A Modification of Rubber Elasticity Theory

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SUMMARY

Based on a reconsideration of the packing conditions in amorphous
polymers, a modification of the statistical theory of rubber elasti-
city is derived. The main assumption is, that the mean square end-
to-end distance of a free chain in the bulk state depends on the di-
mensions of the surrounding chains. The theory describes quite well
the deformation behaviour of real elastomeric networks.

INTRODUCTION

From the statistical theory of rubber elasticity (TRELOAR, 1975)
follows for the change of free energy at the deformation of a net-
work in the simplest case the expression

$$\Delta F = \frac{3}{2} \nu kT \frac{<r^2>_d - <r^2>_i}{<r^2>_o} \tag{1}$$

ν is the number of elastically effective chains, $<r^2>_d$ the mean
square end-to-end distance of the chains in the deformed network,
$<r^2>_i$ the same quantity of the chains in the undeformed, isotropic
network, and $<r^2>_o$ the same quantity, if the chains were not con-
nected and otherwise under the same conditions. kT has the usual
meaning. Eq. (1) follows from the model case of a phantom network,
where the chains can freely intersect each other and themselves. The
crosslinking points however are assumed not to fluctuate and to be
displaced affinely on deformation. With the assumption of fluctua-
ting crosslinks in a phantom network the expression for ΔF is re-
duced by a factor $1-2/f$, where f is the functionality, i.e. the
number of chains emanating from a crosslinking point (GRAESSLEY,
1975).

At a homogeneous deformation in the Cartesian coordinates we have

$$<r^2>_d = <r^2>_i \frac{\lambda_x^2 + \lambda_y^2 + \lambda_z^2}{3} \tag{2}$$

with a relative deformation $\lambda = L/L_i$, with L a length in the de-
formed state and L_i a length in the isotropic undeformed state.
For uniaxial deformation at constant volume we have $\lambda \equiv \lambda_x = \lambda_y^{-2} = \lambda_z^{-2}$
and

$$<r^2>_d = <r^2>_i \frac{\lambda^2 + 2\lambda^{-1}}{3} \tag{3}$$

With Eq. (1) and (3) it follows for the retractive force

$$K = \frac{1}{L_i} \left(\frac{\partial \Delta F}{\partial \lambda}\right)_v = \frac{\nu kT}{L_i} \frac{<r^2>_i}{<r^2>_o} \left(\lambda - \lambda^{-2}\right) \tag{4}$$

and for a quantity, which may be termed reduced stress,

$$\sigma^* \equiv \frac{\sigma}{\lambda - \lambda^{-2}} = \frac{\nu kT}{V} \frac{<r^2>_i}{<r^2>_o} \tag{5}$$

with σ the force per area of the undeformed sample and V the volume.

The stress-strain behaviour of elastomeric networks is usually not in accordance with the statistical theory. In simple elongation, the real behaviour is decribed quite well in a large range of deformation by the empirical MOONEY-RIVLIN-equation (TRELOAR, 1975)

$$\sigma^* = 2 C_1 + 2 C_2 \lambda^{-1} \tag{6}$$

where C_1 and C_2 are constants for a given sample.

The molecular explanation of Eq. (6) is still an open and controversial question. Some authors see it in a contribution of permanently entangled chains to the elastic modulus (FERRY, 1979; GRAESSLEY, 1974). Others see it in a transition from the case of not fluctuating crosslinks to that of fluctuating crosslinks during the deformation or the swelling of the network (RONCA, ALLEGRA, 1975; FLORY, 1977). Furthermore it has been supposed, that the packing conditions or the short range order in amorphous polymers could give an explanation (DI MARZIO, 1962; JACKSON et al. 1966; SCHWARZ 1973, 1977; GEBHARD et al. 1979).

We present a modification of the rubber elasticity theory, which follows from a reconsideration of the packing conditions in amorphous polymers. The main result is, that $<r^2>_o$ in Eq. (1) is replaced by an expression, which depends on deformation.

CHAIN DIMENSIONS

An isolated polymer chain diluted in an athermal low molecular weight solvent will assume all possible conformations with equal probability, if we consider the simple case, that all conformations have the same energy. On concentrating the polymer solution, the mean square end-to-end distance $<r^2>_o$ decreases as the chain overlapping increases and reaches a value $<r^2>_{ob}$ in the bulk state. FLORY suggested that this value is identical with that for the chain in a Θ-solvent and that for the model case of the so-called unperturbed chain, which is characterized by bond lengths, bond angles and rotational potentials, but can otherwise freely intersect itself (FLORY, 1953, 1969). This suggestion has been proved as substantially correct by neutron scattering experiments (MACONNACHIE, RICHARDS, 1978).
Nevertheless a reconsideration of the matter seems necessary. First of all one should see that intrinsic values as the mean optical anisotropy of a chain in direction of the end-to-end vector or the mean ratio of trans and gauche positions are not a priori to be considered as equal in the bulk state or the Θ-solvent condition on

the one hand and the unperturbed model case on the other. Despite of an equal $\langle r^2 \rangle$ the ensemble of the conformations is different. In the bulk state and the Θ-solvent condition the exclusion of conformations for volume reasons is compensated by a higher statistical weight of more closely packed conformations.

According to FLORY, the change of dimensions of chains on changing the athermal solvent content is mainly due to long range interferences, that means volume exclusions between segments, which are far apart within the chain (FLORY, 1953,1969). Monte Carlo simulations show however, that in short chain systems the dimensions also decrease markedly with increasing chain concentration (CURRO, 1974; DE VOS, BELLEMANS, 1975; OKAMOTO, 1976). The effect can still be seen for chains which cannot intersect, but can form an intramolecular contact.
A high degree of intrachain contacts, which is mainly brought about by short back folding, is considered as the necessary condition for the maximum number of conformations in a system of flexible chains in the bulk state. This aspect has been illustrated in an earlier paper, though the conclusions drawn there on rubber elasticity are not correct (SCHWARZ, 1977).

The dimensions of a free chain in the bulk state should increase to some extent, if by a fictitious process the ends of the surrounding chains would be pulled apart, so that these chains are uncoiled and offer a larger actual surface. This follows from the constancy of the sum of intra- and interchain contacts. It is the starting point for the modification of the rubber elasticity theory given in the next chapter.

RUBBER ELASTICITY THEORY

We consider the deformation of a network in the bulk state at constant volume with the assumption that the crosslinking points do not fluctuate. For simplicity we assume equal chain lengths. We divide the total number of chains ν into small groups $\nu_1, \nu_2 ... \nu_n$. The chains within one group should be dispersed randomly in the sample. We assume the fictitious process, that one group of chains after the other is deformed affinely from $\langle r^2 \rangle_i$ to $\langle r^2 \rangle_d$. The change of free energy at the deformation of the first group ν_1 would be

$$\Delta F_1 = \frac{3}{2} \, \nu_1 kT \, \frac{\langle r^2 \rangle_d - \langle r^2 \rangle_i}{\langle r^2 \rangle_o} \tag{7}$$

according to the existing theory (Eq. (1)).
If $\langle r^2 \rangle_i$ differs from $\langle r^2 \rangle_o$, the latter has to be replaced however in Eq. (7) by

$$\langle r^2 \rangle_o^{**} = \langle r^2 \rangle_o + c \, (\langle r^2 \rangle_i - \langle r^2 \rangle_o) \tag{8}$$

This expression describes the adjustment of the mean square end-to-end distance of a free chain in a surrounding of chains, which are not at $\langle r^2 \rangle_o$ but at $\langle r^2 \rangle_i$. The coupling parameter c is between 0 and 1. The value 0 means no coupling between the dimensions, the limiting value 1 means full adjustment of the dimensions, which will not be reached in reality. In a similar way we have to replace in ΔF_n at the deformation of the last group ν_n the $\langle r^2 \rangle_o$ of the simple theory by

$$\langle r^2 \rangle_o^{**} = \langle r^2 \rangle_o + c \; (\langle r^2 \rangle_d - \langle r^2 \rangle_o) \qquad (9)$$

since the free chains of the group ν_n are in a surrounding of chains, which are at $\langle r^2 \rangle_d$. The ΔF values for the groups in between will vary linearly between ΔF_1 and ΔF_n. This yields for the total ΔF at the deformation of the network

$$\Delta F = \frac{\nu}{2}(\Delta F_1 + \Delta F_n) = \frac{3\nu kT}{4} \; (\langle r^2 \rangle_d - \langle r^2 \rangle_i) \left[\frac{1}{\langle r^2 \rangle_o^{*}} + \frac{1}{\langle r^2 \rangle_o^{**}} \right] \quad (10)$$

In the foregoing treatment we assume, that at the deformation of a single chain in the bulk state this chain behaves as a Gaussian chain. The decrease of the number of possible conformations at this process is however not confined to the deformed chain, but occurs in this chain and the surrounding chains.
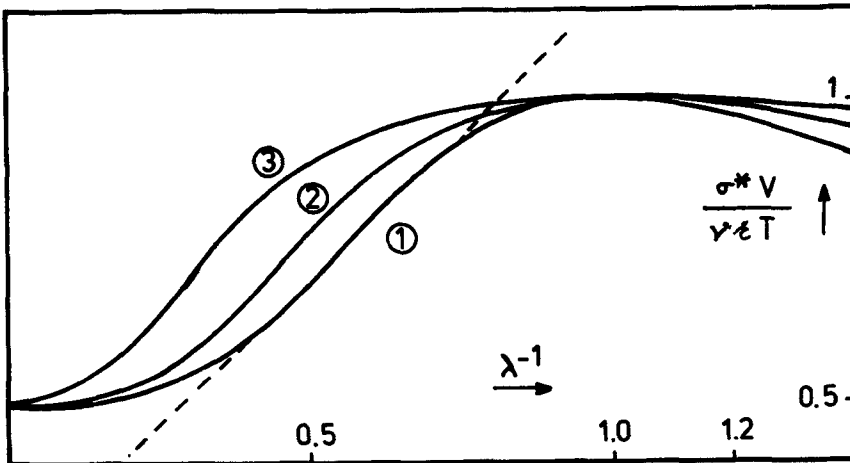

Fig. 1: Dependence of the quantity $\frac{\sigma^{*} V}{\nu kT}$ on λ^{-1} derived from Eq. (11) for the case $\langle r^2 \rangle_i = \langle r^2 \rangle_o$ for the values 0,2 ①; 0,5 ②; 1 ③ of the parameter c.

We assume, that the coupling parameter c increases in bulk polymers with the extent of intrachain contacts. Therefore it should increase at a given polymer with the chain length. On swelling the networks, the coupling parameter c should decrease and vanish. Loops and free chain ends in a network will act as a diluent, since we are concerned with the coupling between elastically effective chains.

A small decrease of c with deformation should exist since c will vanish if the chains are extended to a degree, that no more intra-chain contacts exist. This dependence is neglected in the following treatment. We neglect also a possible effect of anisotropy, since at moderate deformations the molecular anisotropy in elastomeric networks is quite small. In other words we assume some adjustment of the mean dimensions of a free chain to the surrounding chains in consequence of the surface relations, but we neglect a possible adjustment in the orientations of the end-to-end vectors.

For uniaxial deformation follows from Eq. (10) with the left of
the equations (4) and with the assumption of a constant parameter
c for the retractive force

$$K = \frac{\nu kT}{L_i} \frac{<r^2>_i}{<r^2>_o}\left(\lambda-\lambda^{-2}\right)\left[\frac{1}{2}\left(1-c+c\frac{<r^2>_i}{<r^2>_o}\right)-1\right.$$

$$\left. + \frac{1}{2}\left(1-c+c\frac{<r^2>_i}{<r^2>_o}\right)\left(1-c+c\frac{<r^2>_i}{<r^2>_o}\frac{\lambda^2+2\lambda^{-1}}{3}\right)-2\right] \qquad (11)$$

In Fig. 1 is plotted the reduced stress $\sigma^{\#}$ over $\frac{\nu kT}{v}$ versus λ^{-1}
for the case $<r^2>_i = <r^2>_o$ for the values 0,2; 0,5; 1,0 of the
parameter c.

DISCUSSION

The curves of Fig. 1 describe rather well the stress strain beha-
viour of elastomeric networks (TRELOAR, 1975). In the range of
high elongation ($\lambda^{-1} < 0,3$) the theory is not adequate, since
here the parameter c will decrease markedly. Otherwise the beha-
viour of real networks is determined in this range by the limited
chain extensibility (TRELOAR, 1975). In the range of moderate elon-
gations, ($0,9 > \lambda^{-1} > 0,4$), where usually the MOONEY-RIVLIN equation
(6) can be applied, a slight curvature can be seen in Fig. 1.
The consideration of a slight dependence on λ of
the parameter c or the compensating effect of non-Gaussian beha-
viour of shorter chains, which increases gradually with λ and cross-
linking density (TRELOAR,1975), could lead to more straight lines.
Otherwise the experimental results on networks of polymethylene
show a curvature as in Fig. 1 (GENT,VICKROY,1967). The dotted
straight line on the curve for c = 1 gives a ratio $C_2/C_1 \approx 3,5$
on application of Eq. (6). This is the order of magnitude of the
high values of this ratio, which are found at some polymers, as
polymethylene at low crosslinking density (GEBHARD et al. 1979;
MARK, 1975). The decrease of C_2/C_1 , which is found on increas-
ing crosslinking density at a given polymer (TRELOAR,1975;GEBHARD
et al. 1979;MARK,1975), is equivalent to a decrease of the parame-
ter c and therefore consistent with this theory.A closer relation
exists however between the parameter c and $C_2/(C_1 + C_2)$ rather
than to C_2/C_1.

One can see from Eq. (11) and from Fig. 1, that the modulus at
$\lambda \longrightarrow 1$, or approximately $2(C_1 + C_2$), is in accordance with the
simple theory and has to be used for the determination of the cross-
linking density, and not the value $2C_1$, as is usually done.

On swelling, the ratio C_2/C_1 decreases and vanishes (TRELOAR,1975),
as it should, since the coupling of dimensions between the elasti-
cally effective chains decreases and vanishes. At the same time the
modulus at $\lambda \rightarrow 1$ should decrease more as it should with the assump-
tion of a constant $<r^2>_o$. Computer simulation shows, that the
increase of $<r^2>_o$ on dilution is not to neglect at the conditions
we deal with on the swelling of elastomeric networks (DE VOS,BELLE-
MANS, 1975).The larger the ratio C_2/C_1 in the bulk state or the
chain length is, the larger should be the decrease of the modulus
on swelling. From the data of DE VOS and BELLEMANS one can esti-

mate for chains of 1000 links on a cubic lattice an increase of $\langle r^2 \rangle_0$ by a factor of about 1,8 on diluting the chains with a low molecular weight athermal solvent to a volume fraction of polymer $v_2 = 0,25$. This chain length might be approximately adequate to a chain length of 2000 bonds or 500 monomer units in a low cross-linked natural rubber network, which has a ratio $C_2/C_1 \approx 1$ in the bulk state. So the decrease of the modulus on swelling due to an increase of $\langle r^2 \rangle_0$ might be in the order of magnitude to explain the experimental results. From these it appears as if $2C_1$ and not $2(C_1 + C_2)$ would be in accordance with the statistical theory, while $\langle r^2 \rangle_0$ is considered to remain constant (TRELOAR, 1975).

It is generally found, that networks prepared by crosslinking highly streched or crystalline material or by crosslinking in solution, followed by a removal of the solvent, have a very small value of C_2/C_1. The reason is still unknown. A possible explanation could be, that these systems contain many elastically ineffective chains, which act as a diluent.

The value of C_2/C_1 differs markedly for different polymers at comparable crosslinking densities (GEBHARD et al., 1979; MARK, 1975). The hypothesis, on which this theory is based, is that the coupling parameter c is determined by the extent of intrachain contacts. So it follows, that the extent of intrachain contacts should be larger in polymers with high values of C_2/C_1, as polymethylene, compared to polymers with low values of C_2/C_1, as natural rubber. This connection can not be proved at this time, but there are some indications in favour of it. C_2/C_1 increases with decreasing mean cross-sectional area of the chains, that means, with increasing chain length per volume unit (BOYER, MILLER). Chains with lower cross-sectional area have less bulky side groups. They might be more able to build intrachain contacts by short back folding, which is in our opinion the main source of those contacts. With decreasing chain cross-sectional area, or increasing C_2/C_1, the short range order in the bulk state increases (GEBHARD et al. 1979). This orientational short range order, determined by stress-optical measurements, reflects somehow a change of the packing conditions in dependence of the polymer structure.

With the consequences of this modification of rubber elasticity theory on thermoelasticity and stress-optical behaviour we will deal later.

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