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(11) A modified equation for S would be required if constraint release is important, but here for simplicity we disregarded it.
(12) One can assume that the tube segments at the chain ends are oriented due to the nematic interaction. In this case, one has to solve the boundary value problem similar to that of Merrill et al. In this paper, we do not pursue this model since the essential aspects of the nematic interaction is accounted for by eq 17.
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(14) Precisely speaking, due to the effect of constraint release, $\tilde{S}_S(t)$ depends on ϕ_L, but this dependence would be much less than that for $\tilde{Q}_S(t)$.

Increase of the Mobility of Knotted Macromolecules

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A basic feature of polymer dynamics is the entanglements. Entanglements are of importance in concentrated polymer solutions and gels and are examined in connection with, e.g., diffusive motion of polymers.[1,2] However, a simple example is already provided by self-entangled macromolecules, which give rise to knots. In this note we focus on knotted macromolecules. Experimentally, the production of knotted polymers has very recently become possible by treating relaxed circular DNA molecules with topoisomerases.[3] With this method one obtains (at least for small numbers of crossings) all topologically possible forms.[4] This fortunate fact opens now the possibility of relating theoretical predictions to experiments. We note that for each knot its minimal number of crossings (usually designated as "nodes") is an important topological characteristic quantity; evidently any knot may take forms with more crossings—but these may be disentangled without cutting the knot. Now, diffusion experiments show that the knots are separable according to their number of nodes. Firstly, one observes that knots with a larger number of nodes diffuse faster, which is intuitively understandable because of the compactness of a knot with many nodes.[5] Furthermore, in addition to this, knots with the same number of nodes have closely similar friction coefficients: especially for electrophoresis in agarose gel, where the mobility of the knots increases linearly with the number of nodes.[3]

To examine the diffusional behavior of knotted molecules theoretically, we first remark that the wealth of topologically possible patterns is hardly amenable to an exact treatment. Thus, here we consider only knots with all nodes pulled together. Such a pattern can be simply modeled by a flexible polymer chain with Gaussian statistics under the restrictions of being closed and forming as many loops emerging from a center as there are nodes in the knot. This model can be viewed as being made from a star-branched molecule by replacing the linear star arms by closed loops (compare Figure 1). Hence, our pattern displays both star and ring aspects.

For dilute solutions, it is now straightforward to obtain the friction coefficient (which is proportional to the inverse of the diffusion coefficient) for such patterns. Following Kirkwood,[6] the friction coefficient f (which is the proportionality factor between the total mean force $\mathbf{F}$ on the molecule and its mean velocity $\mathbf{u}$, i.e., $\mathbf{F} = f\mathbf{u}$) is approximately given by

$$f = N\zeta\left[1 + \frac{\zeta}{6\pi\eta N}\sum_{\mu,\nu=1}^{n}\int_0^{N_\mu}\mathrm{d}t\int_0^{N_\nu}\mathrm{d}s\ \langle R^{-1}(\mu t,\nu s)\rangle\right]^{-1} \tag{1}$$

In eq 1, ζ denotes the friction constant for one monomer, N_μ is the number of monomers on the μth loop, N is the total number of monomers, and n denotes the number of loops. The viscosity of the solvent, is η, and $R^{-1}(\mu t,\nu s)$ is the inverse distance between the sth monomer on the νth loop and the tth monomer on the μth loop. To calculate the configurational average of the inverse distance, one has to consider the distribution function for the distance vector $\mathbf{R}(\mu t,\nu s)$ between the monomers:[7,8]

$$P(\mathbf{R}(\mu t,\nu s)) = \left[\frac{3\det D}{2\pi a^2\det C}\right]^{3/2}\exp\left[-\frac{3\det D}{2a^2\det C}(\mathbf{R}(\mu t,\nu s))^2\right] \tag{2}$$

Here, a denotes the bond length, and the symmetric $(n + 1) \times (n + 1)$ matrix $\mathbf{C}$ is given by the elements $C_{\alpha\beta}$, which equal (for $\nu \geq \mu$)

$$(1 - \delta_{\mu\nu})[\sum_{m=\mu}^{\nu-1} N_m + s - t] + \delta_{\mu\nu}|t - s|$$

if $\alpha = \beta = n + 1$

$$N_\alpha\delta_{\alpha\beta} \tag{3}$$

if $1 \leq \alpha,\beta \leq n$, and

$$\sum_{m=1}^{n}\sum_{p=1}^{N_m}[\varphi_{\nu,s}(m,p) - \varphi_{\mu,t}(m,p)][\varphi_{\alpha,N_\alpha}(m,p) - \varphi_{\alpha-1,N_{\alpha-1}}(m,p)]$$

if $1 \leq \alpha \leq n$ and $\beta = n + 1$, where

$$\begin{aligned}\varphi_{\lambda,x}(m,p) &\equiv 1 \qquad \text{if } m < \lambda,\ 1 \leq p \leq N_m \\ &\qquad\qquad \text{or if } m = \lambda,\ 1 \leq p \leq x \\ &\equiv 0 \qquad \text{otherwise}\end{aligned} \tag{4}$$

The $n \times n$ matrix $\mathbf{D}$ is given by $D_{\alpha\beta} = N_\alpha\delta_{\alpha\beta}$ for all $1 \leq \alpha,\beta \leq n$. From eq 3 and 4 one calculates the ratio of the determinants

$$\begin{aligned}\det C/\det D &= |t - s| - (t - s)^2/N_\mu \qquad \text{if } \mu = \nu \\ \det C/\det D &= t + s - s^2/N_\nu - t^2/N_\mu \qquad \text{if } \mu \neq \nu\end{aligned} \tag{5}$$

Because the mean inverse distance results in

$$\langle R^{-1}(\mu t,\nu s)\rangle = (6/\pi a^2)^{1/2}(\det D/\det C)^{1/2} \tag{6}$$

the double sum reads in the continuum limit

$$\sum_{\mu,\nu}\int_0^{N_\mu}\mathrm{d}t\int_0^{N_\nu}\mathrm{d}s\ \langle R^{-1}(\mu t,\nu s)\rangle = (6\pi/a^2)^{1/2}[\sum_\mu N_\mu^{3/2} + \sum_\mu\sum_{\nu\neq\mu}(N_\nu N_\mu)^{1/2}(N_\nu^{1/2} + N_\mu^{1/2} - (N_\nu + N_\mu)^{1/2})] \tag{7}$$

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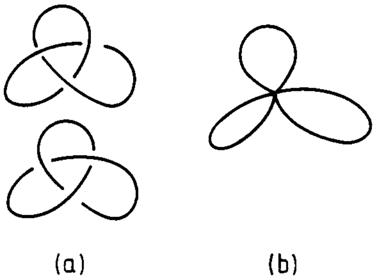

Figure 1. (a) Two topologically inequivalent knots with three nodes. (b) Our model, with all nodes pulled together.

The expression for the friction is obtained by inserting eq 7 into eq 1. It coincides with the special case ($q = 0$) of eq 13–15 of ref 9, in which the friction coefficient for multiple ring molecules was evaluated; see also ref 10 for a summary of useful formulas.

Now we consider the case of equal numbers of monomers per loop: $N_\mu = N/n$. The friction coefficient f then equals (for $N \gg 1$)

$$f \approx (6\pi N)^{1/2}\eta a/y(n) \tag{8}$$

where y is defined by

$$y(n) \equiv n^{1/2}(2 - 2^{1/2})(1 + 1/(n2^{1/2})) \tag{9}$$

The friction coefficient for linear polymers is

$$f(\text{linear}) \approx (6\pi N)^{1/2}\eta a 3\pi/8 \tag{10}$$

Hence the friction coefficient for the molecule with n loops then reads

$$f(n\ \text{loops})/f(\text{linear}) = 8n^{1/2}/(3\pi(2^{1/2}n + 1)(2^{1/2} - 1)) \tag{11}$$

and decreases roughly with the inverse square root of the number of nodes. The friction vanishes in the limit of large n, because more and more monomers are concentrated in the center and the molecule becomes pointlike. This is a consequence of the neglect of the excluded volume. Equation 11 may be contrasted to the relation which gives the decrease of the friction of star-branched polymers with n arms of equal length (and fixed numbers of constituting monomers), which reads[11]

$$f(n\ \text{arms})/f(\text{linear}) = n^{1/2}/((n + 2^{1/2})(2^{1/2} - 1)) \tag{12}$$

Qualitatively, we find thus a close resemblance between the diffusional behavior of star-branched molecules and of our model for knotted molecules in dilute solution. Furthermore, the difference of the friction coefficients of the n loop molecule and of the molecule formed from n linearly connected rings is also not too large for small n (for $n < 10$ less than 50%).[9] The latter is given by

$$f(n\ \text{rings})/f(\text{linear}) = (8/3\pi)[n^{-1/2} + (4/\pi)n^{-3/2} \times \sum_{k=1}^{n-1}\sum_{l=1}^{n-k}(2 \arcsin (l^{-1/2}) - (l + 1)^{1/2} \arcsin l^{-1})]^{-1} \tag{13}$$

As a proposal, we hence suggest to check experimentally whether in dilute solutions the diffusional motion of knots is well described by eq 11. In order to render more evident the connection between the friction coefficients for the three cases (molecules with n loops, molecules with n linearly connected rings, and star-branched molecules with n arms), we plot these in Figure 2 for values of n between 1 and 10. Here the parallelity in the behavior of molecules with n loops and molecules with n arms becomes evident.

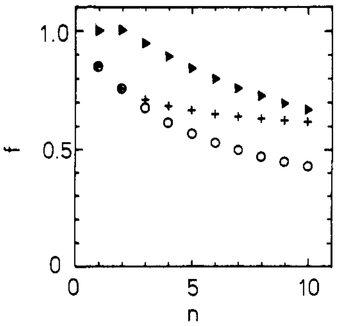

Figure 2. Friction coefficient f for the n-loop polymer (eq 11, circles), the star-branched polymer with n arms (eq 12, triangles), and n linearly connected rings (eq 13, crosses). The values are normalized with respect to the friction coefficient for the linear polymer of identical molecular weight.

If the hydrodynamic interaction is totally screened and entanglements are neglected, the diffusion coefficient (calculated in the Rouse model) is independent of the number of nodes. In our model, calculated for dilute solutions, the diffusion coefficient grows with the number n of nodes, e.g., $n^{1/2}$, eq 11. However, as experimentally determined, the diffusion coefficient of knotted DNA molecules in gels grows faster than this, being roughly linear with the number of nodes. This fact may be related to the importance of entanglements in the diffusion through polymer networks like gels. As a reminder,[2,12,13] in gels star-branched molecules with n arms should have a diffusion coefficient proportional to $n \exp(C/n)$, where C is a positive constant (compare eqs III.19′ and II.6 of ref 2). This would lead for small C to a roughly linear increase in the diffusion constant with the number of nodes. Possibly an analysis along the lines of ref 14, whose authors study diffusion of ring molecules, may lead to a result for knotted polymers close to the $n \exp(C/n)$ behavior, i.e., more in line with the experimental findings. In any case, the replacement of a linear chain by a loop has a deep effect on the mechanism of the motion through a network. We view the description of this motion as an interesting subject which—thanks to the recent experiments—is worth further theoretical investigations.

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