The strain dependence of elastomer loss modulus: Rubber elasticity and the structure of polymer networks

I. P. Borodin* and T. N. Khazanovicht
Institute of Chemical Physics, Academy of Sciences of the USSR, 117977 Moscow, USSR
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Using the theory of the strain dependence of elastomer loss modulus in the transition zone, it was shown that measurement of this dependence in the non-Gaussian strain region allows more reliable conclusions about the network structure to be drawn than is possible from the equilibrium stress–strain dependence. On the basis of the experimental data obtained by Meinecke, the structural characteristics related to the length and coiling ratio distributions, $\overline{Nh^2/\bar{N}\bar{L}^2}$ and $\overline{Nh^4/\bar{N}\bar{L}^4}$, were determined for two elastomers, where N is the number of links in an elastically active chain, L is its contour length, h is the end-to-end distance and the bars mean averaging over the network. The supposition made by Mullins and Morris, namely that the equilibrium stress–strain dependence in both Gaussian and non-Gaussian regions can be described by the phantom-chain theory with addition to the Mooney–Rivlin term, is thus verified.

(Keywords: polymer networks; rubber elasticity; viscoelasticity; large strains; non-Gaussian chains)

NOTATION

A function of phase coordinates
a equilibrium distance between adjacent beads
B function of phase coordinates
C_g, C_l, C_t elasticity coefficients of a spring
C_1, C_2 Mooney–Rivlin constants
$D_z, D_l, D_x, D_y, D_t, D_g$ diffusion constants of a bead
E'' loss modulus
$F_i(N_k)$ functions of number of segments
G transition probability in the space of slow variables
g the number of a slow mode
H Hamiltonian
h end-to-end distance of a chain
$I(\omega)$ spectral density
i number of the atom
$J_{\alpha\beta}$ component of momentum flux
k number of the mode
$\mathbf{k}$ coordinate vector
$L(t)$, $\bar{L}$ current and average lengths of a sample
L contour length of a chain
N_c number of chains in a network
N_e number of links between entanglements
N_k number of Kuhn segments in a chain
N_ν number of linkages in the νth chain
n number of subchains in a chain
p number of atoms in a subchain
$\mathbf{p}_i^{(\nu)}$ momentum of the ith atom in the νth chain
P_e equilibrium distribution of slow coordinates
$Q_{ik}^{(\nu)}$ component of the matrix transforming into collective modes
$\mathbf{q}_k^{(\nu)}$ collective mode
$\mathbf{q}_k$ normal mode
q a set of slow coordinates
$\mathbf{R}_i$ radius vector of a bead
$\mathbf{R}_i^{(0)}$ equilibrium value of $\mathbf{R}_i$
$\mathbf{r}_i^{(\nu)}$ radius vector of the ith atom in the νth chain
T period, absolute temperature
$T_{\alpha\beta}$ components of the tensor of dissipative momentum flux
t time
U potential of a spring
V volume of a sample
$\bar{\dot{W}}$ average power dissipated during a period
W_e conditional equilibrium distribution
α,β numerical coefficients
$\delta_{\alpha\beta}$ Kronecker delta
ζ structural parameter of a network
θ angle to the z-axis
λ extension ratio
ν number of the chain in a network
ρ_i deviation of the radius vector of a bead from its equilibrium position
τ_0 relaxation time of local motion
τ_k relaxation time of the kth mode
ϕ effective potential
ω circular frequency
σ true stress

INTRODUCTION

In a series of experiments[1–5] it was found that, if a small oscillating strain is superimposed on an elastomer

* On leave from Kostroma Technological Institute, USSR.
† To whom correspondence should be addressed.

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extended λ times, the loss modulus increases with λ. This point, however, needs to be clarified, since the loss modulus at finite strains is not defined uniquely.

Let $L(t)$ be the length of a sample at time t, so that

$$\bar{L}=(1/T)\int_0^T L(t)\,dt$$

is the length averaged over the period of the oscillating strain. Then

$$(L(t)-\bar{L})/\bar{L}=\varepsilon\cos\omega t \qquad (1)$$

$$(\omega=2\pi/T)$$

If we define the extension ratio as $\lambda=\bar{L}/L_0$, where L_0 is the non-extended length, then (1) becomes

$$L(t)/L_0=\lambda(1+\varepsilon\cos\omega t) \qquad (2)$$

The loss modulus is defined so that the average power dissipated during a period within a unit volume changes as the square of the oscillating strain amplitude:

$$\dot{W}=\omega E''\varepsilon^2/2 \qquad (3)$$

Under this definition, which is invariant to λ, the amplitude of the true viscous stress is proportional to ε. In the experiments mentioned above, just the value E'' of (3) increases with strain.

The observed dependence of E'' on λ in the transition zone of frequencies was theoretically explained[7,8] to be due to finite extensibility of the chains. This theory is based upon a general relation between the viscous stress tensor and the time-dependent correlation functions of the dissipative momentum flux[9-11], these functions having been calculated using the intuitive model of beads and springs.

In the present work this model is substantiated for the transition zone. Also evidence is given that the E''–λ dependence contains information on the network structure and on the properties of strongly extended polymer chains. The information obtained is to a great extent free of topological constraints, which are significant in the case of the σ–λ dependence (σ is the equilibrium stess) see, e.g., ref. 12). Therefore, comparison of the E''–λ and σ–λ dependences allows the role of the constraints to be estimated for strongly extended elastomers.

THEORY

In order to make the general theory[9-11] applicable to polymer systems, chemical bonds between rigid groups are to be simulated by proper non-additive and non-central potentials. Then the Hamiltonian H of the system includes both the usual van der Waals interactions and the potential energy of chemical bonds. In the references mentioned, the radius of the interatomic interaction was taken to be necessarily finite, though this condition is not applicable to potentials simulating chemical bonds. But, in fact, it is sufficient to use the condition that the correlation radius of atomic motions is finite. According to the theory[9-11] the loss modulus defined by (3) is expressed in terms of time correlation functions as

$$E''(\omega)=\frac{\omega}{k_BTV}\int_0^\infty dt\cos\omega t(\langle T_{zz}(t)T_{zz}(0)\rangle+\tfrac{1}{2}\langle T_{xx}(t)T_{xx}(0)\rangle$$

$$+\tfrac{1}{2}\langle T_{xx}(t)T_{yy}(0)\rangle-2\langle T_{zz}(t)T_{xx}(0)\rangle) \qquad (4)$$

where k_B is the Boltzmann constant, T is the temperature, V is the sample volume,

$$T_{\alpha\beta}=J_{\alpha\beta}-\langle J_{\alpha\beta}\rangle \qquad (5)$$

are the components of the tensor of dissipative momentum flux, the z axis is along the extension axis, and the angular brackets mean averaging over the canonical distribution at a given λ, the cylindrical symmetry of uniaxial extension being taken into account in (4). The tensor of the microscopic momentum flux can be written as

$$J_{\alpha\beta}=\sum_\nu\sum_{i=1}^{N_\nu}\left(p_{i\alpha}^{(\nu)}\frac{\partial H}{\partial p_{i\beta}^{(\nu)}}-r_{i\alpha}^{(\nu)}\frac{\partial H}{\partial r_{i\beta}^{(\nu)}}\right) \qquad (6)$$

where ν is the number of the chain in a network consisting of N atoms, and $p_i^{(\nu)}$ and $\mathbf{r}_i^{(\nu)}$ are the momentum and the radius vector of the ith atom in the νth chain. (For short, any rigid group is here referred to as an atom.) Since the crosslinks consist of several atoms, they can be separated so that every atom belongs to a definite chain. Formula (6) can be shown to be valid for non-central and non-additive interactions[13,14].

The calculations of the loss modulus in (4) can be essentially simplified if we restrict ourselves to rather low frequencies $\omega\ll\tau_0^{-1}$, τ_0 being the expectation time of a conformational transition (or the relaxation time of local motions in polymer chains). For time correlation of two functions of phase coordinates, A and B, which depend on both fast and slow variables, the following relation is valid for $t\gg\tau_0$:

$$\langle A(t)B(0)\rangle\simeq\langle\langle A\rangle_{q(t)}\langle B\rangle_{q(0)}\rangle \qquad (7)$$

Here $\langle A\rangle_q$ is the conditional average at given values of slow variables q. The condition of slowness means that

$$|\langle A\rangle_{q(t+\tau_0)}-\langle A\rangle_{q(t)}|\ll|\langle A\rangle_{q(t)}| \qquad (8)$$

Let us consider the spectral density

$$I(\omega)=\int_0^\infty dt\exp(i\omega t)\langle A(t)B(0)\rangle$$

at $\omega\ll\tau_0^{-1}$. Then considering (7) and (8) we have

$$I(\omega)\approx\int_0^{\tau_0} dt\langle A(t)B(0)\rangle+\int_0^\infty dt\exp(i\omega t)\langle\langle A\rangle_{q(t)}\langle B\rangle_{q(0)}\rangle$$

Therefore, within the accuracy of an additive constant, the spectral density is the Fourier transform of the reduced time correlation function (7).

The slow variables are collective variables, which we define as

$$\mathbf{q}_0^{(v)} = N_v^{-1} \sum_{i=1}^{N_v} \mathbf{r}_i^{(v)} \qquad \mathbf{q}_k^{(v)} = \sum_{i=1}^{N_v-1} Q_{ki}^{(v)} (\mathbf{r}_{i+1}^{(v)} - \mathbf{r}_i^{(v)})$$
$$Q_{ki}^{(v)} = (2/N_v)^{1/2} \sin(ik\pi/N_v) \qquad (k = 1, 2, \ldots, N_v - 1) \tag{9}$$

As was shown when studying the relaxation properties of a series of analytically solvable models[15-17] and of models simulated by the methods of molecular and Brownian dynamics (see, e.g., refs. 18 and 19), the relaxation times of collective variables (9) are longer the less is the k number. These relaxation times correspond to those in the Rouse model[20] at $1 \leqslant k \ll N_v$ (see also ref. 6). Hence we assume that all $\mathbf{q}_g^{(v)}$ with $g = 0, 1, \ldots, p \ll N_v$ are the only slow variables in the system, while all those with $k > p$ and all momenta are fast variables.

Following Doi and Okano[21], averaging over fast variables is done by introducing a conditional distribution of fast variables for given slow variables

$$W_e(\Gamma/\mathbf{q}^t) = Z^{-1} \exp(-H/k_B T) \delta(\mathbf{q} - \mathbf{q}^t)/P_e(\mathbf{q}^t)$$

where Γ is the point in the phase space of the system, the $\mathbf{q}$ vector with no index means all the set of $\mathbf{q}_g^{(v)}$,

$$Z = \int d\Gamma \exp(-H/k_B T)$$

and

$$P_e(\mathbf{q}^t) = Z^{-1} \int d\Gamma \exp(-H/k_B T) \delta(\mathbf{q} - \mathbf{q}^t)$$

is the equilibrium distribution in the space of slow variables. Integrating $J_{\alpha\beta} W_e(\Gamma/\mathbf{q}^t)$ with due regard for the vanishing of W_e at boundaries of the phase space, we obtain

$$\langle J_{\alpha\beta} \rangle_{\mathbf{q}} = -\sum_v \sum_{g=0}^{p} q_{g\alpha}^{(v)} \frac{\partial \phi}{\partial q_{g\beta}^{(v)}} + \frac{N_c \rho k_B T}{V} \delta_{\alpha\beta} \tag{10}$$

where

$$\phi = -k_B T \ln P_e(\mathbf{q}^t) \tag{11}$$

is the effective potential and N_c is the number of chains in the network.

The problem becomes further simplified if we restrict ourselves to the transition zone of frequencies that correspond to semilocal motion, i.e. to the modes with $1 \ll g \ll N_v$ (see, e.g., ref. 6). The condition of semilocality becomes $(N_v/N_e) \ll g \ll N_v$, provided that the average distance between entanglements is $N_e < N_v$. So, we consider a limited time interval in which the relaxation connected with local motions $g \sim N_v$ has already finished, while that related to the motions whose scale is commensurable with the whole chain $g \sim (N_v/N_e)$ has not yet developed. The motions with $g \gg (N_v/N_e)$ are not sensitive to topological constraints producing entanglements (tubes) (see, e.g., refs. 12 and 22).

The other advantage of the transition zone is that relaxation of semilocal modes in long chains does not depend on the conditions of fixing the chain ends. Hence, the semilocal motions of different chains are not correlated and the correlation function (4) can be represented as a sum of correlation functions of separate chains. In this case the semilocal modes are equivalent to the bead–spring model.

In order to illustrate this fact, let us divide the chain into n subchains. For collective modes (9) with $k \ll n$ we can write

$$\mathbf{q}_k = \sum_{i=1}^{n} \sum_{\substack{j= \\ (i-1)p+1}}^{ip} Q_{kj} (\mathbf{r}_{j+1} - \mathbf{r}_j) \simeq \sum_{i=1}^{n} Q_{ki,p} (\mathbf{R}_{i+1} - \mathbf{R}_i) \tag{12}$$

here $p = N/n$, the index v being omitted for short. Then $\mathbf{q}_k$ can be expressed using the coordinates of the subchain ends $\mathbf{R}_i$; also $\mathbf{R}_i$ can be expressed using $\mathbf{q}_k$ by the inverse transform and can be also considered as slow variables. In this case, (10) coincides with the result by Doi and Okano[21] for $\alpha \neq \beta$. The additional diagional term on the right-hand side of (10), which can be considered as the pressure of $N_c p$ links, does not contribute to the dissipative momentum flux, owing to definition (5). The fact that semilocal motions are not sensitive to topological constraints is verified by experiments on scattering of neutrons in polymer melts. These experiments showed that the relaxation of motions whose scales are smaller than distances between entanglements are described by the Rouse model (see, e.g., ref. 23).

All that said, the effective potential of a chain (11) can be written as

$$\phi = \sum_{i=0}^{n} U(|\mathbf{R}_{i+1} - \mathbf{R}_i|) \tag{13}$$

There are also some other arguments showing that the bead–spring model can be used to calculate the loss modulus of an elastomer in the transition zone. In ref. 24 we have modified the potential ϕ so that the equilibrium σ–λ dependence in the Gaussian region of extension is closer to the experimental dependence, this modification having been found to affect the loss modulus weakly. When entanglements were simulated by points capable of forming rather weak linkages, the processes of breakage and formation of entanglements proved to be of no importance in the transition zone[25].

All these arguments concern free or weakly extended chains, but we believe that they are also valid for greater extensions for which the effects of limited extensibility of chains become essential, i.e. the springs in the model become nonlinear.

The micro-Brownian motions of beads in extended chains are, in fact, the fluctuations around equilibrium positions $\mathbf{R}_i^{(0)}$. Since strong fluctuations are hardly probable, the effective potential (13) can be expanded into powers of deviations from the equilibrium positions $\rho_i = \mathbf{R}_i - \mathbf{R}_i^{(0)}$ restricted to the second-order terms.

Here the normal modes

$$\mathbf{q}_k^* = \sum_{i=1}^{n-1} 2 \left(\frac{2}{n}\right)^{1/2} \sin\left(\frac{k\pi}{2n}\right) \sin\left(\frac{ik\pi}{n}\right) \rho_i \tag{14}$$

which correspond to the condition of fixed chain ends, are convenient to use. In the coordinate system where the chain ends are on the z axis

$$\phi = \phi_0 + \tfrac{1}{2} \sum_{k=1}^{n-1} [C_l q_{kz}^{*2} + C_t (q_{kx}^{*2} + q_{ky}^{*2})] \tag{15}$$

where $\phi_0=\phi$ if all the beads are in their equilibrium positions, the 'elastic coefficients' $C_l=U''(a)$, $C_t=U'(a)/a$, $a=|\mathbf{R}_{i+1}^{(0)}-\mathbf{R}_i^{(0)}|$.

In analogy with the non-Gaussian theory of rubber elasticity[26] we restrict ourselves to two non-Gaussian terms in the expansion of the effective potential U in powers of the coiling ratio h/L, h being the distance between the chain ends and L the contour length. So, remembering that $h=na$ (see (13))

$$U=\tfrac{1}{2}C_g a^2[1+\alpha(na/L)^2+\beta(na/L)^4+\ldots] \qquad (16)$$

where $C_g=3k_BTn/\langle h^2\rangle$ is the known 'elastic coefficient' of a Gaussian subchain. The numerical factors α and β depend on the chain model; in particular, $\alpha=3/10$ and $\beta=33/175$ for a freely jointed chain. To calculate the time correlation functions of the reduced momentum flux (10), the transition probability G in the space of normal modes (14) must be known. The supposition of $\mathbf{q}_k^*$ being slow means that G must satisfy the diffusion equation. As Gotlib and Darinskii[27] have shown, the mobility of a chain may decrease with extension and become anisotropic because the fraction of *gauche* conformers decreases.

According to (15), the diffusion equation is

$$\frac{\partial G}{\partial t}=\sum_{k=1}^{n-1}\sum_{\alpha=1}^{3}\frac{D_\alpha}{2\tau_k C_g D_g}\left(k_BT\frac{\partial^2 G}{\partial q_{k\alpha}^{*2}}+C_\alpha\frac{\partial}{\partial q_{k\alpha}^*}(q_{k\alpha}^*G)\right) \qquad (17)$$

here $D_z\equiv D_l$, $D_x=D_y\equiv D_t$, $C_z\equiv C_l$, $C_x=C_y\equiv C_t$, τ_k and D_g are respectively the relaxation time of the kth normal mode and the bead diffusion coefficient in a Gaussian chain. The reduced correlation functions of a chain can be calculated using (10), (15) and (17) in a standard way, provided the dependence of the diffusion constants on a is known. Using the model of freely jointed segments, which can flip in pairs around the axis passing through the points where segments are attached to the main chain, it was shown[8] that $D_\alpha\sim C_\alpha^{-1}$. In this case the correlation times of normal modes $\tau_k C_g D_g/C_\alpha D_\alpha$ do not depend on the chain extension. If a weak correlation of orientation in adjacent chains is included in the model, the relaxation times become shorter during extension. When the motions follow the mechanism of accumulation of weak vibrations, mobilities stay constant under extension[27]. Therefore, to estimate how the changes in mobilities affect the loss modulus, two limiting cases must be considered, viz. a freely jointed chain whose relaxation times are constant and a chain with constant diffusion coefficients whose relaxation times decrease very strongly with extension.

In order to obtain the correlation functions of a whole network it is necessary to transform from the chain coordinate system to the laboratory one and to know the orientation distribution function of the end-to-end vectors in a deformed network. Furthermore, it is necessary to know how the equilibrium positions of beads in strained and non-strained states are interconnected. For our calculations we have taken the displacements from equilibrium positions $\mathbf{R}_i^{(0)}$ to be affine, although this is not true for a non-Gaussian network[28]. But out assumption is justified since we restrict ourselves to weakly non-Gaussian networks, which, as shown by Wang and Guth[26], are approximately affine. We must also mention here work[29,30] in which the network extension was simulated by the Monte Carlo method. As shown therein the average extension of chains is proportional to changes in the sample dimensions until the average coiling ratio is less than 0.8.

Calculating the time correlation functions within the accuracy of the first two non-Gaussian terms using the above concepts we obtain the following expansions for the loss modulus in accordance with (4):

(a) for the case of constant relaxation times

$$E''(\omega,\lambda)=E_g''(\omega)[1+\tfrac{4}{15}\overline{\zeta^2}(2\lambda^2+\lambda^{-1}) +\tfrac{1}{875}\overline{\zeta^4}(846\lambda^4-24\lambda+564\lambda^{-2})+\ldots] \qquad (18)$$

(b) for the case of the constant mobilities

$$E''(\omega,\lambda)=E_g''(\omega)[1+\tfrac{3}{10}\overline{\zeta^2}\lambda^2 +\tfrac{3}{7000}\overline{\zeta^4}(1275\lambda^4-370\lambda+712\lambda^{-2})+\ldots] \qquad (19)$$

Here the network is supposed to be perfect, $E_g''(\omega)$ is the loss modulus in the model of Gaussian subchains, the values of α and β in (16) are taken in accordance with the model of freely jointed segments, and the bar means averaging over the network:

$$\overline{\zeta^{2n}}=\frac{1}{N_c}\sum_{\nu=1}^{N_c}(h_\nu/L_\nu)^{2n}(N_\nu/\bar{N})$$

$$\bar{N}=\sum_{\nu=1}^{N_c}(N_\nu/N_c)$$

When obtaining (19) we used the fact that $E_g''(\omega)\sim\omega^{1/2}$ in the transition zone (see, e.g., ref. 6). The E''–λ dependences for the two limiting cases of (18) and (19) proved to be close to one other. It means that during extension the mobilities change much more weakly than do elastic constants. Just the latter fact provides the growth of E'' under extension.

DISCUSSION

As follows from (18) and (19), from the E''–λ dependences the moments $\overline{\zeta^{2n}}$ can be determined, which control the tension distribution of chains in non-deformed states. This distribution together with the distribution contour lengths characterizes the network structure. The same moments $\overline{\zeta^{2n}}$ are also present in the equilibrium dependence of true stress σ on λ in the non-Gaussian region of deformations. If the coefficients of the effective potential (16) are taken from the model of freely jointed segments and under the conditions of affinity, the theory of phantom non-Gaussian chains[26] gives

$$\sigma=C_1(\lambda^2-\lambda^{-1})[1+\tfrac{9}{25}(\overline{\zeta^4}/\overline{\zeta^2})(\lambda^2+\tfrac{4}{3}\lambda^{-1})+\ldots] \qquad (20)$$

where the elastic constant of the theory of Gaussian chains can be written as

$$C_1=N_c k_B T\bar{N}_k\overline{\zeta^2}/V \qquad (21)$$

$\bar{N}_k$ being the number of Kuhn segments in a chain consisting of $\bar{N}$ links. As mentioned in the Introduction

the theory of phantom chains disagrees with experiments because of steric interactions. But a satisfactory theory including this influence does not exist yet. On the contrary, as shown above, the relations (18) and (19) are not affected by topological constraints. The most doubtful point in the derivation of these relations is the assumption of affinity. One more factor that can make the assumption of affinity wrong is the slow motions within the network, this phenomenon not being clearly understood up to now. But the motions mentioned can result in slow fluctuations of equilibrium positions. To estimate the contribution of slow fluctuations, a simple example is considered in the Appendix. It is shown (see (A.3)) that the values of moments $\overline{\zeta^{2n}}$ vary slightly, but for sufficiently long chains this variation is negligible.

For illustration we have considered the experimental data of Meinecke[2], though they hardly fit our conditions since they correspond to the low-frequency part of the transition zone just near the plateau boundary. *Figure 1* shows the E''–λ dependence for a vulcanizate of natural and styrene–butadiene rubbers. The values of the parameters obtained are: $E_g''=0.36$ MPa, $\overline{\zeta^2}=0.11$, $\overline{\zeta^4}=0.012$ for SBR; and $E_g''=0.245$ MPa, $\overline{\zeta^2}=0.06$, $\overline{\zeta^4}=0.0054$ for NR. Describing the same experimental data by (19) we obtain $E_g''=0.39$ MPa, $\overline{\zeta^2}=0.15$, $\overline{\zeta^4}=0.0023$ for SBR.

As mentioned above, the theory gives the loss modulus to an accuracy of an undetermined constant, which, in turn, may depend on strain. Therefore, to check the theory, measurements at various frequencies are needed.

Rather a long time ago Mullins[31] and Morris[32] attempted to describe the equilibrium σ–λ dependence over a wide range of λ including the non-Gaussian region. It was done in the same way as for the Gaussian region, i.e. by summing the expression for σ taken from the phantom-chain theory with the Mooney–Rivlin term C_2/λ. Since in this work three fitting parameters were used, the results obtained therein seem not to be very reliable. In our case, having determined $\overline{\zeta^2}$ and $\overline{\zeta^4}$ we can restrict ourselves to only two parameters, C_1 and C_2, just as in the Gaussian range. This approach was used to describe the σ–λ dependences (since Meinecke[2] has measured those) and E''–λ dependences on the same samples. As shown in *Figure 2*, the experimental data are well described by the sum of (20) and the Mooney–Rivlin term.

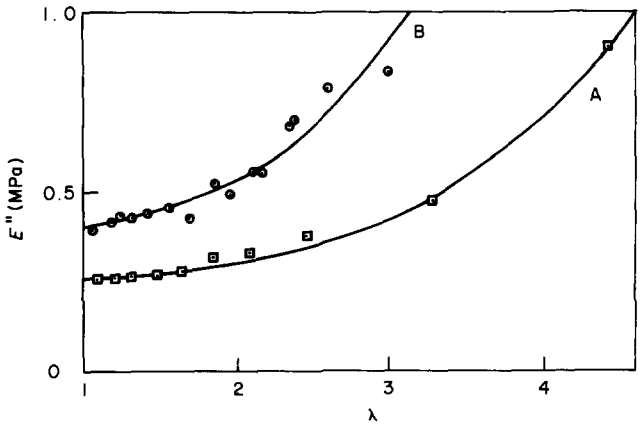

Figure 1 Dependence of the loss modulus E'' on λ as calculated using (18): ○, □, experimental data of Meinecke[2]; curve A, NR, $T=-26$°C; curve B, SBR, $T=25$°C, frequency 1 Hz

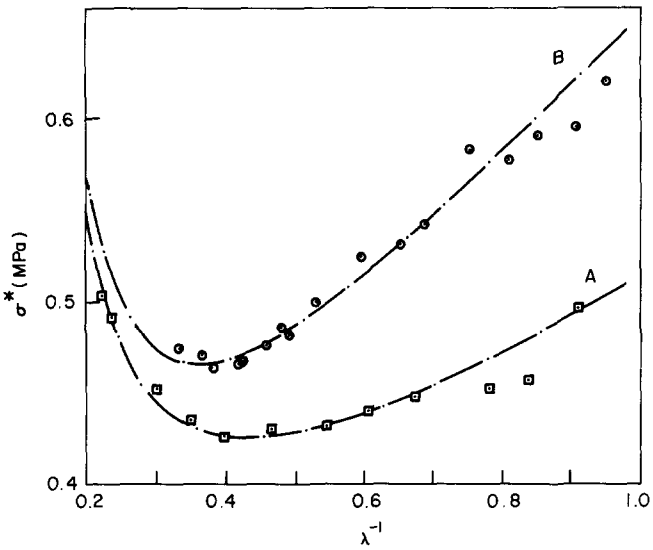

Figure 2 Dependence of the reduced strain $\sigma^*=\sigma/(\lambda^2-\lambda^{-1})$ on λ^{-1} plotted according to (20): curve A, NR, $C_1=0.28$ MPa, $C_2=0.21$ MPa; curve B, SBR, $C_1=0.25$ MPa, $C_2=0.39$ MPa; ○, □, experimental data of Meinecke[2]

Therefore, in the region of large strains, the theory of phantom chains is much more precise than in the Gaussian region. This is due to the fact that at large strains the variations of chain entropy induced by internal interactions are much greater than those connected with steric interactions of chains. In this connection it is worth mentioning the comment made by the late I. M. Lifshits that an exact theory of rubber elasticity will originate from considering the regions of ultimate extensions.

CONCLUSION

A new method of studying network structure can stem from the measurements of deformational dependence of the loss modulus. The data obtained by this method can also be useful in developing the theory of rubber elasticity. However, a series of preliminary studies must be done. It is necessary to find out at what extension the concept of semilocal modes remains valid and the model of beads and nonlinear springs is applicable. This can be done using the method of Brownian dynamics. Also the orientations and coiling ratio distributions of chains in strongly extended networks must be calculated. As mentioned above, the latter problem can be solved within the framework of the phantom-chain theory. Certainly we also need measurements of E''–λ dependences in elastomers of various network structures over a wide range of frequencies with simultaneous measurements of σ–λ dependences and birefringences.

APPENDIX

Let us consider two polymer chains with ends fixed at points A and C while point B can fluctuate (see *Figure 3*). The motion of this point is slower than micro-Brownian motions of chains AB and BC. During the characteristic time of those motions the point B scarcely moves from its position, and hence it may be considered to be fixed. Let us take B to be fixed so that the angle between $\mathbf{h}_1$ and $\mathbf{h}$ is θ. As an example we take the correlation function $\langle T_{zz}(t)T_{zz}(0)\rangle$ of the chain AB, which was calculated in refs. 7 and 8. In the coordinate system whose z-axis goes

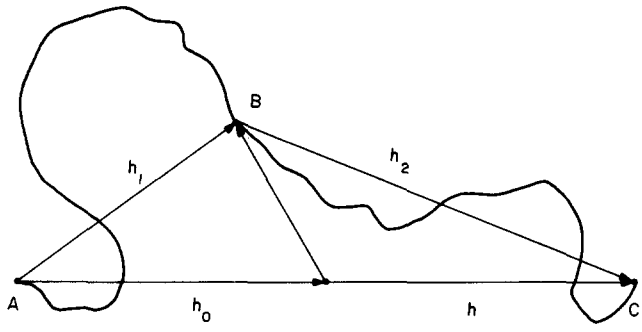

Figure 3 Slow fluctuation of the middle point in a chain

through the points A and C, this function for a chain with constant relaxation times is

$$\langle T_{zz}(t)T_{zz}(0)\rangle = K_g(t)[1+12\alpha(h_{1z}/L)^2 + 4(15\beta-7\alpha^2)(h_{1z}/L)^4 + 12(3\beta-2\alpha^2)(h_{1x}^2+h_{1y}^2)h_{1z}^2/L^4+\ldots] \quad (A.1)$$

Here it is taken into account that $h_{1z}=h_1\cos\theta$, $K_g(t)$ is the correlation function of a Gaussian chain, $\alpha=0.3$ and $\beta=33/175$.

We introduce the deviation of $\mathbf{h}_1$ from the equilibrium value $\mathbf{h}_0$: $\mathbf{h}_1=\mathbf{h}_0+\Delta\mathbf{h}_1$, $\mathbf{h}_0=h\mathbf{k}$. By analogy with (15) we expand the effective potential energy of the system involved in powers of deviations up to the second-order terms

$$\phi_h=\phi_h^0+\tfrac{1}{2}\sum_{i=1}^{2}[C_{lh}\Delta h_{iz}^2+C_{th}(\Delta h_{ix}^2+\Delta h_{iy}^2)] \quad (A.2)$$

Here ϕ_h^0 is the value of ϕ_h at equilibrium, $C_{lh}=U''(h_0)$, $C_{th}=U'(h_0)/h_0$ and $U(h_0)$ is the effective potential of interaction of points A, B and B, C at equilibrium for which we take the dependence (16).

Calculating the moments $\overline{\Delta h_{i\alpha}^n}$ in (A.1) under the approximations assumed, we obtain

$$\langle T_{zz}(t)T_{zz}(0)\rangle = K_g(t)[F_1(N_k)+\tfrac{18}{5}(h_0/L)^2F_2(N_k) + \tfrac{1539}{175}(h_0/L)^4F_3(N_k)+\ldots]$$

where

$$F_1(N_k)=1+1.2N_k^{-1}+3.9N_k^{-2}+\ldots$$
$$F_2(N_k)=1+5.1N_k^{-1}-3.6N_k^{-2}+\ldots \quad (A.3)$$
$$F_3(N_k)=1-3.8N_k^{-1}+1.8N_k^{-2}-\ldots$$

Here N_k is the number of segments in the chain. If we assume that the point B is fixed in its most probable position, all F_i are unity. Therefore, the contribution of fluctuations of the point B decreases with increasing N_k and may be neglected for sufficiently long chains.

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