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Iterative Convolution Determination of the Mobility of Knotted Macromolecules

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ABSTRACT: A statistical mechanical calculation of the mobility of a knotted macromolecule is presented on the basis of the iterative convolution approximation utilizing the Kirkwood–Riseman estimate of the translational friction coefficient. The linear relationship between mobility and the irreducible number of nodes or loops observed experimentally is confirmed. The magnitude of the diffusion coefficient appears to be a sensitive function of the excluded-volume processes operating within the entanglement, while the linear behavior derives from the specification of the central core of the knot from which the solvent is largely excluded.

Introduction

The systematic experimental investigation of the mobility of knotted macromolecules has recently become possible following the treatment of relaxed circular DNA molecules with topoisomerases,[1] enabling the production, in principle, of all topologically possible forms and, in particular, knotted macromolecules of any specified minimal number of "nodes" or "crossings".[2] This number is an important topological characteristic of the self-entanglement, and although a knot may contain more nodes, there is evidently an irreducible number n to which the system may be disentangled without cutting the knot.

Moreover, when such an entanglement is pulled tight to form a central knot, then n equals the number of loops formed (Figure 1a). Having thus identified an n-loop knot, we also recognize an n-loop entanglement representing the delocalized version of the knot in which the central region is progressively teased apart, yet the n loops still remain clearly identifiable. The parameters we use to classify the structure of the entanglement are n, representing the number of loops or crossings, N_μ, representing the number of monomers in the μth loop, and $\langle R_c\rangle$, the mean radius of the central core region within which the nodes or crossings occur (Figure 1b).

There are a number of experimentally established results relating to the diffusion of knotted macromolecules, and it is the purpose of this investigation to establish a theoretical description of the diffusion process based on Kirkwood's concept of the friction constant. A recent similarly based investigation by Matuschek and Blumen[3] also sought to provide a theoretical description of knotted macromolecule mobility, however they totally neglect excluded volume effects which we consider crucial in the specification of the friction constant: we shall make detailed comparisons of their results with ours and with the experimental data that is currently available.

In a recent series of experiments Dean et al.[1] performed gel electrophoresis of DNA knots formed in nicked DNA rings by *Escherichia coli* DNA topoisomerase I. It was found that electrophoresis of the knots forms a ladder of DNA bands, and knots with the same number of nodes migrate to the same band. The organization of the nodes of a knot appeared to have little effect on its electrophoretic mobility. Electron microscopy of the knots extracted from each band provided unequivocal evidence that they had segregated according to the number of nodes within each knot. Dean et al.[1] concluded that, despite the variety of shapes possible for a knot with many nodes, the mobility of a knot in a gel is determined exclusively by the number of its nodes. Their experiments revealed a linear relationship between knot mobility and the number of nodes for rings of given molecular weight. Adventitious nodes formed due to accidental flopping of DNA are irrelevant: the mobility bears a linear relationship to the irreducible number of nodes, n, that characterize the entanglement. Knots with a small number of nodes have a lower mobility, presumably because of the different frictional aspect presented by a delocalized, disentangled structure versus a more compact, tightly knotted configuration. Indeed, the mobility presumably maximizes in the limit of large n when the entanglement has formed a compact knot from which the surrounding solvent is totally excluded.

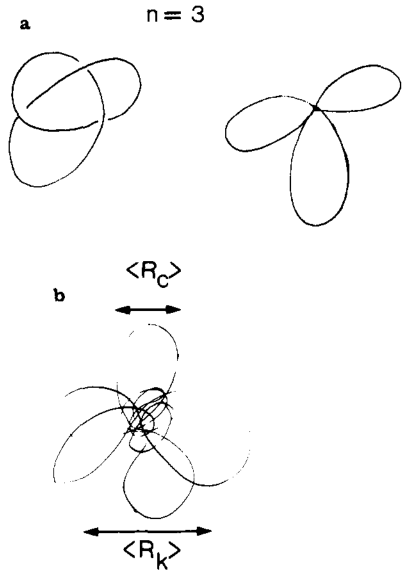

Figure 1. (a) Geometry of a knotted entanglement having an irreducible number (n = 3) of nodes. If such an entanglement is pulled tight to form a central knot, the system forms an n-loop entanglement. In this case n = 3. (b) Parameters involved in the specification of the entanglement geometry.

Friction Coefficient

If the center of gravity of a polymer molecule immersed in a solvent moves with a mean velocity **u** and is subject to a force **F** exerted by the surrounding fluid, then they are related by

$$\mathbf{F} = f\mathbf{u} \qquad (1)$$

where $\mathbf{F} = \sum_{i=1}^{N}\langle \mathbf{F}_i\rangle$ is the sum of the mean forces exerted

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on the N individual monomer units, averaged over all internal configurations of the chain. The translational friction coefficient, f, of the molecule is related to the diffusion constant via the Einstein relation

$$D = kT/f \tag{2}$$

The uniform steady flow of the surrounding fluid is perturbed in the vicinity of the polymer chain, and the change in flow at any point arises as the cooperative sum of perturbations arising from each of the monomers constituting the macromolecule. The hydrodynamic interaction between the centers and the perturbation of the fluid flow has been calculated by Oseen[4] and utilized by Kirkwood and Riseman[5] in an estimate of the friction coefficient for a polymeric molecule.

We present here an outline of the development of the central equation of Kirkwood and Riseman for the friction coefficient. We refer the reader elsewhere[5,6] for a full discussion and restrict ourselves here to those aspects of immediate concern for the theoretical description of the mobility of self-avoiding, knotted macromolecules.

If $\mathbf{u}_i$ is the velocity of the ith monomer in the molecule and $\mathbf{v}_i$ is the velocity of the fluid at that point if the monomer were not present, then the force exerted by the monomer on the fluid is

$$\mathbf{F}_i = \zeta(\mathbf{u}_i - \mathbf{v}_i) \tag{3}$$

where ζ is the translational friction coefficient of the ith monomer and, of course, depends on both the nature of the fluid and the monomer itself. Now, $\mathbf{v}_i$ arises from two contributions

$$\mathbf{v}_i = \mathbf{v}_i^0 + \mathbf{v}_i' \tag{4}$$

where $\mathbf{v}_i^0$ is the intrinsic flow velocity of the fluid in the absence of the entire molecule and $\mathbf{v}_i'$ is the sum of the Oseen perturbations to the flow arising from all the other j ($\neq i$) monomers in the chain

$$\mathbf{v}_i' = \sum_{\substack{j=1\\ j\neq i}}^{N} \mathbf{T}_{ij}\mathbf{F}_j \tag{5}$$

where $\mathbf{T}$ is the Oseen tensor. We then have from eqs 3 and 4

$$\mathbf{F}_i = \zeta(\mathbf{u}_i - \mathbf{v}_i^0) - \zeta\sum_{\substack{j=1\\ j\neq i}}^{N} \mathbf{T}_{ij}\mathbf{F}_j \tag{6}$$

If there is no original velocity field $\mathbf{v}_i^0 = 0$ and $\langle \mathbf{u}_i\rangle = \mathbf{u}$, then configurationally averaging over the macromolecule the mean force exerted by segment i on the fluid is

$$\langle \mathbf{F}_i\rangle = \zeta\mathbf{u} - \zeta\sum_j \langle \mathbf{T}_{ij}\mathbf{F}_j\rangle \tag{7}$$

Approximating $\mathbf{T}_{ij}$ by its configurational average $\langle \mathbf{T}_{ij}\rangle$ and setting $\langle \mathbf{T}_{ij}\mathbf{F}_j\rangle = \langle \mathbf{T}_{ij}\rangle\langle \mathbf{F}_j\rangle$, we have in the Kirkwood–Riseman approximation for the Oseen hydrodynamic interaction tensor

$$\langle \mathbf{T}_{ij}\rangle = \frac{1}{6\pi\eta_0}\langle R_{ij}^{-1}\rangle \tag{8}$$

where η_0 is the viscosity of the solvent and R_{ij}^{-1} is the reciprocal distance between the ith and jth monomers within the macromolecule. For the entire molecule we then have

$$\sum_{i=1}^{N}\langle \mathbf{F}_i\rangle = N\zeta\mathbf{u} - \frac{\zeta}{6\pi\eta_0}\sum_i\sum_j \langle R_{ij}^{-1}\rangle\langle \mathbf{F}_j\rangle \tag{9}$$

which with eq 1 may be rewritten in terms of the friction coefficient as

$$f + \frac{f\zeta}{6\pi\eta_0}\sum_i\sum_j \langle R_{ij}^{-1}\rangle = N\zeta$$

i.e.

$$f = N\zeta\left[1 + \frac{\zeta}{6\pi\eta_0 N}\sum_i\sum_j \langle R_{ij}^{-1}\rangle\right]^{-1} \tag{10}$$

or, in terms of the diffusion coefficient (eq 2)

$$\frac{D}{kT} = \frac{1}{N\zeta}\left[1 + \frac{\zeta}{6\pi\eta_0 N}\sum_i\sum_j \langle R_{ij}^{-1}\rangle\right] \tag{11a}$$

The reduced diffusion coefficient may be expressed in the form

$$D^* = A + B\sum_i\sum_j \langle R_{ij}^{-1}\rangle \tag{11b}$$

where $A = (N\zeta)^{-1}$ and $B = (6\pi\eta_0 N^2)^{-1}$. Since we are interested in the relation of the configurational properties of the knot embodied in $\sum_i\sum_j\langle R_{ij}^{-1}\rangle$ to the reduced diffusion coefficient D^*, we neglect the system-dependent parametric factors A and B: instead, we investigate the double sum over the configuration-averaged reciprocal separations $\sum_i\sum_j\langle R_{ij}^{-1}\rangle$ as a function of knot classification. We restrict ourselves in the present analysis to situations in which the electrophoretic field is sufficiently small as not to physically distort the entanglement.

Clearly $\sum_i\sum_j\langle R_{ij}^{-1}\rangle$ is a highly sensitive function of monomer separation, particularly for the confined configurations that characterize the entanglements under investigation here. We anticipate that the correct specification of excluded-volume effects will be crucial in the estimate of the translational diffusion constant or friction coefficient. Random-walk representations in which excluded-volume processes are totally neglected will obviously tend to overestimate the reciprocal separations and will not reflect their modification with the increasing monomer density associated with progressively complicated entanglements.

Description of the Entanglement

The topological specification of a knot has received considerable attention, and it would appear that the identification of a true knot may be made only in a formal sense, which does not readily lend itself to a convenient physical representation suitable for the present calculations. Here, for the purposes of qualitative description, we model the entanglement as n interacting loops (Figure 2), with one specified monomer per loop (the "key" monomer) being required to remain within a range $R > \sigma$ of specified key monomers on the other loops. σ is the monomer diameter and equals the bond length. We shall later identify the mean-radial distance of the key monomers from the center of the knot as $\langle R_c\rangle$. As R increases, the entanglement may vary from a tight, close-packed central region surrounded by loops to a looser structure with no identifiable knot as such. Care must be taken that the choice of R is sufficiently large as to permit physically possible monomer-packing densities in the central core region of the entanglement, particularly for large loop numbers n. In the present study we choose R

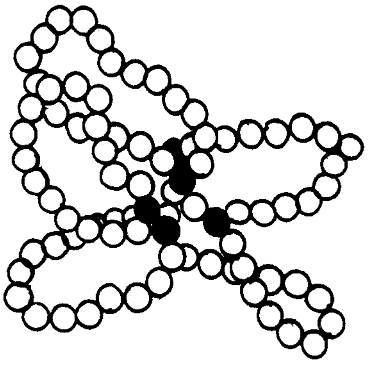

Figure 2. Hard-sphere loop representation of a knotted entanglement (n = 5). The filled segments represent the "key monomers" that are constrained to remain within R of each other.

= 3σ, 5σ, and 10σ, representing progressive delocalization of the entanglement. The calculation of the mean inverse monomer separation required for the determination of the friction constant (eq 10) may now proceed on the basis of the iterative convolution approximation,[8] which takes account of the excluded-volume processes operating both within and between the loops constituting the entanglement.

It should be pointed out that the inverse separations within the entanglement required in the Kirkwood–Riseman estimation of the friction coefficient are particularly sensitive to the excluded-volume features of the system, and a Gaussian representation of the type proposed recently by Matuschek and Blumen in which self-avoidance is totally neglected would appear to be inappropriate for any calculation based as sensitively as this one upon reciprocal separations (cf. eq 11b). Since self-interaction within and between the loops is neglected in the Gaussian description of the entanglement, the principal axes of the loops do not reflect their crowding or elongation with increasing n despite the high monomer densities in the vicinity of the central entanglement. This is considered a crucial aspect in the adequate description of the configurational properties of the system and, indeed, involves precisely those configurations for which a Gaussian description is least appropriate. Moreover, in the absence of excluded volume, the central knot reduces to a *point* in Matuschek and Blumen's calculation—and they only consider the case of tight, pointlike central knots. The neglect of the frictional contribution arising from the finite-sized central knot undoubtedly accounts at least in part for their systematic underestimate of the friction constant of pointlike knots to which the entire entanglement reduces in the case of large n.

Another important feature of the entanglements embodied in the present description is the *internal mobility* of the macromolecule. For all but tightly knotted molecules, the n-loop entanglement is essentially a configurationally mobile structure, as directly confirmed by electron microscopy[1] of complex knots in circular DNA tied by topoisomerase. This configurational mobility of the entanglement is an important aspect of any configurational average taken over the molecule, particularly for the reciprocal separations required in the estmation of the friction coefficient and the related diffusion constant. It is appropriate to mention that none of the knots reported by Dean et al.[1] revealed the tightly knotted form adopted by Matuschek and Blumen[3] in their calculations but rather the delocalized structures of the qualitative form considered here.

As outlined above, we model the entanglement as a system of loosely coupled flexible rings, the "key monomer" on each of which is required to remain within R of each other. Excluded-volume effects between and within rings are embodied in the iterative convolution (IC) description of the monomer–monomer correlations. Here, however, we regard any pair of loops to be immersed in a "solvent" of monomers arising from the presence of the other $n - 2$ loops, which constitute the entanglement.

Specification of the number of monomers per loop, N_μ, the number of loops, n, and the core radius, $\langle R_c \rangle$, enables a uniform monomer density within the entanglement to be estimated from which the effective potential of mean force, Ψ, which operates between monomers, can be estimated on the basis of the Ornstein–Zernike equation in the Percus–Yevick approximation. We shall describe this aspect of the calculation in detail below.

Iterative Convolution (IC) Approximation

The IC approximation has been applied to a wide range of three-dimensional continuum polymer problems ranging from linear sequences through ring, star, ladder, and polynematic systems to adsorption at boundaries and the determination of scattering functions. From the outset the objective of the IC approach was to predict the configurational properties—mean-square length, radius of gyration, etc.—purely on the basis of a knowledge of the monomer–monomer interaction functions. The technique applies equally to heterogenous and homogeneous sequences whether they be idealized hard-sphere interactions or more realistic central, nonsaturating functions. Moreover, since the numerical evaluation of the integrals is based upon fast Fourier transform processes, the scattering function of the system is determined automatically. In virtually every case we complement the IC determinations with parallel Monte Carlo simulations and the agreement is generally good to excellent. While the IC technique is undoubtedly an approximation, it does nevertheless appear to give good account of the excluded-volume features of short to intermediate length sequences without the unrealistic confinement that characterizes the lattice-based analyses.

As Matuschek and Blumen observe,[3] geometrically the knot problem has many similarities with star systems in which the branches are replaced by loops and in their Gaussian representation the central vertex is a point knot. Here we model the entanglement in terms of the IC approximation, but on the basis of a system of coupled interacting loops as outlined above. Discussion of the iterative convolution approximation has been presented elsewhere,[8] and it is inappropriate to reiterate the details here. The IC technique is based upon the calculation of the normalized spatial probability distributions or correlation functions $Z(ij|N)$, which develop between any pair of monomers i,j within the N-mer. With a knowledge of the complete set of Z-functions operating between each pair of monomers in the system, virtually all configurational properties of the system may be immediately determined, including the scattering function. The only input required for the determination of the Z-functions is a specification of the monomer–monomer pair potentials, $\Phi(ij)$, operating between each pair ij. The equation that relates the interaction potential to the probability distribution is[8]

$$Z(ij|N) = H(ij) \prod_{k=1}^{2N_\mu}{}' \int Z(ik|N)\, Z(kj|N)\, \mathrm{d}k \qquad (12)$$

where

$$H(ij) = \exp(-\Phi(ij)/kT) \qquad (13)$$

Π' represents the formation of the geometrical mean of the convolution integrals, and kT is the Boltzmann factor. The upper limit, $2N_\mu$, represents the total number of monomers in the two representative interacting loops. Quite simply, eq 12 asserts that the spatial probability distribution, $Z(ij|N)$, between segments i and j within the N-mer arises from the "direct" correlation $H(ij) = \exp(-\Phi(ij)/kT)$, modified by the presence of "indirect" correlation between i and j via a third segment $k \neq i,j$. Because, in a polymer, each segment participates differently depending upon its location within the sequence, we take the *mean* along the chain of these third particle effects. In fact, we take the geometrical mean designated by Π' (see ref 8), whereupon eq 12 describes the development of the direct correlation between i and j modulated by the mean field of the other segments in the sequence. With an appropriate specification of the Φ-functions, which, apart from describing the i,j monomer–monomer interaction, also express the $i,i+1$ sequential connectivity of the system (and hence its geometry), we are now in a position to iteratively evaluate eq 12. This is most conveniently achieved by means of fast Fourier transform techniques, which incidentally yield the scattering function of the system. We direct the reader to the literature for a more detailed description of the technique and its application.[8,9]

For simplicity we restrict the calculations reported here to entanglements whose n loops all have the same number of monomers N_μ per loop. We determine the mean radius, $\langle R_c \rangle$, of the central core region. Two identical loops of N_μ segments and whose key segments are within R of each other are allowed to interact, and their spatial distributions are determined on the basis of eq 12. Again, for simplicity, all monomer–monomer interactions are taken to be hard-sphere functions, although there would be no difficulty in principle in assuming more realistic interactions. The mean distance of the key segments from the origin may be readily determined and an estimate of the core radius, $\langle R_c \rangle$, formed. The interference of two rings at this stage is taken to be representative of the loop–loop interaction operating within the entanglement, and although ideally all n loops should be included in the determination of $\langle R_c \rangle$, such a calculation would be prohibitive. We note in passing that Matuschek and Blumen effectively set R and $\langle R_c \rangle = 0$ in assuming a pointlike central core to the entanglement.

A similar calculation of the radial segment density distribution provides an estimate of $\langle R_k \rangle$, the mean radius of the entire entanglement from which we may form estimates of ρ_c and ρ_k, the mean segment densities of the entanglement in the core and outer loop regions, respectively. The quantity ρ_k represents a crucial parameter in the subsequent calculations, as we shall now show.

We have already observed that the full calculation of the simultaneous interaction of all n loops would be prohibitively difficult. Accordingly, in this calculation we consider the interaction of two representative loops in a "solvent" of monomers at number density ρ_k, the "solvent" representing the remaining $n - 2$ loops of the entanglement. The presence of the solvent modifies the hard-sphere interaction $\Phi \rightarrow \Psi$, the so-called potential of mean force familiar in the statistical description of dense fluids. The effective monomer interaction $\Psi(r,\rho_k)$ in a "solvent" at density ρ_k is readily calculable and may be determined on the basis of the Ornstein–Zernike and Percus–Yevick equations of fluid statistical mechanics via the direct correlation function. The transition $\Phi \rightarrow \Psi$ for the hard-sphere monomers in this calculation is shown in Figure 3, from which we see the effective interaction develops a weak attraction followed by a longer range oscillation.[9] This structure may be directly attributed to screening effects in the presence of a solvent, which modifies the direct interaction between two monomers taken in isolation: the net effect of this modified interaction will be an ellipticity in the loop dimensions, which will modify the estimates of the mean reciprocal separations $\langle R_{ij}^{-1} \rangle$. We have previously reported the application of these equations in earlier IC descriptions of polymers immersed in a solvent and refer the reader to those publications for a detailed description.[9] Suffice it to say here that the OZ–PY equations in conjunction with the IC approximation appear to provide a good description of solvent influences on the prediction of polymer configuration, and we apply the procedure here with confidence.

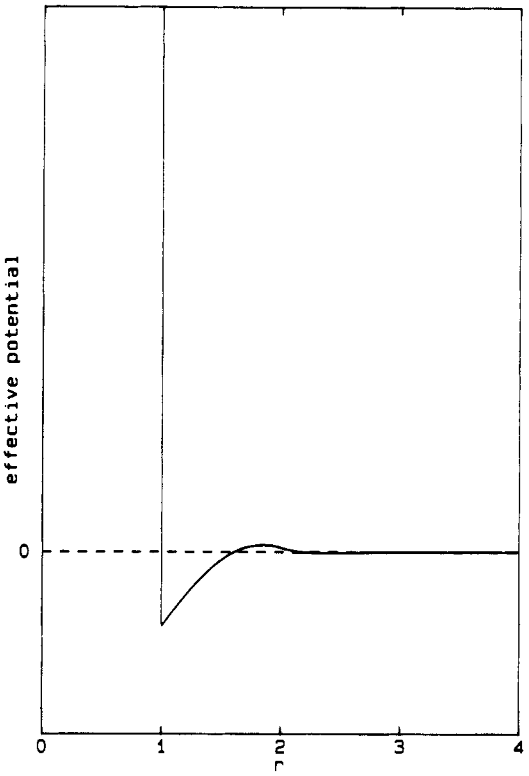

Figure 3. Effective interaction, $\Psi(r)$, between two hard-sphere monomers in a solvent of identical particles. The amplitude and range of the oscillation, which arises from screening processes, increases with increasing solvent density. Screening effects induce a weak effective attraction between hard-sphere monomers at close separations.

To further clarify the role of excluded volume in these determinations of knot mobility, we repeat the IC calculations with the monomer diameter $\sigma = 0$, corresponding to zero excluded volume. The random-walk entanglement is still treated as a system of coupled loops, with their key monomers confined to within a range R of each other. Intra- and inter-ring interferences arising from excluded-volume effects no longer arise, however. We anticipate that the double sum $\sum_i \sum_j \langle R_{ij}^{-1} \rangle$, which determines the mobility of the entanglement, will be substantially larger on the basis of the much closer separations that may arise in the absence of excluded volume. This latter calculation should be distinguished from that of Matuschek and Blumen in which they effectively set $R = 0$, corresponding to a pointlike central knot. We specifically investigate $R = 0$ and 3 bond lengths for the zero excluded-volume ($\sigma = 0$) case: however, we note that even for $R = 0$ the IC calculations will differ slightly from the random-walk descriptions of Matuschek and Blumen since their Gaussian representations do not strictly apply to the finite entanglements investigated here.

The parameters of a given calculation are N_μ, the number of monomers in a loop, n, the number of loops (and hence $nN_\mu = N$, the total number of monomers in the entanglement), and R, the maximum separation of any two "key" monomers. On this basis, the spatial correlation function, and hence the mean reciprocal separation, $\langle R_{s_\mu t_\nu}\rangle$, between monomers s and t on loops μ and ν, may be calculated using eq 12. All inter- and intraloop mean reciprocal separations need to be determined for insertion in the Kirkwood–Riseman equation, and this may be done once we have determined the Z-functions:

$$\langle R_{ij}^{-1}\rangle = 4\pi\int_0^\infty R_{ij}^{-1} Z(ij|N)\, R_{ij}^{2}\, \mathrm{d}R_{ij} \qquad (14)$$

Results and Discussion

As we might expect, the ellipticity of the loops increases as the knot tightens (i.e., as R decreases) for given number of loops, n. This indicates the correct qualitative behavior of the IC and OZ–PY approximations adopted here. Noninterating Gaussian representations of the entanglement necessarily yield an ellipticity of zero, regardless of the total number of loops and the tightness of the entanglement, and such a shortcoming seriously undermines the Gaussian estimates of $\langle R^{-1}\rangle$, which is highly sensitive to short-range monomer–monomer separations, particularly at large n. Again, Gaussian estimates of the mean reciprocal separations are strictly appropriate only for loops for which N_μ is very large, not for the finite loops with which we are concerned here. Of course, in the Rouse model in which hydrodynamic interaction is totally screened and entanglements entirely neglected, the diffusion coefficient is independent of the number of nodes or loops. On the basis of their Gaussian description, Matuschek and Blumen find that the diffusion coefficient grows as $n^{1/2}$, while experimentally[1] it is found that the diffusion coefficient of knotted DNA molecules in a gel shows a stronger linear dependence upon n. A consequence of their neglect of excluded-volume leads Matuschek and Blumen to the conclusion that the friction coefficient *vanishes* at large n since all the monomers are then concentrated in a pointlike central knot. Of course, these authors recognize that this is a shortcoming of their analysis, based as it is upon a tightly knotted Gaussian representation of the entanglement, and they attribute their weaker dependence of the diffusion coefficient to that observed experimentally at least in part to the neglect of excluded volume.

In Figure 4 we show the results of our excluded-volume IC estimates of the n dependence of the diffusion coefficient for three different tightnesses: $R = 3\sigma, 5\sigma, 10\sigma$, corresponding to progressive disentanglement of the central core region of the knot. The diffusion coefficient may be expressed in reduced form as

$$D^* = A + B\sum_i\sum_j\langle R_{ij}^{-1}\rangle$$

where

$$A = (N\zeta)^{-1}$$

$$B = (6\pi\eta_0 N^2)^{-1}$$

Rather than become involved with estimates of the parameters A and B, we concern ourselves here with $\sum\sum\langle R_{ij}^{-1}\rangle$, which contains all the n dependence of the system: this we plot against the number of loops n (Figure 4). Now, ideally we would wish to partition the total number of segments N in a given entanglement into various numbers n of loops. However, generally there will not be many (N_μ,n) combinations yielding precisely N, and so we have afforded ourselves a little latitude in choosing (N_μ,n) combinations that yield $N \pm \Delta$, where $\Delta \lesssim 5\%$. This allows us considerably more partitionings of $\sim N$ monomers into n loops, although at the price of some scatter in the calculated points. Even so, their distribution is quite systematic, rising slightly for $N+$ segments and falling for $N-$. A linear least-squares fit to the data yields a convincing linear dependence of the diffusion coefficient

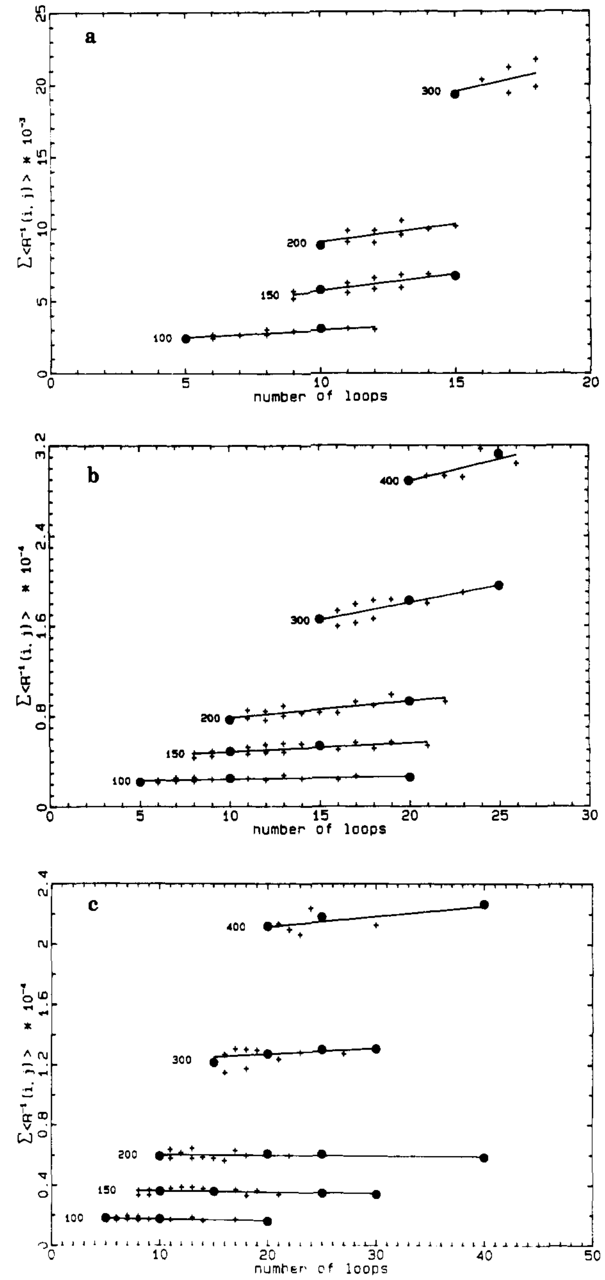

Figure 4. n (loop number) dependence of the mobility for hard-sphere entanglements for various confinements R of the key segments. The solid points represent loop partitionings of exactly N ($100 \leq N \leq 400$) monomers; the pluses represent loop partitionings for systems of $N \pm \Delta$ monomers where $\Delta < 5\%$. The data points appear consistent with a linear least-squares fit, suggesting an n^1 dependence, as observed experimentally. The results indicate an increasing sensitivity to n as the radius R of the central entanglement decreases: (a) $R = 3\sigma$, (b) $R = 5\sigma$, (c) $R = 10\sigma$.

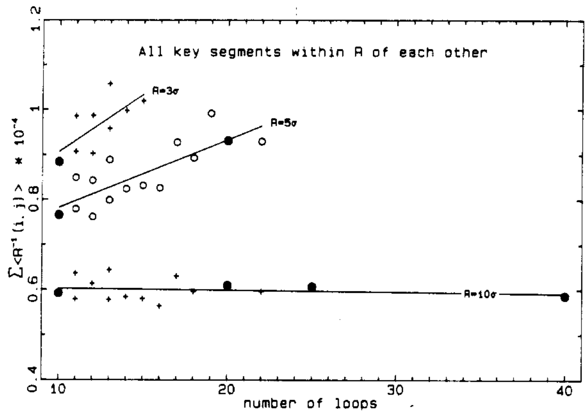

Figure 5. Increasing sensitivity to loop partitioning for self-avoiding entanglements of $N \sim 200$ hard-sphere monomers with increasing tightness of the central knot. The solid points correspond to systems of exactly N monomers.

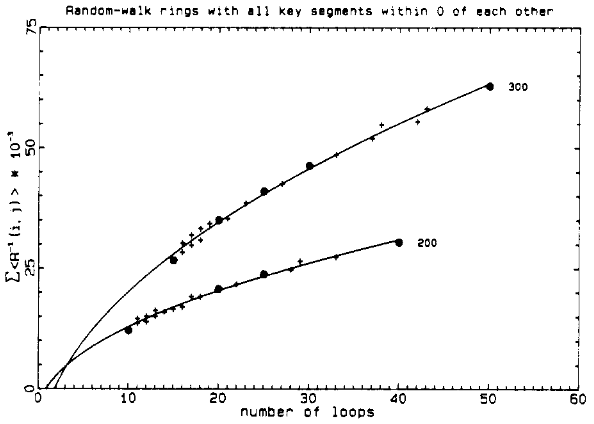

Figure 6. n (loop number) dependence of the mobility of random-walk loops for $R = 0$ corresponding to a tight central point knot. These results exhibit an $n^{1/2}$ dependence (confirmed by a logarithmic plot (Figure 7)) in concurrence with the results of Matuschek and Blumen. A least-squares fit to the data of the form $a + bn^{1/2}$ is indicated and is seen to fit well. The solid points correspond to systems of exactly N monomers.

upon loop number, as observed experimentally. Indeed, knots with a large number of nodes (for given N) diffuse faster because of the compactness of a knot with many nodes, and this too is observed experimentally. Moreover, we observe that with increasing tightness a given size entanglement shows an increasing sensitivity to the partitioning into loops, as would be expected intuitively (Figure 5). Conversely, as the entanglement relaxes (R increasing), the molecule presents a greater frictional aspect to the solvent and the diffusion coefficient decreases and ultimately shows an indifference to the partitioning of the entanglement into n loops.

In Figure 6 we show the corresponding IC results for the case of zero excluded-volume ($\sigma = 0$) with $R = 0$. The entanglement is again modeled as a system of coupled loops, although interference effects do not arise of course. The Matuschek and Blumen model closely corresponds to the case $R = 0$, the remaining distinction between the two treatments being attributable to their assumption of Gaussian statistics for the configurational estimates $\langle R_{ij}^{-1} \rangle$. It is apparent that for a knot of given molecular weight $\sum\sum\langle R_{ij}^{-1} \rangle$ is orders of magnitude larger than its excluded-volume counterpart—a feature we attribute directly to the much larger reciprocal separations arising when $\sigma = 0$. For $R = 3$ the calculated points remain consistent with a linear dependence upon n and the overall behavior is qualitatively similar to that of the excluded-volume systems, while at

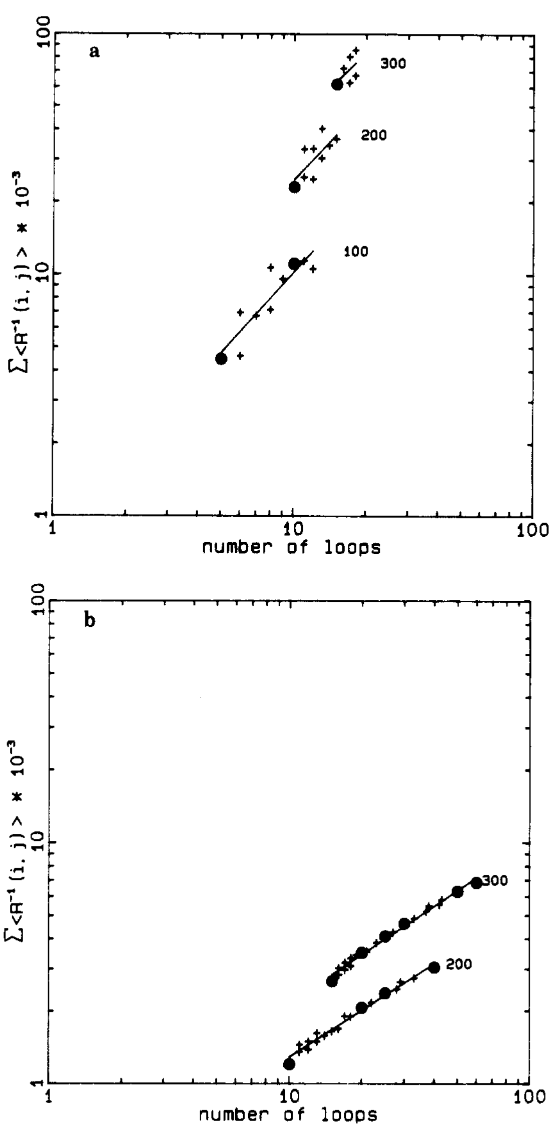

Figure 7. Logarithmic plots of the n dependence for hard-sphere and random-walk entanglements: (a) hard sphere, $R = 3$; (b) random walk, $R = 0$. All hard-sphere and random-walk systems having $R > 0$ exhibit an n^1 dependence, while for random-walk entanglements having $R = 0$ corresponding to a tight, point-like central knot, they show an $n^{1/2}$ dependence. The solid points correspond to systems of exactly N monomers.

$R = 0$ the zero excluded-volume system recovers the $n^{1/2}$ dependence predicted by Matuschek and Blumen. The logarithmic plots in Figure 7 clearly illustrate the two n dependences. We conclude that excluded-volume processes do not, in themselves, account for the linear n dependence of the mobility observed experimentally but that the *magnitude* of the diffusion coefficient does depend sensitively upon the excluded volume operating within the macromolecule.

The linear n dependence appears to be associated with the compactness of the central core region: the denser the core region the more solvent is excluded and the lower the friction coefficient. The weaker n dependence reported by Matuschek and Blumen would appear to arise from their underestimate of the development of the core region of the entanglement as n increases due to their assumption of a point knot. Certainly as our entanglements delocalize (R increasing) the n-dependence weakens and eventually the mobility becomes n-independent, regardless of excluded-volume effects. Presumably for sufficiently disentangled systems the knot becomes qualitatively indistinguishable from a linear nonentangled chain for which, of course, $n = 0$. The *magnitude* of the diffusion constant, however, remains a sensitive function of excluded volume.

As Matuschek and Blumen observe,[3] there should be many similarities between the diffusion of looped entanglements and star-branched molecules of functionality n. A number of workers[11] suggest that star molecules should have a diffusion coefficient proportional to $n \exp(C/n)$, where C is a positive constant. For sufficiently small C this would also yield a roughly linear dependence upon n, and Matuschek and Blumen surmise that an analysis along similar lines may well yield a theoretical result in better agreement with the experimental findings. However, we maintain that the inclusion of excluded-volume features together with a more realistic description of the configurational features of the entanglement yields the correct linear dependence upon n, as observed experimentally.

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References and Notes

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