Equation of state of real networks*

Hanns-Georg Kilian
Abteilung für Experimentelle Physik der Universität Ulm, Oberer Eselsberg, 7900
Ulm/Donau, West Germany
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The effects of mutual interactions between the chains of a molecular network are taken into account by a van der Waals approach for an 'ideal conformational gas'. The utility of the new equations of state can be judged by their ability to describe the results of a set of different known experiments. Thus, it is shown that the retractive force of a real network seems to be not only intramolecular in its origins.

INTRODUCTION

A high degree of success has been achieved in the theory of rubber elasticity[1-5,31-37,39]. Nevertheless, some properties of rubber elastic systems cannot quantitatively be described. Most of the known approaches are based on the assumption that the conformational changes of the chains are not dependent on the mutual interactions between the network chains. A proof of this assumption is considered to be given by the recent neutron-scattering experiments[31,32]. However, it might be reasonable to expect a certain contribution by interactions between the chains of a network to the deformational energy.

Here, we present a thermomechanical description of molecular networks which is closely related to the concepts developed by van der Waals in his theory of real gases. The ideal network is treated as an 'ideal conformational gas'. Applying mutual interactions between 'quasi-particles' we thus arrive at a van der Waals representation of a 'real conformational gas'.

DEFORMATION ENERGY

The elastic free energy of a Gaussian network related to the initially isotropic state is obtained as[2,4]:

$$W = NkT(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)/2 \qquad (1)$$

the network being composed of N chains. For simple elongation along the x-axis, let $\lambda = \lambda_x = L/L_0$ and $\lambda_y = \lambda_z = V\lambda^{-1/2}/V_0$ where L and V are the length and volume of the elongated sample and L_0 is the length at volume V_0 in the reference state, specified by $\lambda = 1$. For convenience, we define the deformation function:

$$\psi(\lambda) = (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)/2 = (\lambda^2 + 2/\lambda - 3)/2 \qquad (2)$$

The 'phantom chains' of the ideal network chains are considered not to occupy any space. Without chemical structure the mass of the chains is taken to be uniformly distributed over their length. In the absence of internal elasticity, the chains realize their isoenergetic conformations without any handicaps. The relative force is given by

$$f(\lambda) = (NkT/L_0)\psi^\lambda \qquad (3)$$

with

$$\psi^\lambda \equiv \partial\psi/\partial\lambda = \lambda - \lambda^{-2} \qquad V/V_0 \simeq 1 \qquad (4)$$

The sole retained quantity pertaining to the network structure is N. Only the total number of chains matter, thus indicating their statistical equivalence. For equilibrium conditions, each chain has the same energy in the statistical average (equipartition of energy). Any understanding of the physical properties of the ideal network is closely related to the fact that microscopic kinetic energy is the only form of energy which is present.

QUASI-PARTICLE REPRESENTATION

From equation (1) the energy in the state of reference is obtained as:

$$W(\lambda = 1) = (3/2)NkT \qquad (5)$$

thus indicating that the unloaded equilibrium state of the ideal network may be represented by 'free particles' having three degrees of freedom of the kinetic energy, independent of their being localized in the network.

Employing an r-space representation of the statistics we arrive at the total energy within the ith phase-space cell of a network in simple extension.

$$\varepsilon_i^* = \varepsilon_i + \varphi(\lambda) \qquad (6)$$

with ε_i being determined by quantum mechanical arguments. $\varphi(\lambda)$ describes a cooperative deformational energy which is considered to be uniformly imposed onto network chains independent of their ε_i values.

The partition function Z is then defined by:

$$Z = \exp\{-\varphi(\lambda)/kT]\Sigma \exp\{-\varepsilon_i/kT\} \qquad (7)$$

with a definite number of phase-space cells. The pro-

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bability of a given configuration of the chains is found to be independent of the state of deformation according to:

$$n_i = \frac{N}{Z} \cdot \mathrm{e}^{-\varphi/kT - \varepsilon_i/kT} = N\mathrm{e}^{-\varepsilon_i kT}/\Sigma \mathrm{e}^{-\varepsilon_i/kT} \qquad (8)$$

as a consequence of the simple structure of equation (6) with its invariant term for deformation energy. For the internal energy, we arrive at the expression:

$$u = NkT\frac{\partial}{\partial T}\ln Z = N\left\{\varphi - T\frac{\partial \varphi}{\partial T} + \Sigma \varepsilon_i \mathrm{e}^{-\varepsilon_i/kT}/\Sigma \mathrm{e}^{\varepsilon_i/kT}\right\} \qquad (9)$$

Thus, for an ideal network with $\varphi = 0$ we are led to:

$$u = N\langle \varepsilon_i \rangle \qquad (10)$$

indicating that the internal energy of a Gaussian network is identical to equation (5) providing that the average energy of a single chain $\langle \varepsilon_i \rangle$ is equal to $3kT/2$. This can be derived from the law of equipartition according to which an average contribution of $kT/2$ is obtained for each degree of freedom of the kinetic energy[6]. A generalization of equation (10) can be obtained if additional internal degrees of freedom of the chains are introduced thus having the partition function

$$Z^* = \mathrm{e}^{-\varphi/kT}\Sigma \mathrm{e}^{-\varepsilon_i/kT}\Sigma \mathrm{e}^{-\varepsilon_k^{(i)}/kT} \qquad (11)$$

with $\varepsilon_k^{(i)}$ designating the corresponding energies.

STATISTICAL MEANING OF THE DEFORMATION FUNCTION

We are now seeking an expression for the configuration of the deformed network with a maximum entropy. From equation (6):

$$S = kN\ln N + k\alpha N + k\beta U$$

$$\beta = (kT)^{-1} \qquad (12)$$

with α and β being Lagrange parameters; allowing N to be constant, but permitting U to change:

$$\mathrm{d}S = kN\mathrm{d}\alpha + kU\mathrm{d}\beta + k\beta \mathrm{d}U \qquad (13)$$

On logarithmic differentiation of

$$N = \mathrm{e}^{-\alpha}\mathrm{e}^{-\varphi \cdot \beta}\Sigma \mathrm{e}^{-\varepsilon_i \beta} \qquad (14)$$

and allowing a change in the total number of phase-space cells ($\mathrm{d}\Sigma$), we obtain:

$$\mathrm{d}\alpha + \frac{U}{N}\mathrm{d}\beta - \frac{\mathrm{d}\Sigma}{\Sigma} = 0 \qquad (15)$$

where $\mathrm{d}\Sigma/\Sigma$ is used as the representation of the relative change in the number of phase-space cells. Hence, equation (13) may be rewritten accordingly:

$$\mathrm{d}S = k\beta \mathrm{d}U + kN\mathrm{d}\Sigma/\Sigma \qquad (16)$$

Using the Gibbs equation for simple elongations at constant volume ($L_0 \equiv 1$):

$$T\mathrm{d}S = \mathrm{d}U - F\mathrm{d}L = \mathrm{d}U - NkT\mathrm{d}\psi(\lambda) \qquad (17)$$

and comparing this expression with equation (16), we are led to the instructive equation:

$$\mathrm{d}\Sigma/\Sigma = -\mathrm{d}\psi(\lambda) \qquad (18)$$

where equation (3) has been employed.

Equation (18) gives the meaning of the deformation function. For simple elongation, a decrease of the number of phase-space cells is predicted, simply expressed by the corresponding change of the deformation function.

STRUCTURE OF THE PHASE-SPACE

We take advantage of the statistics of ideal gases[6] where it has been shown using Liouville's theorem that N may be written as:

$$N = \mathrm{e}^{-\alpha}(V/\Delta\tau)\Sigma' \mathrm{e}^{-\varepsilon_j \beta} \qquad (19)$$

thus indicating the independence of the 'q space' and the 'p space', the physical space and the space of momenta resp. The prime is attached to Σ as a reminder that the summation has only to be performed in the p space. $\Delta\tau$ is the size of the cells in the q space. From equation (19) the following relation is obtained:

$$\mathrm{d}\Sigma/\Sigma = \mathrm{d}V/V \qquad (20)$$

If the volume is diminished by adiabatic compression, the total energy of the particles must be distributed over a reduced number of phase-space cells, thus heating up the gas.

We have the opportunity of an analoguous treatment of the ideal network if the following factorization is permitted:

$$N = \mathrm{e}^{-\alpha}(V/\Delta\tau)(V_c/\Delta\tau_c)\Sigma' \mathrm{e}^{-\varepsilon_j \beta} \qquad (21)$$

The structure of the phase-space is thus characterized by three independent parts, the q space, the momenta space and the configuration space, the c space having 'volume' V_c, with cells of volume $\Delta\tau_c$. We do not intend to discuss the statistical nature of this factorization. We will consider equation (21) to be justified for a Gaussian network by analogy with the treatment of ideal gases[6]. Now, by logarithmic differentiation of equation (21) with invariant N and V we arrive for an isochoric process at:

$$\mathrm{d}\alpha + \frac{U}{N}\mathrm{d}\beta + \mathrm{d}V_c/V_c = 0 \qquad (22)$$

The Gibbs equation takes the form of equation (17), with the aid of which the following expression is obtained:

$$\mathrm{d}V_c/V_c = \mathrm{d}\Sigma/\Sigma = -\mathrm{d}\psi(\lambda) \qquad (23)$$

where equation (16) has also been used. Stretching an ideal rubber in its isoenergetic conformations under adiabatic conditions, the total number of cells is diminished thus yielding an increase in temperature.

REAL NETWORK

It is profitable to present the equations of state in an unconventional form. For an ideal gas we arrive at:

$$p = NkT/V = (NkT/\Sigma)\mathrm{d}\Sigma/\mathrm{d}V \qquad (24)$$

while the ideal network is represented by:

$$f = -(NkT/L_0)(1/\Sigma)\mathrm{d}\Sigma/\mathrm{d}\lambda \qquad (25)$$

the equivalence of these two equations of state is evident. Using the phase space representation we arrive at the van der Waals equation of state:

$$p = \frac{NkT}{V-b^*} - \frac{a^*}{V^2} = \frac{NkT}{(\Sigma\mathrm{d}V/\mathrm{d}\Sigma - b^*)} - \frac{a^*}{\Sigma^2}\left(\frac{\mathrm{d}\Sigma}{\mathrm{d}V}\right)^2 \qquad (26)$$

where effects due to the infinite volume of the particles are related to b^*, while cohesive attractions determine the value of the parameter a^*. Hence, by analogy, we are led to the following equation of state for real networks:

$$f = \frac{NkT}{\left(-\Sigma\dfrac{\mathrm{d}\lambda}{\mathrm{d}\Sigma} - b\right)} - \frac{a_0}{\Sigma^2}\left(\frac{\mathrm{d}Z}{\mathrm{d}\lambda}\right)^2 \qquad (27)$$

The force must grow to infinitely large values if the chains attain their maximum lengths. Because of the finite volume of the chains a complicated situation is expected to occur in highly drawn systems. Nevertheless, the maximum elongation observed is useful for the interpretation of the phenomenological parameter b. The parameter a, however, should express interactions between the chains in the real network.

Using the concept of quasi-particles, no assumptions are involved as to the actual conformations of the chains. There is only a need for thermodynamically autonomous equilibrium subsystems which are statistically equivalent in the sense of the law of equipartition. Hence, even correlations which might affect the conformations in a real network must not devalue this concept. Using equation (18), equation (27) may be cast in the form:

$$f = (NkT/L_0)/((\psi^{\lambda})^{-1} - b) - a_0(\psi^{\lambda})^2 \qquad (28)$$

With $f \to \infty$ for $\lambda \to \lambda_m$ we arrive at:

$$b = (\psi^{\lambda}(\lambda_m))^{-1} \equiv (\psi^{\lambda}_m)^{-1} \qquad (29)$$

allowing the formulation of an equation of state for real networks:

$$f = \frac{NkT}{L_0}\psi^{\lambda}\{\psi^{\lambda}_m/(\psi^{\lambda}_m - \psi^{\lambda}) - a\psi^{\lambda}\}$$

$$a = a_0 L_0/NkT \qquad (30)$$

The simplicity of this 'three-parameter' equation of state is attractive. Moreover, there is hope for relating λ_m to the average molecular weight of the chains, M_c, which, however, also determines the value of $NkT = \rho RT/M_c$ (ref 2).

COMPARISON WITH EXPERIMENT

The extent to which the predictions of the equation of state are confirmed by experiment will now be considered.

Uniaxial elongation and compression

For the purpose of determining the parameter λ_m we consider the network to be composed of free chains, yielding:

$$y = \lambda_m^2 \qquad (31)$$

with y designating the number of links in the chains. Hence the front factor NkT may be expressed as:

$$NkT = \rho RT/yM_0 = \rho RT/\lambda_m^2 M_0 \qquad (32)$$

where M_0 is the molecular weight of a single link, the monomer unit. The quality of the theoretical description of experiments on gum-vulcanized rubber published by Treloar[7] is demonstrated in *Figures* 1 and 2. The parameter a turns out to be positive, representing attractive interactions between the quasi-particles. These interactions are then predicted to be strongly increased with increasing elongation. In principle the occurrence of a phase transition is predicted.

However, a fully satisfying fit of the data in the range of uniaxial compression can only be achieved if the following modification of the parameter a is introduced:

$$a = a_1(1 - a_2/\lambda^2) \qquad (33)$$

The improvement of the theoretical representation of the data by using equation (33), can be seen from curve B in *Figure* 2. Thus, on account of equation (33), a non-linear dependence of $f/(\lambda - \lambda^{-2})$ on λ^{-1} is obtained in agreement

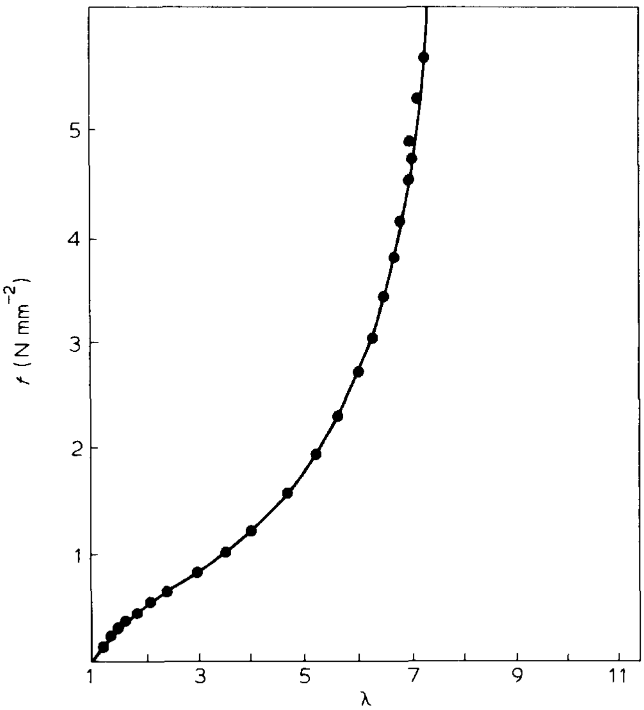

Figure 1 Simple elongation for natural rubber[2,7]. The full line has been calculated with the aid of equation (31) using the parameters: a = 0.2; λ_m = 9.8; T = 295K; NkT/L_0 = 35.8 N mm^{-2}

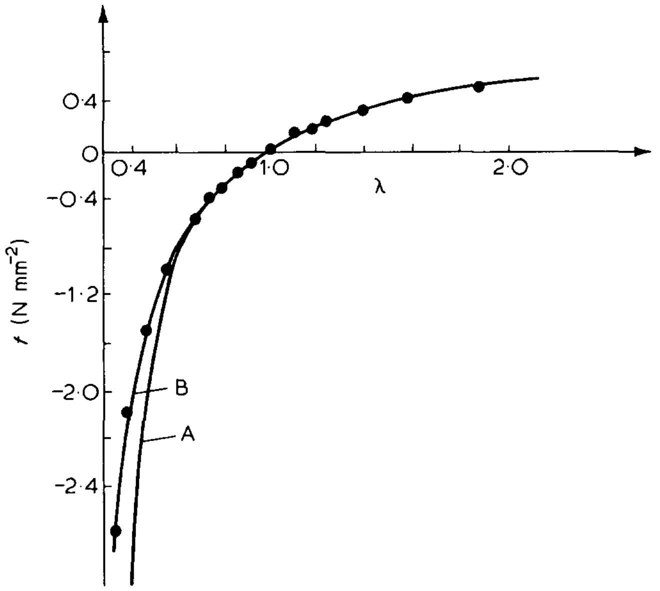

Figure 2 Complete extension and compression curve[2,7]. The full line represents the theoretical relation (31) with the parameters assigned to the same values as given in *Figure 1*: A, with invariant a = 0.2; B, $a = a_1\,(1 - a_2/\lambda^2)$ with a_1 = 0.2 and a_2 = 0.1

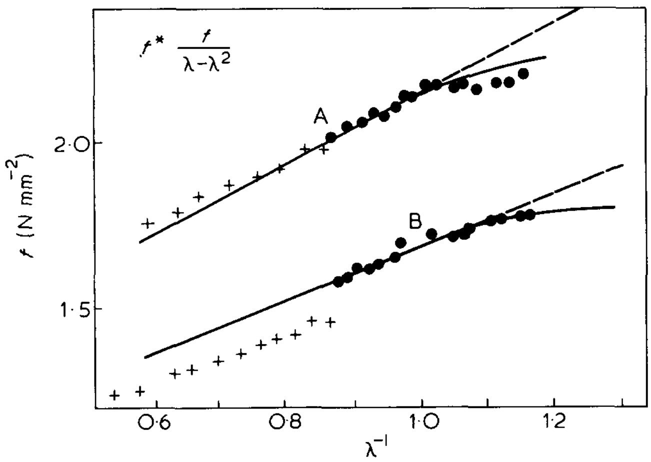

Figure 3 Reduced force $[f^*] = f/\lambda - \lambda^2$ of poly(dimethyl siloxane) *versus* λ^{-1} various degrees of crosslinking according to Erman and Flory[33]. The full lines are computed with the aid of equation (30) with a defined in equation (33), using the parameters: NkT/M_0L_0 = 35.9 N mm^{-2}: A, λ_m = 12; B, λ_m = 14.5; a_1 = 0.24; a_2 = 0.15

with experiments reported by Erman, Flory[33] and Rehage[34]. Calculations are presented in *Figure* 3 compared with the Erman–Flory data.

Hence, from this phenomenological description, we can see that at least three parameters are necessary above the total uniaxial deformation behaviour. The molecular statistical meaning of these parameters might be illuminated from the statistical theory of rubber elasticity developed by Ronca and Allegra[35] and by Flory[36,37].

Pure shear

The description of any type of homogeneous deformation should be possible with the aid of equation (31) in terms of deformation functions which define the physical circumstances. In pure shear, one of the principal extension ratios is held fixed, thus leading to a derivative of the deformation function (5):

$$\psi^{\lambda}(\lambda) = \lambda - \lambda^{-3} \qquad (34)$$

From an inspection of *Figure* 4, curve B, it is seen that the data of Treloar[7] are fairly well represented by the use of equation (31) with invariant parameters a and λ_m.

Equibiaxial tension

In equibiaxial tension, two of the principal stresses and accordingly, two of the stretches, are equal, thus yielding the derivative of the deformation function[5]:

$$\psi^{\lambda}(\lambda) = \lambda - \lambda^{-5} \qquad (35)$$

For homogeneous deformations the marcoscopic $\lambda_m^{\exp}$ should be determined from the average stretching which occurs along the chains. Deforming a sheet, the measured elongation $\lambda_m^{\exp}$ might be related to the average maximum elongation of the chains according to:

$$\lambda_m^{\exp} = \gamma \lambda_m \qquad (36)$$

where γ should depend on the functionality of the crosslinks as well as on the network structure. Its correct value is difficult to assess. The degree of agreement attained with $\gamma = 0.77$ is shown in *Figure* 4, curve C.

Hence, for the quantitative description of the total set of mechanical experiments presented at least four parameters are necessary: λ_m, γ, a_1, a_2.

SHORT CHAIN NETWORK

For systems with short chains it is questionable whether the λ_m adjustment is sufficient for taking into account the increasing impediments with regard to the conformational abilities of the chains in the network. A comparison with theoretical results is interesting. For making

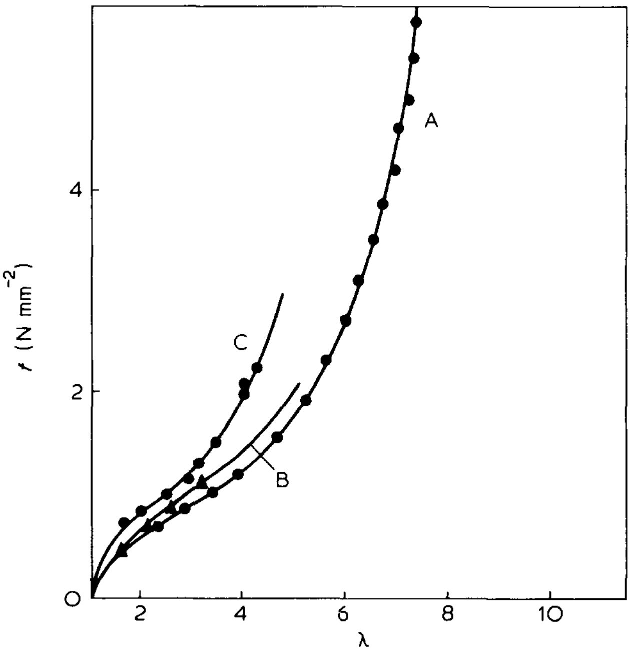

Figure 4 Theory compared with Treloar's data[2] at room temperature: A, in simple tension; B, pure shear with the same set of parameters as given in *Figure 1*; C, in equibiaxial tension with $m_{\exp} = \gamma\,\lambda_m$; γ = 0.77

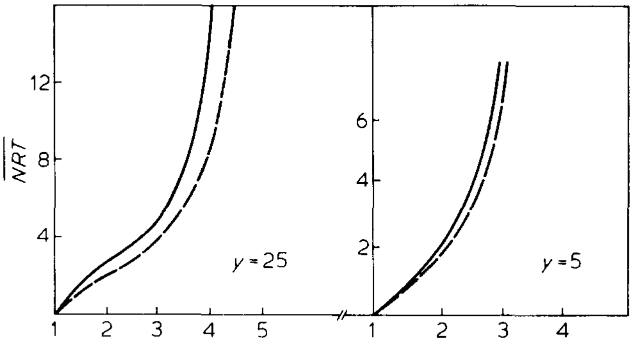

Figure 5 Simple elongations of short chain networks. Comparison of the 3-chain model calculations (broken lines)[2,8] with theoretical curves from equation (30) (full lines) using $a = 0.2$ = constant and y values as indicated

this estimate it might be reasonable to let the parameter a be invariant. Only the chain lengths of the network must be varied when we take the set of parameters obtained from the above description. It is then clear from *Figure* 5 that calculations using equation (31) are capable of reproducing the results which have been derived from the 'three-chain model'[2,8].

For the purpose of testing the meaning of this result, we have computed the extension forces of various rubber-elastic systems with different chain lengths, which have been measured by Flory *et al.*[9]. Adjusting the parameter y_{eff} we may compare these data with the degree of polymerization which has been calculated from the molecular weights reported. From *Figure* 6 it is readily seen that the relation given in equation (32) does not hold for real networks with short chains. This discrepancy should also be related to the increasing influence of the volume of the chains themselves. These conclusions, which are in qualitative agreement with expectations on physical grounds, illustrate the general meaning of the parameter λ_m which seems not only to be related to the chain length in the short-chain network, but takes volume effects of the chains themselves into account equally well.

THERMODYNAMIC REPRESENTATION

A more crucial test of the validity of the equation of state derived is provided by its thermodynamic consequences. Hence, we have to derive the energy- as well as the entropy-elastic components of the force according to its phenomenological representations:

$$f=\left(\frac{\partial H}{\partial L}\right)_{P,T}+T\left(\frac{\partial S}{\partial L}\right)_{P,T}=f_h+f_s \tag{37}$$

and

$$f=\left(\frac{\partial U}{\partial L}\right)_{V,T}+T\left(\frac{\partial S}{\partial L}\right)_{V,T}=f_e+f_s \tag{38}$$

with U, H and S being the internal energy, the enthalpy and the entropy respectively.

In the preceding discussions it has been tacitly assumed that the conformations of the chains are isoenergetic. This is, in general, not correct. Hence, let us modify the equation of state, equation (30), and account for energy differences between rotational isomeric states by incorporating the term[39,2,3]:

$$f=\frac{NkT}{L_0}\frac{\langle r^2\rangle}{\langle r_0^2\rangle}\cdot\psi^\lambda[B-a\psi^\lambda];$$

$$B=\psi_m^\lambda/(\psi_m^\lambda-\psi^\lambda) \tag{39}$$

The temperature dependence of $\langle r^2\rangle$, the mean-square end-to-end distance of the network chains, is governed by the thermal expansion of the sample, while $\langle r_0^2\rangle$, the mean-square end-to-end distance for a set of free chains in the bulk state, is determined by the energy differences between rotational isomeric states, thus being a characteristic of the chain structure.

From thermodynamics, it follows that the relative enthalpy contribution to the force, f, is given by[2]:

$$f_h/f=1-(T/f)(\partial f/\partial T)_{P,L} \tag{40}$$

while the relative energy contribution is obtained from:

$$f_e/f=1-(T/f)(\partial f/\partial T)_{V,L} \tag{41}$$

The changes of the force associated with a change of temperature are obtainable from equation (39):

$$\left(\frac{\partial f}{\partial T}\right)_{P,L}=\frac{f}{T}\left\{1-T\frac{\partial\ \ln\ \langle r_0^2\rangle}{\partial T}-\frac{\beta T}{\lambda^3-1}+\right.$$

$$\left.+\frac{T(B^2-2a\psi^\lambda)}{\psi^\lambda(B-a\psi^\lambda)}\frac{\partial\psi^\lambda}{\partial T}\right)+\frac{2}{3\lambda^3}\frac{\beta T a_2\psi^\lambda}{(B-a\psi^\lambda)}\Bigg\} \tag{42}$$

with:

$$\left(\frac{\partial\psi^\lambda}{\partial T}\right)_{P,L}=-\beta/3(\lambda+2\lambda^{-2});$$

$$\beta=\left(\frac{\partial\ln V}{\partial T}\right)_{P,L}=3\left(\frac{\partial\ln L_0}{\partial T}\right)_{P,L};$$

$$a=a_1\cdot(1-a_2/\lambda^2) \tag{43}$$

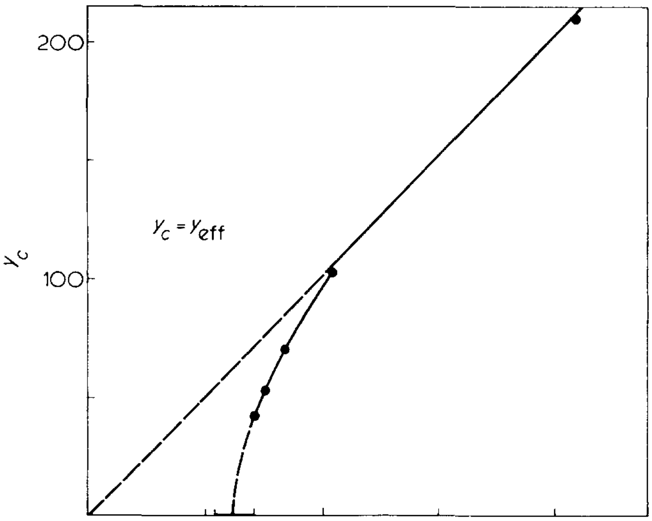

Figure 6 Chain length parameter y_c of rubber-networks calculated from the molecular weights reported by Flory *et al.*[9] against the theoretical y_{eff} which has been adjusted to calculate the retraction forces with the aid of equation (31) with $a = 0.2$ = constant

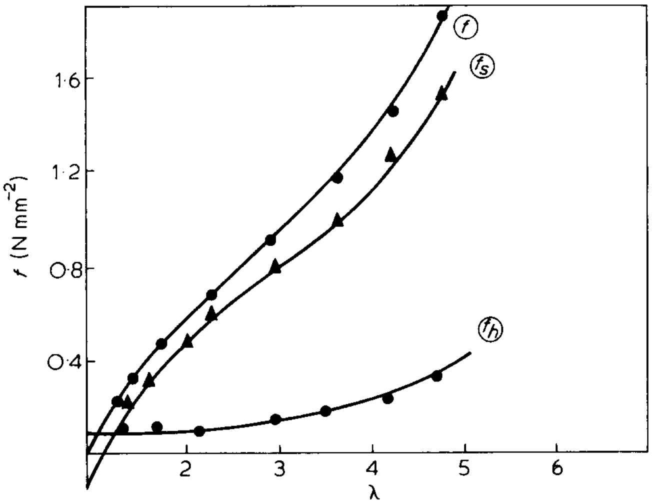

Figure 7 Plot of f_h (broken line), f_s and F accompanying extension of rubber according to Anthony, Caston and Guth[15]. Full and broken lines calculated from equations (39), (44) and (45) with $a = 0.2$; $\lambda_m = 9.8$; $\beta = 4.5 \times 10^{-4}$ deg^{-1} ^{3}; d ln$\langle r_0^2 \rangle$/dT = 4.1×10^{-4} deg^{-1} ^{3}

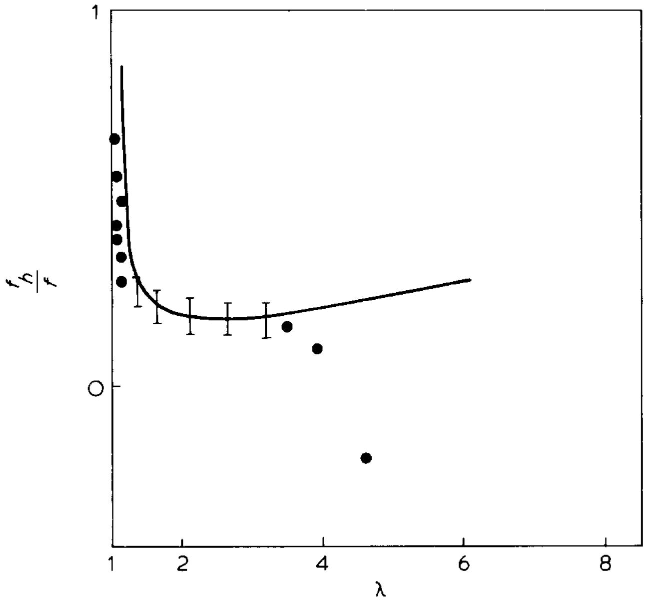

Figure 8 Relative enthalpy contribution f_h/f to the force for natural rubber in simple extension[18–21]. Full lines calculated by equation (44) using the parameters listed in *Figure 7*

where β defines the bulk coefficient of expansion. Hence, the fractional contribution f_h/f becomes:

$$\frac{f_h}{f} = T\left[\frac{\mathrm{d}\ln\langle r_0^2\rangle}{\mathrm{d}T} + \beta\left\{(\lambda^3-1)^{-1} + \frac{B^2-2a\psi^\lambda}{\psi^\lambda(B-a\psi^\lambda)}\left(\frac{\lambda+2\lambda^{-2}}{3}\right) - \frac{2a_2\psi^\lambda\lambda^{-3}}{3(B-a\psi^\lambda)}\right\}\right] \tag{44}$$

while f_e/f may be expressed as:

$$f_e/f = T\mathrm{d}\ln\langle r_0^2\rangle/\mathrm{d}T \tag{45}$$

The results indicate that, in general, the retractive force contains energetic contributions. For f_h/f, volume changes enter into the thermoelastic phenomena, whereas the energy differences between rotational isomeric states appear in any process under discussion.

Figure 7 shows that the modified equation (39) is capable of reproducing the experiments of Anthony *et al.*[15] assigning $\partial\ln\langle r_0^2\rangle/\partial T$ and β, the bulk expansion coefficient to 0.41×10^{-3} deg^{-1} ^{3} and 4.5×10^{-4} deg^{-1}. For sufficiently small elongations f_h is almost constant taking values near $f_h = 0.095$ N mm^{-2}. Thus, the fractional contributions f_h/f show a sharp rise as the strain approaches zero in contradiction to the asymptotic behaviour of f_e/f (see *Figures* 8 and 9).

We would like to stress the point that for small deformations marked contributions to f_h/f appear which are definitely related to the number of holes which must be formed during deformation if internal equilibrium is maintained[38]. Analogous effects have been observed in simple extension experiments performed in a stretching calorimeter on polycrystalline steel[17]. In this case, we conclude that at the beginning of the extension energetic changes arise which originate from the defined modifications of the phonon spectrum.

VOLUME CHANGES DUE TO STRESS

Particular interest is directed at an understanding of the changes in volume observed in simple elongation experiments on natural rubber[2,3,25,26]. They are related to the defined change of the concentration of holes during the deformation as discussed in the preceding section.

$$(\partial V/\partial L)_{P,T} = (\partial f/\partial P)_{T,L} \tag{46}$$

it follows from equation (39) that:

$$\left(\frac{\partial V}{\partial L}\right)_{P,T} = F \cdot x\left[\frac{1}{\lambda^3-1} + \frac{B^2-2a\psi^\lambda}{\psi^\lambda(B-a\psi^\lambda)}\,\frac{\lambda+2\lambda^{-2}}{3} - \frac{2\psi^\lambda \cdot a_2\lambda^{-3}}{3(B-a\psi^\lambda)}\right] \tag{47}$$

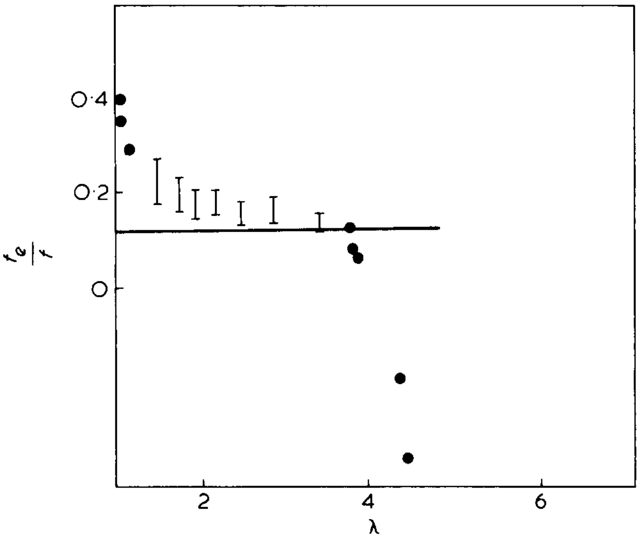

Figure 9 Calculated relative energy contribution f_e/f to the force for natural rubber in simple extension (full line) computed using equation (45) and compared with the data shown in *Figure 8*

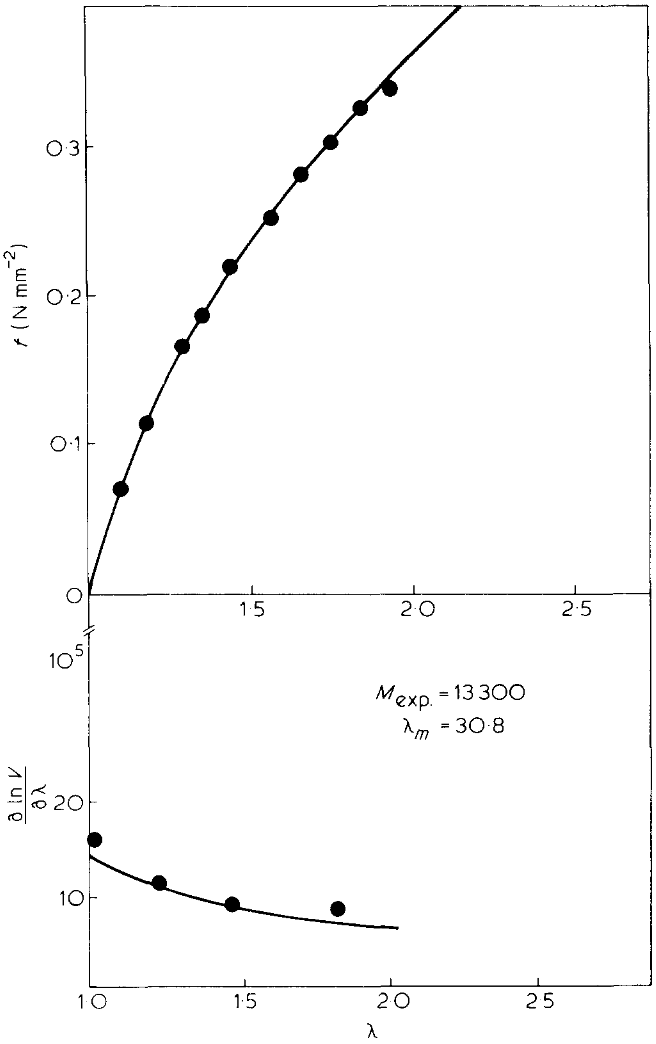

Figure 10 Extension force and volume dilation coefficient of natural rubber (Allen *et al.*[2,26]) full line calculated by equations (39) and (47) with the parameters λ_m = 30.8; a_1 = 0.2; a_2 = 0.1; NkT/L_0 = 28 N mm^{-2}; T = 293K; $L_0V^{-1}x$ = 2.6 x 10^{-4} mm^2 N^{-1}; M_{exp} = 13 300 (λ_m = $(M_{exp}/14)^{1/2}$

where

$$x = -(\partial \ln V/\partial P)_{T,L} = -3\left(\frac{\partial \ln L_0(p)}{\partial P}\right)_{T,L} \qquad (48)$$

is the bulk compressibility. It appears profitable to compare experimental results[2,25,26] with our prediction that:

$$(\partial \ln V/\partial \lambda)_{P,T} = -L_0V^{-1}(\partial f/\partial P)_{T,L} \qquad (49)$$

For natural rubber at finite extensions, the theoretical values fit the data approximately (*Figures* 10 and 11). λ_m has been calculated from the experimental M_{exp} with the aid of $\lambda_m = (M_{exp}/M_0)^{1/2}$. For any further discussion of the correspondence there is need of a more accurate discussion of the front factor, based on properly synthesized rubber–elastic systems[40].

In summary, the results from our studies on natural rubber support the view that the retractive force is not only intramolecular in origin. The theory is able to account satisfactorily for its pressure dependence and its dilatation behaviour.

PHASE TRANSITION

It is useful to examine the occurrence of the phase transition in real networks while we are not considering the stress- and orientation-induced crystallization. Considerations pointing in the same direction have been published by Müller, who discussed the simple extension of partly crystallized systems[27].

The stability of real networks is limited on the same grounds as those for real gases. But is is important to recognize that the phase transition of an oriented network should occur in the configurational space.

Without discussing this at the moment and taking $a = a_0 y$ we arrive at the state diagram shown in *Figure* 12. If the energetical components are sufficiently strong, simple homogeneous elongation is not possible: under the conditions of thermodynamic equilibrium the coexistence of two macroscopic phases each with a definite ratio of elongation is predicted. Macroscopic necking is a proper process of the new phase with different orientation of the chains. On stretching, the neck is then predicted to run over the total sample at constant force and temperature. The force can be increased only when the transition is accomplished.

FINAL CONSIDERATIONS

Under the premises that the stored elastic free energy resides within the chains of an ideal network and that thus the stress originates therein, the elastic energy may be taken as the sum of the individual chains constituting the network. Implementation of the theory requires that a connection be established between the configurations of the chains and the macroscopic strain. Now, representation of $f(\lambda)$ by equation (39) clearly implies a modification of this concept in that van der Waals

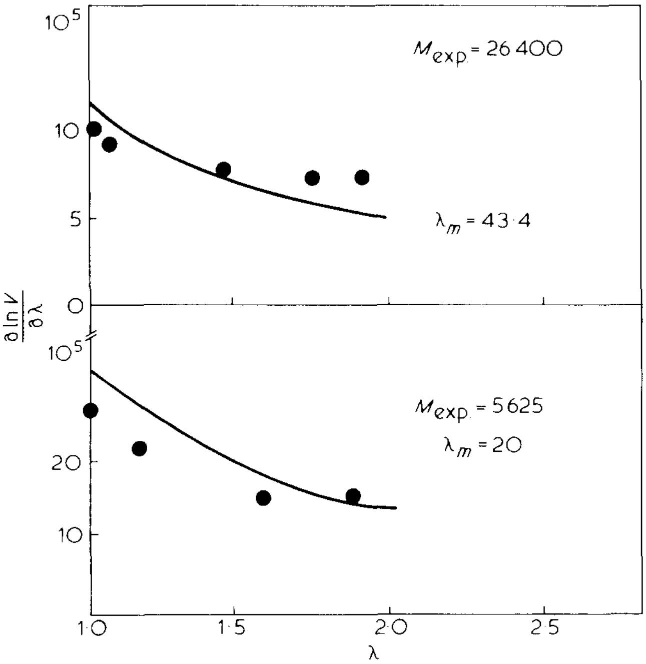

Figure 11 Volume dilation coefficient of natural rubber (Allen *et al.*[2,26]). Full lines calculated with the aid of equation (47) using the same parameters listed in *Figure 11* but varying the chain length as indicated, M_{exp} designating the experimental values, M the values used to obtain the best fit of the calculation to the data

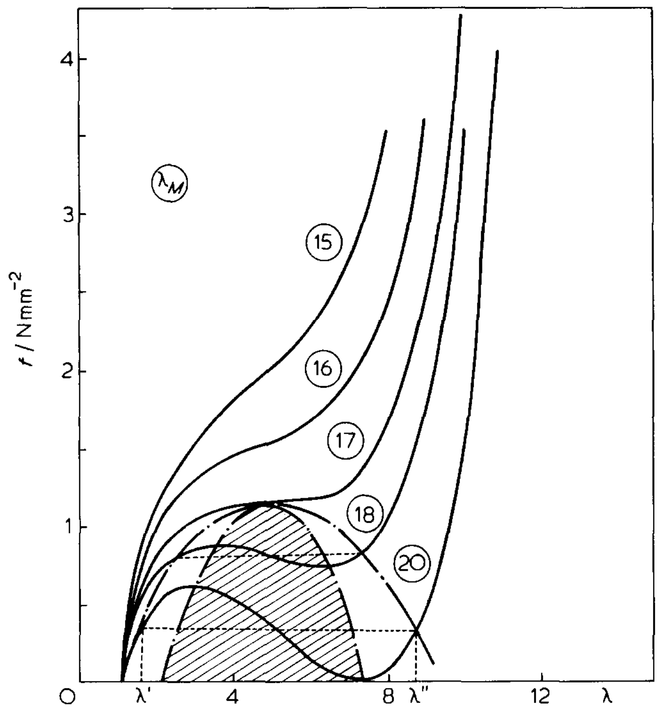

Figure 12 Phase diagram for real network calculated with the aid of equation (39) using $NkT/L_0\ \langle r^2\rangle/\langle r_0^2\rangle$ = 35.9 N mm^{-2} and $a = a_0 y$ with a_0 = 0.2

interactions between the chains are allowed to occur. But expressing equation (39) as follows:

$$f=\frac{NkT}{L_0}\frac{\langle r^2\rangle}{\langle r^2\rangle_0}\cdot\psi^{\lambda}\frac{\psi_m^{\lambda}}{\psi_m^{\lambda}-\psi^{\lambda}}-a_0\psi^{\lambda 2} \qquad (52)$$

with

$$a_0=\frac{NkT}{L_0}\cdot\frac{\langle r^2\rangle}{\langle r_0^2\rangle}\cdot a \qquad (53)$$

a_0 may also be related to the chains of the network, thus, maintaining their basic autonomy.

The orientation pattern of the chain segments will be discussed elsewhere. First results obtained from measurements of the birefringence and of the anisotropy of thermal diffusivity seem to indicate that the attraction term in equation (52) does not contribute. Hence, it is hoped to prove the consistency of the new equation of state with the neutron scattering results. A distinct influence of the interactions on the configurations of the chains is expected from the fact that the model presented corresponds to a description of a molecular network as a conformational gas with weak interactions.

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NOMENCLATURE

W	reversible deformation energy
N	number of chains in the network
k	Boltzmann constant
λ_i	extension ratio in direction i
V_0	volume in the reference state
V	volume of the deformed sample
L_0	length in the reference state
L	length of the deformed sample
f	extension force
$\psi(\lambda)$	deformation function
$\psi^{\lambda}(\lambda)$	derivative of $\psi(\lambda)$
ε_i	energy in the phase-space cell
$\varphi(\lambda)$	deformation potential of a single chain
Z	partition function
n_i	statistical weight in ith phase space cell
S	entropy
U	internal energy
$V, \Delta\tau$	q space volume and its cell volume
Σ'	sum in the momentum space
$V_c, \Delta\tau_c$	volume of configurational part of the phase space and its cell-volume

p	macroscopic pressure
a, b, a^*, b^*	van der Waals parameters
λ_m	maximum extension ratio
$\psi_m^\lambda \equiv \psi^\lambda(\lambda_m)$	the derivative of the deformation function for λ_m
M_0	molecular weight of the chain link
y	number of links within the chains
R	gas constant
m	mass
β	bulk thermal expansion coefficient in the isotropic reference state
f_h, f_e, f_s	enthalpy, energy and entropy changes of f