

An efficient model for extensible semiflexible polymers

September 11, 2012

Abstract

We present a model for semiflexible polymers in Hamiltonian formulation which interpolates between a Rouse chain and wormlike chain. Both models are realized as limits for the parameters. The model parameters can also be chosen to match the experimental force-extension curve for double-stranded DNA. Near the ground state of the Hamiltonian, the eigenvalues for the longitudinal (stretching) and the transverse (bending) modes of a chain with N springs, indexed by p , scale as $\zeta_p^{\parallel} \sim (p/N)^2$ and $\zeta_p^{\perp} \sim p^2(p-1)^2/N^4$ respectively for small p . The eigenspectrum for the longitudinal modes are the same as those of the Rouse modes. The dynamics is also formulated in terms of the Rouse modes, enabling to focus on the most relevant slow modes of the system.

1 Introduction

There are many models for the equilibrium behavior of long polymers but few for their dynamics. The celebrated Rouse model describes the temporal behavior of the chain by a set of (Rouse) modes in a harmonic potential. Such a Rouse (or fantom) chain is however too flexible to describe the behavior of biological polymers. For instance the persistence length of a Rouse chain is zero, while e.g. dsDNA persist in its orientation over some hundred base pairs. It is easy to dress the Rouse model with a term that suppresses bending of the chain, while preserving the dynamics in the form of a set of Rouse modes. However, the behavior of such a chain under an external force, i.e. the force extension curve, does still not correspond to that of the semiflexible biopolymers, as it responds to the force as an harmonic spring, while the semiflexible chain has a characteristic rapid increase of the extension for small forces, crossing over to a slow linear increase with the force. Clearly Rouse-type chains have too little rigidity against longitudinal forces.

An opposite approach is to represent the biopolymer as worm-like chain [1], which is a continuum description with the appropriate stiffness against bending. The worm-like chain (WLC) keeps a fixed contour length and only undergoes transversal undulations. A microscopic realization of the worm-like chain is the model in which the monomers are connected by rigid bonds. The bending stiffness is incorporated in the hamiltonian by a term suppressing the

angle between two successive bonds. The rigidity of the bonds guarantees the invariance of the contour-length under the possible motion of the monomers. We refer to this model as the “jointed chain” (in analogy with the well known freely-jointed chain [2]). A refinement is to let the bond length vary with the external force. Such an “extensible jointed chain” can very well reproduce the measured force-extension curve of biopolymers by an appropriate choice of the bending stiffness. A model close to the extensible jointed chain has recently been introduced by Kierfeld et al. [3], who extensively treat its equilibrium properties.

However, the dynamics of jointed chains is quite involved, as the motion of the monomers is strongly constrained by the rigidity of the bonds, which introduces unphysical long-range correlation. E.g. the motion between the end monomers of the chain is correlated due to the constant length of the contour.

Thus a polymer model that can treat the dynamics of biological polymer fragments, such as occurring in networks, is quite welcome. These fragments are of the order of the persistence length, rendering a continuum description not adequate and a description on base-pair level necessary. In this paper we propose such a model combining to a large extent the mathematical simplicity of the Rouse model, while describing accurately the experimental force-extension curve.

The hamiltonian for our flexible and extensible chain reads:

$$\mathcal{H} = \frac{\lambda}{2} \sum_{n=1}^N (|\mathbf{u}_n| - d)^2 - \kappa \sum_{n=1}^{N-1} \mathbf{u}_n \cdot \mathbf{u}_{n+1} - \mathbf{F} \cdot \mathbf{L}. \quad (1)$$

Here \mathbf{u}_n is the bond vector between monomer $n - 1$ and n and \mathbf{L} the end-to-end vector

$$\mathbf{u}_n = \mathbf{r}_n - \mathbf{r}_{n-1}, \quad \mathbf{L} = \mathbf{r}_N - \mathbf{r}_0 = \sum_{n=1}^N \mathbf{u}_n. \quad (2)$$

\mathbf{r}_n is the position of the n -th monomer ($n = 0, 1, \dots, N$). \mathbf{F} is a force tending to orient and stretch the chain. The first term in (1) is a single-bond harmonic interaction, providing the length scale d and the energy parameter λ . The second term is a nearest-neighbor-bond interaction giving the model a bending stiffness measured by κ . The above defined hamiltonian is the simplest of a class of hamiltonians with bond interactions, not only between nearest neighbors as in (1), but also longer-ranged interactions. If we set $d = 0$ the model reduces to that of Marques and Frederickson [4] (with slightly different boundary conditions). As we mentioned above such a Rouse-like model does not have an acceptable force-extension curve. We will argue that a finite d changes the properties from being rather unrealistic to realistic. The difference between our model and that of Kierfeld et al.[3] is minor as far as the equilibrium properties are concerned. However the difference is major with respect to the dynamics. While in Kierfeld et al. the bending energy only depends on the angle between the bonds in our case it depends on the bond vectors. The angles are dynamically very inconvenient parameters: changing one angle while keeping the others fixed involves the motion of a whole segment of the chain. In contrast monomers positions can be changed independently, only changing the incident bond vectors of that monomer.

In this paper we discuss the mechanical and statistical properties of the model. Also we formulate the dynamical equations for the monomer positions, as well as those for an equivalent description in terms of the modes of the system. In a subsequent study we design an efficient scheme for the solution of the dynamical equations and report on extensive simulations of the model.

2 The parameters of the model

By varying the parameters d, λ and κ we cover a wide range of physical systems. We can eliminate the value of a finite d from the problem by scaling \mathbf{u}_n with d . Then the hamiltonian reads

$$\mathcal{H} = \frac{\lambda d^2}{2} \sum_{n=1}^N (|\mathbf{u}_n| - 1)^2 - \kappa d^2 \sum_{n=1}^{N-1} \mathbf{u}_n \cdot \mathbf{u}_{n+1} - d\mathbf{F} \cdot \sum_{n=1}^N \mathbf{u}_n. \quad (3)$$

Thus d can be absorbed in the parameters λ, κ and F . Therefore d does not show up in the expressions for the static and dynamic properties. To translate the properties to a real chain one has to multiply the bond vectors with a well chosen d . The form (3) shows that $d = 0$ is a singular point of the hamiltonian (1). Amongst others, the case $d = 0$ has a lowest energy state in which all bond lengths vanish.

As our main interest is describing biological polymers, which have a fairly rigid bond length and a large persistence length, we consider large values of λ and κ . So it is useful to consider the ratio between λ and κ as characteristic for the model. As we will see their common magnitude couples to the temperature. So we write

$$\kappa = \nu \lambda \quad (4)$$

and the hamiltonian gets the form that we will use in this paper:

$$\mathcal{H}^* = \frac{\mathcal{H}}{\lambda d^2} = \left[\frac{1}{2} \left(\sum_{n=1}^N (|\mathbf{u}_n| - 1)^2 - \nu \sum_{n=1}^{N-1} \mathbf{u}_n \cdot \mathbf{u}_{n+1} \right) - \mathbf{f} \cdot \sum_{n=1}^N \mathbf{u}_n \right], \quad (5)$$

with the abbreviation

$$\mathbf{f} = \mathbf{F}/(\lambda d). \quad (6)$$

Equilibrium is governed by the ratio $\mathcal{H}/k_B T$, which we write as

$$\frac{\mathcal{H}}{k_B T} = \frac{\mathcal{H}^*}{T^*} \quad (7)$$

where the reduced temperature T^* equals

$$T^* = k_B T / (\lambda d^2) \quad (8)$$

Thus the combination λd^2 is absorbed in the reduced temperature T^* . We will discuss the model in terms of the dimensionless parameters T^*, ν and f . Stability of the hamiltonian requires that $\nu < 1/2$. Large values of λ manifest themselves in low values of T^* . This makes the bond length fairly constant. Assuming a constant bond length reduces the model to the jointed chain and

indeed the force-extension curve of our model closely follows that of the (extensible) jointed chain.

For the analysis of the model we split the hamiltonian in three parts according to the power in which the bond vectors (or bead positions) occur:

$$\mathcal{H}^* = \mathcal{H}_h^* + \mathcal{H}_s^* + N/2. \quad (9)$$

The last term is a trivial constant having no influence, neither on the statics nor on the dynamics. We will pay no further attention to it. The first term, which would be the full (force-free) hamiltonian if we were to set $d = 0$, can be written as a matrix, sandwiched with the bead positions

$$\mathcal{H}_h^* = \frac{1}{2} \sum_{m,n}^N H_{m,n} \mathbf{r}_m \cdot \mathbf{r}_n. \quad (10)$$

The term \mathcal{H}_s represents the stabilizing force and has the form

$$\mathcal{H}_s^* = - \sum_{n=1}^N [u_n + \mathbf{f} \cdot \mathbf{u}_n]. \quad (11)$$

The first term in (11), involving the contour length of the chain, plays an essential role in stabilizing the chain. It prevents however an exact diagonalization of the model, which is possible for the harmonic terms.

3 Groundstate Properties

The dynamics of the model is our main interest. There are a number of equilibrium properties which are important for the dynamical analysis. We summarize them here.

3.1 The groundstate configuration

The groundstate or lowest energy configuration prevails at low T^* . With a non-vanishing external force, the chain starts to align itself with the force and the configuration becomes a straight line. All bond vectors point in the direction of \mathbf{f} and may be written as $\mathbf{u}_n = u_n \hat{\mathbf{f}}$. The values of the length u_n follow from minimization of the energy, leading to the equations

$$\left(\begin{array}{r} u_1 - \nu u_2 = 1 + f, \\ -\nu u_1 + u_2 - \nu u_3 = 1 + f, \\ \dots \\ -\nu u_{N-2} + u_{N-1} - \nu u_N = 1 + f, \\ -\nu u_{N-1} + u_N = 1 + f. \end{array} \right) \quad (12)$$

Note that the solution for $f \neq 0$ follows from that for $f = 0$ by multiplying all u_n by $1 + f$. A set of equation of the type (12) can be solved by the standard technique of the generating function. The solution reads

$$u_n = \frac{1 + f}{1 - 2\nu} \left[1 - \frac{\cosh\{\alpha(N + 1 - 2n)\}}{\cosh\{\alpha(N + 1)\}} \right], \quad (13)$$

with $\cosh(2\alpha) = 2/\nu$. In the bulk the value approaches

$$b(f) = \frac{1+f}{1-2\nu}. \quad (14)$$

Near the ends the bond become somewhat shorter. The value $b = b(0)$ is an important (numerical) value by which d has to be multiplied in order to match the experimental bond length a . In other words $d = a/b$. We find that for small T^* , b is still close to the value (14).

3.2 Eigenmodes near the groundstate

The groundstate energy responds harmonically to small deviations, yielding a quadratic increase in the energy. We first discuss the force free case. One can find the Hessian matrix by twice differentiating the Hamiltonian with respect to the positions of the monomers. As the dependence on the monomer positions is exclusively through the bond vectors, we use the rule

$$\frac{\partial}{\partial \mathbf{r}_n} = \frac{\partial}{\partial \mathbf{u}_n} - \frac{\partial}{\partial \mathbf{u}_{n+1}}, \quad (15)$$

and define the bond matrix

$$\mathbf{B}_{m,n} = \frac{\partial^2 \mathcal{H}^*}{\partial \mathbf{u}_m \partial \mathbf{u}_n}. \quad (16)$$

The indices in the matrix B run between $1 \leq m, n \leq N$. We extend the matrix by putting the elements equal to zero, whenever one of the indices equals 0 or $N + 1$. The Hessian matrix M is then obtained as

$$\mathbf{M}_{m,n} = \mathbf{B}_{m,n} - \mathbf{B}_{m,(n+1)} - \mathbf{B}_{(m+1),n} + \mathbf{B}_{(m+1),(n+1)}. \quad (17)$$

$M_{m,n}$ runs in the interval $0 \leq m, n \leq N$.

Let us first consider the part of B which is due to the contribution \mathcal{H}_h^* . This part is diagonal in the vectorial indices and the scalar matrix multiplying the unit tensor \mathbf{I} reads

$$B_{mn} = \begin{pmatrix} 1 & -\nu & 0 & 0 & \cdots \\ -\nu & 1 & -\nu & 0 & \cdots \\ 0 & -\nu & 1 & -\nu & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \end{pmatrix}. \quad (18)$$

Using the property

$$\sin \left[\frac{m(n+1)\pi}{N+1} \right] + \sin \left[\frac{m(n-1)\pi}{N+1} \right] = 2 \cos \left(\frac{m\pi}{N+1} \right) \sin \left(\frac{mn\pi}{N+1} \right), \quad (19)$$

it is easy to see that the eigenvalue equation has the form

$$\sum_{n=1}^N B_{mn} \sin \left(\frac{mn\pi}{N+1} \right) = \theta_m \sin \left(\frac{mn\pi}{N+1} \right), \quad (20)$$

with θ_m given by

$$\theta_m = \left[1 - 2\nu \cos \left(\frac{m\pi}{N+1} \right) \right]. \quad (21)$$

Note that (20-21) are also satisfied for the ends of the chain ($m, n = 0, N$) since we can trivially extend the summation to the interval $0 \leq m, n \leq N$.

Using Eq. (20) and similar trigonometric relations, we arrive at the eigenvalues for M_{mn}

$$\sum_{n=0}^N M_{pn} \cos \left[\frac{(n+1/2)\pi}{N+1} \right] = \zeta_p \cos \left[\frac{(p+1/2)\pi}{N+1} \right], \quad (22)$$

with ζ_p given by

$$\zeta_p = 2 \left[1 - \cos \left(\frac{p\pi}{N+1} \right) \right] \theta_p. \quad (23)$$

Next we consider the influence of the stabilizing force \mathcal{H}_s^* . Since

$$\mathbf{B}_{i,j}^s = -\frac{\partial^2}{\partial \mathbf{u}_i \partial \mathbf{u}_j} \sum_{n=1}^N u_n. \quad (24)$$

evaluation of the derivative yields

$$\mathbf{B}_{i,j}^s = -\delta_{i,j} \frac{1}{u_i} \left(\mathbf{I} - \frac{\mathbf{u}_i \mathbf{u}_i}{u_i^2} \right). \quad (25)$$

This tensor projects out the longitudinal eigenmodes and is unity for the transversal modes. Longitudinal and transversal relate to the direction of the vector \mathbf{u}_j . Thus the longitudinal modes are given by (20-21). We put this in formula

$$\lambda_p^l = \zeta_p \quad (26)$$

as ζ_p is going to play a different role in the dynamics.

The two transversal modes are corrected by the term (25), which is diagonal in the matrix indices. The diagonal contribution to B of the quadratic terms in the Hamiltonian equals 1. So if we define

$$q_i = (1 - 1/u_i), \quad (27)$$

q_i becomes the diagonal matrix element. The transverse modes for \mathbf{B} follow from the diagonalization of this matrix, which has to be carried out numerically. One gets an impression of the eigenvalue spectrum by using the bulk value

$$1/u_i \simeq 1 - 2\nu \quad (28)$$

for each diagonal element. Then the modes of the bond matrix have again the shape (20) and the eigenvalues are

$$\theta_p^t = \nu \left[1 - \cos \left(\frac{p\pi}{N+1} \right) \right]. \quad (29)$$

This formula covers the spectrum closely, provided that we replace for the low modes p by $p - 1$ in the argument of the cos. Note that upon this substitution

the eigenvalue for $p = 1$ vanishes. This is a general property of the eigenmode in the force free case, due to invariance of the energy under an overall rotation.

The dynamical matrix has then transversal eigenmodes of the form (22) and the eigenvalue equals

$$\lambda_p^t = 2 \left[1 - \cos \left(\frac{p\pi}{N+1} \right) \right] \theta_p^t. \quad (30)$$

An external force changes the shape of the modes and the eigenvalues. The transversal mode for $p = 1$ no longer vanishes. The effects of a force have to be incorporated numerically.

3.3 The persistence length

The persistence length derives from the orientation correlation function

$$O_{i,j} = \langle \hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j \rangle. \quad (31)$$

Asymptotically $O_{i,j}$ decays exponentially and the exponent defines the persistence length. It is dominantly dependent on ν (or κ). For the large values of λ (or small values of T^*), one gets a good impression of the orientation correlation function, by taking the bond lengths as rigid, i.e. by studying the extensible jointed chain, for which the orientation correlation function can be exactly calculated (see Appendix A). One finds for the persistence length l_p

$$\frac{l_p}{a} = -\frac{1}{\log[\coth(r) - 1/r]} \quad \text{with} \quad r = b^2 \nu / T^*. \quad (32)$$

Note that only κ determines this persistence length, since λ , which is buried both in ν and T^* , drops out. So a given persistence length sets the ratio ν/T^* . This expression gives the persistence length as the number counting the monomers over which the orientation persists.

3.4 The force-extension curve

The most informative quantity is the force-extension curve. It is the response of the end-to-end vector \mathbf{L} on the external force. It follows from the partition function

$$Z_f = \text{Tr} \exp -\mathcal{H} / (k_b T) \quad (33)$$

as

$$\langle \mathbf{L} \rangle = \left\langle \sum_{n=1}^N \mathbf{u}_n \right\rangle = \frac{\partial \log Z}{\partial \mathbf{f}}. \quad (34)$$

This quantity is difficult to simulate, since it fluctuates strongly with a long relaxation time. The limits of weak and strong forces are however easy to understand. For weak forces we may treat the external force as a perturbation, with the lowest order result

$$\log Z \simeq \log Z_0 + \frac{1}{2T^*} \langle ([\mathbf{f} \cdot \mathbf{L}]^2) \rangle_0. \quad (35)$$

The subscript 0 indicates the forceless values. Thus the response is linear in \mathbf{f} :

$$\langle \mathbf{L} \rangle \simeq \langle \mathbf{L} \mathbf{L} \rangle_0 \cdot \mathbf{f} / T^* = \mathbf{f} \langle L^2 \rangle_0 / 3T^*. \quad (36)$$

In the forceless average only the diagonal components survive. The mean-squared-average of the end-to-end vector can be related to the persistence length for chains many times longer than the persistence length:

$$\langle L^2 \rangle_0 = 2Nb(0)l_p. \quad (37)$$

The combination $L_c = Nb(0)$ is the contour length and thus one gets for the initial slope in the large N limit

$$\frac{\langle \mathbf{L} \rangle}{L_c} \simeq \frac{2l_p}{3T^*} \mathbf{f}. \quad (38)$$

One sees from this expression that for low T^* the slope of the rise is steep for two reasons: the small factor T^* in the denominator and large l_p in the numerator.

In the large force limit we may use the result (14). The chain will be stretched in the force direction and the bond will be elongated accordingly, with the result

$$\frac{\langle \mathbf{L} \rangle}{L_c} \simeq (1 + f) \hat{\mathbf{f}}. \quad (39)$$

As a note in passing we point out on the basis of equation (14) that the groundstate gives this result for all forces. Thus for $\mathbf{f} = \mathbf{0}$ there is a residual value for the extension. This holds only for $T = 0$ as for all $T \neq 0$ the end-to-end vector will vanish for $f = 0$, due to rotational invariance. Indeed the point ($f = 0, T = 0$) is singular and the value of $\langle \mathbf{L} \rangle$ depends on the way this point is approached.

The complete curve will be a smooth transition between the fast initial rise (till L is of the order Nb) and the slow rise of (20), manifesting itself when f becomes of the order 1. Remember that f is the real force F divided by λd . Thus forces f of order 1 are huge on a real scale when the polymer is stiff or λ large. In between, there is a quasi-plateau with the value Nb .

3.5 Choice of the parameters

The model parameters ν and T^* can be chosen such that the force-extension curve of the model is in good agreement with that of biopolymers. Wang et al. give the following empirical formula for biopolymers, such as dsDNA:

$$\frac{Fl_p}{k_B T} = \frac{1}{4} \left[1 - \frac{\langle L \rangle}{L_c} + \frac{F}{K_0} \right]^{-2} - \frac{1}{4} + \frac{\langle L \rangle}{L_c} - \frac{F}{K_0}. \quad (40)$$

This equation contains two polymer-specific parameters: the persistence length l_p and the constant K_0 . As we have mentioned earlier the experimental l_p has to be combined with the bond length a to a dimensionless quantity, for which

our model gives the value (32). So for the biological stiff polymers T^* is small, making r large and l_p/a equal to r . So as first equation we get

$$r = \frac{l_p}{a} = \frac{b^2 \nu}{T^*}. \quad (41)$$

The other experimental quantity K_0 is turned into a dimensionless combination z :

$$z = \frac{aK_0}{k_B T}. \quad (42)$$

This constant manifests itself only for large forces. The behavior of the extension for large forces is somewhat hidden in the implicit equation (40). In order to make it explicit, we write the equation in parametric form. We introduce the auxiliary parameter s and for the force the parameter x :

$$x = \frac{F l_p}{k_B T}, \quad s = \frac{\langle L \rangle}{L_c} - \frac{F}{K_0}, \quad (43)$$

such that extension and force can be written as function of s :

$$\frac{\langle L \rangle}{L_c} = s + \frac{x(s)}{r z}, \quad \text{with} \quad x(s) = \frac{1}{4(1-s)^2} - \frac{1}{4} + s. \quad (44)$$

The parameter s runs in the interval $0 < s < 1$, small s corresponding to small forces and s close to 1, to large forces. For $s = 1 - \epsilon$, with ϵ small, one has, according to (44) $x \simeq 1/(4\epsilon^2)$. Then the force-extension curve obtains the form

$$\frac{\langle L \rangle}{L_c} \simeq 1 + \frac{x}{r z}. \quad (45)$$

We compare this with the strong force behavior of our model as given by (39). Relating the experimental force to our parameter f we have

$$x = \frac{f \lambda d l_p}{\lambda d^2 T^*} = \frac{l_p b f}{a T^*} = \frac{r b f}{T^*}. \quad (46)$$

The two expressions (45) and (39) are the same if

$$\frac{b}{T^*} = z. \quad (47)$$

We now have two equations, (41) and (47), for the two hamiltonian parameters T^* and ν . Solving them leads to the explicit relations

$$T^* = \frac{2r + z}{z^2} \quad \text{and} \quad \nu = \frac{r}{2r + z}. \quad (48)$$

For dsDNA the persistence length is about 40 nm. Wang et al. [5] report for the force constant a value around $K_0 = 1200$ pN. So with a monomer distance $a = 0.33$ nm and at room temperature $k_B T = 4$ pN nm, we get as representative values

$$r = 120 \quad \text{and} \quad z = 100. \quad (49)$$

This gives for ν and T^* as model parameters for dsDNA

$$T^* = 0.034 \quad \text{and} \quad \nu = 0.35. \quad (50)$$

4 The dynamical Equations

The dynamical equations for the beads are the Langevin equations for particles in a high viscous medium:

$$\frac{d\mathbf{r}_n}{dt} = -\frac{1}{\xi} \frac{\partial \mathcal{H}}{\partial \mathbf{r}_n} + \mathbf{g}_n(t). \quad (51)$$

Here ξ is the friction coefficient and \mathbf{g}_n is a random noise force, with correlation function

$$\langle \mathbf{g}_n(t) \mathbf{g}_m(t') \rangle = \frac{2k_B T}{\xi} \mathbf{I} \delta_{n,m} \delta(t - t'), \quad (52)$$

where \mathbf{I} is the unit tensor. The strength of the correlation is determined by the fluctuation-dissipation relation.

We make the equations dimensionless by introducing a reduced time τ :

$$\tau = t\lambda/\xi. \quad (53)$$

The equations then obtain the form

$$\dot{\mathbf{r}}_m(\tau) = - \sum_{n=0}^N H_{m,n} \mathbf{r}_n(\tau) + \mathbf{h}_m(\tau) + \mathbf{g}_m(\tau) + \mathbf{f}(\delta_{n,0} - \delta_{N,n}), \quad (54)$$

where the dot stands for differentiation with respect to τ . \mathbf{h}_m derives from the stabilizing term \mathcal{H}_s , given in (10), reading

$$\mathbf{h}_m = \frac{\partial |\mathbf{u}|_m}{\partial \mathbf{r}_m} + \frac{\partial |\mathbf{u}|_{m+1}}{\partial \mathbf{r}_m} = |\hat{\mathbf{u}}_m| - |\hat{\mathbf{u}}_{m+1}|. \quad (55)$$

$\hat{\mathbf{u}}_n$ is the unit vector in the direction of the bond n . The dimensionless random forces have the correlations

$$\langle \mathbf{g}_n(\tau) \mathbf{g}_m(\tau') \rangle = 2T^* \mathbf{I} \delta_{n,m} \delta(\tau - \tau'). \quad (56)$$

The center-of-mass position, defined as

$$\mathbf{R}_{cm} = \frac{1}{N+1} \sum_{n=0}^N \mathbf{r}_n, \quad (57)$$

is not affected by the interaction between the beads and is only influenced by the random forces. It fluctuates due to the random forces as a Brownian particle. In the route via the Rouse modes it will disappear completely from the problem.

5 Rouse Modes

Diagonalizing the matrix $H_{m,n}$ gives modes relevant for the system. Since H is symmetric and positive definite, all its eigenvalues are real and non-negative. This means that all the modes, but one, are associated with a decay exponent ζ_p . Only the mode corresponding to the center-of-mass has a zero eigenvalue

and decouples from the dynamic equations (the sum over the columns of $H_{m,n}$ vanishes).

The eigenmodes \mathbf{R}_p of the matrix H induce an orthogonal transformation of the positions \mathbf{r}_n . The label p runs through the integers $p = 0, 1, \dots, N$. For $p = 0$ we have a mode corresponding to the center-of-mass

$$\mathbf{R}_0 = (N + 1)^{1/2} \mathbf{R}_{cm}. \quad (58)$$

The other modes are given by the expression

$$\mathbf{R}_p = \left(\frac{2}{N + 1} \right)^{1/2} \sum_{n=0}^N \cos \left(\frac{p(n + 1/2)\pi}{N + 1} \right) \mathbf{r}_n. \quad (59)$$

The modes are normalized such that the transformation from \mathbf{r}_n to \mathbf{R}_p is orthonormal. For that reason we have put the factor in front of \mathbf{R}_{cm} in (58). One recognizes the modes \mathbf{R}_p as the modes of the Rouse model. The Rouse modes for other models have turned out to be an important tool for analyzing the properties of a polymer chain [6]. The Rouse modes diagonalize the part \mathcal{H}_n^* of the hamiltonian. The eigenvalues are, according to (23),

$$\zeta_p = 2 \left[1 - \cos \left(\frac{p\pi}{N + 1} \right) \right] \left[1 - 2\nu \cos \left(\frac{p\pi}{N + 1} \right) \right], \quad (60)$$

showing that the slow modes vanish as $(p/N)^2$ for small p .

As the Rouse modes diagonalize the dynamic matrix H , it can be written as

$$\sum_{m,n=0}^N H_{m,n} \mathbf{r}_m \cdot \mathbf{r}_n = \sum_{p=0}^N \zeta_p R_p^2, \quad (61)$$

with ζ_p given by (60). We point out that \mathbf{R}_p is an exact eigenmode of $H_{m,n}$ because of the special structure of the boundaries of the the matrix.

The inverse transformation reads

$$\mathbf{r}_n = \mathbf{R}_{cm} + \left(\frac{2}{N + 1} \right)^{1/2} \sum_{p=1}^N \cos \left(\frac{(n + 1/2)p\pi}{N + 1} \right) \mathbf{R}_p. \quad (62)$$

The advantage of these linear relations between the Rouse modes and the monomer positions, is that we can switch between either of two representations of the configuration to whichever is more convenient.

By applying the transformation to the equations (53) they become

$$\dot{\mathbf{R}}_p(\tau) = -\zeta_p \mathbf{R}_p(\tau) + \mathbf{H}_p + \mathbf{F}_p + \mathbf{G}_p(\tau). \quad (63)$$

Here \mathbf{H}_p is the transform of \mathbf{h}_n defined in (55):

$$\mathbf{H}_p = \left(\frac{2}{N + 1} \right)^{1/2} \sum_{n=0}^N \cos \left(\frac{(n + 1/2)p\pi}{N + 1} \right) \mathbf{h}_n. \quad (64)$$

The external force on the Rouse modes gets the form

$$\mathbf{F}_p = -2 \cos \left(\frac{p\pi}{2(N + 1)} \right) \mathbf{f}. \quad (65)$$

As the transformation to Rouse variables is orthogonal, the correlation function of \mathbf{G}_p equals

$$\langle \mathbf{G}_p(\tau) \mathbf{G}_q(\tau') \rangle = 2T^* \mathbf{I} \delta_{p,q} \delta(\tau - \tau'). \quad (66)$$

Without \mathbf{H}_p the Rouse modes are exact eigenmodes with decay coefficient ζ_p .

We make the scheme more explicit by inserting (55) into (64) and combining the two terms, yielding

$$\mathbf{H}_p(\tau) = - \sum_{n=1}^N M_{p,n} \hat{\mathbf{u}}_n(\tau), \quad (67)$$

where the matrix $M_{p,n}$ is defined as

$$M_{p,n} = 2 \left(\frac{2}{N+1} \right)^{1/2} \sin \left(\frac{p\pi}{2(N+1)} \right) \sin \left(\frac{np\pi}{N+1} \right). \quad (68)$$

The bond vectors are likewise expressed in terms of the Rouse variables using (62):

$$\mathbf{u}_n = - \sum_{q=1}^N \mathbf{R}_q M_{q,n}. \quad (69)$$

By these steps the relation between the stabilizing force and the Rouse modes has been made operational. We note that the operations have the character of a sinus fourier transform and therefore the technique of the fast fourier transform can be applied in both relations (67) and (69).

In concluding the discussion of the Rouse modes, we elaborate on the relation between the modes of the bond matrix $B_{m,n}$, introduced in (18) and the Rouse modes. To make this relation more transparent, we introduce modified Rouse modes as

$$\tilde{\mathbf{R}}_p = -2 \sin \left(\frac{p\pi}{2(N+1)} \right) \mathbf{R}_p. \quad (70)$$

Then relation (69) can be written as

$$\mathbf{u}_n = \left(\frac{2}{N+1} \right)^{1/2} \sum_{p=1}^N \sin \left(\frac{np\pi}{N+1} \right) \tilde{\mathbf{R}}_p. \quad (71)$$

The transformation from the $\tilde{\mathbf{R}}_p$ to the \mathbf{u}_n is also orthogonal and self-dual:

$$\tilde{\mathbf{R}}_p = \left(\frac{2}{N+1} \right)^{1/2} \sum_{n=1}^N \sin \left(\frac{np\pi}{N+1} \right) \mathbf{u}_n. \quad (72)$$

This provides actually a short-cut to derive (60). The harmonic energy is on the one hand with (18) given by

$$\sum_{m,n} B_{m,n} \mathbf{u}_m \cdot \mathbf{u}_n = \sum_{p=1}^N \theta_p \tilde{\mathbf{R}}_p \cdot \tilde{\mathbf{R}}_p \quad (73)$$

and on the other hand it also equals

$$\sum_{m,n} H_{m,n} \mathbf{r}_m \cdot \mathbf{r}_n = \sum_{p=1}^N \zeta_p \mathbf{R}_p \cdot \mathbf{R}_p. \quad (74)$$

With relation (70) between the modified Rouse modes and the Rouse modes, relation (60) immediately follows.

6 Discussion

We feel that our model fills a gap in the spectrum of models with respect to the dynamics of polymers for the the following reasons.

1. With only two adaptable parameters T^* and ν , the model interpolates between a worm-like chain and the Rouse model. This is important for the dynamics of fragments of biological polymers such as dsDNA, which neither are wormlike nor are well described by a Rouse model. The combination ν/T^* controls the persistence length and with $T^* \rightarrow 0$ one approaches the wormlike chain.
2. The empirical force-extension curve for biological polymers as proposed by Wang et al. [5] contains also two adaptable parameters: persistence length l_p and the force constant K_0 . In Section 3.5 we show how to make a map between between l_p and K_0 on the one hand and our model parameters T^* and ν on the other hand. The correspondence between the force-extension curve of our model and that of Wang et al. is excellent, as Fig. 1 shows.
3. The equilibrium properties of the model are close to that of the model of Kierfeld et al. [3]. The difference is that we use for the bending energy the inner product of two adjacent bond vectors, while (commonly) the cosine of the angle between the bonds is used. Our model allows to have the monomer positions as unconstrained dynamical variables, whereas it is awkward to formulate the dynamics in terms of the angles.
4. The dynamics of the model admits a description in terms of modes, showing clearly the wide scala of time scales from short for high-indexed modes till very long for the important low-indexed modes. Two types of modes exist: for polymers much shorter than the persistence length, the mechanical modes (described in Section 3.2) are relevant. For longer chains the Rouse modes are the more convenient representation.

In a subsequent paper we describe the results of simulations of this model for realistic parameters T^* and ν , applying to dsDNA. We there show how the simulation can be speeded up by orders of magnitude permitting to study chains of the order of 1000 base pairs. There it is also shown that the slowest mode is the rotational diffusion of the orientation, with a relaxation time going up as N^3 and that the other modes, often claimed as increasing with N^4 , are limited by the orientational diffusion.

Acknowledgement. The authors are indebted to Debrabata Panja for numerous stimulating discussions and providing the simulation data of Fig. 1.

A The extensible jointed-chain

In this appendix we discuss the properties of the chain in which the bonds all have the length $b(f) = b(1 + f)$. The f dependence of this bond length derives from the stretching of the bonds due to the force. Fixing the bond

length reduces the degrees of freedom to the orientations of the bonds, given by the polar angle θ_n between the bond and the direction of the force and the azimuth angle ϕ_n in a plane perpendicular to the force. So the hamiltonian reduces to

$$\frac{\mathcal{H}}{k_B T} = \frac{1}{2T^*} \left(N(b(f) - 1)^2 - 2\nu b(f)^2 \sum_{n=1}^{N-1} \cos \theta_{n,n+1} - 2b(f)f \sum_{n=1}^N \cos \theta_n \right) \quad (75)$$

$\theta_{n,n+1}$ is the angle between the bonds n and $n+1$. We observe that, apart from a trivial additive term, the hamiltonian contains two dimensionless parameters

$$\gamma = b(f)^2 \nu / T^*, \quad \text{and} \quad w = b(f)f / (2T^*). \quad (76)$$

The partition function thus is obtained as

$$Z = \text{Tr} \exp \left[\gamma \sum_{n=1}^{N-1} \cos \theta_{n,n+1} + 2w \sum_{n=1}^N \cos \theta_n \right], \quad (77)$$

where the trace is an integration over all angles θ_n, ϕ_n . For the evaluation we use the expansion in terms of the Legendre polynomials

$$\exp(\gamma z) = \sum_l (2l+1) q_l(\gamma) P_l(z), \quad (78)$$

with the $P_l(z)$ the l th Legendre polynomial. The coefficients $q_l(\gamma)$ are recovered as the integrals

$$q_l(\gamma) = \frac{1}{2} \int_{-1}^1 dz \exp(\gamma z) P_l(z). \quad (79)$$

These elementary integrals, related to the modified half-integer Bessel-functions, can be calculated successively using the recurrence relations between the Legendre polynomials. A Legendre polynomial is subsequently expanded in the bond angles as

$$(2l+1) P_l(\cos \theta_{n,n+1}) = 4\pi \sum_m Y_{l,m}(\theta_n, \phi_n) Y_{l,m}^*(\theta_{n+1}, \phi_{n+1}), \quad (80)$$

with the $Y_{l,m}$ as spherical harmonics. The advantage of this expression is that the relative angle between the bonds is expressed in terms of products of function of the the angles of the bonds in a fixed coordinate system.

Next we formulate the partition function as a matrix product. The first step is the integration over the azimuth angles ϕ_n . The angle ϕ_1 appears only in the first joint between 1 and 2. So its integration selects the term $m=0$, as all the higher m integrate to zero. This implies that also the angle ϕ_2 disappears from the product, since

$$Y_{l,0}(\theta_1, \phi_1) Y_{l,0}^*(\theta_2, \phi_2) = \frac{2l+1}{4\pi} P_l(\cos \theta_1) P_l(\cos \theta_2). \quad (81)$$

Subsequently one can integrate over ϕ_2 and so on, each integration over an azimuth angle contributing a factor 2π .

The remaining integration over the θ_n is of the type with $z = \cos \theta$

$$T_{k,l}(2w) = \frac{[(2k+1)(2l+1)]^{1/2}}{2} \int_{-1}^1 dz P_k(z) \exp(2wz) P_l(z). \quad (82)$$

The numerical factor in front of the integral is inserted to yield the property

$$T_{k,l}(2w) = \sum_n T_{k,n}(w) T_{n,l}(w), \quad (83)$$

which follows from the completeness of the Legendre polynomials and which is convenient for symmetrizing the coming matrix product.

We now define the transfer matrix

$$S_{k,l}(w, y) = \sum_n T_{k,n}(w) q_n(y) T_{n,l}(w), \quad (84)$$

which allows us to write the partition function as

$$Z = (4\pi)^N \langle \chi | S^{N-1} | \chi \rangle, \quad (85)$$

with the definition of the initial state $|\chi\rangle$

$$|\chi_l\rangle = T_{l,0}. \quad (86)$$

Note that we have used the property (83) to make the definition of $B_{k,l}$ symmetric.

By expression (85) the problem of calculation the partition function is reduced to finding the eigenvalues of the matrix $S_{k,l}$. For very long chains the largest eigenvalue will dominate. However, since the persistence length is long, this limit will only be reached when the chain has several thousands of bonds. Therefore we also investigate the finite chain for which one has to take into account all the eigenvalues. The eigenvalues and eigenfunctions are obtained from the equations

$$\sum_n S_{k,n} \psi_n^\alpha = \lambda_\alpha \psi_k^\alpha. \quad (87)$$

Then we use the representation

$$S_{k,n} = \sum_\alpha \psi_k^\alpha \lambda_\alpha \psi_n^\alpha, \quad (88)$$

Note that for small w , i.e. for weak forces, the matrix $T_{k,l}$ reduces to $\delta_{k,l}$ because the definition is just the orthogonality relation between Legendre polynomials. Then the eigenvalues of $S_{k,l}$ are given by the factor $q_l(y)$ and one of their properties is that they decrease with increasing l . Thus for $w \simeq 1$, i.e. forces $f \simeq T^*$, it suffices to restrict the matrix S to a finite square in the upper-left corner. This simplifies the problem considerably since, both for the $q_l(y)$ and the $T_{k,l}(w)$, simple recursion relation exist, enabling to construct them from the first few values. Even for larger w one does not need to include an excessive number of states to get an accurate answer.

The partition function itself is not the main goal of the above exercise. We now apply this approach to the calculation of the force extension curve and

the orientation correlation function. For the former we need the sum of the averages of $\cos \theta_j$ (see (18)). The appearance of $\cos \theta_j$ means the extra matrix $t_{k,l}$ at position j in the matrix product, with

$$t_{k,l} = \frac{[(2k+1)(2l+1)]^{1/2}}{2} \int_{-1}^1 dz P_k(z) z P_l(z) \quad (89)$$

This integral equals

$$t_{k,l} = \frac{k\delta_{k-1,l} + (k+1)\delta_{k+1,l}}{[(2k+1)(2l+1)]^{1/2}} \quad (90)$$

As we plan to take the eigenfunctions S as basis, we transform the matrix $t_{k,l}$ to that basis

$$t^{\alpha,\beta} = \sum_{k,l} \psi_k^\alpha t_{k,l} \psi_l^\beta. \quad (91)$$

In the same way we transform the χ vector

$$\chi^\alpha = \sum_k \psi_k^\alpha T_{k,0}. \quad (92)$$

The partition function is now obtained as

$$Z = (4\pi)^N \sum_{\alpha} \chi^\alpha \lambda_\alpha^{N-1} \chi^\alpha. \quad (93)$$

The numerator of the end-to-end vector gives the sum over all positions of the $\cos \theta_j$, or matrices t in the product. We may write this as

$$\langle \sum_j \cos \theta_j \rangle = \frac{1}{Z} \sum_{\alpha,\beta} \chi^\alpha U_{\alpha,\beta} t^{\alpha,\beta} \chi^\beta. \quad (94)$$

The factor $U_{\alpha,\beta}$ accounts for all the ways the t can be put on the bonds. On the left of the t one will have the state α and on the right β . So $U_{\alpha,\beta}$ is given by

$$U_{\alpha,\beta} = \lambda_\beta^{N-1} + \lambda_\alpha \lambda_\beta^{N-2} + \dots + \lambda_\beta \lambda_\alpha^{N-2} + \lambda_\alpha^{N-1}. \quad (95)$$

Dividing (94) by N will give the extension, i.e. the ratio between the end-to-end vector and the contour length. As mentioned in the limit of an infinite chain we may restrict the summations over α and β to $\alpha = \beta = 0$.

For the orientation correlation we consider the infinitely long chain, as its definition should not be muddled by finite-size effects. We repeat the definition of the orientation correlation for the approximation considered in this appendix

$$O_{i,j} = \langle \hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j \rangle = \langle \cos \theta_i \cos \theta_j + \sin \theta_i \sin \theta_j \cos(\phi_i - \phi_j) \rangle. \quad (96)$$

The first term gives the contribution of the longitudinal component, the second gives the transversal component (with respect to the force direction). We restrict ourselves to the first contribution, since we are mostly interested the persistence length of the force-free chain for which the eigenvalue problem is trivial. Without an external force the longitudinal and transversal components are equal. The appearance of two terms $\cos \theta_i$ and $\cos \theta_j$ gives an insertion of

the matrix $t_{k,l}$ at the bonds i and j . Outside the interval $i - j$ the chain is in the state ψ^0 . Inside the interval it may be in any of the eigenstates ψ^α of S . Thus we arrive at the expression for the average

$$\langle \cos \theta_i \cos \theta_j \rangle = \sum_{\alpha} \chi^0 t^{0,\alpha} (\lambda_{\alpha}/\lambda_0)^{|i-j|} t^{\alpha,0} \chi^0. \quad (97)$$

For the force-free chain this expression reduces considerably. As we mentioned for $w = 0$ the matrix $T_{k,l}$ reduces to $\delta_{k,l}$ and each l is an eigenstate of $S_{k,l}$ with eigenvalue $q_l(\gamma)$. Therefore the t matrix with upper indices is the same as the one with lower indices. Moreover the t matrix couples only nearby states. So the summation over α is restricted to $\alpha = 1$. The largest and the next eigenvalue read

$$q_0(\gamma) = \frac{\sinh \gamma}{\gamma}, \quad q_1(\gamma) = \frac{\cosh \gamma}{\gamma} - \frac{\sinh \gamma}{\gamma^2}. \quad (98)$$

Therefore the expression for the orientation function reduces to

$$\langle \cos \theta_i \cos \theta_j \rangle = (q_1(\gamma)/q_0(\gamma))^{|i-j|}/3. \quad (99)$$

One observes that the correlation decays exponentially with the persistence length l_p

$$l_p = -\frac{1}{\log(q_1(\gamma)/q_0(\gamma))} = -\frac{1}{\log(\coth \gamma - 1/\gamma)}. \quad (100)$$

Large γ gives the value $l_p \simeq \gamma$. This will be used in the parameter match between our model and dsDNA.

References

- [1] O. Kratky and G. Porod, Recl.Trav. Chim. Pays-Bas **68** (1949) 1106;
J. Wilhelm and E. Frey, Phys. Rev. Lett. **77** (1996) 2581.
- [2] See e.g. Flory, P.J. (1969) *Statistical Mechanics of Chain Molecules*, Wiley, ISBN 0-470-26495-0; reissued 1989, ISBN 1-56990-019-1.
- [3] J. Kierfeld, O. Niamploy, V. Sa-yakanit and R. Lipowsky, Eur. Phys. J. E. **14**, (2004) 17-34.
- [4] C. M. Marques and G. H. Fredrickson, J. Phys. II France **7** (1997) 1805.
- [5] M. D. Wang, H. Yin, R. Landick, J. Gelles and S. M. Block, Biophys. Journ. **72** (1997) 1335-1346.
- [6] G. T. Barkema, D. Panja, and J. M. J. van Leeuwen, J. Chem. Phys. **134** (2011) 154901.

Gerard T. Barkema Institute for Theoretical Physics, Universiteit Utrecht, Leuvenlaan 4, 3584 CE Utrecht, The Netherlands,
Instituut-Lorentz, Universiteit Leiden, Niels Bohrweg 2, 2333 CA Leiden, The Netherlands

J. M. J. van Leeuwen Instituut-Lorentz, Universiteit Leiden, Niels Bohrweg 2, 2333 CA Leiden, The Netherlands

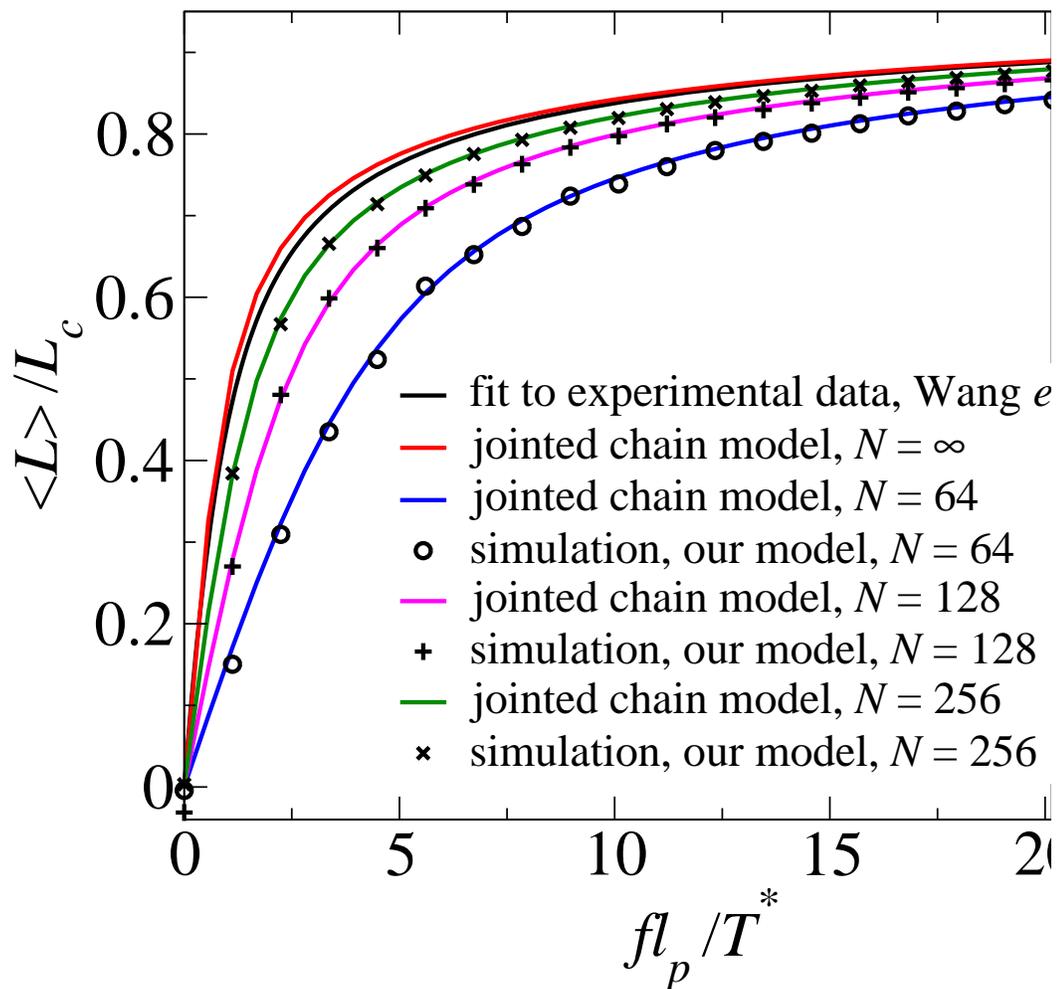


Figure 1: Force extension curves for our model for $N = 64, 128$ and 256 , compared to the jointed chain model defined earlier in the main text for the same N -values and to the experimental data by Wang *et al.* [5]. The agreement between our model (simulation) and the jointed chain (calculation) is excellent, evidently both models exhibit strong finite-size effects.