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UN MODELO INTERPRETATIVO DEL COMPORTAMIENTO TERMOELASTICO DE MATERIALES RETICULADOS

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Abstract- Molecular networks may be considered as elastic fluids, the conformational abilities of which are adecuately characterized with the aid of the model of a Van der Waals conformational gas with weak interactions. The internal properties are submitted to the conditions of internal equilibrium, thus, having their changes uniquely related to the global transformations of the network upon deformation. The global properties are at least determining the limits of stability which are expressed in the Van der Waals approach by formulating of a reduced equation of state of real networks. It will be discussed on hand of thermo-elastic measurements and its quantitative description what is in need for a full and self-containing phenomenological description of molecualr networks.

Key words: Thermo-elastic, networks

Resumen- Los materiales de estructuras moleculares reticuladas pueden considerarse como fluidos elásticos, pues su comportamiento conformacional es adecuadamente caracterizado mediante un modelo conformacional gaseoso, con interacciones débiles, tipo Van der Waals. Las propiedades internas son comprendidas en las condiciones de equilibrio interno, asi, los cambios relativos son sólo respecto a las transformaciones globales de los sistemas reticulados, es decir, de sus deformaciones. Estas propiedades globales, al menos, determinan los limites de estabilidad los cuales son expresados en la aproximación de Van der Waals mediante la formulación de una ecuación reducida de estado de sistemas reticulados reales. Se discute en base a mediciones de propiedades termo-elásticas y a su descripción cuantitativa, necesaria para una descripción fenomenológica particular y global de los sistemas moleculares reticulados.

Palabras clave: Termoelasticidad, reticulados

INTRODUCTION

It was the ingenious idea of Kuhn and Grün [1,2] to consider a real chain a mathematically defined fiber occupying no volume, having no internal structure, thus, without interactionand with ideal penetration abilities realizing each isoenergetical conformation with the same a priori probability. This "phantom chain" remains a physical system because of having its mass continuously distributed over the total fiber. This abstract model is congenial to the definition of a mass point, a model successfully used in the classical mechanics [3]. It is a logical consequence that the phantom chain is characterized by an invariant statistical shape storing kinetical energy only the amoung of wich is in proportion to the absolute temperature. The usefulness of this conception was manifested by the outstanding success of the theory of a Gaussian network [1,2,4] in describing basicly correct the elastic properties of real networks at sufficiently small elongations.

It has, on the other hand, readily been noted that the Gaussian model is totally unacceptable for large deformations approaching full extension of the chains [1,2,4]. Hope was nevertheless engendered from the results of non-Gaussian treatments [1,2,4] that the approximation of the actual situation by the Gaussian theory should be satisfactory throughout the range of ordinary interests [5]. Improvements of the satatistical theory are thus often developed proceeding from the Gaussian approach [6,13].

In any case, a complete and self-contained statistical theory of the thermoelasticity of real networks which is covering the total range of strains is still missing. This situation is provokingthe questionwhether there might be a chance to develop at least a phenomenological description which is fully characterizing thr objetive of this paper is to consider the momentary situation in this concern.

THERMODYNAMICS

By virtue of our interests in reversible deformation processes of initially isotropic bodies, we anticipate that we shall be concerned with the differential form of the fundamental equation [2,4,14]

$$dU = TdS - pdV + f dL \qquad (1)$$

where: U is the fundamental function U(S,V,L,N) defined in its natural coordinates; S is the entropy, V the volume ; L the longh and N as the number of particles which is considered to be constant (dN=0). Recalling the definition of the quasi-static heat flux

$$dQ = TdS \qquad (2)$$

we learn from equation (1) that for a thermodynamically complete description the energy transfer during deformation must be know embracing heat and work-exchange with appropriate reservoirs.

Referring to literature we arrive by the use of the Legendre-transformes of equation (1), [14]

$$dF = -SdT + f dL \qquad (3)$$

and

$$dG = -SdT - Vdp + f dL \qquad (4)$$

at the thermodynamic equations of state [2,4,15,16,17].

Isothermal-isochoric

$$f = f_g + f_s$$

$$f_g \equiv \left(\frac{\partial U}{\partial L}\right)_{T,V} = f - T\left(\frac{\partial f}{\partial T}\right)_{L,V}$$

$$f_s \equiv -T\left(\frac{\partial S}{\partial L}\right)_{T,V} = T\left(\frac{\partial f}{\partial T}\right)_{L,V} \qquad (5)$$

Isotermal-isobaric

$$f = f_b + f_s$$

$$f_b \equiv \left(\frac{\partial H}{\partial L}\right)_{T,P} = f - T\left(\frac{\partial f}{\partial T}\right)_{L,P}$$

$$f_s \equiv -T\left(\frac{\partial S}{\partial L}\right)_{T,P} = T\left(\frac{\partial f}{\partial T}\right)_{L,P} \qquad (6)$$

Hence, one can draw from force - temperature measurements, conveniently carried out at fixed length and pressure, thermodynamic characteristics of the molecular networks. By integration under constant temperature and pressure conditions we are led to

$$Q = T\Delta S_{T,P} = \left(\int f_s dL\right)_{T,P} \qquad (7)$$

and correspondingly

$$W = \left(\int f dL\right)_{T,P} \qquad (8)$$

We can provide a convenient form of characterizing elastic systems. To these purposes we are defining the characteristic ratio [19,20]

$$\eta = \frac{Q}{W} = \frac{\Delta U}{W} - 1 \qquad (9)$$

Two idealized limiting models can, on principle, be discussed:

The ideal energy-elastic system

Here we postulate the validity of the condition

$$\eta = 0; \quad \Delta U = w \qquad (10)$$

which expresses that the reversible work is totally transferred into internal energy, ΔU.

The ideal entropy-elastic system

Another type of elastic system can be defined by assuming that,

$$\eta = -1; \quad \Delta U = 0 \tag{11}$$

such that the deformational processes are considered to occur under invariant internal energy conditions. The work exchanged is totally transformed into an adequate change of the entropy of the system. A well know system of this type is the ideal gas.
We will see that the above frame permits us to characterize elastic systems in a particularly convenient manner by always referring to one of the limiting odels. Let us proceed therefore to the consideration of concrete elastic systems, beginning with the discussion of an isotropic Hookian body.

The isotropic Hookian Solid

The system elements are assumed to be "iocalized" such that the strain-energy function in the mode of simple elongation is parabolic having its minimun potential-energy in the unstrained state. Hence , we are led to

$$W = K(L - Lo)^2/2 \tag{12}$$

where K is the modulus of the (quai-) isotropic elastic body, Lo is the length in the unstrained state. Simply elongating to L, the Hookian law of an isotropic system is obtained

$$f = \left(\frac{\partial W}{\partial L}\right)_{T,P} = K\left(L - L_0\right) \tag{13}$$

We have to be aware that the length in the fiducial state, Lo, is dependent on the variables T and p. Let us suppose that the thermal expansion of the unstrained system is to the first approximation described by the use of the linear thermal expansion coefficient, ß, defined by

$$\beta = d \ln Lo/dT \tag{14}$$

Neglecting the variation of K on the temperature, we then are led to the thermodynamic equations of state of a Hookian system in the mode of simple elongation

$$f\text{b} = K(L\text{-}Lo) - K\beta TLo \tag{15}$$
$$f\text{s} = K\beta TLo$$

We recognize a typical symmetry in respect to that terms which are describing the transformation of intrinsic properties of the Hookian solid showing thermal expansion. This can easily be demonstrated by the use of n which is now obtained to be given by [18,19,20,21,22]

$$\begin{aligned} n &= Q/W \\ &= [K\beta T(L\text{-}Lo).Lo]/[K(L\text{-}Lo)^2/2] \\ &= 2\beta T/\varepsilon \end{aligned} \tag{16}$$

with $\varepsilon = (l\text{-}Lo)/Lo$ as the elastic strain. In the limits of $\beta \to 0$, we arrive at the heuristical system with ideal energy-elasticity (n = 0), only displaying a defined change of the internal energy produced by an affine transformation of the "static lattice configuration". Then, it is to be noted that the transformation of the lattice dynamics [19,20,23] which is by its unharmonics originating the macroscopic thermal expansion, is submitted to the condition

$$\left(\frac{\partial H^{(i)}}{\partial L}\right)_{T,P} \cong \left(\frac{\partial U^{(i)}}{\partial L}\right)_{T,P} = T\left(\frac{\partial S^{(i)}}{\partial L}\right)_{T,P} = K\beta TL_0 \tag{17}$$

The index (i) is added as a reminder that contributions of internal freedoms to the extensive state functions should only be taken into consideration. Equation (17) must necessarily be fulfilled if a GIbbs-function in the variables (T,p,L,N) is existent (14,17). Taking the phonons as quasi-particles, equation (17) is expressing that according to the conditions of internal equilibrium all phonons are transformed under the condition that the changes of potential and kinetical energies are necessarily identical [17,18].
An analogue condition of internal equilibrium can be shown to be valid on heating an ensamble of quantum

mechanical harmonic oscillators. In this case we have

$$\partial U^{(1)} / \partial \beta_0 = T \partial S^{(1)} / \partial \beta_0 \qquad (18)$$

with ßo = 1/(kT). This is exhibiting the same symmetry which is always imposed onto changes of "localized" internal states under the condition of internal equilibrium.

It is further to be noted that these trasformations of the internal properties do not affect the thermodynamic stability of the Hookian body. We find immediately

$$\left(\partial f / \partial L\right)_{T,P} = K > 0 \qquad (19)$$

Hence, a Hookian solid with linear thermal expansion is absolutely stable in all states of deformation.

It is interesting to prove the quality of the above approach because of the provocative simplicity. It is seen from the plot in **figure 1** that n(ε) defined in equation (16) is indeed correctly describing the data published by Göritz [19]. This is fascinating because there is no fitting parameter available. ß, the phenomenological coefficient of thermal expansion in the unstrained, isotropic state is solely determining the transformation of "internal properties" during quasistatic deformation.

Moreover it is seen from the plot in **figure 1** that at smallest extensions internal properties are in the first place affected. Their transformation is related to a defined increase in the anharmoniticity of the interaction potentials durin extension, thus, bringing about an adiabatic cooling of elastic solid on elongation [18,23]. This happens because of the necessity of distributing the total kinetical energy over an increasing number of phonon states the energy levels of which are continuously lowered with elongation.

Hence,we arrive at the hypothesis that global properties in the elastic solid must be modified if limited thermodynamic stability in deformed states will be described. In view of this question it is attractive to study molecular networks. Here, we will be in the position of also discussing the limits of stability what might also influence strategies in describing solid-state deformation at large elongations.

Networks

In this section we consider the thermo-elastic properties of networks proceeding from the heuristical model of an ideal network (Gaussian network) to real networks by systematic and logical improvements.

Gaussian Networks

The properties that are defining the ideal network are the best recalled by the use of the simplifying sketch shown in figure 2. Gaussian chains in its equilibrium conformation (maximum of entropy of the representative coil) are forming a network with pointlike fixed nonfluctuating crosslinks [1,2,4]. Postulating an affine transformation of these crosslinks [1,2,4] a distint orientation of the chain-end vectors is needed accompanied by a defined dilatation **(fig.2)** [1]. Having Gaussian chains as phantom-chains, the energy stored in the network is kinetical only. Hence, we may consider this phantom network to be adequately represented as an **ideal conformational gas** [25,26]. This hypothesis can the best be proven by studying the thermo-elastic properties. The deformational potential in the mode of simple elongation should correspond to that of an isotropic continuous [27]

$$W_i(\lambda) = \left(\overline{G}/2\right)\left(\lambda^2 + 2/\lambda - 3\right) : \lambda = L/L_0 \qquad (20)$$

where λ is the macroscopic strain in direction of the stress. The elongation should occur under constant volume conditions too. The entropic nature of energy changes upon deformation can only be taken into consideration by appropriate specification of the modulus

$$\overline{G} = \overline{G}_0 T \qquad (21)$$

it is the advantage of the molecular statistic treatment of the Gaussian network [1,2,4] that $\overline{G}$ can uniquely be related to temperature as well as to the number of chains, hence, delivering the relation

$$\overline{G} = \overline{G}_0 T = NkT \qquad (22)$$

which is equivalent to the fact that each chain in the isotropic state is storing in the average the same amount the kinetical

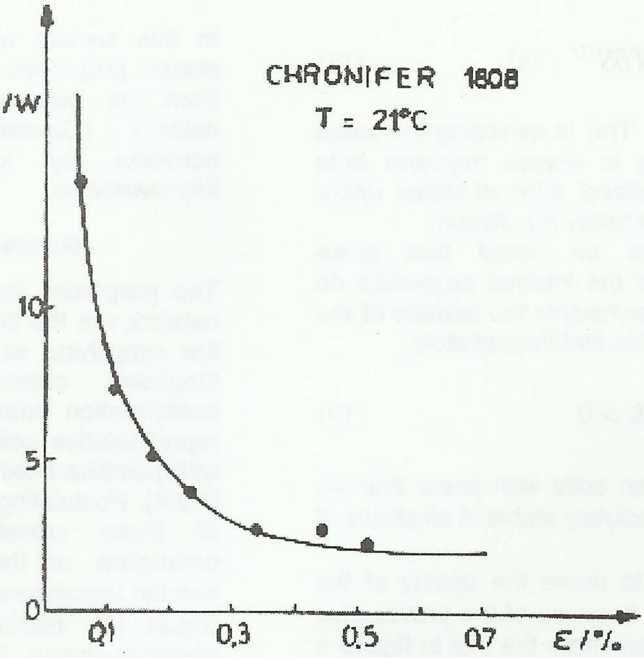

Fig.1 : Plot of n versus ε for steel wire (Chronifer 1808) according to D. Göritz [19] deformed in simple elongation at room temperature. The solid line is computed with the of equation (16) (ß= 4,05 x 10-5 deg^{-1})

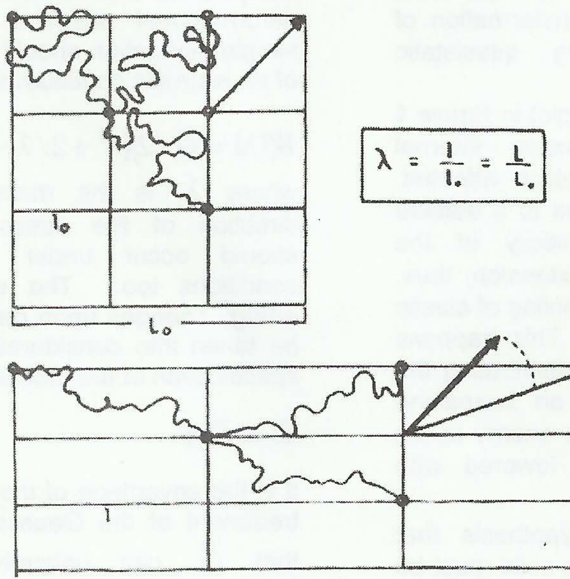

Fig.2: Illustration of the affine transformations of an isotropic network. An idealized representation of the fiducial state is drawn out in the upper part of this figure. The chain end vectors are then tranformed as shown in the lower part where the orientational and dilational transformation of a distincd chain-end-to-end vector is to be seen.

energy of conformation being equal to 3/2 kT [18,25].
With equation (20) we are led to the mechanical eqution of state of an ideal network

$$f = \left(G_0 / L_0\right)TD; D = \lambda - \lambda^2 \qquad (23)$$

By the use of the definitions (5) and (6) the thermo-elastic equation of states are thus abtained to be equal to

$$f_b = 0 \qquad (24)$$

$$f_s = T\left(\frac{\partial f}{\partial T}\right)_{L,P} \equiv f \qquad (25)$$

Hence, we easily derive

$$\eta = Q/Wi = -1 \qquad (26)$$

THis result is underlining that the ideal network must be considered as an ideal entropy-elastic system.

The global properties of the Gaussian network model are defined by postulating phantom-chains, having no volume, no internal structure, no interactions, thus, being physically characterized by having their mass continuouslydistributed over the fiber-like chains themselves. This abstract conception is in direct contrast to the real situation dictated in condensed matter.
A sustantial step to the right understanding of realnetworks has be done by various authors especially by P.J. Flory [2,15,16,17]. It was introduced to consider the thermal expansion as well as the contributions of non-isoenergetic rotational isomers. The second step is directed to a corection the "standard state" of networks. We demonstrate this the best by defining the new deformation potential

$$W = <r^2>/<r_o^2>.Wi \qquad (27)$$

$<r^2>/<ro^2>$is very often called the "memory term" relating the squared average of the actual chain-end-to-end vector in the network to the corresponding vector of a freely-jointed chain having non isoenergetical rotational isomers [2,4,28-32].

The belonging thermo-elastic equations of state are equal to

$$f_b = f\left[T\frac{d\,ln<r_0^2>}{dT} + \frac{3\beta T}{\lambda^3 - 1}\right] \qquad (28)$$

$$f_s = f\left[1 - T\frac{d\,ln<r_0^2>}{dT} + \frac{3\beta T}{\lambda^3 - 1}\right] \qquad (29)$$

Because of observing the same symmetry in respect to the terms originated by internal freedoms as discussed in prior sections, we arrive at the conclusions.

-The global properties of ideal networks with thermal expansion etc. are represented as an ideal conformational gas.

-Internal deformation afeccted properties are "anharmonic interactions" in the macomolecular fluid as well as the configurations of the rotational isomers.

With the same arguments as used in the discussion of the thermo-elasticity of the Hookian body, we find then that the ideal network with internal properties as defined here is absolutely stable.
It is interesting to check utility of the above approach. The stress-strain behaviour appears to be correctly predicted for small extensions up to λ =1,3 - 1,4 what is exemplified in **figure 3A**. What is fascinating is the observation that the "Flory-approach" is indeed also correctly describing thermo-elasticity of real networks in the range of sufficiently small elongations. This is demonstrated in **figure 3B**. We thus find that real networks behave at small elongations in respect to the conformational abilities of their chains like an ideal conformational gas; the volume, the finite length of the chains, their interactions are of no measurable importance. The internal properties are submitted to the conditions of internal equilibrium, thus, contributing "potential"

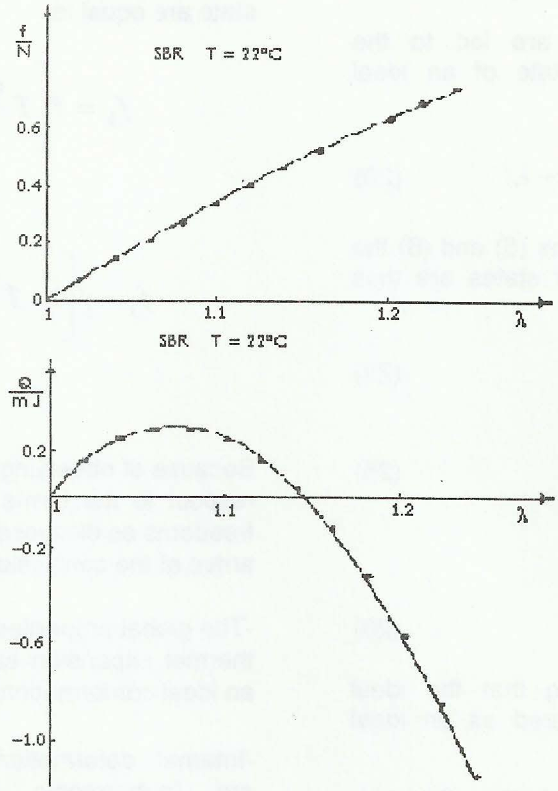

Fig 3: Styrene butadiene rubber (SBR) in simple elongation at small strains at room temperature according to G.Höhne et al [33]. A) stress-strain curves: The solid line is computed with the aid of equation $f=\overline{G}\ D$, $\overline{G}=(\rho RT/M)\langle r^2\rangle/\langle r_o^2\rangle = 4{,}1\text{x}10\text{-}3\text{N}$; B) Q(λ) computed using equtions (29) and (7) with ß=2,6x10-4 K-1; d $\ln\langle r_o^2\rangle/dT=0$ K-1.

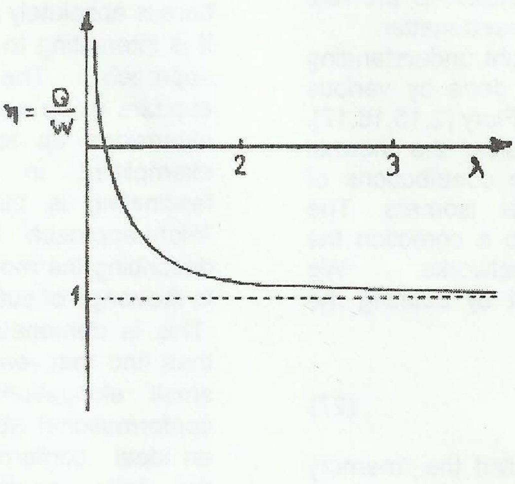

Fig.4: η(λ)de SBR at room temperature according to G.Höhne et al [33] in the range of small strains. The solid is computed with the set of parameters as given in the capture of figure 3, the dotted line is indicating the ideal network with ß=0

and "kinetical" energy of deformation as demanded by equation (17).

The above hypothesis is also illustrated in **figure 4**. We observe a thermo-elastic inversion which is expressed in $\eta(\lambda)$ by its change in sign. This inversion is deeply related to the fact that at smallest λ's the production of "holes" is dominant compared with globally considered change of conformation. Hence, we are led to the conclusion that the volume of molecular networks must necessarily be increased on deformation if the internal properties remain that of a fluid [2,10,15,35,36]. The correctnees of this interpretation is manifested for sufficiently small elongations (see figure 5) using the relation [2]

$$\Delta V/V = 3\chi NkT <r^2> (1-\lambda^{-1})/[V <r_o^2>] \qquad (30)$$

where 3χ is the isothermal bulk compressibility at constant length defined by

$$\chi = -(\partial \ln L_o/\partial P)_{L,T} \qquad (31)$$

From these results we find the Gaussian approach as an adequate description of the thermoelastic properties of rubbers at sufficiently small extensions:

Here, the global properties are indeed indistinguishable from the predictions of the ideal network theory provided that the chains are sufficiently long [2,4]. Although represented as an ideal conformational gas we find internal properties regulated by the conditions of internal equilibrium,thus, being in a defined dependence upon the global deformation processes. This should for example also influence the trans-gauche configurations in rubbers, if we let the trans-conformation be the energetically lower-valued rotational isomer, we derive from equation (17) with

$$\left(\frac{\partial H^{(l)}}{\partial L}\right)_{T,P} < 0 \qquad (32)$$

for simple elongation that

$$T\left(\frac{\partial S^{(l)}}{\partial L}\right)_{T,P} < 0 \qquad (33)$$

An increased ordering of the rotational isomers may appear favouring stretching induced crystallization in such networks.

Yet,there are no doubts about the limits of the attractive approach presented. This is ilustrated with documentary evidence in **figure 5** and **figure 6.**

Thus, we are led to the question whether and appropriate improvement of the simplest model in the global range, represented by the concept of an ideal conformational gas, can establish a more satisfying approach to the data.

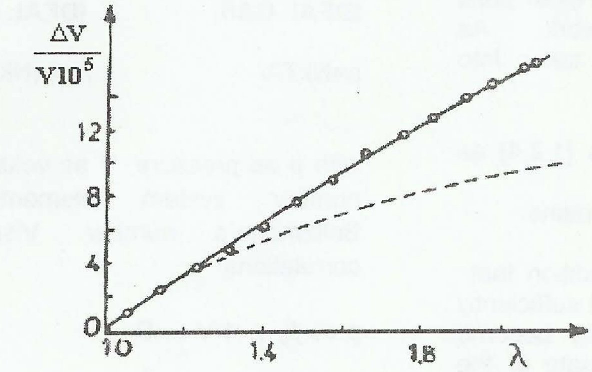

Fig.5: ΔV/V against λ according to Christensen et al [35].The doted fine is calculated employing equation (30) with $3\chi(NkT/V)<r^2>/<r_o^2>=1{,}5x10-4$ according to Treloar [2].

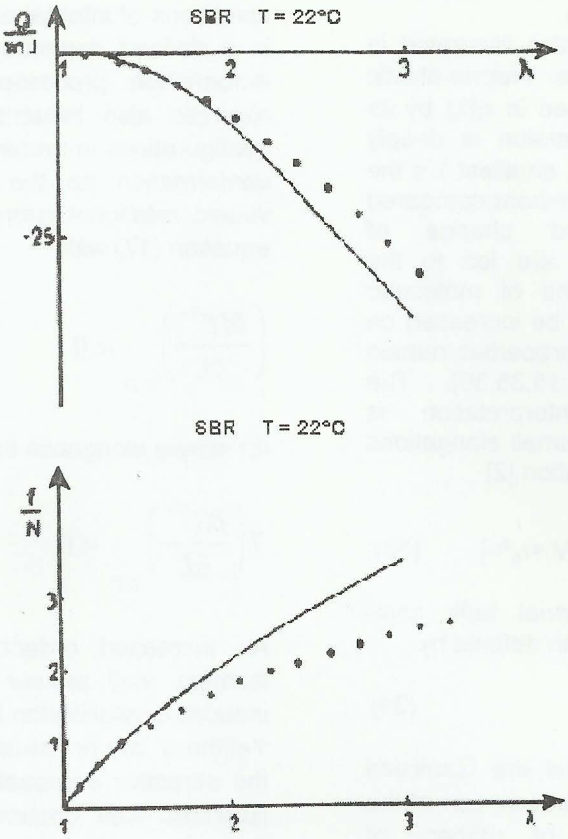

Fig 6: Thermo-elastic properties of SBR at room temperature according to G. Höhne et al [33]. A) stress-strain data ;the solid line computed B) Q(λ) -data; the solid line calculated for a Gaussian network; in both calculations the same set of parameters as indicated with the calculations shown in figure 3 and 4, has been used.

The Van der Waals-approach

An adequate mechanical equation of state should be more exacting at large extensions than that of a Gaussiannetwork. As essential aspects it should be taken into consideration:

-The finite length of the chains [1,2,4] as well as.
-Global interaction between the chains.

It is moreover a necessary condition that the new equation of state must at sufficiently small elongations asympto-tically become identical with the equation of state of the ideal network; All of the above aspects can be considered by a van der Waals equation of state of networks [17,18,25,26].

Comparing the equation of states of the ideal systems

IDEAL GAS	**IDEAL NETWORK**
$p=NkT/V$	$f_o = (NkT/L_o)D$

with p as pressure, V as volume, N as the number system elements and k Boltzmann`s number. Visualizing the correlations

$p \leftrightarrow f_o$; $1/V \leftrightarrow D$

it is easy to formulate, proceeding from the van der Waals equation of state of real gases,

$p = NkT/(V-\mathbf{b}) - \mathbf{a}/V^2$ (34)
the corresponding equation for real networks

$f_o = NkT/[L_o(1/(1/D - 1/D_m)] - a_o/(1/D^2)$ (35)

which we prefer to write in its extended form

$$f = \frac{f_0}{A_0} = \frac{\rho RT}{\lambda_m^2 M_{st}} * \frac{<r^2>}{<r_0^2>} D(B - aD) \quad (36)$$

where

$D = \lambda - \lambda^{-2}$

$B = D_m/(D_m - D)$; (37)

$D_m = \lambda_m - \lambda_m^{-2}$; $\lambda_m = L_{MAX}/L_0$ (38)

we recognize from equation (36) that the front factor group is identical with the equations of state of the Gaussian network. we have only rewritten the front-factor by using the density ρ and the average molecular weight of the chains [1,2]

$M = n_{st} M_{st}$ (39)

This cuantity may be expressed as the product of theaverage number of statistical segments, n_{st}, times the molecular weight of this unit, M_{st}. In the Gaussian approach the maximum strain of such a chain should be given by [37]

$\lambda_m^2 = n_{st}$ (40)

The global properties of the network are substantially modified by factor in the brackets being determined by both of the van der Waals coefficients

λ_m and $a = a_o/\overline{G}$, letting $\overline{G}$ be written as

$\overline{G} = (RT\rho/\lambda_m^2 M_{st}) <r^2>/<r_0^2>$.

It is seen from equations (37) and (38) that λ_m is defined in the limit of extremely large extensions $\text{limit}_{\lambda\to\lambda m} f = \infty$.

This heuristical state corresponds to a basic singularity: Infinitely large forces would be necessary bring the rubber comprised of chains of finite lengths into this state, the characteristic λ_m of which is, thus, uniquely related to the average chain length in the network. The parameter a is a least empirically describing "global" interactions between the chains restricing definitely their conformational abilities [25,26].

The thermo-elastic equations of state are then equal to [38]

$f_b = f.T\phi$

$f_s = f(1 - T\phi)$ (41)

with

$$\phi = \beta - \mu + \frac{\overline{D}}{D} + \frac{\overline{B} - a\overline{D} - \overline{a}D}{B - aD}$$

$$\frac{\partial \ln <r^2>}{\partial T} = 2\beta; \frac{\partial \ln <r_0{}^2>}{\partial T} = \mu;$$

$$\overline{D} \equiv \frac{\partial D}{\partial T} = \frac{\partial D}{\partial \lambda}\frac{\partial \lambda}{\partial T}; \frac{\partial \lambda}{\partial T} = -\beta\lambda$$

$$\frac{\partial D}{\partial \lambda} = 1 + 2\lambda^{-3}$$

$$\overline{a} \equiv \frac{\partial a}{\partial T} = -\frac{a_0}{\overline{G}^2}\left(\frac{\partial \overline{G}}{\partial T}\right) + \overline{G}\left(\frac{\partial a_0}{\partial T}\right)$$

$$\overline{B} \equiv \frac{\partial B}{\partial T} = \frac{1}{D_m - D}\left(\overline{D}_m + B\left(\overline{D} - \overline{D}_m\right)\right)$$

$$\overline{D}_m \equiv \frac{\partial D_m}{\partial T} = \frac{\partial D_m}{\partial \lambda_m}\frac{\partial \lambda_m}{\partial T}; \frac{\partial D_m}{\partial \lambda_m} = 1 + 2\lambda_m^{-3}$$

$$\frac{\partial \lambda_m}{\partial T} = -\lambda_m \beta$$

Comparison with experiments

First we demonstrate the quality of the fit to stress-strain data for various rubbers. **In figure 7** the "mooney" plot of experimental force-extension data for peroxid crosslinked rubbers published by Mullins [39] is shown. Letting $a = a_0/\overline{G} = 0{,}26$ be invariant, we arrive with the λ_m's as indicated with each curve at a very satisfying representation of these data. The upturn at larger extensions is clearly the effect of finite extensibility of the chains [1,2,4,41,44] described by a proper value of λ_m [18,25,38,40]. It is to be noted that this fit is based on the assumption of having identically sized statistical segments in all the systems involved.

It should be emphasized that λ_m and a can be obtained from the fit to the shape of the stress-strain data [37], thus, bringing about the outstanding possibility of determining the size of the statistical segments, M_{st}, from the discussion of the absolute force, provided that the memory term is equal to one and that the functionality corrections [7,45-51] are known.

From the representation shown in **figure 8** the topological relationships between these stress-strain curves is readily visualized. All these data can satisfyingly be fitted with equation (36) delivering λ_m-and a- values which have all together the same order of magnitude **(table 1).**

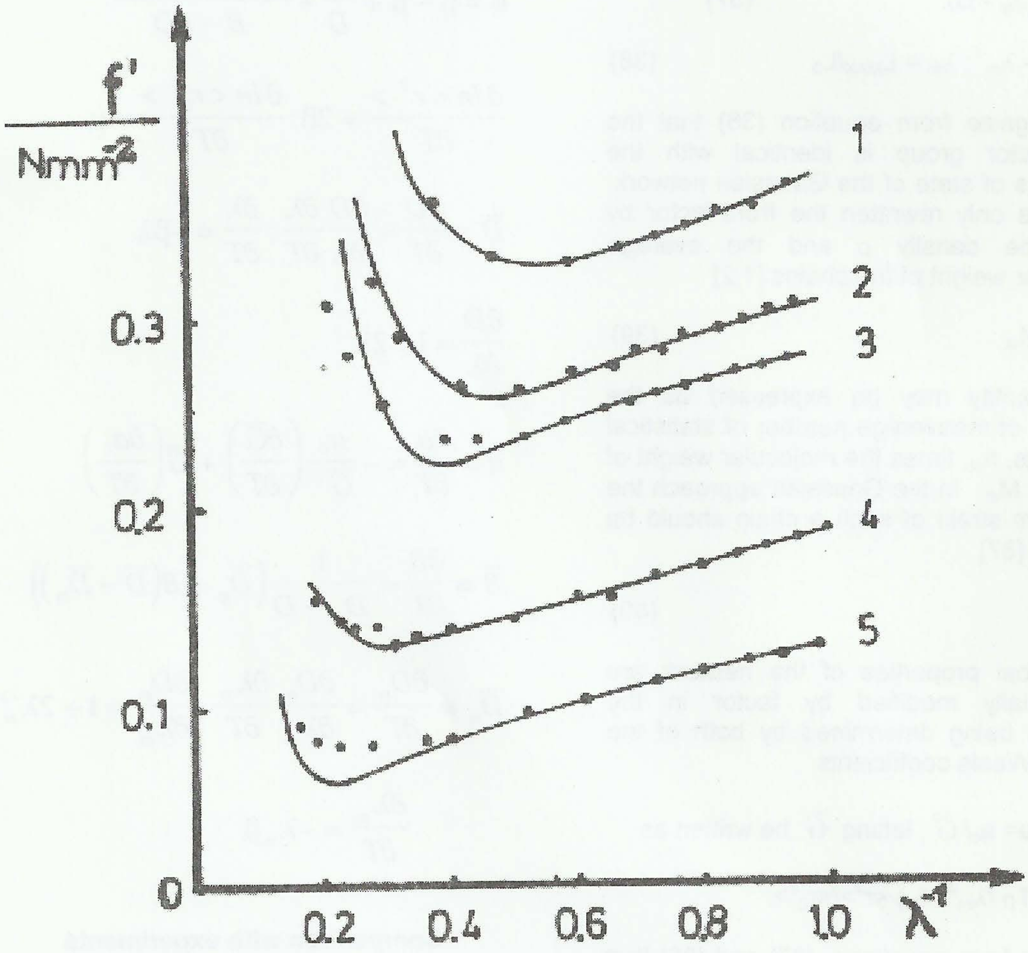

Fig. 7: "Mooney" plot of $[f*] = f/D$- Data according to Mullins [39] against λ^{-1} for peroxide-crosslinked rubbers containing (1) 5%; (2) 4%; (3) 3%; (4) 2%; (5) 1% peroxide. The solid lines have been calculated with the aid of equation (36) employing the following set of parameters. $(RT\rho) <r^2>/<r_0^2>/M_{st}$ = 0,166 Nmm^{-2}, a = 0,26 and (1)λ_m = 6,65; (2)λ_m = 7,3; (3)λ_m = 7,7; (4)λ_m = 9,4; (5)λ_m = 11,5

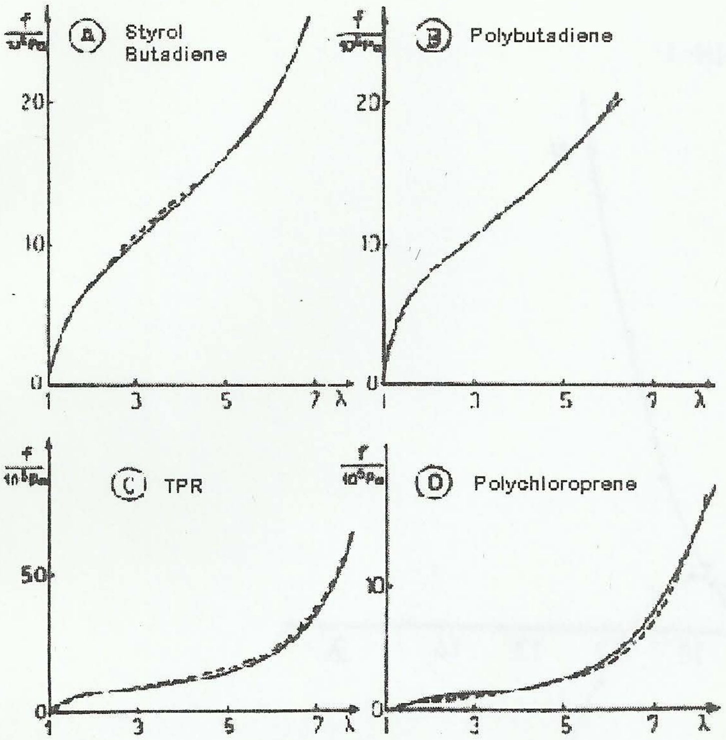

Fig.8: Stress-strain data at room temperature for various rubbers in simple extension according to Eisele et al [37]. (A) SBR; (B) PB; (C) TPR ; (D) polychloropreno as listed in table 1 [52]

Table 1:

System	$\overline{G}$ /10^6 Pa	λ_m	a
(A) styrene-butadiene rubber (SBR)	0,359	8,8	0,2
(B) polybutadiene (PB)	1,15	12,5	0,24
(C) poly-transpentenamer (TPR)	0,595	11,0	0,24
(D) polychloropreno	0,595	8,8	0,21

Hence, we are led to the conclusion that the van der Waals corrections of the "global" network properties are proper modifications of the situation in molecular networks allowing a fit of the stress-strain data within the total range of extensions.

The thermo-elastic behaviour

Given the fact that the stress-strain behaviour of real networks is fully understood with the van der Waals approach, we are faced with the question of whether the thermo-elastic properties can also be treated within this framework. The quality of the fit to data can be seen **from figure 9 [38].** From the plot in **figure 10** it will be noted that the experiments can fairly well be represented up to largest extensions. We want to stress here that this phenomenological coefficients ß = d ln Lo/dT and μ = d ln <ro²>/dT. We thus arrive at the finding that real networks behave like elastic fluids up to largest extensions provided that crystallization does not occur [2].

The volume changes

Since the work of Gee [15] the description of the changes of volume which accompany

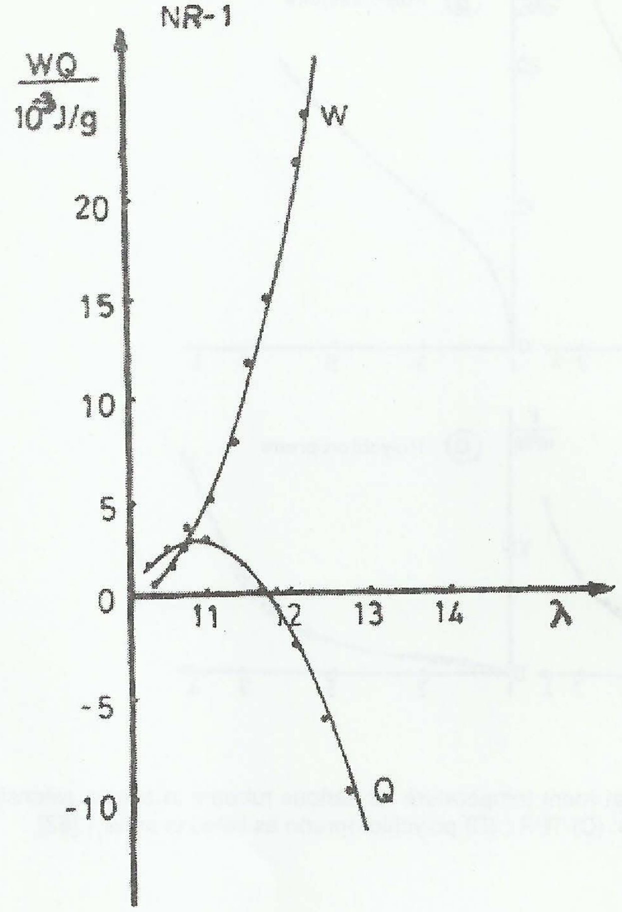

Fig. 9: Plot of W(λ) and Q(λ) for natural rubber in simple elongation at room temperature according to [5,38]. The solid lines have been computed with the equation (7), (36),(39) and (41) with the parameters:

$\overline{G}$ /Jg^{-1}	λ$_m$	a	β/K^{-1}	μ/K^{-1}
0,359	10	0,2	22 x 10^{-4}	9,6 x 10^{-4}

the applications of stress, under constant pressure conditions, has been one of the central issues [2]. Making use of the Maxwell relation (43) with p as the hydrostatic pressure we immediately derive from the equation of state (36)

$$\left(\frac{\partial f}{\partial p}\right)_{L,T} = \left(\frac{\partial V}{\partial L}\right)_{P,T} \tag{43}$$

$$\left(\frac{\partial V}{\partial L}\right)_{T,P} = f\left[\chi + \left(\frac{\partial \ln < r_0^2 >}{\partial p}\right)_{T,L} - D/D - \frac{B - \bar{a}D - aD}{B - aD}\right] \tag{44}$$

where

$$\overline{D} \equiv \frac{\partial D}{\partial p} = \left(\frac{\partial D}{\partial \lambda}\right)\left(\frac{\partial \lambda}{\partial T}\right); \frac{\partial \lambda}{\partial p} = \chi\lambda$$

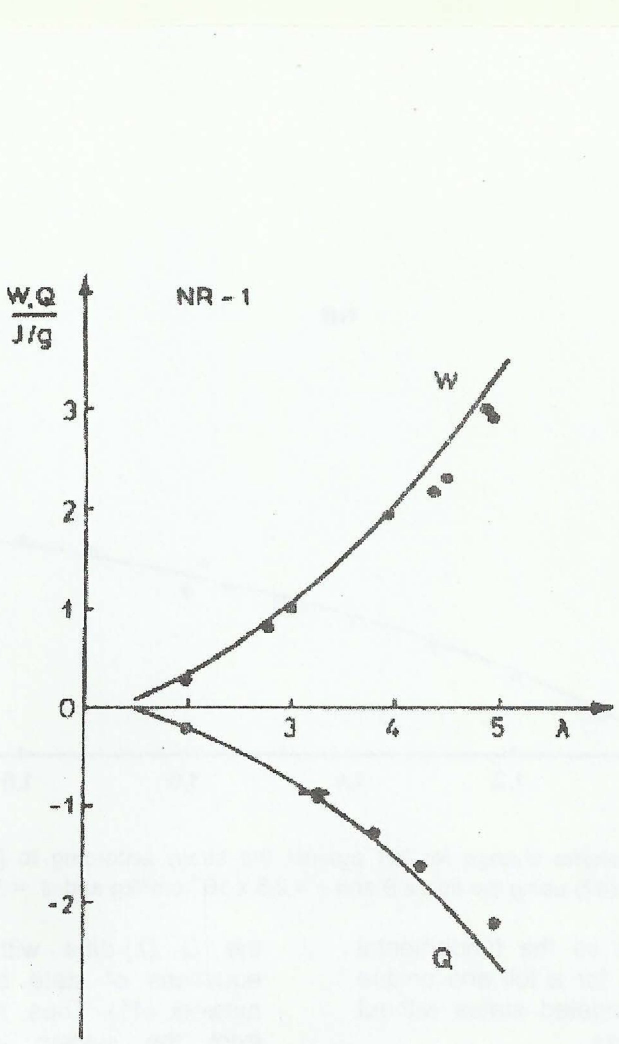

Fig. 10: The same system as given in figure 9 at larger extensions.

$$\overline{D}_m \equiv \left(\frac{\partial D_m}{\partial \lambda_m}\right)\left(\frac{\partial \lambda_m}{\partial p}\right); \frac{\partial \lambda_m}{\partial p} = \chi \lambda_m$$

$$\overline{B} \equiv \frac{1}{D_m - D}\left(\overline{D}_m + B\left(\overline{D} - \overline{D}_m\right)\right)$$

$$\overline{a} \equiv \left(\frac{\partial a}{\partial p}\right)_{L,T} \qquad (45)$$

Here the isothermal linear coefficient of compressibility at constant length has been defined as

$$\chi = -\left(\partial \ln L_0 / \partial p\right)_{T,L} \qquad (46)$$

By integration we are then led to

$$\Delta V / V = V^{-1} \int_{L_0}^{L} \left(\partial V / \partial L_O\right)_{T,P} dL \qquad (47)$$

It may by recalled that the Gaussian theory does not in general provide a satisfactory quantitative basis for the interpretation of the volume changes at larger extensions [2]. It may thus be taken as a sustantial prove of the quality of the van der Waals approach whether a quantitative fit to the data can be achieved by means of the equations (44) or (47). For natural rubber vulcanizates the experimental values of dilatation coefficient can indeed satisfyingly be calculated not showing discrepancies as obtained for the Gaussian approach [2] **(fig.11).** From the results presented up to now it can thus be concluded:

Real rubbers behave on isothermal isbaric uniaxial extension up to largest elongations like an elastic fluid the conformational abilities of which are properly characterized using the model of a van der Waals conformational gas with weak interactions. Conditions of internal equilibrium are strictly regulating the transformation of intrinsic properties , thus, producing the thermo-elastic inversion as well as defined changes of the volume. This is at least indicating that a Gibbs-function of such

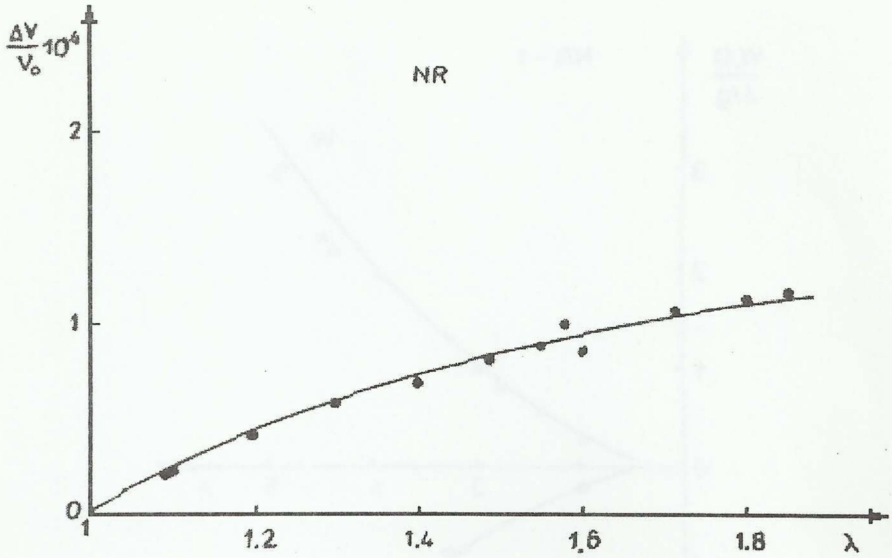

Fig.11: The relative volume change for NR against the strain according to [35,5]. The solid line is computed with equation (47) using the figure 9 and χ = 2,5 x 10^{-4} cm²/kg and $\bar{a}$ = $\partial a/\partial p$ = 6 x 10^{-5} χ[4]

systems should exist as the fundamental function which allows for a full and unique description of all elongated states without crystallization processes.

Rotatoric freedoms

Having now described the thermo-elasticity of real networks at room temperature, we proceed to consider the dependence upon temperature. The measurement of isothermal energy transfer during simple elongation of a styrene-butadiene-rubber obtained with a stretching micro-calorimeter at various temperatures [33] display a surprising effect **(see figure 12)**

B). At T=90 °C a thermo-elastic inversion is found dissappeared in spite of observing a thermal expansion coefficient of approximately the same size as determined at room temperature [33]. In the limits to smallest elongations ($\lambda \rightarrow 1$) η (λ) has changed sign, thus, indicating an inversion of the reversible transformation properties of internal freedoms in the SBR network at temperatures above room-temperature **(fig. 13)** It is to be noted that the stress-strain behaviour can nevertheless satisfyingly be computed with the aid of the equation of state defined by equation (36). This is shown in figure 12A. On the other hand, there is no possibility at all to manage a fit to the Q (λ)-data with the thermo-elastic equations of state of a van der Waals network (41). Thus, heat must be emitted from the system to the reservoir by additional strain dependent internal properties of "rotatoric nature" because of not giving any contribution to the reversibly stored elastic energy of deformation. From the laws of thermodynamics we thus have

$$T\, dS^{(r)} = \delta Q_{rev}^{(r)} = dU^{(r)} \qquad (48)$$

with $dS^{(r)}$ and $dU^{(r)}$ as the entropy and internal energy

changes of the rotators.For the isothermal simple extension (with $dV^{(r)}$ = 0) we than are led to

$$T\left(\frac{\partial S^{(r)}}{\partial L}\right)_{T,P} = \left(\frac{\partial U^{(r)}}{\partial L}\right)_{T,P} \qquad 49)$$

what again is expressing the presence of internal equilibrium with its equally sized changes of kinetical and of potential energy in all quasi-static steps of deformation.

The rotatoric oscillations are considered to be excited at temperature T > Tr, con Tr designating the freezing temperature of the rotatoric oscilators. To calculate these effects we accept the approximative Dolitlle type equation:

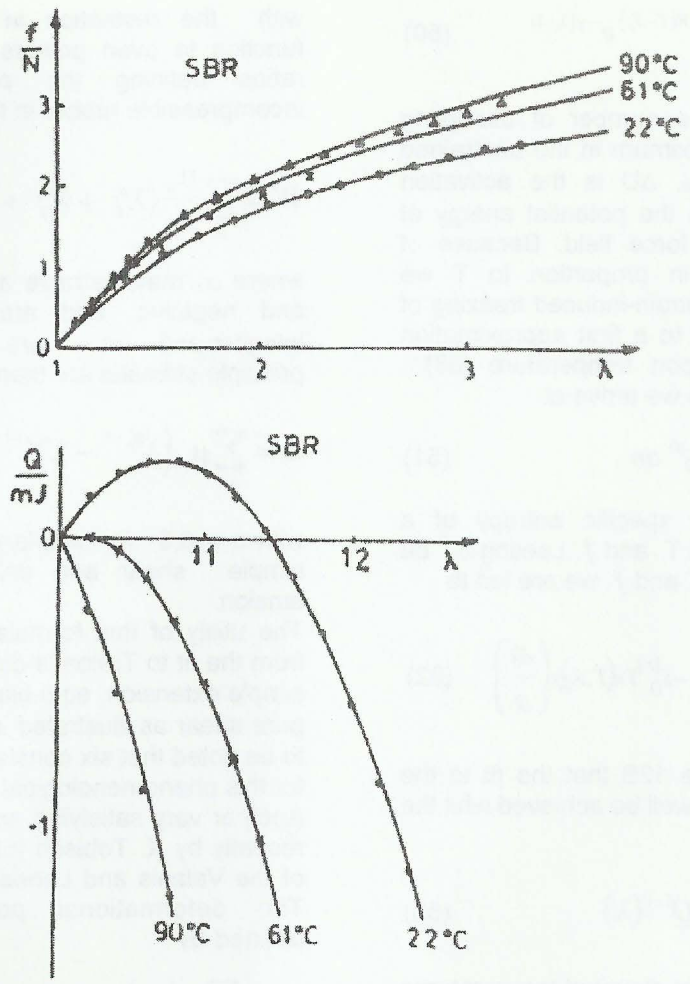

Fig.12: The thermo-elastic data of SBR in the deformational mode of simple elongation; each curve according to (33). The solid lines have been computed with the equations (36),(41),(42) and (53) using the set of parameters: figure 12A: ∫(λ) curves, figure 12B: Q(λ) curves, $\overline{G}\ L_0^2$ = 0,041 n; λ_m = 14; a = 0,2, β = 2,6 x 10 -4 K-1, μ = 0, ΔU = 480 J/mol; γ = 2,5, $S_0^{(r)} n_{or}$ = 4,8 x 10 -8 J/K

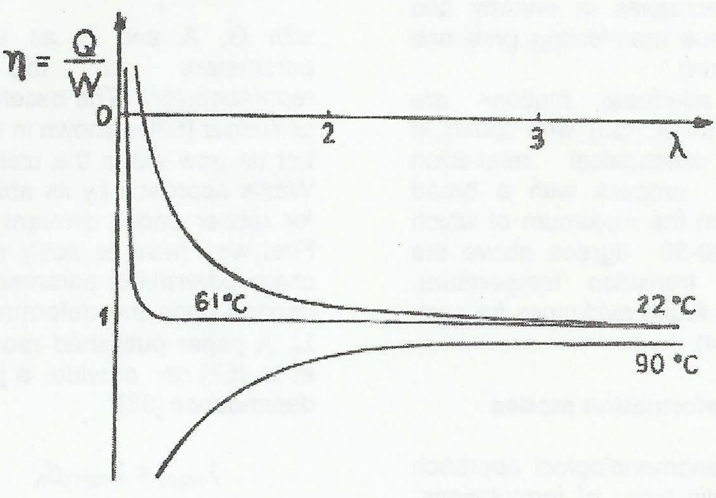

Fig.13: Plot of η(λ) for the same SBR as presented in figure 12

$$\eta(T,\lambda) = n_{or} e^{-\Delta U \; R(T-T_r)} e^{-\gamma(\lambda-1)} \qquad (50)$$

where $\eta(T,\lambda)$ is the number of oscillating rotators with its maximum in the unstrained state equal to η_{OR}, ΔU is the activation energy, $\gamma(\lambda-1)RT$ is the potential energy of the rotator in the force field. Because of having the force in proportion to T we recognize that the strain-induced freezing of the rotators should to a first approximation be independent upon temperature [33]. Using this approach we arrive at

$$T\, dS^{(r)} = \delta Q^{(r)} = T\, S_0^{(r)}\, dn \qquad (51)$$

where $S_0^{(r)}$ is the specific entropy of a rotatoric oscilator at T and f. Leeting $S^{(r)}$ be independent upon T and f we are led to

$$\partial Q^{(r)} = T\left(\frac{\partial S^{(r)}}{\partial \lambda}\right)\frac{\partial \lambda}{\partial} = -S_0^{(r)} T\eta(T,\lambda)\gamma\left(\frac{\partial \lambda}{\partial}\right) \qquad (52)$$

We see from figure 12B that the fit to the data can now farly well be achieved whit the aid of

$$\partial Q = L_0 \int f d\lambda + \partial Q^{(r)}(\lambda) \qquad (53)$$

The new situation at elevated temperatures can thus be pictorialized in terms of local rotatoric oscillations which will continuously be activated at $T > T_r$. The process wich will then occur during elongation, is a defined restriction of these internal motions with equally sized decreases in entropy and internal energy, thus manifesting presence of internal equilibrium.

Occurrence of adequate motions are reported by stoll et al. [53] who found in dielectric and mechanical relaxacion measurements a process with a broad frecuency spectrum the maximum of which should appear 30-50 dgrees above the quasi-static glas transition temperature. Monnerie has also found evidences for such motions at $T>T_r$ [54].

Different deformation modes

An interesting phenomenological approach expanding the "rivlin type of formulations" [2] was made by Ogden [55] who dispensed with the restriction in the stress-strain function to even powers of the extension ratios defining the potencial for an incompressible rubber in the general form

$$W = \sum_n \frac{\mu_n}{\alpha_n}\left(\lambda_1^{a_n} + \lambda_2^{a_n} + \lambda_3^{a_n} - 3\right) \qquad (54)$$

where α_n may be have any values positive and negative, and are not necessarily integers,and μn are constants. The principle stresses are then of the form

$$\sigma = \sum_n \mu_n\left(\lambda^{a_n - 1} - \lambda^{a_n c - 1}\right) \qquad (55)$$

with c = 0,5 for simple extension, c=1 for simple shear and c=2 for equi-biaxial tension.

The utility of this formulation can be seen from the fit to Treloar's data [56] obtained in simple extension, equi-biaxial extension and pure shear as illustrated in **figure 14a**. It is to be noted that six constants are necessary for this phenomenological representation.

Another very satisfying approach was given recently by K. Tobisch [63,64] on the basis of the Valanis and Landel hypothesis [65]. The deformational potential is then defined by

$$W = \sum \omega(\lambda_i) \qquad (56)$$

employing the empirical relations

$$\omega(\lambda_i) \equiv 2G\int_1^{\lambda_i} e^{A(u^2-1)}\, du - \frac{B}{2}\left(1-\lambda_i^{-2}\right) \qquad (57)$$

with G, A and B as the characteristic parameters of this mathematical representation. The excellent fit to the data of Treloar [59] is shown in **figure 14b**.

Let us now judge the utility of the van der Waals approach by its ability to fit the data for rubber under different types of strain. First we have to notily that the maimum chain extensibility parameter should clearly depend upon the deformational mode [25]. λ_m A paper published recently by Edwards et al. [57] can provide a justification of the dependence [58]

$$\lambda_{m(n)} = \lambda_{m(1)} d_n$$

Table 2

	$\lambda_{m(i)}$	$D_{(i)}$	d_n
Simple extension	$\lambda_{m(1)}$	$\lambda - \lambda^{-2}$	1
Pure shear	$\lambda_{m(1)}$	$\lambda - \lambda^{-3}$	1
Equi biaxial extension	$\lambda_{m(1)} / \sqrt{2}$	$\lambda - \lambda^{-5}$	$2^{-1/2}$
Equi-triaxial extension	$\lambda_{m(1)} / \sqrt{3}$	$3(\lambda - 1)$	$3^{-1/2}$

Dm(i) has the analytical form as $D_{(i)}$,
λ has only he substituted by $\lambda_{m(i)}$.

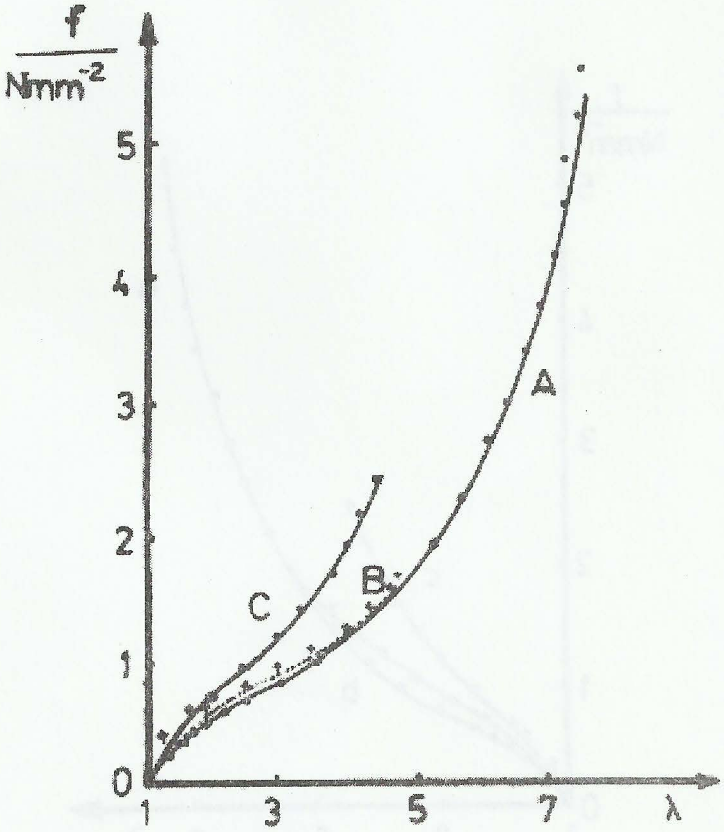

Fig.14a: Representation of data for simple extension and equibiaxial extension by Treloar [59] on the basis of equations (56) and (57) according to (55) using the parameters $\alpha1$ =1,3; $\alpha2$ =5,0; $\alpha3$ = -2,0; $\mu1$ = 6,3; $\mu2$ =0,012; $\mu3$ = -0,1; [μ] = kg cm^{-2}

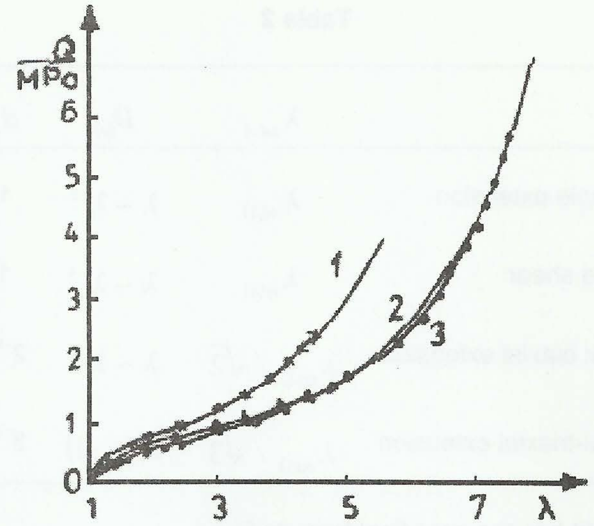

Fig 14b: The same data as given in figure 14a according to Treloar (59) computed ourgoing from the equaling (56) and (57) according to K. Tobisch [64]

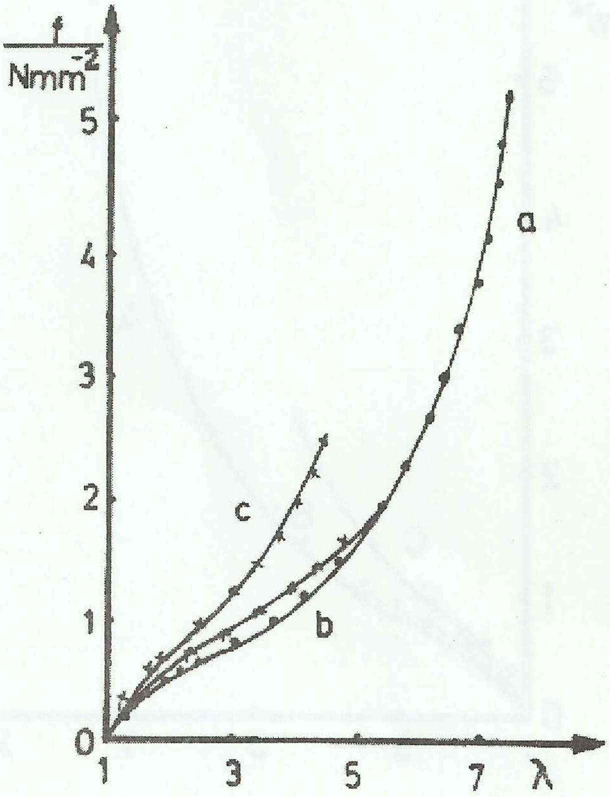

Fig.15: Representation of data for (a) simple elongation, (b) simple shear and (c) equibiaxial extension according to Treloar [2]. The solid lines have been calculated with the aid of the equations (36) employing (a)$D = \lambda - \lambda^{-2}$, $\overline{G}$ =0,365 Nmm^{-2}.$\lambda_{m(1)}$ =10,8, a =0,19; (b) $D = \lambda - \lambda^{-3}$, $\lambda_m \equiv \lambda_{m(1)}$, (c) $D = \lambda - \lambda^{-5}$, $\lambda_{m(2)} \equiv \lambda_{m(1)}/2^{1/2}$

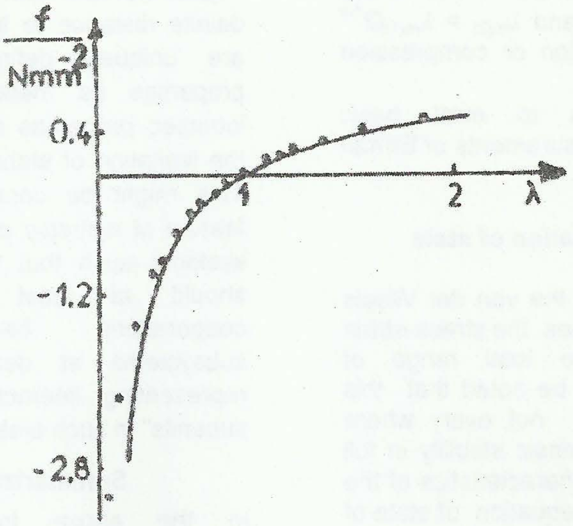

Fig.16: Complete extension and compression curve according to Treloar [2]. Calculated with the aid of equation (36) using the parameters, ξ =0,365 N mm =10,8, a = 0,19, for $\lambda < 1$: $\lambda_{m(2)} \equiv \lambda_{m(1)}/2^{1/2}$

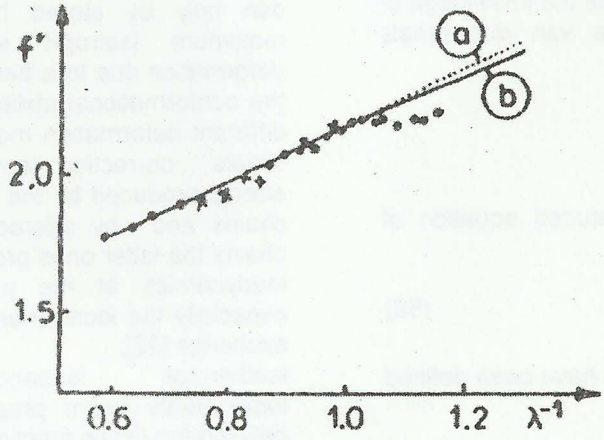

Fig 17: Reduced force [$f^{\bullet}$] of poly-(dimethylsiloxane) vs λ^{-1} according to Erman and Flory [60]. The full lines are computed with the aid of equation (36), using $\overline{G}$ = 2,18 N mm-2; λ_m =14,5; a =0,24. For <1 the calculations with $\lambda_{m(2)} \equiv \lambda_{m(1)}/2^{1/2}$
corresponds to the solid line, While the dotted line has been obtained with $\lambda_{m(1)}$

with d_n designed to the values as given in **table 2**. This is a first approximation because of the lack of an adequate "single-chain treatmen" of the van der Waals approach.

Under these circunstances, the degree of agreement as shown in **figure 15**, must be considered as very satisfactory. This is elucidating that the reasons behind the differences in the stress-strain behaviour in different conformation abilities of the chains of finite lengths.

For uniaxial extension and compression we arrive at a fit as drawn out in **figure 16** which is seen to be in poorer agrrment with the data at larger degrees of compression.

The dependence of $f^{\bullet} = f/D$ over λ^{-1} is on principle predicted to be asymmetric if the maximum strains $\lambda_{m(1)}$ and $\lambda_{m(2)} = \lambda_{m(1)}/2^{1/2}$ are used in the dilatation or compression range **(fig. 17)**.
Hence, there seems to exist basic correspondence to measurements of Erman and Flory [60].

The reduced equation of state

For all rubbers studied, the van der Waals equation of state describes the stress-strain behaviour within the total range of elongations. But it is to be noted that this equation of state does not every where satisfy the criteria of intrinsic stability in full correspondencs to the characteristics of the classical van der Waals equation of state of real gases [14]. The consequences of this fact can be discussed in a very general fashion by the use of the reduced equation of state which has recently be derived by Vilgis et al.[59]. The formulation of this equation of state based on the knowledge of the critical data of the van der Waals network

$$T_C = 8/27\, a_0 D_m$$
$$D_c = D_m/3$$
$$f_c = a_0 D_m^2/27$$

is leading us to the reduced equation of state

$$c = d\,(8t/(3-d)-3d) \tag{59}$$

where reduced variables have been defined accordingly

$$f' = f'/f_c;\ d = D/D_C\ ;\ t = T/T_C \tag{60}$$

From the plot drawn our in figure 18 we realize that all rubbers of practical interest are stable in the total range of elongations because of being in sufficiently large distances to the limit of stability which is also drawn out in **figure 18**.
Hence, in the mode of simple elongation the occurrence of aphase transition is predicted [25]. This concept properly extended, might also deliver an understanding of the necking process [61] often observed in "cold drawn" samples deformed at temperatures below their glas transition [62]

What we want to stress here is only the new aspect that real networks turn out to be in a deinite distance to limits of stability which are uniquely defined by their global properties as "network properties". The intrinsec properties are not contributing to the limitation of stability of these systems.
This might be considered as a general feature of isotropic or quasi-isotropic clasic systems such that their limits of stability should at least be originated by cooporations between appropriate subsystems at deformation which are representing interacting "global structural subunits" in such elastic systems.

Summarizing remarks

In the above treatments we have experienced the presence of a hierarchic principle: The stress-strain behaviour is governed by global network properties with their characteristics the best describedas a Van der Waals conformational gas. Work can only by stored by diminishing the maximum isotropic state entropy on deformation due to a belonging reduction of the conformational abilities of the chains in different deformation modes. The Van der Waals correction terms are related to effects produced by the finite length of the chains and by interactions between the chains the latter ones probably originated by thedynamics at the junctions regulating especially the local energy and momentum exchange [26].
Isothermal isobaric deformation experiments seem properly by described defining the Gibbs function G(T,p,L,N) which has with N= const. the differential form

$$dG = -S\,dT + V\,dp + f\,dL \tag{61}$$

thus, implicating the existence of three equations of state [14].

$$S = S\,(T,p,L) \qquad V = V(T,p,L)\ ; \qquad f = f(T,p,L) \tag{62}$$

The totality of all three equations of state is only equivalent to the fundamental equation and contains all thermodynamic information about the system. Any single equation of state contains then necessarily less information. Relationships known as Maxwell relations [2,14,17], derived from

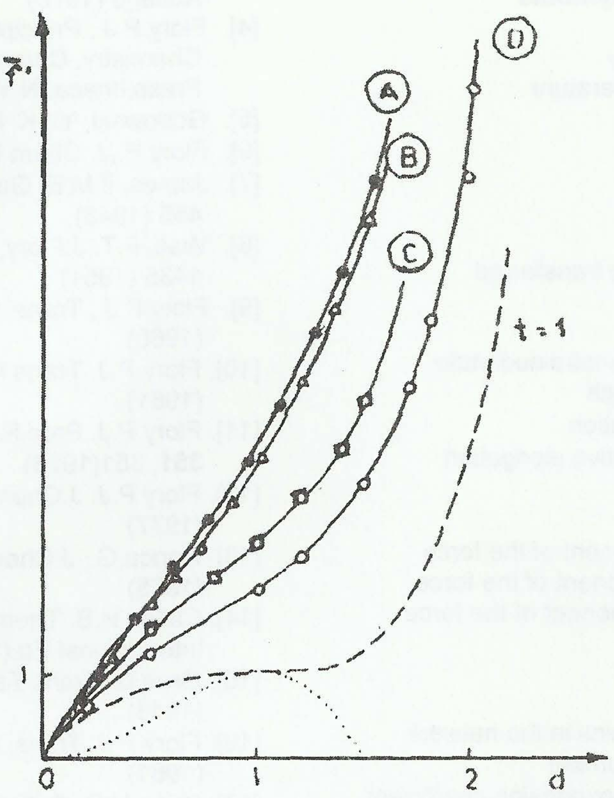

Fig.18: The f" plot against $d = D/D_c$, $t = 1$ corresponds to the critical isotherm. The dotted line is giving the limits of stability. Actual rubbers are represented by the curves. (A) $D_m = 10$; a = 0,2; $t = 1{,}685$ with $D_c = 3.33$; $T_c = 177{,}8$ K and $f_c/NK = 0{,}74$ (Natural Rubber and Polychloropre. (B) $D_m = 8{,}5$; a = 0,24; $t = 1{,}66$ with $D_c = 2{,}83$; $T_c = 181{,}3$ K and $f_c/NK = 0{,}64$ (Polybutadiene). (C) $D_m = 7{,}5$; a = 0,36; $t = 1{,}25$ with $D_c = 2{,}5$; $T_c = 240$ K and $f_c/NK = 0{,}75$ (Styrene-Butadiene Rubber). (D) $D_m = 13{,}5$; a = 0,18; $t = 1{,}39$ with $D_c = 4{,}5$; $T_c = 216$ K and $f_c/NK = 1{,}2$ (Styrene-Butadiene Rubber); full lines: calculated with equation (5)), points: experimental values

the condition of integrability, deliver differential correlations between the state function involved.

$$\left(\frac{\partial S}{\partial L}\right)_{T,P} = \left(\frac{\partial f}{\partial T}\right)_{L,P} \qquad (63)$$

or

$$\left(\frac{\partial V}{\partial L}\right)_{T,P} = \left(\frac{\partial f}{\partial p}\right)_{L,T} \qquad (64)$$

In this situation it is, nevertheless, evident that an analysis of a rubberelastic system with the aid of the thermo-elastic equations of state only (see eq. (41)) can on principle not provide a complete characterization of the rubber as it is exemplified in the discussion of deformational induced transformations of rotatoric oscilations. In addition, the knowledge of the pressure-dependence of the nework properties on deformation is wanted for making the description complete.

It has already been indicated that no generally accepted molecular interpretation of the thermo-elastic properties of molecular networks has yet beenadvanced. In this view, the importance knowing the Gibbs-function the existence of which can be drawn from all of the above results, is that it provides a basis for improvements of the statistical theory. A central problem is clearly to arrive at an understanding of the global properties of van der Waals networks, in particular the physics behind the interaction parameter a. Finite chain entensibility as well as interactions between the chains are both of elementary significance in discussions which will be directed to an understanding of the limits of stability.

List of symbols

U	internal energy
T	absolute temperature
S	entropy
V	volume
G	free enthalpy
F	free energy
W	work
Qrev	heat reversibly transferred
p	pressure
L	actual length
Lo	length in the unstrained state
lmax	maximum length
λ	relative elongation
λ_m	maximum relative elongation
ε	strain
f	force
f_g	energy component of the force
f_s	entropy component of the force
f_h	enthalpy component of the force
K	modulus
$\overline{G}, \overline{G}_0$	shear moduli
N	number of chains in the network
k	Boltzmanns number
β	linear thermal expansion coefficient
χ	isothermal compressibility
$\langle r^2\rangle/\langle r_o^2\rangle$	memory term
$\eta = Q/W$	
$D = \lambda-\lambda^{-2}$	
$D_m = \lambda_m-\lambda_m^{-2}$	
$B = D_m/(D_m - D)$	
n_{st}	number of Kuhn-segments
M_{st}	molecular weigth of the Kuhn-segment
ρ	density
R	gas constant
$\lambda_{m,a}$	van der Waalsparameters
ΔU	activation energy
$n(T, \lambda)$	number of activated "rotators"
γ	potential energy parameter
T_r	freezing temperature
T_c, D_c, f'_c	critical parameters
f', d, t	reduced variables

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