A mean-field model for semiflexible chains

B.-Y. Ha and D. Thirumalai
Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742

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We derive a mean-field model for a semiflexible chain using a functional integral approach. The resulting model satisfies the global constraint $\langle \mathbf{u}^2(s)\rangle = 1$ rather than the hard constraint that $\mathbf{u}^2(s)=1$ for all s. The function $\mathbf{u}(s)$ is the tangent vector $\partial\mathbf{r}/\partial s$, where $\mathbf{r}(s)$ represents the conformation of the chain and s is the arc length. © *1995 American Institute of Physics.*

I. INTRODUCTION

The random walk model for neutral polymer is perhaps the simplest mathematical model for long flexible chains.[1] The tremendous progress made in the theoretical understanding of configurational and dynamical properties of flexible polymer systems becomes possible because systematic calculations using the random walk model can be carried out at least in principle.[2] This model is the minimal representation of real polymers that adequately describes the global properties of several polymeric systems. The model views the flexible polymer chains as a Brownian curve. In the discrete representation, a flexible chain can be modeled as one for which angles between successive chain segments are not correlated. Since the orientations of chain segments are independent, the segment vectors have the Markovian property so that the mean squared end-to-end distance is proportional to the number N of segments of size a in the chain. In the continuous limit this chain becomes a Brownian curve. The position vector of this chain is capable of undergoing arbitrary changes in direction and thus the tangential vectors are not well defined. Many polymeric molecules, however, exhibit internal stiffness, thus restricting the allowed values of the angles between two successive segments. For such polymers, called semiflexible or stiff chains, the angles between segments are not uncorrelated, as is the case for flexible chains, but exhibit nonvanishing spatial correlations. A mathematical description of such chains should incorporate the effects of chain stiffness without violating homogeneity condition.

The effect of excluded volume can also be modeled for flexible chains. Although historically the importance of excluded volume was recognized sometime ago, the introduction of the Edwards to represent the effect of this short range interaction made possible systematic calculation of various static and dynamic properties using field theoretical methods.[2] In this paper, in which we focus on representations of semiflexible chains; the excluded volume effects will be ignored.

A simple way to account for the stiffness of a semiflexible chain is to constrain the angles between two successive segments θ to be fixed. The value of θ depends on the local stiffness of the chain. This prescription leads to the freely rotating chain model. If we describe the configurations of a polymer chain by the set of position vectors $\{\mathbf{r}_n\}=(\mathbf{r}_0,...,\mathbf{r}_N)$ or alternatively by the set of segment vectors $\{\Delta\mathbf{r}_n\}=(\mathbf{r}_1-\mathbf{r}_0,...,\mathbf{r}_N-\mathbf{r}_{N-1})$, then the spatial correlation, $\langle \Delta\mathbf{r}_n\cdot\Delta\mathbf{r}_{n-1}\rangle$, in the freely rotating chain has the assigned value $a^2\cos\theta$. In the continuous limit ($a\to 0$, $\theta\to 0$, $N\to\infty$, $Na=L$) the freely rotating chain becomes the so-called wormlike chain.[3] In this case, the ratio $2a/\theta^2$ defines the *persistence length* l_p, which is the typical length scale over which the chain changes its direction appreciably. Other conformational properties of such a model are well known in the literature.[3–8]

The spatial correlations $\langle \Delta\mathbf{r}_n\cdot\Delta\mathbf{r}_m\rangle$, which characterize the properties of a semiflexible chain, decay exponentially as $\exp(-a|n-m|/l_p)$. Thus the conformational properties of a semiflexible chain beyond the length scale l_p reduce to those of flexible chains, i.e., one can view the stiff chain as being made up of several rigid segments of length l_p that are freely joined. However because of the intrinsic skeletal stiffness of many synthetic polymers as well as biopolymers one needs to develop a model that explicitly builds effects due to chain bending. The chain stiffness turns out to be a relevant parameter to the isotropic-nematic transition condition in liquid-crystalline polymers.[9] Even for an isolated chain, the chain stiffness should be taken into account in the description of the local properties of polymer chains. This is especially important in polyelectrolytes. The scaling behavior of the electrostatic persistence length l_e is known to depend on the rigidity of the chain.[10,11] Many biological molecules and short chains of otherwise flexible chains also belong to the class for which the chain stiffness plays an important role.

A number of theoretical models have been introduced in the literature to account for chain stiffness. The earliest model for stiff chains is the wormlike chain (also known as Kratky–Porod model) in which the angles between successive chains are constrained.[3] Although physically reasonable this model has not yielded analytically tractable results for equilibrium and dynamical properties. Harris and Hearst introduced a ''simplified model'' of stiff chains in which the tangent vector $\mathbf{u}(s)=\partial\mathbf{r}/\partial s$ was allowed to fluctuate as opposed to having the constraint $\mathbf{u}^2(s)=1$ for all s.[5] It has been noted that the resulting model does not represent homogeneously stiff chains. More recently a model that does not suffer from this restriction was proposed by Lagowski, Noolandi, and Nickel[12] using a functional integral formalism. These authors showed that the resulting model yielded the mean squared end-to-end distance in agreement with Kratky–Porod. The spatial correlations decay exponentially with a slightly shorter value of the persistence length.

In this paper we show that a model for stiff chains proposed by Lagowski, Noolandi, and Nickel (LNN) (Ref. 12)

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results from a stationary phase evaluation of certain functional integrals that occur in an appropriate field theory [cf. Eq. (8)]. Our approach is systematic and can be applied to other polymeric systems exhibiting more complicated interactions. The spirit of the theory presented here is in the same vein as the Mauer and Saupe theory of liquid crystals.[13] We should note that Winkler *et al.*[14] have obtained a model for stiff chains using the maximum entropy principle. These authors did not notice that their model in the continuum limit is identical to that of LNN. Furthermore their method appears more cumbersome than the standard functional integral approach presented here. In the next section the basic derivation is presented and a few concluding remarks are given in Sec. III.

II. MEAN-FIELD MODEL

A. Flexible chains

The basic methodology can be illustrated using the simpler example of a flexible chain. This is a limiting case of a stiff chain as the rigidity vanishes. The probability function for the flexible chain conformations without excluded volume interactions can be written as

$$\Psi\{\mathbf{r}_n\}=\prod_{n=1}^{N}\psi(\Delta\mathbf{r}_n), \tag{1}$$

where $\psi=\delta(|\Delta\mathbf{r}|-a)/4\pi a^2$ denotes the random distribution of a segment vector of length a. We can now rewrite the probability weight in Eq. (1) by introducing auxiliary fields λ_n as

$$\Psi\{\mathbf{r}_n\}\propto\int_{-i\infty}^{i\infty}\prod_{n=1}^{N}d\lambda_n\ \exp\left\{-\sum_{n=1}^{N}\frac{\lambda_n}{a}[(\Delta\mathbf{r}_n)^2-a^2]\right\}. \tag{2}$$

We now show that a stationary phase evaluation of the free energy of the chain described by above weight leads to the probability weight for the Brownian chain. This approximation amounts to relaxing the locally enforced constraint of $(\Delta\mathbf{r}_n)^2=a^2$ to a globle one, $\langle(\Delta\mathbf{r}_n)^2\rangle=a^2$, and the validity of the approximation can be justified *a posteriori* as $a\to 0$. The free energy F of a noninteracting flexible chain can be written as

$$\exp(-F/k_BT)=\text{ const }\int_{-i\infty}^{i\infty}\prod_{n=1}^{N}d\lambda_n\exp\,(-\mathscr{F}\{\lambda_n\}), \tag{3}$$

where the free energy functional $\mathscr{F}\{\lambda_n\}$ is defined by

$$\mathscr{F}\{\lambda_n\}\equiv-\ln\left[\int\prod_{n=1}^{N}d\mathbf{r}_n\ \exp\left(-a^{-1}\sum_{n=1}^{N}\lambda_n\mathbf{r}_n^2\right)\right]-a\sum_{n=1}^{N}\lambda_n=\sum_{n=1}^{N}\left(\frac{3}{2}\ln\lambda_n-\lambda_n a\right)+\text{ const }. \tag{4}$$

In the above equation, the order of the $\mathbf{r}_n$ and λ_n integrations is interchanged. So far the formulation is exact. If we denote the trajectory λ_n along which the integrand in Eq. (3) has its maximum value by λ_n^{cl}, then the free energy can be expanded around this stationary phase trajectory, λ_n^{cl}. In the following discussions the superscript cl will be omitted. In the mean-field theory for which the constraint is imposed only on an average, we retain only the leading term in this expansion and neglect correction terms to this. By setting the partial derivative of the free energy functional $\mathscr{F}\{\lambda_n\}$ with respect to λ_n, we get the stationary phase condition,

$$\frac{\partial}{\partial\lambda_n}\mathscr{F}\{\lambda_n\}=0\Rightarrow\lambda_n=\frac{3}{2a},\quad 0\leqslant n\leqslant N. \tag{5}$$

The independence of λ_n on n reflects the symmetry of the problem of an ideal flexible chain. Since the delta function can be also represented as $\delta(\mathbf{r})=\lim_{a\to 0}(3/2\pi a^2)^{3/2}\exp(-\mathbf{r}^2/2a^2)$, the saddle-point evaluation becomes very accurate in the continuum limit, $a\to 0$. Thus long flexible chains, i.e., $N\gg 1$ can be well described by the following weight in the continuum limit:

$$\Psi[\mathbf{r}(s)]\propto\exp\left[-\frac{3}{2a}\int_0^L ds\left(\frac{\partial\mathbf{r}}{\partial s}\right)^2\right], \tag{6}$$

where $\Psi[\mathbf{r}(s)]$ is written in the functional integral notation and is referred to as the Wiener measure. By treating the random fields $\lambda(s)$ at the mean field level, the microscopic constraints conjugate to the fields $\lambda(s)$, which ensure that the chain segments are connected but otherwise randomly distributed, are relaxed to the global ones. This results in the expected probability weight given in Eq. (6) for a long flexible chain and is the Wiener measure obtained in the path integral description of a diffusion equation.

B. Stiff chains

The approach described above can be extended to semiflexible chains. In these calculations we assume that the stretching of two connected chain segments are not important so that there is no coupling between this degree of freedom and the bending degree of freedom.[15] In this case, the weight in Eq. (1) needs to be modified so that it yields nonvanishing correlations $\langle\Delta\mathbf{r}_n\cdot\Delta\mathbf{r}_{n-1}\rangle=a^2\theta^2=2a^3/l_p$. This can be achieved if we multiply the weight in Eq. (1) by the Boltzman weight $\exp(l_p a^{-3}\Sigma_{n=1}^{N-1}\Delta\mathbf{r}_{n+1}\cdot\Delta\mathbf{r}_n)$ corresponding to the local interactions between adjacent segments. This term favors parallel alignment of adjacent segments over bent configurations. In the λ_n representation of the probability weight, this can be rewritten as $\exp[-\frac{1}{2}l_p a^{-3}(\Delta\mathbf{r}_{n+1}-\Delta\mathbf{r}_n)^2]$ with a redefinition of λ_n. Then the weight associated with a particular configuration of a semiflexible chain becomes

$$\Psi\{\mathbf{r}_n\}\propto\int_{-i\infty}^{i\infty}\prod_{n=1}^{N}d\lambda_n\ \exp\left\{-\sum_{n=1}^{N}\frac{\lambda_n}{a}[(\Delta\mathbf{r}_n)^2-a^2]-\frac{l_p}{2a^3}\sum_{n=1}^{N-1}(\Delta\mathbf{r}_{n+1}-\Delta\mathbf{r}_n)^2\right\}. \tag{7}$$

In the continuum limit, this can be written in the functional integral notation as

$$\Psi[\mathbf{u}(s)] \propto \exp\left[-\frac{l_p}{2}\int_0^L ds\left(\frac{\partial \mathbf{u}}{\partial s}\right)^2\right]\prod_{0\le s\le L}\delta[\mathbf{u}^2(s)-1], \tag{8}$$

where $\mathbf{u}(s)\equiv\partial\mathbf{r}(s)/\partial s$ is a unit tangent vector. The properties associated with the weight $\Psi[\mathbf{u}(s)]$ are well-known in the literature.[3–8] The random variable $\mathbf{u}(s)$ describes the rotational Brownian motion on a unit sphere, $\mathbf{u}^2=1$. If we let $P(\mathbf{u}_s,\mathbf{u}_{s'};s',s)$ be the probability that $\mathbf{u}(s')=\mathbf{u}_{s'}$ when $\mathbf{u}(s)=\mathbf{u}_s$, then this function obeys a diffusion equation on the unit sphere. The solution of the diffusion equation can be expanded in terms of spherical harmonics. This enables us to compute the following correlation:

$$\langle \mathbf{u}(s')\cdot\mathbf{u}(s)\rangle = \exp(-|s'-s|/l_p). \tag{9}$$

This correlation along with the Markovian property of $\mathbf{u}$ lead to the mean squared end-to-end distance given by

$$\langle R^2\rangle = \int_0^L\int_0^L ds\,ds'\langle \mathbf{u}(s')\cdot\mathbf{u}(s)\rangle = 2l_pL - 2l_p^2(1-e^{-L/l_p}). \tag{10}$$

Even though the results given in Eq. (9) and Eq. (10) are exact, the use of Eq. (8) to describe nonideal semiflexible chains turns out to be quite formidable. The major difficulty arises because of the constraint $\mathbf{u}^2(s)=1$. One encounters similar difficulty in other physical systems described by the nonlinear σ model[16] for which the magnitude of a spin $\mathbf{S}$ is held fixed, $\mathbf{S}^2=$const. Thus it is of very practical interest to obtain a tractable model for such constrained systems. We will extend the stationary phase approach adopted for the flexible chain to obtain a tractable meanfield model for a semiflexible chain.

In our stationary phase approach, the field λ_n is treated as a parameter to be determined. The dependence of λ_n on n depends on the problem under consideration. The free energy functional for an ideal semiflexible chain can be written as

$$\mathscr{F}\{\lambda_n\} = -\ln\int\prod_{n=1}^N d\mathbf{r}_n\ \exp\left(-\frac{E}{k_BT}+a\sum_{n=1}^N\lambda_n\right), \tag{11}$$

where E is given in a matrix form

$$\frac{Ea}{k_BT} = \zeta^T Q\zeta, \tag{12}$$

with $\zeta\equiv\{\mathbf{r}_1,...,\mathbf{r}_N\}^T$. The $3N\times 3N$ matrix Q is defined by

$$Q_{nm} = \lambda_n\delta_{nm} - \frac{l_p}{2a^2}(1+\delta_{nm\pm1}). \tag{13}$$

Then the free energy $\mathscr{F}$ is given by

$$\mathscr{F}\{\lambda_n\} = \frac{3}{2}\ln(\det\ Q) - a\sum_{n=1}^N\lambda_n + \text{const}. \tag{14}$$

The stationary phase evaluation of λ_n amounts to minimizing the free energy with respect to λ_n, i.e.,

$$\frac{\partial}{\partial\lambda_n}\mathscr{F}\{\lambda_n\} = 0 \Rightarrow \frac{3}{2}\frac{\partial\ln(\det\ Q)}{\partial\lambda_n} = a, \quad 1\le n\le N. \tag{15}$$

It can be easily shown that the minimization condition in Eq. (15) amounts to requiring $\langle\mathbf{u}^2\rangle=1$ in the continuous limit. This follows because Eq. (15) can be rewritten as $\partial\mathscr{F}/\partial\lambda_n = \langle(\Delta\mathbf{r}_n)^2/a^2\rangle - 1$. This is a set of simultaneous equations for the unknown parameters λ_n for which we can not find an analytical solution. An examination of the structure of the matrix Q, however, leads to the following properties of λ_n which satisfy the above equation; $\lambda_1=\lambda_N\neq\lambda_2=,\cdots,=\lambda_{N-1}$. For our purposes it suffices if λ_n can be chosen so that $\langle\mathbf{u}^2(s)\rangle=1$ and other conformational properties are reproduced. If all λ_n are equal to each other, as is the case for the flexible chain, then the chain described by the probability weight in Eq. (7) shows inhomogeneity, i.e., the chain fluctuates more strongly at both ends than elsewhere. Having recognized the translational asymmetry in the problem of a semiflexible chain, it is convenient to rewrite λ_n as follows: $\lambda_1=\lambda_N=\lambda+\delta/a$, $\lambda_n=\lambda(2\le n\le N-1)$. With these simplifications, the weight for the semiflexible chain at the level of a stationary phase approximation becomes

$$\Psi[\mathbf{u}(s)] \propto \exp\left[-\lambda\int_0^L ds\,\mathbf{u}^2(s) - \frac{l_p}{2}\int_0^L ds\left(\frac{\partial\mathbf{u}}{\partial s}\right)^2 - \delta(\mathbf{u}_0^2+\mathbf{u}_L^2)\right]. \tag{16}$$

This functional is exactly identical in form to that proposed by LNN. The explicit expression for $\det Q$ and thus the saddle-point conditions for λ and δ can be obtained by setting a recursion relation in N. Alternatively, we can exploit an analogy between the path integral in Eq. (16) and the harmonic oscillator in quantum mechanics.[17] If $Z(\mathbf{u}_0,\mathbf{u}_L;L)$ is the propagator of a harmonic oscillator of a mass l_p and a frequency $(2\lambda/l_p)^{1/2}$, we can rewrite the free energy as

$$\begin{aligned}\mathscr{F}[\lambda,\delta] &= -\ln\int d\mathbf{u}_0 d\mathbf{u}_L \exp[-\delta(\mathbf{u}_0^2+\mathbf{u}_L^2)] \\ &\quad\times Z(\mathbf{u}_0,\mathbf{u}_L;L) - (L\lambda+2\delta) + \text{const} \\ &= \frac{3}{2}\ln\left\{\left[\delta\ \sinh\ L\left(\frac{2\lambda}{l_p}\right)^{1/2} + \left(\frac{\lambda l_p}{2}\right)^{1/2}\right.\right. \\ &\quad\left.\left.\times\cosh\ L\left(\frac{2\lambda}{l_p}\right)^{1/2}\right]^2 - \frac{\lambda l_p}{2}\right\} - \frac{3}{2}\ln\left(\frac{\lambda l_p}{2}\right)^{1/2} - \frac{3}{2} \\ &\quad\times\ln\left[\sinh\ L\left(\frac{2\lambda}{l_p}\right)^{1/2}\right] - (L\lambda+2\delta) + \text{const}.\end{aligned} \tag{17}$$

A little algebra leads to the following stationary phase conditions for λ and δ:

$$\left(\frac{\lambda l_p}{2}\right)^{1/2} = \delta = \frac{3}{4}. \tag{18}$$

Note here that the values of λ and δ do not depend on the contour length L of a chain. Since the stationary phase condition is imposed on λ, only one of l_p or λ is independent.

To understand features implied by the weight in Eq. (16), let us compute the correlation $\langle\mathbf{u}(s)\cdot\mathbf{u}(s')\rangle$. Using the Markovian property of $\mathbf{u}$, the correlation can be computed,

$$\langle \mathbf{u}(s)\cdot\mathbf{u}(s')\rangle = \frac{\int \mathscr{D}[\mathbf{u}]\mathbf{u}(s)\cdot\mathbf{u}(s')\Psi[\mathbf{u}]}{\int \mathscr{D}[\mathbf{u}]\Psi[\mathbf{u}]}$$

$$= \exp(-|s'-s|/l_0), \tag{19}$$

where $l_0 \equiv \frac{2}{3} l_p$. A direct consequence of the above correlation is $\langle \mathbf{u}^2\rangle = 1$ and thus the constraint $\mathbf{u}^2 = 1$ is enforced only on an average in the weight given in Eq. (16). The above correlation can be compared with one in Eq. (9) obtained with the exact weight. A comparison of Eq. (19) and Eq. (9) shows that the persistence length for the approximate model for stiff chains [cf. Eq. (16)] is smaller by a factor of $\frac{2}{3}$. The plausible reason for this is the following: In the original model the constraint condition is $\mathbf{u}^2(s) = 1$ for all values of s. The model obtained by enforcing the global condition $\langle \mathbf{u}^2\rangle = 1$ allows for unrestricted (restricted only on an average) fluctuations in $\mathbf{u}$ thus allowing for configurations that would be prohibited by the restricted condition $\mathbf{u}^2(s) = 1$. Thus we would expect l_0 to be less than l_p. Winkler *et al.*[14] have obtained exactly the same result [see their Eq. (4.18)] using the maximum entropy principle. Since they also only enforce the constraint on an average the resulting theory, as described here, should be viewed as mean-field like. If l_0 is understood as a new definition of the persistence length, then the stationary phase weight in Eq. (16) predicts the same conformational behaviour as the exact one in Eq. (8). It is worth noting that for a chain described by this weight with $\delta = 0$, the above correlation holds only for $0 \ll s, s' \ll L$. This is because of the excess end fluctuations in this case.

For practical purposes it's more convenient to use a translationally symmetric model for a semiflexible chain, i.e., one described by $\Psi[\mathbf{u}(s)]$ in Eq. (16) with $\delta = 0$. For ring polymers for which the periodic condition $\mathbf{u}(0) = \mathbf{u}(L)$ and the closure relation $\int_0^L \mathbf{u}(s)ds = 0$ are imposed, we expect all the $\lambda(s)$ to be equal or $\lambda(s)$ should be independent of s. In this case, the free energy $\mathscr{F}$ can be written compactly with $\mathscr{H} \equiv \lambda\mathbf{u}^2 + \frac{1}{2} l_p (\partial\mathbf{u}/\partial s)^2$ as follows:

$$\mathscr{F}[\lambda] = -\ln \mathrm{tr}\left\{ \delta\left[\int_0^L \mathbf{u}(s)ds\right] e^{-L\mathscr{H}}\right\} - L\lambda$$

$$= 3\ln\left[\sinh L\left(\frac{\lambda}{2l_p}\right)^{1/2}\right] - \frac{3}{2}\ln(L\lambda) - L\lambda$$

$$+ \text{ const}. \tag{20}$$

Now the stationary phase condition reads

$$\left(\frac{l_p\lambda}{2}\right)^{1/2} = \frac{3}{4}\left[\coth L\left(\frac{\lambda}{2l_p}\right)^{1/2} - \frac{1}{L}\left(\frac{2l_p}{\lambda}\right)^{1/2}\right]. \tag{21}$$

Here we have L-dependent condition for λ. This is because only paths which satisfy the periodic boundary condition $\mathbf{u}(L) = \mathbf{u}(0)$ contribute to the free energy $\mathscr{F}$. The periodic boundary condition is also incorporated in the correlation of $\mathbf{u}(s)$, i.e.,

$$\langle \mathbf{u}(s')\cdot\mathbf{u}(s)\rangle$$

$$= \frac{\cosh[(L-2|s'-s|)/2l_0'] - 2l_0'/L\cdot\sinh(L/2l_0')}{\cosh(L/2l_0') - 2l_0'/L\cdot\sinh(L/2l_0')}, \tag{22}$$

where $l_0' \equiv (l_p/2\lambda)^{1/2}$. Note here that $\langle \mathbf{u}(s+L)\cdot\mathbf{u}(s)\rangle = \langle \mathbf{u}^2(s)\rangle = 1$. In the limit of $L\to\infty$, however, the ring conditions are irrelevant. That is the stationary phase condition and the correlation given above reduce to those of open chains. This can be checked by taking the limit $L\to\infty$ in above equations for the ring polymers. Alternatively, for large L, we can use the following formula:[18]

$$e^{-L\mathscr{H}} = e^{-LE_0}\{|0\rangle\langle 0| + \mathscr{O}[e^{-L(E_1-E_0)}]\}, \tag{23}$$

where $E_0 = \frac{3}{2}(2\lambda/l_p)^{1/2}$ and $E_1 = \frac{5}{2}(2\lambda/l_p)^{1/2}$. The ground state denoted by $|0\rangle$ corresponds to the lowest eigenvalue E_0 of $\mathscr{H}$ and is assumed to be unique and isolated. As $L\to\infty$, this expression is dominated by the ground state. The term $\mathrm{tr}\exp(-L\mathscr{H})$ can be easily computed to yield the stationary phase condition, i.e., $(\lambda l_p/2)^{1/2} = \frac{3}{4}$. Similarly the correlation of $\mathbf{u}$ can be computed as follows:

$$\langle \mathbf{u}(s')\cdot\mathbf{u}(s)\rangle = \exp[-(E_1-E_0)(s'-s)]$$

$$= \exp(-|s'-s|/l_0). \tag{24}$$

An alternative model (without derivation) for ring segments has been proposed earlier.[19] This involves modifying the original Harris–Hearst model for open chains. Huber *et al.* have computed quasielastic scattering for a modified version of this model.[20]

III. CONCLUSIONS

In this paper we have provided a derivation of the model for stiff chains introduced by Lagoiwski, Noolandi, and Nickel.[12] These authors sought to eliminate certain deficiencies associated with the model of the sort suggested by Harris and Hearst.[5] LNN started from the weight given by

$$\Psi[\mathbf{u}] \propto \exp\left[-\frac{3}{2a}\int_0^L ds\,\mathbf{u}^2(s) - \frac{l_p}{2}\int_0^L ds\left(\frac{\partial\mathbf{u}}{\partial s}\right)^2\right]. \tag{25}$$

The first term in the exponent accounts for the segment distribution while the second one corresponds to the bending energy. By noting that inhomogeneity is associated with the chain described by this weight, they added a term $-\delta(\mathbf{u}_0^2 + \mathbf{u}_L^2)$ in the exponent to suppress excess end fluctuations. The same stationary phase conditions in Eq. (18) were obtained to ensure $\langle \mathbf{u}^2(s)\rangle = 1$. More recently, the same model was suggested by Winkler, Reineker, and Harnau using the maximum entropy principle supplemented by the method of Lagrangian multipliers to account for the constraints.[14] The stationary phase scheme used here is a longer version of a brief result on the model of a semiflexible chain reported in our earlier work describing the calculation of electrostatic persistence length of a polyelectrolyte chain.[11] We believe that this saddle-point approach is systematic and straightforward way of dealing with constrained systems and can be extended to polymer chains in more complicated circumstances. Our theory also offers justification for the meanfield model for stiff chains proposed in earlier studies.[12]

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