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ORIGINAL CONTRIBUTION

G. Glatting
R.G. Winkler
P. Reineker

Freely jointed chain with variable segment number and length

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Prof. Dr. P. Reineker (✉) · R.G. Winkler
G. Glatting
Abteilung Theoretische Physik
Universität Ulm
Albert-Einstein-Allee 11
89081 Ulm, Germany

Abstract The configurational properties of a molecular chain are investigated. The chain consists of rigid rod segments, which are consecutively correlated. This correlation is described by a two-state model. In the first state, neighboring segments are freely hinged together, whereas in the second state they are parallel. The partition function and the force-extension relation are calculated. They show significant differences as compared to the usual results for a freely jointed chain. Thus the experimentally observed force-extension relation of polymeric networks built up of such chains might be affected.

Key words Freely jointed chain – stiff chain – two-state model – partition function – force-extension relation

Introduction

Polymer molecules are usually modeled by the wellknown freely jointed chain [1–5]. This model assumes that a polymer chain behaves equivalently to a chain of N rigid rod segments of length l which are freely hinged together. Recently, we generalized this model by dropping the rigid segment assumption [6–8], however, the restriction to a fixed number of segments (N) was maintained. But there is no physical reason why flexibility should occur only at distinct points of the chain and why there should exist just N flexible points [9]. In contrast, it is very reasonable to assume that N depends on temperature T, because for $T \to 0$ the single polymer molecule is rigid and for increasing temperature T the flexibility of the chain increases. Such effects are important for the conformational behavior of stiff molecules with flexible links [10, 11] and biomolecules undergoing rod-to-coil transitions [12, 13].

In this paper we extend the usual statistical treatment by representing the orientational states of consecutive segments via a two-state model. In section 2 we introduce the model and in section 3 we determine the mean square end-to-end distance. The approximate partition function and force-extension relation of a single chain are calculated within this model in section 4. Section 5 summarizes our findings.

Model

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

$$H(\{\vec{p}_i, \vec{R}_i\}) = \sum_{i=0}^{M} \frac{\vec{p}_i^{\,2}}{2m} + \sum_{i=1}^{M} V_1(\vec{R}_i - \vec{R}_{i-1}) + \sum_{i=2}^{M} V_2(\vec{R}_i - \vec{R}_{i-1}, \vec{R}_{i-1} - \vec{R}_{i-2}) \,. \quad (1)$$

In this Hamiltonian we take into account nearest neighbor interactions by V_1 and restrictions of the relative orientations of consecutive segments by V_2. The general expression for the canonical partition function of this polymer molecule is given by

$$Z(T) = \int \prod_{i=0}^{M} d^d p_i d^d R_i \exp\left\{ -\frac{H(\{\vec{p}_i, \vec{R}_i\})}{k_B T} \right\} \delta(\vec{R}_0)\,\delta(\vec{p}_0))\,. \tag{2}$$

The δ-functions fix the first mass point at the origin of the coordinate system. k_B is the Boltzmann constant and T the temperature. To simplfy this equation, we introduce difference vectors

$$\vec{b}_i = \vec{R}_i - \vec{R}_{i-1}, \quad i = 1, 2, 3, \ldots, M \tag{3}$$

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

$$Z(T) = \int \prod_{i=1}^{M} d^d p_i d^d b_i \exp\left\{ -\frac{H(\{\vec{p}_i, \vec{b}_i\})}{k_B T} \right\}. \tag{4}$$

In the following, we denote $\vec{b}_i$ as bond length. In terms of the bond coordinates $\vec{b}_i$ the Hamiltonian reads

$$H(\{\vec{p}_i, \vec{b}_i\}) = \sum_{i=0}^{M} \frac{\vec{p}_i^{\,2}}{2m} + \sum_{i=1}^{M} V_1(\vec{b}_i) + \sum_{i=2}^{M} V_2(\vec{b}_i, \vec{b}_{i-1})\,. \tag{5}$$

For dimension $d = 3$ the potential V_1 of the single bond is chosen as

$$V_1(\vec{b}) = \frac{\kappa}{2}(|\vec{b}_i| - l_0)^2\,, \tag{6}$$

i.e., the potential $V_1(\vec{b})$ has been expanded to second order (compare [14] page 239); l_0 is the length of the covalent bond between consecutive carbon atoms. Because the carbon atoms are connected by covalent bonds, i.e., $\kappa l_0^2 \gg k_B T$, we approximate

$$e^{-\frac{\kappa}{2k_B T}(|\vec{b}| - l_0)^2} \sim \left(\frac{2\pi k_B T}{\kappa}\right)^{\frac{1}{2}} \delta(|\vec{b}|) - l_0)\,. \tag{7}$$

This expression is proportional to the single segment partition function of the three dimensional freely jointed chain of rigid rods. Inserting in Eq. (4) and integrating over all momenta yields

$$Z(T) = Z_0(T) \int d^3 b_1 \frac{\delta(|\vec{b}_1| - l_0)}{4\pi l_0^2} \sum_{i=2}^{M} \left\{ d^3 b_i \frac{\delta(|\vec{b}_i| - l_0)}{4\pi l_0^2} \times \left[1 + (e^{-\frac{V_2(\vec{b}_i, \vec{b}_{i-1})}{2k_B T}} - 1) \right] \right\} \tag{8}$$

with

$$Z_0(T) = (2\pi m k_B T)^{\frac{3M}{2}} \left(\frac{2\pi k_B T}{\kappa}\right)^{\frac{M}{2}} (4\pi l_0^2)^M\,. \tag{9}$$

In Eq. (8), we introduced the term $[\exp\{-\frac{V_2}{k_B T}\} - 1]$, which takes into account the interaction of consecutive segments. This term is chosen in analogy to the calculation of real gases with interaction between pairs of atoms. In order to have a tractable analytic form we assume

$$\exp\left\{ -\frac{V_2(\vec{b}_i, \vec{b}_{i-1})}{k_B T} \right\} - 1 \simeq \frac{4\pi c}{\sin\theta_i} \delta(\theta_i - \theta_{i-1}) \times \delta(\phi_i - \phi_{i-1}), \quad i = 2, \ldots, M\,. \tag{10}$$

θ_i and ϕ_i are the angular coordinates of $\vec{b}_i$. c is a measure of the interaction strength and therefore depends on temperature and approaches zero for $T \to \infty$. Equation (10) forces two consecutive bonds in the same direction in such a way that they behave as a single bond with double length. Thus, expression (10) may be interpreted as the weight (probability) of a second state of the connection between two bonds: the first state is the freely jointed one.

Within this approximation the evaluation of Eq. (8) yields

$$Z(T) = Z_0(T)\,[1 + c]^{M-1}\,. \tag{11}$$

Instead of Eq. (10) we could have used $V_2(\vec{b}_i, \vec{b}_{i-1}) = \frac{\mu}{2}(\vec{b}_i - \vec{b}_{i-1})^2$, where the parameter μ describes the strength of the angular potential [4, 15, 16]. The parameter μ is related to the average angle $\theta = arcos(\vec{b}_i \vec{b}_{i-1})$ between successive bonds [16]. In the continuum limit the partition function would be equivalent to the wormlike chain model discussed in [16–20].

In this paper we apply, in a sense, a cruder approach, because we are less interested in describing chains of variable stiffness (there are other models which are more appropriate for that purpose [16, 19, 20]); instead, our analysis is directed towards the understanding of the statistical properties of chains, where flexibility occurs at arbitrary points along the chain. Results of related calculations can be found in [21–24].

In the next sections we calculate the mean square end-to-end distance and the force-extension relation for the above model.

Mean square ends-to-end distance

The mean square end-to-end distance is given by

$$\langle \vec{R}^2 \rangle = \frac{Z_0(T)}{Z(T)} \int d^3 b_1 \frac{\delta(|\vec{b}_1| - l_0)}{4\pi l_0^2} \prod_{i=2}^{M} \left\{ d^3 b_i \frac{\delta(|\vec{b}_i| - l_0)}{4\pi l_0^2} \times \left[1 + \frac{4\pi c}{\sin\theta_i} \delta(\theta_i - \theta_{i-1}) \delta(\phi_i - \phi_{i-1}) \right] \right\} \times \left(\sum_{j=1}^{M} \vec{b}_j \right)^2, \tag{12}$$

since

$$\vec{R} = \sum_{j=1}^{M} \vec{b}_j\,. \tag{13}$$

Expression (12) is simplified in a first step by integrating over the angular dependent δ-functions and combining all parallel consecutive bonds to a segment of length $k_i l_0$. Then, we obtain

$$\langle \vec{R}^2 \rangle = \frac{1}{[1+c]^{M-1}} \sum_{N=1}^{M} c^{M-N} \sum_{\{k_i\}} \int \left(\prod_{i=1}^{N} d^3 b_i \frac{\delta(|\vec{b}_i| - l_0)}{4\pi l_0^2} \right) \times \sum_{i=1}^{N} k_i^2 \vec{b}_i^2 \,. \tag{14}$$

This expression is the mean square end-to-end distance of a freely jointed chain of N segments of different lengths $k_i l_0$. The sum with subscript $\{k_i\}$ stands for the N sums over all possible lengths of segments, with the constraint that the total length $M l_0$ is fixed, i.e.

$$\sum_{i=1}^{N} k_i = M \,. \tag{15}$$

From (14) we obtain by straightforward calculation (note: segments are freely jointed, but of different lengths)

$$\langle \vec{R}^2 \rangle = \frac{1}{[1+c]^{M-1}} \sum_{N=1}^{M} c^{M-N} \sum_{\{k_i\}} \left\{ \sum_{i=1}^{N} k_i^2 l_0^2 \right\} . \tag{16}$$

Exchanging the summations over i and $\{k_i\}$ yields ($\sum_{\{k_i\}} f(\{k_i\})$) is independent of the index i, therefore, we replace k_i by k_1)

$$\begin{aligned} \langle \vec{R}^2 \rangle &= \frac{l_0^2}{[1+c]^{M-1}} \sum_{N=1}^{M} c^{M-N} N \sum_{\{k_i\}} k_1^2 && (17) \\ &= \frac{M l_0^2}{[1+c]^{M-1}} \sum_{N=1}^{M} c^{M-N} \binom{M-1}{N-1} \times \frac{2M-(N-1)}{N+1} \,, && (18) \end{aligned}$$

where we used Eq. (48) from the appendix. Equation (18) is approximately evaluated by assuming that the dominant contribution comes from the maximum term. Then we arrive at

$$\langle \vec{R}^2 \rangle \simeq M l_0^2 [1 + 2c] \,, \tag{19}$$

which is correct only in the high temperature limit (many segments exist). From Eq. (10) we see that $c \to 0$ in the limit $T \to \infty$. So we obtain the usual freely jointed chain result in this limit. In the low temperature $c \gg 1$; then we obtain from the first terms of the sum in (18)

$$\langle \vec{R}^2 \rangle \simeq (M l_0)^2 \left[1 - \frac{M}{3c} + \frac{M^3}{12c^2} \right] , \tag{20}$$

showing that the polymer chain is nearly stretched in this case, because $M l_0 = L$ is just the maximum length of the chain.

As an interpolation formula between Eqs. (19) and (20), we get by use of a Padé-approximation

$$\langle \vec{R}^2 \rangle \simeq M l_0^2 \frac{1 + 2c + \frac{12}{M} c^2}{1 + \frac{6}{M} c + \frac{12}{M^2} c^2} \,. \tag{21}$$

This formula describes the transition of the polymer molecule from the rigid rod state, i.e., $c = \infty$, to the freely jointed state given by $c = 0$.

Special case: N fixed

A result contained in our calculation is the mean square end-to-end distance for a freely jointed chain with fixed contour length $M l_0 = L$ and segment number N, but with variable segment lengths. In order to obtain this result we have to drop the sum over N in (18) (as well as the corresponding sum in $Z(T) = [1 + c]^{M-1}$). Thus, we find

$$\langle \vec{R}^2 \rangle_N = (M l_0)^2 \left(\frac{2}{N+1} - \frac{1}{M} \frac{N-1}{N+1} \right) . \tag{22}$$

This expression is a generalized version of an earlier result by Rieger [25, 26] who calculated the continuous case, which corresponds to $M \to \infty$ with fixed $M l_0 = L$ in our calculation. In order to compare this "fluctuating" segment lengths model with the one with fixed segment lengths, we introduce the mean segment length $l_N = \frac{M}{N} l_0$ and obtain

$$\langle \vec{R}^2 \rangle_N = N l_N^2 \frac{N}{N+1} \left\{ 2 - \frac{N-1}{M} \right\} \simeq 2 N l_N^2 \,. \tag{23}$$

Obviously, the factor 2 is due to the fact that segment lengths are not fixed.

Partition function and force-extension relation

In order to calculate the partition function for fixed end-to-end distance we have to multiply Eq. (8) by a δ-function in the following way:

$$\begin{aligned} Z(\vec{R}, T) = Z_0(T) \int d^3 b_1 \frac{\delta(|\vec{b}_1| - l_0)}{4\pi l_0^2} \prod_{i=2}^{M} \Bigg\{ d^3 b_i \frac{\delta(|\vec{b}_i| - l_0)}{4\pi l_0^2} \\ \times \left[1 + \frac{4\pi c}{\sin\theta_i} \delta(\theta_i - \theta_{i-1}) \delta(\phi_i - \phi_{i-1}) \right] \Bigg\} \\ \times \delta\left(\vec{R} - \sum_{j=1}^{M} \vec{b}_j \right) . \end{aligned} \tag{24}$$

Replacing $\delta(\vec{R} - \sum_{j=1}^{M} \vec{b}_j)$ by its Fourier transform and integrating thereafter over all bond coordinates yields

$$Z(\vec{R}, T) = Z_0(T) \sum_{N=1}^{M} c^{M-N} \frac{1}{(2\pi)^3} \int d^3 k e^{i\vec{k}\vec{R}} \times \sum_{\{k_i\}} \left\{ \prod_{i=1}^{N} \frac{\sin(k l_0 k_i)}{k l_0 k_i} \right\} . \tag{25}$$

The sum over the k_i cannot be determined exactly, therefore we approximate it by $k_i = \langle k_i \rangle = \frac{M}{N}$, i.e., we substitute the real segment length k_i for given N by its mean value. The mean segment length is calculated in the appendix (see Eq. (42)). Now, we can use the general partition function for a chain of equal segment lengths given in [7]. We obtain ($N \gg 1$)

$$Z(\vec{R},T) \propto \sum_{N=1}^{M} \binom{M-1}{N-1} N^{\frac{3}{2}} c^{M-N} \exp\left\{-N\left[\beta l \frac{R}{L} + \ln\left(\frac{\sinh(\beta l)}{\beta l}\right)\right]\right\} \tag{26}$$

with $\beta l = L^{-1}(\frac{R}{L})$ and $l = \frac{M}{N} l_0$. $L(x)$ is the Langevin function.

One could approximate this sum by its maximum term. In this case the factor $N^{\frac{3}{2}}$ would be neglected. Another possibility is to neglect the power $N^{\frac{3}{2}}$ in (26) directly, because the contribution of the factorial and exponential terms dominate. Then we get

$$Z(\vec{R},T) \propto \exp\left\{-\beta l \frac{R}{L} + \ln\left(\frac{\sinh(\beta l)}{\beta l}\right)\right\} \left\{c + \exp\left[-\beta l \frac{R}{\mathrm{L}} + \ln\left(\frac{\sinh(\beta l)}{\beta l}\right)\right]\right\}^{M-1} \tag{27}$$

for the partition function with fixed end-to-end distance R.

The force is calculated from the free energy according to

$$f = \frac{dF}{dR} = -k_B T \frac{d \ln[Z(R,T)]}{dR}, \tag{28}$$

resulting in

$$\frac{f l_0}{k_B T} = L^{-1}\left(\frac{R}{L}\right)\left\{\frac{1}{1 + c\exp\{\beta l \frac{R}{L} - \ln(\frac{\sinh(\beta l)}{\beta l})\}} + \frac{1}{M}\left[\frac{c}{c + \exp\{-\beta l \frac{R}{L} - \ln(\frac{\sinh(\beta l)}{\beta l})\}}\right]\right\} \tag{29}$$

If we compare this force-extension relation with that of the usual freely jointed chain, we see that the extension and the temperature dependence have changed. First, there is a reduction in the force with extension proportional to c and to the extension itself. Secondly, the temperature dependence is altered in such a way that the force increases faster than linearly with increasing temperature T for fixed extension R. Also, this effect is stronger for greater extension. For $T \rightarrow \infty$ we recover the usual freely jointed chain because then $c \rightarrow 0$.

In Fig. 1 we plot the force-extension relation according to Eq. (29) for some values of the parameter c. The decrease of the force compared to the usual freely jointed chain is obvious.

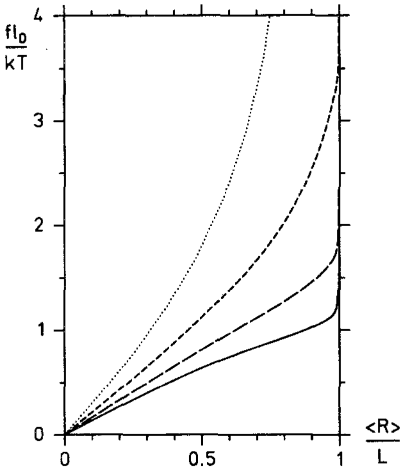

Fig. 1 Force-extension relation for a chain consisting of an arbitrary number of segments but with fixed contour length (see Eq. (29)). (···): $c = 0$, i.e., the inverse Langevin function; (- - -); $c = 4$; (– – –): $c = 8$; (——): $c = 12$

Summary and conclusions

We investigated the configurational properties of a polymer chain, taking into account correlations between successive bonds by a two-state model. Our approach leads to a partition function and mean square end-to-end distance corresponding to a freely jointed chain with segments of different lengths. The lengths and the number of these segments vary under the constraint of fixed contour length of the chain. This is the main difference between our approach and the various other treatments of wormlike chains [16–19, 27]. Another difference is the fact that the flexibility occurs at discrete points of the molecule in contrast to the continuous curvature of wormlike models. Therefore, the introduced parameter c may not be related to the curvature of the polymeric chain, but to the mean number of N of freely jointed segments. Thus, the transition from flexible to rigid rod behavior is not caused by a change in curvature, but by the reduction of the mean number of freely jointed segments of the chain.

For fixed number of segments N and contour length $M l_0 = L$ but varying lengths of the individual segments, we show that the mean square end-to-end distance is twice that of a freely jointed chain consisting of fixed identical segments.

If we compare the above results with the simple theory of freely jointed chains we obtain the following differences. Firstly, the temperature dependence of the force-extension relation is not proportional to T, but this effect is not strong as long as c is small, which is the limit for our approximations. Secondly, the force is reduced during extension, due to a decrease of the average number of segments. This feature of a single chain automatically gives the experimentally observed decrease of the modulus in the Mooney–Rivlin plot for a network, as is shown in [7]. Although there exist many models correctly describing Mooney–Rivlin behavior [6, 28–30], this clearly shows that the properties of a network are influenced by single chain features. Therefore, network models should be investigated taking into account different single chain properties.

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Appendix

In this appendix we calculate some moments of the sum over all segment lengths $\sum_{\{k_i\}}$ introduced in (14). Because of the constraint

$$M = \sum_{i=1}^{M} k_i \,, \tag{30}$$

i.e., the sum over all segment lengths is the total length of the polymer chain, the sum has the general form

$$\sum_{\{k_i\}} \cdots = \sum_{i_{N-1}=N-1}^{M-1} \; \sum_{i_{N-2}=N-2}^{i_{N-1}-1} \cdots \sum_{i_1-1}^{i_2-1} \cdots \,, \tag{31}$$

where k_l is the length of the l-th segment and i_l is the index of the mass point between segment number l and $(l+1)$. Therefore, we have

$$k_l = (i_l - i_{l-1}), \quad l = 1, 2, \ldots N \,. \tag{32}$$

The following relations for binomial coefficients are used [31]:

$$\sum_{i=k}^{n} \binom{i}{k} = \binom{n+1}{k+1} \,, \tag{33}$$

$$\sum_{k=1}^{n} k = \frac{n}{2}(n+1) \tag{34}$$

and

$$\sum_{k=1}^{n} k^2 = \frac{n}{6}(n+1)(2n+1) \,. \tag{35}$$

1. Zero$^{\text{th}}$ moment

First, we calculate the zero$^{\text{th}}$ moment of expression (31), because we need it later in Eqs. (42) and (48). Result:

$$G_N = \sum_{i_{N-1}=N-1}^{M-1} \; \sum_{i_{N-2}=N-2}^{i_{N-1}-1} \cdots \sum_{i_1-1}^{i_2-1} 1 = \binom{M-1}{N-1} \,. \tag{36}$$

Proof by complete induction.
Starting point:

$$G_2 = \sum_{i_1-1}^{i_2-1} 1 = (i_2 - 1) = \binom{i_2-1}{2-1} \,. \tag{37}$$

Induction step:

$$G_{N+1} = \sum_{i_N=N}^{i_{N+1}-1} G_N = \binom{M-1}{N} \,. \tag{38}$$

2. Mean segment length

For the first moment of segment number one, we obtain, because $k_1 = i_1 - i_0$, $i_0 = 0$,

$$G_N = \sum_{i_{N-1}=N-1}^{M-1} \; \sum_{i_{N-2}=N-2}^{i_{N-1}-1} \cdots \sum_{i_1-1}^{i_2-1} i_1 = \binom{M-1}{N-1} \frac{M}{N} \,. \tag{39}$$

Proof by complete induction.
Starting point:

$$G_2 = \sum_{i_1-1}^{i_2-1} i_1 = \frac{i_2}{2}(i_2 - 1) = \binom{i_2-1}{2-1} \frac{i_2}{2} \,. \tag{40}$$

Induction step:

$$G_{N+1} = \sum_{i_N=N}^{i_{N+1}-1} G_N = \binom{i_{N+1}}{N+1} = \binom{M-1}{N} \frac{i_{N+1}}{N+1} \,. \tag{41}$$

Therefore, we obtain for the mean segment length

$$\langle k_i \rangle = \frac{M}{N} \,. \tag{42}$$

3. Mean square segment length

The second moment of the first segment is $(k_1 = i_1 - i_0 = i_1)$

$$G_N = \sum_{i_{N-1}=N-1}^{M-1} \; \sum_{i_{N-2}=N-2}^{i_{N-1}-1} \cdots \sum_{i_1-1}^{i_2-1} (i_1)^2$$

$$= \binom{M-1}{N-1} \frac{M[2M - (N-1)]}{N(N+1)} \tag{43}$$

$$= 2! \binom{M}{N+1} + \binom{M}{N} \,. \tag{44}$$

Proof by Complete induction.

Starting point:

$$G_2 = \sum_{i_1 - 1}^{i_2 - 1} i_1^2 = \frac{i_2}{2}(i_2 - 1)$$

$$= \binom{i_2 - 1}{2 - 1} \frac{i_2[2i_2 - (2 - 1)]}{2 \cdot 3} . \qquad (45)$$

Induction step:

$$G_{N+1} = \sum_{i_N = N}^{i_{N+1} - 1} G_N = \sum_{i_N = N}^{i_{N+1} - 1} \left\{ 2! \binom{i_N}{N + 2} + \binom{i_N}{N} \right\} \qquad (46)$$

$$= 2! \binom{i_{N+1}}{N + 2} + \binom{i_{N+1}}{N + 1} . \qquad (47)$$

Thus the mean square segment length is

$$\langle k_i^2 \rangle = \frac{M}{N} \frac{2M - (N - 1)}{N + 1} . \qquad (48)$$

The limiting cases $N = 1$ and $N = M$ yield correctly

$$\langle k_i^2 \rangle_{N=1} = M^2 , \quad \langle k_i^2 \rangle_{N=M} = 1 . \qquad (49)$$

References

1. Kuhn W (1934) Kolloidzeitschr 68:2
2. Kuhn W, Grün F (1942) Kolloidzeitschr 101:248
3. Treloar LRG (1946) Trans Farady Soc 42:77
4. Volkenstein MV (1963) Configurational Statistics of Polymeric Chains, John Wiley & Sons, New York
5. Treloar LRG (1975) The Physics of Rubber Elasticity, Clarendon Press, Oxford
6. Glatting G (1992) Ph D Thesis, Universität Ulm, Germany
7. Glatting G, Winkler RG, Reineker P (1993) Macromolecules 26:6085
8. Glatting G, Winkler RG, Reineker P (1993) Makromol Theory Simul. 3:575
9. Khokhlov AR, Semenov AN (1984) Macromolecules 17:2678
10. Pfannenmüller B, Schmidt M, Ziegast G, Mazsuo K (1984) Macromolecules 17:710
11. Aharoni SM (1988) Macromolecules 21:185
12. Poland D, Scheraga HA (1970) Theory of Helix-Coil Transitions in Biopolymers. Academic Press, New York
13. Wiegel FW (1983) In: Domb C, Lebowitz JL (eds) Phase Transitions and Critical Phenomena VI. Academic Press, New York
14. Weiner JH (1983) Statistical Mechanics of Elasticity, John Wiley & Sons, New York
15. Flory PJ (1989) Statistical Mechanics of Polymeric Chains, John Wiley & Sons, New York
16. Winkler RG, Reineker P, Harnau L (1994) J Chem Phys 101: in press
17. Kratky O, Porod G (1949) Recl Trav Chim Pays-Bas 68:1106
18. Harris RA, Hearst JE (1966) J Chem Phys 44:2595
19. Saito N, Takahashi K, Yunoki Y (1967) J Phys Soc Jap 22:219
20. Yamakawa H (1971) Modern Theory of Polymer Solution, Harper & Row, New York
21. Mansfield ML (1986) Macromolecules 19:854
22. Muroga Y (1988) Macromolecules 21:2751
23. Huber K (1989) Macromolecules 22:2750
24. Garcia Molina JJG, Garcia de la Torre J (1986) J Chem Phys 84:4026
25. Rieger J (1988) Ph D Thesis, Universität Saarbrücken, Germany
26. Rieger J (1993) Polym Bull 30:617
27. Soda K (1973) J Phys Soc Jap 35:866
28. Higgs PG, Gaylord RJ (1990) Polymer 31:70
29. Glatting G, Winkler RG, Reineker P (1994) Macromol Symp 81:129
30. Glatting G, Winkler RG, Reineker P (1994) J Chem Phys 101:2532
31. Bronstein IN, Semendjajew KA (1981) Taschenbuch der Mathematik, Harry Deutsch, Frankfurt/Main