Topological Origin of Reptation: A Collective Motion of Local Knots

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ABSTRACT: The local-knot model proposed in previous works is extended to include the Brownian motion of polymer chains. As a model of Brownian motion, the so-called "local-jump model" is used. It is shown that the diffusion constant for a local knot is given by $D_{\xi\xi} = K\delta(\nu_l)^{1/2}$, where K is a universal constant near unity, ν_l, the average size of the local chains, and δ, a new molecular constant named the "topological diffusion parameter", which is expressed in terms of jump probability p_J and displacement $\Delta_J\xi$ of a local chain by jump J. The reptation is assigned to a collective motion of local knots along a polymer chain. It is found that there is no direct correlation among reptations of different polymer molecules. The disengagement time τ_d and the sedimentation constant D_s are computed; the results are $\tau_d = N^3/\pi^2K\delta\nu_l^{3/2} \sim M^3/M_l^{3/2}$ and $D_s = \bar{b}^2K\delta(\nu_l)^{1/2}/3Nn_l \sim M_l^{3/2}/M^2$, where $\bar{b}$ is the effective bond length, N the length of the polymer chains, and n_l the number of the local chains per polymer molecule and M and M_l are the molecular weight of the polymer and local chains. The M dependence of τ_d and D_s agrees with but M_l (or M_e) dependence is different from that of the Doi–Edwards theory. The M_l dependence is further transformed into concentration dependence: $\delta\tau_d \sim c^{1.3-1.5}$ and $D_s/\delta \sim c^{-1.3--1.5}$. The molecular origin of reptation is argued, and a question is presented on the basic assumption of the Doi–Edwards theory that the diffusion constant of reptation is given by $k_BT/N\zeta_0$.

I. Introduction

A. Background. The concept of reptation has been applied to the viscoelastic and transport properties of concentrated polymer solutions and melt with great success. In 1971, de Gennes[1] proposed the reptation model of a polymer chain that is allowed to move in a rigid tube formed by surrounding chains. A major result of the theory is the prediction of sedimentation constant D_s of a reptating polymer chain, $D_s \sim M^{-2}$. Doi and Edwards[2] later applied this model to the viscoelastic properties; their results are summarized in their recent monograph.[3] One of the difficulties of the reptation theory is the predicted viscosity law $\eta \sim M^3$, which conflict the experimental law, $\eta \sim M^{3.4}$; a similar discrepancy occurs in the terminal relaxation time τ_e.[3] A few modifications of the model have been proposed to improve the M dependence of η and τ_e; Doi[4] considers contour length fluctuation of the tube, and Klein[5] considers configurational change of the tube due to constraint release in the intermediate part of a polymer chain (tube renewal); the latter model was further developed by Daoud and de Gennes[6] and Graessley.[7] These are partial modifications of the reptation theory, but the concept of reptation itself is subjected to criticism, because it is based on the extremely simplified model of polymer motion.

The formulation of reptation from a more fundamental physical basis has been presented by Curtiss and Bird,[8] Hess,[9] and Fixman.[10] Starting form kinetic equations in the full phase space of many chains, these authors derived diffusion equations in the curvilinear spaces parallel and orthogonal to the contours of the polymer chains; the reptation is assigned to the motion in the parallel direction. Curtiss and Bird[8] assumed that the diffusion coefficients in the parallel and orthogonal direction are different and show that the model goes from the Rouse to reptation-like as the orthogonal friction increases with increase of M and c. Hess[9] obtained a similar result for a polymer model with the excluded volume but without ad hoc assumptions; his theory however remains a difficulty in that entanglement disappears in the Θ state. Fixman[10] assumed a drag force due to the surrounding polymer matrix on a probe chain moving along the chain contour and obtained $D_s \sim M^{-2}$ and $\eta \sim M^{3.5}$, which agree with experiments. It will however be shown in this work that there is no direct correlation among reptations of different polymer chains. Although these authors presented different ways of formulating reptation, the origin of reptation is still not understood well. Recently, Kolinski et al.[11] performed computer simulations of condensed polymers and found that a probe chain moves more in the orthogonal direction than in the parallel direction, in contradiction to the assumption of the tube model. Further studies are necessary to understand the origin and nature of reptation.

In this series of works, entanglement is studied from a more basic physical foundation. We consider that entanglement is topological in nature and that it has a relationship to much wider properties of polymers than the viscoelastic and transport phenomena; they should include at least the rubber elasticity of network polymers and various properties of ring polymers. All of these problems should be treated by a unified theory of entanglement, but the tube model is not sufficient for it. As for the ring polymers, there have so far been two experimental data that may be connected to their topological behavior, i.e., the abnormality of the Θ temperature and the second virial coefficients of the dilute solutions of ring polystyrene[12] and the formation of catenated polymers,[13] in each of which the tube model seems to be inoperative. We have so far constructed a topological theory of entanglement, in which topological invariants such as the Gauss integral (GI) are considered explicitly in the statistical mechanical equations; the theory covers a wide range of the entanglement phenomena such as the dynamics of weakly entangled polymers,[14] the elastic and thermodynamic properties of network polymers,[15] and dilute solution properties of ring polymer.[16] Recently, we have proposed a new entanglement model, "the localized Gauss integral model", which is applied to the plateau time region[22] of highly entangled polymers. By definition, application of the theory is limited to quasi-equilibrium quantities, such as G_N or M_e measured in the plateau region. In this work, this model is extended to include the

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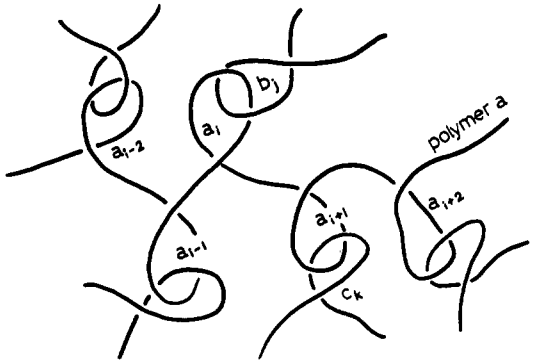

Figure 1. Entanglement of chain a divided into local knots, (a_i, b_j), (a_{i+1}, c_k), ...

Brownian motion of polymer chains.

B. Local-Knot Model (Localized Gauss Integral Model). Before discussing the main subject of this work, we first review the physical background of the local-knot model presented in the previous papers.[17] This model was previously called the "localized Gauss integral model", but it will hereafter be called "local-knot model", because the latter name seems to represent more directly the nature of the model. This model is based on the assumption that entanglement of concentrated polymer chains, which looks very complicated as a whole, may be decomposed into local two-body entanglements (local knots) as shown in Figure 1. In the figure, each polymer chain, say a, is divided into many "local chains", ..., a_i, a_{i+1}, ..., which are entangling with other local-chains, b_j, c_k, ... to form local knots (a_i, b_j), (a_{i+1}, c_k), ... In principle, more complex knots formed by three or more local chains will appear, but they may be neglected because their occurrence probabilities are far smaller than that of the two-body knots. The entanglement state of a local knot (a_i, b_j) is represented by the GI

$$T_{a_i b_j} = \frac{1}{4\pi}\int_{a_i}\int_{b_j} \frac{[\dot{\mathbf{r}}_{a_i}(s) \times \dot{\mathbf{r}}_{b_j}(s')][\mathbf{r}_{a_i}(s) - \mathbf{r}_{b_j}(s')]}{|\mathbf{r}_{a_i}(s) - \mathbf{r}_{b_j}(s')|^3}\, ds\, ds' \tag{1}$$

where $\mathbf{r}_{a_i}(s)$ and $\mathbf{r}_{b_j}(s')$ are vector coordinates of points s and s' on the local chains and the integrations are performed along their contours. It is convenient to divide the local chains into submolecules p, q, ... and rewrite eq 1 as follows:

$$T_{a_i b_j} = \sum_{p\in a_i}\sum_{q\in b_j} \Theta_{pq} \tag{2}$$

where Θ_{pq} is the GI in regard to submolecular pair (p, q). Let us consider how the entanglement state of (a_i, b_j), which is initially in state A of Figure 2, changes into B or C; clearly, the whole entanglements of a or b must be untied before changing the enganglement state of (a_i, b_j). In the previous work,[17] the local chains are defined in the so-called "plateau time region", which is longer than τ_e, the onset time of entanglement restriction, but sufficiently shorter than τ_d, the disengagement time of the tube model.[3] It is assumed that, in this time region, GIs of the all local knots should be conserved as an average or, more precisely, they should fluctuate around integer number 0, 1, 2, ... according to their state B, A, C, ...; this phenomenon was called the "localization of GI" in the previous work.[17] When the local knots are conserved they behave like cross-links and form a transient network all over the system. As the time passed beyond the plateau time region, "reptation" begins and renewal of local knots occurs initially at the terminal and then proceeds to the inner parts of polymer

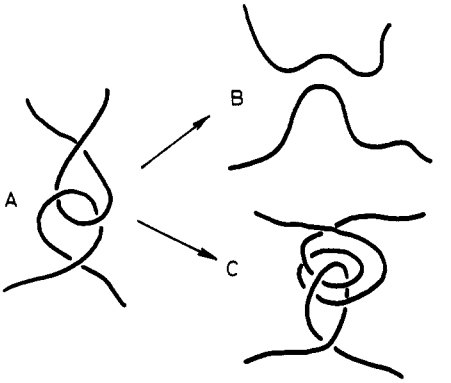

Figure 2. Various topological states of a local knot; state A cannot be changed into B or C unless the whole entanglements of the polymer chains are untied.

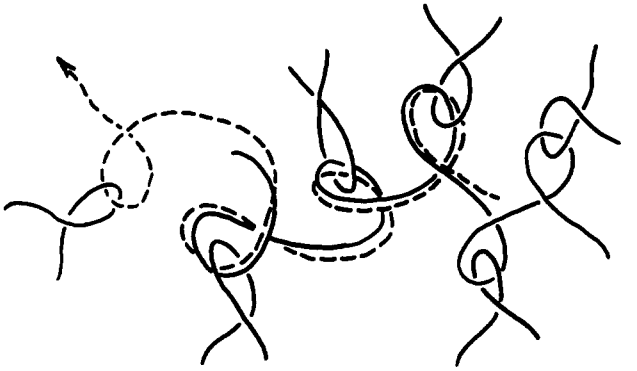

Figure 3. "Reptation" in the local-knot model.

chains as shown in Figure 3. The local-knot model is therefore a type of the transient network models of entanglement.[22]

Now, equilibrium distribution function of $T_{a_i b_j}$ is computed by the same method as used in the ring and network polymers.[16,15] It was shown in the previous works[16,17] that $P(T,\mathbf{r})$, the probability density for $T_{a_i b_j}$ to take value T under the condition that the distance between the centers of a_i and b_j is equal to $\mathbf{r}$, is expressed in terms of contact probabilities among the submolecules. The expression of $P(T,\mathbf{r})$ contains a new molecular parameter called the "topological interaction parameter γ", which is defined by[16,17]

$$\gamma = \langle \Theta_{pq}^2 \rangle / \bar{b}^3 z^2 \tag{3}$$

where z is the number of main-chain bonds per submolecule and $\bar{b}$ is the effective bond length. In the previous work,[17] it is assumed that (a_i, b_j) forms a local knot when $|T_{a_i b_j}|$ is larger than a certain positive number $T_0 \sim 0.5$; T_0 was equated to 0.5 in the previous work, but generally speaking, it should be considered as an adjustable parameter near 0.5. The probability density $\epsilon(\mathbf{r})$ for (a_i, b_j) to form a local knot is given by

$$\epsilon(\mathbf{r}) = \int_{|T|\geq T_0} P(T,\mathbf{r})\, dT \tag{4}$$

The average molecule weight, M_l, of the local chains is determined by

$$(c/M_l)\int \epsilon(\mathbf{r})\, d\mathbf{r} = 1 \tag{5}$$

where c is the weight concentration. The left-hand side of eq 5 represents the average number of entanglement partners per local chain; eq 5 indicates that M_l is determined so that each local chain entangles with exactly one other local chain as an average. By definition, M_l

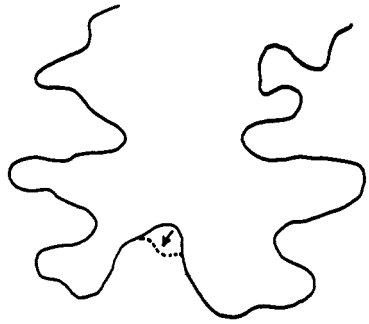

Figure 4. Local-jump model of polymer motion.

represents the molecular weight between adjacent entanglements, which is usually identified with the empirical parameter

$$M_e = ck_BT/G_N \tag{6}$$

According to the previous work,[17] M_1 is roughly equal to the two-thirds of M_e:

$$M_1 \approx 0.65M_e \tag{7}$$

This model has been applied to the calculation of G_N, and the parameter γ is determined for many polymers by using their bulk G_N.[17] Now, we consider the dynamics of the local-knot model.

II. Motion of Local Knots in a Frozen Matrix of Ring Chains

First, we consider a simple system composed of a linear chain moving in a matrix of ring chains; the rings are models of local knots and have random conformations, and their molecular weight is determined by eq 5. To simulate the Browninan motion of highly entangled polymers, we assume that the rings are frozen and only the linear chain is allowed to move in the matrix. As elementary processes of the Brownian motion, we consider the so-called "local-jump model", in which the motion of polymer chains is generated by Markoffic jumps in their small parts (local jumps) as shown in Figure 4. In this model, hydrodynamic interactions among segments are neglected, and the model should be applied to highly concentrated or melt polymers alone. This model has been used in computer simulations of entangled polymers.[11,18,20,21] In this model, chains are restricted on a lattice, say, a simple cubic lattice, on which their Brownian motion is generated by a set of rules of local jumps; Figure 5 shows an example of local-jump J that has been used in the computer simulations.[18,20,21] In application of this model to our systems, it is necessary that the average size, n_J, of chains taking part in the local jumps is sufficiently smaller than that of the local chains (or rings in this section); this requirement seems to be satisfied in the most entangled systems.

It is convenient to imagine that we are performing a computer simulation. In the simulation, it is required that no polymer chain should cross each other during the local jumps. This requirement is naturally satisfied in our model by considering the change of T_{a_ib} induced by the local jumps, where a_i is the ith local chain of a, and b is one of the rings. Now suppose that jump J occurs in a *nonterminal* part of a_i, changing its partial conformation α into α' as shown in Figure 6A. Since T_{a_ib} is an line integral along a_i and b, it is written after the jump as follows:

$$\int_{a'_i}\int_b = \int_{a_i}\int_b + \int_{\bar{\alpha}\alpha'}\int_b \tag{8}$$

where a'_i is the contour of a_i after the jump and $\bar{\alpha}\alpha'$ is the loop formed by $\bar{\alpha}$ (which is the same as α but has the opposite direction) and α'. Note that the integration along $\bar{\alpha}$ in the second term on the right-hand side of eq 8 cancels exactly the integration along α in the first term. The first term on the right-hand side represents T_{a_ib} before the jump, and the second term represents its variation induced. The second term must be equal to zero by the definition of GI, since b and $\bar{\alpha}\alpha'$ are loops and never linked together from the requirement that no polymer chains should go across each other during the local jumps; i.e.

$$\Delta T_{a_ib} \equiv \int_{a'_i}\int_b - \int_{a_i}\int_b = \int_{\bar{\alpha}\alpha'}\int_b = 0 \tag{9}$$

This is the topological restrictive condition in our model. (In fact, if crossing occurred during a local jump, loops b and $\bar{\alpha}\alpha'$ would be linked together and ΔT_{a_ib} would be equal to ± 1, which is as large as T_{a_ib} itself; see Figure 7.) When a jump occurs in a *terminal* part of a_i, on the other hand, ΔT_{a_ib} is not zero but takes a considerable value, because $\bar{\alpha}\alpha'$ is no longer a loop (see Figure 6B). This means that T_{a_ib} changes only when local jumps occur in the terminal

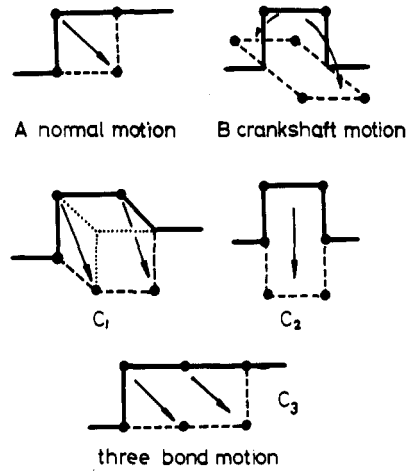

Figure 5. Elementary processes of the simple cubic lattice model. Normal motion A alone is considered in the original Verdier's model;[18,34] crankshaft motion B is added to by Kovac;[19,20] three-bond motions C_1, C_2, and C_3 are further added by Kolinski et al.[21]

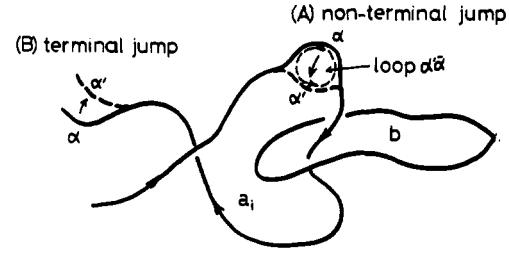

Figure 6. Local-jumps occurring in a_i. In nonterminal jump A, $\alpha'\alpha$ forms a complete loop, whereas in a terminal jump B, $\alpha'\bar{\alpha}$ is not a loop. For nonterminal jump A, $\Delta_J T_{a_ib} = 0$, and for a terminal jump B, $\neq 0$. The arrows represent direction of the integrations in the definition of GI.

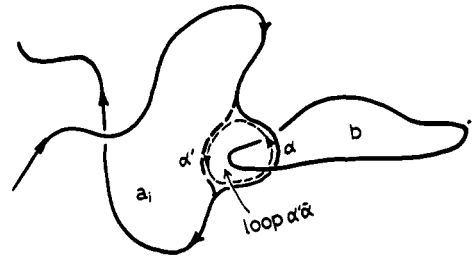

Figure 7. Inhibited local jump. If crossing occurred during a local jump, loop $\alpha'\bar{\alpha}$ would be linked to b as shown in the figure. For this jump, $\Delta_J T_{a_ib} = \pm 1$. The arrows represent direction of the integrations in the definition of GI.

parts or that the motion of $T_{a_i b}$ is very slow, since terminal jumps occur seldom.

It is difficult however to treat the large change of $T_{a_i b}$ induced by the terminal jumps. We therefore modify the definition of $T_{a_i b}$ slightly, so that both terminal and nonterminal jumps lead to a small and steady variation of $T_{a_i b}$. First, we consider that local chain a_i is composed of main-chain bonds, $\mathbf{b}_j$, rather than submolecules, p; this modification is necessary when indicating the exact position of local jumps along chain a. In accordance with this modification, $\Theta_{p,q}$ appearing on the right-hand side of eq 2 is replaced by $\theta_{j,p}$, the GI in regard to the main-chain bond $\mathbf{b}_j$ of chain a and submolecule p of ring b. Second, the head positions of the local chains are indicated by continuous number ξ instead of integer number i. In the original definition of the local chains, main-chain bonds (or submolecules) have an equal weight, but in the modified version, they are multiplied by the following weight factor:

$$U_{j,\xi} = \begin{cases} \sin[\pi(j-\xi)/\nu_1] & \text{for } \xi \le j \le \xi + \nu_1 \\ 0 & \text{otherwise} \end{cases} \quad (10)$$

where j is the index of the main-chain bonds and ν_1 is the average number of main-chain bonds per local chain. In this definition, the weight factors of the terminal bonds are so small that terminal jumps scarcely contribute to the motion of the local chains. Hereafter, local chains are designated by a_ξ, and the modified GI for pair (a_ξ, b) is defined by

$$T_{a_\xi b} = \sum_{j \in a} \sum_{p \in b} U_{j,\xi} \theta_{j,p} \quad (11)$$

where the summations should be performed over all main-chain bonds in a and submolecules in b. We can generally show that the variation of $T_{a_\xi b}$ induced by local jumps is always of the order of n_J/ν_1 for both terminal and nonterminal jumps. To show this, we consider the local jumps shown in Figure 5. When a jump occurs at a terminal part of a local chain, it does not contribute to the motion of $T_{a_\xi b}$ since the weight $U_{j,\xi}$ is almost zero at the terminals. When jump A in Figure 5 occurs at nonterminal element j, $\theta_{j-1,p}$ and $\theta_{j,p}$ jump to $\theta'_{j-1,p}$ and $\theta'_{j,p}$ and the variation of $T_{a_\xi b}$ is given by

$$\Delta_J T_{a_\xi b} = \sum_{p \in b} [U_{j-1,\xi}(\theta'_{j-1,p} - \theta_{j-1,p}) + U_{j,\xi}(\theta'_{j,p} - \theta_{j,p})] = U_{j-1,\xi} \sum_{p \in b} (\theta'_{j-1,p} + \theta'_{j,p} - \theta_{j-1,p} - \theta_{j,p}) + (U_{j,\xi} - U_{j-1,\xi}) \sum_{p \in b} (\theta'_{j,p} - \theta_{j,p}) \quad (12)$$

Sum $\sum_{p \in b}(\theta'_{j-1,p} \pm \theta'_{j,p} - \theta_{j-1,p} - \theta_{j,p})$ is just equal to the GI for loop b and $\alpha\alpha'$ and disappears exactly because $\alpha\alpha'$ never links to b (see Figure 6). With use of eq 10, eq 12 is rewritten by

$$\Delta_J T_{a_\xi b} \approx (\pi/\nu_1) U'_{j,\xi} \sum_{p \in b} (\theta'_{j,p} - \theta_{j,p}) \sim \nu_1^{-1} \quad (13)$$

where

$$U'_{j,\xi} = \cos[\pi(j-\xi)/\nu_1] \quad (14)$$

Generally, jump J changes $\theta_{j,p}$ into $\theta'_{j,p}$ ($j_c - n_J/2 < j \le j_c + n_J/2$), and the variation of $T_{a_\xi b}$ associated with this jump is given by

$$\Delta_J T_{a_\xi b} \approx (\pi/\nu_1) U'_{j_c,\xi} \sum_{j \in J} \sum_{p \in b} (k - j_c)(\theta'_{j,p} - \theta_{j,p}) \sim n_J/\nu_1 \quad (15)$$

where j_c is the central element of jump J and $\sum_{j \in J}$ is the summation over the all bonds that are changed by jump J. It is important that the topological restrictive condition, eq 9, is a necessary condition in deriving eqs 13 and 15. The condition eq 9 is therefore equivalent to stating that $\Delta T_{a_\xi b}$ should be of the order n_J/ν_1. Since $|\Delta_J T_{a_\xi b}|$ is much smaller than $|T_{a_\xi b}|$ itself, we may expect that the Fockker–Planck equation holds in the the diffusion motion of $T_{a_\xi b}$. From this consideration, a simultaneous diffusion equation for the Rouse coordinates and "entanglement coordinates", which are equivalents to the present $T_{a_\xi b}$ was derived and the sedimentation constant was computed in the previous work.[14] In that work, however, the localization of the GI has been neglected and the theory should be applied to weakly entangled systems (i.e., $c < c_c$ or $M < M_c$) alone. In highly entangled systems as considered here, localization of the GI occurs and the reptation motion appears; in such system, we must take a different approach as describe now.

First, we consider how to find the local chains and how to determine their positions, ξ, along the chain in an imaginary computer simulation. When conformations of the all-polymer chains are given, we can calculate $T_{a_\xi b}$ for any ξ and ν_1, where ξ is an unknown variable and ν_1 ($=M_1/M_0$) has been already determined by eq 5. As the lower limit of fluctuation of $T_{a_\xi b}$, the appropriate value $T_{\min}$ (which must be smaller than T_0) is assumed, and if $T_{a_\xi b}$ satisfies condition

$$|T_{a_\xi b}| \ge T_{\min} \quad (16)$$

pair (a_ξ, b) is nominated as a local knot. Position ξ is determined by the following condition:

$$\partial T_{a_\xi b}/\partial \xi = 0 \quad (17)$$

If assumed $T_{\min}$ is too large, some local knots will be overlooked, while if it is too small, too many false local knots will be listed as local-knot candidates. In the computer simulation, a rather small value of $T_{\min}$ is assumed and the evolution of a time average of $T_{a_\xi b}$ is observed; if (a_ξ, b) is a false local knot, time average of $T_{a_\xi b}$ will decrease rapidly to zero and it is removed from the list. Repeating this process, we can in principle find the all local knots in the system. In this theory, however, $T_{\min}$ does not appear explicitly and it is sufficient to note that local knots are certainly determined in this manner.

Now, let $\Delta_J T_{a_\xi b}$ and $\Delta_J \xi$ be respectively the changes of $T_{a_\xi b}$ and ξ induced by jump J. By the jump, $T_{a_\xi b}$ moves to $T'_{a_\xi b} = T_{a_\xi b} + \Delta_J T_{a_\xi b}$, of which the first derivative in regard to ξ at point $\xi' = \xi + \Delta_J \xi$ is written

$$\frac{\partial T'_{a_\xi b}}{\partial \xi'} = \frac{\partial T_{a_\xi b}}{\partial \xi} + \Delta_J \xi T^{(\xi\xi)} + \Delta_J T^{(\xi)} + \dots \quad (18)$$

where $T^{(\xi\xi)}$ and $\Delta_J T^{(\xi)}$ are derivatives of $T_{a_\xi b}$ and $\Delta_J T_{a_\xi b}$ in regard to ξ:

$$T^{(\xi\xi)} = \frac{\partial^2 T_{a_\xi b}}{\partial \xi^2}, \quad \Delta_J T^{(\xi)} = \frac{\partial \Delta_J T_{a_\xi b}}{\partial \xi}, \quad \text{etc.} \quad (19)$$

The left-hand side of eq 18 disappears, since eq 17 holds also at point ξ'. Since the first terms on the right-hand side of eq 18 disappear, $\Delta_J \xi$ is given in the first order of $\Delta_J T^{(\xi)}$ by

$$\Delta_J \xi = -\Delta_J T^{(\xi)}/T^{(\xi\xi)} = U_{j_c,\xi} \sum_{j \in J} \sum_{p \in b} (j - j_c)(\theta'_{j,p} - \theta_{j,p})/T_{a_\xi b} \quad (20)$$

Now, *if $\Delta_J \xi$ is a simple Markoffic process*,[25] the diffusion constant for the Brownian motion of ξ along chain a is

given by

$$D_{\xi\xi} = {}^1/_2\langle \sum_{J\in a_\xi} p_J(\Delta_J\xi)^2\rangle_{a_\xi b} \tag{21}$$

where p_J is the probability for jump J to occur in unit time, $\sum_{J\in a_\xi}$ is the summation over all possible local jumps in a_ξ, and $\langle\ \rangle_{a_\xi b}$ represents the average over equilibrium configuration of a_ξ and b. Although we have assumed that the surrounding ring chains are frozen, the average in regard to the conformation of b is necessary because we consider the average behavior of numerous systems that have an equivalent topological state. Introducing eq 20 into the right-hand side of eq 21, we find the following term:

$$\sum_{p\in b}\sum_{p'\in b}\langle Y_{Jp}Y_{Jp'}\rangle_{a_\xi b} \tag{22}$$

where

$$Y_{Jp} = \sum_{j\in J}(j - j_c)(\theta'_{j,p} - \theta_{j,p}),\quad \text{etc.} \tag{23}$$

At this point, we note that Y_{Jp} is a quantity very similar to Θ_{pq}. In the equilibrium topological problems,[16,17] the similar quantity $\langle\Theta_{pq}\Theta_{p'q'}\rangle$ appears, for which we have introduced the following approximation:

$$\Theta_{pq}\Theta_{p'q'} \approx \begin{cases}\langle\Theta_{pq}{}^2\rangle\delta(\mathbf{d}_{pq}) & \text{for } p = p' \text{ and } q = q'\\ 0 & \text{otherwise}\end{cases} \tag{24}$$

where $\mathbf{d}_{pq}$ is the distance vector between the centers of p and q. This approximation comes from the following: (1) $\langle\Theta_{pq}\Theta_{p'q'}\rangle$ disappears rapidly with increase of $|p - p'|$ and $|q - q'|$ and, when the submolecules are sufficiently large, $\langle\Theta_{pq}{}^2\rangle$ alone is significant; (2) $\Theta_{pq}{}^2$ decreases as $|\mathbf{d}_{pq}|^{-4}$. Since Y_{Jp} is almost like Θ_{pq}, we can use a similar approximation:

$$Y_{Jp}Y_{Jp'} \approx \begin{cases}\langle Y_{Jp}{}^2\rangle\delta(\mathbf{d}_{j_cp}) & \text{for } p = p'\\ 0 & \text{otherwise}\end{cases} \tag{25}$$

where $\mathbf{d}_{j_cp}$ is the distance vector between the centers of jump J and submolecule p, and $\langle\ \rangle$ is an average over the equilibrium conformation of p. With use of eq 25, $D_{\xi\xi}$ is rewritten by

$$D_{\xi\xi} = \delta_1 C(\nu_1) \tag{26}$$

with

$$\delta_1 \equiv \frac{1}{2z\bar{b}^3}\sum_{j\ \text{at}\ j_c} p_J P_J^0\langle Y_{Jp}{}^2\rangle \tag{27}$$

$$C(\nu_1) \equiv (z\bar{b}^3/T_{a_\xi b}{}^2)\sum_{j\in a_\xi}\sum_{p\in b} U_{j,\xi}{}^2 P_{a_\xi b}(O_{jp}) \tag{28}$$

where P_J^0 is the equilibrium probability of appearing such configurations that permit jump J, $P_{a_\xi b}(O_{jp})$ is the contact probability between bond $\mathbf{b}_j$ of a_ξ and submolecule p of b, $\sum_{j\ \text{at}\ j_c}$ is the summation over all jumps in which the central bond is $\mathbf{b}_{j_c}$, and z is the size of the submolecules. Replacing submolecule p by bond $\mathbf{b}_j$ of ring chain b, eq 28 is rewritten by

$$C(\nu_1) = (\bar{b}^3/T_{a_\xi b}{}^2)\sum_{j\in a_\xi}\sum_{k\in b} U_{j,\xi}{}^2 P_{a_\xi b}(O_{jk}) \tag{29}$$

where $P_{a_\xi b}(O_{jk})$ is the contact probability between $\mathbf{b}_j$ and $\mathbf{b}_k$. Although we have so far considered the modified local chain, in which $\mathbf{b}_j$ are multiplied by weight factor $U_{j,\xi}$, it is more consistent to replace a_ξ by a ring chain of the same size as b, since a_ξ and b are both models of the local chains. Approximating $P_{a_\xi b}(O_{jk})$ by the contact probability between elements of two rings of length ν_1, $(9/\pi\nu_1\bar{b}^2)^{3/2}$, and omitting $U_{j,\xi}$ on the right-hand side of eq 29, we find

$$C(\nu_1) = (9/\pi)^{3/2}\nu_1{}^{1/2}/T_{a_\xi b}{}^2 \approx 4.849\nu_1{}^{1/2} \tag{30}$$

In obtaining the numerical coefficient, we have considered that $|T_{a_\xi b}|$ is roughly equal to unity by definition.

Another quantity, δ_1, must be independent of the size of the submolecules, z, since $D_{\xi\xi}$ and $C(\nu_1)$ are both independent of z. It is also independent of ν_1. In these points, δ_1 resembles parameter γ and it is hereafter called the "topological diffusion parameter". They are both molecular parameters characterizing topological features of polymers. The main difference is that γ is almost independent of the environmental parameters (T, c, or the free volume of the system),[16,17] while δ dependents strongly on them, since its expression contains jump probability p_J. In the computer simulations,[18,20,21] the unit of time is chosen such that all kinds of local jumps are tried once per bond per unit time; in this definition, p_J is roughly given by the probability for destination sites to be vacant, or

$$p_J \approx (1 - c)^{n_J - 1} \tag{31}$$

For example, let us consider Kovac's model,[19,20] in which normal motion A and crankshaft motion B (Figure 5) are considered. In this work, it is sufficient to consider motion A alone, since B seldom occurs.[19] We then have

$$\delta_1 \approx 0.8(1 - c)\gamma'$$
$$\gamma' = \langle(\theta_{jp}' - \theta_{jp})^2\rangle/2z\bar{b}^3 \approx \langle\theta_{jp}{}^2\rangle/z\bar{b}^3 \approx \gamma \tag{32}$$

where γ is defined by eq 3. Diffusion coefficient $D_{\xi\xi}$ is then given by

$$D_{\xi\xi} \approx 3.879(1 - c)\gamma\nu_1{}^{1/2}$$

(Kovac's model in frozen matrix) (33)

At this point, one may ask why crankshaft motion B, which plays a very important role in Kovac's model, does not contribute to the diffusion of the local knots. This question will be answered in section V. Finally we point out that $D_{\xi\xi}$ is proportional to $\nu_1{}^{1/2}$ or that long local chains are more mobile than short ones; this agrees with our experience that loose knots are more easily untied than tight knots.

III. Motion of Local Knots in Many-Chain Systems

Now, we consider more general systems composed of linear chains entangling strongly with each other. Let a_ξ and b_η be local-chains of a and b, respectively, which are forming a local knot and of which head positions local at ξ and η. For simplicity, we neglect the fluctuation of the size of the local chains and assume that it is always equal to ν_1. In analogy with eq 11, a modified GI for the local chain pair (a_ξ, b_η) is defined by

$$T_{a_\xi b_\eta} = \sum_{j\in a}\sum_{k\in b} U_{j,\xi}U_{k,\eta}\theta_{jk} \tag{34}$$

where $U_{j,\xi}$'s are the weight defined by eq 10 and θ_{jk} is the GI in regard to bond $\mathbf{b}_j$ (of a) and $\mathbf{b}_k$ (of b). When jump J_a occurs in a_ξ or jump J_b in b_η, variations of $T_{a_\xi b_\eta}$ are given by

$$\Delta_{J_a} T_{a_\xi b_\eta} \approx U_{j_c,\xi} \sum_{k\in b} U_{k,\eta} X_{J_a k} + (\pi/\nu_1) U_{j_c,\xi}' \sum_{k\in b} U_{k,\eta} Y_{J_a k}$$

$$\Delta_{J_b} T_{a_\xi b_\eta} \approx (\pi/\nu_1) U_{k_c,\eta}' \sum_{j\in a} U_{j,\xi} Y_{J_b j} + U_{k_c,\eta} \sum_{j\in a} U_{j,\xi} X_{J_b j} \tag{35}$$

with

$$X_{J_a k} = \sum_{j\in J_a} (\theta_{jk}' - \theta_{jk})$$
$$X_{J_b j} = \sum_{k\in J_b} (\theta_{jk}' - \theta_{jk})$$
$$Y_{J_a k} = \sum_{j\in J_a} (j - j_c)(\theta_{jk}' - \theta_{jk})$$
$$Y_{J_b j} = \sum_{k\in J_b} (k - k_c)(\theta_{jk}' - \theta_{jk}) \tag{36}$$

where j_c and k_c are respectively the central bonds of jump J_a and J_b. $Y_{J_a k}$ and $Y_{J_b j}$ are essentially the same quantities as Y_{Jp} introduced in section II (cf. eq 23), and $X_{J_a k}$ and $X_{J_b j}$ are the GI in regard to the loops formed by the local jumps and bond $\mathbf{b}_j$ or $\mathbf{b}_k$. In section II, the first terms on the right-hand side of eq 35 disappear because one of the local chains is a complete loop and is frozen, and its bonds are multiplied by an equal weight; in the present systems, however, they do not disappear because the local chains are not loops, both being in motion, and their bonds are multiplied by uneven weight U. We note here that

$$X_{J_a k} \sim d_{j_c k}^{-3} \tag{37}$$

where $d_{j_c k}$ is the distance between the center of jump J_a and bond $\mathbf{b}_k$. Since $X_{J_a k}$ and $X_{J_b j}$ decrease more rapidly than θ_{jk} ($\sim d_{jk}^{-2}$) or $Y_{J_a k}$ ($\sim d_{j_c k}^{-2}$), only such bonds that come very close to the center of the local jumps contribute significantly to the first terms on the right-hand side of eq 35. Let j^* and k^* be *locally* nearest bonds to the center of jump J_b and J_a, respectively, and let p and q be such parts of chains, of length z, that are composed of bond $\mathbf{b}_j$ ($j^* - z/2 < j \le j^* + z/2$) of chain a or $\mathbf{b}_k$ ($k^* - z/2 < k \le k^* + z/2$) of chain b. The term "*locally* nearest" means that $\mathbf{b}_{j^*}$, say, is the nearest bond to the center of J_b in part p but not necessarily the nearest one in a_ξ; there may be many locally nearest bonds in a_ξ. The first terms on the right-hand side of eq 35 are now rewritten as follows:

$$\sum_{j_c\in a_\xi} \sum_{k\in b_\eta} U_{j_c,\xi} [U_{k^*,\eta} \sum_{k\in q} X_{J_a k} + \sum_{k\in q} (U_{k,\eta} - U_{k^*,\eta}) X_{J_a k}] \tag{38}$$

where $\sum_{k^*\in b_\eta}$ is the summation over the all locally nearest bonds in b_η. Sum $\sum_{k\in q} X_{J_a k}$ represents the GI for q and loop $\alpha\alpha'$ and should almost disappear because $\alpha\alpha'$ is much smaller than q. Neglecting the first term in the brace of eq 38, eq 35 is rewritten by

$$\Delta_{J_a} T_{a_\xi b_\eta} \approx (\pi/\nu_1)[U_{j_c,\xi} \sum_{k^*\in b_\eta} U_{k^*,\eta}' Y_{J_a q}' + U_{j_c,\xi}' \sum_{k\in b_\eta} U_{k,\eta} Y_{J_a k}]$$

$$\Delta_{J_b} T_{a_\xi b_\eta} \approx (\pi/\nu_1)[U_{k_c,\eta} \sum_{j^*\in a_\xi} U_{j^*,\xi}' Y_{J_b p}' + U_{k_c,\eta}' \sum_{j\in a_\xi} U_{j,\xi} Y_{J_b j}] \tag{39}$$

with

$$Y_{J_a q}' = \sum_{k\in q} (k - k^*) X_{J_a k} \qquad Y_{J_b p}' = \sum_{j\in p} (j - j^*) X_{J_b j} \tag{40}$$

Now, the head positions of the local chains, ξ and η, are determined by the following local maximum conditions:

$$\partial T_{a_\xi b_\eta}/\partial\xi = 0, \quad \partial T_{a_\xi b_\eta}/\partial\eta = 0 \tag{41}$$

The local jumps lead the Brownian motions of a_ξ and b_η along a and b. Let $\Delta_J T_{a_\xi b_\eta}$, $\Delta_J\xi$, and $\Delta_J\eta$ be respectively the change of $T_{a_\xi b_\eta}$, ξ, and η induced by jump J, where J is either J_a or J_b. By jump J, $T_{a_\xi b_\eta}$ moves to $T_{a_\xi b_\eta}' = T_{a_\xi b_\eta} + \Delta_J T_{a_\xi b_\eta}$, of which first derivatives at point $\xi' = \xi + \Delta_J\xi$ and $\eta' = \eta + \Delta_J\eta$ are written as

$$\frac{\partial T_{a_\xi' b_\eta'}}{\partial \xi'} = \frac{\partial T_{a_\xi b_\eta}}{\partial \xi} + \Delta_J\xi T^{(\xi\xi)} + \Delta_J\eta T^{(\xi\eta)} + \Delta_J T^{(\xi)} + \dots$$

$$\frac{\partial T_{a_\xi' b_\eta'}}{\partial \eta} = \frac{\partial T_{a_\xi b_\eta}}{\partial \eta} + \Delta_J\xi T^{(\eta\xi)} + \Delta_J\eta T^{(\eta\eta)} + \Delta_J T^{(\eta)} + \dots \tag{42}$$

where $T^{(\xi\xi)}$, $T^{(\xi\eta)}$, $\Delta_J T^{(\xi)}$, etc., are derivatives of $T_{a_\xi b_\eta}$ at point ξ and η:

$$T^{(\xi\xi)} = \frac{\partial^2 T_{a_\xi b_\eta}}{\partial\xi^2}, \quad T^{(\xi\eta)} = \frac{\partial^2 T_{a_\xi b_\eta}}{\partial\xi\,\partial\eta}, \quad \Delta_J T^{(\xi)} = \frac{\partial \Delta_J T_{a_\xi b_\eta}}{\partial\xi}, \quad \text{etc.} \tag{43}$$

The left-hand side of eq 42 disappears, since eq 41 should hold at point ξ' and η'. Since the first terms on the right-hand side of eq 42 also disappear, $\Delta_J\xi$ and $\Delta_J\eta$ are given in first order of $\Delta_J T^{(\xi)}$ and $\Delta_J T^{(\eta)}$ as follows:

$$\Delta_J\xi = -\frac{T^{(\eta\eta)}\Delta_J T^{(\xi)} - T^{(\eta\xi)}\Delta_J T^{(\eta)}}{T^{(\xi\xi)}T^{(\eta\eta)} - (T^{(\xi\eta)})^2} \approx -\Delta_J T^{(\xi)}/T^{(\xi\xi)}$$

$$\Delta_J\eta = -\frac{T^{(\xi\eta)}\Delta_J T^{(\xi)} + T^{(\xi\xi)}\Delta_J T^{(\eta)}}{T^{(\xi\xi)}T^{(\eta\eta)} - (T^{(\xi\eta)})^2} \approx -\Delta_J T^{(\eta)}/T^{(\eta\eta)} \tag{44}$$

In obtaining these equations, we have considered that $T^{(\xi\eta)}$ is far smaller than $T^{(\xi\xi)}$; this is shown as follows: (1) With use of eq 10, we find

$$T^{(\xi\xi)} = T^{(\eta\eta)} = (\pi/\nu_1)^2 \sum_{j\in a_\xi} \sum_{k\in b_\eta} U_{j,\xi} U_{k,\eta} \theta_{jk} = (\pi/\nu_1)^2 T_{a_\xi b_\eta}$$

$$T^{(\xi\eta)} = (\pi/\nu_1)^2 \sum_{j\in a_\xi} \sum_{k\in b_\eta} U_{j,\xi}' U_{k,\eta}' \theta_{jk} \tag{45}$$

(2) The sum appearing in the expression of $T^{(\xi\xi)}$ is just equal to $T_{a_\xi b_\eta}$, which is of the order of unity, while that in $T^{(\xi\eta)}$ almost disappears because $U_{j,\xi}'$ and $U_{k,\eta}'$ have a node that leads cancellation in the summations in regard to j and k. Now, *if $\Delta_J\xi$ and $\Delta_J\eta$ are simple Markov process*,[25] diffusion constants associated with their motions are given by

$$D_{\xi\xi} = {}^1/_2\{\sum_{J_a\in a_\xi} p_{J_a} \langle[\Delta_{J_a}\xi]^2\rangle_{a_\xi b_\eta} + \sum_{J_b\in b_\eta} p_{J_b} \langle[\Delta_{J_b}\xi]^2\rangle_{a_\xi b_\eta}\} = D_{\eta\eta}$$

$$D_{\xi\eta} = {}^1/_2\{\sum_{J_a\in a_\xi} p_{J_a} \langle\Delta_{J_a}\xi\Delta_{J_a}\eta\rangle_{a_\xi b_\eta} + \sum_{J_b\in b_\eta} p_{J_b} \langle\Delta_{J_b}\xi\Delta_{J_b}\eta\rangle_{a_\xi b_\eta}\} \tag{46}$$

where p_{J_a} and p_{J_b} are occurrence probabilities of J_a and J_b, and $\langle\ \rangle_{a_\xi b_\eta}$ is an average over all possible configuration of the local chains. $D_{\xi\eta}$ is the off-diagonal element of the diffusion coefficient tensor for reptation motions of a_ξ and b_η, and its magnitude represents the degree of correlation between them.

Insertion of eqs 39 and 44 into the right-hand side of eq 46 leads generally to such terms as $\langle Y_{J_a k} Y_{J_a k'}\rangle_{a_\xi b_\eta}$ and

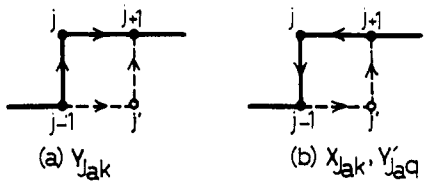

Figure 8. Different symmetries of X_{J_ak}, Y_{J_ak}, and Y'_{J_aq} for normal motion A. Y_{J_ak} represents line $j-1 \rightarrow j+1$, while X_{J_ak} and Y'_{J_aq} represent loop $j-1 \rightarrow j' \rightarrow j+1 \rightarrow j \rightarrow j-1$; due to this difference, $\langle Y_{J_ak} Y'_{J_aq} \rangle$ disappears.

$\langle Y_{J_aq} Y_{J_aq'} \rangle_{a_\xi b_\eta}$. The latter term, $\langle Y_{J_aq} Y_{J_aq'} \rangle_{a_\xi b_\eta}$, should disappear or at least should be far smaller than the former, because Y_{J_ak} and $Y_{J_aq'}$ belong to different symmetry classes as shown in Figure 8. In analogy with eq 25, we can use

$$Y_{J_aq'} Y_{J_aq'} \approx \begin{cases} \langle (Y_{J_aq'})^2 \rangle \delta(\mathbf{d}_{j_cq}) & \text{for } q = q' \\ 0 & \text{otherwise} \end{cases} \quad (47)$$

With use of eqs 25 and 47, we find

$$D_{\xi\xi} = {}^1/_2 \sum_{J_a \in a_\xi} p_{J_a} \{ \sum_{k^* \in b_\eta} (U_{j_c,\xi}' U_{k^*,\eta}')^2 P(O_{j_c k^*}) \langle (Y_{J_aq'})^2 \rangle + \sum_{k \in b_\eta} (U_{j_c,\xi} U_{k,\eta})^2 P(O_{j_c k}) \langle (Y_{J_ak})^2 \rangle \} + {}^1/_2 \sum_{J_b \in b_\eta} p_{J_b} \{ \sum_{j^* \in a_\xi} (U_{j^*,\xi} U_{k_c,\eta})^2 P(O_{j^* k_c}) \langle (Y_{J_bp'})^2 \rangle + \sum_{j \in a_\xi} (U_{j,\xi}' U_{k_c,\eta}')^2 P(O_{j k_c}) \langle (Y_{J_bj})^2 \rangle \}$$

$$D_{\xi\eta} = {}^1/_2 \sum_{J_a \in a_\xi} p_{J_a} \{ \sum_{k^* \in b_\eta} U_{j_c,\xi} U_{j_c,\xi}' U_{k^*,\eta} U_{k^*,\eta}' P(O_{j_c k^*}) \langle (Y_{J_aq'})^2 \rangle + \sum_{k \in b_\eta} U_{j_c,\xi} U_{j_c,\xi}' U_{k,\eta} U_{k,\eta}' P(O_{j_c k}) \langle (Y_{J_ak})^2 \rangle \} + {}^1/_2 \sum_{J_b \in b_\eta} p_{J_b} \{ \sum_{j^* \in a_\xi} U_{j^*,\xi} U_{j^*,\xi}' U_{k_c,\eta} U_{k_c,\eta}' P(O_{j^* k_c}) \langle (Y_{J_bp'})^2 \rangle + \sum_{j \in a_\xi} U_{j,\xi} U_{j,\xi}' U_{k_c,\eta} U_{k_c,\eta}' P(O_{j k_c}) \langle (Y_{J_bj})^2 \rangle \} \quad (48)$$

where $P(O_{jk})$'s are contact probabilities between bonds $\mathbf{b}_j$ and $\mathbf{b}_k$. All summations appearing in the expression of $D_{\xi\eta}$ have the form $\sum_{j \in a_\xi} U_{j,\xi} U_{j,\xi}'$ or $\sum_{k \in b_\eta} U_{k,\eta} U_{k,\eta}'$, which disappear exactly since U and U' have different symmetries. Hence, we find the following important result:

$$D_{\xi\eta} = 0 \quad (49)$$

This equation indicates that *there is no frictional drag among reptations of polymer chains even if they are entangling strongly with each other.*[26] This seems to be natural, considering that the contours of a_ξ and b_η are random walks, which are almost independent of each other, and $\Delta_J \xi$ and $\Delta_J \eta$ are measured along these contours.

Quantity $P(O_{j_c k^*})$ is the contact probability between $\mathbf{b}_{j_c}$ and $\mathbf{b}_{k^*}$, where $\mathbf{b}_{k^*}$ is the central bond of short chain q. We may then introduce the following substitution into the right-hand side of eq 48:

$$\sum_{k^* \in b_\eta} P(O_{j_c k^*}) \rightarrow \sum_{q \in b_\eta} P(O_{j_c q}) \rightarrow z^{-1} \sum_{k \in b_\eta} P(O_{j_c k}), \quad \sum_{J_a \in a_\xi} \rightarrow \sum_{j_c \in a_\xi} \sum_{J \text{ at } j_c} P_J^0 \quad (50)$$

where $\sum_{J \text{ at } j_c}$ is the summation over all local jumps of which central bonds is $\mathbf{b}_{j_c}$, and P_J^0 is the equilibrium probability of occurrence of such conformations that permit jump J. By these substitutions, we find

$$D_{\xi\xi} = \delta C(\nu_1) \quad (51)$$

with

$$\delta = \delta_1 + \delta_2$$

$$C(\nu_1) = C_1(\nu_1) + C_2(\nu_1) \quad (52)$$

δ_1 is defined by eq 27, and δ_2, $C_1(\nu_1)$, and $C_2(\nu_1)$, by

$$\delta_2 = (2z^2 \bar{b}^3)^{-1} \sum_{J \text{ at } j_c} p_J P_J^0 \langle (Y'_{J_q})^2 \rangle \quad (53)$$

$$C_1(\nu_1) = (\bar{b}^3 / T_{a_\xi b_\eta}{}^2) \sum_{j \in a_\xi} \sum_{k \in b_\eta} (U_{j,\xi} U_{k,\eta})^2 P_{a_\xi b_\eta}(O_{jk})$$

$$C_2(\nu_1) = (\bar{b}^3 / T_{a_\xi b_\eta}{}^2) \sum_{j \in a_\xi} \sum_{k \in b_\eta} (U'_{j,\xi} U'_{k,\eta})^2 P_{a_\xi b_\eta}(O_{jk}) \quad (54)$$

Quantity δ_2 is similar to δ_1, and C_1 and C_2 to C introduced in section II. By definition, $D_{\xi\xi}$ must be independent of z, since it is chosen arbitrarily. Since δ_1, C_1, and C_2 are all independent of z, so must be δ_2. Both δ_1 and δ_2 are determined by the chemical structure of polymer chains and the environmental parameters but independent of the topological state of the system. Quantity δ defined by eq 52 is the "topological diffusion parameter" in the many chain systems. In section II, δ_1 has been computed for Kovac's model,[19] but calculation of δ_2 is difficult and needs much computational work, which will be done in future papers. The other quantity, C, is almost the same as that introduced in section II (cf. eqs 29 and 30). Generally we get $C(\nu_1) = K(\nu_1)^{1/2}$ or

$$D_{\xi\xi} = K \delta \nu_1{}^{1/2} \quad (55)$$

where K is an universal constant of $O(1)$ and is independent of polymer species and environment.

Let us consider again that all chains other than a are frozen and only a is allowed to move. In this case, the diffusion constant of a_ξ is given by the terms come from jump J_a alone on the right-hand side of eqs 46 or 48; hence

$$D_{\xi\xi} = \delta_1 C_1(\nu_1) + \delta_2 C_2(\nu_1) \quad \text{(in frozen matrix)} \quad (56)$$

The first term is essentially identical with $D_{\xi\xi}$ of the model in section II. The second term represents correction due to the incomplete topological restriction of the matrix of this section (i.e., the matrix is made of ring chains in section II, while it consists of linear chains in this section). Considering the nature of these models, we may expect that the second term is similar to the first term. When chain b also moves, it gives extra term $\delta_1 C_2 + \delta_2 C_1$, which is similar to the right hand side of eq 56. Thus, the motion of local knots in a mobile matrix is faster than but similar to that in a frozen matrix. Equation 55 again shows that $D_{\xi\xi}$ of large local chains is larger than that of smaller ones or that loose knots are more easily untied than tight knots.

IV. Reptation: Collective Motion of Local Knots

A. Diffusion Constant of Reptation. Now, let us consider a collective motion of the local knots along chain a. Suppose that local chain a_{ξ_1}, a_{ξ_2}, a_{ξ_3}, ..., distribute along a in this order as shown in Figure 9. As the local chains move at random along a, they may overlap each other and may even go across their neighbors temporally, but their order must be conserved as an average. This means that repulsive forces act among neighboring local chains. These forces come from higher topological invariants that have so far been neglected. To see the origin of the repulsive forces, suppose that two neighboring local chains, a_i and a_{i+1}, along a form local knots with surrounding local chain b_j and c_k, respectively, as shown in Figure 1. In the real systems, two-body topological invariants (such as GI) as

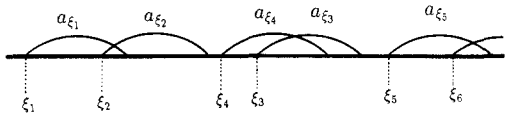

Figure 9. Transient arrangement of local chains, a_{ξ_1}, a_{ξ_2}, ..., on polymer a; ξ_1, ξ_2, ..., represent the head positions of the local chains in the index-number space of the main-chain bonds. The local chains may overlap with each other and may even go across their neighbors (as a_{ξ_3} and a_{ξ_4} in the figure) transiently, but their overall order must be conserved until the whole entanglement of a is unknotted.

well as three- and four-body invariants among a_i, a_{i+1}, b_j, and c_k should be conserved. Although we do not know at present how to treat such higher invariants, it seems evident that they keep the average order of the local chains along polymer chains and thus introduce effective repulsive forces among neighbors. In this work, however, we do not need the explicit form of these forces. When n_l particles (or local-chains in this case) diffuse on a line (or along a polymer chain), keeping their order due to repulsive interactions, the diffusion coefficient of their collective motion is given by n_l^{-1} time of that of single particle; this result is independent of the details of the interaction among them. This collective motion correspond to the reptation in our model. The diffusion constant of the reptation is therefore given by

$$D_r^{lk} = D_{\xi\xi}/n_l = K\delta\nu_l^{1/2}/n_l \sim M_l^{3/2}/M \qquad (57)$$

where lk stands for local knot, and n_l is the average number of local chains per polymer chain. D_r^{lk} may be compared with the diffusion constant of reptation in the Doi–Edwards model:[3]

$$D_c^{DE} = k_BT/\zeta_0 N \sim M_e^0/M \quad \text{(Doi–Edwards)} \qquad (58)$$

where ζ_0 is the friction constant per main-chain bond and M_e is the empirical molecular weight between entanglements defined by eq 5. Considering the physical meaning of the tube and the local-knot model, the molecular weight between entanglements is equated to M_l in the former model and to M_e in the latter. Since M_l and M_e are essentially the same quantity, this discrimination is rather formal and may be neglected in the latter discussion. Equations 57 and 58 show that the M dependence of D_r^{lk} and D_c^{DE} is the same but M_e (M_l) dependence is different. The latter difference, however, means nothing at this stage since the reptation of the two models is different. (Remember that the reptation of our model occurs in the index-number space of the bonds while that of the tube model occurs in a tube fixed to the lab space.) Comparison should be made for observable quantities such as disengagement time τ_d or sedimentation constant D_s, which are computed now.

B. Disengagement Time, τ_d. For simplicity, we neglect the so-called leakage effect (or the partial dissipation of entanglements due to the motion of surrounding polymer chains). This effect may play an important role in quantitative discussion but neglected in this work, because our main interest is to study the topological origin of reptation. We start with the disengagement problem. We first note that once the diffusion coefficient of reptation is given by eq 57 or 58, further treatments are more or less the same in the tube and local-knot model, although their molecular origins are different. We follow the treatments of the monograph of Doi and Edwards.[3] For disengagement time τ_d, their calculation holds as it is in the present model, if D_c^{DE} and L, the contour length of the tube, are replaced by D_r^{lk} and N, respectively, in the present model; τ_d is given by eq 6.13 of their monograph,[3] or in the present notations, by

$$\tau_d = \begin{cases} L^2/\pi^2 D_c^{DE} = NL^2\zeta_0/\pi^2 k_BT \sim M^3/M_e & \text{(Doi–Edwards)} \\ N^2/\pi^2 D_r^{lk} = N^3/\pi^2 K\delta\nu_l^{3/2} \sim M^3/M_l^{3/2} & \text{(local knot)} \end{cases} \qquad (59)$$

The M dependence of τ_d is the same but the M_e (M_l) dependence is different in the two models.

C. Sedimentation Constant D_s. To compute D_s, we must consider a more elaborate translation between the tube and the local-knot model. Let us consider the transient network picture of the local-knot model discussed in the Introduction. In the plateau times region, our model looks like a network polymer in which the local knots behave like cross-links. In this time region, it is sufficient to consider quasi-equilibrium positions of the center of the local chains, averaging the all other degrees of freedom. As time passes beyond the plateau time region, the reptation motion occurs. In the local-knot model, the reptation is originally defined in the index-number space, ξ, of the main-chain bonds, or when observed in the lab space, it occurs along the precise contour of the main chain; when the motion is averaged over a time scale comparable to the plateau time region, we will observe a "reptation" along a line connecting the quasi-equilibrium positions of the centers of the local chains; we call the line a "coarse-grained contour", which corresponds to the contour of the "tube" in the tube model. In the previous work,[17] the persistent length of the coarse-grained contour of the local-knot model, a^{lk}, has been determined by the local mechanical-equilibrium conditions; it is simply given by[27]

$$a^{lk} = \bar{b}\nu_l^{1/2} \qquad (60)$$

Since the original reptation of the local-knot model occurs along a line of length N and the reptation in the lab system, along the course-grained contour of length $n_l a^{lk}$ ($=N\bar{b}/\nu_l^{1/2}$), the diffusion constant of the original reptation motion, D_r^{lk}, should be multiplied by the square of the contraction ratio, $\bar{b}/\nu_l^{1/2}$. Hence, the diffusion constant of the reptation in the lab system, D_c^{lk}, is given by

$$D_c^{lk} = (\bar{b}^2/\nu_l)D_r^{lk} = (k_BT/\zeta_t)\nu_l^{1/2}/N \sim M_l^{1/2}/M \qquad (61)$$

where ζ_t is the "topological friction parameter" defined by

$$\zeta_t = k_BT/\bar{b}^2K\delta \qquad (62)$$

ζ_t is a molecular parameter determined by the chemical structure of polymer chains and environmental parameters but independent of M or M_l. M_l dependence of D_c^{lk} is still different from the M_e dependence of D_c^{DE}.

In the coarse-grained version of the local-knot model, n_l, a^{lk}, and D_c^{lk} should be equated respectively to n_e ($=M/M_e$), a ($=b\nu_e^{1/2}$), and D_c^{DE} of the Doi–Edwards model. Although these parameters are different, calculation of D_s can be done formally by the same method. Since D_s is given by $D_c^{DE}/3N_c$ in the Doi–Edwards theory,[3] we find

$$D_s = \begin{cases} D_c^{DE}/3n_e = k_BT/3\zeta_0 N n_e \sim M_e/M^2 & \text{(Doi–Edwards)} \\ D_c^{lk}/3n_l = k_BT\nu_l^{1/2}/3\zeta_t N n_l \sim M_l^{3/2}/M^2 & \text{(local knot)} \end{cases} \qquad (63)$$

The M dependence of D_s is the same but M_e (M_l) dependence is again different in the two models.

V. Discussion

A. M, M_l, and c Dependence of τ_d and D_s. From the nature of the local-knot model, calculation of diffusion and viscoelastic properties can be performed essentially

by the same method as used in the tube model. We may therefore expect that phenomenological features, such as the stress–strain relationships or relaxation behaviors, of the two models are essentially the same. Further treatment of the local-knot model is however postponed to the future work. We discuss here the physical meanings of the results obtained in the previous sections.

M dependence of τ_d and D_s: According to eqs 59 and 63, τ_d and D_s are proportional to M^3 and M^{-2}, respectively, in the two models. The M dependence of D_s is consistent with experiments.[28] Disengagement time τ_d cannot be observed directly in experiments, but it is usually compared with the terminal relaxation time, τ_e. The M dependence of τ_d given by eq 59 deviates considerably from the well-known 3.4 power law.[22] This discrepancy has been a matter of debate for many years, and it is believed that the extra 0.4 power will be explained by a partial modification of the reptation model. This problem is however out of the scope of the present work. At this stage, it is sufficient to note that the M dependence of the local-knot model is the same as that of the original tube model.

M_e (M_l) dependence of τ_d and D_s: Since M_l is roughly proportional to M_e, the M_l dependence of the local-knot model may be compared with the M_e dependence of the tube model. As seen from eqs 59 and 63, the M_e (M_l) dependence of τ_d and D_s are different in the two models. This discrepancy reflects the difference in their mechanism of reptation. In the tube model, it is assumed that each chain moves in an imaginary tube formed by surrounding chains. In the original model due to de Gennes,[1] no specific future of the tube is assumed except that it restricts the motion of the chains and its contour is Gaussian; de Gennes argued that the friction constant of the reptation should be proportional to M^{-1}.[1] Later, Doi and Edwards[3] introduced another assumption that the friction constant of the reptation should be given by $N\zeta_0$ (eq 58); this is equivalent to assuming that the tube is completely slippery so that the friction constant of a segment in the tube is identical with ζ_0, the friction constant without restriction. In view of the local-knot model, however, this assumption is wrong, since D_c^{lk} is independent of ζ_0. The frictional resistance to the reptation motion in the local-knot model comes from the restriction that GIs of the local knots should be conserved as an average. This picture is rather close to the original model of de Gennes.[1,24] In the local-knot model, polymers are characterized by two molecular parameters, γ and ζ_t (or δ), both of which originate in the topological nature of the polymer chains; the usual parameters b and ζ_0 should be applied to dilute solutions or high-frequency phenomena. This idea is quite different from the usual assumption that behaviors of polymers are determined by b and ζ_0 even in the entangled systems. Although the local-knot model is still an assumption, it seems inevitable to introduce such new parameters as γ and ζ_t, so long as we take a topological approach. From this consideration, eq 58 is doubtful. Although numbers of calculations and discussions have been presented on a basis, directly or not, of eq 58, their reassessment would be necessary from this point of view. It must also be added that although some of the molecular interpretation of the Doi–Edwards theory is doubtful, most of their results, particularly their constitution equations, are right at least in the first approximation.

c dependence of τ_d and D_s: The M_e (M_l) dependence of τ_d and D_s may be observed as their c dependence in experiments. Their c dependence comes from ζ_t (or δ) and ν_l, but the former's contribution should be neglected in the present discussion, since it represents the environmental effects that are irrelevant to entanglement. We consider therefore the following reduced quantities:

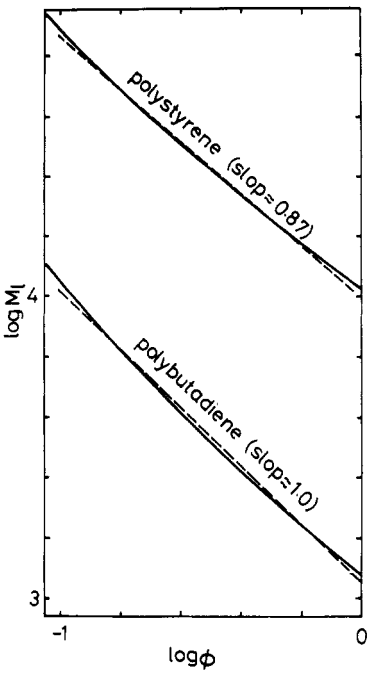

Figure 10. Concentration dependence of m_l, where ϕ is the volume fraction of the polymer chains or $c = \rho\phi$, and ρ is the density of the undiluted polymers.

$$\bar{\tau}_d = \tau_d/\zeta_t \sim M_l^{3/2} \qquad \bar{D}_s = D_s\zeta_t \sim M_l^{-3/2} \tag{64}$$

In experiments, they may be compared with τ_d/ζ_0 and $D_s\zeta_0$, since it is expected that ζ_t and ζ_0 depend similarly on the environmental parameters. In the previous work,[17] M_l has been computed for many polymers and two typical examples are shown in Figure 10 (as for details of the calculation, see ref 30). In the figure, ϕ represent the volume fraction of polymer chains. From the figure, we find

$$M_l \sim c^{-0.87- -1.0} \tag{65}$$

or from eqs 64 and 65

$$\bar{D}_s \sim c^{-1.3- -1.5} \qquad \bar{\tau}_d \sim c^{1.3-1.5} \tag{66}$$

Their c dependence comes purely from entanglement. This equation should be applied to melt and concentrated polymer solutions, for the excluded-volume effects have been neglected.

B. Why Crankshaft Motions Do Not Contribute to the Reptation. Finally, we consider the remaining problem in section II, which is associated with the strange behavior of the simple cubic lattice model (SCLM). Verdier[34] found that when normal motion A (Figure 5) alone is considered in computer simulations of SCLM, its motion is drastically slowed down as the excluded volume is introduced. Since the chain was isolated in the simulations, this must be an intramolecular effect. This problem is solved by Hilhorst and Deutch,[35] who showed that SCLM have a kind of local-conformational memory called extrema that cannot be removed by motion A alone; they also suggested that the extrema can be removed by introducing crankshaft motion B (Figure 5). Later, Kovac showed that the self-diffusion constant of entangled SCLM in fact increases drastically by adding a small amount of the crankshaft motions, say a few percent of the total local jumps.[19] Evidently, the crankshafts work as a catalyst for dissolving extrema. So, why do the

crankshafts not contribute significantly to the reptation of SCLM? The answer is simple: the crankshafts are the catalyst for the extrema but not for the local knots; in Kovac's model, the crankshafts occur frequently enough to remove the extrema rapidly but their contribution to the local knot motion is still small. We must farther point out that the extrema is, so to say, a *bugbear* arisen from artificial restrictions on the chain motion, and our theory should be applied to real polymers and *good* polymer models that are not haunted.

VI. Summary

The local-knot model introduced in the previous work[17] is extended to include the Brownian motion of polymer chains. Diffusion coefficient tensors $D_{\xi\xi}$ and $D_{\xi\eta}$ for local-chain a_ξ and b_η moving along chain a and b are derived with the use of the topological restrictive condition. It is found that

$$D_{\xi\xi} \sim M_l^{1/2} \qquad D_{\xi\eta} = 0 \tag{I}$$

where M_l is the molecular weight of the local chain. The first equation shows that longer local chains move more rapidly than shorter ones, and the second equation shows that there is no correlation among reptations of different polymer chains.

The reptation is assigned to a collective diffusion of local knots along a polymer chain. The diffusion constant of the reptation, D_c, the disengagement time, τ_d, and the sedimentation constant, D_s, are computed in the approximation of neglecting fluctuations and the leakage effect. For example, the diffusion constants are computed for Kovac's model used in computer simulations. The M, M_l, and c dependences of these quantities are summarized as follows:

$$D_c \sim M_l^{1/2}/M \tag{II}$$

$$\tau_d \sim M^3/M_l^{3/2} \qquad D_s \sim M_l^{3/2}/M^2 \tag{III}$$

$$\tau_d/\zeta_t \sim c^{1.3-1.5} \qquad D_s\zeta_t \sim c^{-1.3--1.5} \tag{IV}$$

The M dependence agrees with Doi–Edwards theory, but the M_l dependence does not. The latter discrepancy reflects the difference in the mechanism of the reptation in the two models. It is argued that (1) the phenomenological features of the local-knot model are essentially the same as those of Doi-Edwards model but (2) their molecular origins are quit different and (3) entanglement should be characterized by two topological parameters (γ, ζ_t), which are independent of the usual parameters ($\bar{b}$, ζ_0), and finally (4) a question is posed concerning the basic assumption of Doi–Edwards theory that the friction constant of the reptation is given by $N\zeta_0$.

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(25) Strictly speaking, $\Delta_j\xi$ is not a simple Markoffic process but has a short-time memory. We have however neglected it for simplicity, since its introduction can be done formally and leads to no essential change in the theory.
(26) Although the direct correlation among reptations is neglected by eq 49, there may appear indirect correlations when a simultaneous diffusion equation of the whole local knots is considered explicitly.
(27) In the previous work,[17] the persistent length of the coarse-grained contour is given by $a^{lk} = \bar{b}\nu_l^{1/2}$, where $\bar{b}$ is given by

$$\bar{b} = b\left(\frac{1+\cos\tilde{\theta}}{1-\cos\tilde{\theta}}\right)^{1/2} \tag{67}$$

where $\tilde{\theta}$ is the average bond angle of the line connecting the quasi-equilibrium positions of the centers of the local chains. Although it has not been mentioned explicitly in the previous work, $\bar{b}$ is exactly equal to $\bar{b}$, the effective bond length.
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(30) In the local-knot model, the relationship between M_l and c is determined by eq 9, which corresponds to eqs 4.12, 6.4, and 6.5 of the previous paper.[17] The model and notations in the previous paper are slightly different from those in the present work. Previous eqs 6.5, 4.12, and 6.4 are written in terms of the present notations as follows:

$$(c/\nu_l M_0)(\nu_l\bar{b})^3 E_l(X) = 1$$

$$E_l(X) = \int\int_{|T|\geq 0.5} P(T,\mathbf{r})\,dT\,d\mathbf{r}$$

$$X = (8\gamma)^{-1/2}\nu_l^{-1/4} \tag{68}$$

where $\mathbf{r}$ is the coordinate vector measured in the unit of $\bar{b}\nu_l^{1/2}$. ($T_0 = 0.5$ is assumed for simplicity.) In the previous work,[17] $E_l(X)$ was computed numerically as a function of X. When M_0, $\bar{b}$, and γ are given for a polymer, we can computer M_l as a function of c using eq 68 and Table I of $E_l(X)$ given in the previous paper.[17] In Figure 9, log M_l of polystyrene (PS) and polybutadiene (PB) are plotted against log ϕ, where ϕ is the volume fraction of the polymer chains. Average slopes are estimated to be 0.87 (PS) and 1.0 (PB) in the region $0.1 \leq \phi \leq 1.0$; the slopes of the most polymers come between these two values.
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