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Matrix models of discretely bending, stiff polymers

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Abstract

Polymer models which make use of the Ising model and transfer matrix techniques remind us, for example, of the work of Flory [Statistical mechanics of chain molecules, 1969] and Zimm and Bragg [J Chem Phys, 31 (1959) 526]. We investigate the properties of some such polymer models where the chain conformation can be described solely by an Ising-like parameterization and a set of independent, predetermined bond direction vectors or by a Potts-like model for directions of bond vectors on a lattice, with the specific aim of understanding more closely the connection of constraints and forces on the chain ends for polymers which, in general, are of arc length corresponding to their persistence lengths. Instances of these models are directed helical walks, random sequential walks, bimodally distributed in direction walks or relatively short, stiff chains fixed into a network. The behavior of this model under deformation in statistical mechanics and its dynamical properties under Glauber dynamics are discussed.

Keywords: Statistical mechanics; Stiff polymers

1. Introduction

The recent interest in biologically motivated physics and the properties of the very stiff molecules such as actin, or other, softer chains which have as a feature some persistence length, has brought models for such molecules into the limelight. Not only are they interesting from the aspect of liquid crystalline behavior but especially from their mechanical properties when they form networks, as in cells [3,4]. Networks of short and stiff polyamide chains can also be synthesized [5]. It has been shown that the molecules assume new configurations by rotation about a certain bond, indicating a jump-like (almost discrete) re-orientation which can be modeled in an Ising-like fashion [6]. During the deformation of the molecule in such a network it is important to take into account the constraints imposed on the chain ends by the junctions connecting the molecule to the rest of the network.

Further complexity can be introduced when double-stranded chains are viewed. For example, some chains can be viewed as combinations of stiff helices and flexible coils as first studied by Zimm and Bragg [2,7] and in numerous descendents of their model. For semiflexible, double-stranded molecules (in Refs. [8,9]) both the torsional and bending rigidities play an important role in the final statistical conformations of the chain. Such models can be applied to investigate the conformational properties of DNA. The advances in experimental micromanipulation techniques have also recently caused the investigation of the Zimm–Bragg model for a force–extension relationship [10].

Frequently, a continuum formulation for stiff polymers is used in the form named after Kratky and Porod where a walk with a constraint on the magnitude of the tangent can be introduced and the partition function is calculated in the following manner:

$$Z_{\mathrm{KP}} = \int \mathscr{D}\mathbf{r}(s)\exp\left[-\frac{\kappa}{2}\int_0^N \mathrm{d}s\left(\frac{\partial^2 r}{\partial s^2}\right)^2\right]\times\prod_s \times\delta\left[\left(\frac{\partial r}{\partial s}\right)^2-1\right]. \tag{1.1}$$

Here κ is the bending rigidity and the Dirac delta function constrains the tangent vector of the chain to be equal to 1 in magnitude. The arc length s varies from 0 to N. The averaged end-to-end vector squared is then given by the

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expression:

$$\langle R^2\rangle = 2\ell_p N - 2\ell_p^2(1 - e^{-N/\ell_p}). \quad (1.2)$$

However, the constraint upon the tangent above makes this expression very difficult to handle analytically such that in many cases only a mean-field approach to the constraint or a perturbative treatment around the limit of a straight rod is used. Subject to such approximations of the constraint the stiffness is no longer fully controlled. One aspect of a continuum or discretely formulated model of a polymer configuration is that it will show stiffness at short length scales and will be Gaussian at scales larger than the persistence length. Important ingredients for the formulation of such a model are the definition of a local probability (or energy) of bending and a probability for two neighbors on a chain to be both bent.

Of course, there exist many different models and texts describing polymer chains and the transitions from local bending to the Gaussian chain. The reader may refer to Flory's book [1], references therein, and to other standard textbooks.

Another interesting question emerges as to the conformational sequences in molecules where the local properties of conformation are distributed in some way [11]. There are further difficulties with interactions in molecules which show any stiffness.

In this paper we investigate models in which the polymer consists of bonds of a fixed and finite length. Each bond also has a finite number of permissible orientations. The models share the property that they are accommodated in a matrix formalism for which statistical properties may be calculated in a fashion analogous to the transfer matrix of the Ising case (see, for example, Ref. [12]). The use of these methods for polymer problems is not new, of course, since the work by Zimm and Bragg modeling the helix-coil transition of polypeptides [2] and, especially, Flory's rotational isomeric state (RIS) model [1].

Here we connect the Ising variable description to conformational information of the polymer, such as an end-to-end distance, with forces and possible constraints applied to the end-points. The chain we model can be thought to consist of compact stiff sections and straight, stiff sections. Constraints and forces on the ends are used to model the inclusion of the chain in a network with stiff junctions. This differs from the Zimm–Bragg idea in that separated compact or helical sections are still orientationally coupled in the present case. Propagators for end-to-end distances in the Zimm–Bragg helix-coil system have recently been formulated by Muthukumar [13] and Carri and Muthukumar [14] in the investigation of the phase behavior of more complicated systems. Tamashiro and Pincus [10] have investigated the Zimm–Bragg model with an external force term $-\mathbf{F}\cdot\mathbf{R}_{\text{end-to-end}}$ added to the Hamiltonian. Here we show how such contributions can be computed with correlations between compact sections of polymer.

The RIS model, whose foundations are essentially the same as for the models presented here, has been used in the past overwhelmingly in the computation of the value of the coefficient C_∞ or for averages such as $\langle R^4_{\text{end-to-end}}\rangle$ for various polymers. We indicate how one can compute more general properties which might be applicable to Aharoni's polyamide networks [5] or to descriptions of polyelectrolyte chains in bad solvent. (Polyelectrolyte chains in bad solvent are believed to show a 'pearl necklace' structure, i.e. compact 'beads' connected by relatively straight 'strings' of polymer [15–17].)

In short, we argue that the idea of the RIS and related models is analytically useful in complex problems requiring the use of stiff polymer chains. In particular, we record here results (obtained by the usual methods) for such models of chains with an applied force, constrained directions of the ends of the polymer and which might still exhibit stiffness over their length. Eqs. (2.30) and (2.32) can be viewed as the main results of this paper.

2. Model

In the model the conformation of the chain is given by a set of N Ising variables $\{\sigma_i = \pm 1\}_{i=1}^N$ in conjunction with a sequence of unit vectors $(\hat{t}_0, \hat{t}_1, \hat{t}_2, \ldots)$. A value $\sigma_j = -1$ indicates that the jth bond is straight and $\sigma_j = +1$ that it has been bent along a definite direction, which is the next in the sequence of unit vectors above. Consequently each $+1$ Ising spin leads to a change in direction of the chain. The number of these orientational changes is equal to the number of spins of value $+1$ and it is also equal to the number of unit vectors $\hat{t}_i$. We present a schematic representation of the conformations for a given sequence as follows:

$$\begin{bmatrix} \text{Spin variables :} & \sigma_N & \sigma_{N-1} & \cdots & \sigma_{i+2} & \sigma_{i+1} & \sigma_i & \sigma_{i-1} & \sigma_{i-2} & \sigma_{i-3} & \sigma_{i-4} & \cdots \\ & +1 & -1 & \cdots & -1 & +1 & -1 & -1 & -1 & +1 & -1 & \cdots \\ \text{bend/straight :} & \text{ⓑ} & \text{Ⓢ} & \cdots & \text{Ⓢ} & \text{ⓑ} & \text{Ⓢ} & \text{Ⓢ} & \text{Ⓢ} & \text{ⓑ} & \text{Ⓢ} & \cdots \\ \text{bond vector :} & \hat{t}_{k+1} & \hat{t}_k & \cdots & \hat{t}_4 & \hat{t}_4 & \hat{t}_3 & \hat{t}_3 & \hat{t}_3 & \hat{t}_2 & \hat{t}_2 & \cdots \end{bmatrix}. \quad (2.1)$$

The conformation of the polymer molecule is then illustrated (for another series of bent and straight sections) in Fig. 1. It can be viewed as a two-state RIS model.

Indicating the length of any consecutive series of -1

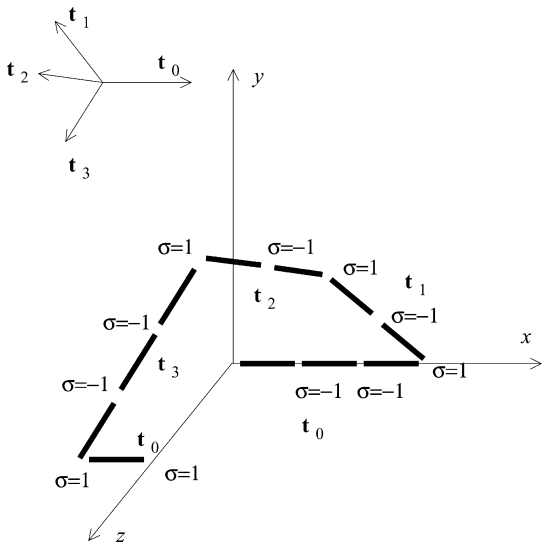

Fig. 1. The model of the chain whose conformation is given by an Ising model and an independent predetermined sequence of bond directions. Each time a spin $+1$ is encountered along the spin sequence determines the next direction followed. The bond unit vector sequence indicates the new direction the end of the chain follows until another spin $+1$ occurs. In this way the deformation of the chain is described by a conformation and an independent set of vectors, indicated in the top, left-hand corner.

spins by an integer $\ell \geq 1$, it is equivalent to describe the conformation of the chain by a set $\{\ell_0, \ell_1, \ell_2, \ldots\}$ together with the unit vectors. For example, the above series from σ_{i-3} to σ_i has a length equal to 4. In general there are m such lengths (and m such unit vectors) for $m-1$ spins of value $+1$ on the chain. The total displacement of the ends of the chains can be written as:

$$\mathbf{r} = \sum_{m'=0}^{m} a\ell_{m'}\hat{\mathbf{t}}_{m'}. \tag{2.2}$$

Each segment has a length a. A similar expression holds for the displacements of intermediate points of the chain.

We choose a simple conformational (Ising) Hamiltonian for the noninteracting chain:

$$H_I = A\sum_{i=1}^{N}\sigma_i\sigma_{i+1} + \frac{B}{2}\sum_{i=1}^{N}(\sigma_i + \sigma_{i+1}). \tag{2.3}$$

The meaning of this Hamiltonian in terms of the cartoon (2.1) can be understood by referring to the underlying magnetic model. The parameter B, representing the external magnetic field in the usual Ising model, here represents the propensity of the chain to have bent or straight elements. A large, positive B will statistically favor straight segments instead of bends. The parameter A responsible for the ferromagnetic or anti-ferromagnetic nature of the magnetic interpretation, determines whether adjacent spins prefer the same or opposite directions. Formulation of the chain in this way leads to a manner in which sequences of bends $\sigma_i = +1$ can be correlated. It is possible to interpret the chain in terms of 'bunched up' and 'stretched out' regions. The correlations were historically used to model the pentane effect [1].

This description may be a useful form in which to investigate polymers under competing interactions such as, for example, polyelectrolyte chains in a bad solvent. The pearl necklace structure has been proposed for such chains [15–17]. The model should enable one to go beyond the scaling approaches to such problems as in Refs. [16,17]. We present a possible scheme for calculations with interactions in Appendix D.

The distribution of the set $\{\ell_m\}$ can be found by means of transfer matrices and the end-to-end vector distribution depends upon the choice of the sequence of unit vectors.

Here we assume that the bond either lets the molecule continue in a straight line or rotates it through only one specific angle. If the molecules were attached at one end, such a rotation means that the remainder of the molecule on the side of the bond not attached, would undergo a twist. A further rotation farther down the molecule could then mean that the direction of the chain after such a twist would be spatially different that after only the first rotation. Thus, flexural information is also part of the molecular conformation in a very elementary way. Consequently, we choose the unit vectors according to very simple and cyclically repeating rules. A right-handed, clockwise 90° rotation would give a sequence leading to a helix $\hat{x}, \hat{y}, \hat{z}, \hat{x}, \ldots$ Another choice is that the bond directions take on the unit vectors perpendicular to the side of a tetrahedron, and the sequence of unit vectors becomes $\hat{t}_0, \hat{t}_1, \hat{t}_2, \hat{t}_3, \hat{t}_0, \hat{t}_1, \ldots$ where the respective vectors are:

$$\hat{t}_0 = [1, 0, 0], \tag{2.4a}$$

$$\hat{t}_1 = \left[-\frac{1}{3}, \frac{2\sqrt{2}}{3}, 0\right], \tag{2.4b}$$

$$\hat{t}_2 = \left[-\frac{1}{3}, -\frac{\sqrt{2}}{3}, \sqrt{\frac{2}{3}}\right], \tag{2.4c}$$

$$\hat{t}_3 = \left[-\frac{1}{3}, -\frac{\sqrt{2}}{3}, -\sqrt{\frac{2}{3}}\right]. \tag{2.4d}$$

In the remainder of this section, we shall use this cyclical realization of the unit vectors. Ideally, we wish to find the generating function of the end-to-end distance

$$\mathscr{G}_h \equiv \langle e^{\mathbf{h}\cdot\mathbf{r}}\rangle = \left\langle e^{a\mathbf{h}\sum\ell_m\cdot\hat{\mathbf{t}}_m}\right\rangle \tag{2.5}$$

and its dependence on the probabilities given by the Ising Hamiltonian. A chain under external forces and the structure factor are also related to this expression.

In what follows we shall assume that all lengths are scaled in terms of a, and we therefore set $a = 1$. In accordance with the cyclic properties of the unit vectors mentioned above, we can define:

$$\hat{t}_{m'} \equiv \hat{t}_{m' \bmod 4}. \tag{2.6}$$

The partition function is given by using the transfer matrix which is familiar from elementary statistical mechanics texts

$$\mathfrak{T}_{\sigma,\sigma'} = \exp\left(-A\sigma\sigma' - \frac{B}{2}(\sigma+\sigma')\right) = \begin{pmatrix} T_{++} & T_{+-} \\ T_{+-} & T_{--} \end{pmatrix}, \tag{2.7}$$

to give

$$Z_N = \mathrm{Tr}(\mathfrak{T}^N), \tag{2.8}$$

which is easily evaluated to give:

$$Z_N = \lambda_+^N + \lambda_-^N. \tag{2.9}$$

This can be approximated for large N in the usual manner by the larger eigenvalue λ_+^N. Here $\lambda_\pm$ comes from the transfer matrix approach and is given by:

$$\lambda_\pm = \mathrm{e}^{-A}\cosh B \pm \sqrt{\mathrm{e}^{-2A}\sinh^2 B + \mathrm{e}^{2A}}. \tag{2.10}$$

The statistics of the bends in the present model are given completely by the one-dimensional Ising model. The cyclic set of vectors ($\hat{\mathbf{t}}_\mathbf{i}$) carries information concerning the physical locations of the polymer bonds. It represents the memory the chain has of its previous direction.

We denote the four possible directions for each bond by a column vector with four entries:

$$\hat{t}_0 \rightarrow \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad \hat{t}_1 \rightarrow \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \quad \hat{t}_2 \rightarrow \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad \hat{t}_3 \rightarrow \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}. \tag{2.11}$$

When $\sigma = -1$, i.e. when the direction of the polymer does not change, the column vector representing a given direction of the bond i, t_i transforms with the unit matrix:

$$t_{i+1} \leftarrow \mathbb{1}\, t_i. \tag{2.12}$$

In the case of the change in direction, the correct cyclic behavior is reproduced by multiplying by the non-symmetric matrix

$$\mathbf{m} = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \tag{2.13}$$

as follows:

$$t_{i+1} \leftarrow \mathbf{m} t_i. \tag{2.14}$$

In this way one can see that $\hat{t}_1 = \mathbf{m}\hat{t}_0$, $\hat{t}_2 = \mathbf{m}^2\hat{t}_0$, $\hat{t}_2 = \mathbf{m}\hat{t}_1$, etc.

Due to the cyclic nature of the sequence of directions $\mathbf{m}^4 = \mathbb{1}$, which means that the inverse of $\mathbf{m}$ is $\mathbf{m}^3$. Furthermore, we know (using obvious notation) that

$$(t_0^{\mathrm{T}} + t_1^{\mathrm{T}} + t_2^{\mathrm{T}} + t_3^{\mathrm{T}})\mathbf{m}^n t_0 = 1, \tag{2.15}$$

for arbitrary $n \in \mathbb{Z}$. The $4\otimes 2$ representation is now used in the expression for the partition function for a chain whose first bond points in a specified direction:

$$Z_N = (1,1,1,1)\left\{\mathrm{Tr}_\sigma \begin{pmatrix} \mathbf{m}\,\mathrm{e}^{-A-B} & \mathbb{1}\,\mathrm{e}^{A} \\ \mathbf{m}\,\mathrm{e}^{A} & \mathbb{1}\,\mathrm{e}^{-A+B} \end{pmatrix}^N\right\}\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \equiv (1,1,1,1)\{\mathrm{Tr}_\sigma \mathbb{T}^n\}\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}. \tag{2.16}$$

Eventually we wish to compute free energies for Hamiltonians containing force, twist, or bending terms such as might be of use in a network of stiff chains. First, we illustrate the present approach by an elementary calculation which is also accessible by other methods. In Section 2.2 we proceed to more general cases.

2.1. Example: end-to-end directional correlation

Eq. (2.16) is clearly the same partition function as Eq. (2.9) because of the property (2.15). The directional end-to-end average is then:

$$\langle t_N \cdot t_1 \rangle = \frac{1}{Z_N}\left[(1,0,0,0) - \tfrac{1}{3}(0,1,0,0) - \tfrac{1}{3}(0,0,1,0) - \tfrac{1}{3}(0,0,0,1)\right] \times \{\mathrm{Tr}_\sigma \mathbb{T}^N\}\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} = \left[\frac{4}{3Z_N}(1,0,0,0)\{\mathrm{Tr}_\sigma \mathbb{T}^N\}\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}\right] - \frac{1}{3}. \tag{2.17}$$

This correlation can be calculated by noting that $\mathbf{m}$ is really simply a symbol indicating a change of backbone direction. Multiplying the matrices and taking the trace would result in

an expression containing sums of powers of **m**. The direction constraints on the ends mean that only certain powers of **m** need to be considered. The matrix expression multiplied by the two vectors above has the important feature that only terms in $\mathbf{m}^{4n}$ for integral n survive. It is possible to extract only terms to fourth powers from a series. Consider any function $f(x)$ which can be expressed as some power series in x such that $f(x) = \sum_{k=0} c_k x^k$. The following sum can be constructed:

$$f(x)+f(-x)+f(\mathrm{i}x)+f(-\mathrm{i}x) = \sum_{k=0} c_k x^k (1+(-1)^k+\mathrm{i}^k+(-\mathrm{i})^k) = 4\sum_{\ell=0} c_{4\ell} x^{4\ell}. \quad (2.18)$$

By defining the following

$$\lambda_{\pm}(x) = \frac{1}{2}\mathrm{e}^{-A}(x\,\mathrm{e}^{B}+\mathrm{e}^{-B}) \pm \sqrt{2x\sinh 2A + \frac{1}{4}\mathrm{e}^{-2A}(x\,\mathrm{e}^{B}+\mathrm{e}^{-B})^2}, \quad (2.19)$$

the average (2.17) is calculated explicitly as:

$$\langle t_N \cdot t_1\rangle = \left(\frac{1}{3}\right)\frac{\lambda_+^N(1)+\lambda_-^N(1)+\lambda_+^N(-1)+\lambda_-^N(-1)+\lambda_+^N(\mathrm{i})+\lambda_-^N(\mathrm{i})+\lambda_+^N(-\mathrm{i})+\lambda_-^N(-\mathrm{i})}{\lambda_+^N(1)+\lambda_-^N(1)} - \frac{1}{3}$$
$$= \left(\frac{1}{3}\right)\frac{\lambda_+^N(-1)+\lambda_-^N(-1)+2\,\mathrm{Re}[\lambda_+^N(i)]+2\,\mathrm{Re}[\lambda_-^N(i)]}{\lambda_+^N(1)+\lambda_-^N(1)}, \quad (2.20)$$

$$\mathrm{Re}\left(\frac{\lambda_+(\mathrm{i})}{\lambda_+}\right)^N = \exp\left\{N\ln\left[\left(\sqrt{\left(\frac{1}{2}\mathrm{e}^{-A-B}+R^{1/4}\cos\frac{\theta}{2}\right)^2+\left(\frac{1}{2}\mathrm{e}^{-A+B}+R^{1/4}\sin\frac{\theta}{2}\right)^2}\right)\mathrm{e}^{\mathrm{i}\phi}\right] - N\ln\lambda_+\right\}, \quad (2.23a)$$

$$\langle t_N \cdot t_1\rangle \approx \frac{1}{3}\sum_{\alpha=1}^{6}\left[\frac{\lambda_\alpha}{\lambda_+}\right]^N. \quad (2.21)$$

In the last line we have employed the shorthand notation $\{\lambda_\alpha\} \equiv \{\lambda_+(-1), \lambda_-(-1), \lambda_+(\mathrm{i}), \lambda_-(\mathrm{i}), \lambda_+(-\mathrm{i}), \lambda_-(-\mathrm{i})\}$ and made use of the fact that for large N the larger eigenvalue $\lambda_+ \equiv \lambda_+(1)$ dominates the expression for the trace.

The expression for the bond-angle correlation (2.20) must be real. The emergence of powers of complex numbers, such as $\lambda_\pm(\pm\mathrm{i})$, reveals the nature of the model in that such terms can give rise to oscillatory behavior in dependence of N since a high level of coherence of the Ising variables will reveal the cyclic nature of the bonding directions.

Assuming, for the sake of simplicity the (ferromagnetic) case, where $A < 0$, the first two terms associated with $\lambda_\pm(-1)$ give rise to a contribution:

$$\frac{1}{3}\sum_{\alpha=1,2}\left[\frac{\lambda_\alpha}{\lambda_+}\right]^N$$
$$= \left[\frac{-\mathrm{e}^{-A}\sinh B+\sqrt{-2\sinh 2A+\mathrm{e}^{-2A}\sinh^2 B}}{\mathrm{e}^{-A}\cosh B+\sqrt{2\sinh 2A+\mathrm{e}^{-2A}\cosh^2 B}}\right]^N$$
$$+\left[\frac{-\mathrm{e}^{-A}\sinh B+\sqrt{-2\sinh 2A+\mathrm{e}^{-2A}\sinh^2 B}}{\mathrm{e}^{-A}\cosh B+\sqrt{2\sinh 2A+\mathrm{e}^{-2A}\cosh^2 B}}\right]^N$$
$$\approx \exp\left[-N\ln\left(\frac{-\mathrm{e}^{-A}\sinh B+\sqrt{-2\sinh 2A+\mathrm{e}^{-2A}\sinh^2 B}}{\mathrm{e}^{-A}\cosh B+\sqrt{2\sinh 2A+\mathrm{e}^{-2A}\cosh^2 B}}\right)\right]$$
$$= \exp(-N/\ell_{\mathrm{p1}}). \quad (2.22)$$

This defines the persistence length ℓ_{p1}. There are also other lengths in the system associated with the complex arguments in the average (2.21). These lengths are associated with the decay of any periodicity of the bending.

For example, we give the real part of $\lambda_+(i)$, which equals

with

$$\phi = \arctan\left[\frac{\frac{1}{2}\mathrm{e}^{-A+B}+R^{1/4}\sin\frac{\theta}{2}}{\frac{1}{2}\mathrm{e}^{-A-B}+R^{1/4}\cos\frac{\theta}{2}}\right], \quad (2.23b)$$

$$\theta = \arctan\left[\frac{-4\left(\sinh 2A+\frac{1}{4}\mathrm{e}^{-2A}\right)}{\mathrm{e}^{-2A}\sinh 2B}\right], \quad (2.23c)$$

$$R = 4\left(\sinh 2A + \frac{1}{4}\mathrm{e}^{-2A}\right)^2 + \tfrac{1}{4}e^{-4B}\sinh^2 2B. \qquad (2.23d)$$

2.2. Forces applied to constrained chain ends

A stiff chain joined stiffly to a network at both ends can be subjected to both forces and torsion by the junctions, which also constrain the directions of the two end segments of the chain in question. Pulling or pushing the chain ends leads to an additional term $\Delta H = -\mathbf{F}\cdot\mathbf{R}_{\text{end-to-end}}$ in the Hamiltonian. For simplicity we choose the ends to be constrained to the directions $\mathbf{t}_0$ and the force also directed along this vector, $\mathbf{F}/k_\mathrm{B}T = f\mathbf{t}_0$. Under these conditions the partition function can be expressed as

$$Z_N(f;0,0) = (1,0,0,0)$$

$$\mathrm{Tr}_\sigma\left\{\mathbf{u}\begin{pmatrix}\mathbf{m}\,\mathrm{e}^{-A-B} & \mathbb{1}\mathrm{e}^{A}\\ \mathbf{m}\,\mathrm{e}^{A} & \mathbb{1}\,\mathrm{e}^{-A+B}\end{pmatrix}\right\}^N\begin{pmatrix}1\\0\\0\\0\end{pmatrix}, \qquad (2.24)$$

with

$$\mathbf{u} = \begin{pmatrix}\mathrm{e}^{f} & 0 & 0 & 0\\ 0 & \mathrm{e}^{-f/3} & 0 & 0\\ 0 & 0 & \mathrm{e}^{-f/3} & 0\\ 0 & 0 & 0 & \mathrm{e}^{-f/3}\end{pmatrix}. \qquad (2.25)$$

The matrix $\mathbf{u}$ assigns the correct weights to the segments.

2.2.1. Very strong stretching

We consider an extremely simplifying scenario, where the force f tends to a very large value, enabling the use of the approximation:

$$\mathbf{u} \simeq \begin{pmatrix}\mathrm{e}^{f} & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\end{pmatrix}. \qquad (2.26)$$

We can calculate the partition function easily:

$$Z_N^{f\gg}(f;0,0) = (1,0,0,0)$$

$$\mathrm{Tr}_\sigma\left\{\begin{pmatrix}\mathrm{e}^{f} & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\mathbf{m}\,\mathrm{e}^{-A-B} & \mathbb{1}\,\mathrm{e}^{A}\\ \mathbf{m}\,\mathrm{e}^{A} & \mathbb{1}\mathrm{e}^{-A+B}\end{pmatrix}\right\}^N\begin{pmatrix}1\\0\\0\\0\end{pmatrix}$$

$$= (1,0,0,0)\mathrm{Tr}_\sigma\left\{\begin{pmatrix}\mathrm{e}^{f} & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\mathbf{m}\,\mathrm{e}^{-A-B} & \mathbb{1}\,\mathrm{e}^{A}\\ \mathbf{m}\,\mathrm{e}^{A} & \mathbb{1}\,\mathrm{e}^{-A+B}\end{pmatrix}\right\}^{N-1}$$

$$\times\begin{pmatrix}1\\0\\0\\0\end{pmatrix}\times\begin{pmatrix}0 & \mathrm{e}^{A+f}\\ 0 & \mathrm{e}^{-A+B+f}\end{pmatrix}. \qquad (2.27)$$

Continuing to multiply out the directional column vector from the right then leads to:

$$Z_N^{f\gg}(f;0,0) = \mathrm{Tr}_\sigma\begin{pmatrix}0 & \mathrm{e}^{A+f}\\ 0 & \mathrm{e}^{-A+B+f}\end{pmatrix}^N = \mathrm{e}^{-N(A-B-f)}. \qquad (2.28)$$

This is the expected fully stretched configuration, as $\partial \ln Z_N^{f\gg}/\partial f = N$.

2.2.2. Small forces

When considering small forces the following expansion of $\mathbf{u}$ in terms of f will be used:

$$\mathbf{u} = \mathrm{e}^{-f/3}\left[\mathbb{1} + \frac{4f}{3}\begin{pmatrix}1 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\end{pmatrix} + \mathcal{O}(f^2)\right]. \qquad (2.29)$$

In the expression for the partition function we express the

matrix product contributions to first order in f :

$$Z_N^{f\ll}(f;0,0,0) = (1,0,0,0)\mathrm{Tr}_\sigma$$

$$\times\left\{ \mathrm{e}^{-f/3}\left[\mathbb{1} + \frac{4f}{3}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}\right]\begin{pmatrix} \mathbf{m}\,\mathrm{e}^{-A-B} & \mathbb{1}\,\mathrm{e}^{A} \\ \mathbf{m}\,\mathrm{e}^{A} & \mathbb{1}\,\mathrm{e}^{-A+B} \end{pmatrix}\right\}^N$$

$$\times\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \simeq (1,0,0,0)\mathrm{Tr}_\sigma\,\mathrm{e}^{-Nf/3}\left\{\begin{pmatrix} \mathbf{m}\,\mathrm{e}^{-A-B} & \mathbb{1}\,\mathrm{e}^{A} \\ \mathbf{m}\,\mathrm{e}^{A} & \mathbb{1}\,\mathrm{e}^{-A+B} \end{pmatrix}^N\right.$$

$$\left. + \frac{4f}{3}\sum_{n=0}^{N-1}\begin{pmatrix} \mathbf{m}\,\mathrm{e}^{-A-B} & \mathbb{1}\,\mathrm{e}^{A} \\ \mathbf{m}\,\mathrm{e}^{A} & \mathbb{1}\mathrm{e}^{-A+B} \end{pmatrix}^n\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}(1,0,0,0)\right.$$

$$\left.\times\begin{pmatrix} \mathbf{m}\,\mathrm{e}^{-A-B} & \mathbb{1}\,\mathrm{e}^{A} \\ \mathbf{m}\,\mathrm{e}^{A} & \mathbb{1}\,\mathrm{e}^{-A+B} \end{pmatrix}^{N-n}\right\}\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}. \tag{2.30}$$

The summation term above relates the linear force contribution to a sum of products of two end-constrained sections of polymer chain. Consequently, it is necessary to keep only integral fourth power terms in $\mathbf{m}$ for each factor. In the 'place-holder formalism' one calculates

$$\mathrm{Tr}_\sigma\begin{pmatrix} x\,\mathrm{e}^{-A-B} & \mathrm{e}^{A} \\ x\,\mathrm{e}^{A} & \mathrm{e}^{-A+B} \end{pmatrix}^n\begin{pmatrix} x'\,\mathrm{e}^{-A-B} & \mathrm{e}^{A} \\ x'\,\mathrm{e}^{A} & \mathrm{e}^{-A+B} \end{pmatrix}^{N-m},$$

keeping fourth powers of both x and x'. This reduces the calculation to familiar techniques again. One can then evaluate the free energy difference for small forces as a function of N

$$\ln Z_N^{f\ll}(f;0,0) - \ln Z_N(0;0,0) = fk(N). \tag{2.31}$$

2.2.3. Grand canonical formalism

The summations arising due to the inclusion of $\mathbf{u}$ in computing Eq. (2.24) become more tedious when higher powers of the force need to be considered. It is often useful to transform to the grand canonical formalism with the help of the fugacity z :

$$\mathscr{Z}(f;0,0) = \sum_{N=0}^{\infty} z^N Z_N(f;0,0)$$

$$= \sum_{N=0}^{\infty}(1,0,0,0)$$

$$\mathrm{Tr}_\sigma\left\{z\mathbf{u}\begin{pmatrix} \mathbf{m}\,\mathrm{e}^{-A-B} & \mathbb{1}\,\mathrm{e}^{A} \\ \mathbf{m}\,\mathrm{e}^{A} & \mathbb{1}\,\mathrm{e}^{-A+B} \end{pmatrix}\right\}^N\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

$$= (1,0,0,0)$$

$$\mathrm{Tr}_\sigma\left[\mathbb{1} - z\mathbf{u}\begin{pmatrix} \mathbf{m}\,\mathrm{e}^{-A-B} & \mathbb{1}\,\mathrm{e}^{A} \\ \mathbf{m}\,\mathrm{e}^{A} & \mathbb{1}\,\mathrm{e}^{-A+B} \end{pmatrix}\right]^{-1}\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}. \tag{2.32}$$

The computation of this and related derivatives, therefore, requires the inversion of an 8×8 matrix.

2.3. Variation on model: changes of bond-direction sequences

The model has been presented as following a definite rule of sequences of the bond directions. This was motivated by the reasoning that the nature of the chemical bonds of the molecule permitted exactly two states at each bond and entailed a twist of the molecule when there was bending. This led to a definite sequence of the orientations of bonds.

Are there models where different sequences to $\{\ldots,\hat{t}_0,\hat{t}_1,\hat{t}_2,\hat{t}_3,\hat{t}_0,\ldots\}$ may occur—such as, for example, $\{\ldots,\hat{t}_0,\hat{t}_3,\hat{t}_2,\hat{t}_1,\hat{t}_0,\ldots\}$, or mixtures of them? Indeed, the definite, sequential structure, or the specific way in which the polymer winds, is not necessary in the formalism. The formalism developed in the preceding parts of the paper can be adapted to include different options for winding.

We consider a molecule which has three possible rotations of a bond one of which is a straight conformation. We can label these rotations in analogy to the work above by a three-state Potts-like variable: $\sigma = 0$, 1, or 2, corresponding to straight conformation and two rotations. If, for the sake of simplicity, we again review the bond directions as restricted to the set of four tetrahedral vectors $\{\hat{\mathbf{t}}_\mathbf{i}\}$, we can associate with a state $\sigma = 1$ a rotation given by $\mathbf{m}$ (cf. equation (Eq. (2.13)) and with the state $\sigma = 2$ a rotation $\mathbf{m}^{-1} = \mathbf{m}^3$. The schematic representation would then read

as follows:

$$
\begin{array}{lcccccccccccc}
\text{Potts variables :} & \sigma_N & \sigma_{N-1} & \cdots & \sigma_{i+2} & \sigma_{i+1} & \sigma_i & \sigma_{i-1} & \sigma_{i-2} & \sigma_{i-3} & \sigma_{i-4} & \cdots \\
 & 0 & 0 & \cdots & 1 & 1 & 2 & 2 & 0 & 0 & 1 & \cdots \\
\text{bend/straight :} & \text{ⓢ} & \text{ⓢ} & \cdots & \text{ⓑ} & \text{ⓑ} & \text{ⓑ} & \text{ⓑ} & \text{ⓢ} & \text{ⓢ} & \text{ⓑ} & \cdots \\
\text{bond vector matrix :} & \mathbb{1} & \mathbb{1} & \cdots & \mathbf{m} & \mathbf{m} & \mathbf{m}^3 & \mathbf{m}^3 & \mathbb{1} & \mathbb{1} & \mathbf{m} & \cdots \\
\text{bond direction :} & \cdots & & & \hat{t}_0 & \hat{t}_3 & \hat{t}_2 & \hat{t}_3 & \hat{t}_0 & \hat{t}_0 & \hat{t}_0 & \cdots
\end{array}
\tag{2.33}
$$

After a suitable choice of weights for different nearest-neighbor configurations the partition function for the model would be determined by the usual transfer matrix approach for the 3×3 matrix. Bond-angle correlations would also be computed in a manner exactly analogous to the methods shown in this section, excepting that one would have to deal with larger matrices with entries of both $\mathbf{m}$ and $\mathbf{m}^3$.

Some simple alternative methods are noted in Appendix A.

3. Formulation of dynamics

The dynamics of helix-coil transitions for the Zimm–Bragg model have been investigated extensively (amongst many others, see, for example, Refs. [18–21]). In general, in such systems one is interested in the nucleation and growth of helical or coiled regions. Since one might expect it to be more favorable for a helical bond to be appended to one side of an already existing helical region than forming spontaneously inside a coiled region, researchers have introduced kinetic coefficients for nucleation, extending and receding helical regions. However, the insertion of a unit helix or coil or the shortening of a section hardly influences the overall conformation of the Zimm–Bragg chain.

In contrast to this, a change of state of ± 1 to ∓ 1 at a segment often brings about a large conformational change in the molecule of the preceding sections. If we are to continue following the analogy to Ising spin systems, one can introduce dynamics by means of Glauber dynamics [22] as expressed by a Master equation for the spins. Due to the reasons mentioned above, Glauber dynamics are not considered suitable for the helix-coil models. In our case, torsion or applied stress might, in the simplest scenario, lead to independent flipping of the states of bonds, although it is to be expected that hydrodynamic or inertial effects would tend to decrease this tendency to bend spontaneously. Nevertheless, since the energetics of the model above differ in no way from the Ising model, we simply transcribe Glauber's results for our purposes.

Using the ideas of Glauber is the simplest scenario in which dynamics can be introduced. Here one would also expect formation of double kinks spontaneously or *single kinks diffusing* [23] along the chain with sinks and sources at the ends to be more applicable. Such considerations will be the subject of a future publication.

By assigning α as the rate of spin flips and following Glauber [22] in the definition of the parameters:

$$\eta = \tanh A, \tag{3.1}$$

$$\gamma = \tanh 2A, \tag{3.2}$$

the average magnetization of the kth spin of the model is given by Eq. (89) in Ref. [22]:

$$\langle \sigma_k(t) \rangle = \mathrm{e}^{-\alpha(t-t_0)} \sum_j q_j(t_0) I_{k-j}(\gamma\alpha(t-t_0)) + B\alpha \frac{1-\eta^2}{1+\eta^2} \int_{-t_0}^{t} \mathrm{d}t' [\mathrm{e}^{-\alpha(1-\gamma)(t-t')}]. \tag{3.3}$$

Here the $I_n(x)$ are the modified Bessel functions of the first kind, with the asymptotic behavior:

$$I_n(x) \sim \frac{\mathrm{e}^x}{\sqrt{2\pi x}}. \tag{3.4}$$

The answer (3.3) above can be related to a measure of the persistence length, $\tilde{\ell}_\mathrm{p}$, by means of:

$$\frac{3N}{\tilde{\ell}_\mathrm{p}} \simeq \langle M(t) \rangle = \left\langle \sum_i q_i(t) \right\rangle. \tag{3.5}$$

Consequently, any initial specific configuration of spins $\{q_i(0)\}$ tends exponentially quickly towards the equilibrium average:

$$\langle M(t) \rangle = \mathrm{e}^{-\alpha(1-\gamma)t} \sum_j q_j(0) - BN \frac{1-\eta^2}{1+\eta^2} \frac{1}{1-\gamma} [\mathrm{e}^{-\alpha(1-\gamma)t} - 1] \to BN \frac{1-\eta^2}{1+\eta^2} \frac{1}{1-\gamma}, \text{ for } t \gg 1. \tag{3.6}$$

Some systems will require non-thermal 'activation energies' to overcome the barriers of reconformation which can be achieved by the application of an external stress (modeled by Δ previously). This is the case in polyamide networks, for example. We refer to Refs. [5,6].

4. Summary

We have investigated a simple model of discrete, stiff polymers with directionally constrained ends and applied force. The RIS-type model was formulated as two *decoupled* parts, one an Ising model and the other a given set of unit vectors indicating the directions. Although the use of an Ising formalism and transfer matrices (see Appendix B) is familiar to polymer physics, we argue that this method is still useful for current problems in understanding force–extension relationships in stiff polymer networks.

We also indicate in Appendix D how interactions could be treated approximately and have argued that the two-parameter model might give insights into conformations previously only achieved by means of scaling argument or simulations.

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Appendix A. Another approach for calculations

A.1. End-to-end distances

Using the four tetrahedral unit vectors as the basic directions and the condition that $\sum_{m'=1}^{m} \ell_{m'} = N$ (expressing the preservation of the total length of the chain) with $m = \sum_{i=1}^{N} (\sigma_i + 1)/2 \geq 4$ (the number of $+1$ spins on the chain) the generating function for the end-to-end distance is given by:

$$\langle \mathrm{e}^{+\mathbf{h}\cdot\mathbf{r}} \rangle = \langle \mathrm{e}^{+\mathbf{h}\cdot\hat{\mathbf{t}}_0(\ell_0+\ell_4+\cdots)+\cdots+\mathbf{h}\cdot\hat{\mathbf{t}}_3(\ell_3+\ell_7+\cdots)} \rangle. \tag{A1}$$

It is necessary to express the Ising Hamiltonian in terms of the sequence of ℓ_is with the probability distribution $P\{\ell_0, \ldots, \ell_i, \ldots, \ell_j, \ldots\}$. Since there is no external i-dependent field it is clear that this probability distribution is permutation-invariant:

$$P\{\ell_0, \ldots, \ell_i, \ldots, \ell_j, \ldots\} = P\{\ell_0, \ldots, \ell_j, \ldots, \ell_i, \ldots\}. \tag{A2}$$

This means that if $m \geq 4$ the fact that only nearest-neighbor interactions are considered can lead to a regrouping of all the spins which enables one to rewrite the generating function Eq. (2.5) as:

$$\mathscr{G}_{\mathbf{h}} = \mathscr{G}_{\mathbf{h}}^{(m\geq 4)} + \mathscr{G}_{\mathbf{h}}^{(m<4)}. \tag{A3}$$

We define the quantity $Z_N^{(0)}$ which expresses the statistical weight of a straight sequence of N steps terminated by a bend at either end:

$$Z_N^{(0)} = \left(T_{++} - \frac{T_{+-}^2}{T_{--}} \right) \delta_{N,1} + \left(\frac{T_{+-}}{T_{--}} \right)^2 T_{--}^N. \tag{A4}$$

The contribution for $m \geq 4$ for Eq. (A3) is:

$$\mathscr{G}_{\mathbf{h}}^{(m\geq 4)} = \frac{1}{Z_N} \mathrm{Tr}\left[\mathrm{e}^{+\mathbf{h}\cdot\hat{\mathbf{t}}_0(\ell_0+\ell_4+\cdots)} Z_{\ell_0}^{(0)} Z_{\ell_4}^{(0)} \cdots \right] \times \cdots \times \mathrm{Tr}\left[\mathrm{e}^{+\mathbf{h}\cdot\hat{\mathbf{t}}_3(\ell_0+\ell_7+\cdots)} Z_{\ell_3}^{(0)} Z_{\ell_7}^{(0)} \cdots \right]. \tag{A5}$$

The condition $L_0 + \cdots + L_3 = N$ must hold. The property of the unit vectors that $\hat{\mathbf{t}}_0 + \hat{\mathbf{t}}_1 + \hat{\mathbf{t}}_2 + \hat{\mathbf{t}}_3 = 0$ will also be used. It is now straightforward to include the possibilities of $m < 4$ which augment the above equation by

$$\mathscr{G}_{\mathbf{h}}^{(m<4)} = \frac{\mathrm{e}^{\mathbf{h}\cdot\hat{\mathbf{t}}_0 N} T_{+-}^2 T_{--}^{N-2}}{Z_N} + \sum_{\ell=1}^{N-1} \times \frac{\mathrm{e}^{\mathbf{h}\cdot\hat{\mathbf{t}}_0 \ell + \mathbf{h}\cdot\hat{\mathbf{t}}_1 (N-\ell)} Z_{\ell}^{(0)} Z_{N-\ell}^{(0)}}{Z_N} + \sum_{\ell=1}^{N-2} \sum_{\ell'=1}^{N-1-\ell} \times \frac{\mathrm{e}^{\mathbf{h}\cdot\hat{\mathbf{t}}_0 \ell + \mathbf{h}\cdot\hat{\mathbf{t}}_1 \ell' + \mathbf{h}\cdot\hat{\mathbf{t}}_2 (N-\ell-\ell')} Z_{\ell}^{(0)} Z_{\ell'}^{(0)} Z_{N-\ell-\ell'}^{(0)}}{Z_N}, \tag{A6}$$

to give the full expression for Eq. (A1). Performing the sum over all L_αs under the length constraint leads to Eq. (2.5), the end-to-end generating function. This equation is, however, only relevant for our sequence of *four* repeating unit vectors. The average end-to-end distance squared can be calculated by means of taking the derivative of the generating function $\mathscr{G}_{\mathbf{h}}$ as follows:

$$\langle R^2 \rangle = \left[\frac{\delta^2 \mathscr{G}_{\mathbf{h}}}{\delta \mathbf{h}^2} \right]_{\mathbf{h}=0}. \tag{A7}$$

The calculations of of Eqs. (A5) and (A6) can be facilitated by the usual procedure of computing expressions in the grand ensemble.

An easier approach than the full calculation above follows immediately by application of correlations of the type (2.21) because:

$$\langle R^2 \rangle = \left\langle \left(\sum_{i=1}^{N} \hat{t}_i \right)^2 \right\rangle = N + 2 \sum_{i<j} \left\langle \hat{t}_i \cdot \hat{t}_j \right\rangle \approx N + \frac{2}{3} \sum_{\alpha=1}^{6} \sum_{k=1}^{N} (N-k) \left(\frac{\lambda_\alpha}{\lambda_+} \right)^k = N + \frac{2}{3} \sum_{\alpha=1}^{6} \times \left\{ \frac{(\lambda_\alpha/\lambda_+)^N}{(1-(\lambda_\alpha/\lambda_+))^2} + \frac{(\lambda_\alpha/\lambda_+)[(1-(\lambda_\alpha/\lambda_+))N - 1]}{(1-(\lambda_\alpha/\lambda_+))^2} \right\}. \tag{A8}$$

This behaves in the expected manner, because when $(\lambda_\alpha/\lambda_+) = 1$ the equations for the end-to-end distance

squared (A8) give $\langle R^2\rangle \propto N^2$. If the terms $\sum_\alpha (\lambda_\alpha/\lambda_+)^N$, for large N, vanish, the random walk behavior is recovered.

The Kuhn length ℓ of the random walk is the square root of the prefactor of the term linear in N of $\langle R^2\rangle$ in the random walk limit. For the present model it is:

$$\ell^2 = 1 + \frac{2}{3}\sum_{\alpha=1}^{6}\frac{(\lambda_\alpha/\lambda_+)[1-(\lambda_\alpha/\lambda_+)]}{(1-(\lambda_\alpha/\lambda_+))^2}. \tag{A9}$$

A.2. Persistence and step-lengths

The persistence length of a walk is defined as that length after which two tangent vectors become decorrelated. If we write the tangent vector at each site as $\hat{\mathbf{d}}_i$, we wish to compute: $\langle \hat{\mathbf{d}}_i\cdot\hat{\mathbf{d}}_{i+m}\rangle \sim \exp(-m/\ell_p)$, where ℓ_p is the persistence length. By splitting our expressions for the generating function into two regimes we have already indirectly defined the correlation length because for the case of $\mathscr{G}_{\mathbf{h}}^{(m\geq 4)}$ all four unit vectors are equally distributed meaning that $\langle \hat{\mathbf{d}}_i\cdot\hat{\mathbf{d}}_{i+m}\rangle = 0$. Consequently, $\mathscr{G}_{\mathbf{h}=0}^{(m<4)}$ then gives the probability that a chain of N segments has a statistical end-to-end length proportional to N, i.e. is rod-like.

We can now introduce a simple definition of the average persistence length of the model:

$$\tilde{\ell}_p = \lim_{N\to\infty}\sum_{\ell=1}^{N-1}\left(\frac{Z_{N-\ell}(T_{+-}^2 T_{--}^{\ell-2}\ell)}{Z_N}\right)$$

$$\simeq \left(\frac{T_{+-}}{T_{--}}\right)^2\frac{\lambda_+}{(T_{--}-\lambda_+)^2}. \tag{A10}$$

The fact that only + values appear in the expression for the persistence length comes from the usual assumption of large N. We see that for the case where $A = 0$ that the expression for $\tilde{\ell}_p$ reduces to $\tilde{\ell}_p \simeq (1+\exp(-2B))\exp(2B)$ which is equal to the inverse of the probability of a spin being in the state $+1$ (for $A = 0$).

The magnetization and the pair magnetization are easily computed from the free energy by differentiation:

$$\nu_1 \equiv \frac{1}{N}\sum_{i=1}^{N}\langle\sigma_i\rangle = -\frac{1}{N}\frac{\partial \ln Z}{\partial B}, \tag{A11}$$

$$\nu_2 \equiv \frac{1}{N}\sum_{i=1}^{N}\langle\sigma_i\sigma_{i+1}\rangle = -\frac{1}{N}\frac{\partial \ln Z}{\partial A}. \tag{A12}$$

They can be used to calculate the average number of $+1$ spins $\nu_+ \equiv (\nu_1+1)/2$ and the average number of adjacent kinks $\nu_{++} \equiv (\nu_2+2\nu_1+1)/4$. Consequently $a(\nu_+)^{-1}$ is also a measure of the average length of a straight sequence of segments. The ratio ν_{++}/ν_+ should then give an indication of the degree of clustering of bends. A value of $\nu_{++}/\nu_+ \simeq 1$ means that there are many long straight sections interspersed by highly coiled regions, while $\nu_{++}/\nu_+ \simeq 0$ would indicate that the kinks are well-spaced.

Another interesting average is the spin–spin correlation function

$$\langle\sigma_i\sigma_{i+m}\rangle = Z^{-1}\,\mathrm{Tr}(\mathbf{T}^i\boldsymbol{\sigma}\mathbf{T}^m\boldsymbol{\sigma}\mathbf{T}^{N-i-m-2}\mathbf{T}_3) \sim \mathrm{e}^{-\xi N}, \tag{A13}$$

which comes from the usual Ising model coherence length $\xi = -\max\{1,(\ln\lambda_+/\lambda_-)^{-1}\}$. Since λ_- becomes zero as $A\to 0$ the coherence length then reaches a minimum.

Appendix B. Matrix formulations for bond-vector directions

It is well known that the transfer matrix method is applicable to a variety of one-dimensional models showing more than two states per site. We remind of examples of this possibility in this section.

The models which we mention in this section simply relate the orientations of consecutive bonds of the chain. A polymer chain with unit length bonds $|\mathbf{b}_i| = 1, \forall i \in \{0,N\}$ exists an a cubic lattice. Consequently, each bond vector of the polymer is described by a positive or negative unit vector:

$$\mathbf{b}_i = \begin{cases}\pm\hat{\mathbf{x}}\\ \pm\hat{\mathbf{y}}\\ \pm\hat{\mathbf{z}}\end{cases}. \tag{B1}$$

Therefore, the orientation variable has six possible states. The stiffness is modeled by an energetic interaction between neighbors. At this point it is important to note that the variables of the bonds in this second type of model differ significantly from that of the main model of the main text, in that the variables here are the orientations of the bond vectors. In the formulations presented hereafter the ideas of clustering of bends, etc. which are used for the model in the main text, are not applicable.As a first example we choose the form of the interaction energy between nearest neighbors:

$$E_{i,i+1} = \alpha\mathbf{b}_i\cdot\mathbf{b}_{i+1}. \tag{B2}$$

The partition function for the walk then becomes

$$Z_\alpha = \sum_{\{\mathbf{b}_i\}}\prod_{i=1}^{N}\mathrm{e}^{-\beta\alpha\mathbf{b}_i\cdot\mathbf{b}_{i+1}} = \mathrm{Tr}\,\mathfrak{T}_2^N, \tag{B3}$$

with the transfer matrix:

$$\mathfrak{T}_2 \equiv \begin{pmatrix} \mathrm{e}^{-\beta\alpha} & 1 & 1 & \mathrm{e}^{+\beta\alpha} & 1 & 1\\ 1 & \mathrm{e}^{-\beta\alpha} & 1 & 1 & \mathrm{e}^{+\beta\alpha} & 1\\ 1 & 1 & \mathrm{e}^{-\beta\alpha} & 1 & 1 & \mathrm{e}^{+\beta\alpha}\\ \mathrm{e}^{+\beta\alpha} & 1 & 1 & \mathrm{e}^{-\beta\alpha} & 1 & 1\\ 1 & \mathrm{e}^{+\beta\alpha} & 1 & 1 & \mathrm{e}^{-\beta\alpha} & 1\\ 1 & 1 & \mathrm{e}^{+\beta\alpha} & 1 & 1 & \mathrm{e}^{-\beta\alpha}\end{pmatrix}. \tag{B4}$$

The free energy is readily computed to be:

$$-\beta F = \ln\{(2\cosh(\beta\alpha)+4)^N + 2(2\cosh(\beta\alpha)-2)^N + 3(2\sinh(\beta\alpha))^N\}. \quad \text{(B5)}$$

We define the generating function for correlations by

$$G_{j,k,\mathbf{g}} \equiv \sum_{\{\mathbf{b}_i\}} \left\{ \left[\prod_{i=1}^{N} \mathrm{e}^{-\beta\alpha \mathbf{b}_i\cdot\mathbf{b}_{i+1}} \right] \mathrm{e}^{\mathbf{g}\cdot\sum_{i=j}^{k}\mathbf{b}_i} \right\}, \quad \text{(B6)}$$

which can be evaluated by defining an appropriate matrix, $\mathfrak{T}_{\mathbf{g}}$ and computing the trace:

$$G_{j,k,\mathbf{g}} = \mathrm{Tr}(\mathfrak{T}_{\mathbf{g}}^{M}\mathfrak{T}_{2}^{N-M}) \text{ with } M = |k-j|. \quad \text{(B7)}$$

An even simpler transfer matrix can be constructed by assigning a uniform energy penalty, E, with a Boltzmann factor $a \equiv \exp(-\beta E) \leq 1$, for any neighboring configuration which is not straight:

$$\mathfrak{T}_3 = \begin{pmatrix} 1 & a & a & a & a & a \\ a & 1 & a & a & a & a \\ a & a & 1 & a & a & a \\ a & a & a & 1 & a & a \\ a & a & a & a & 1 & a \\ a & a & a & a & a & 1 \end{pmatrix}. \quad \text{(B8)}$$

In this sense the model favors the forward direction above any of the other bond orientations. This formulation gives a partition function

$$Z_3 = (5a+1)^N + 5(1-a)^N, \quad \text{(B9)}$$

an end-to-end squared average

$$\langle R_{x,a}^2\rangle = \{12(1-a)^N aN^2 + [(2a+1)(5a+1)^N - 2(1-a)^N a - (1-a)^N]N\}/[9a(5a+1)^N + 45(1-a)^N a], \quad \text{(B10)}$$

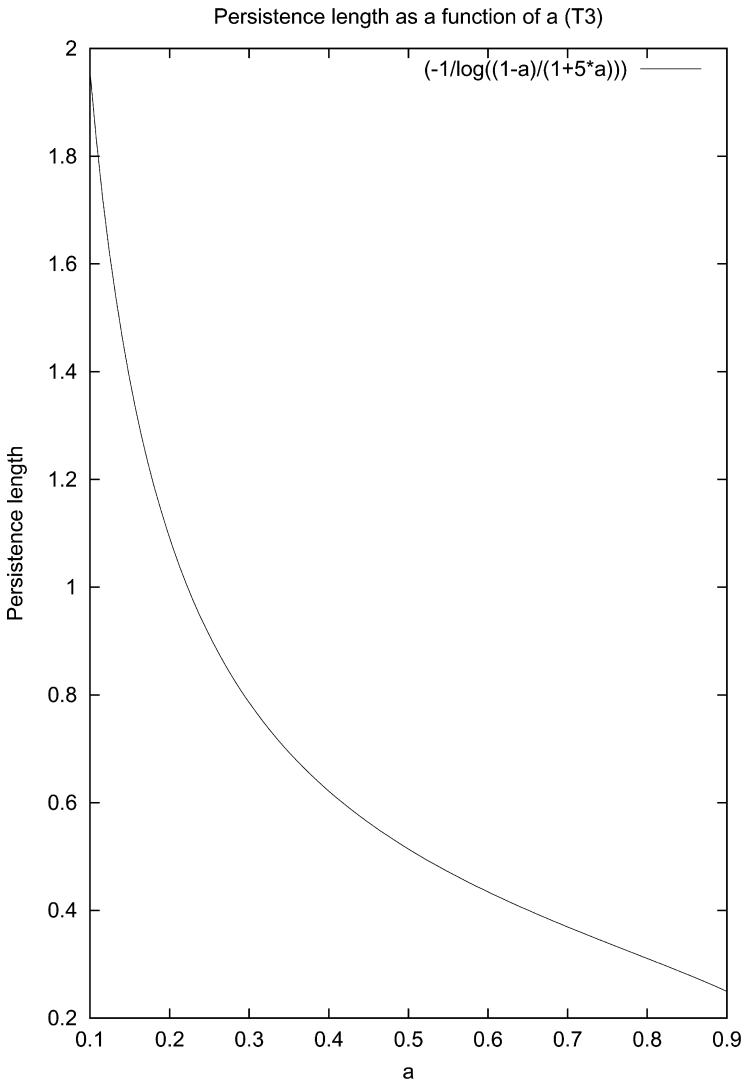

Fig. 2. The persistence length of Eq. (B11) as a function of $a = \exp(-\beta E)$.

a persistence length

$$\ell_{\mathrm{p},a} = -\frac{1}{\ln\left(\dfrac{1-a}{5a+1}\right)} \tag{B11}$$

and an effective spring constant for small forces:

$$k_{\mathrm{eff}} = [3\langle R_x^2\rangle]^{-1}. \tag{B12}$$

The definition for k_{eff} is given in Eqs. (C4) and (C5) in Appendix C. It has been computed from the linear term in the force of the average end-to-end distance of a chain which has been subjected to an extending force:

$$\langle R_{x,a}(\mathbf{f})\rangle = \frac{\left\langle \sum_i \mathbf{b}_i \, \mathrm{e}^{\mathbf{f}\cdot\sum_j \mathbf{b}_j}\right\rangle}{\left\langle \mathrm{e}^{\mathbf{f}\cdot\sum_j \mathbf{b}_j}\right\rangle}. \tag{B13}$$

Details of the calculations are given in Appendix C.

Eq. (B10) produces the expected limits:

$$\lim_{a\to 1^-} \langle R_x^2\rangle = \frac{n}{3}, \tag{B14}$$

$$\lim_{a\to 0^+} \langle R_x^2\rangle = \frac{n^2}{3}. \tag{B15}$$

The expression for the persistence length (B11) also strives to zero for no energetic penalty for bending and towards an infinite value when a straight configuration is highly favored as shown in Fig. 2. A plot of the linear spring constant is shown in Fig. 3.

It is possible to introduce a large number of models for different types of situations along the vein of the formulations in this section. We mention another two possibilities.

1. The first is for a model with the usual stiffness, favoring a forward-direction above a perpendicular alignment of adjacent bonds, and ascribing a probability of 0 to two adjacent bonds being anti-parallel. The relevant transfer matrix is:

$$\mathfrak{T}_4 = \begin{pmatrix} 1 & a & a & 0 & a & a \\ a & 1 & a & a & 0 & a \\ a & a & 1 & a & a & 0 \\ 0 & a & a & 1 & a & a \\ a & 0 & a & a & 1 & a \\ a & a & 0 & a & a & 1 \end{pmatrix}. \tag{B16}$$

2. *Non-symmetric* matrices are also permissible. They can be used to express tendency towards the formation of helical conformations of the molecule, i.e. sequences of bonds of the type $\{x, y, z, x, y, \ldots\}$ or $\{-x, -y, -z, -x, -y, \ldots\}$ with a certain probability. A transfer matrix which would permit this is:

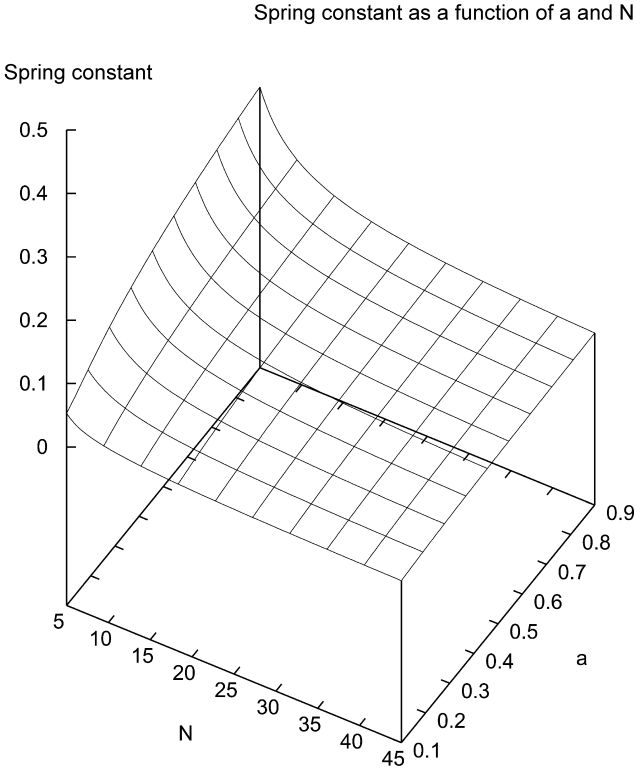

Fig. 3. The linear spring constant of the chain modeled by Eq. (B10). The y scale is for $a = \exp(-\beta E)$, whereas the x-axis represents the number of bonds in the chain. The *linear* contribution to the elasticity increases as the chain becomes more Gaussian and the number of bonds decreases.

$$\mathfrak{T}_5 = \begin{pmatrix} p & 0 & 1-p & 0 & 0 & q \\ 1-p & p & 0 & q & 0 & 0 \\ 0 & 1-p & p & 0 & q & 0 \\ 0 & 0 & q & p & 0 & 1-p \\ q & 0 & 0 & 1-p & p & 0 \\ 0 & q & 0 & 0 & 1-p & p \end{pmatrix}. \tag{B17}$$

The qs here, simply, couple positive and negative directions in some manner.

All these specific examples show the variety which can be accommodated by such types of models.

Appendix C. $\mathfrak{T}_3$

The mathematics required to derive the relevant quantities can be found in numerous introductory texts. They are summarized here only briefly.

In order to compute the end to end distance of, for

example, the x-components, we introduce a matrix

$$S = \begin{pmatrix} e^{g/2} & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & e^{-g/2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}, \tag{C1}$$

for a generating function:

$$Z_{a,g} = \mathrm{Tr}\mathfrak{T}_{3,g}^{N} = \mathrm{Tr}(S\mathfrak{T}_3 S)^N = \sum_{\varepsilon} \lambda_{\varepsilon,g}^{N}. \tag{C2}$$

Here the sum over ε is over the six eigenvalues of $S\mathfrak{T}_3 S$ which depend upon g. Consequently, the averaged end-to-end distance is:

$$\begin{aligned} \langle R_x^2 \rangle &= \frac{1}{Z_{a,0}} \left(\frac{\partial^2}{\partial g^2} Z_{a,g} \right)_{g=0} \\ &= \frac{1}{Z_{a,0}} \left\{ \sum_{\varepsilon} N \left(\frac{\partial^2 \lambda_{\varepsilon,g}}{\partial g^2} \right)_{g=0} \lambda_{\varepsilon}^{N-1} + N(N-1) \sum_{\varepsilon} \right. \\ &\quad \left. \times \left(\frac{\partial \lambda_{\varepsilon,g}}{\partial g} \right)_{g=0}^{2} \lambda_{\varepsilon}^{N-2} \right\}. \end{aligned} \tag{C3}$$

By similar logic one can view the average end-to-end distance of a chain subject to a force along the x-axis g as:

$$\langle R_x(g) \rangle = \frac{\dfrac{\partial}{\partial g} Z_{a,g}}{Z_{a,g}}. \tag{C4}$$

The linear contribution to the extension due to the force can be extracted:

$$k_{\mathrm{eff}}^{-1} = \left(\frac{\partial}{\partial g} \frac{\dfrac{\partial}{\partial g} Z_{a,g}}{Z_{a,g}} \right)_{g=0}. \tag{C5}$$

This can be expressed in terms of eigenvalues and be computed readily.

The persistence length is computed analogously to the correlation length in the Ising model. Taking $\hat{\mathbf{t}}_i$ as the unit vector of the ith bond and by defining

$$\mathbf{t} = \begin{pmatrix} \hat{\mathbf{x}} & 0 & 0 & 0 & 0 & 0 \\ 0 & \hat{\mathbf{y}} & 0 & 0 & 0 & 0 \\ 0 & 0 & \hat{\mathbf{z}} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\hat{\mathbf{x}} & 0 & 0 \\ 0 & 0 & 0 & 0 & -\hat{\mathbf{y}} & 0 \\ 0 & 0 & 0 & 0 & 0 & -\hat{\mathbf{z}} \end{pmatrix}, \tag{C6}$$

one can write:

$$\begin{aligned} \langle \hat{\mathbf{t}}_i \cdot \hat{\mathbf{t}}_{i+p} \rangle &= \frac{1}{Z_a} \mathrm{Tr}[\mathfrak{T}_3^{N-p} \mathbf{t} \cdot \mathfrak{T}_3^{p} \mathbf{t}] \\ &= \frac{\dfrac{(5a+1)^p}{3(1-a)^{p-n}} + \dfrac{(1-a)^p}{3(5a+1)^{p-n}} + \dfrac{4(1-a)^n}{3}}{(5a+1)^n + 5(1-a)^n} \\ &\quad \times \to \left(\frac{1-a}{5a+1} \right)^p, N \to \infty. \end{aligned} \tag{C7}$$

Appendix D. Interactions

An interaction term in the Hamiltonian of the previously analyzed models would require the computation of quantities such as the Helmholtz free energy

$$e^{-\beta F} = \sum_{\{\sigma_i\}} \exp\left[-\beta H_0 - \beta \sum_{i<j} V\left(\sum_{k=i+1}^{j} \mathbf{b}_k \right) \right], \tag{D1}$$

where H_0 is any of the varieties of Ising Hamiltonians previously introduced.

In order to compute the effect of interactions in the model, use of the Feynman–Bogoliubov variational principle can be made using as the variational Hamiltonian, H_{v}, corresponding to another Ising model with parameters with altered stiffness of the polymer chain. In so doing the average

$$\begin{aligned} &\left\langle \beta \sum_{i<j} V\left(\sum_{k=i+1}^{j} \mathbf{b}_k \right) \right\rangle_{\mathrm{v}} \\ &= \left\langle \beta \sum_{i<j} \int \mathrm{d}^3 k \tilde{V}(\mathbf{k}) e^{i\mathbf{k} \cdot \sum_{l=i+1}^{j} \mathbf{b}_l} \right\rangle_{\mathrm{v}}, \end{aligned} \tag{D2}$$

needs to be computed with H_{v}, where

$$\left\langle \beta e^{i\mathbf{k} \cdot \sum_{l=i+1}^{j} \mathbf{b}_l} \right\rangle_{\mathrm{v}} = G_{i,j,i\mathbf{k}}/Z, \tag{D3}$$

is related to the generating function of Eq. (B6). The variational free energy can then be computed in the usual manner by approximating the k-integration and minimizing for the Ising-model interaction parameter.

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