amylose, and this finding is verified by conformational energy calculations.[38,40] Molecular models for maltose triacetate reveal an almost identical range of conformation space free of serious steric conflicts. To the extent that only those interactions present in the maltose moiety are responsible for determining the unperturbed chain dimensions, amylose triacetate should resemble amylose or carboxymethylamylose. To the extent that conformations involving longer range interactions, such as occur in helical portions of amylose, make important contributions to the average chain properties, amylose triacetate will not resemble amylose. The probable crystalline helical structure of amylose triacetate involves fewer than five glucose units per turn,[34] but there is no evidence for retention of this conformation in dilute solution. The observation that $C_\infty$ for NaCMA falls between those for amylose and amylose triacetate is thus consistent with the model proposed for NaCMA which involves a moderate disruption of the helical sequences of native amylose.

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# Theory of Long-Chain Molecules with Partial Flexibility

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ABSTRACT: The conformation of a linear, semiflexible, long-chain molecule in a Θ solvent is described in terms of the theory of Markoffian processes due to Uhlenbeck and Ornstein. The model exhibits correct behavior in both the limiting cases of a completely flexible chain and a thin rigid rod, and gives a fair approximation to the wormlike chain at intermediate degrees of stiffness. In contrast to the wormlike chain, the present model permits analytical evaluation of all the higher moments of the end-to-end distance and thus offers a useful treatment of the angular distribution function for intensity of Rayleigh scattering.

## I. Introduction

The conformation of linear, incompletely flexible, long-chain molecules in dilute solution in a Θ solvent is usually characterized by the spatial correlation between different points on the chain. The approach of the conformation of a long-chain molecule, in the limit of a sufficiently long chain, to that of an assembly of normally distributed point masses is well established. Moreover, when chain flexibility is introduced as a parameter, the resulting non-Gaussian conformation can be described in terms of the well-known "wormlike" chain[2-5] or a related model.[6,7]

The conformation of a polymer chain is conveniently represented, as in Figure 1, in terms of the set of position vectors, $\mathbf{r}(s)$, drawn from an arbitrary origin to points along the chain contour designated by a parameter $0 \leq s \leq L$ running from one end of the chain of length $L$ consisting of $n$ segments. In the wormlike chain models, the statistical fluctuations in length of a chain $\mathbf{r}(s) - \mathbf{r}_0$, with $\mathbf{r}_0$ designating $\mathbf{r}(0)$, are assumed to be attributable entirely to a slight bending of the chain. In this paper we consider a different correlation scheme, in which, instead of seeking the physical mechanism for the fluctuations in length, we merely assume the resultant fluctuations to be random. The outcome is that our correlation function introduces a dependence of $\mathbf{r}(s) - \mathbf{r}_0$ on the most probable value $\langle \mathbf{r}(s) - \mathbf{r}_0 \rangle_{\mathbf{u}_0}$, with the orientation of the first chain segment vector $\mathbf{u}_0 = (\partial \mathbf{r}/\partial s)_{s=0}$ specified.

In sections II, III, and IV, we will develop the statistical picture of our model in a derivation based on the diffusion process described by Uhlenbeck and Ornstein.[8,9] The validity, and the limitations, of the "O-U process," as it is often called, are discussed for our application. In section V, our model is compared with others. It is shown that while the features of all these models are contained in our model as specific limiting cases, independent assumptions made in our derivation give rise to some new aspects not possessed by the previous models.

The present work was inspired by the fact that the diffusion process discussed by Uhlenbeck and Ornstein obviates a difficulty encountered in the description of ordinary Brownian motion wherein the particle velocity appears to approach infinity as the time lapse becomes very short. The importance of this property of the model will be made apparent by consideration

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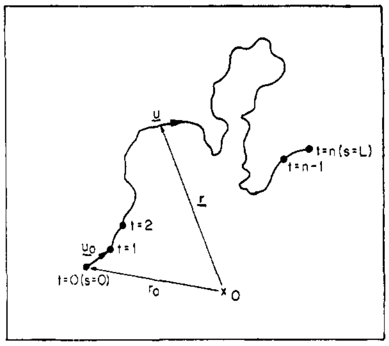

Figure 1. A polymer chain of $n$ segments with total contour length $L$ is described in dual fashion, by parameters $s$ and $t$ which range over $0 \leqq s \leqq L$ and $0 \leqq t \leqq n$, respectively. The position vector **r** and the chain orientation vector **u** are also shown.

of the corresponding roles played by the time sequence in diffusion and the link number parameter in the polymer chain.

## II. The Chain Model

The process of generating stepwise the conformation of a long-chain molecule without self-exclusion can be shown immediately to conform to the stationary Markoffian process of diffusion of a particle, by noting the analogy of the link number parameter in the former process with the time-sequence parameter in the latter. The contour of our chain molecule, a three-dimensional curve, is expressed in terms of a set of position vectors, $\mathbf{r}(s)$, defined at each point on the contour specified by a timelike parameter $0 \leq s \leq L$, where $L$ is the length of the chain. At each point $s$ on the contour, we define the derivative of the position vector at that point, $\mathbf{u}(s) = \mathrm{d}\mathbf{r}(s)/\mathrm{d}s$, which is the spatial orientation vector of the chain contour at that point (Figure 1). The parameter $s$ obviously stands in a one-to-one relation to the link-number parameter $0 \leq t \leq n$, with $n$ the total number of segments in a chain. In consequence, all expressions in the $s$ space are tantamount to their counterparts in the $t$ space. Since $\mathbf{u}(s)$ is a unit vector, we have

$$\mathbf{u}(s)\cdot\mathbf{u}(s) = \overline{\mathbf{u}(s)\cdot\mathbf{u}(s)} = 1 \qquad (1)$$

for the entire ensemble of randomly oriented chain molecules. Then, from $\mathbf{u}(t) = \mathbf{u}(s)(\mathrm{d}s/\mathrm{d}t)$, we obtain by averaging over the distribution of **u**

$$\overline{\mathbf{u}(t)\cdot\mathbf{u}(t)} = \overline{(\mathrm{d}s/\mathrm{d}t)^2} = b^2 \qquad (2)$$

where $b$ is the root-mean-square unit step length along the chain contour. It follows that $L$, the length of the chain, is related to $n$, the total number of segments in the chain, by $L = nb$.

We have a "phase space" spanned by the vectors $\mathbf{r}(s)$, $\mathbf{u}(s)$. From the analogy with the theory of diffusion of free particles we assume that the resulting conformation $\mathrm{f}(\mathbf{r}(s), \mathbf{u}(s), s)$ of the chain will evolve with respect to $s$ in this phase space through the Fokker–Planck equation[9]

$$\frac{\partial}{\partial s}\mathrm{f}(\mathbf{r},\mathbf{u},\mathbf{r}_0,\mathbf{u}_0,s) = \mathrm{div}_{\mathbf{u}}(q\cdot\mathrm{grad}_{\mathbf{u}}\mathrm{f}) + \mathrm{div}_{\mathbf{u}}(\beta\mathrm{f}\mathbf{u}) - \mathbf{u}\cdot\mathrm{grad}_{\mathbf{r}}\mathrm{f} \qquad (3)$$

where $q$ and $\beta$ are the truncated variance and mean displacement of the "particle" in the phase space in a small "time" $\Delta s$. The boundary conditions are those for free diffusion. The parameter $\beta$, which appears in the second term on the right-hand side of eq 3, corresponds to the friction constant in the theory of Brownian motion. We note at this point that in the particular phase space under consideration, the definition of $q$ in eq 3 makes it identical with the reciprocal of the so-called persistence length of a wormlike chain, or the mean projection of the infinitely long chain on the direction of the first chain segment. On the other hand, the boundary condition associated with the process expressed by eq 3 leads to the relation

$$\frac{q}{\beta} = {}^1/_3\overline{\mathbf{u}(s)\cdot\mathbf{u}(s)} = {}^1/_3 \qquad (4)$$

showing that $q/\beta$ is a constant of the system, as in the original O–U process of diffusion of particles. Since the factor 3 in eq 4 is simply due to the dimensionality of the $\mathbf{u}(s)$ space, we see from eq 4 that in our phase space the quantity $\beta$ itself is identified with the reciprocal of the persistence length of a wormlike chain; to wit

$$\beta^{-1} = a \qquad (5)$$

where $a$ is the persistence length.

Although the quantities $q$ and $\beta$ in eq 3 can in general vary with $s$ or **u**, letting aside the precluded possibility of their dependence on **r** on account of the general assumption that the process is homogeneous, we hereafter treat these quantities as constants following the theory by Uhlenbeck and Ornstein, which does not specify the "force" that keeps the vectors $\mathbf{u}(s)$ randomly oriented. Consequently, moments higher than the second derived from the probability distribution function f of eq 3, of which we shall make use later, cannot in general be obtained correctly on the basis of the present assumption. This constitutes an inherent limitation on the applicability of the O–U process to polymer chains; but, as will be seen, correct results are obtained in limiting cases.

The solution for the O–U process given by eq 3 has been obtained[8,9] in the form

$$\mathrm{f}(\mathbf{r},\mathbf{r}_0,\mathbf{u}_0,s) = \left[\frac{\beta^3}{2\pi q(2\beta s - 3 + 4e^{-\beta s} - e^{-4\beta s})}\right]^{3/2} \times \exp\left\{-\frac{\beta^3|\mathrm{R}(s)|^2}{2q(2\beta s - 3 + 4e^{-\beta s} - e^{-2\beta s})}\right\} \qquad (6)$$

where

$$\mathrm{R}(s) = \mathbf{r}(s) - \mathbf{r}_0 - \frac{\mathbf{u}_0}{\beta}(1 - e^{-\beta s}) \qquad (7)$$

and

$$\frac{\mathbf{u}_0}{\beta}(1 - e^{-\beta s}) = \langle\mathbf{r}(s) - \mathbf{r}_0\rangle_{\mathbf{u}_0} \qquad (8)$$

To be precise, the distribution function f of eq 6 is obtained by integrating in a stochastic sense the solution f of eq 3 over **u**. Note the difference in the explicit variables in the two expressions for f. As can be seen above, $\mathbf{R}(s)$ is the deviation of the end-to-end distance $\mathbf{r}(s) - \mathbf{r}_0$ of the chain from the most probable value for a given orientation $\mathbf{u}_0$ of the first chain segment. The subscript $\mathbf{u}_0$ in eq 8 indicates that the mean is taken over an ensemble of conformations of a chain starting at $s = 0$, all with the same chain orientation $\mathbf{u}_0$. The distribution function $f(\mathbf{r}, \mathbf{r}_0, \mathbf{u}_0, s)$ of eq 6, which is the fundamental solution of the process described by eq 3, approaches the well-known Gaussian form

$$\lim_{s>>\beta^{-1}} f(\mathbf{r},\mathbf{r}_0,\mathbf{u}_0,s) \rightarrow f_\infty(\mathbf{r},\mathbf{r}_0,s) =$$

$$\left(\frac{\beta^2}{4\pi q s}\right)^{3/2} \exp\left\{-\frac{\beta^2|\mathbf{r}(s)-\mathbf{r}_0|^2}{4qs}\right\} \quad (9)$$

in the case of a long chain, and $\delta(\mathbf{r} - \mathbf{r}_0)$ in the case of a short chain. In the Appendix we shall further consider the bases of the assumptions of our model discussed in this section.

## III. Moments of the Chain Length Distribution

The juxtaposition of eq 6, 7, and 8 makes it apparent that the operation $\langle \ldots \rangle_{\mathbf{u}_0}$ introduced in eq 8 is formally equivalent to taking the mean of the quantity under consideration over the distribution function $f(\mathbf{r}, \mathbf{r}_0, \mathbf{u}_0, s)$ of eq 6. Consequently, the moments of $\mathbf{R}(s)$ with respect to $f(\mathbf{r}, \mathbf{r}_0, \mathbf{u}_0, s)$ are the central moments of the end-to-end distance $\mathbf{r}(s) - \mathbf{r}_0$ of the chain. We shall hereafter denote the $k$th moments with respect to $f(\mathbf{r}, \mathbf{r}_0, \mathbf{u}_0, s)$ of $\mathbf{r} - \mathbf{r}_0$ and $\mathbf{R}$ by $m_k$ and $\mu_k$, respectively; and in particular, $m_1$ will be written as $m$.

The $m_k$ thus calculated are for a chain with the initial segment given an arbitrarily specified orientation $\mathbf{u}_0$. To obtain physically meaningful quantities, we have to average $m_k = \langle(\mathbf{r} - \mathbf{r}_0)^k\rangle_{\mathbf{u}_0}$ again over $\mathbf{u}_0$. To distinguish this new average from $\langle\ \rangle_{\mathbf{u}_0}$, we introduce the notation $\langle\ \rangle$. Furthermore, a doubly averaged value $\langle\langle\ \rangle_{\mathbf{u}_0}\rangle$ will be simply denoted by $\langle\langle\ \rangle\rangle$, when this simplification will invite no confusion. Remembering that the orientation vector $\mathbf{u}(s)$ is a unit vector, with its spatial orientation arbitrary, we write

$$\langle \mathbf{u}_0^{2k-1}\rangle = 0 \quad (10)$$

$$\langle \mathbf{u}_0^{2k}\rangle = 1 \quad (11)$$

where $k = 1, 2, 3, \ldots.$ On account of these relations, we get, in the $s$ space

$$\langle m^{2k-1}\rangle = 0 \quad (12)$$

$$\langle m^{2k}\rangle = \left(\frac{1 - e^{-\beta s}}{\beta}\right)^{2k} \equiv m_2^k \quad (13)$$

where $k = 1, 2, 3, \ldots,$ and

$$\mu_{2k-1} = 0 \quad (14)$$

$$\mu_{2k} = \frac{(2k+1)!!}{2^k}\left(\frac{2q(2\beta s - 3 + 4e^{-\beta s} - e^{-2\beta s})}{\beta^3}\right)^k$$

$$= \frac{(2k+1)!!}{3^k}\left(\frac{2\beta s - 3 + 4e^{-\beta s} - e^{-2\beta s}}{\beta^2}\right)^k \equiv$$

$$\frac{(2k+1)!!}{3^k}\mu_2^k \quad (15)$$

where $k = 1, 2, 3, \ldots,$ and where we have made use of the notation

$$(2N)!! = (2N)(2N-2)(2N-4)\ldots 4.2 = 2^N N!$$

$$(2N-1)!! = (2N-1)(2N-3)\ldots$$

$$3.1 = (2N)!/(2N)!!$$

where $N = 1, 2, 3, \ldots.$

Putting these expressions into the well-known relations[10] between $m_k$'s and $\mu_k$'s we have, after assorting terms

$$\langle\langle(\mathbf{r}(s) - \mathbf{r}_0)^{2k-1}\rangle\rangle \equiv \langle l^{2k-1}\rangle = m_{2k-1} = 0 \quad (16)$$

$$\langle\langle(\mathbf{r}(s) - \mathbf{r}_0)^{2k}\rangle\rangle \equiv \langle l^{2k}\rangle =$$

$$(2k)!\sum_{n=0}^{k}\frac{(2n+1)}{n!(2k-2n)!}(m_2)^{k-n}\left(\frac{\mu_2}{6}\right)^n \quad (17)$$

$$\langle l^{2k}\rangle = (-1)^k(\mu_2/3)^k\{H_{2k}(i\sqrt{3m_2/\mu_2}) -$$

$$H_{2k}''(i\sqrt{3m_2/\mu_2})\} \quad (17a)$$

where $k = 1, 2, 3, \ldots,$ and $H_n(x) = (-1)^n e^{x^2/2}(\mathrm{d}^n/\mathrm{d}x^n)(e^{-x^2/2})$ is the Hermite polynomial of order $n$ and $i$ denotes $\sqrt{-1}$. These relations yield

$$\langle(\mathbf{r}(s) - \mathbf{r}_0)^2\rangle_{\mathbf{u}_0} = \mu_2 + \mathbf{u}_0^2 m_2 \quad (18)$$

$$\langle l^2\rangle = \mu_2 + m_2 = [2(\beta s - 1 + e^{-\beta s})/(\beta s)^2]s^2 \quad (19)$$

and

$$\langle l^4\rangle = (1/3)(5\mu_2^2 + 18\mu_2 m_2 + 3m_2^2) \quad (20)$$

$$= [\gamma(\beta s)/(\beta s)^4]s^4$$

where

$$3\gamma(x) = 20x^2 - 24x - 6 + (48 + 8x)e^{-x} -$$

$$(88 - 16x)e^{-2x} + 56e^{-3x} - 10e^{-4x} \quad (21)$$

The values of $\langle l^{2k}\rangle/s^{2k}$ for $k = 1, 2, 3$ are illustrated as solid lines in Figure 2.

In the limits $\beta s \gg 1$ and $\beta s \ll 1$, since

$$m_2/s^2 = \{[1 - \exp(-\beta s)]/(\beta s)\}^2 \rightarrow$$

$$\begin{cases} 1/(\beta s)^2 \text{ (when } \beta s \gg 1) & (22) \\ 1 \text{ (when } \beta s \ll 1) & (23) \end{cases}$$

and

$$\mu_2/s^2 = [2\beta s - 3 + 4\exp(-\beta s) - \exp(-2\beta s)]/(\beta s)^2 \rightarrow$$

$$\begin{cases} 2/\beta s \text{ (when } \beta s \gg 1) & (24) \\ 2\beta s/3 \text{ (when } \beta s \ll 1) & (25) \end{cases}$$

we find from eq 17 and 17a in conjunction with eq 19

$$\langle l^{2k}\rangle/s^{2k} \rightarrow \begin{cases} \dfrac{(2k+1)!!}{3^k}\left(\dfrac{2}{\beta s}\right)^k \sim \dfrac{(2k+1)!!}{3^k}\dfrac{\langle l^2\rangle^k}{s^{2k}} & \\ \qquad\qquad \text{(when } \beta s \gg 1) & (26) \\ 1 \text{ (when } \beta s \ll 1) & (27) \end{cases}$$

both of which are well-known results. However, as is expected (see section II) and is apparent in Figure 2, the behavior of $\langle l^{2k}\rangle/s^{2k}$ becomes peculiar for $\beta s$ of order unity. The two regions where the model exhibits the expected behavior are $\beta s \ll 1$ (rigid chain limit) and $\beta s \gg 1$ (flexible chain limit).

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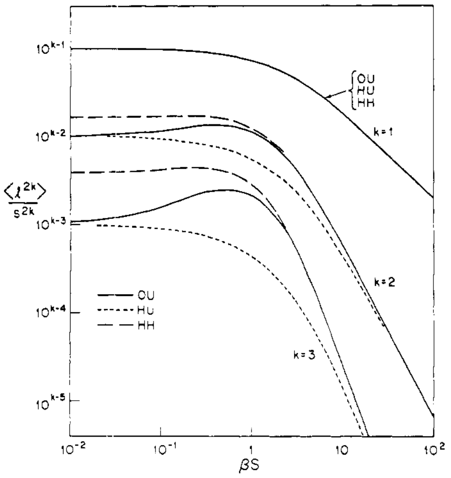

Figure 2. The $2k$th moments of the end-to-end distance for our model (solid lines) as compared with those of the wormlike chain model of Hermans and Ullman (dotted lines) and the Harris and Hearst model (dashed lines). Curves are shown for $k = 1$, $k = 2$, $k = 3$.

As is well known, the mean-square radius of gyration, which we denote by $R_G{}^2$, of a chain molecule consisting of a total of $n_0 = s/b$ segments is related to the mean-square end-to-end distance of subchains composed of segments $i$–$j$ through the relation

$$R_G{}^2 = \frac{1}{n_0{}^2}\sum_{j=1}^{n_0}\sum_{i<j}^{n_0}\overline{(\mathbf{r}_j - \mathbf{r}_i)^2} \tag{28}$$

Our procedure of first averaging over an individual partial ensemble of conformations with a given $\mathbf{u}_0$ and then averaging again for the entire ensemble is equivalent to the averaging process over the entire ensemble of randomly oriented chain molecules required by eq 28. Application of the result of eq 19 to eq 28 leads to the well-known expression[5]

$$R_G{}^2 = \frac{2}{(\beta s)^4}\left[\frac{(\beta s)^3}{6} - \frac{(\beta s)^2}{2} + \beta s - 1 + \exp(-\beta s)\right]s^2 \tag{29}$$

with the limiting behavior

$$R_G{}^2/s^2 \rightarrow \begin{cases} 1/3\beta s \text{ (when } \beta s \gg 1) & (30)\\ 1/12 \text{ (when } \beta s \ll 1) & (31)\end{cases}$$

## IV. The Light Scattering Function

As an immediate consequence of knowledge of all the moments of the end-to-end distance for a chain of length $s = n_0 b$, we can obtain $P(\theta)$, the angular distribution function for intensity of Rayleigh scattering, for our ensemble of O–U chains. The function $P(\theta)$ for an ensemble of molecules randomly oriented in space is defined as

$$P(\theta) = \frac{1}{n_0{}^2}\sum_{i,j=1}^{n_0}\sum_{i\neq j}^{n_0}\overline{\frac{\sin(hr_{ij})}{hr_{ij}}} \tag{32}$$

where $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$ and $h = (4\pi/\lambda_0)\sin(\theta/2)$, with $\lambda_0$ the wavelength of incident light and $\theta$ the scattering angle. We write for our ensemble of O–U chains, for the reason given in connection with eq 28

$$P(\theta) = \frac{1}{s^2}\int_0^s\int_0^s\left\langle\left\langle\frac{\sin(hr_{s'})}{hr_{s'}}\right\rangle\right\rangle ds_1 ds_2 \tag{33}$$

where $r_{s'} = |\mathbf{r}(s_2) - \mathbf{r}(s_1)|$.

The integrand of eq 33 is computed with the help of eq 17a

$$\left\langle\left\langle\frac{\sin(hr_{s'})}{hr_{s'}}\right\rangle\right\rangle = \sum_{k=0}^{\infty}(-1)^k\frac{h^{2k}\langle l_{s'}{}^{2k}\rangle}{(2k+1)!} =$$

$$\sum_{k=0}^{\infty}[1/(2k+1)!](h^2\mu_2{}^0/3)^k \times$$

$$\{H_{2k}(i\sqrt{3m_2{}^0/\mu_2{}^0}) - H_{2k}{}''(i\sqrt{3m_2{}^0/\mu_2{}^0})\} \tag{34}$$

where the superscript to $m_2$ and $\mu_2$ specifies that these quantities refer to a subchain of length $s'$. The limiting forms corresponding to eq 26 and 27 are

$$\left\langle\left\langle\frac{\sin(hr_{s'})}{hr_{s'}}\right\rangle\right\rangle \rightarrow$$

$$\begin{cases}\exp\left(-\dfrac{1}{3(\beta s')}(hs')^2\right) \sim \exp\left(-\dfrac{h^2\langle l^2{}_{s'}\rangle}{6}\right) & \text{(when } \beta s' \gg 1) \quad (35)\\[2ex] \dfrac{\sin(hs')}{hs'} \text{ (when } \beta s' \ll 1) & (36)\end{cases}$$

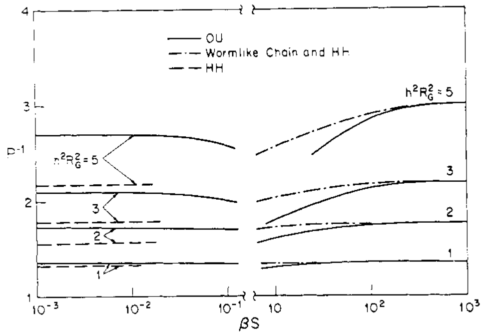

Figure 3. The dependence of $P^{-1}(\theta)$ on $h^2R_G{}^2$ and $\beta s$ for our model (O–U), the wormlike chain model of Peterlin, and the Harris and Hearst model (H–H).

These limiting forms subsequently lead to the known limiting forms of $P(\theta)$, that is, Debye's expression for flexible coils[5]

$$P(\theta) = \frac{2}{\Omega_1{}^2}(\Omega_1 - 1 + e^{-\Omega_1}) \tag{37}$$

$$\Omega_1 = h^2R_G{}^2 \cong h^2s/3\beta \text{ (when } \beta s \gg 1)$$

and Neugebauer's result[5] for thin rods

$$P(\theta) = 2\sum_{n=0}^{\infty}\frac{(-12\Omega_2)^n}{(2n+2)!(2n+1)} = \frac{Si(2X)}{X} - \left(\frac{\sin X}{X}\right)^2 \tag{38}$$

$$\Omega_2 = h^2R_G{}^2 \cong h^2s^2/12$$

$$X = (3\Omega_2)^{1/2} \text{ (when } \beta s \ll 1)$$

respectively.

The solid lines in Figure 3 exhibit the behavior of

$P^{-1}(\theta)$ *vs.* $\beta s$ for fixed values of $h^2R_G{}^2$, that is, fixed values of $\theta$. The smaller values of $h^2R_G{}^2$ are chosen because of the slow convergence of the series involved in the general expression of $P(\theta)$, as can be seen in eq 34. In the region where neither $\beta s \gg 1$ nor $\beta s \ll 1$ is satisfied, $P(\theta)$, as well as the parameter $h^2R_G{}^2$, are no longer derived from our model, as we have remarked in the preceding section. The approach of $P^{-1}(\theta)$ to the known limiting values in both regions of $\beta s$ is marked. The values of $P^{-1}(\theta)$ calculated from eq 38 in the limit of a thin rod for the curves shown are 1.359, 1.746, 2.116, 2.714 for $\Omega_2$ equal to 1, 2, 3, 5, respectively.

## V. Comparison with other Models

So far, a new chain model has been described on the basis of the Markoffian statistics of the O–U process. Although the derivation is self-contained, the resulting model is closely related to other models used for long chain molecules. First of all, the relation of our model to an ordinary Gaussian chain can be seen from eq 9. In the limit of a very long chain, the conformation of a chain no longer depends on the value of $\langle \mathbf{r}(s) - \mathbf{r}_0\rangle_{\mathbf{u}_0}$ and the O–U chain is itself a Gaussian coil.

The statistics of the chain in our model is characterized by a constant $\beta$, the reciprocal of which, as we noted in section II, is the persistence length in the wormlike chain model. Comparison of eq 19 and 29 with the corresponding relations for the wormlike chain suggests that the relation of $\beta$ to $\lambda$ is simply

$$\beta \approx 2\lambda \quad \text{(wormlike chain model)} \tag{39}$$

The approximate equality symbol in eq 39 is used here for the special purpose of indicating that the relation refers to the formal equivalence among the expressions of only the second moments of the end-to-end distance and the radius of gyration pertinent to the two theories under consideration. Equation 39 conforms with eq 5, the stiffness parameter $\lambda$ being half the reciprocal of the persistence length of the wormlike chain. The higher moments of the end-to-end distance that have been calculated with the wormlike chain model are different from our eq 17. For example, instead of eq 20 and 21, Hermans and Ullman[8] obtained

$$\frac{\langle l^4\rangle_{\mathrm{HU}}}{s^4} = \frac{5}{3w^2} - \frac{26}{9w^3} + \frac{(e^{-6w} - 1)}{54w^4} + \frac{2(1 - e^{-2w})}{w^4} - \frac{e^{-2w}}{w^3} \tag{40}$$

where $w = \lambda s$, for the wormlike chain. Similarly, inversion of their expression for the Laplace transform of $\langle l^6\rangle$ yields[11]

$$\frac{\langle l^6\rangle_{\mathrm{HU}}}{s^6} = \frac{35}{9w^3} - \frac{259}{18w^4} + \frac{226}{9w^5} - \frac{6143}{324w^6} + \frac{21}{10w^4}e^{-2w} + \frac{639}{50w^5}e^{-2w} + \frac{4743}{250w^6}e^{-2w} - \frac{1}{54w^5}e^{-6w} - \frac{1}{81w^6}e^{-6w} + \frac{1}{4500w^6}e^{-12w} \tag{41}$$

The notation $\langle l^k\rangle_{\mathrm{HU}}$ refers to $(\mathbf{r}(s) - \mathbf{r}_0)^k$ averaged over all possible conformations of the wormlike chain. The moments calculated with eq 40 and 41 together with the relation between $\beta$ and $\lambda$ given by eq 39 are shown as the dotted lines in Figure 2. These moments have the same values as eq 17 in either of the limits corresponding to very flexible or very rigid chains, as expected. The greatest deviations of the O–U model from the wormlike chain appear from Figure 2 to occur at $\beta s = 1$. At that point, our value of $\langle l^4\rangle^{1/4}$ is about 20% too large while $\langle l^6\rangle^{1/6}$ is about 30% too large.

Peterlin has discussed the light-scattering function for the wormlike chain model.[5] This function coincides with that obtained here in the limit of large $\beta s$ since the wormlike chain model yields a relation for the mean-square end-to-end distance identical with eq 19 if $\beta = 2\lambda$, and Peterlin's assumption that all the higher moments of the end-to-end distance are related to the second moment in Gaussian fashion is consistent with eq 35. However, the approach described by Peterlin, like other similar treatments, fails to give a correct light-scattering function in the rigid-rod limit for which the higher moments are not so related. The values of $P^{-1}(\theta)$ calculated from his theory are illustrated as dotted lines in Figure 3.

Finally, we mention a related model for a partially flexible chain proposed by Harris and Hearst,[6] which for convenience we shall denote as the H–H model. Since their treatment makes the coefficients in their starting equation constants for a given chain, the higher moments obtained from their model cannot be accurate without further knowledge of the mechanism of fluctuation. This is the same kind of predicament that we encounter in our treatment. More significantly, however, as Hearst, *et al.*, point out,[12] the second moments of the end-to-end distance and the radius of gyration of the H–H model, both of which depend on a constant $\beta$ (not to be confused with our $\beta$), are not the same as those of other models; a simple numerical juxtaposition reveals that $\beta$ of their model calculated by eq 39 of ref 5 and the corresponding quantity of the wormlike chain calculated by eq 43 of the same paper differ considerably when the stiffness parameter $2\lambda L$ is of the order of unity, although the two $\beta$'s are identical in the limit of a very stiff chain and approach each other in the limit of a very flexible chain. The behavior of $\beta$ in the H–H model arises from the dependence of $\beta$ on another constant $\alpha$, the determination of which is based on a relation valid only for a very stiff chain.

In order to compare our model with that of H–H, we shall for convenience ignore the above complexity and simply apply eq 39. The higher moments in the H–H model are assumed to be related in a Gaussian fashion to the second moment, regardless of the flexibility of the chain.[7] Under this assumption, the limiting forms of the quantities in the H–H scheme when $\beta s \ll 1$ are

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(11) S. Heine, O. Kratky, G. Porod, and P. J. Schmitz, *Makromol. Chem.*, **44**, 682 (1961).

(12) J. E. Hearst, R. A. Harris, and E. Beals, *J. Chem. Phys.* **45**, 3106 (1966).

$$P(\theta)_{\mathrm{HH}} \rightarrow \frac{1}{s^2}\int_0^s\int_0^s \exp(-h^2(s_1 - s_2)^2/6)\, \mathrm{d}s_1\mathrm{d}s_2 = \frac{1}{2\Omega}(2\sqrt{2\Omega}\ \mathrm{erf}(\sqrt{2\Omega}) - 1 + e^{-2\Omega}) = \sum_{n=0}^{\infty}\frac{(-2\Omega)^n}{(n+1)!(2n+1)} \qquad (42)$$

$$\Omega = h^2s^2/12$$

where $\mathrm{erf}(x) = \int_0^x e^{-t^2}\,\mathrm{d}t$, and

$$\frac{\langle l^{2k}\rangle_{\mathrm{HH}}}{s^{2k}} \rightarrow \frac{(2k+1)!!}{3^k} = \frac{(2k+1)!!}{3^k}\frac{\langle l^2\rangle^k{}_{\mathrm{HH}}}{s^{2k}} \qquad (43)$$

Equation 43, which coincides with eq 26, is derived by comparing eq 42 with the first equality in eq 34. Equation 42 reduces to eq 38 if we identify $\Omega_2$ of eq 38 according to eq 43 as

$$\Omega_2{}^k = \frac{(2k+1)!!}{3^k}\Omega^k \qquad (44)$$

where $k = 1, 2, 3, \ldots$. The values of the moments of the mean-square end-to-end distance and the Rayleigh scattering function of the H–H model are illustrated as dashed lines in Figures 2 and 3, respectively, where we assumed eq 39 to hold. The values of $P^{-1}(\theta)_{\mathrm{HH}}$ calculated from eq 42 for the curves presented in Figure 3 are 1.309, 1.571, 1.795, 2.175 for $\Omega$ equal to 1, 2, 3, 5, respectively. The behavior of the dashed curves in Figure 3 is in general agreement with the observation by Hearst and Harris.[7]

## VI. Discussion

We have noted that while our model for a linear, long-chain molecule with incomplete flexibility retains correct limiting behavior, it fails to describe correctly quantities associated with the chain conformation for intermediate values of $\beta s$. Hearst and Harris[7] also find that their correlation function for the intermediate values of $\lambda L$ behaves differently from that of Kratky and Porod, but this must occur primarily because of the difference in the mean-square end-to-end distances in the H–H model and in the wormlike chain (see section V).

The failure of our model for intermediate values of $\beta s$ is due to its incomplete physical correspondence with a stiff polymer chain. For truly random-flight chains with absolutely no correlation in direction of successive links, the analogy to the Brownian motion of a free particle is mathematically well established;[13] but when chain stiffness is introduced the analogy cannot be preserved. The path $\mathbf{r}(s)$ of the Brownian particle is a nondifferentiable space curve,[14] but the wormlike chain corresponds to a path with a continuous first derivative. The inertia of the Brownian particle assures correct rodlike limiting behavior for small $\beta s$, but this evidently offers no guarantee for the intermediate stages.

Despite this limitation, the present model offers the practical advantage that all higher moments of the end-to-end distance can be obtained analytically without difficulty, although not with complete accuracy save at the limits of rigid rod or flexible coil. For applications in which explicit knowledge of the higher moments is required, our model offers a tractable and useful approximation to the conformational behavior of stiff chains without excluded volume.

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## VII. Appendix

The original O–U process involves a random velocity function with respect to time, $\mathbf{u}(t)$, that fluctuates with respect to both magnitude and direction. In our adaptation of the O–U process, however, we made use of the fact that the tangent vector is a unit vector, as expressed in eq 1. It is to be noted in this respect that the derivative of a position vector of a continuous space curve with respect to the running parameter of the curve can essentially assume any value except zero. This is because the choice of the running parameter is to some degree *arbitrary*. We then choose in particular a normalized parameter $s$ as described by eq 1. In doing so, we *de facto* lump the lengthwise fluctuation of $\mathbf{u}(s)$ into the statistically averaged quantity $b$ of eq 2, which in turn is treated as a constant of the model throughout the paper. Insofar as the specific choice of the timelike parameter $s$ is capable of recovering the increment of $\mathbf{r}(s)$ from $\mathbf{u}(s)$, *i.e.*, $\mathrm{d}\mathbf{r}(s) = \mathbf{u}(s)\mathrm{d}s$, our application of the O–U process to the problem of the polymer chain still seems justifiable.

It is amusing to remark that eq 5 is just the Nyquist relation for our essentially linear system, and to speculate that an extension to a slightly nonlinear system[15] might afford better approximations to the higher moments.

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(13) For example, E. W. Montroll, *Ann. Math. Stat.*, **18**, 18 (1947).

(14) For example, D. R. Cox and H. D. Miller, "The Theory of Stochastic Processes," John Wiley & Sons, Inc., New York, N. Y., 1965.

(15) See, for example, the techniques described by N. G. van Kampen in "Fluctuation Phenomena in Solids," R. E. Burgess, Ed., Academic Press, New York, N. Y., Chapter 5.