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Freely jointed chains in external potentials: analytical computations

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Abstract. Freely jointed chains in external potentials are crude representations of macromolecular systems in interaction with electrostatic fields, surfaces, walls and interfaces. We show how the canonical partition function of these models can be computed analytically and how the independent motion approximation (IMA) may be applied. In particular, the chain stretched at both ends is studied with IMA and new results are obtained for entropic elastic constants and force/extension relations, including the dependence on the degree of polymerization. These new results are in good agreement with molecular dynamics computations.

1. Introduction

The freely jointed chain is an off-lattice model of an ideal polymer. This model was proposed more than 50 years ago by Kramers [1, 2] and is used frequently in polymer physics for a crude description of linear connectivity (see, for instance, [3]): nevertheless, a rigorous computation of the freely jointed chains canonical partition function is recent [4, 5].

In previous papers [4, 5] we computed the canonical partition function of a chain by taking explicitly all holonomic constraints into account and showed that integration over the velocities of the monomers leads to a coupling between nearest-neighbour bond vectors. In this paper, we study the freely jointed chain in an external potential. Our aim is to extract the influence of the coupling between nearest-neighbour bonds induced by holonomic constraints on some properties of these systems as the entropic elastic constants and the force/extension relations [6]. Another objective is to derive general analytical expressions that may be used for all one-dimensional potentials.

In the context of mean field theory, the complicated interaction between molecules and environment is simplified by considering the interaction of the molecules with an external field. This crude approximation of a real system is interesting since it gives a good qualitative description of the system properties. For our problem, interaction between the chain and external field is described by using the potential energy of each monomer of the chain. If the potential energy has no special symmetry, the problem is not very interesting because it is too general and very little can be said. This is why we restrict ourselves to the study of potential energies that depend only on one coordinate of the monomer following a fixed direction of the configuration space. This simplification restricts the generality of our results: nevertheless, this choice is sufficiently general to apply to a wide range of problems, such as polymers in a uniform field [7, 8] or stretched under a flow [9, 10], and polymers in interaction with (im-)penetrable surfaces [11] or in a one-dimensional periodic potential (smectic) [12], etc.

The paper is organized as follows. In section 2, we study the general problem of a freely jointed chain in one-dimensional external potentials, we establish analytical relations for partition function of these systems and show how the independent motion approximation (IMA) [5] can be implemented. In section 3, we study explicitly, with the new analytical results obtained in section 2, the problem of a freely jointed chain stretched at both ends. These results show that entropic elastic constants are 3% larger than those predicted by the independent link approximation (ILA). With these computations we can also extract the dependence on the degree of polymerization of the chain. These results allow us to estimate in which conditions one must take into account the dynamical part of holonomic constraints and since these results are analytic one is able to control the accuracy of approximations.

In a forthcoming paper we compare the analytical results obtained in this paper with numerical computations obtained using molecular dynamics (MD) and Monte Carlo algorithms [13].

2. Analytical computation of the canonical partition function

Before we explicitly examine freely jointed chains stretched at both ends, we study the general problem of a chain in an external field. We consider that the interaction between the chain and the field is described via the potential energy U_i of each monomer X_i of the chain. The total potential energy of the chain is given by $U = \sum_{i=0}^N U_i$. The analytical form of the potential energy U_i is chosen such that it depends only on the monomer coordinates Z_i following a fixed direction \hat{e}_z of the space.

Although the choice of one-dimensional potential energy restricts the generality of the discussion, it does allow us to study a wide range of problems, including polymers in constant electrostatic fields and polymers in interaction with penetrable surfaces (for instance polymers at the interface between two solvents) or with impenetrable walls. Of course, for each of these problems one has to take into account a more precise model and an analytical form for the potential energy.

In section 2.1 we make the analytical computation of the canonical partition function of a freely jointed chain in an external potential. The analytical computation is valid as long as an analytical expression for the potential energy is not needed, thus the results of section 2.1 can be applied to systems of freely jointed chains other than simply chains stretched at both ends.

In section 2.2 we show how the IMA can be implemented to study this kind of problem. It appears that IMA is a generalization of ILA. As is explained in the section 2.2 and with the formalism developed in [5], one can use the results of this paper for all freely jointed chains with an arbitrary mass sequence.

2.1. Analytical results

We consider a freely jointed chain (homopolymer) in an external field. The monomers of the chain interact via holonomic constraints and with the external field described via a potential energy $U(\{Z_i\}_{0 \leq i \leq N})$, where $\{Z_i\}_{0 \leq i \leq N}$ are the monomer coordinates following the axis of the field. The canonical partition function of this system is

$$Q_N^{(d)}(U) = C_{\text{ind}} \frac{(ha^2)^N}{h^{(N+1)d}} \int_{\varphi_N} d\mathbf{r}_0 d\mathbf{p}_0 \prod_{n=1}^N d\mathbf{u}_n d\mathbf{p}_n \delta(\mathbf{u}_n^2 - a^2) \delta((\mathbf{p}_n - \mathbf{p}_{n-1}) \cdot \mathbf{u}_n) \\ \times \exp\left(-\frac{\beta}{2m} \sum_{n=0}^N p_n^2 - \beta U(\{Z_n\}_{0 \leq n \leq N})\right)$$

where C_{ind} is the indistinguishability factor of both directions of the monomer labelling and $\delta(x)$ the Dirac distribution.

Integration over momenta is done as for the free freely jointed chains [4, 5] and leads to the result

$$\begin{aligned}
 Q_N^{(d)}(U) &= C_{\text{ind}} \frac{1}{h^{(N+1)d}} \left(\frac{h}{2\pi}\right)^N \left(\frac{2\pi m}{\beta}\right)^{\frac{d}{2}(N+1)} a^{Nd} \int \prod_{n=1}^N d\Omega_n \exp\left(-\frac{ma^2}{\beta} \sum_{n=1}^N \Omega_n^2\right) \\
 &\quad \times \int d\mathbf{r}_0 \prod_{n=1}^N d\hat{\mathbf{u}}_n \delta(\hat{\mathbf{u}}_n^2 - 1) \\
 &\quad \times \exp\left(\frac{ma^2}{\beta} \sum_{n=1}^{N-1} \Omega_n \hat{\mathbf{u}}_n \cdot \Omega_{n+1} \hat{\mathbf{u}}_{n+1} - \beta U(\{Z_n\}_{0 \leq n \leq N})\right). \tag{1}
 \end{aligned}$$

Because of the axial symmetry of the potential energy, it is advantageous to separate the unitary bond vectors $\hat{\mathbf{u}}_i$ in axial and radial part. We set

$$\begin{cases} \mathbf{r}_0 = \mathbf{r}_{0\perp} + Z_0 \hat{\mathbf{e}}_z \\ \hat{\mathbf{u}}_n = \eta_n \hat{\mathbf{w}}_n + z_n \hat{\mathbf{e}}_z \end{cases} \quad \text{for } 1 \leq n \leq N \tag{2}$$

which inverts as

$$\begin{cases} \mathbf{r}_{0\perp} = \mathbf{r}_0 - (\mathbf{r}_0 \cdot \hat{\mathbf{e}}_z) \hat{\mathbf{e}}_z \\ Z_0 = \mathbf{r}_0 \cdot \hat{\mathbf{e}}_z \\ \eta_n \hat{\mathbf{w}}_n = \hat{\mathbf{u}}_n - (\hat{\mathbf{u}}_n \cdot \hat{\mathbf{e}}_z) \hat{\mathbf{e}}_z \\ z_n = \hat{\mathbf{u}}_n \cdot \hat{\mathbf{e}}_z \end{cases} \quad \begin{matrix} \text{for } 1 \leq n \leq N \\ \text{for } 1 \leq n \leq N. \end{matrix} \tag{3}$$

By expressing the integral over the spatial part of the phase space with the new variables $(\eta_n, \hat{\mathbf{w}}_n, z_n)$ one gets

$$\begin{aligned}
 \int d\mathbf{r}_0 \prod_{n=1}^N d\hat{\mathbf{u}}_n \delta(\hat{\mathbf{u}}_n^2 - 1) \dots &= \int d\mathbf{r}_{0\perp} dZ_0 \prod_{n=1}^N \int_{-1}^1 dz_n \int_0^1 d\eta_n \eta_n^{(d-2)} \\
 &\quad \times \int d\hat{\mathbf{w}}_n \delta(\eta_n^2 \hat{\mathbf{w}}_n^2 + z_n^2 - 1) \dots \tag{4}
 \end{aligned}$$

and with the relations

$$\begin{aligned}
 \delta(\eta_n^2 \hat{\mathbf{w}}_n^2 + z_n^2 - 1) &= \delta(\hat{\mathbf{w}}_n^2 - 1) \delta(\eta_n^2 + z_n^2 - 1) \\
 &= \frac{1}{2(1 - z_n^2)^{\frac{1}{2}}} \delta(\hat{\mathbf{w}}_n^2 - 1) (\delta(\eta_n - (1 - z_n^2)^{\frac{1}{2}}) + \delta(\eta_n + (1 - z_n^2)^{\frac{1}{2}}))
 \end{aligned}$$

we find that

$$\begin{aligned}
 \int d\mathbf{r}_0 \prod_{n=1}^N d\hat{\mathbf{u}}_n \delta(\hat{\mathbf{u}}_n^2 - 1) \dots \\
 = \int d\mathbf{r}_{0\perp} dZ_0 \prod_{n=1}^N \int_{-1}^1 (1 - z_n^2)^{\frac{(d-3)}{2}} dz_n \int d\hat{\mathbf{w}}_n \delta(\hat{\mathbf{w}}_n^2 - 1) \dots \tag{5}
 \end{aligned}$$

The unitary vectors $\{\hat{\mathbf{w}}_n\}_{1 \leq n \leq N}$ are in the hyperplan of $(d - 1)$ -dimensions perpendicular to the axis of the field, while the vectors $\{\hat{\mathbf{u}}_n\}_{1 \leq n \leq N}$ are the unitary vectors parallel to the bond vectors of the chain.

The contribution of the spatial part of the phase space to the canonical partition function is now given by

$$\int \mathbf{dr}_{0\perp} dZ_0 \int_{-1}^1 \prod_{n=1}^N (1 - z_n^2)^{\frac{(d-3)}{2}} dz_n \exp(-\beta U(\{Z_n\}_{0 \leq n \leq N})) \times \exp\left(\frac{ma^2}{\beta} \sum_{n=1}^{N-1} \Omega_n \Omega_{n+1} z_n z_{n+1}\right) \int d\hat{\omega}_n \delta(\hat{\omega}_n^2 - 1) \times \exp\left(\frac{ma^2}{\beta} \sum_{n=1}^{N-1} \Omega_n \Omega_{n+1} (1 - z_n^2)^{\frac{1}{2}} (1 - z_{n+1}^2)^{\frac{1}{2}} \hat{\omega}_n \cdot \hat{\omega}_{n+1}\right). \tag{6}$$

As for the general freely jointed chain (heteropolymer) [5], we can compute the integral over the $\hat{\omega}$ vectors by using a result due to Stanley [14]. With

$$y_n = \frac{ma^2}{\beta} \Omega_{n-1} \Omega_n (1 - z_n^2)^{\frac{1}{2}} (1 - z_{n+1}^2)^{\frac{1}{2}}$$

integrations over the $\hat{\omega}$ vectors give

$$S_{d-1}(1) \left(\frac{1}{2}\right)^{(N-1)} (2\pi)^{\frac{d-1}{2}(N-1)} \prod_{n=2}^N y_n^{\frac{3-d}{2}} I_{\frac{d-3}{2}}(y_n) \tag{7}$$

where $I_\mu(x)$ are modified Bessel functions.

In the following we set

$$\begin{cases} b_n = (1 - z_n^2)^{\frac{1}{2}} \\ \gamma_n = \left(\frac{ma^2}{\beta}\right) \Omega_n. \end{cases} \tag{8}$$

The partition function is now written as

$$\mathcal{Q}_N^{(d)}(U) = 2C_{\text{ind}} \left(\frac{mkT}{2\pi\hbar^2}\right)^{\frac{d}{2}} \left(\left(\frac{1}{2}\right)^{\frac{2}{d-1}} \frac{ma^2kT}{\hbar^2}\right)^{\frac{N}{2}(d-1)} \left(\frac{1}{2}\right)^{\frac{(d-1)}{2}} \frac{1}{\Gamma\left(\frac{d}{2}\right)} J_N^{(d)}(U) \tag{9}$$

where the non-integrated part, depending on the external potential, is given by

$$J_N^{(d)}(U) = \frac{S}{V} \frac{S_{d-1}(1)}{S_d(1)} \left(\frac{1}{2}\right)^{\frac{1}{2}(N-1)} \int dZ_0 \int_{-1}^1 \prod_{n=1}^N b_n^{(d-3)} \exp(-\beta U(\{Z_n\}_{0 \leq n \leq N})) \times \tilde{J}_N^{(d)}(\{z_n\}_{1 \leq n \leq N}) \tag{10}$$

and $\tilde{J}_N^{(d)}(\{z_n\}_{1 \leq n \leq N})$ is defined by

$$\tilde{J}_N^{(d)}(\{z_n\}_{1 \leq n \leq N}) = \int \prod_{n=1}^N d\gamma_n \prod_{n=2}^N (b_{n-1} b_n \gamma_{n-1} \gamma_n)^{\frac{3-d}{2}} \prod_{n=2}^N I_{\frac{d-3}{2}}(b_{n-1} b_n \gamma_{n-1} \gamma_n) \times \exp\left(-\sum_{n=1}^N \gamma_n^2 + \sum_{n=2}^N z_{n-1} z_n \gamma_{n-1} \gamma_n\right). \tag{11}$$

The main difficulty in computing the latter integral comes from the coupling between γ_n and γ_{n+1} . Setting

$$\begin{cases} \omega_n = b_{n-1} b_n \gamma_{n-1} \gamma_n & \text{for } 2 \leq n \leq N \\ \omega_1 = \gamma_1 \end{cases} \tag{12}$$

and inverted as

$$\begin{cases} \gamma_n = A_n \omega_n & \text{for } 2 \leq n \leq N \\ \gamma_1 = \omega_1. \end{cases}$$

where

$$A_n = \frac{1}{b_n} (b_1)^{(-1)^{(n-1)}} \prod_{p=1}^{(n-1)} (\omega_{n-p})^{(-1)^p}$$

we cancel this complicated coupling.

The recurrence relation between A_n and A_{n-1} :

$$\frac{1}{A_n} = b_{n-1} b_n A_{n-1} \omega_{n-1} \quad \text{for } 3 \leq n \leq N \tag{13}$$

holds all information about the linear connection of monomers. Making the transformation (12) in equation (11) we find

$$\begin{aligned} \tilde{J}_N^{(d)}(\{z_n\}_{1 \leq n \leq N}) &= \int d\omega_1 \exp(-\omega_1^2) \int \prod_{n=2}^N d\omega_n \\ &\times \exp\left(-A_n^2 \omega_n^2 + \frac{z_{n-1} z_n}{b_{n-1} b_n} \omega_n\right) A_n \omega_n^{\frac{3-d}{2}} I_{\frac{d-3}{2}}(\omega_n). \end{aligned} \tag{14}$$

$\tilde{J}_N^{(d)}(\{z_n\}_{1 \leq n \leq N})$ is similar to the constant $J_N^{(d)}$ appearing in the computation of the free freely jointed chain canonical partition function [4], but computed for $(d - 1)$ instead of d . This is not very surprising because integration over the \hat{w} vectors, and the axial and radial parts decomposition are equivalent to considering that the chain is a heteropolymer in a space of dimension $(d - 1)$ coupled, via some holonomic constraints, to a random walk in one dimension.

Following the method used for free freely jointed chains [5] we set

$$\begin{aligned} \tilde{f}_N^{(d)} &= A_N \int d\omega_N \exp\left(-A_N^2 \omega_N^2 + \frac{z_{N-1} z_N}{b_{N-1} b_N} \omega_N\right) \omega_N^{\frac{3-d}{2}} I_{\frac{d-3}{2}}(\omega_N) \\ &= \left(\frac{1}{2}\right)^{\frac{d-3}{2}} \frac{A_N}{\Gamma(\frac{d}{2} - 1) \Gamma(\frac{1}{2})} \int_{-1}^1 dt_N (1 - t_N^2)^{\frac{d}{2} - 2} \\ &\times \int_{-\infty}^{+\infty} d\omega_N \exp\left(-A_N^2 \omega_N^2 + \left(t_N + \frac{z_{N-1} z_N}{b_{N-1} b_N}\right) \omega_N\right). \end{aligned} \tag{15}$$

The computation of the Gaussian integral gives

$$\tilde{f}_N^{(d)} = \left(\frac{1}{2}\right)^{\frac{d-3}{2}} \frac{1}{\Gamma(\frac{d}{2} - 1)} \int_{-1}^1 dt_N (1 - t_N^2)^{\frac{d}{2} - 2} \exp\left(-\frac{1}{4A_N^2} \left(t_N + \frac{z_{N-1} z_N}{b_{N-1} b_N}\right)^2\right). \tag{16}$$

and with the relation

$$\begin{aligned} \exp\left(-\frac{1}{4A_N^2} (t_N + B_N)^2\right) &= \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{1}{4}\right)^n \left(\frac{1}{A_N^2}\right)^n (t_N + B_N)^{2n} \\ &= \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{1}{4}\right)^n \left(\frac{1}{A_N^2}\right)^n \sum_{p=0}^{2n} \binom{2n}{p} t_N^p B_N^{2n-p} \end{aligned} \tag{17}$$

we compute the integral over t_N :

$$\tilde{f}_N^{(d)} = \left(\frac{1}{2}\right)^{\frac{d-3}{2}} \sum_{n_1=0}^{\infty} \frac{1}{n_1!} \left(\frac{1}{4}\right)^{n_1} \sum_{k_1=0}^{n_1} \binom{2n_1}{2k_1} \left(\frac{z_{N-1} z_N}{b_{N-1} b_N}\right)^{2(n_1-k_1)} \left(\frac{1}{A_N}\right)^{2n_1}. \tag{18}$$

We use the recurrence relation (13) between A_N and A_{N-1} to obtain

$$\begin{aligned} \tilde{f}_N^{(d)} &= \left(\frac{1}{2}\right)^{\frac{d-3}{2}} \sum_{n_1=0}^{\infty} \frac{1}{n_1!} \left(\frac{1}{4}\right)^{n_1} \sum_{k_1=0}^{n_1} \binom{2n_1}{2k_1} \\ &\quad \times \frac{\Gamma(k_1 + \frac{1}{2})}{\Gamma(k_1 + \frac{d-1}{2})} (z_{N-1}z_N)^{2(n_1-k_1)} (b_{N-1}b_N)^{2k_1} A_{N-1}^{2n_1} \omega_{N-1}^{2n_1}. \end{aligned} \tag{19}$$

$\tilde{f}_{N-1}^{(d)}$ is defined inductively from $\tilde{f}_N^{(d)}$ by

$$\begin{aligned} \tilde{f}_{N-1}^{(d)} &= A_{N-1} \int d\omega_{N-1} \exp\left(-A_{N-1}^2 \omega_{N-1}^2 + \frac{z_{N-2}z_{N-1}}{b_{N-2}b_{N-1}} \omega_{N-1}\right) \omega_{N-1}^{\frac{3-d}{2}} I_{\frac{d-3}{2}}(\omega_{N-1}) \tilde{f}_N^{(d)} \\ &= \left(\frac{1}{2}\right)^{\frac{d-3}{2}} \sum_{n_1=0}^{\infty} \frac{1}{n_1!} \left(\frac{1}{4}\right)^{n_1} \sum_{k_1=0}^{n_1} \binom{2n_1}{2k_1} \frac{\Gamma(k_1 + \frac{1}{2})}{\Gamma(k_1 + \frac{d-1}{2})} \\ &\quad \times (z_{N-1}z_N)^{2(n_1-k_1)} (b_{N-1}b_N)^{2k_1} \\ &\quad \times \left(\frac{1}{2}\right)^{\frac{d-3}{2}} \frac{A_{N-1} A_{N-1}^{2n_1}}{\Gamma(\frac{d}{2}-1)\Gamma(\frac{1}{2})} \int_{-1}^1 dt_{N-1} (1-t_{N-1}^2)^{\frac{d}{2}-2} \\ &\quad \times \int_{-\infty}^{+\infty} d\omega_{N-1} \omega_{N-1}^{2n_1} \exp\left(-A_{N-1}^2 \omega_{N-1}^2 + \frac{z_{N-2}z_{N-1}}{b_{N-2}b_{N-1}} \omega_{N-1}\right). \end{aligned} \tag{20}$$

The computation of the integral over ω_{N-1} is straightforward. We have

$$\begin{aligned} \tilde{f}_{N-1}^{(d)} &= \left(\frac{1}{2}\right)^{\frac{d-3}{2}} \sum_{n_1=0}^{\infty} \frac{1}{n_1!} \left(\frac{1}{4}\right)^{n_1} \sum_{k_1=0}^{n_1} \binom{2n_1}{2k_1} \frac{\Gamma(k_1 + \frac{1}{2})}{\Gamma(k_1 + \frac{d-1}{2})} (z_{N-1}z_N)^{2(n_1-k_1)} (b_{N-1}b_N)^{2k_1} \\ &\quad \times \left(\frac{1}{2}\right)^{\frac{d-3}{2}} \frac{1}{\Gamma(\frac{d}{2}-1)} \sum_{n_2=0}^{\infty} \frac{1}{n_2!} \left(\frac{1}{4}\right)^{n_2} \frac{\Gamma(n_1+n_2 + \frac{1}{2})}{\Gamma(n_2 + \frac{1}{2})} \left(\frac{1}{A_{N-1}}\right)^{2n_2} \\ &\quad \times \int_{-1}^1 dt_{N-1} (1-t_{N-1}^2)^{\frac{d}{2}-2} \left(t_{N-1} + \frac{z_{N-2}z_{N-1}}{b_{N-2}b_{N-1}}\right)^{2n_2}. \end{aligned} \tag{21}$$

With the binomial formula for $(t_{N-1} + \frac{z_{N-2}z_{N-1}}{b_{N-2}b_{N-1}})^{2n_2}$ we can compute the latter integral, and another use of the recurrence relation (13) gives the result

$$\begin{aligned} \tilde{f}_{N-1}^{(d)} &= \left(\frac{1}{2}\right)^{\frac{d-3}{2}} \sum_{n_1=0}^{\infty} \frac{1}{n_1!} \left(\frac{1}{4}\right)^{n_1} \sum_{k_1=0}^{n_1} \binom{2n_1}{2k_1} \frac{\Gamma(k_1 + \frac{1}{2})}{\Gamma(k_1 + \frac{d-1}{2})} (z_{N-1}z_N)^{2(n_1-k_1)} (b_{N-1}b_N)^{2k_1} \\ &\quad \times \left(\frac{1}{2}\right)^{\frac{d-3}{2}} \sum_{n_2=0}^{\infty} \frac{1}{n_2!} \left(\frac{1}{4}\right)^{n_2} \frac{\Gamma(n_1+n_2 + \frac{1}{2})}{\Gamma(n_2 + \frac{1}{2})} \sum_{k_2=0}^{n_2} \binom{2n_2}{2k_2} \\ &\quad \times \frac{\Gamma(k_2 + \frac{1}{2})}{\Gamma(k_2 + \frac{d-1}{2})} (z_{N-2}z_{N-1})^{2(n_2-k_2)} (b_{N-2}b_{N-1})^{2k_2} A_{N-2}^{2n_2} \omega_{N-2}^{2n_2}. \end{aligned} \tag{22}$$

The latter relation shows that the dependence of $\tilde{f}_{N-1}^{(d)}$ on ω_{N-2} has the same structure as the dependence of $\tilde{f}_N^{(d)}$ on ω_{N-1} ; thus we can compute inductively $\tilde{J}_N^{(d)}(\{z_n\}_{1 \leq n \leq N})$ as a multiple power series expansion. Finally we find

$$\begin{aligned} \tilde{J}_N^{(d)}(\{z_n\}_{1 \leq n \leq N}) &= \Gamma\left(\frac{1}{2}\right) \left(\frac{\Gamma(\frac{1}{2})}{\Gamma(\frac{d-1}{2})}\right)^{(N-1)} \left(\frac{1}{2}\right)^{\frac{(d-3)(N-1)}{2}} \\ &\quad \times \sum_{n_1=0}^{\infty} \frac{1}{n_1!} \frac{(n_1, \frac{1}{2})}{(n_1, \frac{d-1}{2})} \left(\frac{1}{4}\right)^{n_1} \mathfrak{S}_{n_1}^{(d)}(z_{N-1}z_N, b_{N-1}b_N) \end{aligned}$$

$$\begin{aligned}
 & \times \sum_{n_2=0}^{\infty} \frac{1}{n_2!} \frac{(n_1 + n_2, \frac{1}{2})}{(n_2, \frac{d-1}{2})} \left(\frac{1}{4}\right)^{n_2} \mathfrak{S}_{n_2}^{(d)}(z_{N-2}z_{N-1}, b_{N-2}b_{N-1}) \\
 & \dots \\
 & \times \sum_{n_p=0}^{\infty} \frac{1}{n_p!} \frac{(n_{p-1} + n_p, \frac{1}{2})}{(n_p, \frac{d-1}{2})} \left(\frac{1}{4}\right)^{n_p} \mathfrak{S}_{n_p}^{(d)}(z_{N-p}z_{N-p+1}, b_{N-p}b_{N-p+1}) \\
 & \dots \\
 & \times \sum_{n_{N-1}=0}^{\infty} \frac{(n_{N-1}, \frac{1}{2})}{n_{N-1}!} \frac{(n_{N-2} + n_{N-1}, \frac{1}{2})}{(n_{N-1}, \frac{d-1}{2})} \left(\frac{1}{4}\right)^{n_{N-1}} \mathfrak{S}_{n_{N-1}}^{(d)}(z_2z_1, b_2b_1) \tag{23}
 \end{aligned}$$

where

$$\mathfrak{S}_n^{(d)}(a, b) = b^{2n} {}_2F_1\left(-n, \frac{3-d}{2} - n; \frac{1}{2}; \frac{a^2}{b^2}\right). \tag{24}$$

In equation (23) one can observe that the analytical structure of the expansion is similar to the structure of the expansion corresponding to a free freely jointed chain in a space of dimension $(d - 1)$. The coupling between the chain in $(d - 1)$ dimensions and the random walk in one dimensions is expressed with the set of variables $\{z_n\}_{1 \leq n \leq N}$.

One should remember that in the computation leading to equation (23) from equation (1) no approximation was made, and thus the result for $\tilde{J}_N^{(d)}(\{z_n\}_{1 \leq n \leq N})$ is analytical. At this stage of the computation, because the coupling between the random walk and the chain appears explicitly, we need an analytical expression for the potential energy. Of course, in most cases, the analytical form of the potential energy would lead to a complicated integral that we cannot compute analytically. This new analytical result allows us to define new approximations for related problems.

Before illustrating these results on the problem of the freely jointed chain stretched at both ends, we show that equation (23) with equations (10) and (9) are in agreement with the analytical results obtained for the free freely jointed chains in $(d - 1)$ and d dimensions [4, 5].

For the free freely jointed chain in d -dimensions, the external potential should be chosen such that

$$\exp(-\beta U(\{Z_n\}_{0 \leq n \leq N})) = 1 \tag{25}$$

with the result that

$$\begin{aligned}
 & \int_{-1}^1 (1 - z^2)^{\frac{(d-3)}{2}} dz \mathfrak{S}_n^{(d)}(xz, (1 - x^2)^{\frac{1}{2}}(1 - z^2)^{\frac{1}{2}}) \\
 & = \Gamma\left(\frac{1}{2}\right) \frac{\Gamma(n + \frac{d-1}{2})}{\Gamma(n + \frac{d}{2})} \sum_{k=0}^n \binom{n}{k} x^{2(n-k)} (1 - x^2)^k \\
 & = \Gamma\left(\frac{1}{2}\right) \frac{\Gamma(n + \frac{d-1}{2})}{\Gamma(n + \frac{d}{2})} (x^2 + (1 - x^2))^n = \Gamma\left(\frac{1}{2}\right) \frac{\Gamma(n + \frac{d-1}{2})}{\Gamma(n + \frac{d}{2})}.
 \end{aligned}$$

We find that

$$\int_{-1}^1 \prod_{n=1}^N (1 - z_n^2)^{\frac{(d-3)}{2}} dz_n \tilde{J}_N^{(d)}(\{z_n\}_{1 \leq n \leq N}) = (2\pi)^{\frac{1}{2}(N-1)} \left(\int_{-1}^1 (1 - z_1^2)^{\frac{(d-3)}{2}} dz_1 \right) J_N^{(d)}. \tag{26}$$

Since

$$\begin{aligned}
 & \int_{-1}^1 (1 - z_1^2)^{\frac{(d-3)}{2}} dz_1 = \frac{\Gamma(\frac{1}{2})\Gamma(\frac{d-1}{2})}{\Gamma(\frac{d}{2})} \\
 & S_{d-1}(1) = \frac{2(\Gamma(\frac{1}{2}))^{(d-1)}}{\Gamma(\frac{d-1}{2})}
 \end{aligned}$$

and

$$(2\pi)^{\frac{d-1}{2}(N-1)} = (2\pi)^{\frac{d}{2}(N-1)} \left(\frac{1}{2\pi}\right)^{\frac{1}{2}(N-1)}$$

we have

$$S_{d-1}(1) \left(\frac{1}{2\pi}\right)^{\frac{1}{2}(N-1)} \int_{-1}^1 \prod_{n=1}^N (1 - z_n^2)^{\frac{(d-3)}{2}} dz_n \tilde{J}_N^{(d)}(\{z_n\}_{1 \leq n \leq N}) = S_d(1) J_N^{(d)}. \tag{27}$$

Therefore we recover the results of [4, 5] and have established that

$$Q_N^{(d)} = Q_N^{(d)}(U \equiv 0).$$

To obtain a free freely jointed chain in $(d - 1)$ dimensions, let

$$\exp(-\beta U(\{Z_n\}_{0 \leq n \leq N})) = \delta(Z_0) \prod_{n=1}^N \delta(z_n). \tag{28}$$

Thus we find

$$\int_{-1}^1 \prod_{n=1}^N (1 - z_n^2)^{\frac{(d-3)}{2}} dz_n \prod_{n=1}^N \delta(z_n) \tilde{J}_N^{(d)}(\{z_n\}_{1 \leq n \leq N}) = J_N^{(d-1)} \tag{29}$$

and

$$\int dZ_0 \delta(Z_0) = 1.$$

To recover the partition function of a free freely jointed chain in $(d - 1)$ dimensions one has also to impose that the monomer momentum be perpendicular to a fixed direction \hat{e}_z : i.e., one has to include a term as

$$\prod_{n=0}^N \delta(\mathbf{p}_n \cdot a \hat{e}_z).$$

in the computation. These constraints freeze the degrees of freedom of the system along the \hat{e}_z -direction and with $C_{\text{ind}} = 1/2!$ we have

$$Q_N^{(d-1)}(0) = Q_N^{(d)}(\delta(Z_0) \prod_{n=1}^N \delta(z_n) \prod_{n=0}^N \delta(\mathbf{p}_n \cdot a \hat{e}_z)).$$

2.2. IMA

Following the study performed for free freely jointed chains (homopolymer [4] and heteropolymers [5]), it is convenient to define some diagrammatic rules to simplify analytical expressions such as equation (23). These diagrammatic rules also show explicitly the technical difficulties encountered in the computation of $Q_N^{(d)}(U)$.

Following our previous papers, we define diagrammatic rules involving sites and lines:

- (a) As in the case of free freely jointed chains, the ‘propagators’ between two neighbouring sites are defined by:

$$\left(n + p, \frac{1}{2}\right) \equiv n \text{ --- } p \equiv p \text{ --- } n. \tag{30}$$

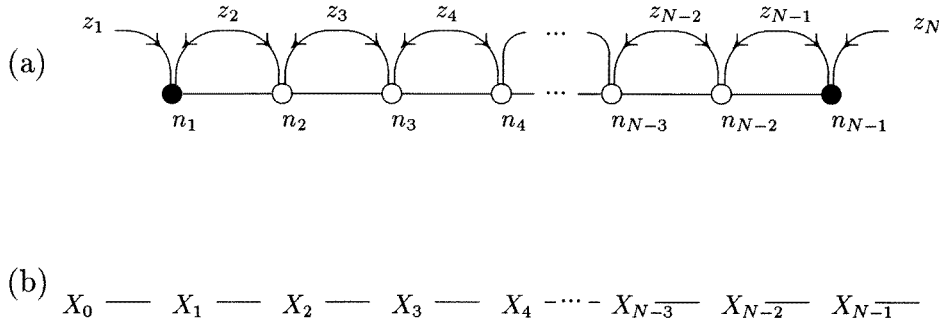


Figure 1. (a) Diagram for $\tilde{J}_N^{(d)}(\{z_n\}_{1 \leq n \leq N})$. (b) Primary structure of the freely jointed chain; the i th site of (a) corresponds to the trimer $X_{i-1} - X_i - X_{i+1}$.

(b) Since variables z_p and z_{p+1} are non-trivially coupled together via the multiplicity n_p of a site, one must define the diagrammatic rule for sites with the variables z_p and z_{p+1} appearing in the diagram. The diagram for a site with a multiplicity n_p is therefore defined by:

$$\begin{array}{c} z_p \\ \swarrow \\ \circ \\ \searrow \\ z_{p+1} \\ n_p \end{array} \equiv \frac{1}{n_p!} \frac{1}{(n_p, \frac{d-1}{2})} \left(\frac{1}{4}\right)^{n_p} \mathfrak{S}_{n_p}^{(d)}(z_p z_{p+1} + 1, (1 - z_p^2)^{\frac{1}{2}} (1 - z_{p+1}^2)^{\frac{1}{2}}).$$

(31)

(c) For the ending sites, the diagram is directly given by the definition of propagator and site:

$$\begin{array}{c} z_p \\ \swarrow \\ \bullet \\ \searrow \\ z_{p+1} \\ n_p \end{array} \equiv (n_p, \frac{1}{2}) \begin{array}{c} z_p \\ \swarrow \\ \circ \\ \searrow \\ z_{p+1} \\ n_p \end{array} \equiv \frac{z_p}{0} \begin{array}{c} z_p \\ \swarrow \\ \circ \\ \searrow \\ z_{p+1} \\ n_p \end{array}.$$

(32)

With these rules, equation (23) can be rewritten as a single diagram (see figure 1).

In equation (31), the circle defining the site has exactly the same meaning as the site defined for a homopolymer [4] since we recover at the beginning of the right-hand side of equation (31) the definition of a site for a free freely jointed chain in $(d - 1)$ dimensions.

The coupling between neighboring sites and between the variables $\{z_n\}_{1 \leq n \leq N}$, as is shown in figure 1(a), is a consequence of the linear connection of the monomer (cf figure 1(b)). A natural way to obtain a first approximation of this function is to cancel the coupling by disconnecting the sites. In doing this, the complicated diagram of figure 1(a) is reduced to a product of simple diagrams each involving only one site.

Because a site is associated to a trimer, for example the i th site is associated to the trimer $X_{i-1} - X_i - X_{i+1}$, the disconnecting of sites is physically equivalent to considering that the movement of the monomer X_i is influenced only by the movement of its nearest neighbours: the monomers X_{i-1} and X_{i+1} . This is why we call this approximation the independent motion approximation. The IMA is improved by considering tetramers, pentamers and more generally n -mers, instead of trimers [5]. This scheme of approximation has been shown to be very accurate for the computation of canonical partition function of free freely jointed chains [4, 5].

When the chain interacts with an external field, this approximation should be quite a good approximation if the potential energy of each monomer is small compared with its kinetic energy. Thus IMA should be valid for weak interactions and at high temperature. On the other hand, if the interaction of a monomer with the external field is strong enough, then the movement of this monomer will strongly perturb the movement of monomers other than its closest neighbours; thus, if at least one monomer in the chain has a strong interaction with the external field, the IMA is not accurate.

The diagrammatic rule (32) shows how we can disconnect two neighbouring sites. First, we cut the propagator of equation (30) and take the value 0 for the multiplicity on the left of the propagator and keep the true value of n for the site on the left of the propagator; for the value p on the right of the propagator, we keep the true value of p for both the site and the right-hand side of the propagator. Second, one must disconnect the coupling induced by z_{p+1} . This is done by considering that z_{p+1} stay connected to the site n_{p+1} and for the site n_p , z_{p+1} be changed into a constant y_0 not equal to 0 or to 1.

By using this procedure and according to equation (32), $\tilde{J}_N^{(d)}(\{z_n\}_{1 \leq n \leq N})$ is approximated by

$$\tilde{J}_N^{(d)}(\{z_n\}; y_0)|_{1(l)} = J_0 \left(\sum_{n_{N-1}=0}^{\infty} \begin{array}{c} z_{N-1} \quad z_N \\ \swarrow \quad \searrow \\ \bullet \\ n_{N-1} \end{array} \right) \prod_{p=1}^{N-2} \left(\sum_{n_p=0}^{\infty} \begin{array}{c} z_p \quad y_0 \\ \swarrow \quad \searrow \\ \bullet \\ n_p \end{array} \right) \tag{33}$$

with

$$J_0 = \Gamma\left(\frac{1}{2}\right) \left(\frac{\Gamma(\frac{1}{2})}{\Gamma(\frac{d-1}{2})}\right)^{(N-1)} \left(\frac{1}{2}\right)^{\frac{(d-3)}{2}(N-1)}.$$

In equation (33) one can note that the role played by the ending trimers of the chain $X_0 - X_1 - X_2$ and $X_{N-2} - X_{N-1} - X_N$ are not equivalent. This is, of course, an artefact of the approximation. To correct this misleading behaviour one has to again make the same approximation, but now by disconnecting the neighbouring sites to the right. Thus one obtains $\tilde{J}_N^{(d)}(\{z_n\}; y_0)|_{1(r)}$ which has an analytical expression similar to equation (33). Then $\tilde{J}_N^{(d)}(\{z_n\}; y_0)|_1$ is given by the geometrical average of $\tilde{J}_N^{(d)}(\{z_n\}; y_0)|_{1(l)}$ and $\tilde{J}_N^{(d)}(\{z_n\}; y_0)|_{1(r)}$. It is worthwhile to mention that if all monomers have the same mass then $\tilde{J}_N^{(d)}(\{z_n\}; y_0)|_{1(l)}$ is equal to $\tilde{J}_N^{(d)}(\{z_n\}; y_0)|_{1(r)}$ thus to $\tilde{J}_N^{(d)}(\{z_n\}; y_0)|_1$ [5]. As is shown in equation (33), the last site (or the first) is connected to z_{N-1} and z_N (resp. z_1 and z_2). A final approximation is needed to evaluate with the same precision the contribution of all sites: thus, we make

$$\sum_{n_{N-1}=0}^{\infty} \begin{array}{c} z_{N-1} \quad z_N \\ \swarrow \quad \searrow \\ \circ \\ n_{N-1} \end{array} \approx \sum_{n_{N-1}=0}^{\infty} \left(\begin{array}{c} z_{N-1} \quad y_0 \\ \swarrow \quad \searrow \\ \bullet \\ n_{N-1} \end{array} \right) \times \left(\begin{array}{c} y_0 \quad z_N \\ \swarrow \quad \searrow \\ \circ \\ 0 \end{array} \right) \tag{34}$$

and the same approximation for the first site when we disconnect to the right.

Finally an approximation of the spatial contribution to the canonical partition function is given by integration of $\tilde{J}_N^{(d)}(\{z_n\}_{1 \leq n \leq N}; y_0)|_1$ over the variables $\{z_n\}_{1 \leq n \leq N}$ and by taking $y_0 \rightarrow 0$

$$J_N^{(d)}(U)|_1 = \lim_{y_0 \rightarrow 0} \left(\int_{-1}^1 \prod_{n=1}^N (1 - z_n^2)^{\frac{(d-3)}{2}} dz_n \exp(-\beta U) \tilde{J}_N^{(d)}(\{z_n\}; y_0)|_1 \right). \quad (35)$$

3. The freely jointed chain stretched at both ends

The freely jointed chain stretched at both ends is an ideal chain on which a force $-\mathbf{f}$ is applied on the ‘first’ monomer and a force \mathbf{f} on the ‘last’ monomer. An example of this kind of system is given by a chain with the first monomer carrying an electric charge $-q$ and the last monomer carrying a charge $+q$ in a constant and uniform electric field $\mathbf{E} = E \hat{z} (E > 0)$, where we neglect the interaction between charges carried by the first and the last monomers [15].

Another example of such systems is given in micromanipulation of DNA molecules. In these experiments one end of a DNA molecule is attached to a surface, while the other end is attached to a small magnetic bead used to put the polymer under uniform tension [16, 17].

The forces acting on the freely jointed chain are given by

$$\mathbf{f}_N = qE \hat{z} = f \hat{z} \quad \text{and} \quad \mathbf{f}_0 = -\mathbf{f}_N = -qE \hat{z} = -f \hat{z} \quad (36)$$

and a straightforward computation gives the potential energy of the chain as

$$U_{\text{syst}} = U_0 + U_N = f(Z_0 - Z_N) = -fa \sum_{n=1}^N z_n. \quad (37)$$

In the following we set

$$\alpha = \frac{af}{kT}.$$

Because one needs to define arbitrarily the first monomer as the monomer carrying the charge $-q$, we lose the indistinguishability of direction of the monomer labelling. On the other hand, since we neglect the charge interaction between the first and the last monomers, the indistinguishability of both directions of labelling must be recovered when $\alpha = 0$. Thus, when expanding the canonical partition function as a power series in α , one should divide the first term of the series by the indistinguishability factor to obtain the limit $\alpha \rightarrow 0$ correctly from the series expansion.

3.1. The ILA

The standard method of approximation to compute the canonical partition function of the chain stretched at both ends is to consider that the stretching potential of equation (37) tends to orient each bond along the force. In this approximation each bond is considered independently of the other bonds, and in particular one loses the coupling between neighbouring bonds induced by the kinematic part of the holonomic constraints (cf equation (1)).

In this section we give the principal results obtained with this approximation for the chain stretched at both ends (see [18], ch X, appendix B or [3] ch I, section 8). A straightforward computation gives the canonical partition function as

$$Z_{\text{ILA}} = \left(4\pi \frac{\sinh \alpha}{\alpha} \right)^N. \quad (38)$$

The free energy is given by

$$F_{\text{ILA}} = -kT \ln Z_{\text{ILA}} = cte - NkT \ln \frac{\sinh \alpha}{\alpha} \quad (39)$$

the force/extension relation is defined by

$$\langle X \rangle_{\text{ILA}} = - \left(\frac{\partial F_{\text{ILA}}}{\partial f} \right)_{N,V,T} = Na \left(\coth \alpha - \frac{1}{\alpha} \right) = NaL(\alpha), \quad (40)$$

where $L(x)$ is the Langevin function, and the susceptibility by

$$\chi_{\text{ILA}} = \left(\frac{\partial \langle X \rangle_{\text{ILA}}}{\partial f} \right)_{N,V,T} = \frac{Na^2}{kT} \left(\frac{1}{\alpha^2} - \frac{1}{\sinh^2 \alpha} \right). \quad (41)$$

In d -dimensions, the same approximation gives for the canonical partition function

$$\begin{aligned} Z_{\text{ILA}}^{(d)} &= \left(S_d(1) \int_0^\pi d\theta \sin^{(d-2)} \theta e^{\alpha \cos \theta} \right)^N \\ &= \left(2 \frac{(\Gamma(\frac{1}{2}))^d \Gamma(\frac{d-1}{2})}{\Gamma(\frac{d}{2})} \right)^N \left(\left(\frac{2}{\alpha} \right)^{\frac{d}{2}-1} I_{\frac{d}{2}-1}(\alpha) \right)^N. \end{aligned}$$

The free energy, the force/extension relation and the susceptibility are computed as for $d = 3$.

The ILA is frequently used for crude description of the elasticity of macromolecular systems. In some systems, like a network of long polymer chains [19] or DNA molecules [16], the entropic contribution to the free energy is partially taken into account with the ILA. In particular, the force/extension relations in the entropic regime computed by Monte Carlo algorithms are well fitted with ILA [20]. This is not in disagreement with the computations performed in section 2, because in Monte Carlo simulation most algorithms sample only the spatial part of the phase space, and thus corrections induced by the dynamical part of the holonomic constraints are forgotten. On the other hand, molecular dynamics algorithms sample the whole phase space: then the corrections to ILA predicted by the analytical computation of the previous section are relevant in these numerical computations. In a paper in preparation we shall present molecular dynamics computations of freely jointed chains stretched at both ends coupled to a Nosé–Hoover thermostat [21] and compare the numerical results with IMA presented in the next section.

3.2. Corrections predicted by IMA

When α is small we may use IMA to evaluate the spatial contribution to the canonical partition function. Thus by disconnecting the sites of the $\tilde{J}_N^{(d)}(\{z_n\}_{1 \leq n \leq N})$ diagram (cf figure 1(a)), following the rules described in section 2.2, and using equations (33) and (34) we find that

$$\tilde{J}_N^{(d)}(\{z_n\}_{1 \leq n \leq N}) \text{ diagram} \simeq \prod_{p=1}^{N-1} \left(\sum_{n_p=0}^{\infty} \begin{array}{c} z_p \quad y_0 \\ \swarrow \quad \searrow \\ \bullet \\ n_p \end{array} \right) \times \left(\begin{array}{c} z_p \quad y_0 \\ \swarrow \quad \searrow \\ \bullet \\ n_p \end{array} \right).$$

This equation is obtained by disconnecting the sites to the left. We consider that all monomers have the same mass: thus IMA to the left gives the same result as IMA to the right. This would not hold if the chain had a heterogeneous mass sequence [5]. For such a model of heteropolymer one must take the geometrical average of both approximations to cancel some unphysical artefacts. Nevertheless, the study of this general case is straightforward with the formalism built in [5].

To obtain $J_N^{(d)}(\alpha)$ from equation (41) we have to compute two integrals:

$$J_0(\alpha; y_0) = \int_{-1}^1 (1 - z^2)^{\frac{1}{2}(d-3)} \exp(\alpha z) \left(\begin{array}{c} z \quad y_0 \\ \swarrow \quad \searrow \\ \bullet \\ 0 \end{array} \right) dz \tag{42}$$

and

$$J_1(\alpha; y_0) = \int_{-1}^1 (1 - z^2)^{\frac{1}{2}(d-3)} \exp(\alpha z) \left(\begin{array}{c} z \quad y_0 \\ \swarrow \quad \searrow \\ \sum_{n=0}^{\infty} \bullet \\ n \end{array} \right) dz. \tag{43}$$

With these integrals $\tilde{J}_N^{(d)}(\alpha)|_1$ is given by

$$J_N^{(d)}(\alpha) = \left(\frac{1}{2}\right)^{\frac{(d-1)}{2}} \frac{S_{(d-1)}(1)}{S_d(1)} \left(\frac{\Gamma(\frac{1}{2})}{\Gamma(\frac{d-1}{2})}\right)^{(N-1)} \left(\lim_{y_0 \rightarrow 0} J_1(\alpha; y_0)\right)^{(N-1)} \lim_{y_0 \rightarrow 0} J_0(\alpha; y_0). \tag{44}$$

For $J_0(\alpha; y_0)$ we find easily that

$$J_0(\alpha; y_0) = J_0(\alpha) = \Gamma\left(\frac{1}{2}\right) \Gamma\left(\frac{d-1}{2}\right) \left(\frac{2}{\alpha}\right)^{\frac{(d-1)}{2}} I_{\frac{d-1}{2}}(\alpha) \tag{45}$$

and for $J_1(\alpha; y_0)$ we expand $e^{\alpha z}$ as a power series in αz and compute the integral. With the result

$$\int_{-1}^1 dz (1 - z^2)^{\frac{1}{2}(d-3)+k} z^{2(n-k)} e^{\alpha z} = \sum_{p=0}^{\infty} \frac{1}{(2p)!} \alpha^{2p} \frac{\Gamma(n - k + p + \frac{1}{2}) \Gamma(k + \frac{d-1}{2})}{\Gamma(n + p + \frac{d}{2})}$$

we find that

$$J_1(\alpha; y_0) = \left(\frac{1}{2}\right)^{\frac{(d-3)}{2}} \left(\Gamma\left(\frac{1}{2}\right)\right)^2 \sum_{p=0}^{\infty} \frac{1}{p!} \frac{1}{\Gamma(p + \frac{1}{2})} \left(\frac{\alpha^2}{4}\right)^p \sum_{n=0}^{\infty} \frac{1}{n!} \frac{\Gamma(n + \frac{1}{2})}{\Gamma(n + p + \frac{d}{2})} \left(\frac{1}{4}\right)^n \times \sum_{k=0}^n \binom{n}{k} \frac{\Gamma(n - k + p + \frac{1}{2})}{\Gamma(n - k + \frac{1}{2})} y_0^{2(n-k)} (1 - y_0^2)^k. \tag{46}$$

With the relation

$$\begin{aligned} \sum_{k=0}^n \binom{n}{k} \frac{\Gamma(n - k + p + \frac{1}{2})}{\Gamma(n - k + \frac{1}{2})} y_0^{2(n-k)} (1 - y_0^2)^k &= \frac{\Gamma(p + \frac{1}{2})}{\Gamma(\frac{1}{2})} (1 - y_0)^n {}_2F_1\left(-n, p + \frac{1}{2}; \frac{1}{2}; \frac{y_0^2}{(1 - y_0^2)}\right) \\ &= \frac{\Gamma(p + \frac{1}{2})}{\Gamma(\frac{1}{2})} {}_2F_1\left(-n, -p; \frac{1}{2}; y_0^2\right) \end{aligned}$$

we have

$$J_1(\alpha; y_0) = \left(\frac{1}{2}\right)^{\frac{(d-3)}{2}} \Gamma\left(\frac{1}{2}\right) \sum_{p=0}^{\infty} \frac{1}{p!} \left(\frac{\alpha^2}{4}\right)^p \times \sum_{n=0}^{\infty} \frac{1}{n!} \frac{\Gamma(n + \frac{1}{2})}{\Gamma(n + p + \frac{d}{2})} \left(\frac{1}{4}\right)^n {}_2F_1\left(-n, -p; \frac{1}{2}; y_0^2\right) \tag{47}$$

and

$$\begin{aligned} \lim_{y_0 \rightarrow 0} J_1(\alpha; y_0) &= \left(\frac{1}{2}\right)^{\frac{(d-3)}{2}} \frac{\Gamma(\frac{1}{2})}{\Gamma(\frac{d}{2})} \sum_{n=0}^{\infty} \frac{1}{n!} \frac{(n, \frac{1}{2})}{(n, \frac{d}{2})} {}_0F_1\left(; n + \frac{d}{2}; \frac{\alpha^2}{4}\right) \\ &= \left(\frac{1}{2}\right)^{\frac{(d-3)}{2}} \frac{\Gamma(\frac{1}{2})}{\Gamma(\frac{d}{2})} \Phi_3\left(\frac{1}{2}; \frac{d}{2}; \frac{1}{4}, \frac{\alpha^2}{4}\right) \end{aligned} \quad (48)$$

where $\Phi_3(a; c; x, y)$ is a Humbert function (cf [22], p 28) defined by an Appell function as

$$\begin{aligned} \Phi_3(a; c; x, y) &= \lim_{\epsilon \rightarrow 0} F_1\left(\frac{1}{\epsilon}, a, \frac{1}{\epsilon}; c; \epsilon x, \epsilon^2 y\right) \\ &= \sum_{n=0}^{\infty} \frac{1}{n!} \frac{(n, a)}{(n, c)} x^n {}_0F_1(; n + c; y) \\ &= \sum_{p=0}^{\infty} \frac{1}{p!} \frac{1}{(p, c)} y^p {}_1F_1(a; p + c; x). \end{aligned} \quad (49)$$

An approximation of the spatial contribution to the canonical partition function is given by

$$J_N^{(d)}(\alpha)|_1 = \left(\frac{1}{2}\right)^{\frac{(d-1)(N-1)}{2}} \frac{\Gamma(\frac{1}{2})\Gamma(\frac{d}{2})}{\Gamma(\frac{d-1}{2})\Gamma(\frac{d}{2})} \left(\frac{\Gamma(\frac{1}{2})}{\Gamma(\frac{d}{2})}\right)^{(N-1)} \left(\Phi_3\left(\frac{\alpha^2}{4}\right)\right)^{(N-1)} \left(\left(\frac{2}{\alpha}\right)^{\frac{(d-1)}{2}} I_{\frac{d}{2}-1}(\alpha)\right) \quad (50)$$

where we have simplified the notations for the hypergeometric functions. With equation (9) the canonical partition function is approximated by

$$Q_N^{(d)}(\alpha) = Q_{\diamond}^{(d)}(V, T) \left(\frac{T}{T_0}\right)^{\frac{N}{2}(d-1)} \left(\Phi_3\left(\frac{\alpha^2}{4}\right)\right)^{(N-1)} \left(\left(\frac{2}{\alpha}\right)^{\frac{(d-1)}{2}} I_{\frac{d}{2}-1}(\alpha)\right) \quad (51)$$

where

$$\begin{cases} Q_{\diamond}^{(d)}(V, T) = \left(\frac{mkT}{2\pi\hbar^2}\right)^{\frac{d}{2}} V \\ T_0 = 2 \left(\frac{1}{\sqrt{2}} \frac{\Gamma(\frac{d}{2})}{\Gamma(\frac{1}{2})}\right)^{\frac{2}{d-1}} \frac{\hbar^2}{kma^2}. \end{cases} \quad (52)$$

The free energy is given by

$$F_N^{(d)}(\alpha) = -kT \ln Q_N^{(d)}(\alpha) \quad (53)$$

and the force/extension relation by

$$\langle \mathbf{R}_N \cdot \hat{\mathbf{e}}_z \rangle = \langle Z \rangle = - \left(\frac{\partial F_N^{(d)}(\alpha)}{\partial f} \right)_{N, V, T} = a \left(\frac{\partial \ln Q_N^{(d)}(\alpha)}{\partial f} \right)_{N, V, T}. \quad (54)$$

For a large degree of polymerization ($N \gg 1$), we may approximate the free energy as

$$F_N = F_{\text{id}}(N, V, T) - NkT \ln \Phi_3\left(\frac{\alpha^2}{4}\right) \quad (55)$$

and with the relation

$$\frac{\partial^p}{\partial y^p} \Phi_3(a; c; x, y) = \frac{\Gamma(c)}{\Gamma(c+p)} \Phi_3(a; c+p; x, y) \quad (56)$$

we compute the force/extension relation as

$$\frac{\langle Z \rangle}{Na} = \frac{1}{d} \alpha \frac{\Phi_3(\frac{1}{2}; \frac{d}{2} + 1; \frac{1}{4}, \frac{\alpha^2}{4})}{\Phi_3(\frac{1}{2}; \frac{d}{2}; \frac{1}{4}, \frac{\alpha^2}{4})}. \tag{57}$$

The susceptibility is given by

$$\chi \frac{kT}{Na^2} = \frac{1}{d} \alpha \frac{\Phi_3(\frac{d}{2} + 1)}{\Phi_3(\frac{d}{2})} \left(\frac{1}{\alpha} + \frac{\alpha}{(d+2)} \frac{\Phi_3(\frac{d}{2} + 2)}{\Phi_3(\frac{d}{2} + 1)} - \frac{\alpha}{d} \frac{\Phi_3(\frac{d}{2} + 1)}{\Phi_3(\frac{d}{2})} \right). \tag{58}$$

In figure 2(a) we show the force/extension relations given by the ILA (equation (40)) and the IMA (equation (57)), while in figure 2(b) the susceptibilities are represented. It appears that both approximations are in very good agreement, the precision of ILA for the force/extension relation compared with IMA is better than 1% and between 2–5% for susceptibilities. IMA is interesting for two reasons. First, by using IMA we can predict the behaviour with the polymerization degree induced by the linear connection of monomer, while ILA cannot give such results. Second, one can build an iterative scheme of approximation with IMA that converges to the analytical result of equation (23) by grouping neighbouring sites in blocks; this scheme is described in [5]. IMA can be considered as a generalization of ILA.

By using ILA for very small α ($\alpha \ll 1$) we find that

$$\frac{\langle X \rangle_{\text{ILA}}}{Na} \sim \left(\frac{1}{d} \alpha - \frac{(d-2)}{(d+2)d^2} \alpha^3 \right) \quad \text{for } \alpha \ll 1. \tag{59}$$

The Hooke elastic constant K_H and the nonlinear elastic constant K_{nl} are defined by

$$f \sim K_H \langle X \rangle + K_{nl} \langle X \rangle^3. \tag{60}$$

Thus, with ILA we find that

$$\begin{cases} K_H^*|_{\text{ILA}} = K_H|_{\text{ILA}} \frac{Na^2}{kT} = d \\ K_{nl}^*|_{\text{ILA}} = K_{nl}|_{\text{ILA}} \frac{N^3 a^4}{kT} = \frac{d^2}{(d+2)}. \end{cases} \tag{61}$$

For $d = 3$ equation (61) gives $K_H^*|_{\text{ILA}} = 3$ and $K_{nl}^*|_{\text{ILA}} = \frac{9}{5}$.

On the other hand, by using IMA with very small α and according to

$$\Phi_3\left(\frac{1}{2}; c; \frac{1}{4}, \frac{\alpha^2}{4}\right) \simeq {}_1F_1\left(\frac{1}{2}; c; \frac{1}{4}\right) + \frac{1}{c} {}_1F_1\left(\frac{1}{2}; c+1; \frac{1}{4}\right) \frac{\alpha^2}{4} \tag{62}$$

we find that

$$\begin{aligned} \frac{\langle Z \rangle}{Na} &\sim \frac{a}{kT} \left(\frac{{}_1F_1(\frac{d}{2} + 1)}{{}_1F_1(\frac{d}{2})} \right) f \\ &+ \frac{1}{2} \frac{Na^4}{(kT)^3} \left(\frac{{}_1F_1(\frac{d}{2} + 1)}{{}_1F_1(\frac{d}{2})} \right)^2 \left(\frac{d}{d+2} \frac{{}_1F_1(\frac{d}{2} + 2) {}_1F_1(\frac{d}{2})}{({}_1F_1(\frac{d}{2} + 1))^2} - 1 \right) f^3. \end{aligned} \tag{63}$$

Thus, with IMA we find for the elastic constants:

$$\begin{cases} K_H^*|_{\text{IMA}} = d \frac{{}_1F_1(\frac{d}{2})}{{}_1F_1(\frac{d}{2} + 1)} \\ K_{nl}^*|_{\text{IMA}} = \frac{d^2}{2} \left(\frac{{}_1F_1(\frac{d}{2})}{{}_1F_1(\frac{d}{2} + 1)} \right)^2 \left(1 - \frac{d}{d+2} \frac{{}_1F_1(\frac{d}{2} + 2) {}_1F_1(\frac{d}{2})}{({}_1F_1(\frac{d}{2} + 1))^2} \right). \end{cases} \tag{64}$$

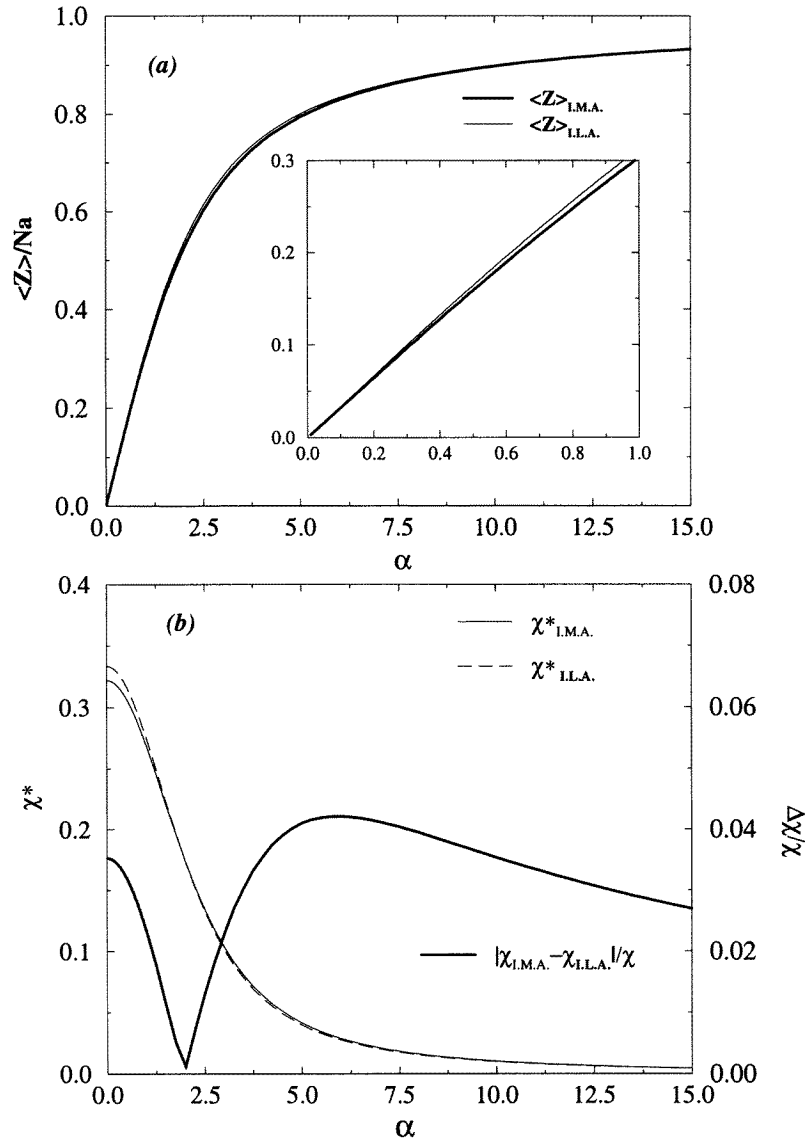


Figure 2. (a) Force/extension relations for the freely jointed chain stretched at both ends obtained by using the ILLA and IMA for $d = 3$ and $N \gg 1$. (b) Susceptibilities obtained by using ILLA and IMA. The reduced susceptibility is defined by $\chi^* = (kT/Na^2)\chi$.

For $d = 3$ these elastic constants are $K_{H}^*|_{IMA} \simeq 3.106$ and $K_{nl}^*|_{IMA} \simeq 1.871$. The difference between $K_{H}^*|_{IMA}$ and $K_{H}^*|_{ILLA}$ can be seen in figure 2(b) when $\alpha \rightarrow 0$.

For small α (i.e. $\alpha < 1$) we may approximate by using Taylor expansion:

$$\left(\frac{2}{\alpha}\right)^{\left(\frac{d}{2}-1\right)} I_{\frac{d}{2}-1}(\alpha) \simeq \frac{1}{\Gamma\left(\frac{d}{2}\right)}(1 + a_2\alpha^2 + a_4\alpha^4 + a_6\alpha^6 + a_8\alpha^8) + o(\alpha^{10}) \tag{65a}$$

$$\Phi_3\left(\frac{\alpha^2}{4}\right) \simeq {}_1F_1\left(\frac{1}{2}; \frac{d}{2}; \frac{1}{4}\right)(1 + \varphi_1\alpha^2 + \varphi_2\alpha^4 + \varphi_3\alpha^6 + \varphi_4\alpha^8) + o(\alpha^{10}) \tag{65b}$$

with

$$\begin{cases} a_2 = \frac{1}{2d} \\ a_4 = \frac{1}{8} \frac{1}{(d+2)d} \\ a_6 = \frac{1}{48} \frac{1}{(d+4)(d+2)d} \\ a_8 = \frac{1}{384} \frac{1}{(d+6)(d+4)(d+2)d} \end{cases}$$

and where the coefficients φ_n are given by equation (49), for instance:

$$\varphi_1 = \frac{1}{2d} \frac{{}_1F_1(\frac{1}{2}; \frac{d}{2} + 1; \frac{1}{4})}{{}_1F_1(\frac{1}{2}; \frac{d}{2}; \frac{1}{4})}.$$

With these approximations we do not recover in the limit $\alpha \rightarrow 0^+$ the indistinguishability of both directions of the monomer labelling, because of the remnescent discernability when $\alpha \neq 0$. Therefore, we have to modify equation (65a) as

$$(1 + P(\alpha^2) + o(\alpha^{10})) \longrightarrow \left(\frac{1}{2!} + P(\alpha^2) + o(\alpha^{10}) \right).$$

With Taylor expansions we found the free energy as

$$F_N(\alpha) = F_{id}(N, V, T) - kT(F_2\alpha^2 + F_4\alpha^4 + F_6\alpha^6 + F_8\alpha^8 + o(\alpha^{10})) \quad (66)$$

where

$$\begin{cases} F_2 = A_2 + (N - 1)\varphi_1 \\ F_4 = A_4 + (N - 1)(\varphi_2 - \frac{1}{2}\varphi_1^2) \\ F_6 = A_6 + (N - 1)(\varphi_3 - \varphi_1\varphi_2 + \frac{1}{3}\varphi_1^3) \\ F_8 = A_8 + (N - 1)(\varphi_4 - \varphi_1\varphi_3 - \frac{1}{2}\varphi_2^2 + \varphi_1^2\varphi_2 - \frac{1}{4}\varphi_1^4) \end{cases}$$

and with

$$\begin{cases} A_2 = \frac{1}{d} \\ A_4 = -\frac{1}{4} \frac{(d+4)}{d^2(d+2)} \\ A_6 = \frac{1}{48} \frac{(5d^2 + 48d + 128)}{(d+4)(d+2)d^3} \\ A_8 = -\frac{1}{192} \frac{(37d^4 + 410d^3 + 1712d^2 + 4224d + 4608)}{(d+6)(d+4)(d+2)^2d^4}. \end{cases}$$

Force/extension relations for small α and for $N \geq 3$ are now given by

$$\frac{\langle Z \rangle}{Na} \simeq \frac{1}{Nd} (Z_1(N)\alpha + Z_3(N)\alpha^3 + Z_5(N)\alpha^5 + Z_7(N)\alpha^7 + o(\alpha^9)) \quad (67)$$

where the $Z_i(N)$ are easily computed from the F_i .

Equation (67) is not valid for $N = 2$, because it has been obtained by using IMA and when $N = 2$ there is no propagator to cut (cf section 2.2). For $N = 2$ and $d = 3$ we found by computing the integral $J_1(\alpha; y_o)$ given by equation (43):

$$\frac{\langle Z \rangle}{2a} = \frac{2}{3}\alpha - 0.33164\alpha^3 + 0.21261\alpha^5 - 0.12892\alpha^7 + o(\alpha^9). \quad (68)$$

In a molecular dynamics [13] using the RATTLE algorithm [23] to take the holonomic constraints into account and the Nosé–Hoover thermostat [21] to perform a sampling in the

canonical ensemble, we have found for $d = 3$ and $N = 20$, $Z_1(20)|_{\text{MD}} = 20.4 \pm 0.1$ and $Z_3(20)|_{\text{MD}} = -1.65 \pm 0.25$, and for $N = 30$, $Z_1(30)|_{\text{MD}} = 30.0 \pm 0.1$ and $Z_3(30)|_{\text{MD}} = -1.5 \pm 0.6$. According to equation (67) we compute $Z_1(20)|_{\text{IMA}} \simeq 20.352$ and $Z_3(20)|_{\text{IMA}} \simeq -1.613$, and $Z_1(30)|_{\text{IMA}} \simeq 30.011$ and $Z_3(30)|_{\text{IMA}} \simeq -2.216$. Thus IMA and MD simulations are in good agreement, while ILA fails to predict any dependence on the degree of polymerization.

In the literature, force/extension relations are frequently defined from susceptibility. That definition allows one to include fluctuations in variations of the extensive variable Z , while equation (57) furnishes only the average of Z in the canonical ensemble. By definition of susceptibility we have

$$\chi kT = \langle \Delta Z^2 \rangle = \langle Z^2 \rangle - \langle Z \rangle^2 \quad (69)$$

and with equations (57) and (58) an analytical expression of $\langle Z^2 \rangle$ can be extracted. From $\langle Z^2 \rangle$ we define a force/extension relation including fluctuations of Z as

$$\langle\langle Z \rangle\rangle = \sqrt{\langle Z^2 \rangle} = g(\alpha). \quad (70)$$

With the Taylor expansion one may also obtain expressions for $g_N(\alpha)$ where the dependence on the degree of polymerization is explicitly included to the accuracy of IMA at first order (i.e. in $1/N$).

Comparison of experimental data, as for instance micromanipulations of DNA molecules, or numerical results obtained by molecular dynamics simulations, with computations performed with IMA must be made with $g_N(\alpha)$ rather than with the force/extension relations given by equations (67) and (57). In figure 3, we have plotted the force/extension relations given by the functions $g_N(\alpha)$ for $N = 12, 20, 50, 100$ and $10\,000$, for $d = 3$. The force/extension relation obtained by using ILA, the MD results for $N = 20$ and $d = 3$ [13], and some experimental points of micromanipulations of DNA molecules extracted from [16] are also represented on this figure.

The function $g_{20}(\alpha)$ is in very good agreement with MD simulation. Experimental points for DNA molecules could be interpreted as though the numbers of ‘effective monomers’ in molecules varied with the amplitude of the force applied to both ends. Since in the experiments of [16] there is no histone octamer left in the molecules after preparation of the sample, the hypothetical ‘effective monomers’ cannot be histones. Nevertheless, when histones are removed from DNA molecules some local structures or secondary structures, such as plectonemic or double helix, are induced to minimize the bending and torsional energies of the molecules. These local structures might perhaps be identified with effective monomers. Thus when the stretching force is increased these local structures would be undone and therefore the numbers of effective monomers is reduced. If a stretching force is strong enough to remove all effective monomers then the true elasticity of the double helix of the DNA molecule would be measured, and as has been shown, this elasticity is quite well described by the worm-like chain (WLC) [24, 25] or the continuous model of Krathy–Porod chains [26].

The mechanism described in the last paragraph is hypothetical because, even with the great experimental skill of the authors of [16, 27], a measurement of the stretching force as small as a few femtonewtons needs more than two hours with the experimental set-up described in [16]: explicitly experimental errors are as large as 5–10% in this regime. In figure 3 the error bars on the experimental points are set to 8% for the force, and to 5% for the extension. The experimental points are not much more than one or two standard deviations of the WLC or ILA force/extension relations; thus, to test the validity of the hypothetical mechanism proposed in the previous paragraph, a higher accuracy and more data in the weak force regime are needed [27].

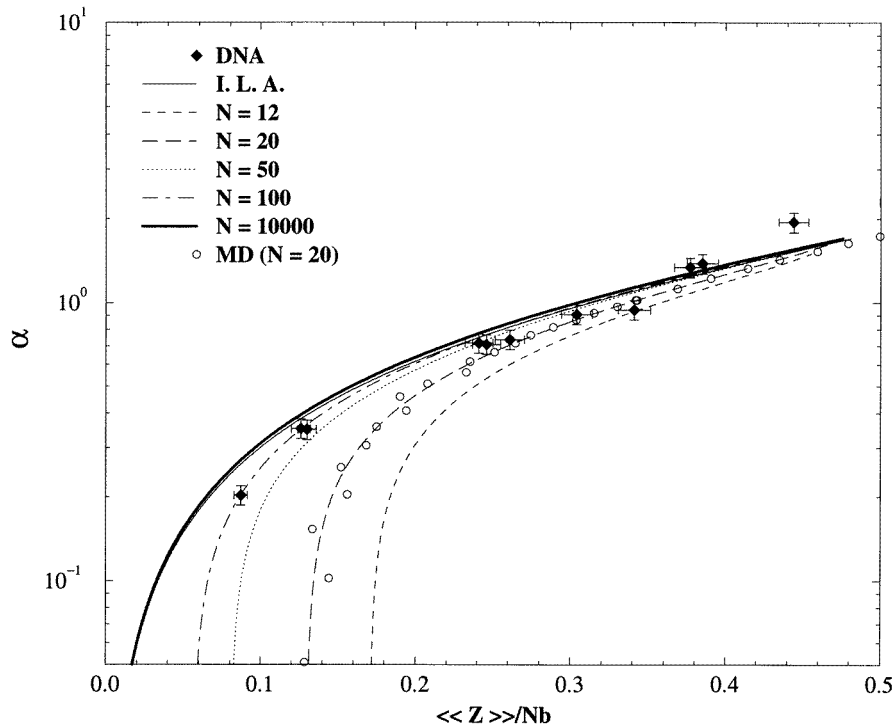


Figure 3. Force/extension relations including fluctuations of the end-to-end distance. The relations obtained with ILA and with IMA for $N=12, 20, 50, 100,$ and $10\,000$ are represented for $d=3$. Open circles are MD results for $N=20$. Filled diamonds are experimental results for a single DNA molecule extracted from [16]. The experimental errors are estimated as 8% for the amplitude of the force and 5% for the extension; $kT/a \simeq 0.038pN$.

4. General discussion

In this work we have presented analytical computations of freely jointed chains in a one-dimensional external field. As was shown recently [4, 5], interactions between the monomers via holonomic constraints induced a coupling between nearest-neighbours; nevertheless, this coupling is simple enough such that the analytical computation of the canonical partition function can still be performed. All computations done in section 2.1 of this paper are analytical and can be applied to any one-dimensional potential. In particular, we have obtained equation (23) from equation (1) in an analytical way: therefore equation (23) holds all information about the linear connectivity of the chain. This result can be useful to define rigorously new approximations for chains in a one-dimensional field. For instance, this result can help to define approximations for the chain stretched at both ends in the strong regime or for polymers stretched under a flow where the ILA fails.

Another interesting result of this paper is to show how one can extend the ILA rigorously to take into account more precisely the linear connection of the chain. This extension is called IMA and by construction, when this approximation is improved by grouping monomers, it converges to the analytical result given by equation (23) [5]. This new scheme of approximation can also be extended very easily to chains with heterogeneous mass sequence. As in ILA, in IMA we consider that the movement of monomers are only slightly influenced by the movement of its neighbours; thus, this kind of approximation is valid only for weak interactions between

the field and monomers or at high temperature.

When applied to the chain stretched at both ends these computations give several new results. The entropic elastic constants of the chain are shown to be 3% higher than those predicted by ILA. These computations allow us to extract the dependence of the properties of the chain on the degree of polymerization N , while ILA cannot predict any dependence on N because each bond is treated on the same footing. In conclusion, since the correction induced by the dynamical part of the holonomic constraints is small, it is recommended for crude theoretical descriptions of some macromolecular systems, like polymers networks, to use ILA instead of IMA, whose analytical functions are more complicated. On the other hand, in MD simulations these corrections are relevant.

As is shown in [4, 5] the phase space of freely jointed chains can be considered as a subset of the phase space of the ideal gas; thus, when we perform MD in Nosé–Hoover or microcanonical ensemble, application of the ergodic hypothesis is not straightforward. As for the ideal gas, there are in the freely jointed chain some degrees of freedom that are not coupled to the dynamics, and then the system does not reach thermalization. This problem will be studied in a forthcoming paper [13].

Finally, the new results, including the dependence on the degree of polymerization, might also explain some experimental features of a single DNA molecule under uniform tension in the entropic regime. The mechanism described very briefly at the end of section 3 is hypothetical. A higher accuracy and more experimental points in the entropic regime would be very useful to validate or invalidate such a mechanism.

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References

- [1] Kramers H 1946 *J. Chem. Phys.* **14** 415
- [2] Fixman M 1974 *Proc. Natl Acad. Sci., USA* **71** 3050
- [3] Grosberg A Y and Khokhlov A R 1994 *Statistical Physics of Macromolecules* ed R Larson and P A Pincus (New York: AIP)
- [4] Mazars M 1996 *Phys. Rev. E* **53** 6297
- [5] Mazars M 1998 *J. Phys. A: Math. Gen.* **31** 1949
- [6] Winkler R G, Reineker P and Scheiber M 1989 *Europhys. Lett.* **8** 493
- [7] Mansfield M 1988 *J. Chem. Phys.* **88** 6570
- [8] Gaveau B and Schulmann L S 1990 *Phys. Rev. A* **42** 3470
- [9] Schurr J M and Smith S B 1990 *Biopolymers* **29** 1161
Perkins T T, Smith D E, Larson R G and Chu S 1995 *Science* **268** 83
- [10] Marciano Y and Brochard-Wyart F 1995 *Macromolecules* **28** 985
- [11] Klushin L I, Skvortsov A M and Gorbunov A A 1997 *Phys. Rev. E* **56** 1511
- [12] Goulding D J and Teixeira P I C 1997 *J. Chem. Phys.* **107** 7530
- [13] Mazars M in preparation
- [14] Stanley H E 1969 *Phys. Rev.* **179** 570
- [15] de Gennes P G 1979 *Scaling Concepts in Polymers Physics* (Ithaca, NY: Cornell University Press)
- [16] Allemand J F 1997 Micro-manipulations de molécules d'ADN isolés *Thèse* l'Université Pierre et Marie Curie
- [17] Smith S B, Finzi L and Bustamante C 1992 *Science* **258** 1122
- [18] Flory P 1953 *Principles of Polymer Chemistry* (London: Cornell University Press)
- [19] Glattig G, Winkler R G and Reineker P 1993 *Macromolecules* **26** 6085
- [20] Webman I, Lebowitz J L and Kalos M H 1981 *Phys. Rev. A* **23** 316

- Ceperley D, Kalos M H and Lebowitz J L 1981 *Macromolecules* **14** 1472
- [21] Nosé S 1991 *Prog. Theor. Phys. Suppl.* **103** 1
- [22] Exton H 1976 *Multiple Hypergeometric Functions and Applications* ed G M Bell (New York: Wiley)
- [23] Andersen H C 1983 *J. Comput. Phys.* **52** 24
- [24] Bustamante C, Marko J F, Siggia E D and Smith S 1995 *Science* **265** 1599
Marko J F and Siggia E D 1995 *Macromolecules* **28** 8759
- [25] Bouchiat C, Wang M D, Allemand J F, Strick T, Block S M and Croquette V in preparation
- [26] Bensimon D, Dhomi D and Mézard M 1998 *Europhys. Lett.* **42** 97
- [27] Croquette V Private communication