way to do the problem, but does have heavy algebraic complexity. Therefore in this paper we use the much cruder method of Flory, which will give the essential features, although by ignoring fluctuations this is well known to overestimate the free energy by a factor of 2.

If there are no slip links, it was shown by Deam and Edwards[7] that the result of the replica method is that given by James and Guth for the phantom network with all its suspect properties of collapsing etc. Hence the minimum of

$$F=k_BT\sum_{i=1}^{3}\lambda_i^2 \tag{2.5}$$

is given by $\lambda_i=0$ *without* any further constraint.

We wish in this paper to present a crude but nevertheless adequate theory to cover not only the slippage but also the inextensibility. How can we do this? It turns out that generalizing the very simplest model of rubber elasticity, that of Flory's affine deformation of crosslinks model, can be very instructive. To see this we go back to the elementary expression for the probability distribution for a Gaussian chain

$$P(\underset{\sim}{R},L)=\left(\frac{3}{2\pi lL}\right)^{3/2}\exp\left\{-\frac{3\underset{\sim}{R}^2}{2lL}\right\} \tag{2.6}$$

which is separable into the three cartesian axis

$$P(\underset{\sim}{R})=\prod_{i=1}^{3}P(X_i) \tag{2.6a}$$

with

$$P(X_i)=\left(\frac{3}{2\pi lL}\right)^{1/2}\exp\left\{-\frac{3X_i^2}{2lL}\right\}$$

In the theory cited above we introduced the slip link constraint by a modified crosslink which allows the slippage along the arc length of the polymer. We try to model the slip link process by the following integral

$$P(X_i)=\int \mathrm{d}\varepsilon P(\varepsilon)\frac{\exp\left\{-\frac{3X_i^2}{2l(L+\varepsilon)}\right\}}{[\frac{1}{3}2l(L+\varepsilon)]^{1/2}} \tag{2.7}$$

while ε is the slippage and $P(\varepsilon)$ is the probability of the arc length of the slippage. For simplicity we use for the probability distribution $P(\varepsilon)$ a rectangular one and we rewrite equation (2.7) as

$$P(X_i)=\int_{-a}^{+a}\frac{\mathrm{d}\varepsilon}{2a}\exp\left\{-\frac{3X_i^2}{2l(L+\varepsilon)}-\tfrac{1}{2}\log(L+\varepsilon)\right\} \tag{2.8}$$

This integral must have the property that is normalized for every value of ε.

It is not easy to maintain the normalization unless we are able to construct an 'effective Gaussian' form for the result of this intregration. After changing $X_i\to\lambda_iX_i$ we expand equation (2.8). λ_i are the principal values of the deformation tensor

$$P(\lambda_iX_i)=\mathcal{N}\int_{-a}^{+a}\frac{\mathrm{d}\varepsilon}{2a}\exp\left\{-\frac{3}{2lL}\sum_{i=1}^{3}\lambda_i^2X_i^2\left(1-\frac{\varepsilon}{L}+\left(\frac{\varepsilon}{L}\right)^2\right)\right.$$
$$\left.-\frac{3}{2}\left(\frac{\varepsilon}{L}-\frac{\varepsilon^2}{2L^2}\right)\right\} \tag{2.9}$$

for averaging the slippage we expand each of the exponentials in ε and ε^2 and find

$$P(\lambda_iX_i)=\mathcal{N}\int_{-a}^{+a}\frac{\mathrm{d}\varepsilon}{2a}\exp\left\{-\frac{3}{2lL}\sum_{i=1}^{3}\lambda_i^2X_i^2\right\}\left\{1+\frac{3}{2lL}\left(\frac{\varepsilon}{L}\right)\sum_{i=1}^{3}\lambda_i^2X_i^2+\right.$$
$$+\frac{1}{2}\left(\frac{3}{2lL}\right)^2\left(\sum_{i=1}^{3}\lambda_i^2X_i^2\right)^2\left(\frac{\varepsilon}{L}\right)^2-\frac{3}{2lL}\left(\sum_{i=1}^{3}\lambda_i^2X_i^2\right)\left(\frac{\varepsilon}{L}\right)^2$$
$$-\frac{3}{2}\left(\frac{\varepsilon}{L}\right)-\frac{3}{2}\left(\frac{3}{2lL}\right)\sum_{i=1}^{3}\lambda_i^2X_i^2\left(\frac{\varepsilon}{L}\right)^2+\frac{15}{8}\left(\frac{\varepsilon}{L}\right)^2$$
$$+O\left[\left(\frac{\varepsilon}{L}\right)^3\right]+O\left[\left(\frac{\varepsilon}{L}\right)^4\right]$$

We perform the integral over the slippage ε. The odd terms in ε vanish and we are left with the even terms. We call for a moment $\int_{-a}^{+a}(\mathrm{d}\varepsilon/2a)\varepsilon^2=\overline{\varepsilon^2}$ and find for the probability $P(\lambda_iX_i)$

$$P(\lambda_iX_i)=\mathcal{N}\exp\left\{-\frac{3}{2lL}\sum\lambda_i^2X_i^2\right\}\left\{1+\frac{\overline{\varepsilon^2}}{L^2}\frac{1}{2}\left(\frac{3}{2lL}\right)^2\left(\sum_i\lambda_i^2X_i^2\right)^2\right.$$
$$\left.-\frac{5}{2}\left(\frac{3}{2lL}\right)\sum_{i=1}^{3}\lambda_i^2X_i^2+\frac{15}{8}\right. \tag{2.10}$$

We calculate the free energy by the usual equation

$$F(\underset{\sim}{\lambda})=-\int \mathrm{d}^3R\,P(\underset{\sim}{R},L)\log P(\underset{\sim}{\lambda}\underset{\sim}{R},L) \tag{2.11}$$

where $P(\underset{\sim}{R},l)$ is the distribution function of the undeformed state. Since we are working only to order $\overline{\varepsilon^2}$ we can use the usual Gaussian for $P(\underset{\sim}{R},L)$.

Performing the integration given in equation (2.11) we find

$$F=\frac{1}{2}\sum_{i=1}^{3}\lambda_i^2-\frac{\overline{\varepsilon^2}}{8L^2}\left\{\left(\sum_{i=1}^{3}\lambda_i^2\right)^2+\ 2\sum_{i=1}^{3}\lambda_i^4-10\sum_{i=1}^{3}\lambda_i^2+15\right\} \tag{2.11a}$$

If we compare this with the result given by the rigorous calculation (Ball *et al.*[5])

$$F=\frac{1}{2}\sum_{i=1}^{3}\left\{\frac{\lambda_i^2(1+\eta)}{1+\eta\lambda_i^2}+\log(1+\eta\lambda_i^2)\right\} \tag{2.12}$$

We see (after some algebra) that equation (2.11a) fits the exact result equation (2.12) to order $(\lambda_i-1)^2$ if we require for $\eta=\overline{\varepsilon^2}/L,\eta$ is a measure for the slippage.

We have now shown that the result of the calculation can be modelled by a simple Flory segment argument, provided that a factor $\frac{1}{2}$ is included to allow for non-affine deformation of the links. It is well known that the Flory argument gives twice the correct value and the paper of Ball *et al.*[5] produces the correct front factor.

For crosslinks, of course, we get the same formula because a crosslink has zero slip, so that in this limit the slip link behaves as a crosslink:

$$F=\tfrac{1}{2}\sum_{i=1}^{3}\lambda_i^2 \tag{2.13}$$

The final free energy of the total system is given by the sum

$$F=\tfrac{1}{2}N_c\sum_{i=1}^{3}\lambda_i^2+\tfrac{1}{2}N_s\sum_{i=1}^{3}\left\{\frac{\lambda_i^2(1+\eta)}{1+\eta\lambda_i^2}+\log(1+\eta\lambda_i^2)\right\} \tag{2.14}$$

This free energy has been used by Thirion and Weil[6] to analyse data in deformed rubbers and they find good agreement with this theory. We can also use equation (2.14) to calculate the force in maximal stretching (using the incompressibility condition $\Pi\lambda_i=1$ and hence the

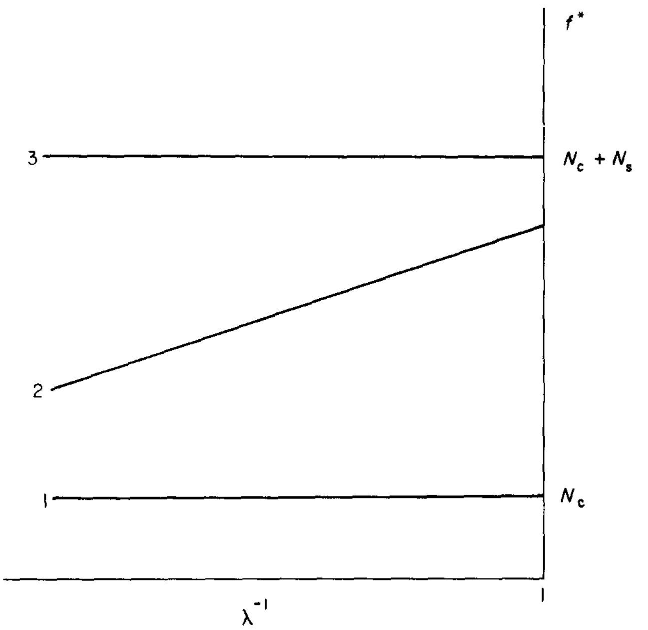


Figure 1 Mooney–Rivlin plot of the reduced force $f^*/(\lambda-\lambda^{-2})$ *versus* λ^{-1} from equation (2.14). (1) Network in which the entanglements act as crosslinks with zero slip ($\eta=0$). (2) Real situation ignoring inextensibility (here with $\eta=0.2$) a number given by the replica theory (Ball *et al.*[5]). (3) Phantom network with a vanishing number slip links, or more realistic, entangled network ($N_s\neq0$) but large slippage ($\eta\to\infty$).

minimum of $F=\lambda+2\lambda^{-2}$ is *now* at $\lambda=1$) which gives

$$f=N_cD+N_s\left(\frac{\lambda}{1+\eta\lambda^2}-\frac{1}{(\lambda+\eta)^2}+\eta\frac{D\lambda}{(1+\eta\lambda^2)(\lambda+\eta)}\right)$$

where $D=\lambda-\lambda^{-2}$ which is conveniently plotted in the Mooney–Rivlin representation $f/(\lambda-\lambda^{-2})$, λ^{-1}. For a discussion of the influence of the parameter we fix the ratio N_c/N_s by a condition $N_s+N_c=1$. In *Figure 1* we see the various ranges involved.

We can see the good agreement with any experimental observations for a low deformation, and the completely wrong behaviour in the high deformation regime, where a sharp rise of the force is expected as in *Figure 4* below.

So we now go to an analysis suggested by the idea of the tube (which is formed by the entanglements and therefore the slip links) which implies the finite extensibility of the chains.

INEXTENSIBILITY

Measurements of the force–extension relationship of rubbers show large deformations with a sharp upturn before the fracture of the sample. Let us first assume a very dilute system for illustration. Consider a single ideal chain under external force. In the low deformation regime the force must be linear in the elongation which is consistent with the simple Gaussian theory of rubber elasticity. At higher deformation this approximation fails since the conformation of the chain is no longer Gaussian. For this purpose Kuhn and Gruen[3] noted that the finite extensibility of the single chain in this model is expressed by using the inverse Langevin function to calculate the force of a single chain

$$f=\frac{3k_BT}{l}\mathscr{L}^{-1}\left(\frac{r}{L}\right) \tag{3.1}$$

which has the properties of the linearity for $r\ll L$ and a singularity for $r=L$. The physical reason for this singularity is given by the fact that at full extension no further conformation for the chain is available so that the probability function goes to zero, unlike the Gaussian distribution function.

Extending this idea of Kuhn and Gruen to a network of such chains gives rise to the non-Gaussian theory of rubber elasticity with a singularity of the force at

$$\lambda_{\max}=\left(\frac{L}{l}\right)^{1/2}$$

for the dilute regime (see ref. 2). The quantity (L/l) is the number of statistical segments of the polymer chain which is extremely large so that the maximum extensibility is much too large for a real system.

We therefore go first to the dense regime of a melt. The viscoelastic properties of a polymer have been extensively studied and many of their properties can be explained by the concept of a tube generated by the other chains surrounding any one polymer. For details of the tube concept see refs. 9, 11 and 12. In this paragraph we apply the concept of the tube to the problem of rubber elasticity in the non-dilute regime. Therefore, when we crosslink the melt we fix the topology of this dense highly entangled polymer system, and we can argue that there is a topological skeleton of the system consisting of the tubes containing each polymer. We can make the tube precise by the concept of the primitive path which can be understood as the centre of this tube (see also ref. 8) representing the dense crosslinked system by the situation given in *Figure 2*. In this Figure the dots represent other chains perpendicular to the paper plane. The entanglements define the primitive path as a random walk of step length a while the real path of the polymer is much larger than the primitive path. The reference chain is assumed to be crosslinked at the endpoints so that no reptation is possible and the tube is fixed in space. If the primitive path is long enough it can be modelled by a random walk and its end to end distance is given by

$$\langle R^2\rangle=N_{pp}a^2=L_{pp}a \tag{3.2}$$

where N_{pp} is the number of primitive path segments, a the step length and L_{pp} the contour length of the primitive path. Since the end-to-end distance of the real polymer and the primitive path are the same, we obtain the relation

$$N_{pp}a^2=Nl^2$$

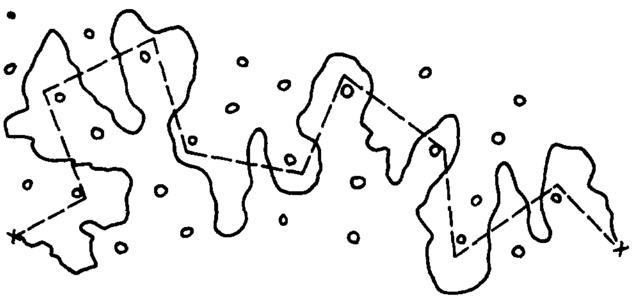


Figure 2 Primitive path model for a crosslinked polymer chain. The circles are chains perpendicular to the paper plane. The dashed line is the centre of the tube (the primitive path, a random walk with the step length a). The polymer is given by the continuous line, and has a much larger contour as the primitive path

or

$$\frac{a^2}{l^2}=\frac{N}{N_{\text{pp}}}\ , \quad \frac{L}{L_{\text{pp}}}=\frac{a}{l} \tag{3.3}$$

where L is the length of the polymer chain and l the step length of the polymer random walk.

The difference $L-L_{\text{pp}}$ of the arc length has gone into the slack which forms the deviations from the primitive path. At the deformation process the primitive path length is increased, and the difference $(L-\tilde{L}_{\text{pp}})$ becomes smaller as some amount of the slack is removed. The deformation then can be increased until all the slack is used up. The deformation of the primitive path length is given by:

$$\tilde{L}_{\text{pp}}=\left(\tfrac{1}{3}\sum_{i=1}^{3}\lambda_i^2\right)^{1/2}L_{\text{pp}} \tag{3.4}$$

which is the Jacobian of a deformed vector $\underset{\sim}{R}'(s)$ (the tangent vector along the path). The maximum extension is then given by the case of full exhaustion of the slack:

$$0=L-L_{\text{pp}}\left(\tfrac{1}{3}\sum_{i=1}^{3}\lambda_i^2\right)^{1/2}_{\max} \tag{3.5}$$

From this it follows that, in a dense system, the maximum elongation is not given by the properties of the total chain, but by the amount of chain in the slack per step of the primitive path. This interesting fact can also be used to determine the tube diameter a in crosslinked systems by measuring the maximum elongation according to equation (3.5).

How can we bring these intuitive ideas into more elaborate mathematics? The mathematical definition of the tube constraint can be modelled by various methods. The most obvious way is to add a harmonic constraint to the Wiener integral and calculate the properties of

$$\left\langle \exp\left\{-\frac{l}{a^4}\int_0^{L_{\text{pp}}} \mathrm{d}s\left[\underset{\sim}{r}(s)-\underset{\sim}{R}\left(\frac{sl}{a}\right)\right]^2\right\}\right\rangle \tag{3.6}$$

where L_{pp} is the tube length between two crosslinks, $\underset{\sim}{r}(s)$ is the real path of the polymer and the tube is given by $R(sl/a)$, the factor l/a^4 is chosen so that the tube diameter $\langle(R(sl/a)-r(s))^2\rangle=a^2$. Similar ideas for the definition of the tube are considered in the next paragraph.

Here we restrict our considerations on the statistics of the slack and estimate the probability distribution of the primitive path.

It is well known that the probability distribution of the slack is given by[12-15]

$$P(\Delta_i)=\frac{1}{\Delta_0}\exp\left\{-\frac{\Delta_i}{\Delta_0}\right\} \tag{3.7}$$

We model the rubber chain by N_{pp} primitive path steps and N_{pp} excursions or slack with an arc length Δ_i. The joint probability of the slack in each segment is then given by

$$P_{\text{s}}=\left(\frac{1}{\Delta_0}\right)^{N_{\text{pp}}}\exp\left\{-\frac{1}{\Delta_0}\sum_{i=1}^{3}\Delta_i\right\} \tag{3.8}$$

The chain length is

$$L=L_{\text{pp}}+\sum_{i=1}^{N_{\text{pp}}}\Delta_i \tag{3.9}$$

and from these two equations we are able to calculate the probability distribution of the primitive path

$$\begin{aligned}P(L_{\text{pp}},L)&=\left\langle\delta\left(L-L_{\text{pp}}-\sum_{i=1}^{N_{\text{pp}}}\Delta_i\right)\right\rangle\\&=\int\cdots\int\prod_{i=1}^{N_{\text{pp}}}\mathrm{d}\Delta_i P_{\text{s}}\delta\left(L-L_{\text{pp}}-\sum_{i=1}^{N_{\text{pp}}}\Delta_i\right)\end{aligned} \tag{3.10}$$

First we evaluate this integral after the usual parametrization of the δ-function

$$\begin{aligned}P(L,L_{\text{pp}})=&\int_{-\infty}^{+\infty}\frac{\mathrm{d}\gamma}{(2\pi)}\int\cdots\int\prod_{i=1}^{N_{\text{pp}}}\mathrm{d}\Delta_i\frac{1}{\Delta_0^{N_{\text{pp}}}}\\&\times\exp\left\{-\sum_{i=1}^{N_{\text{pp}}}\frac{\Delta_i}{\Delta_0}+i\gamma\left(L-L_{\text{pp}}-\sum_{i=1}^{N_{\text{pp}}}\Delta_i\right)\right\}\end{aligned} \tag{3.11}$$

or

$$P(L,L_{\text{pp}})=\int_{-\infty}^{+\infty}\frac{\mathrm{d}\gamma}{2\pi}e^{i\gamma(L-L_{\text{pp}})}\frac{1}{(1+i\gamma\Delta_0)^{N_{\text{pp}}}} \tag{3.12}$$

This can be written as

$$P(L,L_{\text{pp}})=\oint_{\substack{\text{steepest}\\\text{descent}}}\frac{\mathrm{d}\gamma}{2\pi i}\exp\{i\gamma(L-L_{\text{pp}})-N_{\text{pp}}\log(1+i\gamma\Delta_0)\} \tag{3.13}$$

and since N_{pp} is very large, this can be approximated by the method of steepest descent value, giving

$$P(L,L_{\text{pp}})=\frac{1}{\Delta_0(N_{\text{pp}}2\pi)^{1/2}}\exp\left\{-\frac{(L-L_{\text{pp}}-\Delta_0N_{\text{pp}})^2}{2N_{\text{pp}}\Delta_0^2}\right\} \tag{3.14}$$

Defining

$$\overline{L_{\text{pp}}}=L-N_{\text{pp}}a \tag{3.15}$$

and replacing

$$N_{\text{pp}}=\frac{1}{\Delta_0}(L-\bar{L}_{\text{pp}}) \tag{3.16}$$

the above probability function can be written as

$$P(L,L_{\text{pp}})=\frac{1}{\Delta_0^{1/2}(L-\bar{L}_{\text{pp}})^{1/2}}\exp\left\{-\frac{(L-\bar{L}_{\text{pp}})^2}{2\Delta_0(L-\bar{L}_{\text{pp}})}\right\} \tag{3.17}$$

From the equations (3.3) and (3.15) we can estimate

$$\Delta_0=\frac{a^2}{l}-a \tag{3.18}$$

So in our representation the amount of slack chain is not exactly a random walk with mean square end-to-end distance a^2 and arc length Δ_0. This can be true as long as the chain does not leave the tube by this procedure. As long as $(a/l) \gg 1$ we get $\Delta_0 \approx a^2/l$ and the final answer is given by equation (3.17).

If we take the full expression of Δ_0 according to equation (3.19) we find

$$P \sim \frac{1}{L-\bar{L}_{\rm pp}} \exp\left\{ -\frac{(L_{\rm pp}-\bar{L}_{\rm pp})^2}{2(L-\bar{L}_{\rm pp})^2} \right\} \tag{3.19}$$

the singularity in the same place, but with a rather different structure.

The form of equation (3.17) has been given by Edwards[8]. Calculating the resulting free energy with the aid of equation (2.11) we find for the free energy, dropping all deformation independent terms:

$$F = \tfrac{1}{2}N_{\rm c} \left\{ \frac{\sum_{i=1}^{3} \lambda_1^2(1-\alpha)}{\left(1-\frac{\alpha}{3^{1/2}}\left(\sum_{i=1}^{3}\lambda_i^2\right)^{1/2}\right)^z} + z\log\left(1-\frac{\alpha}{3^{1/2}}\left(\sum_{i=1}^{3}\lambda_i^2\right)^{1/2}\right) \right\} \tag{3.20}$$

with $z=1, 2$ according to equation (3.17) or (3.19).

The parameter α is given by

$$\alpha = \left(\frac{l}{a}\right) \tag{3.21}$$

The resulting force of this free energy has been studied by Vilgis and Kilian[16], and there it was found that it fitted large deformation data with the parameter α being about 0.1 for commercial rubbers.

The Mooney plot of this model in uniaxial extension is given in *Figure 3* and we see the correct behaviour for large extensions but it is wrong at low deformations.

From these two different considerations we learn the following: The complete deformation behaviour of rubbers could be understood in the total range of deformation by *basically the same model.* In the low deformation regime the entanglements are responsible for the softening due to the slippage process, for high deformations the tube constraint correctly quantifies inextensibility.

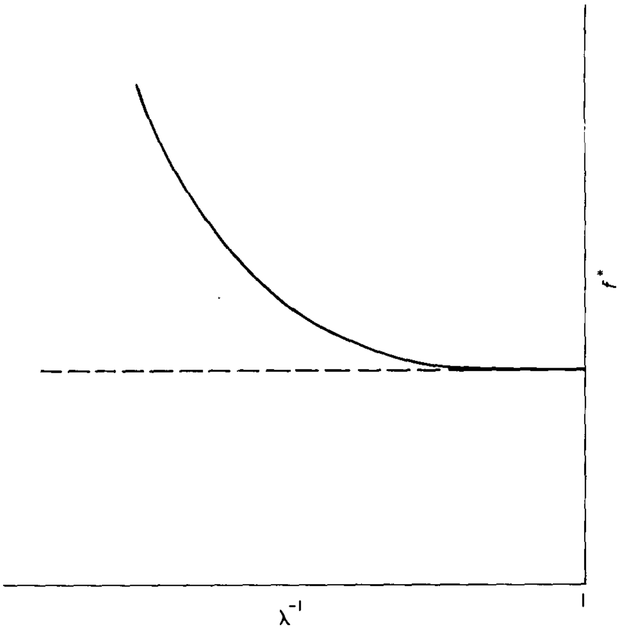


Figure 3 Principal Mooney–Rivlin plot of the force resulting from equation (3.20) with $z=1$

In the next section we put together a more detailed model which connects both processes in order to calculate the final free energy of a deformed rubber.

THE USE OF ROUSE MODES IN MODELLING RUBBER ELASTICITY

As we have now seen entanglements can explain the behaviour for both deformation regimes. We want to use the concept of the tube, generated by the entanglements, to bring both deformation regimes together. The problem in this stage is then to find an amenable mathematical formulation for the tube. A convenient way is to use the dynamics of a single chain. The most simple case is the dynamics of an isolated chain, first given in the famous paper by Rouse[17]. Consider first a diffusing particle, the long time motion of which is governed by the diffusion equation

$$\{\partial_t - D\nabla^2\}P((\underset{\sim}{x},t)=0 \tag{4.1}$$

If a potential is present, say $V(x)$, the equilibrium distribution will be given by

$$P_0 = e^{\beta(F-V(\underset{\sim}{x}))}, \beta^{-1} = k_{\rm B}T$$

This modifies equation (4.1) to

$$\left\{\partial_t - D\frac{\partial}{\partial \underset{\sim}{x}}\left(\frac{\partial}{\partial \underset{\sim}{x}} + \beta\frac{\partial V}{\partial \underset{\sim}{x}}\right)\right\}P=0 \tag{4.2}$$

which is a kind of Fokker–Planck equation.

In the case of a single chain, the equilibrium distribution is given by

$$P_0[\underset{\sim}{r}(s)] = \mathcal{N}\exp\left\{-\frac{3}{2l}\int_a^L {\rm d}s\left(\frac{\partial \underset{\sim}{r}}{\partial s}\right)^2\right\} \tag{4.3}$$

and the exponent acts as a potential so we write for the diffusion equation

$$\left[\partial_t - \int_0^L {\rm d}s\frac{\partial}{\partial \underset{\sim}{r}(s)}D\left\{\frac{\partial}{\partial \underset{\sim}{r}(s)} - \frac{3}{l}\underset{\sim}{r}''(s)\right\}\right]P=0 \tag{4.4}$$

which is the Rouse equation, represented in the continuous notation by a functional differential equation. It is more convenient to write it in terms of the Rouse modes which are the Fourier transform of $\underset{\sim}{r}(s)$. Strictly speaking there is a boundary condition for the dynamics of a single chain with free ends, but for our purposes it is valid to use the familiar complex (i.e. cyclical) notation

$$\underset{\sim}{r}(s) = \sum_{q=1}^{\infty} e^{iqs}\underset{\sim}{r}_q \tag{4.5}$$

Substituting this in the above equations the equilibrium function reads

$$P_0(\{r_q\}) = \mathcal{N}\exp\left\{-\frac{3}{2l}\frac{1}{2\pi}\sum_{q=1}^{\infty} q^2|r_q|^2\right\} \tag{4.6}$$

and in terms of the Rouse modes one has

$$\left\{\partial_t-\sum_q\frac{\partial}{\partial r_q}D\left(\frac{\partial}{\partial r_q}+\frac{3q^2}{2\pi l}r_q\right)\right\}P=0 \tag{4.7}$$

This equation is quite useful because different length scales, represented by q, can be studied separately. It is worth noting that equation (4.7) can be solved exactly by transforming it to Hermite's equation so the similarity to the harmonic oscillator will be recognized. This equation will now be used to divide the problem into two length scales, and it will be used also to define *new* length scales which should be introduced to the problem. For this purpose we look at the physical meaning of equation (4.5). $r(s)$ defines the path of the polymer in real space. Since *all* Fourier components are present (the range of q goes to infinity) this is a function which is capable of being arbitrarily abrupt in its changes of direction. If we now delete the range of q values, and consider

$$R(s)=\sum_{q=1}^{q_0}r_q e^{iqs} \tag{4.8}$$

we smooth the path and remove changes over a scale $s<q_0^{-1}$. The resulting curve can be identified with the primitive path provided that q_0 is taken to a value proportional to a^{-1}. Notice that in the Rouse equation the different q modes are associated with damping of time $\sim q^{-1}$. Thus we can find τ over which modes $q^2>1/\tau$ are excited but $q^2<1/\tau$ are not. If we take τ to be q_0^{-2} in effect we can effect the cut off of equation (4.8). We propose then to take the joint probability of the primitive path and the polymer to be the joint probability of an initial path $R_1(q<q_0)$ and a final path $R_2(q<q_0)$ which is the value taken after the time τ. For $q>q_0 R(q)$ is free all the time.

Therefore, we need to solve the Rouse equation under the condition that the polymer at $t=0$ has a form $R_1(q)$ and at $t=\tau$ has the form $R_2(q)$. We therefore transform the Rouse equation to Hermite's equation by the ansatz:

$$P(\{r_q\})=\exp\left\{-\frac{1}{2\pi}\frac{3}{2l}\sum_q|r_q|^2q^2\right\}Q(\{r_q\}) \tag{4.9}$$

The resulting equation for Q is precisely the equation for a harmonic oscillator

$$\left[\partial_t-D\left\{\sum_q\frac{\partial^2}{\partial r_q\partial r_{-q}}-\frac{1}{4}\left(\frac{3}{2l}\right)^2q^2|r_q|^2+\frac{3}{2l\pi}\frac{1}{2}q^2\right\}\right]Q=0 \tag{4.10}$$

The Green function to this equation is well known[18] and is given by

$$\begin{aligned}Q(\{R_1,R_2\})=&\prod_q\left(\frac{Dq^2t}{\sinh Dq^2t}\right)^{3/2}\\&\times\exp\left\{-\tfrac{1}{2}\sum_q\frac{(R_{q1}^2+R_{q2}^2)\cosh Dq^2t-2R_{q1}R_2}{2\sinh Dq^2t}\right\}\end{aligned} \tag{4.11}$$

The final solution of the Rouse equation is given by putting equations (4.9) and (4.11) together. We now choose the time τ so that the mean distance $\langle(R_{1q}-R_{2q})^2\rangle$ is given by the tube diameter a^2 and bring this new length scale into the problem by putting

$$Dq^2\tau=(q/q_0) \tag{4.12}$$

This relates q_0 to the tube diameter by

$$\frac{l}{a}q_0=\frac{1}{a}\frac{l}{a} \tag{4.13}$$

the same expression given by the mean value of the arc length of the slack Δ_0 in equation (3.18).

Having defined the new length scale we are now able to rewrite the solution of the Rouse equation in the following form

$$\begin{aligned}P(r,R,q)\sim&\exp\left\{-\tfrac{1}{2}\sum_{q=q_0}^{\infty}\frac{3}{2l}q^2|r_q|^2\right\}\\&\times\prod_{q=1}^{q_0}G(r_q,R_q)\exp\left\{-\tfrac{1}{2}\sum_{q=1}^{q_0}\frac{3}{2l}q_2|R_q|^2\right\}\end{aligned} \tag{4.14}$$

where we are now using r_q for the polymer instead of R_1 and R_q for the primitive path instead of R_2.

The first term is the probability distribution for the modes of a free polymer. The second term correlates those modes having $q<q_0$ with the primitive path R_q. The primitive path itself has only modes $q<q_0$, and these have the distribution of the third term, i.e. that of the first q_0 modes of a free polymer. If we integrate out all R_q we must be left with a free polymer; if we integrate out all the r_q we must be left with the first q_0 modes of a free polymer, i.e.

$$\begin{aligned}P[R_q]&=\int d[r_q]P([r_q,R_q,q_0])\\&=\mathcal{N}\exp\left\{-\frac{3}{2l}\frac{1}{2\pi}\sum_{q=1}^{q_0}q^2|R_q|^2\right\}\end{aligned}$$

and

$$\begin{aligned}P[r_q]&=\int d[R_q]P([r_q,R_q,q_0])\\&=\mathcal{N}\exp\left\{-\frac{3}{2l}\frac{1}{2\pi}\sum_{q=1}^{\infty}q^2|r_q|^2\right\}\end{aligned} \tag{4.16}$$

With these equations we can now express and modify inextensibility and slippage.

As we have seen in the previous sections there is a catastrophe in the entropy at a certain deformation. In our equations above there is no singularity in the mean entropy given by

$$\langle S\rangle=\left\langle\frac{3}{2l}\int ds\,R'^2(s)\right\rangle=\left\langle\frac{3}{2l}\frac{1}{2\pi}\sum_{q=1}^{q_0}q^2|R_q|^2\right\rangle \tag{4.17}$$

How can we model this singularity? As shown above the difference between the primitive path and the real path is the important concept. Calculating the mean entropy using equations (4.15) and (4.16) the ratio is given by

$$\frac{S([R])}{S([r])}=\alpha=\frac{l}{a} \tag{4.18}$$

There are many possible models (including of course the exact Langevin) but we want a representation which is amenable to calculations but contains the essential feature of inextensibility. The simplest model with the singularity is

$$P[R]=N\exp\left\{-\frac{3}{2l}\int_0^L ds\frac{R'^2}{1-R'^2}+\gamma R''^2\right\} \tag{4.19}$$

where the normalization $\mathcal{N}$ is complicated and will be discussed after equation (4.21). We have added a bending potential $\gamma R''^2$ due to chain stiffness[19] which guarantees the existence of the Wiener integral for the 'worm-like chain'. This corresponds to the following equation

$$\left[\partial_t - D\sum_q\left\{\frac{\partial^2}{\partial R_q \partial R_q} + h(q,R_q)\right\}\right]P = 0 \qquad (4.20)$$

where $h(q,R_q)$ is the functional derivative of the exponent given in equation (4.19). The difficulty is now to calculate the functional integral given by equation (4.19). The easiest way to do this is to replace $\underset{\sim}{R}'^2$ in the denominator by its mean value in a self consistent manner; we write the equation (4.19) as

$$P[R] = \frac{\exp\left\{-\frac{3}{2l}\int \mathrm{d}s\left(\frac{\underset{\sim}{R}'^2}{1-\langle \underset{\sim}{R}'^2\rangle} + \gamma \underset{\sim}{R}''^2\right)\right\}}{\int \mathscr{D}r \exp\left\{-\frac{3}{2l}\int \mathrm{d}s\left(\frac{R'^2}{1-\langle \underset{\sim}{R}'^2\rangle} + \gamma \underset{\sim}{R}''^2\right)\right\}} \qquad (4.21)$$

where the normalization is now included to be consistent with the model and calculate the mean value of R'^2 by the equation:

$$\langle R^{12}\rangle = \frac{\int \delta R R'^2(s) \exp\left\{-\int \frac{3}{2l}\mathrm{d}s\left(\frac{R'^2}{1-\langle R'^2\rangle} + \gamma R''^2\right)\right.}{\int \delta R \exp\left\{-\frac{3}{2l}\int \mathrm{d}s\left(\frac{\underset{\sim}{R}'^2}{1-\langle \underset{\sim}{R}'^2\rangle} + \gamma \underset{\sim}{R}''^2\right)\right\}} \qquad (4.22)$$

Having adopted this model, because we are working in the range of $q<q_0$ we can now drop the factor $\gamma R''^2$ which guaranteed the existence of our chosen form by damping the large q modes, since they are omitted anyway with the $q<q_0$ condition. From equation (4.22) we get

$$\langle R'^2\rangle \approx q_0^2 l^2 = \left(\frac{l}{a}\right)^2 \qquad (4.23)$$

If we now calculate the entropy under deformation by aid of equation (2.11) and replacing $\underset{\sim}{R}(s) = \underset{\approx}{\lambda}\,\underset{\sim}{R}(s)$

$$F = \int \mathrm{d}^3 R \frac{\int \delta R \exp\left\{-\frac{3}{2l}\int \frac{R'^2}{1-\langle \underset{\sim}{R}'^2\rangle}\right\}}{\prod_s (1-\langle \underset{\sim}{R}'^2\rangle)} \times \log \frac{\int \delta R \exp\left\{-\int \frac{3}{2l}\mathrm{d}s \frac{\underset{\approx}{\lambda}\,\underset{\sim}{R}'^2}{1-\langle \underset{\approx}{\lambda}\,\underset{\sim}{R}'^2\rangle}\right\}}{\prod_s (1-\langle \underset{\approx}{\lambda}^2 \underset{\sim}{R}'^2\rangle)}$$

Evaluating this integral in the *finite* $q<q_0$ condition we get

$$F = \int \prod \mathrm{d}R_q \frac{\exp\left\{-\sum_q \frac{3}{2l}\frac{q^2|R_q|^2}{1-q_0^2 l^2}\right\}}{(1-l^2 q_0^2)} \times \left\{\frac{3}{2l}\frac{\sum_q q^2(\underset{\approx}{\lambda}\underset{\sim}{R}_q)^2}{1-q_0^2 l^2 \sum_i \lambda_i^2} - \log(1-l^2 q_0^2 \sum \lambda_i^2)\right\}$$

and we get the final answer

$$F = \frac{1}{2}\left\{\frac{\sum_{i=1}^{3}\lambda_1^2(1-\alpha^2)}{1-\alpha^2\sum_{i=1}^{3}\lambda_i^2} + \log\left(1-\alpha^2\sum_{i=1}^{3}\lambda_i^2\right)\right\} \qquad (4.24)$$

which gives a singularity determined by the factor as given in the rough model in the third section. Nevertheless the type of the singularity is not quite the same, and the *precise* shape dependence does depend on the model. This, however, is not central to our argument, which is to find a simple model of the singularity. Now we must include slippage which we do with the same arguments given in the second section now using the form of the path integral. As we have seen the probability function for the slippage was given by

$$\prod_{i=1}^{3} P(R,L,a) = \prod_{i=1}^{3} \frac{\exp\left\{-\frac{3R_i^2}{2l(L+a)}\right\}}{(\frac{2}{3}\pi l(L+a))^{1/2}} \qquad (4.25)$$

This function is equivalent to the continuous model

$$P(R,L+a) = \int \mathscr{D}R(s) \exp\left\{-\frac{3}{2l}\int_0^{L+a} R'^2(s)\,\mathrm{d}s\right\} \qquad (4.26)$$

If we assume a to be smaller than L, we can expand this to give

$$P \sim \exp\left\{-\sum_2 \frac{(1+a/L)^2 R'^2 L^2}{L(1+a/L)}\right\} \qquad (4.27)$$

which can be rewritten as a path integral

$$P(R,L) = \int_{-\eta\leqslant\tau(s)\leqslant\eta} \delta\tau(s) \int \mathscr{D}\underset{\sim}{R}(s) \exp\left\{-\frac{3}{2l}\int_0^L R'^2(s)(1+\tau(s))\right\} \qquad (4.28)$$

where function $\tau(s)$ characterizes the slip link. Combining then we arrive at the final probability distribution

$$P = \int_{-\eta\leqslant\tau(s)\leqslant\eta} \delta\tau(s) \int_{\text{path}} D\underset{\sim}{R}(s) \exp\left\{-\frac{3}{2l}\int (1+\tau(s)) \frac{R'^2(s)}{1-\langle R'^2(s)\rangle}\mathrm{d}s\right\} \qquad (4.29)$$

The final resulting free energy for the slip links is given by

$$F_s = \frac{1}{2}N_s\left\{\sum_{i=1}^{3}\left\{\frac{\lambda_i^2(1-\alpha^2)(1+\eta)}{(1-\alpha^2\sum_i \lambda_i^2)(1+\eta\lambda_i^2)} + \log(1+\eta\lambda_i^2)\right\} + \log\left(1-\alpha^2\sum_{i=1}^{3}\lambda_i^2\right)\right\} \qquad (4.30)$$

According to Ball *et al.*[5] we have to add the contribution of pure crosslinks also. This is the same expression as above with $\eta=0$ and we have finally

$$F_c=\tfrac{1}{2}N_c\left\{\frac{\sum_{i=1}^{3}\lambda_i^2(1-\alpha^2)}{1-\alpha^2\sum_{i=1}^{3}\lambda_i^2}+\log\left(1-\alpha^2\sum_{i=1}^{3}\lambda_i^2\right)\right\} \quad (4.31)$$

so that the full free energy of the network is given by

$$F=F_c+F_s \quad (4.32)$$

DISCUSSION OF THE RESULTS

In this section we want to compare this final result given by equations (4.30)–(4.32) with experiment.

Calculating the force in uniaxial extension we arrive at

$$\begin{aligned} f_s=N_s\Bigg\{&\frac{(1+\eta)(1-\alpha^2)\alpha^2 D}{(1-\alpha^2\phi)^2}\left(\frac{\lambda^2}{1+\eta\lambda^2}+\frac{2}{\lambda+\eta}\right)\\ &+\frac{1}{1-\alpha^2\phi}\left(\frac{\lambda}{(1+\eta\lambda^2)^2}-\frac{1}{(\lambda+\eta)^2}\right)\\ &+\eta\frac{D\lambda}{(1+\eta\lambda^2)(\lambda+\eta)}-D\alpha^2\frac{1}{1-\alpha^2\phi}\Bigg\} \end{aligned} \quad (5.1)$$

for the slip links. The functions D and ϕ are given by

$$\phi=\lambda^2+\frac{2}{\lambda} \qquad D=\frac{\mathrm{d}\phi}{\mathrm{d}\lambda} \quad (5.2)$$

For the crosslink contribution we have

$$f_c=N_c D\left\{\frac{1-\alpha^2}{(1-\alpha^2\phi)^2}-\frac{\alpha^2}{1-\alpha^2\phi}\right\} \quad (5.3)$$

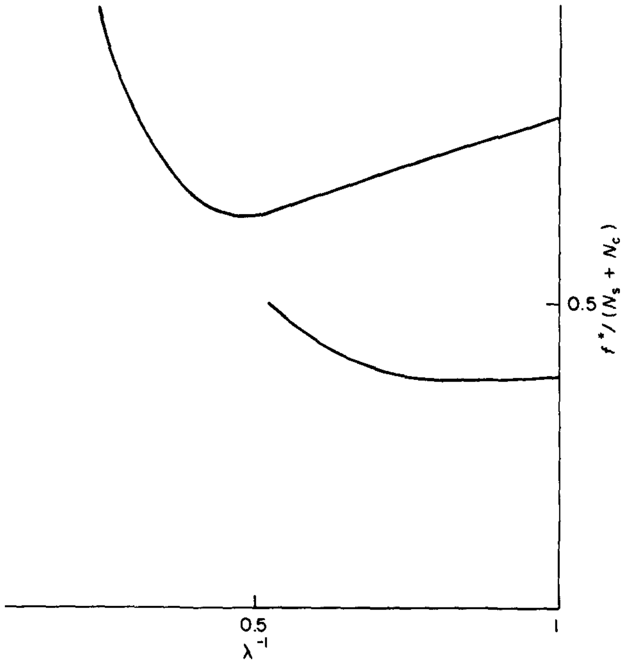


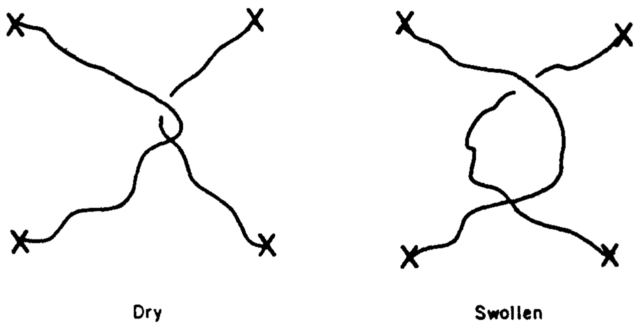
Figure 4 Mooney plot of the force from the above analysis. f^* is normalized by N_s+N_c while the parameters are chosen to be $\alpha=0.1$ and $\eta=0.2$. The curve with zero Mooney slope is given by η large (here $\eta=5$)

and the total force is given by

$$f=f_c+f_s$$

It is quite common to plot the reduced force f^*/D against λ^{-1} which gives *Figure 4*. In this principal figure we have chosen $\eta=0.2$, which was calculated by Ball *et al.*[5], and $\alpha=0.1$, an inextensibility which has been found for many rubbers[16]. We see the principal features of the force. To make the phenomenology complete we should mention that the number of slip links can be estimated from the plateau modulus and so related to the tube dimensions (see equation (6.1)). This estimation (depending on fabrication conditions) gives values of N_c comparable with the number of crosslinks (*cf.* ref. 6).

There is also an interesting fact contained in these results; namely that the slippage depends on the concentration of polymer present. If we swell the system η becomes larger because the amount of phase space is increased. Swelling in a good solvent implies that the 'chain contacts' are reduced:



So if we put $\eta \sim 1/C^2$ we can see that η gets larger. Large η values affect the deformation behaviour as given in *Figure 4* and we find in the experiment results that the Mooney–Rivlin slope reaches its minimum value $C_2 \to 0$ (*cf. Figure 4*).

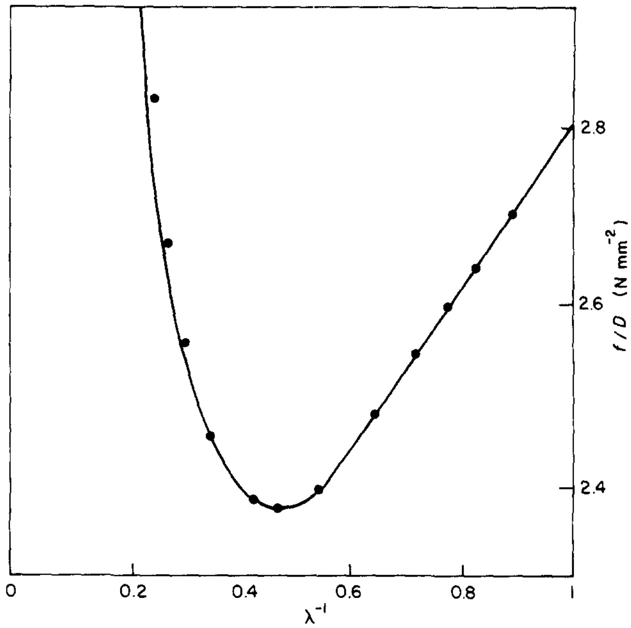


Figure 5 Stress–strain data of natural rubber according to Mullins[21]. The solid line is calculated by the aid of equations (5.1)–(5.3) using the parameters $N_c k_B T=1.2\,\mathrm{N\,mm^{-2}}$, $N_s k_B T=2.1\,\mathrm{N\,mm^{-2}}$, $\eta=0.2$, $\alpha^{-1}=\lambda_{\max}=7.5$

As an experimental example we show a fit to experimental data of Mullins[21] in *Figure 5*. In this example we have used the theoretical value for η ($=0.2$) as given by Ball *et al.*[5] Looking at equations (62) and (63) from the same reference, N_s and N_c can be found approximately from the small deformation regime, while α is found at large deformations. This has been treated also by Vilgis and Kilian[16] and hence the applications on the dependence on the deformation mode are here also applicable. For a complete characterization of a rubber, more information is necessary, nevertheless it is possible with this theory. This characterization starts with the estimation of the number of entanglements by measuring the plateau modulus of the melt before crosslinking. This gives also the ratio a/l by the relaxation times (see ref. 20) which determines the inextensibility. If the rubber is then crosslinked (in the melt) the topology and so N_s are fixed. N_c is then known by the amount of added crosslink molecules (if all react). The amount of slip determines then η which has been estimated to be $\eta=0.2$ from theory and $\eta=0.4$ from Thirion and Weil's work[6].

CONCLUSION

As we have seen from the discussion in the previous section the equation of state is able to explain the deformation behaviour of rubbers over the total range of deformation. Nevertheless, there remains some work to be done to relate all the quantities used in the theory as parameters (for simplicity). This should be possible since we used only one basic molecular model—the entanglement.

In the theoretical model given by the replica calculation, η is a fixed value but this cannot be true for real situation in a network (see the experimental work of Thirion and Weil[6]. Since η is a measurement for the slip it can be related to the length between two crosslinks, since this is the maximum value of slip (see Ball *et al.*[5]). The other quantity $(\langle l/a\rangle^2)$ is very difficult to calculate (this can probably be done by computer), but it is also strongly related to polymer dynamics. As shown by Graessley[20] and Doi and Edwards[4] this quantity occurs also in the reptation time and is therefore related to the relaxation behaviour of the system.

However, the problem of relating N_s and N_c to measurable quantities of the network fabrication still remains. Assuming a homogeneous network and defining c_x as the concentration of the crosslinks and c as the concentration of polymer chains, then the number of slip links can be estimated by use of the plateau modulus

$$N_s = V\left(\frac{c_x}{c_x+2c}\right)\frac{c}{al^2} \qquad c_x=\frac{N_c}{V} \tag{6.1}$$

where V is the total volume.

Since the parameters α and η are caused by the *same* mechanism they should be of the same order: $\alpha=\eta$. However, in all equations of the free energy etc. α^2 always appears so that, for example, in the free energy one has the leading term

$$F\sim\sum_i\frac{\lambda_i^2(1-\alpha^2)(1+\eta)}{(1-\alpha^2\sum\lambda_i^2)(1+\eta\lambda_i^2)}$$

It follows that, since $\alpha^2 \ll \eta$ a positive slope will always be found in the Mooney plot which is in accord with all experiments.

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