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Partition Function and Force Extension Relation for a Generalized Freely Jointed Chain

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ABSTRACT: We introduce a generalized freely jointed chain and calculate analytically its partition function and force extension relation. The generalization allows for arbitrary single segment partition functions and arbitrary dimensions. New quantitative and qualitative features of the chain are obtained for segments with internal structure. As an example we analyze the Mooney–Rivlin plot for the force elongation relation of polymer networks and find excellent agreement with experimental data.

1. Introduction

Polymeric materials, especially elastomers, play an important role for many technological applications. These elastomers consist of a network of long polymer chains, which influence the macroscopic properties. One of the open questions in the description of polymer networks is the underlying mechanism leading to the observed stress–strain behavior.[1,2] In order to understand the network as a whole, it is necessary to know the behavior of its constituents, i.e. the polymer chains, and their interplay.

In a classic paper Kuhn[3] showed that the partition function for a given end-to-end distance of a chain molecule consisting of N grid segments of length l can be approximated by a Gaussian function

$$Z(\vec{R}) = \text{const}\exp\left\{-\frac{3}{2Nl^2}\vec{R}^2\right\} \tag{1}$$

This expression holds for $N \gg 1$ and end-to-end distances $\vec{R}$ small as compared to the maximum chain length Nl. However, especially for stress–strain experiments with elongations up to a factor of 7, one is interested in the partition function of a chain molecule with the extension comparable to the chain length.

This requirement is satisfied in a paper by Kuhn and Grün[4,5] who calculated the "inverse Langevin distribution" for a given end-to-end distance of the freely jointed chain with rigid rod segments:

$$Z(\vec{R}) = B\exp\{-\int_0^R \beta(R)\,\mathrm{d}R\} \tag{2a}$$

$$L(l\beta) = \coth(l\beta) - \frac{1}{l\beta} = \frac{R}{Nl} \tag{2b}$$

B is a constant, and β is defined in the second equation, which is the Langevin function. In eq 2 the finite extensibility of the chain was taken into account by the method of Lagrangian multipliers in the variational derivation of the partition function. This approximation is valid for all R in the limit $N \rightarrow \infty$. Flory[6] improved the prefactor in eq 2, but the general form remained unchanged.

An exact expression for the partition function of a chain molecule consisting of rigid rod segments, valid for arbitrary N and $\vec{R}$, was given by Treloar.[7] However, because of its more compact form the inverse Langevin distribution of Kuhn and Grün is widely used. Although the Kuhn–Grün and the Treloar results are equivalent for $N \rightarrow \infty$ with respect to the force extension relation, it should be noted that the Treloar model describes a chain with a fixed end-to-end distance (three constraints), whereas in the Kuhn–Grün result only the component of the end-to-end distance parallel to the extension is fixed (one constraint).

At this point it is interesting to note that the improvement of eq 2 by Flory[6] would give the correct result if the starting expression by Kuhn and Grün for the projection on the extension axis had been exact. However, since Kuhn and Grün's formula was only an approximation, it is not clear how well Flory's improvement really works.

Although Flory speaks of probabilities, i.e. inverse Langevin distribution, what he indeed calculated was the partition function. That there is in general an important difference between probability distributions and partition functions was shown by Winkler.[8]

In the following we show that the inverse Langevin distribution, i.e. the partition function, can be calculated in a straightforward manner with controlled approximations.[9] Therefore we can give the form of the prefactor in eq 2 within a systematic $1/N$ expansion. In addition our calculation is more general because it allows us to treat the problem of a freely jointed chain without the restriction to rigid rod segments. For that reason one should distinguish various freely jointed chains which differ in their single segment distributions.

The paper is organized as follows: In section 2 we derive the general formula for the partition function of a freely jointed d-dimensional chain consisting of arbitrary segments. Section 3 uses these results to calculate the inverse Langevin partition function in a rigorous manner for a rigid rod segment. In section 4 we determine the partition function of a chain consisting of segments with internal degrees of freedom. A connection of this freely jointed segment to real chains is given in section 5. Section 6 shows that the single segment partition function may influence fundamentally the network properties. Section 7 summarizes our findings and gives an outlook on further applications of our treatment.

2. General Formulation of the Problem and Results

The polymer molecule is described as a chain of $M + 1$ mass points with coordinates $\vec{R}_i$, $i = 0, 1, ..., M$ and momenta $\vec{p}_i$. The mass points represent the backbone of

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the molecule. Then the Hamiltonian has the following form

$$H(\{\vec{p}_i, \vec{R}_i\}) = \sum_{i=0}^{M} \frac{\vec{p}_i^{\,2}}{2m} + V(\{\vec{R}_i\}) \tag{3}$$

In the potential $V(\{\vec{R}_i\})$ all interactions are included as, for example, the covalent bonds between consecutive mass points, the angle restrictions due to nearest neighbor interactions, the excluded volume interaction, and external fields. The canonical partition function of this polymer molecule with a fixed end-to-end distance is given by

$$Z(\vec{R},T) = \int \prod_{i=0}^{M} \mathrm{d}^d p_i \, \mathrm{d}^d R_i \times \\ \exp\left\{-\frac{H(\{\vec{p}_i, \vec{R}_i\})}{k_\mathrm{B}T}\right\} \delta(\vec{R}_0)\delta(\vec{R} - (\vec{R}_M - \vec{R}_0))\delta(\vec{p}_0)\delta(\vec{p}_M) \tag{4}$$

The first δ function fixes the first mass point at the origin of the coordinate system, whereas the second one determines the end-to-end distance of the molecule. The next ones fix the momenta of the end points. k_B is the Boltzmann constant, and T the temperature. To simplify this equation, we introduce the difference vectors

$$\vec{\tilde{b}}_i = \vec{R}_i - \vec{R}_{i-1}, \quad i = 1, 2, 3, ..., M, \quad \vec{\tilde{b}}_0 = \vec{R}_0 \tag{5}$$

and get (after integration over $\vec{R}_0$, $\vec{p}_0$)

$$Z(\vec{R},T) = \int \prod_{i=1}^{M} \mathrm{d}^d p_i \, \mathrm{d}^d \tilde{b}_i \times \\ \exp\left\{-\frac{H(\{\vec{p}_i, \vec{\tilde{b}}_i\})}{k_\mathrm{B}T}\right\} \delta(\vec{R} - \sum_{i=1}^{M} \vec{\tilde{b}}_i)\delta(\vec{p}_M) \tag{6}$$

In the following we refer to $\vec{\tilde{b}}_\mathrm{i}$ as single bond.

Assumptions leading to a freely jointed chain are introduced now as follows: we divide the chain into N *independent* and identical segments; a segment thus contains M/N single bonds. Because of this independency assumption, we have no interaction potential between the segments (i.e. no excluded volume interaction): this may be expressed by the following Hamiltonian

$$H(\{\vec{p}_i, \vec{\tilde{b}}_i\}) = \sum_{i=0}^{M} \frac{\vec{p}_i^{\,2}}{2m} + \sum_{j=1}^{N} V^j(\{\vec{\tilde{b}}_\mathrm{i}\}_j) \tag{7}$$

The upper index j in the potential identifies a specific freely jointed segment and the lower index j reminds us that only the single bonds $\vec{\tilde{b}}_\mathrm{i}$ of the jth segment are included. After the segments are introduced, the $\vec{p}_i$ are still independent, because we use a flexible model.[10] Therefore the $\vec{p}_i$ integrations can be carried out immediately. Since all segments are identical by construction we introduce the "segment partition function"

$$h(\vec{b},T) = \int \prod_{i=1}^{M/N} \mathrm{d}^d \tilde{b}_i \exp\left\{-\frac{V^1(\{\vec{\tilde{b}}_i\}_1)}{k_\mathrm{B}T}\right\} \delta(\vec{b} - \prod_{i=1}^{M/N} \vec{\tilde{b}}_i) \tag{8}$$

and arrive at the approximate canonical partition function

$$Z(\vec{R},T) = \\ (2\pi m k_\mathrm{B}T)^{d(M-1)/2} \int \prod_{j=1}^{N} \mathrm{d}^d b_j \, h(\vec{b}_j, T)\delta(\vec{R} - \sum_{j=1}^{N} \vec{b}_j) \tag{9}$$

This is our generalized expression for the partition function of a freely jointed chain of N identical segments with a fixed end-to-end distance $\vec{R}$. The δ function fixes the end-to-end distance; $h(\vec{b}_j, T)$ is the partition function of one segment.

Introducing the Fourier representation of the δ function in eq 9 yields

$$Z(\vec{R},T) = (2\pi m k_\mathrm{B}T)^{d(M-1)/2} \frac{1}{(2\pi)^d} \int \mathrm{d}^d k \exp\{g(\vec{k})\} \tag{10}$$

with

$$g(\vec{k}) = i\vec{k}\vec{R} + N \ln[\int \mathrm{d}^d b \, h(\vec{b},T)\mathrm{e}^{-i\vec{k}\vec{b}}] \tag{11}$$

Expansion of the exponent about its extremum gives

$$g(\vec{k}) = g(\vec{k}_m) - \frac{N}{2}\sum_{ij} A_{ij}(k_i - k_{mi})(k_j - k_{mj}) + ... \tag{12}$$

with

$$A_{ij} = -\frac{\partial^2}{\partial k_i \partial k_j} \ln[\int \mathrm{d}^d b \, h(\vec{b},T)\mathrm{e}^{-i\vec{b}\vec{k}}]|_{\vec{k}=\vec{k}_m} \tag{13}$$

$\vec{k}_m$ is determined from $\nabla_{\vec{k}} g(\vec{k}_m) = \vec{0}$, which yields

$$\vec{R}/N = i\nabla_k \ln[\int \mathrm{d}^d b \, h(\vec{b},T)\mathrm{e}^{-i\vec{b}\vec{k}}]|_{\vec{k}=\vec{k}_m} \tag{14}$$

The consideration of a freely jointed chain implies $h(\vec{b},T) = \tilde{h}(b,T)$, $b = |\vec{b}|$, which follows from eq 8 and the assumed isotropy of space. Consequently, the integral in eq 14 depends only on $k = |\vec{k}|$, and thus $\vec{k}_m \parallel \vec{R}$. From eq 14 we arrive at the following equation:

$$\bar{L}(\beta) := \frac{\partial}{\partial \beta} \ln[\int \mathrm{d}^d b \, h(\vec{b},T)\mathrm{e}^{\beta\vec{b}\vec{e}_R}] = \frac{R}{N} \tag{15}$$

defining β by ($\vec{R} = R\vec{e}_R$):

$$\vec{k}_m = i\beta\vec{e}_R \tag{16}$$

Solving eq 15 with respect to β gives

$$\beta = -i\vec{k}_m\vec{e}_R = \bar{L}^{-1}(R/N) \tag{17}$$

To evaluate eq 10 we truncate the expansion of $g(\vec{k})$ after the second order (see eq 12). In this way we get

$$Z(\vec{R},T) \approx \left\{\frac{(2\pi m k_\mathrm{B}T)^{d(M-1)}}{(2\pi N)^d \det(\mathbf{A})}\right\}^{1/2} \times \\ \exp\{-\beta R + N \ln[\int \mathrm{d}^d b \, h(\vec{b},T)\mathrm{e}^{\beta\vec{b}\vec{e}_R}]\} \tag{18}$$

A is the matrix defined by eq 13 which must be positive definite because we expanded around a maximum, and det(**A**) is the corresponding determinant. The approximation in the exponent used in deriving eq 18 works very well for $N \gg 1$. As shown in Figure 1, the approximation yields excellent agreement even for $N = 5$ in the case of the segment partition function eq 22.

The elongation dependent force is obtained from the free energy

$$F = -k_\mathrm{B}T \ln Z(R,T) \tag{19}$$

and is given by

$$f(R) = -k_\mathrm{B}T\frac{\mathrm{d} \ln Z(R,T)}{\mathrm{d}R} = k_\mathrm{B}T\left(\beta + \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}R}\ln[\det(\mathbf{A})]\right) \tag{20}$$

where we have used the Gaussian approximation (eq 12) and eq 15 has been taken into account.

3. Chain of Segments without Internal Degrees of Freedom ($N = M$; Ethane-Type Segments): Inverse Langevin "Distribution"

In sections 3 and 4 we investigate the special case of an alkane $(CH_2)_M$ in different approximations.

In the case $N = M$ any correlation between single bonds is totally neglected. This means that we have no internal degrees of freedom within the segment. The potential $V^1(\vec{b})$ of the single segment thus reads

$$V^1(\vec{b}) = \frac{\kappa}{2}(|\vec{b}| - l_0)^2 \tag{21}$$

where the potential $V^1(\vec{b})$ is expanded up to second order (compare ref 10) and l_0 is the length of the covalent bond between consecutive carbon atoms. Because the carbon atoms are connected by covalent bonds κ is very large compared to k_BT. Thus we make the following assumption[8])

$$h(\vec{b},T) = e^{-(\kappa/2k_BT)(|\vec{b}|-l_0)^2} \simeq \left(\frac{2\pi k_B T}{\kappa}\right)^{1/2} \delta(|\vec{b}| - l_0) \tag{22}$$

The left side of eq 22 is just eq 8 with $N = M$. The right hand side of eq 22 is proportional to the single segment partition function of the usual freely jointed chain of rigid rods. In this case the partition function for the identical segments of length l_0 can be written as

$$h(\vec{b},T) = C(T)\,\frac{\delta(|\vec{b}| - l_0)}{4\pi l_0^{\,2}} \tag{23}$$

with

$$C(T) = 4\pi l_0^{\,2}\left(\frac{2\pi k_B T}{\kappa}\right)^{1/2} \tag{24}$$

Inserting in the general expressions, i.e. eqs 13 and 18 of section 2, yields ($d = 3$)

$$Z(\vec{R},T) = \left(\frac{(2\pi m k_B T)^{(M-1)}}{2\pi N}\right)^{3/2}\left(\frac{C(T)^{2N}}{A_{xx}A_{yy}A_{zz}}\right)^{1/2} \times \exp\left\{-\beta R + N\ln\left[\frac{\sinh(l_0\beta)}{l_0\beta}\right]\right\} \tag{25}$$

$$A_{xx} = A_{yy} = l_0^{\,2}\left[\coth(\beta l_0) - \frac{1}{\beta l_0}\right]\frac{1}{\beta l_0} \tag{26}$$

$$A_{zz} = l_0^{\,2}\left[\frac{1}{(\beta l_0)^2} - \frac{1}{\sinh^2(\beta l_0)}\right] \tag{27}$$

The calculation shows that the nondiagonal A_{ij} vanish. Furthermore we have used $\vec{e}_R = \vec{e}_z$. For the special choice eq 23 of the segment partition function eq 25 is equivalent to results obtained by Wang and Guth[11,12] and by Kleinert.[13]

For the force we obtain (see eq 20)

$$f(R) = k_B T\left[\beta + \frac{1}{2}\frac{d}{dR}\ln(A_{xx}A_{yy}A_{zz})\right] \tag{28}$$

$$\beta = \frac{1}{l_0}L_{rr}^{-1}\left(\frac{R}{Nl_0}\right) \qquad L_{rr}(x) = \coth(x) - \frac{1}{x} \tag{29}$$

L_{rr} in eq 29 is the Langevin function where the subscript rr stands for rigid rod. In the limit $N \rightarrow \infty$ it can be shown[9] that the second term in eq 28 vanishes, and $f(R)$ becomes identical to the Kuhn–Grün force extension relation. However, the partition function eq 25 differs from the Kuhn–Grün result (compare eq 2) in this limit.

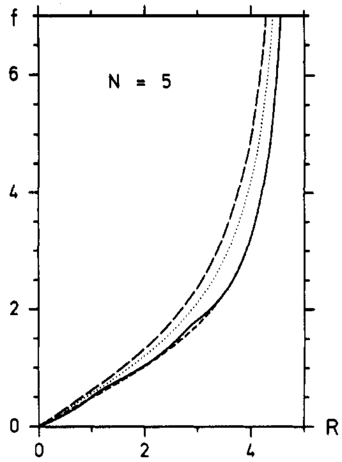

Figure 1. Force dependence on end-to-end distance R for N = 5 segments: (—) exact formula of Treloar; (- - -) our approximation, (···) improved inverse Langevin function (Flory); (— — —): inverse Langevin function (Kuhn–Grün).

In Figure 1 we show the force versus elongation for the Kuhn–Grün, Flory, Treloar, i.e. exact, results and for our result according to eq 28 (including the logarithmic term). Obviously our approximation is very good even in the case $N = 5$, a regime where the Kuhn–Grün and Flory results show significant deviations from the exact expression. We have not pictured the case $N = 10$, where no visible difference between our approximation and the exact result exists, whereas the Kuhn–Grün and Flory results still differ. (The oscillations of the solid line, i.e. the exact result, are due to the discontinuities at $R = 1$ and $R = 3$ caused by the change of the number of terms in the sum occurring in the Treloar formula. In the dynamical treatment of the problem similar discontinuities occur due to special geometric conditions.[14,15]

4. Chain of Segments with Internal Degrees of Freedom ($N = M/3$; Butane-Type Segments)

The lowest order approximation in section 3 of all single bonds being freely jointed is refined in this section in order to improve the results for the partition function. The case $N = M/2$ is not investigated, because for a fixed angle between the two single bonds of a segment we obviously get an expression analogous to eq 23. A difference occurs in the prefactor $C(T)$ and in a scaled segment length $2l_0 \cos(\theta/2)$, with θ being the angle between the single bonds.

The case $N = M/3$ is evaluated in the rotational isomeric state approximation (see ref 6). The single segment partition function is just the partition function of a butane molecule. In the rotational isomeric approximation we have only three different states: *trans* (t), *gauche*$^+$ (g^+), and *gauche*$^-$ (g^-) with degenerate g states; i.e. the g states have the same energy E relative to t and the same length. According to Flory $E \simeq 500$ cal mol^{-1}. The two lengths are obtained by simple vector algebra

$$l_t \simeq 2.5l_0 \qquad l_g \simeq 1.9l_0 \tag{30}$$

where l_0 is the bond length between two carbon atoms. Thus, the segment partition function is given in the rotational isomeric state approximation by

$$h(\vec{b},T) = \text{const}\{\delta(|\vec{b}| - l_t) + 2e^{-E/k_BT}\,\delta(|\vec{b}| - l_g)\} \tag{31}$$

Equation 31 follows from eq 8 by assuming, that the integrand over $\vec{b}_i$ is different from zero and δ-shaped only for the *trans* and the *gauche* states. The constant prefactor is not important in the following calculations and is therefore not specified.

In order to investigate this situation we discuss first the more general case of the partition function for a segment having two possible lengths l and cl ($0 \leq c \leq 1$) with probabilities $1 - w$ and w, respectively. For this generalized single segment partition function we obtain

$$h(\vec{b}) = c(T)\left[(1-w)\frac{\delta(|\vec{b}| - l)}{4\pi l^2} + w\frac{\delta(|\vec{b}| - cl)}{4\pi(cl)^2}\right] \qquad w \in [0,1] \tag{32}$$

The factor $c(T)$ drops from the equation for the force and is thus not important.

Obviously, we obtain the rigid rod segment by setting $w = 0$ or $w = 1$ or, another possibility, $c = 1$. In the present case eq 15 for β reads

$$\frac{R}{Nl} = \frac{(1-w)\cosh(l\beta) + w\cosh(cl\beta)}{(1-w)\sinh(l\beta) + \frac{w}{c}\sinh(cl\beta)} - \frac{1}{l\beta} \tag{33}$$

Expansion of the right hand side for $\beta l \rightarrow \infty$ gives

$$\frac{R}{Nl} \simeq 1 - \frac{1}{\beta l} \tag{34}$$

Solving eq 34 for β and calculating the force from eq 20 for $N \rightarrow \infty$, i.e. neglecting the second term in the bracket, we obtain

$$f = \frac{k_B T}{l}\frac{1}{1 - \frac{R}{Nl}} \tag{35}$$

This shows that the singularity for the force at the maximum extension of the chain is of the same order as in the case $w = 0$, i.e. the usual rigid rod segment with length l. Also the maximum length of the chain Nl depends only on the longer of the two lengths l and cl and not on w and c.

For the expansion of the right hand side of eq 33 for small values of β we get

$$\frac{R}{Nl} = [1 + (c^2 - 1)w]\frac{l\beta}{3} - \left[5(c^2-1)^2w^2 - 3(c^2-1)\left(c^2 - \frac{7}{3}\right)w + 2\right]\frac{l^3\beta^3}{90} + \ldots \tag{36}$$

For small extensions, i.e. $R \ll NL$, we can easily solve eq 36 for βl

$$\beta l = \frac{3}{[1 + (c^2-1)w]}\left(\frac{R}{Nl}\right) + \frac{9}{10}\,\frac{5(c^2-1)^2w^2 - 3(c^2-1)\left(c^2 - \frac{7}{3}\right)w + 2}{[1 + (c^2-1)w]^4}\left(\frac{R}{Nl}\right)^3 + \ldots \tag{37}$$

Since the third order term can exhibit a change in sign depending on the choice of w and c, the model shows a qualitative new feature, as compared to the rigid rod segment, for which the sign of the third order term is always positive (compare $w = 0$).

In Figure 2 we show the two possible regimes in w–c space, separated by the curve

$$c = \sqrt{\frac{5(1-w)}{3-5w}\left[1 - \frac{1}{5}\sqrt{\frac{6}{(1-w)w}}\right]} \qquad w \geq \frac{2}{5} \tag{38}$$

for which the third order term is zero. In regime I the third order term of eq 37 is positive, and in regime II it is negative. In Figure 3 we plot the force extension relation for typical c and w values of both regimes. For regime I this relation is qualitatively the same as the well-known inverse Langevin function, although the modulus depends on c and w. For regime II the increase of the force with extension is weakened by the negative third order term of eq 37. This curve describes qualitatively the behavior of stretched rubber samples. Another difference from the usual freely jointed chain concerns the deviation from linearity. Although $N \gg 1$ in Figure 3, this deviation depends on the chosen parameters of the segment partition function; i.e. the factors in front of $(R/Nl)^\kappa$ (cf. eq 37) are different from the usual freely jointed chain model and depend on the internal degrees of freedom of the single segment.

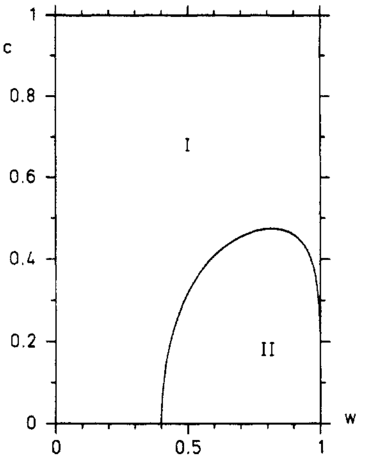

Figure 2. w–c space (compare eq 38); regime I, third order term of eq 37 is positive; regime II, third order term is negative.

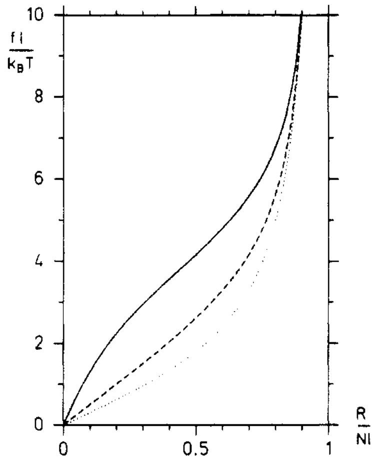

Figure 3. Force extension relation according to eq 33 ($N \gg 1$): (···) $w = 0$, $c = 0.1$, i.e. inverse Langevin function; (- - -) $w = 2/5$, $c = 0.1$, regime I; (—); $w = 4/5$, $c = 0.1$, regime II.

In section 6 we show that if the single chain force extension relation has a negative third order term, as in eq 37, one obtains in the three chain model of Kuhn[1,16] immediately the well-known $c_2 > 0$ in the Mooney equation.[1,17] This means that it is possible to describe the force extension relation of an entropy elastic model network using freely jointed chains as basic network units which consist of segments with two distinct lengths.

Now we calculate the parameters w and c for the butane segment by comparing eqs 31 and 32:

$$c = \frac{l_g}{l_t} \simeq 0.76 \qquad w = \frac{2c^2 e^{-E/k_BT}}{1 + 2c^2 e^{-E/k_BT}} \simeq 0.33 \tag{39}$$

These parameters obviously describe a chain in regime I of Figure 2, but if we compare the results of section 3, i.e. $c = 1$ and w arbitrary, with the values in eq 39, we see that by allowing for additional degrees of freedom in the segments we approach regime II in Figure 2. Therefore it has to be investigated more carefully, if the generalized freely jointed chain behaves as in regime II if we investigate segments with an increasing number of single bonds, taking into account all internal degrees of freedom of a segment. However, the investigation of the pentane segment, i.e. a segment consisting of four monomers, does not yet show any new qualitative feature (although we included the pentane effect[6]).

5. Determination of the Parameters of the Generalized Segments from Macroscopic Quantities

In the literature up to now the segments of the freely jointed chain were not interpreted microscopically, as was done in the sections before, but in a macroscopic way. One starts from a given number of monomers or bonds M with length l_0 and calculates the number N of freely jointed segments and their length l from a comparison with the maximum length $R_{\max}$ and the mean square end-to-end distance $\langle R^2 \rangle$, i.e. with macroscopic quantities:

$$R_{\max} = \alpha M l_0 = Nl \tag{40}$$

$$\langle R^2 \rangle = c_\infty M l_0^2 = N l^2 \tag{41}$$

α and c_∞ depend on the polymer under investigation. For polyethylene Flory obtains[6]

$$\alpha = 0.829 \qquad c_\infty = 6.87 \tag{42}$$

Solving eqs 40 and 41 for N and l shows that 10 bonds of the polyethylene chain correspond to one freely jointed segment of length l.

The approximation that the segment has only a single length, which is its maximum length, is very crude, because 10 monomers obviously have just one configuration with maximum length (all *trans*) but many configurations with shorter lengths. In contrast to the assumption there is a maximum for the number of configurations at a length considerably smaller than the maximum length.

This leads to the idea that the description of the single chain should be improved by releasing the model of the rigid rod segment. To this end we investigate the behavior of segments which, within our model, have two possible lengths (compare section 4).

In our model of section 4 we have to determine the four quantities N, l, w, and c. Therefore we need two additional relations. For these we use $\langle R^4 \rangle$ and the number n of single bonds per segment, which is treated as a parameter. Now we have to solve the following set of equations:

$$R_{\max} = \alpha M l_0 = Nl \tag{43}$$

$$\langle R^2 \rangle = c_\infty M l_0^2 = N l^2 (1 - w + wc^2) \tag{44}$$

$$\frac{\langle R^4 \rangle}{\langle R^2 \rangle^2} = C_4(M) = \frac{5}{3}\left(1 - \frac{1}{N}\right) + \frac{1}{N} \frac{1 - w + wc^4}{(1 - w + wc^2)^2} \tag{45}$$

$$n = \frac{M}{N} = \frac{c_\infty}{\alpha^2 (1 - w + wc^2)} \tag{46}$$

$C_4(M)$ is taken from experiments or very good numerical simulations for real chains. For the polyethylene chain $C_4(M)$ is calculated in ref 6. Special values are for example

$$C_4(100) = 1.54 \qquad C_4(200) = 1.59 \tag{47}$$

Table I. Parameter Values for *n*, l/l_0, *w*, and *c* According to Eqs 50–53 and c_1 and c_2 from Eq 61

n	l/l_0	w	c	c_1	c_2
		0.0	0.1	1.02	-6.00×10^{-3}
		0.4	0.1	1.001	-3.26×10^{-4}
		0.8	0.1	0.616	1.28×10^{-1}
100	82.9	0.994	0.307	1.04	-1.38×10^{-2}
75	62.2	0.989	0.352	1.04	-1.38×10^{-2}
50	41.5	0.978	0.427	1.04	-1.38×10^{-2}
25	20.7	0.977	0.621	1.04	-1.38×10^{-2}

In a $1/M$ expansion we have

$$C_4(M) \simeq \frac{5}{3} - \frac{c_4}{M} + \frac{\tilde{c}_4}{M^2} \tag{48}$$

and

$$c_4 \simeq 18 \qquad \tilde{c}_4 \simeq 533 \tag{49}$$

determined with the help of eq 47. Equation 48 is used up to the order $1/M$ to fit the parameters w and c.

Now we are able to solve eqs 43–46 to get the parameters N, l, w, and c of the freely jointed chain:

$$l = \alpha n l_0 \tag{50}$$

$$N = \frac{M}{n} \tag{51}$$

$$c^2 = \frac{\dfrac{c_\infty}{\alpha^2 n}}{1 - \dfrac{c_\infty}{\alpha^2 n}} \left\{ 1 + \frac{c_\infty}{\alpha^2 n} \left[\frac{c_4}{n} - \frac{5}{3} \right] \right\} \tag{52}$$

$$w = \frac{1 - \dfrac{c_\infty}{\alpha^2 n}}{1 - c^2} \tag{53}$$

In Table I the parameter values for the four cases we investigated are listed ($c_\infty/\alpha^2 \simeq 10$). In Figure 4 we plot the force extension relation, and in Figure 5 we plot the force divided by the extension against the extension.

6. Influence of the Single Chain Properties on an Elastic Network

In this section we show that if the force elongation dependence of the single chain exhibits a negative third order term (compare section 4), this term also exists for the bulk properties, i.e. we have a positive c_2 term in the Mooney–Rivlin equation[17] (see eq 60). For simplicity we carry out this calculation within the three chain model of Kuhn[1,16] in which all chains in the elastomer are replaced by three independent chains with end-to-end distances R_i ($i = x, y, z$) parallel to the coordinate axes. The constraint of constant volume V_0 during uniaxial stretching or compression

$$\lambda_x = \lambda \qquad \lambda_y = \lambda_z = \frac{1}{\sqrt{\lambda}} \qquad \lambda_i = R_i / R_0 \tag{54}$$

gives

$$V_0 = R_x R_y R_z = (\lambda R_0)\left(\frac{1}{\sqrt{\lambda}} R_0\right)\left(\frac{1}{\sqrt{\lambda}} R_0\right) = R_0^3 \tag{55}$$

where R_0 is the unstretched length.

Since in the Kuhn model the three chains are independent, the partition function of the system is the product of the partition functions of the single chains ($R_i = R_0 \lambda_i$):

$$Z_{\text{total}}(\vec{R}) = Z(R_0 \lambda_x) Z(R_0 \lambda_y) Z(R_0 \lambda_z) \tag{56}$$

Therefore we obtain for the force in case of constant volume

$$f_{\text{total}}(R_0\lambda) = -k_BT\frac{\mathrm{d}\ln Z_{\text{total}}}{\mathrm{d}R_x} = f(R_0\lambda) - \frac{1}{\lambda^{3/2}}f\left(\frac{R_0}{\sqrt{\lambda}}\right) \qquad (57)$$

where $f(R_0\lambda)$ is the force for a single chain. If we assume the force of a single chain to be given by (cf. eq 37 with $\nu = 3$ and $\mu = 5$)

$$f(R_0\lambda) = k_BT\beta = \frac{k_BT}{l}\{a\lambda + b\lambda^{\nu} + c\lambda^{\mu} + ...\} \qquad (58)$$

with $\mu > \nu > 1$, we have

$$f_{\text{total}} = \frac{k_BT}{l}a\left(\lambda - \frac{1}{\lambda^2}\right)\left\{1 + \frac{b}{a}\frac{\lambda^{\nu} - \lambda^{-(\nu+3)/2}}{\lambda - \frac{1}{\lambda^2}} + \frac{c}{a}\frac{\lambda^{\mu} - \lambda^{-(\mu+3)/2}}{\lambda - \frac{1}{\lambda^2}}\right\} \qquad (59)$$

$$\simeq \frac{k_BT}{l}\left(c_1 + \frac{c_2 + \bar{c}_2}{\lambda}\right)\left(\lambda - \frac{1}{\lambda^2}\right) \qquad (60)$$

with

$$c_1 = a + (\nu + 1)(\nu + 3)\frac{b}{8} + (\mu + 1)(\mu + 3)\frac{c}{8}$$

$$c_2 = (1 - \nu)(1 + \nu)\frac{b}{8} \qquad \bar{c}_2 = (1 - \mu)(1 + \mu)\frac{c}{8} \qquad (61)$$

Equation 60 is an expansion of eq 59 for $\lambda \simeq 1$, i.e. small elongations.

Comparison of eq 58 with eq 37 in section 4 yields ($\nu = 3$ and $\bar{c}_2 = 0$)

$$a = \frac{3}{[1 + (c^2 - 1)w]}\left(\frac{R_0}{Nl}\right) \qquad (62)$$

$$b = \frac{9}{10}\frac{5(c^2 - 1)^2w^2 - 3(c^2 - 1)\left(c^2 - \frac{7}{3}\right)w + 2}{[1 + (c^2 - 1)w]^4}\left(\frac{R_0}{Nl}\right)^3 \qquad (63)$$

The values for c_1 and c_2 calculated with these formulas for $R_0/Nl = 0.1$ are listed in Table I. Although $c_2 < 0$ for all n, it is important to realize, that this is due to our approximation to third order in eq 37. From Figure 5 it follows obviously that higher order terms give a negative contribution to the force extension relation so that one obtains a Mooney–Rivlin constant $c_2 > 0$ if we do not neglect higher order terms. Usually, the Mooney–Rivlin type of behavior is modeled by the tube model of Edwards et al.[18,19] and by the constrained junction model of Flory.[20] These models describe the intermolecular interactions like entanglements and constraints. According to these models the c_2 effect disappears upon removal of intermolecular contributions by swelling of the network, a fact which is also observed experimentally. In our model no intermolecular interactions are introduced. Nevertheless the sign of $c_2 + \bar{c}_2$ changes from positive to negative for swelling in accordance to experiments. This is due to the proportionalities

$$a \propto R_0 \qquad b \propto R_0^{\nu} \qquad c \propto R_0^{\mu}$$

and the fact that equilibrium length R_0 is increased by the swelling process (note: $a, c > 0$ and $b < 0$). Hence, swelling experiments are not sufficient to distinguish between various effects leading to a change in the stress–strain behavior. In our model the introduction of internal degrees of freedom also explains the c_2 effect.

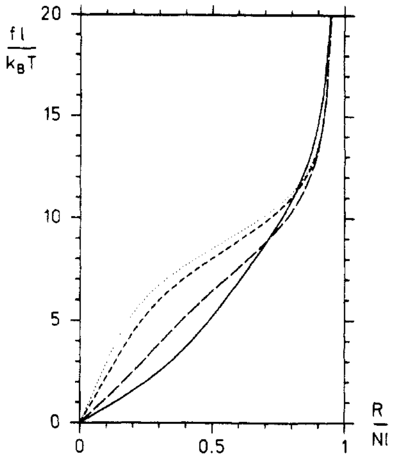

Figure 4. Force extension relation according to eq 33 with parameters from Table I: (···) $n = 100$; (- - -) $n = 75$; (— — —) $n = 50$; (—) $n = 25$.

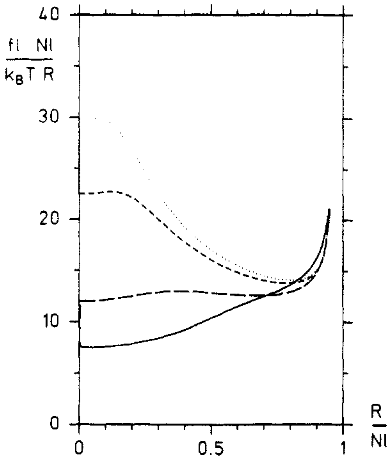

Figure 5. Force/extension versus extension according to eq 33 with parameters from Table I: (···) $n = 100$; (- - -) $n = 75$; (— — —) $n = 50$; (—) $n = 25$.

In Figures 6 and 7 we show a fit to experimental force extension data plotted as force against elongation and in Mooney–Rivlin version.[21,22] The corresponding parameter values are $w = 0.892$ and $c = 8.08 \times 10^{-3}$. The agreement with data is as good as for other theories.[23] In our model the parameters w and c describe the special *chemical structure* of the material. Hence, it is not surprising that these parameters describing PMMA are different from those in Table I obtained for polyethylene.

7. Summary

In the preceding sections we introduced a generalized freely jointed chain description of polymer molecules. We showed that for a single chain quantitative and qualitative new features are obtained by release of the constraint to rigid rod segments.

In section 3 we gave a straightforward derivation of the inverse Langevin partition function (eq 18) *including* the first term of a large N expansion. Although the force calculated with our result is exactly the same as the one of Kuhn and Grün in the limit $N \to \infty$, one should be aware of the fact that the model of Kuhn and Grün describes a different physical system; in their derivation only the component parallel to the end-to-end distance is fixed, whereas in our model all components are fixed. In order to calculate the partition function for the Kuhn and Grün model we have to replace the δ function in eq 6 by

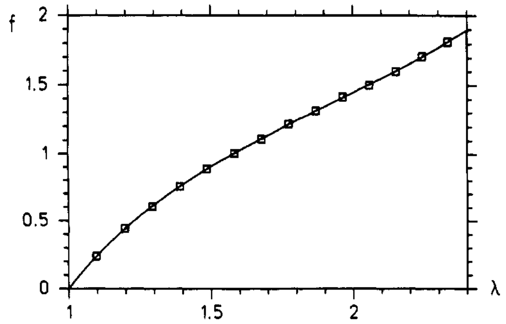

Figure 6. (—) Force extension relation for the three chain model of Kuhn for chains having segments with two distinct lengths with parameters $w = 0.892$, $c = 8.08 \times 10^{-3}$. (□) Experimental values for PMMA.[21]

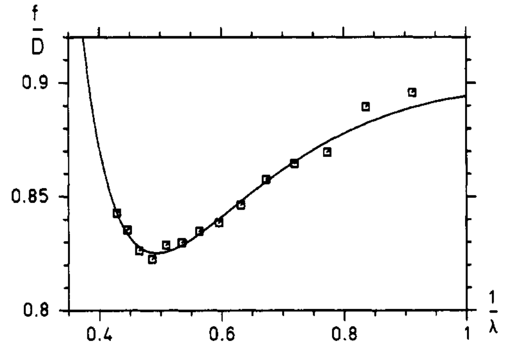

Figure 7. (—) Mooney–Rivlin plot for the three chain model of Kuhn ($D = \lambda - 1/\lambda^2$) for chains having segments with two distinct lengths with parameters $w = 0.892$, $c = 8.08 \times 10^{-3}$. (□) Experimental values for PMMA.[21]

a one-dimensional δ function with argument $(R_z - \sum_i \vec{b}_i \hat{e}_z)$. The result corresponds to eq 25 with $A_{xx} = A_{yy} = 1$.

In the literature up to now the notion of the freely jointed chain is used for a freely jointed chain with rigid rod segments. Due to our new derivation in section 2 we now have to distinguish various freely jointed chains with segments having different internal structure. If we take for example a Gaussian distribution for the single segment length, we obviously get a Gaussian partition function for the total chain. In this case the formulas of section 2 are exact.

The generalized single segment partition function we introduced in eq 32 enables us to take into account short range correlations of the monomers in the segment. This allows us to include the microscopic structure of a molecular chain to some extent in the description of the macroscopic behavior of a rubber sample, which was not possible in the past. As an example we treated the butane segment in section 4, allowing for two possible segment lengths, and showed that the force extension relation is different from, although qualitatively similar to, the case of the usual freely jointed chain consisting of segments with a single length. An important result is that the range of validity of the Gaussian approximation depends on parameters of the chosen segment partition function.

In order to demonstrate the influence of our new model on the uniaxial stretching experiment, we used in section 5 the general expression for a segment with two distinct lengths (introduced in section 4) to improve the freely jointed chain model by the condition that the mean quartic value $\langle R^4 \rangle$ should be the same as for a real (here: polyethylene) polymer molecule. We saw that the force extension relation eq 37 may have a negative third order term in the expansion with respect to extension.

In section 6 we use the three chain model of Kuhn for networks[16] to explicitly connect our single chain to uniaxial extension experiments of elastomers. We obtain excellent agreement with experimental data for the segment length cl being very short and occurring with higher probability w than the longer one. These parameters can be interpreted in the blob model[24] in the following way: in the unstretched state the polymer chain behaves as a freely jointed chain of blobs; these blobs are destroyed during stretching, and the chain ends up as a freely jointed chain of rigid rods. In addition to the uniaxial stretching experiment, our model qualitatively explains the swelling behavior (see section 6). Therefore one cannot decide between the various models on the basis of these experiments.

Within the above description it is also possible to include other constraints as, for example, fixed energy or external fields.[9] Furthermore our treatment allows for a generalization to arbitrary dimensions.[9,25]

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References and Notes

(1) Treloar, L. R. G. *The Physics of Rubber Elasticity*; Clarendon Press: Oxford, U.K., 1975.
(2) Sperling, L. H. *Introduction to Physical Polymer Science*; John Wiley & Sons: New York, 1986.
(3) Kuhn, W. *Kolloid-Z.* **1934**, *68*, 2.
(4) Kuhn, W.; Grün, F. *Kolloid-Z.* **1942**, *101*, 248.
(5) Volkenstein, M. V. *Configurational Statistics of Polymeric Chains*; John Wiley & Sons: New York, 1963.
(6) Flory, P. J. *Statistical Mechanics of Polymer Chains*; John Wiley & Sons: New York, 1989.
(7) Treloar, L. R. G. *Trans. Faraday Soc.* **1946**, *42*, 77.
(8) Winkler, R. G. Ph.D. Dissertation, Universität Ulm, Germany 1989.
(9) Glatting, G. Ph.D. Dissertation, Universität Ulm, Germany 1992.
(10) Weiner, J. H. *Statistical Mechanics of Elasticity*; John Wiley & Sons: New York, 1983.
(11) Wang, M. C.; Guth, E. *J. Chem. Phys.* **1952**, *20*, 1144.
(12) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper & Row Publishers: New York, 1971.
(13) Kleinert, H. *Path Integrals in Quantum Mechanics, Statistics and Polymer Physics*; World Scientific: London, 1990.
(14) Winkler, R. G.; Reineker, P.; Schreiber, M. *Europhys. Lett.* **1989**, *8*, 493.
(15) Reineker, P.; Winkler, R. G.; Siegert, G. R.; Glatting, G. In *Large-Scale Molecular Systems*; Gans, W., Blumen, A., Amann, A., Eds.; Plenum Press: New York, 1991.
(16) Kuhn, W. *Kolloid-Z.* **1936**, *76*, 258.
(17) Mooney, M. *J. Appl. Phys.* **1940**, *11*, 582.
(18) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1987**, *74*, 1802.
(19) Graessley, W. W. *Adv. Polym. Sci.* **1982**, *47*, 67.
(20) Flory, P. J.; Erman, B. *Macromolecules* **1982**, *15*, 800.
(21) Kraus, V.; Kilian, H.-G.; v. Soden, W. *Progress in Colloid & Polymer Science*; Springer: New York, 1992; Vol. 90.
(22) Kraus, V.; Kilian, H.-G. Private communication.
(23) Higgs, P. G.; Gaylord, R. J. *Polymer* **1990**, *31*, 70.
(24) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(25) Glatting, G.; Winkler, R. G.; Reineker, P. Submitted for publication.