NMR spectra give information about the configurational sequences (cotacticity).

Acknowledgment. The author expresses his gratitude to Mrs. A. Vliegen, Mrs. G. Kolfschoten, and Mr. J. Beulen for their enthusiastic assistance.

Registry No. VA–VC copolymer, 9003-22-9.

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On the Statistics and Dynamics of Confined or Entangled Stiff Polymers

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ABSTRACT: The statistics of a wormlike chain of persistence length P and contour length L trapped in a cylindrical pore of diameter D can be understood if a length scale $\lambda \simeq D^{2/3}P^{1/3}$ is introduced ($P \gg D$). If $L \lesssim \lambda$, it is a good approximation to view the chain as being completely rigid. Whenever $L \gg \lambda$, it is convenient to regard the stiff coil as a sequence of rigid links, each of length λ. The free energy involved in forcing a stiff chain into a pore is calculated by scaling arguments. When the chain is confined in a network of mesh size A, we again have $\lambda \simeq A^{2/3}P^{1/3}$. If $L \lesssim \lambda$, it is reasonable to approximate the chain as a completely stiff rod in its reptational and reorientational motion. Whenever $\lambda \lesssim L \lesssim P$, a new region emerges in between the rigid rod and flexible chain limits. Then, the rotational diffusion coefficient scales as L^{-2} instead of L^{-5} as in the rigid rod case. The usual L^{-3} dependence (flexible coil limit) is recovered if $L \gtrsim P$.

Introduction

In spite of its apparent complexity, the dynamics of entangled flexible chains is nowadays understood, semiquantitatively at least, thanks to the seminal ideas of de Gennes[1] and Edwards.[2] One can imagine one of the chains to be confined within a virtual tube[2] formed by the topological restrictions due to the surrounding coils. This test chain reptates, i.e., slithers back and forth along the tube because of Brownian motion, a process that implies a continual modification of the original tube at both its ends (see Chapter 8 of ref 3). Of course, one assumes the restrictive environment to remain fixed during the reptation time, the characteristic time scale of motion of the test chain, but this supposition appears to be reasonable.[4] These concepts have been developed into an extensive theory[5,6] although several authors[6–8] have attempted to amend the basic reptation mechanism because of the (slight) disparity between various theoretical and experimental exponents.[3,9]

Doi[10–12] applied the same reasoning to the dynamics of entangled, rigid rodlike macromolecules. His result is that the rotational diffusion coefficient, D_r, of the rods depends spectacularly on the rod length, L. Experimentally, this appears to be confirmed.[13–16] However, a closer look at the experiments proves that serious discrepancies arise, a fact in large part motivating our own work. At this stage, it is worthwhile to discuss this point in some detail. Zero and Pecora[16] have studied dilute and semidilute solutions of poly(γ-benzyl L-glutamate) in 1,2-dichloroethane by dynamic light scattering. The onset of entanglement as defined by a marked increase in the rotational diffusion coefficient, D_r, occurs at a concentration c^*_{exp} fully 2 orders of magnitude greater than the concentration c^* given by Doi and Edwards.[11] Moreover, the molecular weight dependence of c^*_{exp} is much less than that of c^*. In Figure 5 of ref 16, one can see that at a certain concentration, c^{**}, D_r apparently becomes independent of L. Zero and Pecora argue that the slopes instead of the absolute values within the region $c^*_{\text{exp}} < c < c^{**}$ should be used in order to test the Doi–Edwards theory, but this leaves the large finite value of D_r at c^{**} unexplained. Their equation (V.1) has no bearing on this problem because it refers to a zero value of D_r at a finite concentration. Assuming for the sake of argument that the slopes can be used, one ends up with a numerical discrepancy of the order of 1000 and a significantly smaller dependence of D_r on L. References 13–15 also clearly bear out the inadequacies of applying the congested rigid rod theory of Doi and Edwards to real systems.

One rationalization[17] has been to replace L by an effective smaller length ϵL with $\epsilon = \mathcal{O}(0.1)$. This implies that the rods will start hindering each other only at much higher concentrations. A further implication would be that 100 rods of length L enclosed in a volume of order L^3 are not entangled, which we feel is preposterous. A realistic value of ϵ is perhaps 0.5 but certainly not much lower.

Hydrodynamic screening has also been neglected.[18] This is expected to modify various features of the $D_r(L,c)$ function, but the discrepancies noted above are much too large to be explained in this way.

A third and very likely explanation is the influence of the slight flexibility of real macromolecules near the rod limit as has been alluded to previously.[13–18] Stiff polymers in solution always have a finite persistence length P. One would think that a polymer of length $L = 0.1P$, say, should always behave as a rigid rod. This notion turns out to be incorrect. We shall show that the basic rigidity length scale λ (which we shall call the deflection length) is a function of P and A if the chain is entangled in a network of mesh size A. Whenever $L \lesssim \lambda$, the wormlike polymer behaves effectively as a rigid rod. If $\lambda \lesssim L \lesssim P$, the rotational diffusion coefficient is independent of A and proportional to L^{-2}. The implication for the aforementioned measurements[16] is that an entangled region exists where no dependence of D_r on c should be measured, as is indeed the case. However, the results derived here are preliminary with respect to mutually entangled stiff chains.

In what follows, our objective is to consider the motion of one wormlike chain within a network. An understanding of the statistics obviously precedes the dynamics so we first analyze the equilibrium configurations of confined wormlike coils. The latter topic has in fact never been addressed before (as far as we are aware).

Statistics of Confined Stiff Chains

First, let us consider an unconfined wormlike chain described by the radius vector $\vec{r}(t)$ as a function of the contour distance t from one end to that point. We define the tangential unit vector

$$\vec{u}(t) = \partial\vec{r}(t)/\partial t \tag{1}$$

$$\vec{u}^2(t) = 1 \tag{2}$$

and we let $\vec{u}(0)$ point along the z axis of our Cartesian coordinate system (x, y, z). The statistics of the chain are derived via the free energy of curvature

$$\frac{\Delta F}{k_B T} = \frac{1}{2}P\int_0^L \left(\frac{\partial \vec{u}}{\partial t}\right)^2 \mathrm{d}t \tag{3}$$

where L is the contour length, P the persistence length, T the temperature and k_B Boltzmann's constant.

Yamakawa and Fujii have derived various averages for wormlike coils near the rod limit using eq 3. We shall need[19]

$$\langle \vec{r}^2(t)\rangle = t^2[1 - t/3P + \mathcal{O}(t^2P^{-2})] \tag{4}$$

$$\langle(\vec{r}(t)\cdot\vec{u}(0))^2\rangle = \langle z^2(t)\rangle = t^2[1 - t/P + \mathcal{O}(t^2P^{-2})] \tag{5}$$

Accordingly, the mean-square average deviation away from the z axis due to thermal fluctuations is given by

$$\langle\epsilon^2(t)\rangle = \langle x^2(t) + y^2(t)\rangle = 2\langle x^2(t)\rangle = 2t^3/3P \tag{6}$$

This expression is valid as long as t is rather smaller than P.

We now insert the wormlike chain into a very long cylindrical pore of diameter D. The pore's center axis is placed along the z axis, and we shall also suppose the pore to be relatively thin, i.e., $D \ll P$. Furthermore, it is assumed that the chain does not interact with the pore except for the hard wall repulsion at the pore surface.

A new length scale λ appears via eq 6 when we let the mean-square average deviation be of the same order as $(^1/_2D)^2$. This is the contour length at which the pore boundary starts influencing the wormlike chain statistics markedly.

$$\langle\epsilon^2(\lambda)\rangle \simeq (\tfrac{1}{2}D)^2 \tag{7}$$

$$\lambda^3 \simeq D^2P \tag{8}$$

If $L \lesssim {}^1/_2\lambda$, $\langle\epsilon^2(L)\rangle^{1/2} \ll D$. This implies that the behavior of a wormlike chain of length about ${}^1/_2\lambda$ or smaller is very similar to a completely stiff rod of the same length. When we consider all the possible configurations the stiff chain adopts, i.e., we let $\vec{u}(0)$ become unconstrained also, the very slight deviations from the rigid rod configuration can be neglected. They are, in fact, an order in magnitude smaller than those due to the orientational degrees of freedom allowed within the pore. By analyzing all the accessible configurations, we can readily derive the increase in free energy due to confinement

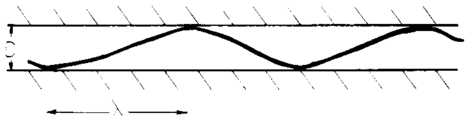

Figure 1. Stiff chain of contour length $L \simeq 0.3P$ trapped in a pore. Even this short piece does not exhibit rodlike behavior.

$$\Delta F_c/k_BT \simeq \ln{(L/D)^2} \qquad (L \lesssim \tfrac{1}{2}\lambda) \tag{9}$$

a result already implicit in Auvray's discussion of infinitely stiff rods.[20] Equation 9 follows from the fact that the number of degrees of freedom decreases from a constant times L^2 in free space to a constant times D^2 within the cylinder.

Starting again from the situation where $\vec{u}(0)$ points along the z axis, we now investigate what happens when we enlarge t beyond λ. First of all $\langle\epsilon^2(t)\rangle \lesssim D^2$ for all t. Hence, eq 6 becomes useless for $t \gtrsim \lambda$ (we are not concerned with the neglect of the higher order terms because $\lambda \ll P$). Equation 6 has of course been derived without taking into account the deflection of the chain by the boundary of the pore. If one realizes that the coil is extremely stiff on a length scale λ, one can immediately surmize that it is deflected back and forth by the cylinder boundary, the characteristic contour length between deflections being of the order of λ on the average (see Figure 1).

If this deflection length were to be much larger than λ, this would imply that the fluctuations were much smaller than those given by eq 6. At the other extreme, a much smaller deflection length would also disagree with eq 6 for in that case a piece of chain of length ${}^1/_2\lambda$, say, would not behave as a rigid rod.

It is plausible to replace the wormlike chain within a pore by a sequence of $L\lambda^{-1}$ links each of length λ. This is consistent as regards the statistical mechanical properties because $\langle\theta^2\rangle_\lambda$, the orientational deviation from the z direction, of such a link scales as $\langle\theta^2(t)\rangle$ at $t = \lambda$ for the original wormlike chain. The latter is given in ref 21 for the unrestricted wormlike chain.

$$\langle\theta^2(\lambda)\rangle \simeq \lambda/P \tag{10}$$

(This equation is correct for contour lengths up to about P for unconfined stiff chains.) Obviously, we have

$$\langle\theta^2\rangle_\lambda \simeq D^2/\lambda^2 \tag{11}$$

which corresponds to eq 10 because of eq 8.

To leading order, we can express the confinement free energy as follows

$$\Delta F_c/k_BT \simeq c_1 \ln{(\lambda/D)^2} + c_2(L/\lambda)\ln{(L/\lambda)} \qquad (\lambda \lesssim L \lesssim P) \tag{12}$$

where c_1 and c_2 are unknown constants of order unity.

The first term on the right-hand side of eq 12 is nothing but the free-energy difference due to the restriction of the first link as given by eq 9 with $L = \lambda$. In order to derive the second term, we first note that the nth link of an unrestricted chain has a mean-square-average orientation with respect to the first given by

$$\langle\theta_n^2\rangle = (n-1)\langle\theta^2\rangle_\lambda \tag{13}$$

A Gaussian law is expected because θ_n is a sum of n random angular displacements. Moreover, eq 13 must be consistent with the angular displacement of the wormlike chain as derived in ref 21 (see eq 10).

$$\langle\theta^2(\lambda n)\rangle \simeq n\lambda/P \qquad (n\lambda \lesssim P) \tag{14}$$

Hence, the decrease in orientational entropy, arising from confinement of the free chain within a pore, can be written as

$$\Delta S \simeq \int_1^{L/\lambda} \mathrm{d}n\, [\log \langle \theta_n{}^2 \rangle - \log \langle \theta^2 \rangle_\lambda] \qquad (15)$$

so that one finally obtains the L-dependent term in eq 12.

As one can see in the derivation of eq 12, it is valid for contour lengths up to about P. For $L \simeq P$ and $P \gg \lambda$, the first term is negligible compared to the second in view of eq 8. Hence, we have

$$\Delta F_c / k_B T \simeq P/\lambda \ln (P/\lambda) \qquad (L = P, P \gg \lambda) \qquad (16)$$

It is easy to obtain the confinement free energy of chains longer than a persistence length. First of all, such an expression must reduce to eq 16 when $L = P$. Second, $\Delta F_c/k_BT$ should be "extensive" whenever the contour length is long enough.[3] In solution, the correlation function expressing the degree of orientational correlation along a stiff chain as a function of contour distance decays with characteristic length P.[21]

$$\langle \vec{u}(t) \cdot \vec{u}(s) \rangle = e^{-|t-s|/P} \qquad (17)$$

Accordingly, whenever $|t - s| \gg P$, the respective chain sections are statistically independent. The same is true for those sections of the stiff chain within the pore that are separated by λ or more. Thus, the confinement free energy should scale as

$$\Delta F_c / k_B T \simeq (L/\lambda) \ln (P/\lambda) \qquad (L \gtrsim P, P \gg \lambda) \qquad (18)$$

If one were to regard the stiff chain in solution as a freely jointed coil of L/P rigid links each of length P and then force such a coil into a pore, one would obtain an expression of the form

$$\Delta F_c / k_B T \simeq (L/P) \ln (P/D)^2 \qquad \text{(incorrect)} \qquad (19)$$

This was derived previously by the author in an unpublished communication. As pointed out by Casassa,[22] eq 19 is a generalization of his own result in ref 23. The reason eq 18 and 19 differ, is that one is not allowed to replace a wormlike chain by another model in an ad hoc way.

Another conceptual difference between the wormlike chain model and the freely jointed link model with link length P is the folding energy, which is zero for the latter when it is forced into a pore. However, the presence of even one "U-turn" for a stiff chain within a cylinder is highly unlikely if $D \ll P$. In that case, its free energy increases by an amount derived with the help of eq 3

$$\frac{\Delta F_f}{k_B T} \geq \tfrac{1}{2} P \int_0^{\frac{1}{2}\pi D} \frac{1}{(\frac{1}{2}D)^2}\, \mathrm{d}t = \frac{\pi P}{D} \qquad (20)$$

which is much larger than unity.

Finally, we note that in eq 18 only an orientational confinement free energy has been taken into account. In reality a spatial confinement term has been neglected. Thus, if we set $D \simeq P$, i.e., $\lambda \simeq P$ in eq 18, we have $\Delta F_c \simeq 0$, which is obviously wrong. If $D \gg P$, a wormlike chain has the same statistical behavior as a Gaussian coil. In the latter case, the confinement free energy is given by[3,24,25]

$$F_c / k_B T \simeq LP/D^2 \qquad (21)$$

From eq 21 one might say that eq 18 has corrections of the order LP^{-1}, which are negligible whenever $P \gg \lambda$. However, a scaling law with a smooth crossover to eq 21 for $D \simeq P$ is impossible because eq 20 implies an additional physical phenomenon precisely at the crossover, viz., lateral folding of the chain.

The scaling analysis presented above is of course fairly limited so a consideration of the distribution functions is certainly called for. As yet, we have not been able to satisfactorily resolve some of the tricky problems associated with the Fokker–Planck type equation[26] for wormlike chains under restrictions of interest to the present work. Nevertheless, at this stage, we can dwell on some dynamical problems.

Reptation and Reorientation of an Entangled Stiff Chain

(a) Rigid Rod Limit. It is useful to briefly rederive the rotational diffusion coefficient D_r for an infinitely stiff, thin rod of length L trapped in a network of characteristic mesh size A. This has been discussed by Doi[10,11] for a mesh of entangled rods and more fully by de Gennes[27] who considered a polymer melt as a network.

At first a test rod is confined by a certain virtual tube of length L and diameter of about A. After a reptation time T_{rep}, it has just left this tube, being now enveloped by a new one. The mean-square-average angular deviation $\langle \theta^2 \rangle$ of the rod during the time T_{rep} is given by

$$\langle \theta^2 \rangle \simeq A^2/L^2 \qquad (22)$$

This results if one assesses the orientational freedom within the original tube. One might suppose that $\langle \theta^2 \rangle$ may well be rather larger because the virtual tubes are actually full of holes of average size A. Thus, if the rod has diffused laterally along a distance A, there would be a nonzero chance of it already slipping into a new tube at an angle $\langle \theta^2 \rangle^{1/2}$ given by eq 22. However, such an event has a very low probability whenever $A \ll L$, and a detailed calculation shows this effect to be negligible.

The reptation time can be expressed as[27]

$$T_{\mathrm{rep}} \simeq \eta_0 L^3 / k_B T \qquad (23)$$

where η_0 is the viscosity of the solvent and not of the gel. The third power dependence on L is explained as follows: (a) the translational friction on a rod should be proportional to L; (b) the time dependence arising from the rod diffusing over its own length should vary as L^2. Dimensional analysis yields the remaining parameter dependence in eq 23.

If the reptational process occurs n times, the total mean-square-average angular deviation of the rod from its original orientation will amount to $n\langle \theta^2 \rangle$. In effect, successive deviations are uncorrelated so we have a Gaussian random process. The reorientational time equal to D_r^{-1} is determined by the condition $n\langle \theta^2 \rangle \simeq 1$. Hence, from eq 22 and 23, we have[27]

$$D_r \simeq A^2 k_B T / \eta_0 L^5 \qquad (24)$$

As pointed out by de Gennes,[27] eq 24 holds only if the usual rotational diffusion is much slower than that described by eq 24, i.e., $D_{\mathrm{rot}} > k_B T/\eta_n L^3$ where η_n is the solution viscosity.

(b) Wormlike Chains. Equation 24 is directly applicable to stiff chains trapped in the same sort of network provided L is short enough

$$D_r \simeq A^2 k_B T / \eta_0 L^5 \quad A \lesssim L \lesssim \lambda;\ A \ll P \qquad (25)$$

where

$$\lambda \simeq A^{2/3} P^{1/3} \qquad (26)$$

which follows from eq 8 and the tacit assumption that the statistics pertain to a stiff chain trapped in an effective tube of diameter A. Equation 25 is valid because the angular deviations due to the finiteness of the persistence

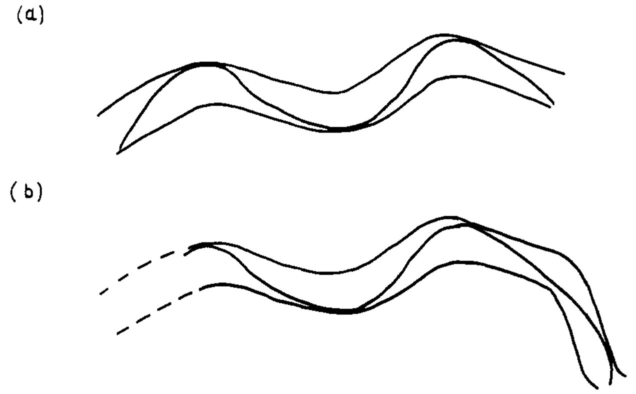

Figure 2. (a) Wormlike chain trapped in a virtual tube due to the confining network. Both coil and tube are characterized by sections of length λ. (b) Modification of (a) after a time T_λ. The chain has shifted along a length of order λ, into a new section of tube.

length are swamped out by those of the whole chain as given by eq 22.

Next we discuss the rotational diffusion of stiff chains longer than the deflection length λ but still shorter than the persistence length P. Our concern here is the general motion on rather long time scales. At any instant the chain statistics is that of equilibrium. Accordingly, our guiding principle is that a wormlike chain within a network viewed at any time is required to obey the statistics described by eq 1–3. In particular, correlation functions of the type given in eq 17 (with $|t - s| \gg \lambda$) determine the chain (and hence the enveloping tube) configurations.

As shown in the previous section, the coil can be conveniently replaced by a sequence of $L\lambda^{-1}$ links of length λ, the angle between successive links being given by eq 11 with A instead of D. After a time T_λ, the chain has diffused along a length λ (see Figure 2). The translational friction is proportional to L whereas a factor of λ^2 arises because the lateral motion is diffusional. Hence, we have

$$T_\lambda \simeq \eta_0 L \lambda^2 / k_B T \qquad (27)$$

Only two links have slightly altered direction during T_λ, the other $(L\lambda^{-1} - 2)$ links remaining in the original tube. Accordingly, the average angular deviation can be expressed as $\lambda L^{-1} \langle \theta^2 \rangle_\lambda \simeq A^2 \lambda^{-1} L^{-1}$. With the aid of eq 26 and 27, we arrive at the following expression for the rotational diffusion coefficient:

$$D_{\rm rot} \simeq k_B T / \eta_0 P L^2 \qquad \lambda \lesssim L \lesssim P \qquad (28)$$

This result can also be derived in a different way. Let the chain reptate over half its own length. One of the chain ends is now situated at the midpoint of the original tube. The orientational deviation $\langle \theta^2 \rangle$ from its original position is given by eq 17, which can be rewritten as eq 10 for $L \lesssim P$

$$\langle \theta^2 \rangle \simeq L/P \qquad P \gtrsim L \gtrsim \lambda \qquad (29)$$

(The numerical coefficient $^1/_2$ has been omitted.) As stated above, the new configuration obeys the usual configurational statistics. The midsection of the coil has an angular deviation from the end point, and thus from its original position, also described by eq 29. (Note that it is now not at the original position of the other end.) Hence, to leading order, the orientational deviation of the whole chain from its original position is given by eq 29. The (semi)reptation time again scales as eq 23 because its derivation holds for any type of linear chain (as long as it is smooth enough). In this way we recover eq 28 via the reasoning used in deriving eq 24.

Several remarks concerning eq 28 are in order: (a) It is valid as long as the reptational–rotational motion is faster than the rotational movement through the viscous gel, i.e., $D_r > k_B T / \eta_n L^3$. (b) Equation 28 matches correctly to eq 24 if $L = \lambda$ as can be seen from eq 26. Equation 28 is incorrect for $L \lesssim {}^1/_2\lambda$. (c) When $L > P$, we should regain the reptational motion of flexible chains.[1,3,5,32]

$$T_{\rm rep}^{-1} \simeq D_r \simeq k_B T / \eta_0 L^3 \qquad L \gtrsim P \qquad (30)$$

This scales correctly with eq 28 when $L = P$.

Concluding Remarks

As is well-known especially because of the work of Casassa,[23–25,28] restriction of the configuration space of polymers plays a major role in determining the distribution or partition coefficient, the ratio of the average pore to bulk concentrations,

$$K = C_p / C_\infty$$

Another factor is the concentration itself.[29,30] For dilute solutions, K for stiff chains in microporous membranes with relatively well-defined cylindrical pores can be evaluated from eq 9, 16, and 18. One might test the theory by measuring the diffusion of double-stranded DNA at high ionic strength through such membranes. Recently, Cannell and Rondelez[31] have attempted to verify the predictions of Daoud and de Gennes[30] by using a flexible polymer such as polystyrene.

Equations 19, 16, and 18 are easily generalized to the case of slitlike pores. In addition, they will be useful in formulating scaling theories of stiff chain adsorption to flat plates as well as the interaction between plates in a solution of wormlike coils.

Equations 24 and 28 can, perhaps, be confirmed by transient electric birefringence of short DNA in, say, a polyacrylamide gel. It will be interesting to see whether there is indeed such a remarkable difference in L dependence in the respective regions as well as a crossover at $A^{2/3}P^{1/3}$.

It is, of course, tempting to transpose the notions of the previous section to the case of a solution of mutually entangled stiff chains. As is now well recognized,[3] such a transposition, even for flexible chains with $A \gg P$, has a number of conceptual difficulties. Accordingly, the following remarks are rather tentative.

First of all, we must ascertain whether P depends on the concentration when $A \ll P$. Real polymers have a finite diameter d so conceivably P might not be invariant. However, Hayter et al.[34] have pointed out that the (strong) interchain interactions in semidilute polyelectrolyte solutions lead to a persistence length of the same order of magnitude as that due to intrachain interactions.[35–37] (The persistence length is derived from a balance between intrachain interactions and thermal energy in dilute solutions,[21,35,36] whereas, otherwise, the fluctuating background of other chains causes random bending forces analogous to the usual thermal excitations.[34]) In the polyelectrolyte case, $A \simeq \kappa^{-1}$ (the Debye length), and also, $d \simeq \kappa^{-1}$.[34,37] Hence, if $d \ll A$ as in the uncharged polymer solution in the isotropic phase, interchain interactions should have almost no influence on P.

Next, we must calculate the mesh size A. For rigid rods, Doi[10,11] has derived the following expression

$$A \simeq 1/cL^2 \qquad (31)$$

based on an equation for the number of rods $N(A_c)$ that envelop a test rod within a distance A_c

$$N(A_c) \simeq c A_c L^2 \qquad (32)$$

i.e., Doi chooses $N(A_c) \simeq 1$ and sets $A \simeq A_c$. Such a choice is rather arbitrary, and one might consider larger values of N and A. In the stiff chain case, the choice of N and A is even more problematic. As can be seen in Figure 1, the number of entanglements (N) along a tube confining a certain wormlike chain must be much larger than $L\lambda^{-1}$,

$$N\lambda \gg L \tag{33}$$

Hence, from eq 26 and 32, we must have

$$cA^{5/3}P^{1/3}L \gg 1 \tag{34}$$

where we have set $A \simeq A_c$ in a rough approximation, and assumed that eq 32 still holds. Equation 34 shows at once that the orientation mechanism of the previous section is useless unless we know that $A(c)$ is large enough. Thus, we need a more detailed theory of the structure of the virtual tube (i.e., a theory of $A(c)$) before we can apply the results of this paper to concentrated stiff polymer solutions.

Just after this paper was written, we received two preprints related to our own work. Doi[38] has derived eq 28 (as well as the numerical coefficient) by analyzing the orientational correlation functions via his method outlined in ref 5. Basically, his conclusions concerning the dynamics of stiff chains in networks are the same as ours. We disagree with Doi on his speculative explanation of the irrelevance of those conclusions to a description of mutually entangled stiff polymers.

The interesting simulation work of Frenkel[39,40] on the dynamic properties of dilute and entangled thin needles in vacuum shows that a critical concentration c^* given by L^{-3} underestimates the real c^*_{comp} by an order of magnitude. Although one might be skeptical about the bearing of these results on the dynamics of dissolved rodlike polymers, it is noteworthy that Doi's same scaling idea[10] can be used for a gas of needles.[39] However, as noted in the Introduction, we need to explain at least two orders of magnitude in c^*/c^*_{exp} so our feeling is that there is still an essential gap in our understanding of almost or fully rigid polymer dynamics.

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