Uniaxiality Induced in a Strained Polymer Network: Theory and Monte Carlo Simulations

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ABSTRACT: Deuterium nuclear magnetic resonance experiments on rubber networks under uniaxial stress display a characteristic feature: A doublet structure for network chains and for free chains diffusing in the network. The doublet structure can be explained in a mean field theory by introducing orientational segmental interactions in the network system. A mean field theory of this kind is explicitly developed for a network system on a cubic lattice. Monte Carlo simulations on a cubic lattice are performed and compared to theory. Segmental interactions are simply introduced by applying the concept of mutually and self-avoiding chains in the simulation. It is confirmed that the segmental interactions introduce a uniaxial segmental orientation in the sense that each segment shows an orientational behavior as being under the influence of a uniaxial external field. The mean field theory is shown to be well reproduced by the simulations. The calculation of the nuclear magnetic resonance spectrum for the model network of the simulation gives a doublet structure only for the case where steric interactions are present.

I. Introduction

In various studies deuterium nuclear magnetic resonance (^{2}H NMR) has been used to analyze the orientational order induced in rubber networks under uniaxial stress.[1-7] The systems studied were mainly poly(dimethylsiloxane) and polybutadiene networks. The main results can be summarized in the following way: the ^{2}H-NMR spectrum of network chains exhibits a characteristic doublet structure which is associated with uniaxial reorientations of chain segments around the applied strain direction. The doublet spacing is proportional to $\lambda^2 - \lambda^{-1}$ in the low deformation limit, where λ denotes the parameter characterizing the strain. Homopolymer chains diffusing in the network show a much more resolved doublet structure but with equal splitting. Also solvent molecules inside the deformed network exhibit a doublet structure.

It has been shown that the classical description of a network[9] cannot explain the existence of such a doublet structure. One of the basic ingredients of this classical model is the assumption of noninteracting, independent polymer chains. References 1, 3, and 8 suggest a natural generalization of the classical description by introducing short-range orientational interactions between two segments of different chains. In the same way as in liquid crystal theories[10] this interaction favors a mutually parallel orientation of two segments in contrast to a perpendicular one. It has been demonstrated[8] that a mean field theory including such a segmental orientation predicts all the experimental results summarized above, since the orientational couplings effectively generate in the system a uniaxial field directed along the applied strain.

There are two basic questions which remain open: first, is such a mean field hypothesis sufficient to describe the orientational segmental behavior correctly, and secondly, what is the nature of the underlying orientational interactions? It is the purpose of this paper to answer these two questions by performing computer simulations. In these simulations, interactions are introduced only by the excluded volume condition, i.e. as steric interactions. Steric interactions are naturally present in a dense polymer system and are supposed to generate effectively orientational interactions, even though the polymers under consideration do not contain any nematogen groups.[11] We will show that in fact steric interactions are sufficient to create orientational interactions which in turn lead to a uniaxial segmental orientation. The mean field description of ref 8 provides quantitative statements concerning various dependencies, as for example, the dependence of the orientational parameter on the strain rate λ. Consequently, our second goal will be to reproduce results of a mean field theory as developed in ref 8.

For this purpose it is sufficient to employ a model which takes into account the assumptions of the mean field theory quoted above and which enables us to introduce steric interactions. Since the assumptions of the theoretical model are actually very simple, it is possible to use the simplest and therefore fastest kind of computer simulation: a Monte Carlo simulation on a cubic lattice.

Orientational behavior in network systems was already analyzed by computer simulations in ref 12. In that work molecular dynamics simulations are applied. This kind of simulation is more sophisticated and therefore much more time consuming than our approach. As a result detailed knowledge about the segmental orientational behavior is not accessible, although the uniaxial character generated by steric interactions is indicated.

In section II we will apply the mean field theory from ref 8 for a network system on a cubic lattice. In section III the Monte Carlo simulation is described. Although the simulation may appear unrealistic and oversimplified, it has to be emphasized that all elements of the theory to be verified are taken into account. So the simulation is perfectly well suited to compare with the present theory, which is done in section IV.

II. Theory

II.1. Connection between ^{2}H-NMR Spectra and Distribution Functions of Local Orientational Order Parameters. Basic concepts of ^{2}H NMR have been developed in numerous references.[13] We only quote from ref 8 the elementary result for the transverse relaxation function $M(t)$:

$$M(t) = M_0\langle \exp(-t/T_2) \cos(\nu_Q \Delta t)\rangle \qquad (1)$$

The angular brackets denote an ensemble average, i.e. an average over the network system. ν_Q is the static

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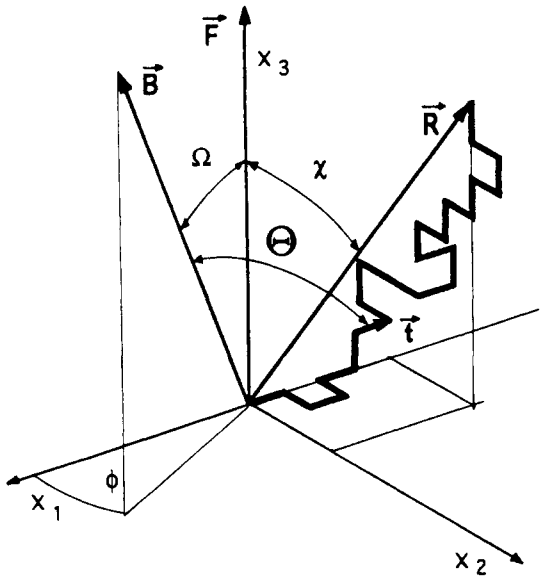

Figure 1. Different angular coordinates used to define the orientation of a segment **t** or of a chain end-to-end vector **R**, with respect to a magnetic field **B** or to the applied force **F**.

quadrupolar interaction constant and T_2 is a characteristic relaxation time. Δ is given by

$$\Delta = \overline{P_2(\Theta)} \tag{2}$$

Θ denotes the instantaneous angle between a given C–D bond and the steady magnetic field **B** (Figure 1). P_2 is the second Legendre polynomial. The overbar denotes a time average over molecular reorientations faster than ν_Q^{-1}. Δ describes the mean orientation of a segment with respect to **B**. If the direction of **B** is identical with a certain symmetry axis, in our case the direction of the force, Δ is called S, the order parameter. The above time average can also be viewed as the average over all conformations accessible to chain molecules in the system. It is this property which makes a statistical theory and a Monte Carlo simulation possible.

The Fourier transform of $M(t)$ provides the spectrum measured in a ^{2}H-NMR experiment. It has been shown[8] that, in the network systems under consideration, T_2^{-1} is small compared to the total width of the spectrum. Hence for performing the Fourier transform the exponential term in eq 1 can be neglected. From eq 1 we get for the spectrum $F(\omega)$

$$F(\omega) \sim \int \mathrm{d}t\, \langle \cos(\nu_Q \Delta t) \rangle \exp(-i\omega t) \tag{3}$$

$$\sim \int \mathrm{d}\Delta\, \mathrm{d}t\, \rho(\Delta) \cos(\nu_Q \Delta t) \exp(-i\omega t) \tag{4}$$

$$\sim \rho(\omega/\nu_Q) + \rho(-\omega/\nu_Q) \tag{5}$$

where in the second step the average over the system has been replaced by an integral over all possible values of Δ occurring in the system, weighted by the distribution function $\rho(\Delta)$. The result shows that the spectrum obtained in a NMR measurement is nothing else but the symmetrized distribution function of the segmental orientation with respect to **B**, except for a scaling factor ν_Q. This connection provides an easy access for theoretical calculations of the spectrum and particularly allows the determination of the spectrum in a computer experiment, as it is described in this article.

II.2. Calculation of the Distribution Function $\rho(\Delta)$ from a Mean Field Single Chain Description. For the statistical description of the segmental orientation in a network, we follow closely the ideas developed in refs 9 and 8 with the difference that we deal with a system on a cubic lattice with segment length 1; i.e. there are only three possible orientations directed along the three unit vectors $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_3$, which form an orthonormal coordinate system. The free energy per segment for a chain of length N with fixed ends under the influence of a uniaxial field is written as (in kT units)

$$F = \sum_{i=1}^{3} (f_i^+ \ln f_i^+ + f_i^- \ln f_i^-) - \beta(f_3^+ + f_3^-) \tag{6}$$

under the constraints

$$(f_i^+ - f_i^-) = x_i/N \tag{7}$$

f_i^+ and f_i^- are the probabilities of finding a segment of the chain under consideration directed along the positive or negative direction of the unit vectors $\mathbf{e}_i$ (i = 1–3), respectively. They are normalized so that

$$\sum_{i=1}^{3} (f_i^+ + f_i^-) = 1 \tag{8}$$

$(f_3^+ + f_3^-)$ corresponds to the usual expression $\cos^2\theta$ for a uniaxial orientational mean field, where θ is the angle between a segment and some fixed direction (the direction of the uniaxial force), which will be the positive $\mathbf{e}_3$-axis throughout this paper.

β is the parameter describing the strength of the uniaxial mean field. The uniaxial field can be viewed as a consequence of short-range orientational interactions between pairs of segments.[8] In this case β can be written as $\beta = u\langle S \rangle$, where u is a parameter describing the short-range orientational interaction and $\langle S \rangle$ is the mean orientation of a segment with respect to $\mathbf{e}_3$ averaged over the total network, so that β depends in a self-consistent manner on the average orientation itself.[8]

x_i (i = 1–3) are the coordinates of the end-to-end vector of the chain under consideration.

Then the quantity to minimize in order to obtain the average orientation of one segment of a particular chain under consideration is given by

$$G = \sum_{i=1}^{3} (f_i^+ \ln f_i^+ + f_i^- \ln f_i^- - \mu_i(f_i^+ - f_i^-) - \epsilon(f_i^+ - f_i^-)) - \beta(f_3^+ + f_3^-) \tag{9}$$

where μ_i and ϵ are Lagrange multipliers associated with the conditions (7) and (8). Note that the ϵ term leads to a contribution independent of the distribution of orientation, and therefore does not play any role in what follows.

The average orientation of one chain segment with respect to a given direction defined by angular coordinates Ω and ϕ is calculated in terms of Ω and ϕ as

$$\Delta = \frac{1}{2}\overline{(3(\sin\Omega \sin\phi t_1 + \sin\Omega \cos\phi t_2 + \cos\Omega t_3)^2 - 1)} \tag{10}$$

The vector **t** with $\mathbf{t}^2 = 1$ represents one segment (Figure 1). For a cubic lattice one has

$$\overline{t_i t_j} = \delta_{ij}(f_i^+ + f_i^-) \tag{11}$$

where δ_{ij} denotes the Kronecker symbol. Using relation 11 in eq 10 one obtains

$$\Delta = \frac{1}{2}(3[\sin^2\Omega\sin^2\phi\,(f_1^+ + f_1^-) + \sin^2\Omega\cos^2\phi\,(f_2^+ + f_2^-) + \cos^2\Omega\,(f_3^+ + f_3^-)] - 1) \quad (12)$$

In a NMR experiment the given direction (Ω,ϕ) is represented by the direction of the constant magnetic field **B**.

For the sake of simplicity we present from now on results only for the case where the magnetic field **B** coincides with the positive $\mathbf{e}_3$-axis. The average segmental orientation Δ is then identical to the order parameter S. Following the steps performed in ref 8 one finds in lowest order for S (see Appendix with $\gamma = 0$)

$$S = \frac{3}{2N^2}P_2(\chi) + \frac{\beta}{3} \quad (13)$$

S depends linearly on the second Legendre polynomial $P_2(\chi)$, where χ is the angle between $\mathbf{e}_3$ and the end-to-end vector of a network chain (Figure 1), together with a constant contribution proportional to the strength of the uniaxial field. We note that the structure of this result is the same as found in the continuous case.[8] Only the numerical factors appearing in front of these terms are different here.

In order to visualize clearly the effect of the uniaxial field on the distribution of the order parameters in the network, and consequently on the NMR spectrum, we discuss first the shape of the distribution function $\rho(\Delta)$, neglecting the influence of the uniaxial field, i.e. setting $\beta = 0$.

Equation 13 is rewritten in terms of Cartesian coordinates

$$S = \frac{3}{4N^2}(2x_3^2 - x_2^2 - x_1^2) + \frac{\beta}{3} \quad (14)$$

The Cartesian coordinates of the end-to-end vectors are usually assumed to follow a Gaussian distribution:[13]

$$h(x_i) = \frac{1}{\sigma\sqrt{2\pi}}\exp\left(-\frac{x_i^2}{2\sigma^2}\right) \qquad \sigma^2 = \langle x_i^2\rangle \quad (15)$$

For the case of a uniaxial strain of the network described by a strain $\lambda = L/L_0$, we assume as usual an affine deformation along $\mathbf{e}_3$, which leads to a modified distribution characterized by the following widths:

$$\sigma_3^2 = \lambda^2\sigma^2 \qquad \sigma_{1,2}^2 = \lambda^{-1}\sigma^2 \quad (16)$$

Using the distributions for the coordinates x_i (eqs 15 and 16), the distribution $\rho(S)$ can now be calculated from eq 14. Figure 2 shows a resulting distribution using continuous values x_i for $\lambda = 2$. The main point is that $\rho(S)$ exhibits a maximum at $S = 0$ even for a strained network, i.e. $\lambda \neq 1$. From eq 5 it follows that the resulting NMR spectrum shows no doublet structure.

On the other hand, if we take into account the constant term arising from the uniaxial field, the resulting $\rho(S)$ will be shifted by the amount $\beta/3$, leading to a maximum at $S = \beta/3$ and a doublet structure in the NMR spectrum. These statements are equally true for a continuous system and a system on a lattice, since they are based on the structure of eq 14, which is the same in both cases.

Note that for a free chain diffusing in the network the first term in the sum in eq 14 vanishes. As a consequence the resulting distribution function will be ideally a δ function peaked at $\beta/3$. The corresponding observed spectrum will consist of a highly resolved doublet with a splitting equal to that of the network chains, as is indeed observed in ref 3.

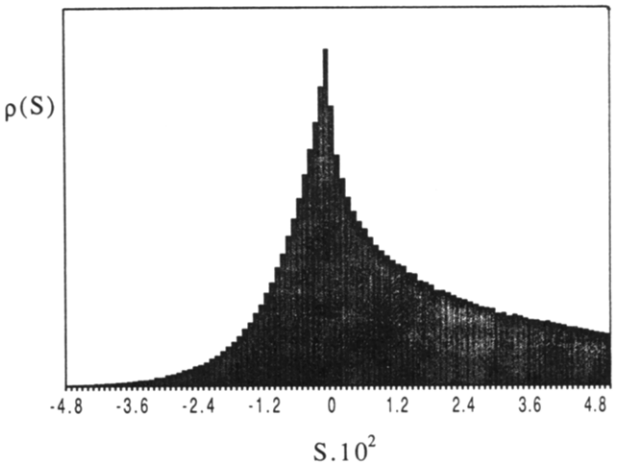

Figure 2. Distribution function $\rho(S)$ of the order parameter S calculated according to eq 14 for $\beta = 0$ ($\lambda = 2$). The calculation has been performed by generating 10^6 times end-to-end coordinates x_1, x_2, and x_3 according to Gaussian distributions and calculating S from each time.

Averaging eq 14 over the network system and using the self-consistency equation $\beta = u\langle S\rangle$, we arrive at the following equation for the average order parameter $\langle S\rangle$ in the system:

$$\langle S\rangle = \frac{1}{1-\frac{u}{3}}\langle S_{cl}\rangle \qquad \langle S_{cl}\rangle = \frac{\langle R_0^2\rangle}{2N^2}(\lambda^2 - \lambda^{-1}) \quad (17)$$

Here $\langle R_0^2\rangle$ is the mean square end-to-end distance of the chains in the network system in the relaxed state. $\langle S_{cl}\rangle$ denotes the average order parameter in a classical system,[9] i.e. without any interactions between different chains.

$\langle S\rangle$ can now be reinserted into eq 14 to obtain finally

$$S = \frac{3}{4N^2}(2x_3^2 - x_2^2 - x_1^2) + \frac{\frac{u}{3}}{1-\frac{u}{3}}\langle S_{cl}\rangle \quad (18)$$

The uniaxial mean field can be viewed as the consequence of local orientational pairwise interactions between segments. In the computer simulations the orientational interactions are introduced by an excluded volume effect. For a cubic lattice model this causes a higher probability for a parallel orientation of two segments than for a perpendicular orientation, because in the latter case there are statistically more possibilities for an overlap of two segments.

II.3. Influence of Intramolecular First-Neighbor Interactions. Two successive segments along one chain behave differently: since steric interactions strictly forbid an orientation of two successive segments in the same direction but with opposite signs while all other possible configurations are allowed, a perpendicular orientation of two successive segments becomes more probable. This results in a somewhat artificial interaction along the chain, specific to the cubic lattice. The mean squared length of the chains should be properly renormalized to implement this finite range interaction (which is indeed contained in the Gaussian assumption) before comparing the resulting orientation S to $\langle S_{cl}\rangle$ (eq 17). Thus, in order to estimate crudely this additional effect, we modify eq 6 by adding a term (the prefactor 6 is introduced for convenience):

$$F = \sum_{s=1}^{N}\left(\sum_{i=1}^{3}(f_{i,s}^{+}\ln f_{i,s}^{+} + f_{i,s}^{-}\ln f_{i,s}^{-}) - \beta\,(f_{3,s}^{+} + f_{3,s}^{-})\right) + 6\gamma\sum_{s=1}^{N-1}\sum_{i=1}^{3}(f_{i,s}^{+}f_{i,s+1}^{-} + f_{i,s}^{-}f_{i,s+1}^{+}) \quad (19)$$

The sum over s represents the sum over the N segments of one chain and γ is an additional parameter describing the strength of the nearest neighbor interactions. For a cubic lattice, where one of six directions is strictly forbidden for an instantaneous move, we expect γ to be positive and not negligible, while for continuous models the influence of this term might be weak and other local effects such as, for example, the local stiffness of a chain dominate.

Following the steps described in the Appendix, we arrive for the inner segments of a network chain in lowest order (in the limit of large N) at

$$S = \frac{1}{1+2\gamma}\left((1+p(\gamma))\frac{3}{4N^2}(2x_3^2 - x_2^2 - x_1^2) + \frac{\beta}{3}\right) \quad (20)$$

$p(\gamma)$ cannot be expressed analytically. One has $p(\gamma = 0) = 0$ and $p(\gamma)$ decreases for decreasing γ and for increasing N. For $N = 30$ and γ taken from a relevant interval $0.2 < \gamma < 0.3$, $p(\gamma)$ varies between 0.04 and 0.07.

The self-consistency condition $\beta = u\langle S\rangle$ leads to

$$\langle S\rangle = \frac{1+p(\gamma)}{1+2\gamma-\frac{u}{3}}\langle S_{cl}\rangle \quad (21)$$

and

$$S = \frac{1}{1+2\gamma}\left((1+p(\gamma))\frac{3}{4N^2}(2x_3^2 - x_2^2 - x_1^2) + \frac{\frac{u}{3}(1+p(\gamma))}{1+2\gamma-\frac{u}{3}}\langle S_{cl}\rangle\right) \quad (22)$$

The explicit calculation performed in the Appendix shows that there is a significant modification of eqs 20 and 22 only for the edge segments of the chain. Equation 22 reflects the fact that the net effect of the first-neighbor interactions is a reduction of the order parameter for each segment. Subsequently, the mean field contribution is affected.

We note that for the orientation of a free chain in the network the first term of the sum vanishes. For the orientation of a single, free segment in a network, the first term of the sum also vanishes and the overall prefactor equals 1. A single, free segment consequently experiences only the pure uniaxial field. Therefore its order parameter is called S_{uniax}:

$$S_{uniax} = \frac{\frac{u}{3}(1+p(\gamma))}{1+2\gamma-\frac{u}{3}}\langle S_{cl}\rangle \quad (23)$$

III. Computer Simulation—Set Up and Performance

A model network in the relaxed state is created as follows: On a cubic lattice a certain number of pairs of lattice sites are randomly distributed, while the relative coordinates between each pair are constrained to follow a (discrete) Gaussian distribution with a given width.

One pair of lattice sites represents the two fixed end points of one chain. Consequently, these end points are connected by occupied lattice sites representing monomers. In this way a chain contour of some fixed length, i.e. of some fixed segment number, is constructed. This procedure of creating chains has not to be totally random, since it serves only as a starting conformation. Relative coordinates are determined by taking into account periodic boundary conditions.[14]

The number of chains, the number of segments per chain, and the size of the lattice have to be chosen so as to fulfill various requirements:

- The chain length has to be large enough in order to be properly described by a statistical theory, as in section II.
- The number of chains has to be large enough so that the distribution of the relative coordinates of the chain end-to-end vectors form a reasonable discrete version of a Gaussian distribution.
- The mean square end-to-end distance has to be of the order of the chain length. This condition fixes the width of the distribution of relative coordinates.
- The density has to be high in order to produce a strong interaction between chain segments.
- The system has to be remarkably larger than the width of the Gaussian distributions of relative coordinates.
- The system has to be as small as possible to allow sufficient sampling over the system within reasonable simulation times.

Taking into account all these requirements, the following parameters were chosen for a network system in the relaxed state: 90 chains with $N = 30$ segments are distributed on a cubic (16,16,16) lattice. Their mean square end-to-end distance equals 30.

For a network under uniaxial stress, characterized by the strain λ, the same procedure as described above is applied with two modifications: the widths of the Gaussian distributions of the relative coordinates are modified according to eq 16, and additionally, the box dimensions are multiplied by λ or $\lambda^{-1/2}$, respectively. Since only integer values are used for box dimensions, the requirement of a deformation which keeps the volume constant cannot be exactly fulfilled. However, for the strain parameters $\lambda = 0.6, 2.0, 3.5$ it was possible to keep the number of lattice sites constant (3200) with a resulting density of 0.87. For the stress parameter $\lambda = 0.4$ a slightly lower density (0.81) was obtained.

Different conformations are created using a Monte Carlo algorithm, which employs so-called L-inversions[15] and modified crankshaft moves, which allow long-range transports of kinks along a chain.[16,17] These types of motion leave the ends of the chain fixed, as required. They are shown to be appropriate for a simulation of cyclic polymer,[17] which should be comparable to a simulation of chains with fixed extremities. It is obvious that for chains with fixed ends the conformational space is much smaller than for free chains, so that sufficient sampling is achieved within very reasonable simulation times. The number of attempted Monte Carlo steps was typically 10^9 per simulation.

A test of the quality of the algorithm and simultaneously a first application is a simulation, where no excluded volume condition is imposed; i.e. one site is allowed to be occupied several times. This corresponds to a network system without interaction. As a result we should reproduce the results of eq 14 with $\beta = 0$.

Since eq 14 is a first order approximation in x_i/N, the order parameter S was determined for those chains, where x_i/N, i = 1–3, is small. The segmental orientation was averaged for each chain separately and according to eq 14 the proportionality factor between S and $^1/_2(2x_3^2 - x_1^2 - x_2^2)$ was calculated. The result for this factor was $(1.75 \pm 0.02) \times 10^{-3}$.

This value has to be compared with the result of the mean field description (eq 14), namely $^3/_2N^2 = 1.67 \times 10^{-3}$. Also the exact result can be obtained in this case by using the exact expression for the number of possible conformations given a certain set of $f_i^{\pm}$ ($Nf_i^{\pm}$ has to be an integer). This exact treatment gives for the proportionality factor of eq 14 the value 1.70×10^{-3} with a small deviation for different end-to-end coordinates (fulfilling $x_i/N \ll 1$).

The deviation between the result of the simulation and the result of the mean field description ($\sim$5%) is acceptable. In particular the proportionality itself is confirmed in the simulation. On the other hand, the deviation from the exact result seems to be systematic and would signify that the employed algorithm does not generate exactly the correct statistical distribution of configurations. Since the order parameter of the first and the last segment of each chain differs significantly from the chain average, it is supposed that the above slight deviation has something to do with the application of the Monte Carlo moves for the end segments.

The exact result differs slightly from the result of the mean field approach, because in the latter one end-to-end vectors are fixed on average whereas in the exact treatment and in the simulations they are fixed rigorously. This might in turn lead to a slight overestimation of the order parameter with respect to the mean field description.

The power of the simulation now lies in the fact that specific interactions in the system can be separately switched on. In this way we are able to apply in one simulation only intramolecular nearest-neighbor interactions and to introduce in another simulation steric interactions by simply applying the condition of self-avoiding and mutually avoiding motions (each site can only be occupied by one monomer). This steric interaction would then generate a pairwise orientational interaction, as proposed in ref 8.

We emphasize that in our simulation the chains are not connected by junctions but are simply fixed at their end points. We repeat that our goal is to verify a statistical theory as in section II and particularly the occurrence of a uniaxial fieldlike effect. However, in this theory there is no concept of junctions as well. The only ingredients are a distribution of fixed end-to-end vectors and an interaction between pairs of segments, all of which are also present in our simulation. For this reason we retain the term network. The reason for abandoning the concept of junctions in our simulation is the following: the existence of multifunctional junctions gives rise to additional effects like a strong influence on the orientational behavior of the segments close to the junctions or an increase in the number of entanglements. These effects are considered as a kind of noise in the present statistical theory and therefore minimized by abandoning real junctions. It is clear however that some entanglements are present.

It is also possible to introduce free chains into the network which are moved using a slithering snake algorithm.[15] In this work we only introduce a single, free segment, which can be viewed as one segment of a polymer or as a solvent of a similar chemical structure as the repeating unit of the polymer. The introduction of single segments instead of free chains has two advantages: first we avoid very long simulations due to the comparatively large conformational space of a free chain, and secondly we are able to visualize directly the effect of the uniaxial field on a segment without the disturbing influence of the first-neighbor intramolecular interactions.

Besides these basic simulations we performed simulations of single free chains of different lengths, where only a first-neighbor interaction is switched on. For the slithering snake algorithm this means that no backward moves are allowed. Different probabilities for a move into the x_1/x_2 or x_3 direction are assigned. In this way a uniaxial field is generated. Its strength β, the parameter appearing in eq 7, is directly related to the given probability. So the net effect of the first-neighbor interaction can be visualized and the parameter γ describing its strength can be calculated.

IV. Results of the Simulation

IV.1. Mean Segmental Orientation of an Isolated, Free Chain with Nearest-Neighbor Interactions under a Given Uniaxial Field. A single free chain under the influence of a uniaxial field is simulated using a slithering snake algorithm with nearest-neighbor interactions as described in the preceding section. The segmental orientation in that case is by construction uniaxial. For a sufficiently long chain (N = 30) the order parameter of a segment in the middle of the chain (S_{15}) obeys the following equation (see eq 20):

$$S_{15} = \frac{\beta}{3}\frac{1}{1+2\gamma} \tag{24}$$

For three different values of $\beta/3$ (0.01, 0.03, 0.1) the above equation was used to determine γ:

$$\gamma = 0.27 \pm 0.01 \tag{25}$$

An explicit calculation of all values for the order parameter S_i for each segment according to the Appendix using this value of γ actually compares very well with the results found in the above simulation. This result confirms the comparatively simple ansatz in eq 19.

IV.2. Mean Segmental Orientation of Network Chains with Only Intramolecular Nearest-Neighbor Interactions. Network chains are simulated without the excluded volume condition, but with the consideration of intramolecular nearest-neighbor interactions. Then γ can be determined by comparison with eq 20 for $\beta = 0$, i.e. without intermolecular steric interactions. The mean orientation S of a segment is calculated for each chain as the average over the 20 inner segments. For those chains where the first order approximation (with respect to x_i/N) in eq 20 is valid, the value of γ was determined:

$$\gamma = 0.21 \pm 0.01 \tag{26}$$

This result and the result above (γ = 0.27) differ appreciably. There are supposedly several reasons for this difference. First of all the value of γ is very sensitive to even small changes of S. The lower γ for the network chains is caused by a larger value of S. For network chains without any interactions it was found that the S of the simulation is larger than the exact result (supposedly due to the algorithm) and, on the other hand, that the exact result is larger than the result of the mean field approach. Both contributions might occur here as well, leading to a value of S too large with respect to eq 20, i.e. to the mean field value.

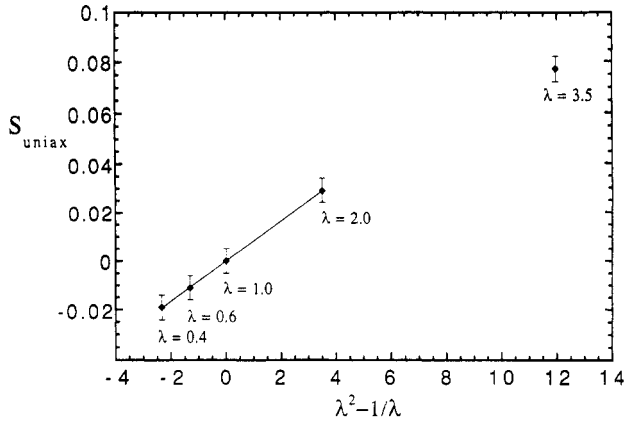

Figure 3. Dependence of the mean orientation of a single, free segment in the network on $\lambda^2 - \lambda^{-1}$, where $\lambda = L/L_0$ is the strain rate. Since a single, free segment experiences the pure uniaxial orientational field, its mean orientation is denoted as S_{uniax}.

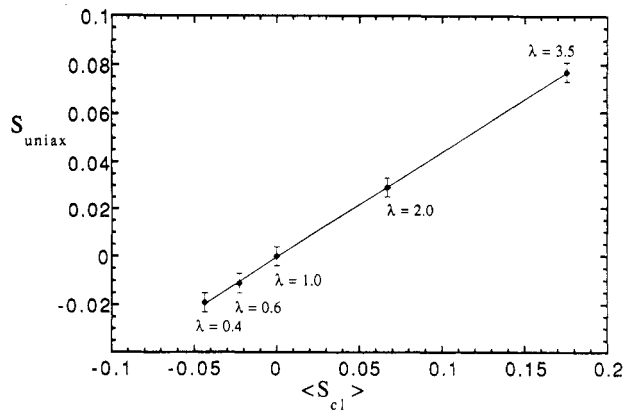
0.1
0.08
0.06
0.04
0.02
0
-0.02
S uniax
λ = 3.5
λ = 2.0
λ = 1.0
λ = 0.6
λ = 0.4
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Figure 4. Mean orientation S_{uniax} of a single, free segment in the network versus $\langle S_{cl} \rangle$. $\langle S_{cl} \rangle$ is the mean segmental orientation averaged over all segments on the basis of a classical description, i.e. without interactions (see eqs 17 and 23).

IV.3. Mean Orientation of a Free, Single Segment in the Network. A free, single segment was introduced networks of different uniaxial strains ($\lambda = 0.4, 0.6, 1.0, 2.0, 3.5$), where the conditions of self-avoiding and mutually avoiding motions was applied between all segments of the system. Following eq 23, the mean orientation S_{uniax} of a free segment should be proportional to $(\lambda^2 - \lambda^{-1})$.

Figure 3 shows that this is indeed the case in our simulation (except for the very high stress rate $\lambda = 3.5$, which exceeds the linear region of eq 23). This is a basic result in the sense that it is demonstrated that the consideration of steric interactions between segments is sufficient to introduce a uniaxial orientation for free segments and consequently for free chains in the network.

The parameter u characterizing the strength of the steric interactions can be estimated from the slope of Figure 4, where S_{uniax} is plotted against $\langle S_{cl} \rangle$. Comparison with eq 23 allows in principle the extraction of the value of u. However, there are two major sources or uncertainty: first the value of the parameter γ cannot be uniquely determined; secondly eq 23 is based on an ensemble average over the network system, wherein all chains are supposed to obey the first order approximation with respect to x_i/N. This is not the case in our simulation. So only a rough estimation of u is given using the values for γ found above (0.21 and 0.27) and taking into account an additional error of 10%, which is the typical deviation between $\langle S_{cl} \rangle$ found in the simulation without interactions and $\langle S_{cl} \rangle$ given in eq 17:

$$0.39 < \frac{u}{3} < 0.51 \tag{27}$$

It is interesting to note that the proportionality between S and $\langle S_{cl} \rangle$ seems to be valid even in the nonlinear regime, i.e. for $\lambda = 3.5$.

IV.4. Distribution Function of the Orientational Parameter *S*. For the case where the average orientation of one segment is determined with respect to an arbitrary direction defined by the angular coordinates Ω and ϕ, the result for this orientation assumes a more complicated form, according to eq 12. However, the uniaxial contribution Δ_{uniax}, i.e. the part which is independent of the coordinates of the end-to-end vectors, can be easily calculated as a function of the angle Ω:

$$\Delta_{uniax} = \frac{1}{1 + 2\gamma} \frac{\beta}{6} (3 \cos^2 \Omega - 1) \tag{28}$$

In an ^{2}H-NMR experiment Ω would be the angle between **B** and the direction of the force, i.e. $\mathbf{e}_3$. As explained in the theoretical section, the maximum of the distribution function of Δ determines the value of Δ_{uniax}. In order to improve the statistics, the final distribution function was calculated for each angle Ω as a sum over various distribution functions for different angles ϕ according to eq 12. Moreover, for the calculation of the distribution function only the 10 inner segments of each chain were taken into account.

As stated in the theoretical section, one obtains by symmetrization of the distribution function $\rho(\Delta)$ the observed spectrum. $\rho(\Delta)$ and the spectrum for $\lambda = 2$ are given in Figures 5 and 6, respectively, where Δ is determined with respect to a direction characterized by a polar angle Ω with $\cos^2 \Omega = {}^2/_3$. The spectrum clearly shows a doublet structure.

Figure 7 shows Δ_{uniax} as a function of ${}^1/_2(3 \cos^2 \Omega - 1)$ for $\lambda = 2$. The dependence on Ω is in perfect agreement with eq 28 and with experiments.[2] It is this plot which shows best the uniaxiality in the system, because only the uniaxial contribution follows the dependence on Ω in eq 28.[2] For example we note that the distribution function exhibits the maximum at $\Delta = 0$ for the angle Ω with $\cos^2 \Omega = {}^1/_3$, the so-called magic angle; i.e. there is no doublet for this angle.

The slope of the plot in Figure 7 gives the value of β and from that the value of u, taking into account the same uncertainities as above:

$$0.39 < \frac{u}{3} < 0.55 \tag{29}$$

The result is in good agreement with the result in section IV.3. This value of $u/3$ is not small with respect to unity, which would correspond to a spontaneous orientation. This may seem rather surprising, since the systems under consideration are by no means nematic polymers. This result means that the excluded volume interactions introduced herein lead to a rather strong enhancement of the induced orientational order. Note also that comparable values were deduced from experiments.[1,8]

V. Conclusions

Monte Carlo simulations of a model polymer network on a cubic lattice were employed to explain the occurrence of a doublet structure of ^{2}H-NMR spectra for free chains and network chains in a strained polymer network. The following results were found:

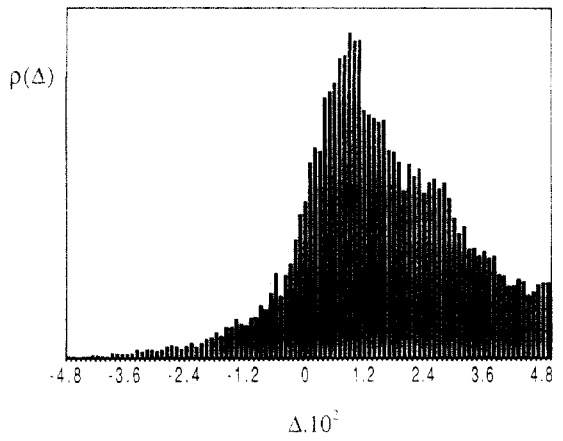

Figure 5. Distribution function $\rho(\Delta)$ of the mean orientation of the network chain segments, computed for $\lambda = 2$. Δ is calculated with respect to a direction characterized by the polar angle Ω with $\cos^2 \Omega = {}^2/_3$.

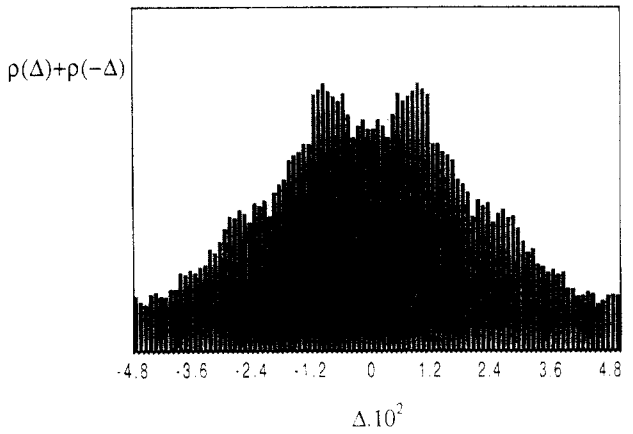

Figure 6. Spectrum $\rho(\Delta) + \rho(-\Delta)$ corresponding to Figure 5.

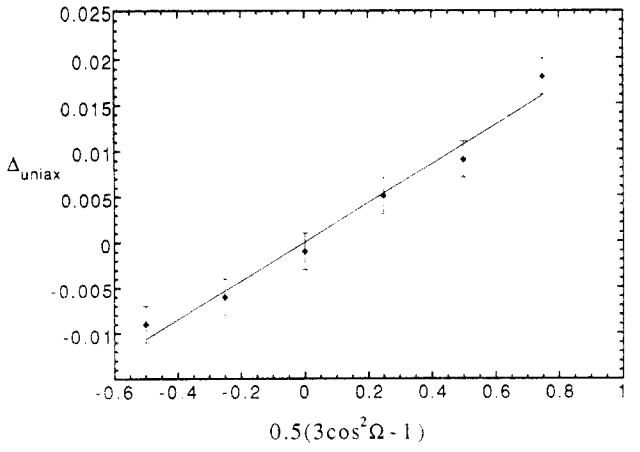

Figure 7. Dependence of the uniaxial part Δ_{uniax} of the mean orientation of the network chain segments on ${}^1/_2(3\cos^2 \Omega - 1)$, for $\lambda = 2$. The orientation is calculated with respect to a given direction which makes the angle Ω with the direction of the strain, for each angle Ω. The large error bars are due to the fact that Δ_{uniax} has to determined from the badly resolved distribution functions $\rho(\Delta)$ (see Figure 5).

(a) The inclusion of *steric interactions* between chain segments is sufficient to generate a uniaxial contribution to segmental orientation of network chains. In particular this contribution leads to a doublet structure in the NMR spectrum.

(b) Segmental steric interactions also generate a uniaxial orientation of free segments in the model network. This corresponds to a uniaxial orientation both of solvent molecules and free chains in real systems which is clearly observed in experiments.[1,3]

(c) A mean field description developed in this article reproduces very well the results found in the simulation. Therefore a mean field description for the continuous case, which has been proposed in ref 8, should describe appropriately the segmental orientational behavior in a real system. In particular the simulations verify the basic outcome of the theory, namely that segmental orientational interactions generate effectively a uniaxial field which causes a doublet in the ^{2}H-NMR spectrum for network chains and for free chains in the network with the same splitting, but better resolved for the latter ones. This result is in accordance with a recent analytic calculation which analyzes the screening of isotropic excluded volume interactions in networks.[18]

(d) Since the employed model does not allow fluctuations of the junctions, it is shown that it is not necessary to introduce these fluctuations in order to explain the doublet structure, as is done in ref 19. For the same reason the existence of dangling ends is not the crucial reason for the doublet structure, as claimed in ref 20. This latter explanation assumes different splittings for network chains and dangling chains and consequently seems to contradict the mean field theory used and verified in this article.

A direct calculation of the orientation dependent steric interactions has been given recently.[21] This approach could be adapted to the problem of this paper.

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Appendix

We start by minimizing the following quantity G in order to obtain the equilibrium probability $f_{i,s}^{\pm}$ for a segment to be directed along the positive or negative direction of $\mathbf{e}_i$:

$$G = \sum_{s=1}^{N}\Big(\sum_{i=1}^{3}(f_{i,s}^{+}\ln f_{i,s}^{+} + f_{i,s}^{-}\ln f_{i,s}^{-} - \mu_i(f_{i,s}^{+} - f_{i,s}^{-}) - \epsilon(f_{i,s}^{+} + f_{i,s}^{-})) - \beta(f_{3,s}^{+} + f_{3,s}^{-})\Big) + 6\gamma\sum_{s=1}^{N-1}\sum_{i=1}^{3}(f_{i,s}^{+}f_{i,s+1}^{-} + f_{i,s}^{-}f_{i,s+1}^{+})$$

All the quantities appearing in this expression are denoted in the same way as in the text (eqs 9 and 19). The derivative of G with respect to $f_{i,s}^{-}$ and $f_{i,s}^{+}$ equals zero at equilibrium:

$$0 = \ln f_{i,s}^{+} - \mu_i - \beta\delta_{3,i} - \epsilon + 6\gamma(f_{i,s+1}^{-} + f_{i,s-1}^{-})$$

$$0 = \ln f_{i,s}^{-} + \mu_i - \beta\delta_{3,i} - \epsilon + 6\gamma(f_{i,s+1}^{+} + f_{i,s-1}^{+}) \qquad s = 2, N-1$$

and

$$0 = \ln f_{i,1}^{-} + \mu_i - \beta\delta_{3,i} - \epsilon + 6\gamma f_{i,2}^{+}$$

and analog equations for $f_{i,1}^{+}$, $f_{i,N}^{-}$ and $f_{i,N}^{+}$.

$\delta_{3,i}$ denotes the Kronecker δ symbol, μ_i is of the order x_i/N, while $\beta = u\langle S\rangle$ is of the order $(x_i/N)^2$ for symmetry reasons. The x_i are the relative coordinates of the end-to-end vector under consideration.

Due to the symmetry of the above equations, $f_{i,s}^{\pm}$ can be expanded around the value $^1/_6$, representing the isotropic case:

$$f_{i,s}^{+} = \frac{1}{6} \pm g_{i,s} + h_{i,s}$$

$g_{i,s}$ and $h_{i,s}$ are of the order x_i/N and $(x_i/N)^2$, respectively.

Introducing the $N*N$ matrix Γ

$$\Gamma = \begin{bmatrix} 0 & \gamma & 0 & 0 \\ \gamma & 0 & \gamma & 0 \\ 0 & \gamma & 0 & \dots \\ 0 & 0 & \gamma & \dots \end{bmatrix}$$

$g_{i,s}$ and $h_{i,s}$ are determed by

$$\sum_{t=1}^{N} (1 - \Gamma)_{s,t} g_{i,t} = \frac{\mu_i}{6}$$

$$\sum_{t=1}^{N} (1 + \Gamma)_{s,t} h_{i,t} = 3g_{i,s}^2 - \sum_{j=1}^{3} g_{j,s}^2 + \frac{\beta}{6}\delta_{3,i} - \frac{\beta}{18}$$

Both equations can be easily solved by inverting the matrices $1 - \Gamma$ and $1 + \Gamma$ numerically. When the constraint

$$\sum_{s=1}^{N} (f_{i,s}^{+} - f_{i,s}^{-}) = 2\sum_{s=1}^{N} g_{i,s} = x_i$$

is applied, the result can be expressed in terms of x_i/N and β. Except for the end segments of a network chain one obtains for the order parameter $S = 3h_3$

$$S = \frac{1}{1 + 2\gamma}\left((1 + p(\gamma))\frac{3}{4N^2}(2x_3^2 - x_2^2 - x_1^2) + \frac{\beta}{3}\right)$$

$p(\gamma)$ is an analytically not expressable function which decreases for decreasing γ and for increasing N. For $N = 30$ and γ taken from a relevant interval $0.2 < \gamma < 0.3$, $p(\gamma)$ varies between 0.04 and 0.07.

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