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Constrained Polymer with Unusual Statistics. Annotations on the Slip-Link Model

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ABSTRACT: The slip-link model has been used by many authors to mimic the restriction of the phase space available to one polymer due to the presence of other polymers in dense polymer samples. In this model it is assumed that the polymer, which is modeled by a random walk, must pass through one or several given points in space. The respective free energy of the system is usually computed via the Gibbs entropy. One thus averages over many degrees of freedom of the polymer chain. I reexamined the slip-link model using the Boltzmann entropy. Unusual statistics were discovered: when considering a polymer with fixed end points, which has to pass through a slip-link with distance R to the respective end points, one finds that the most probable configuration is no longer the one with equal arc length $L/2$ between the slip-link and the respective end points if R drops below a certain critical value. A bifuraction with respect to the most probable configuration is observed in the free energy. The result is found using conventional Gaussian statistics but also, with the aid of Monte Carlo simulations, for chains with finite extensibility and for a slip-link with a finite diameter. In the case of several slip-links, a similar "symmetry breaking" is predicted. It will thus be shown that the tube model and the slip-link approach are *not* equivalent.

1. Introduction

The theory of random walks (RW) has found a wide range of applications in the field of polymer physics. It was shown in the past that the statistics of polymers as regards global properties may be described very well by the use of the concept of RWs[1-3] irrespective of the specific chemical structure of the polymers. Existing theories might be divided into two classes according to their regimes of application: either the non-Markovian aspect of polymer statistics is taken serious, i.e., the excluded-volume effect is accounted for,[2,3] or the polymer is treated as a simple (Markovian) RW subject to certain constraints. The first approach is relevant when discussing the behavior of polymers in dilute form in a good solvent. The second approach applies on the one hand to polymer melts where the excluded-volume effect is screened.[1] On the other hand, it provides in many cases a valuable insight into basic properties that are to be expected in real polymeric systems. We adopt in the following the second point of view and ignore henceforth the influence of excluded-volume constraints. This neglect is justified for we discuss an effect that has been overseen in present theories on dense polymeric systems. In these dense systems screening is active.

One of the major problems when developing a model for polymer melts or cross-linked polymer systems (rubber)—and in a lesser form for polymer solutions—is the consideration of topological constraints due to the one-dimensional connectivity of a polymer, i.e., the obstruction a polymer faces on trying to pass through itself or an adjacent polymer. It must be stressed that this point becomes important when considering the *dynamics* of a polymeric system and must not be confused with the static excluded-volume problem mentioned above. Though the physical origin of both effects is the same, namely the fact that a monomer of the macromolecule occupies a certain volume in space, which must not be pervaded by another part of the same polymer or by a different polymer, presently no model exists which takes into account both effects simultaneously. The consideration of topological barriers within dynamic theories is extremely complex since already the discussion of static properties of knotted curves poses problems that are not yet solved. Presently there are two basic approaches that try to account for these topological constraints: the tube model as proposed by de Gennes[4] and developed by Doi and Edwards[5] and the slip-link (SL) model as used by many authors.[5-13]

In this paper we are concerned with the second model. It will be shown that it provides some unexpected properties with respect to its statistics that were not found in previous work on the slip-link model[5,7,9-13] due to reasons that will be discussed below. These unexpected properties do not emerge from the specific assumptions that are made and therefore might be observable in real polymer samples. Besides possible applications in polymer physics, we want to show that even such a simple model as the Gaussian random walk exhibits surprising statistical behavior when being constrained consisting in a bifuraction of the constrained RW, as was already briefly sketched in ref 10 and 11. The occurrence of such a bifuraction might also be of interest for physicists working in synergetics for we provide another example of a very simple bifurcating system.[16,17]

This paper is organized as follows: In section 2 the main results concerning the constrained RW are derived. A model possessing several slip-links will be considered in section 3. In sections 4 and 5 it will be shown that the observed bifurcation is not specific to the assumption of a continuous chain used in section 2. Section 5 provides a discussion of the results. In the following we make use of the terms (polymer) chain and RW in an interchangeable manner.

2. Chain Constrained by One Slip-Link

The slip-link model[5,7,9-13] can be formulated in the case of one slip-link as follows:[18] a RW (the idealized polymer chain) consisting of N steps of length b is embedded in $\mathbb{R}^d$ where $d \geq 2$. It departs at $\mathbf{R}_0 = \mathbf{0}$, passes through a hoop of negligible diameter located at $\mathbf{R}_1$ and arrives at $\mathbf{R}_2$; see Figure 1. The polymer is allowed to fluctuate (slip) through the hoops. We investigate in the following the statistics of the arc length the chain displays between one of the end points and the SL. For the case that $|\mathbf{R}_2 - \mathbf{R}_1| = |\mathbf{R}_1 - \mathbf{R}_0| =: R$ hold and which I discuss first, one might expect that the probability density function (pdf) for the arc length l_1 or l_2, respectively, which the walk displays between two points, should exhibit a maximum at $l_1 = l_0 := Nb/2$. This guess, however, is deceptive for—once R falls below a critical value R_c—the most probable config-

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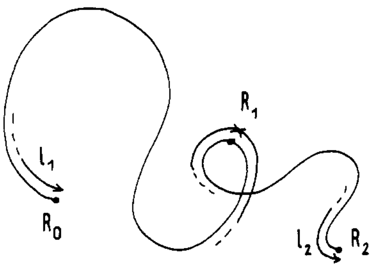

Figure 1. Example of a typical configuration of a random walk with fixed end points, which has to pass through $k = 1$ point (the slip-link).

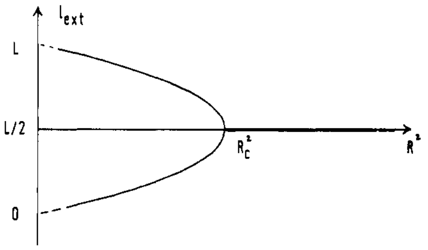

Figure 2. Dependence of the arc length l_{ext}, which the chain displays between one of the end points and the slip-link on the real-space distance between these two points for the case $k = 1$. l_{ext} is the value that maximizes the Boltzmann entropy of the system.

urations are those with an asymmetric distribution of arc lengths, as will be shown presently.

Using the conventional Gaussian pdf, which is approximately valid for $N \gg 1$ and $Nb \ll R$, the pdf for a specific configuration $\{l_1,l_2\}$ subject to the condition $l_1 + l_2 = L \equiv Nb$, with the points $\mathbf{R}_i$ (i = 0–2) being fixed, is given (up to a normalization constant) by the following expression

$$P_1(R,l) \sim [l(L-l)]^{-d/2} \exp\left[-\frac{d}{2}\frac{R^2L}{b}\frac{1}{l(L-l)}\right] \quad (1)$$

where $l \equiv l_1$ and $l_2 = L - l$. The extrema of $P_1(R,l)$ are computed by differentiation of eq 1 with respect to l. One finds easily[14,15] that $P_1(R,l)$ exhibits one or two maxima, respectively, depending on the value of R

$$l_{ext} = L/2 \qquad \text{if } R > R_c$$

$$l_{ext} = L/2 \pm [L^2/4 - LR^2/b]^{1/2} \qquad \text{if } R < R_c \quad (2)$$

where

$$R_c = (Lb/4)^{1/2} \quad (3)$$

l_{ext} is the value of l that extremalizes $P_1(R,l)$. The R dependence of l_{ext} is depicted in Figure 2. This figure is strongly reminiscent of the temperature dependence of the order parameter M in a second-order phase transition, see, e.g., ref 19, if we identify R_c^2 with T_c and $[l_{ext} - L/2]$ with M. That analogy can be further pursued by an analysis of the free energy $F(l)$ of the RW system, computed via the Boltzmann entropy: $F(l) = -kT \ln [P_1(R,l)]$. $F(l)$ is plotted in Figure 3 for values of R below, at, and above R_c. Figure 3 resembles again the order parameter dependence of the free energy of a system exhibiting a second-order phase transition. But this analogy is not very far-reaching: generally, a true phase transition is mathematically realized only in the thermodynamic limit where the number of degrees of freedom of a system tends to infinity. The height of the potential well (when measured in units of kT) between the two bifurcated symmetric states tends to infinity when considering the free energy of a system, which exhibits a true phase transition, and the system is locked to one of the two states with probability 1. The RW system considered here has a finite number of degrees of freedom and therefore does not show a true phase transition. This can be understood when considering the height of the potential barrier $\Delta F = F(L/2) - F(l_{ext})$ in the case $R \le R_c$:

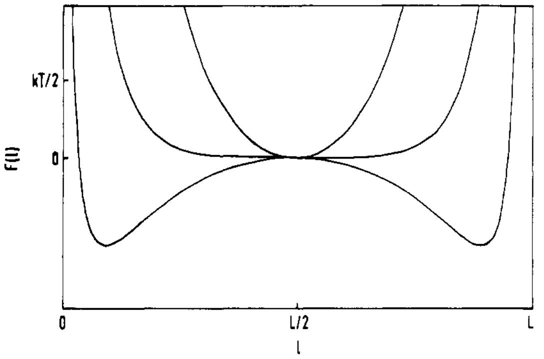

Figure 3. Dependence of the free energy of the constrained random walk system on the arc length, which the walk displays between the origin and the slip-link ($k = 1$) for several values of the real-space distance of the respective points. From top to bottom curves correspond to $R = 1.8R_c$, $R = R_c$, and $R = 0.6R_c$. For the definition of R_c, see text. The dimension of the embedding space is $d = 3$. This figure, as well as Figures 4 and 5, applies to all values of N.

$$\Delta F = \frac{d}{2}kT[1 - R^2/R_c^2 + \ln [R^2/R_c^2]] \qquad \text{for } R \le R_c \quad (4)$$

Equation 4 shows that for all $R > 0$ one finds that ΔF is finite and of the order of kT. This property has important consequences when applied to the dynamics of a polymer chain constrained by a SL, for the arc length l is not anymore confined to l_{ext} but fluctuates. When averaging l over a time period that is large compared with the inverse of the fluctuation frequency ν, one naturally finds $\langle l \rangle = L/2$. The symmetry of the system is thus restored. The time averaging or, equivalently, ensemble averaging corresponds to Gibbs' point of view with respect to the entropy where over all possible configurations with respect to l it is summed. The explanation why the phenomenon predicted here has not been mentioned in previous work on the SL and related models[5,7,9–13] is due to the fact that these authors were concerned directly with Gibbs entropy.

Another point of interest is the behavior of the SL model in the case $r_1 = |\mathbf{R}_1 - \mathbf{R}_0-| \mp |\mathbf{R}_2 - \mathbf{R}_1| = r_2$. The pdf is in this case given by

$$P_1(r_1,r_2,l) \sim [l(L-l)]^{-d/2} \exp\left[-\frac{d}{2b}\left[\frac{r_1^2}{l} + \frac{r_2^2}{L-l}\right]\right] \quad (5)$$

A typical example for the dependence of the free energy $F(l) = -kT \ln[P_1(r_1,r_2,l)]$ on l is shown in Figure 4. The dependence of the height of the potential barrier δ_1 measured from the shallower potential minimum on r_1 and r_2 and the dependence of the difference between the two potential minima δ_2 on r_1 and r_2 are depicted in Figure 5. δ_1 and δ_2 were obtained numerically. Unfortunately it is not possible to derive an analytical expression for the critical values r_1 and r_2 below which two local mimima appear in the free energy because algebraic equations of high order in the relevant parameters would have to be solved.

3. Several Slip-Links

The polymer starts at $\mathbf{R}_0 = \mathbf{0}$, passes through k SLs located at $\mathbf{R}_i$ and ends at $\mathbf{R}_{k+1}$. The points $\mathbf{R}_i$ are visited

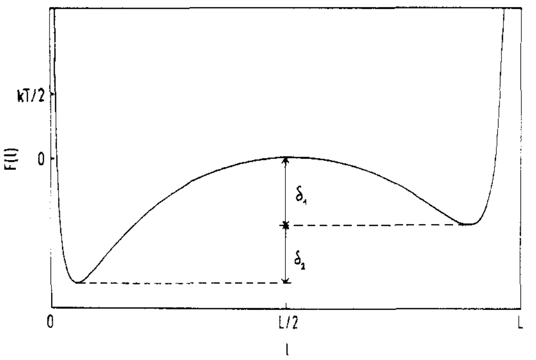

Figure 4. Dependence of the free energy of the constrained random walk system on the arc length, which the walk displays between origin and slip–link ($k = 1$) for $r_1 = 0.5R_c$ and $r_2 = 0.6R_c$ ($d = 3$).

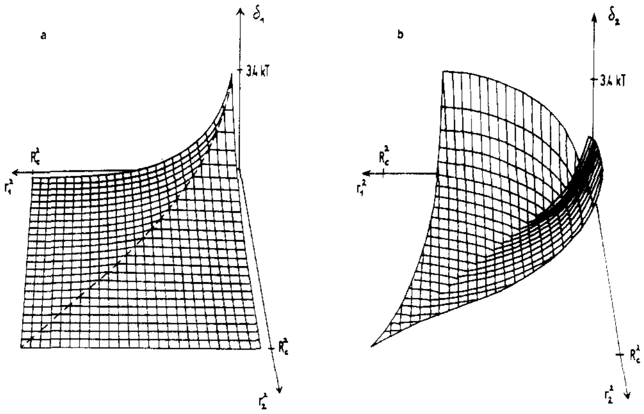

Figure 5. (a) Dependence of δ_1 on r_1 and r_2. The dashed line is defined by eq 4. (b) Dependence of δ_2 on r_1 and r_2. For the definition of δ_1 and δ_2, see Figure 4.

in a consecutive manner according to their index. As a simplification, we assume that $|\mathbf{R}_{i+1} - \mathbf{R}_i| = R$ for $i = 0, 1, ..., k$. The arc length, which the chain displays between the point $\mathbf{R}_{i-1}$ and the point $\boldsymbol{R}_i$, I denote as l_i ($i = 1, ..., k + 2$). The statistics of this model cannot be derived in such an explicit way as in the case $k = 1$, but in the following it will be shown that an instability of the symmetric state where $l_i = l_0 \equiv L/(k + 1)$ (for all i) occurs if R falls below a critical threshold. For that purpose consider the pdf $P_k(\{\mathbf{R}_i\};\{l_i\})_{\mathrm{A}}$ of an asymmetric state where at least one pair (l_i,l_j) can be found with $l_i \mp l_j$ and the pdf $P_k(\{\mathbf{R}_i\};\{l_i\})_{\mathrm{S}}$ of the symmetric state.

$$P_k(\{\mathbf{R}_i\};\{l_i\})_{\mathrm{S}} \sim [\prod_{i=1}^{k+1} L/(k + 1)]^{-d/2} \exp\left[-\frac{d}{2}\frac{R^2}{Lb}(k + 1)^2\right]$$

$$P_k(\{\mathbf{R}_i\};\{l_i\})_{\mathrm{A}} \sim [\prod_{i=1}^{k+1} l_i]^{-d/2} \exp\left[-\frac{d}{2}\frac{R^2}{b}\sum_{i=1}^{k+1} l/l_i\right] \quad (6)$$

The asymptotic behavior of the ratio $\omega = P_k(\{\mathbf{R}_i\};\{l_i\})_{\mathrm{A}}/P_k(\{\mathbf{R}_i\};\{l_i\})_{\mathrm{S}}$ is discussed for small R:

$$\lim_{R\to 0} \omega = \prod_{i=1}^{k+1} (l_0/l_i)^{d/2}$$

When considering the specific asymmetric distribution of the $\{l_i\}$ where, e.g., $l_i = l_0(1 - \epsilon)$, $i = 1, 2, ..., k$, and $l_{k+1} = l_0(1 + k\epsilon)$ with $0 < \epsilon < 1$, one can prove easily that ln $[\omega(R\to 0)] > 0$. This implies that, in the limit $R\to 0$, there exists at least one type of asymmetric state (namely the one considered above) that yields a larger entropy than the symmetric state, i.e., for small R the symmetric state is unstable. Proceeding to the opposite limit where $R \gg 1$, one finds that the asymptotic behavior of ω is dominated by the argument ζ of the exponential appearing in the respective expression for ω

$$\zeta = c[k + 1 - \sum_{i=1}^{k+1} l_0/l_i]$$

where c is a constant with $c > 0$. Upon considering the parametrization $l_i = 1 + \epsilon_i$ I find after some algebra that ζ exhibits a single maximum $\zeta(\epsilon_i{=}0) = 0$ if $\epsilon_i = 0$ for all i, i.e., for the symmetric case. This implies that $\omega(R{\gg}1) < 1$: the symmetric state has the larger entropy.

From these results it follows that also in systems with an arbitrary number of SLs the symmetric distribution $l_i = l_0$ becomes unstable if the separation of the SLs, which are threaded through by the polymer successively, falls below a critical value. Unfortunately, this critical value cannot be deduced from the foregoing analysis.

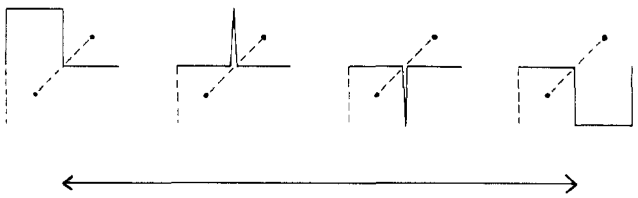

Figure 6. Typical diffusion process through the slip-link is sketched for the Monte Carlo simulation of the constrained chain on square lattice.

4. Constrained Random Walk on a Lattice

In order to examine whether the reported bifurcation is an artifact due to the fact that the Gaussian pdf, which was used in the foregoing sections, does not respect the finite extensibility of a real polymer chain, Monte Carlo (MC) simulations were performed on a RW with a fixed number of steps N, which is placed on the square lattice $\mathbf{Z}^2$. The RW starts at $-R\mathbf{e}_{\mathrm{Z}}$, runs through the origin where the SL is located, and ends at $+R\mathbf{e}_{\mathrm{Z}}$. The separation of the neighboring points along the chain is one lattice spacing. As before, no excluded-volume interaction is respected. MC dynamics are introduced by choosing a point along the RW at random and moving it in such a way on the lattice that the chain remains connected. The topological constraint that the SL imposes is modeled as follows: (i) The chain always possesses a point that is located at the origin. If a move is tried during the simulation that violates this condition, this move is rejected. (ii) If, on the other hand, a move is attempted that sets a point of the chain onto the origin and if this point is separated from the point of the chain in the SL by more than two RW steps, this move is rejected. To allow for fluctuations, the SL may be populated by two points of the chain, which are next to nearest neighbors. The mechanism that yields chain transport through the SL is sketched in Figure 6. The pdf $P_1(R,l)$ is approximated by repeatedly ascertaining the number of steps that the RW takes between one of its end points and the origin. The result is depicted in Figure 7 for several values of R. Again, the bifurcational behavior is observed as in section 2. We conclude that the bifurcation is not specific to the use of the Gaussian pdf. One might argue that the two-dimensional case that was considered is physically not relevant. But as can be seen in eq 1 the bifurcation is predicted for any dimension if $d \geq 2$ when using the Gaussian pdf, and the consideration of the case $d = 2$ by means of the MC simulation rules out the possibility of an artifact due to the fact that the Gaussian pdf does not

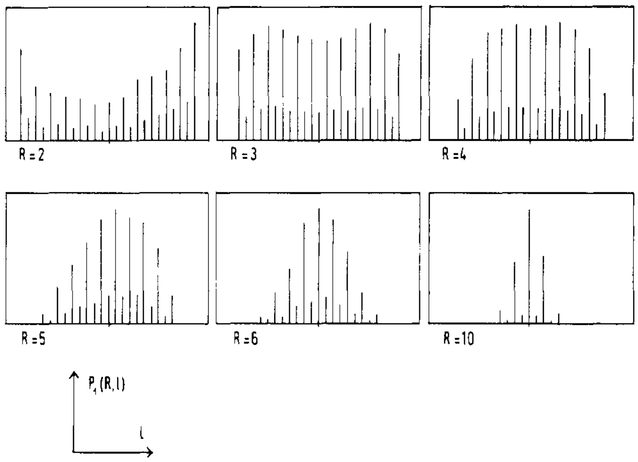

Figure 7. Dependence of the probability density function $P_1(R,l)$ on l for several values of R. Results are obtained via Monte Carlo simulation of a chain with $N = 28$ segments, which is placed on the square lattice and forced to pass through one slip-link.

respect the finite length of the chain.

5. Slip-Link with Finite Diameter

A further point that might be interesting for the polymer physicist is the problem of whether bifurcation still exists if the diameter of the SL is finite. Recall that so far only SLs with a vanishing diameter were considered. This approximation is also made throughout the literature due to mathematical convenience: the SL condition is in that approximation represented by the Dirac δ function. Extension of the analytical formulation to the case of nonzero SL diameter is not possible because of geometric reasons: when computing the entropy of the constrained system, it would be necessary to integrate over the finite area of the SL hoop. But no matter how small this area is, such an integration includes automatically also configurations where the polymer chain threads several times through the hoop (=the integrated area). This fact is due to the self-similar structure of a RW as described by the Gaussian pdf;[2] recall that a RW has fractal dimension $d_f = 2$.

To examine the problem of whether the bifurcational behavior still exists if the polymer is allowed lateral fluctuations in the SL, another Monte Carlo simulation was performed. In contrast to the procedure described in section 4, the polymer is now modeled by the freely jointed chain.[20] The chain consists of N links each being able to point in any direction independently of the other links. This chain is fixed with its end points at $-Re_Z$ and $+Re_Z$ and must pass once and only once through an area defined by a circle with radius r, which is located at the origin. The normal vector of this area is parallel to the z direction. MC dynamics are imposed in the following way: one of the $N - 1$ points of the chain is chosen at random and pivoted by an angle ψ with respect to the line connecting its two neighbors; see Figure 8. The angle ψ is chosen at random from the interval $[0,2\pi[$. The area defining the SL must be pervaded by exactly one link. If a MC step leads to a configuration where this condition is violated, the step is rejected and the algorithm persues with the stored configuration from which this unsuccessful attempt was tried. The approximate pdf for the number of links, which the chain displays between one of its end points and the SL, is found in the same manner as described in section 4. When executing the described MC simulation for several values of r, I find that a bifurcation occurs in all cases. Unfortunately, it is difficult to locate the onset of bifurcation since it takes very long MC runs to obtain good statistics in the interval around the value assumed for R_c.

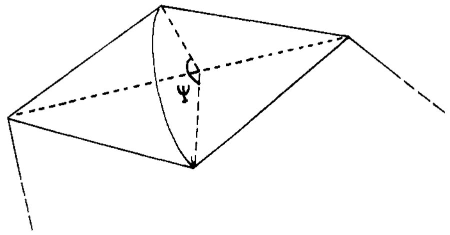

Figure 8. Configurational change during one Monte Carlo step for the freely jointed chain, which is embedded in the three-dimensional space R^3.

But for small R the double maximum as well as the single maximum for large R in the pdf can be clearly seen. The respective figures are qualitatively the same as Figure 7. This shows that the bifurcation is not due to the slightly artificial assumption of confining a point of the polymer to a point in the embedding space but may have physical significance. This point will be discussed in more detail in the following section.

6. Discussion

Let me first mention a technical detail. The examinations in sections 2 and 3 showed that it is important to consider the contour length containing part of the preexponential normalization constant; cf. eq 1, 5, and 6. This apparently trivial remark seems to be important because in many cases it is indeed justified to suppress this constant but *not* in the case of SL models. For example, it has been shown recently[21] that the neglect of this constant partly invalidated Mansfield's calculations on his slip-link model for semicrystalline polymers.[10]

In general, there are two types of conclusions one can draw from the presented results, concerning either existing slip-link theories or the situations in real polymer samples (or both). These points I will discuss presently.

With regard to theories that use the slip-link model, one faces one serious problem: in section 2 it was shown that for values of the distance R between the end point of the chain and the slip-link, which are smaller than the typical dimension of subsegments of the whole chain, contour length fluctuations occur that are typical for the slip-link approach. In an ensemble of chains there will be natural circumstances driving R below this critical threshold. These fluctuations cannot be incorporated in the reptation picture.[1,20] It is thus *not* possible to conclude, as Doi and Edwards did,[5] that the tube model[1,20] and the slip-link model are models that describe the situation in a real polymer sample equivalently. This objection concerns the dynamics of a polymer. The reason why the effect that is discussed in this paper was not found earlier is that the authors of ref 5-13 computed the free energy of a constrained chain via the Gibbs entropy, which yields the *static* properties of the system. From the theoretical approach developed in this paper, it seems to be difficult if not impossible to rederive with the slip-link model some standard results in reptation theory.

There seem to exist natural situations in a real polymer sample for which the slip-link model might indeed be more effective than the tube (reptation) picture. For instance Antonietti and Sillescu[22] reported on experiments on dense polymer systems and proposed the idea of "strangulated" polymers. The points where the polymers are strangulated may provide an example where a *physical* slip-link is realized. In this context the following point may be stressed: in this work I examined exclusively the case where the end points of the polymer were fixed in space. This premise is justified for cross-linked polymers. Nevertheless, it is also possible to study systems where the chain ends are free. Doi and Edwards[5,20] introduce in this context hypothetical phantom forces, which act upon the end points of the chain. This leads in a first approximation to the picture of a chain, with its first and last monomer being fixed.

In conclusion, I have shown that even the simplest approach to the conformational statistics of a polymer chain, namely, the simulation of the real chain by a Gaussian random walk, bears some unexpected subtleties, which can be discovered in a model where the restriction of phase space available to the polymer is realized in a specific way.

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Concept of Intrinsic Chain Stress in Rubber Elasticity

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ABSTRACT: The concept of the entropic axial force exerted by a long-chain molecule loses its clear-cut physical significance, in a dense system, in the presence of inter- and intrachain noncovalent interactions. In order to generalize this concept, it is shown by means of the virial stress formula that the macroscopic stress tensor in a network may be expressed as a sum of individual chain stress contributions. When the individual chain stress tensor is referred to a local coordinate system, with $\bar{x}_1$ in the chain vector direction, we obtain the intrinsic chain stress tensor, $\bar{\chi}_{rs}$. Under reasonable physical assumptions, the tensor $\bar{\chi}_{rs}$ is cylindrical with only $\bar{\chi}_{11}$ and $\bar{\chi}_{22} = \bar{\chi}_{33}$ as nonzero components. The axial component, $\bar{\chi}_{11}$, may be used to define an effective axial force associated with the chain, while the radial components, $\bar{\chi}_{22} = \bar{\chi}_{33}$, represent the effect of noncovalent chain–chain interactions. These concepts are employed in calculations for the affine uniaxial deformation of a simple tetrafunctional network model. It is found that the interchain noncovalent contribution to the stress is nonhydrostatic in the deformed network and varies with deformation due to the variation in chain orientation. In these model calculations these effects lead to departures from the usual Gaussian chain models, which, in a Mooney–Rivlin-type plot, show qualitative similarity to that observed experimentally.

1. Introduction

If we consider the collection of atoms forming a network of a rubberlike solid, we can identify two principal types of atomic interactions: the covalent interactions responsible for the long-chain molecules and the noncovalent interactions active between pairs of atoms of the same chain or of different chains. There are also important rotational potentials producing energy barriers to rotations about bonds, but we do not consider them in this paper.

In the earlier treatments[1] of rubber elasticity, the covalent and noncovalent interactions are regarded as operating on two completely decoupled systems. The covalently bonded chains are treated as entropic springs in tension. The two-body noncovalent interactions, since they are spherically symmetric, are regarded as capable of producing only a hydrostatic or isotropic contribution to the state of stress in the system, whether it is in its undeformed reference state or in a deformed state. The physical picture that results from this decoupling is that of a network of entropic springs immersed in an incompressible liquid, with no direct interaction between the two systems; there is only indirect coupling through the stress boundary conditions.

In several recent papers[2–6] we have been examining this assumption of decoupled systems by means of the computer simulation of atomistic models of polymer melts and networks. We have found two significant modes of direct coupling between the two types of interactions:[5] (i) The noncovalent interactions produce a significant change in the mean force in the covalent bonds. (ii) The covalent structure causes directional screening of the noncovalent interactions so that the latter make a nonhydrostatic contribution to the stress in the system.

These two coupling mechanisms occur on the atomic scale. In this paper, we present some theoretical considerations underlying a third mechanism, which operates on

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