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Effects of a Nematic-Like Interaction in Rubber Elasticity Theory

Jean-Pierre Jarry* and Lucien Monnerie

Laboratoire P.C.S.M., Ecole Supérieure de Physique et Chimie de la Ville de Paris, 75231 Paris Cedex 05, France. *Received November 7, 1978*

ABSTRACT: A modified theory of rubber elasticity is proposed which includes anisotropic intermolecular interactions favoring the alignment of neighboring chain segments. These interactions are described in the mean field approximation by an intermolecular potential having the same form as that used for the study of nematic phases. It is shown that such interactions increase orientation of chain segments but do not significantly alter the stress–strain behavior of a network. Finally, experimental consequences of the theory are discussed.

In recent years, the local structure of amorphous polymers has been a subject of considerable interest. In the rubbery state, the stress-induced orientation distribution of chain segments should be very sensitive to the presence of local order. The second moment S of this distribution has been calculated by Roe and Krigbaum[1] in the framework of the classical gas-like theory[2,3] of rubber elasticity. Observation of deviations from this theory is a way to approach the problem of local order in rubbers. A few data are already available in this respect. Fukuda, Wilkes, and Stein[4] reported values of the stress-optical coefficient which are too high in dry rubbers and which are reduced upon swelling. They suggested that this inconsistency could be due to some local order. Besides, the fluoresence polarization technique[5-6] has been recently extended to the study of rubbers and preliminary results[7] also show that S is anomalously higher in dry networks than in swollen ones.

This emphasized the need for a modified theory of rubber elasticity including intermolecular interactions which could give rise to anisotropic packing of chain segments. Di Marzio[8] and Jackson[9] et al. developed lattice models with anisotropic interactions which enhance the alignment of neighboring segments. Their aim was not to study orientational properties of networks but rather to account for the additional C_2 term of the phenomenological Mooney–Rivlin equation:

$$\sigma = (C_1 + C_2/\lambda)(\lambda^2 - \lambda^{-1})$$

where σ is the true stress and λ the extension ratio. Both models lead to a ratio C_2/C_1, proportional to $1/N$ (N being the number of segments per chain), which is much smaller than experimental values ($C_2/C_1 \simeq 1$). The Di Marzio theory was improved by Tanaka and Allen[10] who showed that his C_2 term should be doubled. Recently, de Gennes[11] discussed the behavior of polymeric networks containing nematogenic segments near the isotropic–nematic transition.

In the present work, the chain segments of usual rubbers are considered as cylindrically symmetric objects submitted to a weak nematic-like interaction. Segment–segment interactions are described in terms of a thermodynamic potential of the same form as that introduced in the study of nematic phases.[12,13] The stress–strain and orientation–strain relations are derived for uniaxial stretching. It is concluded that such interactions principally increase the orientation and that the mechanical behavior is not significantly altered, according to the results of Di Marzio, Jackson, and Tanaka and Allen. Finally, experimental procedures are discussed which should allow one to distinguish between nematic-like interaction and entanglement effects.

General Considerations

In a uniaxial medium, the intermolecular potential U_{12}[13] between two molecules or chain segments, which behave as cylindrically symmetric objects, depends on the intermolecular distance r_{12} and on the angles Θ_1 and Θ_2 between the molecular axes and the symmetry axis of the medium.

It can be expanded in the form:

$$U_{12} = \sum_{l\,\text{even}} u_l(r_{12}) P_l(\Theta_1) P_l(\Theta_2) \qquad (1)$$

where $P_l(\Theta)$ are Legendre polynomials.

Restricting the development to the first anisotropic term ($l = 2$), one obtains a contribution F_{int} to the free energy per molecule:

$$F_{\text{int}} = -\tfrac{1}{2} U \langle \mathrm{P}_2(\Theta) \rangle^2 = -\tfrac{1}{2} U S^2 \qquad (2)$$

where S is the second moment of the molecular distribution function and U is a positive parameter of interaction.

As a preliminary step, let us consider a chain of N segments interacting with a uniaxial medium of axis Z, the end-to-end vector $\mathbf{R}$ lying in the Z direction (Figure 1).

The free energy per segment can be expanded in the form:

$$F = aS^2 + bS^3 + \ldots + cr^2 + dr^4 + \ldots + er^2S + fr^2S^2 + gr^4S + \ldots \qquad (3)$$

where S is the second moment of the surrounding medium and $r^2 = R^2/NR_0^2$, R_0^2 referring to the free chain. The first set of terms characterizes the nematic-like interaction[14] and the second one describes the usual entropic elasticity.[2] cr^2 is the dominant Gaussian term $c = {}^3/_2 kT$ and dr^4 is the first non-Gaussian term corresponding to a possible increase in the tension when the chain approaches its limit of extension. The remaining coupling terms arise from the alteration of chain elasticity due to intermolecular in-

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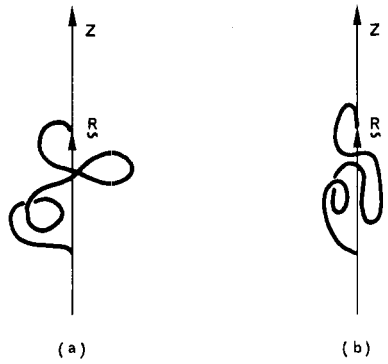

Figure 1. Schematic representation of chain conformations: (a) isolated chain, (b) chain interacting with a uniaxial medium. Its conformation tends to an unidimensional folding along Z.

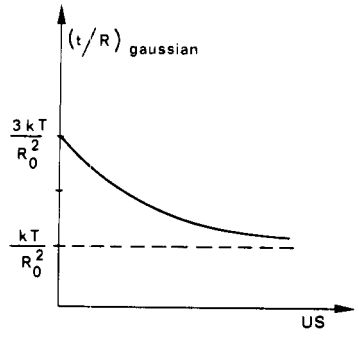

Figure 2. Schematic evolution of the Gaussian chain stiffness $t/R = (2/R_0^2)(c + eS + fS^2)$ with increasing interaction.

teraction. As a matter of fact, they modify the tension t at the chain ends:

$$t = \frac{\partial}{\partial R}(NF) = \frac{2}{R_0^2}(c + eS + fS^2 + \ldots)R + \frac{4}{NR_0^4}(d + gS)R^3 + \ldots \quad (4)$$

The signs of the coupling terms can be simply predicted from the symmetry properties of the interaction which privileges the $\pm Z$ direction of the segments: An isolated tridimensional chain tends toward the unidimensional state when submitted to nematic-like interaction (Figure 1). The first Gaussian term of eq 4 must then decrease from $3kT/R_0^2$ to kT/R_0^2 when interaction increases. It is thus obvious from Figure 2 that e is negative (as previously shown by de Gennes[11]) and f is positive. Moreover, g is negative since the non-Gaussian term is smaller for unidimensional chains than for tridimensional ones.[15]

The free energy per segment is finally rewritten with explicit signs on the form:

$$F = AS^2 - BS^3 + \ldots + Cr^2 + Dr^4 + \ldots - Er^2S + Fr^2S^2 - Gr^4S + \ldots \quad (5)$$

Let us now consider an assembly of mutually interacting chains, all having the same end-to-end vector **R**. Such a situation is not a realistic description of a polymeric network but it simply reveals the main properties of an ensemble of flexible self-interacting chains. For a given value of **R**, the second moment of the orientation distribution of the chain segments is determined by:

$$\left(\frac{\partial F}{\partial S}\right)_r = 0$$

Hence:

$$S = \frac{E}{2A}r^2 + \alpha r^4 + \ldots \quad (6)$$

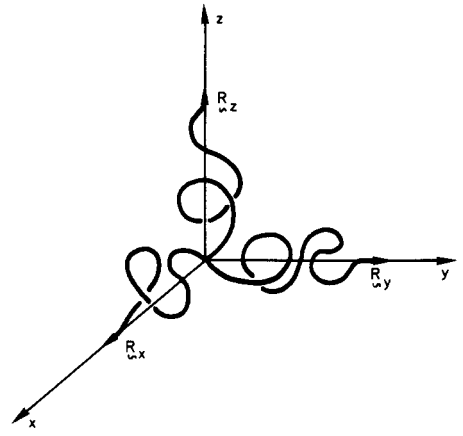

Figure 3. Representation of the three identical chains in a three-chain cell. The end-to-end vectors are mutually perpendicular.

where α is a coefficient depending on A, B, E, F, and G.

Placing eq 6 into eq 5, the free energy is obtained as a function of R only:

$$F = Cr^2 + \left(D - \frac{E^2}{4A}\right)r^4 + \ldots \quad (7)$$

The broad conclusions to be drawn from the above results (eq 6 and 7) are the following: (i) A nematic-like interaction does not affect the first term of F (eq 7) which dominates the stress–strain behavior in the Gaussian range ($r^4 << r^2$). Therefore it cannot be a plausible cause of the C_2 deviation from the classical theory. Mechanical effects of this interaction arise only at high elongation where a lowering of the non-Gaussian chain stiffness (second term of eq 7) can be expected. (ii) The second moment S is obviously increased by interaction but it remains proportional to r^2 in the Gaussian range as in the classical theory which predicts:[1]

$$S = \tfrac{3}{5}r^2 + O(r^4)$$

At high elongation, the curvature of S is governed by the coefficient α of eq 6 which can be positive or negative according to the values of B, F, and G.

These conclusions are quite general and model independent, but they remain qualitative. They will be confirmed and stated more precisely by the study of a completely calculable model.

Three-Chain Model. For the derivation given in this section, we need the following basic assumptions: (1) The chains consist of N freely jointed segments of length a. (2) The nematic-like interaction acts between these segments and is taken into account in the mean field approximation by eq 2. (3) As usually assumed in the classical theory, the end-to-end vectors are affinely deformed by stretching.

The mean field treatment and the affine assumption seem to be reasonable for elastomers where orientation correlations, if they exist, should be very short range.

In order to facilitate the mathematical treatment, we will consider the stretching along Z of the three-chain model first introduced by James and Guth[16] (Figure 3).

In these conditions, the free energy of a three-chain cell is:

$$F = \sum_{u=X,Y,Z} NkT \int f_u \ln f_u \, d\Omega - \tfrac{3}{2}NkTUS^2 \quad (8)$$

where Ω represents the orientation of a segment. In this equation, the sum corresponds to the conformational entropy and involves the segmental orientation distribution f_u of the chain whose end-to-end vector $\mathbf{R}_u$ is directed along

axis u ($u = X, Y, Z$). The distribution functions f_u are determined by specifying that F is a minimum for all variations of f_u which satisfy the constraints:

$$\int f_u \, d\Omega = 1 \tag{9}$$

$$\int \cos \alpha_u f_u \, d\Omega = R_u/Na \tag{10}$$

where α_u is the angle between a segment and axis u. We thus obtain:

$$f_u = Z_u^{-1} \exp(\mu_u \cos \alpha_u + {}^3/_2 US \cos^2 \alpha_z) \tag{11}$$

Z_u and μ_u are Lagrange multipliers determined by conditions 9 and 10.

The procedure for obtaining the segmental second moment S for the whole network and the stress σ as functions of the elongation ratio λ is given in Appendix I. The calculation is based upon the expansion of the partition functions Z_u in series of r_u and US. The final results, which suppose the affine deformation of the vectors $\mathbf{R}_u$, are:

$$S = \frac{1}{1-V}\frac{1}{5N}(\lambda^2 - \lambda^{-1})\left(1 + K\frac{\lambda^2}{N} + \dots\right) \tag{12}$$

with $K = {}^5/_7[12 - 18V(1-V)^{-1} + 5V^2(1-V)^{-2}]$

$$\sigma = \frac{\rho kT}{N}\left[(\lambda^2 - \lambda^{-1}) + \frac{1}{5N}\frac{V}{1-V}(\lambda - \lambda^{-2}) + \frac{2}{5N}\left(3 - \frac{V}{1-V}\right)(\lambda^4 - \lambda^{-2})\right] \tag{13}$$

where ρ is the segment density.

In these equations, $V = U/5$ characterizes the intensity of interaction. The value $V = 0$ corresponds to the classical theory (no interaction) and $V = 1$ corresponds to the critical temperature of spontaneous isotropic–nematic transition.

In the Gaussian range ($\lambda^2/N << 1$), eq 12 and 13 reduce to:

$$S = \frac{1}{1-V}\frac{1}{5N}(\lambda^2 - 1/\lambda) \tag{14}$$

$$\sigma = \frac{\rho kT}{N}(\lambda^2 - 1/\lambda) \tag{15}$$

According to the conclusions of the previous section, S is increased by interaction through the front factor $(1-V)^{-1}$. On the contrary, σ is not modified. The proportionality between S and σ is preserved:

$$S = \frac{\sigma}{5(1-V)\rho kT} \tag{16}$$

These results agree with those derived by Tanaka and Allen,[10] our factor $(1-V)^{-1}$ corresponding to their coefficient Λ (eq 21 of ref 10).

In the non-Gaussian range, second-order terms of eq 12 and 13 must be taken into consideration. The curvature of the plot of S against $(\lambda^2 - 1/\lambda)$ is determined by the coefficient K (eq 12) which is positive at $V < 0.47$ and $V > 0.73$ and negative for $0.47 < V < 0.73$. The second term of eq 13 is a negligible C_2-like term ($C_2/C_1 \sim 1/N$), analogous to the results of Di Marzio and Jackson. The sole mechanical interaction effect is the lowering of the third term of eq 13 which follows from the induced decrease of the chain stiffness. It should be noted that the sum of the second and third terms in eq 13 has the same form as the correcting term derived by Tanaka and Allen (eq 27 of ref 10).

These results have been established for perfectly regular networks. As shown in Appendixes II and III, the existence of free chains or the polydispersity of network chains (i.e., distribution of strand lengths) lead to minor corrections and do not change the main conclusions.

Experimental Consequences. Experimental evidence of the existence of nematic-like interactions in usual rubbers should be obtained from measurements of σ and S in the Gaussian range. According to the classical theory, variations of temperature or swelling ratio must have a minor influence on the C_1-like components σ_1 and S_1 of σ and S. If a nematic-like interaction is present in dry rubber, it should be strongly reduced upon swelling (as it is in nematic phases). Thus S_1 should decrease by addition of a small amount of diluent, without significant modification of σ_1. A decreasing temperature is expected to enhance interactions and increase S_1, the component σ_1 being only slightly modified. It should be noted that the above effects differ from that arising from changes in the entanglement density. Such change would modify both S_1 and σ_1 in the same ratio through the front factor $1/N$.

Stress–optical coefficient data reported by Fukuda et al.[4] are consistent with the presence of nematic-like interactions. However, birefringence measurements can be strongly perturbed by anisotropic internal field effects and their interpretation in terms of the second moment S seems to be very difficult. We believe that other experimental techniques, such as linear dichroism and fluorescence polarization, which are much less sensitive to internal field, could bring more conclusive information. We are therefore presently using fluorescence polarization to study the influence of temperature and swelling on orientation of labeled elastomers.

Acknowledgment. We are indebted to Professor P. G. de Gennes for his valuable advice and to Dr. R. Ullman for helpful discussions.

Appendix I. Derivation of Orientation and Stress in the Three-Chain Model

The partition functions Z_u appearing in eq 11 are determined by condition 9:

$$Z_Z(\mu_Z, \upsilon) = \frac{\pi}{2i\upsilon}\exp\left(-\frac{\mu_Z^2}{4\upsilon}\right) \times \left[\operatorname{erf}\left(i\upsilon^{1/2} + i\frac{\mu_Z}{2\upsilon^{1/2}}\right) - \operatorname{erf}\left(-i\upsilon^{1/2} + i\frac{\mu_Z}{2\upsilon^{1/2}}\right)\right] \tag{A1}$$

$$Z_X(\mu_X, \upsilon) = \int_0^{2\pi} \exp(\upsilon \cos^2 \varphi) Z_Z(\mu_X, -\upsilon \cos^2 \varphi) \, d\varphi \tag{A2}$$

where $\upsilon = {}^3/_2 US$. The second moments S_u of the segments belonging to chains $\mathbf{R}_u$ are derived from eq A1 by use of:

$$S_u = \frac{3}{2}\frac{\partial}{\partial \upsilon}(\ln Z_u) - \frac{1}{2}$$

From an appropriate expansion[17] of erf(X), one obtains:

$$S_Z = {}^1/_{15}\mu_Z^2 - {}^2/_{315}\mu_Z^4 + {}^2/_{15}\upsilon + {}^4/_{315}\upsilon\mu_Z^2 + {}^4/_{315}\upsilon^2 + \dots \tag{A3}$$

$$S_X = -{}^1/_{30}\mu_X^2 + {}^1/_{315}\mu_X^4 + {}^2/_{15}\upsilon - {}^2/_{315}\upsilon\mu_X^2 + {}^4/_{315}\upsilon^2 + \dots \tag{A4}$$

The variables μ_u are then expressed as functions of the reduced lengths $r_u = \mathbf{R}_u/Na$ by use of condition 10 which yields:

$$\mathbf{r}_u = \frac{\partial}{\partial \mu_u}(\ln Z_u)$$

Hence:

$$\mu_Z = 3r_Z[1 - {}^4/_{15}v + {}^3/_5 r_Z^2 + \ldots] \quad \text{(A5)}$$

$$\mu_X = 3r_X[1 + {}^2/_{15}v + {}^3/_5 r_X^2 + \ldots] \quad \text{(A6)}$$

Substituting eq A5 and A6 into A3 and A4, the second moments S_u are written as series expansions of powers of r_u and v. The second moment S

$$S = {}^1/_3 S_Z + {}^2/_3 S_X \quad \text{(A7)}$$

is then given by:

$$S = {}^1/_5(r_Z^2 - r_X^2) + {}^1/_5 US + {}^{12}/_{175}(r_Z^4 - r_X^4) + {}^1/_{35}(US)^2 - {}^6/_{175}US(3r_Z^2 - 4r_X^2)$$

Solving this equation and using the affine deformation hypothesis:

$$r_Z^2 = \lambda^2/N \qquad r_X^2 = \lambda^{-1}/N \quad \text{(A8)}$$

one obtains eq 12.

In order to calculate the stress σ, the free energy F of a three-chain (eq 8) cell is first rewritten in the form:

$$F = NkT\sum_u [{}^1/_2 US + \mu_u r_u - \ln Z_u] - {}^3/_2 NkTUS^2$$

substitution of eq A1, A2, A5, and A6 leads to:

$$F = {}^3/_2 NkT[5(V - V^2)S^2 - 2VS(r_Z^2 - r_X^2) + (r_Z^2 + 2r_X^2) + {}^3/_{10}(r_Z^4 + 2r_X^4) + \ldots]$$

Using eq 12 and A8, the free energy of a cell takes the final form:

$$F = {}^3/_2 NkT\left[(\lambda^2 + 2\lambda^{-1}) + \frac{1}{10N}\frac{V}{1-V}(2\lambda + \lambda^{-2}) + \frac{1}{10N}\left(\frac{3}{2} - \frac{V}{1-V}\right)(\lambda^4 + 2\lambda^{-2})\right]$$

The free energy F_V per unit volume is:

$$F_V = (\rho/3N)F$$

where ρ is the number of segments per unit volume. Equation 13 of the text is derived from:

$$\sigma = \lambda \frac{\partial}{\partial \lambda} F_V$$

Appendix II. Effect of Free Chains

Here, we consider a network containing three-chain cells and free chains whose end-to-end distances are not submitted to deformation conditions. If the unit volume contains ρq segments of network chains and $\rho(1 - q)$ segments of free chains, the free energy is:

$$F_V = \frac{\rho q kT}{3}\sum_u \int f_u \ln f_u \, d\Omega + \rho(1-q)kT\sum \int f_f \ln f_f \, d\Omega - (\rho/2)US^2$$

where f_f is the orientation distribution of free chains.

F_V is minimized with respect to the variations of f_u as in the case of perfect network. For the free chains, condition 10 is removed and the minimization yields:

$$f_f = Z_f^{-1} \exp(3US\cos^2 \alpha_Z/2) \quad \text{(A9)}$$

The derivation of the stress σ and the overall second moment S is then carried out as in Appendix I, replacing eq A7 by:

$$S = (q/3)\sum S_u + (1 - q)S_f$$

where S_f is the second moment of the free chain segments. The final results are:

$$S = \frac{q}{1-V}\frac{1}{5N}(\lambda^2 - \lambda^{-1})\left(1 + K'\frac{\lambda^2}{N}\right) \quad \text{(A10)}$$

with $K' = {}^5/_7[12q - 18qV(1 - V)^{-1} + 5V^2(1 - V)^{-2}]$

$$\sigma = \frac{\rho q}{N}kT\left[(\lambda^2 - \lambda^{-1}) + \frac{q}{5N}\frac{V}{1-V}(\lambda - \lambda^{-2}) + \frac{2}{5N}\left(3 - \frac{qV}{1-V}\right)(\lambda^4 - \lambda^{-2})\right] \quad \text{(A11)}$$

The main effect of free chains is to reduce both S and σ by the front q ($q < 1$) in accordance with the fact that free chain segments are oriented only by interaction and not by end-to-end stretching. In the Gaussian range, the orientation–stress relationship (eq 16) is preserved. It follows that the main conclusions of the text are not changed when free chains are taken into account.

Appendix III. Effect of Polydispersity

We now consider a polydisperse network containing ν_i chains of N_i segments per unit volume. According to eq 8, the free energy F_V is:

$$F_V = kT\sum_{i,u}\rho_i\left[{}^1/_3 \int f_{iu} \ln f_{iu} \, d\Omega - {}^1/_2 US^2\right]$$

where $\rho_i = \nu_i N_i$ is the segment density relative to chains of length N_i and f_{iu} is the orientation distribution of the chains of length N_i whose end-to-end vectors lie in the direction u.

The derivation of the second moments S_{iu} is carried out as in Appendix I. The mean second moment S is calculated from:

$$S = {}^1/_3(\sum_{i,u}\rho_i S_{iu})/(\sum_i \rho_i) \quad \text{(A12)}$$

instead of eq A7.

Assuming the affine deformation for all chains, one finally obtains:

$$S = \frac{1}{1-V}\frac{1}{5\langle N\rangle}(\lambda^2 - \lambda^{-1})\left(1 + K''\frac{\lambda^2}{\langle N\rangle}\right) \quad \text{(A13)}$$

with $K'' = {}^5/_7[12\langle N^{-1}\rangle\langle N\rangle - 18V(1 - V)^{-1} + 5V^2(1 - V)^2]$

$$\sigma = \frac{\rho kT}{\langle N\rangle}\left[(\lambda^2 - \lambda^{-1}) + \frac{1}{5\langle N\rangle}\frac{V}{1-V}(\lambda - \lambda^{-2}) + \frac{2}{5\langle N\rangle}\left(3\langle N^{-1}\rangle\langle N\rangle - \frac{V}{1-V}\right)(\lambda^4 - \lambda^{-2})\right] \quad \text{(A14)}$$

These results show that the behavior of polydisperse networks should not be strongly different from that of perfect networks, even if short chains are present. Indeed, all interaction terms in eq A13 and A14 involve the mean value $1/\langle N\rangle$ (and not $\langle 1/N\rangle$) which is not much sensitive to short chains. In the Gaussian range, the effect of polydispersity is simply to change the front factor $1/N$ into $1/\langle N\rangle$ for both S and σ, so that the orientation–stress relationship (eq 16) is again preserved.

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Wormlike Chains Near the Rod Limit: Translational Friction Coefficient

Takashi Norisuye,* Masanori Motowoka, and Hiroshi Fujita

Department of Polymer Science, Osaka University, Toyonaka, Osaka, 560 Japan.
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ABSTRACT: The translational friction coefficient, Ξ, of the Kratky–Porod (KP) wormlike chain near the rod limit is calculated according to the Yamakawa–Fujii formulation of the Oseen–Burgers method, with a wormlike sausage model assumed for the chain. Here wormlike sausage means a wormlike cylinder capped with hemispheres at its ends. The resulting expression for Ξ converges to the Stokes law at the limit of $L = d$, where L is the contour length and d is the diameter of the sausage. Its comparison with the Yamakawa–Fujii expression, which ignores end effects, shows that end corrections to Ξ are unexpectedly small. In fact, the Yamakawa–Fujii theory is accurate down to as short a chain as $L/d \sim 4$.

Among others,[1-5] the most accurate formulation of the translational friction coefficient, Ξ, of the Kratky–Porod wormlike chain[6] (KP chain) is one worked out by Yamakawa and Fujii[5] with a model that they call the wormlike cylinder. However, it is still incomplete in that it neglects contributions from the ends of the cylinder. Judging from a study by Broersma[7] on straight cylinders, one may anticipate that end effects on hydrodynamic behavior should become significant as the KP chain gets shorter. The purpose of the present paper is to estimate such effects on Ξ, using a wormlike sausage model for the KP chain. This model is a wormlike cylinder capped with two hemispheres at its ends, as illustrated in Figure 1. It is assumed that the central axis of the sausage has a flexibility characteristic of the KP chain. We also assume that the cross-section of each hemisphere perpendicular to the central axis stays circular in whatever way the sausage is deformed. Our calculation will be restricted to the sausage near the rod limit, because by so doing the previously derived moments[8] $\langle \mathbf{R}^{2m}(\mathbf{R}\cdot\mathbf{u}_0)^n \rangle$ (m,n = 0, 1, 2, ...) for the KP chain can be applied to calculate the mean reciprocal distance $\langle |\mathbf{R} - \mathbf{r}|^{-1} \rangle$, which is basic to the evaluation of Ξ by the Yamakawa–Fujii formula.[5] Various symbols appearing here will be explained in the text.

Mean Reciprocal Distance

As in the Yamakawa–Fujii formulation, we measure all lengths in units of the Kuhn statistical length $2q$, where q is the persistence length of a given KP chain.

Consider two points x and y on the central axis or contour of a wormlike sausage and place the origin of Cartesian coordinates (X,Y,Z) at the point x (see Figure 1). Let the spherical coordinates of $\mathbf{R}$ and $\mathbf{u}_0$ be denoted by $\mathbf{R} = (R, \Theta, \Phi)$ and $\mathbf{u}_0 = (1, \theta_0, \phi_0)$, respectively. Here, as shown in Figure 1, $\mathbf{R}$ is the distance between the points x and y, and $\mathbf{u}_0$ is the unit vector for the tangent to the contour at the point x. An orthogonal curvilinear coordinate system (ξ,η,ζ) may be defined in such a way that the ξ, η, and ζ axes are in the directions of $\mathbf{e}_{u_0}$, $\mathbf{e}_{\theta_0}$, and $\mathbf{e}_{\phi_0}$, respectively, where $\mathbf{e}$ denotes a unit vector. Let the components of $\mathbf{R}$ in this coordinate system be denoted by R_ξ, R_η, and R_ζ:

$$\mathbf{R} = (R_\xi, R_\eta, R_\zeta) \tag{1}$$

It is a simple operation to show that

$$R_\xi = R[\cos\theta_0 \cos\Theta + \sin\theta_0 \sin\Theta \cos(\Phi - \phi_0)]$$

$$R_\eta = R[-\sin\theta_0 \cos\Theta + \cos\theta_0 \sin\Theta \cos(\Phi - \phi_0)]$$

$$R_\zeta = R \sin\Theta \sin(\Phi - \phi_0) \tag{2}$$

where $R = |\mathbf{R}|$. Let $\mathbf{r}$ be the radius vector at the point x. If the angle that it makes with the η axis is denoted by β, the ξ, η, and ζ components of $\mathbf{r}$ are given by

$$\mathbf{r} = (0, r\cos\beta, r\sin\beta) \tag{3}$$

Equations 1 and 3 may allow $|\mathbf{R} - \mathbf{r}|^{-1}$ to be written in the form

$$|\mathbf{R} - \mathbf{r}|^{-1} = 1/[R^2 + r^2 - 2r(R_\eta \cos\beta + R_\zeta \sin\beta)]^{1/2} \tag{4}$$

The mean reciprocal distance $\langle |\mathbf{R} - \mathbf{r}|^{-1} \rangle$ is given by[5]

$$\langle |\mathbf{R} - \mathbf{r}|^{-1} \rangle = \int \langle |\mathbf{R} - \mathbf{r}|^{-1} \rangle_\beta G(\mathbf{R},\mathbf{u}_0;t)\, d\mathbf{R}\, d\mathbf{u}_0 \tag{5}$$

where $G(\mathbf{R},\mathbf{u}_0;t)$ is a distribution function ($t = |x - y|$) and

$$\langle |\mathbf{R} - \mathbf{r}|^{-1} \rangle_\beta = \frac{1}{2\pi}\int_0^{2\pi} |\mathbf{R} - \mathbf{r}|^{-1}\, d\beta \tag{6}$$

The integral in eq 6 with eq 4 can be evaluated to give

$$\langle |\mathbf{R} - \mathbf{r}|^{-1} \rangle_\beta = \frac{1}{(R^2 + r^2)^{1/2}} \sum_{m=0}^{\infty} \frac{(4m-1)!!}{4^m (m!)^2} \left(\frac{Rr\sin\theta}{R^2 + r^2} \right)^{2m} \tag{7}$$

where θ is the angle between the vectors $\mathbf{R}$ and $\mathbf{u}_0$, and $(4m$

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