A path integral approach to the dynamics of random chains

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In this work the dynamics of a freely jointed random chain with small masses attached to the joints is studied from a microscopic point of view. The chain is treated using a stringy approach, in which a statistical sum is performed over all two dimensional trajectories spanned by the chain during its fluctuations. In the limit in which the chain becomes a continuous curve, the probability function for such a system coincides with the partition function of a generalized nonlinear sigma model. The cases of open or closed chains in two and three dimensions are discussed. In three dimensions it is possible also to introduce some rigidity at the joints, allowing the segments of the chain to take only particular angles with respect to a given direction.

I. INTRODUCTION

In this paper the dynamics of a random chain subjected to thermal fluctuations at fixed temperature $T$ is discussed. This problem is usually treated phenomenologically, regarding the fluctuations of the chain as a stochastic process which may be described with the help of Langevin equations or, alternatively, of Fokker-Planck equations [1]. This approach leads to the well known models of Rouse [2] and Zimm [3] which allow a satisfactory understanding of the main properties of polymers in solutions. One major drawback of these coarse grained models is, that they suffer from the presence of rigid constraints. The Rouse and Rouse–Zimm equation consider only chains bead spring models of chains, where the local spring is
infinitely extensible. In the framework of continuous models the Rouse equation for example is nothing but the stochastic equation (Langevin equation) for the classical Wiener measure, which yields paths which do not have a well defined tangent vectors \([1]\). These problems have been tackled by various attempts, see e.g. \([4, 5]\). However, the correct use of rigid constraints in (stochastic) dynamics requires some mathematical effort \([6, 7]\), in contrast to the static cases where rigid constraints can be implemented by Dirac delta functions in the partition function.

However, it seems to be too difficult to extend these approaches, therefore we follow here some different routes. Moreover the use of dynamic constraints for (stochastic dynamics equation) is always problematic.

Here the dynamics of random chains is considered from a microscopic point of view. The chain is represented as a set of freely jointed segments of fixed lengths. Small masses are attached at the joints. The goal is to construct the probability function \(\Psi[\text{Conf}_f, \text{Conf}_i]\) of this system. Roughly speaking this function measures the probability that a chain starting from a given initial conformation \(\text{Conf}_i\) at the time \(t_i\) arrives to a given final conformation \(\text{Conf}_f\) at time \(t_f\). During its motion from the initial to the final conformation the chain spans a two dimensional surface. In this way one obtains a stringy formulation of the chain dynamics, which is based on path integrals \([8]\). The chain “world-sheet” is a rectangle whose sides are given by the length of the chain and the time interval \(\Delta t = t_f - t_i\).

The basic ingredient in the construction of the probability function \(\Psi[\text{Conf}_f, \text{Conf}_i]\) is the energy of a discrete freely jointed chain with \(N\) segments. While it is easy to add external and internal interactions acting on the segments of the chain, the complicated form of the kinetic energy poses serious obstacles to the possibility of computing the probability function analytically. The kinetic energy is in fact nonlinear and has an intrinsically non-Markoffian nature. This is due to the fact that the velocity of each segment in the chain depends on the velocities of the other segments. In this situation, it is difficult to isolate in the energy a linear term which could give raise to a propagator, so that even perturbative calculations are not allowed. Luckily, the expression of the kinetic energy simplifies considerably after performing the limit in which the chain becomes a continuous curve. The final form of the probability function which one obtains in this limit closely resembles the partition function of a nonlinear sigma model \([9]\). The difference with respect to the standard nonlinear sigma model is that in the latter case the modulus of the fields is constrained, while in the present
case the constraint involves the modulus of the derivative of the fields with respect to the arc-length of the chain. This constraint is related to our assumption that the lengths of the segments is fixed.

Within our formalism it is possible to add constraints to the trajectory of the chain with the help of Dirac $\delta$–functions as in the case of the statistical mechanics of random chains [10]. Here we have considered just the simplest example of constraints, namely the requirement that the trajectory of the chain is closed. Besides, it is easy to treat non-homogeneous chains, in which both lengths of the segments and the masses located at the points are arbitrary. The probability functions is constructed for two and three dimensional random chains. In three dimensions one may introduce further constraints, which fix for instance the lengths of the projections of the segments on the $z$ axis. In this way we are able to discuss also rigid chains, in which the segments are allowed to form only a given angle with respect to the $z$ axis.

The material presented in this paper is divided as follows. In Section II the expression of the kinetic energy of a discrete chain with $N$ segments is derived in two dimensions using a recursive method. The rules of the passage to the continuous limit are established. After this limit is performed, important simplifications occur. To further simplify the problem, one of the ends of the chain is fixed at a given point. Moreover, it is supposed that the distributions of masses and segment lengths along the chain are uniform. It is shown that under these assumptions the kinetic energy of the continuous chain may be written in terms of free complex scalar fields subjected to a constraint. The origin of this constraint is the requirement that the lengths of the segments are constant. In Section III the classical solutions of a free chain are studied. In Section IV a stringy approach to the dynamics of the chain in two dimensions is established. The probability function is constructed using path integrals. The resulting model closely resembles a nonlinear supersymmetric model. The problem of fixing various boundary conditions, including the case of closed chain trajectories, is discussed. A perturbative approach based on the expansion of the fields describing the statistical fluctuations over a classical background is provided. In Section V the results of Sections II–IV are extended to three dimensional chains. In Section VI chains with constant bending angles are investigated. Finally, in Section VII our conclusions are presented.
II. THE ENERGY OF A FREE CHAIN

Let us consider a chain of $N$ segments of fixed lengths $l_2, \ldots, l_N$ in the two dimensional plane. Each segment $P_{i+1}P_i$ is completely specified by the positions of its end points $P_{i+1}$ and $P_i$. In cartesian coordinates $(x, y)$ these positions are given by the radius vectors:

$$\mathbf{r}_i = (x_i, y_i) \quad i = 1, \ldots, N$$ (1)

The segments are joined together at the points $P_l$, where $2 \leq l \leq N - 1$, see Fig. 1, while $P_1$ and $P_N$ are the ends of the chain. Moreover, at each point $P_i$, with $i = 1, \ldots, N$, a mass $m_i$ is attached. In the following we restrict ourselves to the case of a free chain. We will see below that the addition of interactions is straightforward.

To compute the kinetic energy of the above system, it is convenient to pass to polar coordinates $l_i, \varphi_i$ as follows:

$$x_n = \sum_{i=1}^{n} l_i \cos \varphi_i \quad y_n = \sum_{i=1}^{n} l_i \sin \varphi_i \quad (n = 1, \ldots, N)$$ (2)

The $\varphi_i$ is the angle formed by segment $i$ with the $y-$axis, see Fig. 1. All the radial coordinates $l_i$ are constants for $i = 2, \ldots, N$. The only exception is the length $l_1(t)$ which denotes the distance of the point $x_1, y_1$ from the origin. Since this distance is not fixed, $l_1 = l_1(t)$ is allowed to vary with the time $t$. From Eq. (2) the velocity components of the $n-$th segment may be written as follows:

$$\dot{x}_n = -\sum_{i=1}^{n-1} l_i \dot{\varphi}_i \sin \varphi_i - l_n \dot{\varphi}_n \sin \varphi_n + \dot{l}_1 \cos \varphi_1 \quad (n = 2, \ldots, N)$$ (3)

$$\dot{y}_n = \sum_{i=1}^{n-1} l_i \dot{\varphi}_i \cos \varphi_i + l_n \dot{\varphi}_n \cos \varphi_n + \dot{l}_1 \sin \varphi_1 \quad (n = 2, \ldots, N)$$ (4)

$$\dot{x}_1 = -l_1 \dot{\varphi}_1 \sin \varphi_1 + \dot{l}_1 \cos \varphi_1$$ (5)

$$\dot{y}_1 = l_1 \dot{\varphi}_1 \cos \varphi_1 + \dot{l}_1 \sin \varphi_1$$ (6)

Separating the contribution coming from the first $n - 1$ variables, the kinetic energy $K_n$ of the $n-$th segment can be expressed in terms of the kinetic energy $K_{n-1}$ of the $(n - 1)-$th segment:

$$K_n = \frac{m_n}{m_{n-1}}K_{n-1} + \frac{m_n}{2}l_n^2 \dot{\varphi}_n^2 + m_n \sum_{i=1}^{n-1} l_i \dot{\varphi}_n \dot{\varphi}_i \cos(\varphi_i - \varphi_n) + m_n l_n \dot{\varphi}_n \dot{l}_1 \sin(\varphi_1 - \varphi_n)$$ (7)
FIG. 1: A chain with $N$ segments. Let us note that the end point $P_1$ is not bound to stay at a fixed distance with respect to the origin of the cartesian reference system.

It is possible to solve the above recursion relation to find an expression of $K_n$. If we do that, at the end the total kinetic energy of the discrete chain:

$$K_{disc}^{2d} = \sum_{n=1}^{N} K_n$$

becomes:

$$K_{disc}^{2d} = \frac{M}{2} \left( \hat{\phi}_1^2 + \hat{\phi}_1^2 \right) + l_1 \hat{\phi}_1 \sum_{n=1}^{N} \sum_{k=1}^{n-1} m_n l_{n-k+1} \hat{\phi}_{n-k+1} \cos(\varphi_{n-k+1} - \varphi_1)$$

$$+ l_1 \sum_{n=1}^{N} \sum_{k=1}^{n-1} m_n l_{n-k+1} \hat{\phi}_{n-k+1} \sin(\varphi_1 - \varphi_{n-k+1})$$

$$+ \sum_{n=1}^{N} \sum_{k=1}^{n-1} \frac{1}{2} \hat{\phi}_{n-k+1}^2 + \sum_{n=1}^{N} \sum_{k=1}^{n-1} \sum_{i=2}^{n-k} m_n l_{n-k+1} l_i \hat{\phi}_{n-k+1} \hat{\phi}_i \cos(\varphi_{n-k+1} - \varphi_i)$$

(9)

where $M = \sum_{n=1}^{N} m_n$ is the total mass of the chain [15].

We wish now to perform the limit in which the chain of $N$ segments becomes a continuous system [16]. To this purpose, it is convenient to consider the indices $i, k, n, \ldots$ appearing in Eq. (9) as discrete variables taking values in a one dimensional lattice with $N$ points. Quantities $f_i$ carrying the index $i$ may be interpreted as functions of $i$. Their variations $\Delta f_i$ are given by: $\Delta f_i = f_{i+1} - f_i$. Clearly, $\Delta i = 1$, i.e. the spacing between two neighboring points in the lattice is 1. In order to proceed, we rescale the distances in the lattice in such a way that the spacing in the new lattice will be $a$. To this purpose, we
perform the transformations \( i \rightarrow s_i, \ f_i \rightarrow f(s_i) \) where the new variable \( s_i \) has variation \( \Delta s_i = s_{i+1} - s_i = a \). The next step is to compute the kinetic energy of Eq. (9) in the limit \( N \rightarrow \infty, \ a \rightarrow 0 \), while the product \( Na \) remains finite, let’s say \( Na = L \), where \( L \) denotes the total length of the chain. Clearly, in this limit the right hand side of Eq. (9) will diverge unless we suppose that the masses \( m_i \) and the lengths \( l_i \) of the segments are going to zero in a suitable way. Reasonable assumptions are:

\[
l_i \rightarrow l(s_i) = a \rho_l(s_i) \quad m_i \rightarrow m(s_i) = a \rho_m(s_i) \quad (10)
\]

where \( \rho_l(s_i) \) and \( \rho_m(s_i) \) are respectively the distribution of length and of mass within the chain. Here we allow for segments of different lengths \( l(s_i) \) and for points \( P_i \) of different masses \( m(s_i) \). To be consistent with our settings, the distributions \( \rho_l(s_i) \) and \( \rho_m(s_i) \) must be normalized as follows:

\[
\sum_{i=1}^{N} \rho_l(s_i) \Delta s_i = L \quad \sum_{i=1}^{N} \rho_m(s_i) \Delta s_i = M \quad (11)
\]

At this point we are ready to pass to the continuous limit. Functions of discrete variables will be substituted with functions of continuous variables, while sums will be replaced with integrals according to the following rules:

\[
f(s_i) \rightarrow f(s) \quad \sum_{i=1}^{N} \Delta s_i \rightarrow \int_{0}^{L} ds \quad (12)
\]

After a few calculations one finds:

\[
K_{disc}^{2d} \rightarrow K^{2d} \quad (13)
\]

where

\[
K^{2d} = K^{2d}(t) = \frac{M}{2} (I_1^2(t) \dot{\varphi}_1^2(t) + \dot{I}_1^2(t)) + \dot{\varphi}_1(t) l_1(t) \int_{0}^{L} d\rho_m(s) \int_{0}^{s} d\rho_l(s-u) \dot{\varphi}(t, s-u) \cos(\varphi(t, s-u) - \varphi_1(t)) \\
+ \dot{I}_1(t) \int_{0}^{L} d\rho_m(s) \int_{0}^{L} d\rho_l(s-u) \dot{\varphi}(t, s-u) \sin(\varphi_1(t) - \varphi(t, s-u)) \\
+ \int_{0}^{L} d\rho_m(s) \int_{0}^{s} d\rho_l(s-u) \int_{0}^{s-u} d\rho_l(v) \dot{\varphi}(t, s-u) \dot{\varphi}(t, v) \cos(\varphi(t, s-u) - \varphi(t, v)) \quad (14)
\]

and

\[
\int_{0}^{L} d\rho_l(s) = L \quad \int_{0}^{L} d\rho_m(s) = M \quad (15)
\]
Eq. (14) may be simplified by performing in the integrals in \( du \) the following change of variables:

\[
\begin{align*}
 u' &= s - u \\
 du' &= -du
\end{align*}
\]  

and then using the formula:

\[
\int_0^L ds \int_0^s du' f(u') = \int_0^L ds (L - s) f(s)
\]  

which is valid for any integrable function \( f(s) \). As a result, we obtain:

\[
\begin{align*}
 K^{2d} &= \frac{M}{2} (\dot{I}_1^2(t) \dot{\varphi}_1^2(t) + \dot{\varphi}_1(t) I_1(t)) \\
 &+ \dot{\varphi}_1(t) I_1(t) \int_0^L ds (L - s) \rho_m(s) \rho_l(s) \dot{\varphi}(t, s) \cos(\varphi(t, s) - \varphi_1(t)) \\
 &+ \dot{I}_1(t) \int_0^L ds (L - s) \rho_m(s) \rho_l(s) \dot{\varphi}(t, s) \sin(\varphi_1(t) - \varphi(t, s)) \\
 &+ \int_0^L ds (L - s) \rho_m(s) \rho_l(s) \int_0^s du \rho_l(u) \dot{\varphi}(t, s) \dot{\varphi}(t, u) \cos(\varphi(t, s) - \varphi(t, u))
\end{align*}
\]  

For simplicity, we suppose the length and mass distributions in the chains are uniform. As a consequence, we put:

\[
\begin{align*}
 \rho_l(s) &= 1 \\
 \rho_m(s) &= \frac{M}{L}
\end{align*}
\]  

The first of Eqs. (19) implies (see Eq. (10)):

\[
\begin{align*}
 l_i &= a \\
 i &= 2, \ldots, N
\end{align*}
\]  

Remembering the definition of the length distribution in Eq. (10), it is easy to realize that the first of Eqs. (19) implies that all segments of the chain have the same length. As a further simplification, we will study the case in which the point \( P_1 \) is fixed, so that

\[
\dot{l}_1 = \dot{\varphi}_1 = 0
\]  

From the above assumptions and from Eq. (18), we find that the total energy \( H_0 \) of the ideal chain is given by:

\[
\begin{align*}
 H_0(\varphi) &= \frac{M}{L} \int_0^L ds (L - s) \int_0^s du \dot{\varphi}(t, s) \dot{\varphi}(t, u) \cos(\varphi(t, s) - \varphi(t, u))
\end{align*}
\]  

In view of a future path integral treatment of the dynamics of the chain, it will be convenient to use cartesian coordinates, because of the complications involved with polar coordinates...
in the path integral approach. To this purpose, we rewrite Eq. (22) with the help of the well
known trigonometric formula:

\[
\cos(\varphi(t, s) - \varphi(t, u)) = \frac{1}{2} \left( e^{i\varphi(t,s)}e^{-i\varphi(t,u)} + e^{-i\varphi(t,s)}e^{i\varphi(t,u)} \right)
\] (23)

Introducing new complex variables

\[
\Phi(t, s) = \int_0^s du e^{i\varphi(t,u)} + l_1 e^{i\varphi_1}
\] (24)

\[
\bar{\Phi}(t, s) = \int_0^s du e^{-i\varphi(t,u)} + l_1 e^{-i\varphi_1}
\] (25)

one finds after simple calculations:

\[
H_0(\varphi) = M^2 L \int_0^L ds \frac{\partial \Phi(t, s)}{dt} \frac{\partial \bar{\Phi}(t, s)}{dt}
\] (27)

Now the expression of the energy has become simpler, but the new fields \(\Phi(s,t)\) and \(\bar{\Phi}(s,t)\)
are not independent and have a complicated dependence on the true degree of freedom \(\varphi(t, s)\)
as shown by Eqs. (24) and (25). For this reason, it is preferable to assume that \(\Phi(t, s)\) and
\(\bar{\Phi}(t, s)\) are independent complex fields subjected to the constraint [17]:

\[
\partial_s \Phi(t, s) \partial_s \bar{\Phi}(t, s) = 1
\] (28)

It is easy to check that Eqs. (24) and (25) provide exactly the solution of the constraint (28). At this point the energy \(H_0(\varphi)\) may be rewritten in the simple form:

\[
H_0(\Phi, \bar{\Phi}) = M^2 L \int_0^L ds \frac{\partial \Phi(t, s)}{dt} \frac{\partial \bar{\Phi}(t, s)}{dt}
\] (29)

where \(\Phi, \bar{\Phi}\) are treated as independent complex degrees of freedom subjected to the condition (28). This constraint can be imposed for instance by means of a Lagrange multiplier.

Instead of the complex coordinates \(\Phi, \bar{\Phi}\) one may also exploit real coordinates \(x, y\):

\[
x(t, s) = \int_0^s du \cos \varphi(t, u) + l_1 \cos \varphi_1 = \frac{1}{2} (\Phi(t, s) + \bar{\Phi}(t, s))
\]

\[
y(t, s) = \int_0^s du \sin \varphi(t, u) + l_1 \sin \varphi_1 = \frac{1}{2i} (\Phi(t, s) - \bar{\Phi}(t, s))
\] (30)

It is easy to see that \(x(t, s)\) and \(y(t, s)\) correspond in the continuous case to the discrete
coordinates \(x_n\) and \(y_n\) of the point \(P_n\) given by Eq. (2). Written in terms of the real variables
\(x(t, s)\) and \(y(t, s)\) the functional \(H_0(\Phi, \bar{\Phi})\) and the constraint (28) become respectively:

\[
H_0(x, y) = M^2 L \int_0^L ds (x^2(t, s) + y^2(t, s))
\] (31)
and
\[(\partial_s x(t, s))^2 + (\partial_s y(t, s))^2 = 1\] (32)

In the discrete case this constraint corresponds to the condition:
\[(x_i - x_{i-1})^2 + (y_i - y_{i-1})^2 = a^2 \quad i = 2, \ldots, N\] (33)

In the future it will be convenient to exploit the vector notation:
\[\mathbf{R}(t, s) = (x(t, s), y(t, s))\] (34)

and
\[H_0(x, y) = H_0(\mathbf{R}) = \frac{M}{2L} \int_0^L ds \dot{\mathbf{R}}^2(t, s)\] (35)

If \(s = 0\), it is clear from Eq. (30) that the point \(\mathbf{R}(t, 0)\) is fixed for every time \(t\) at the location:
\[\mathbf{R}(t, 0) = (l_1 \cos \varphi_1, l_1 \sin \varphi_1)\] (36)

This is in agreement with the assumption of Eq. (21), where it is supposed that \(l_1\) and \(\varphi_1\) are constant in time.

### III. THE CLASSICAL EQUATIONS OF MOTION

We wish to give a “stringy” interpretation of the chain dynamics, in which the chain moves during a time interval \([t_i, t_f]\) from an initial conformation \(\Phi_i(s)\) to a final conformation \(\Phi_f(s)\). During this motion, the chain spans a two dimensional portion of the plane \((x, y)\), whose points are described by the “complex coordinates” \(\Phi(t, s), \bar{\Phi}(t, s)\). The chain “world-sheet” is delimited by the range of the variables \(t\) and \(s\): \(t_i \leq t \leq t_f\) and \(0 \leq s \leq L\). The situation is depicted in Fig. 2. Following this strategy, we define the chain action:
\[\mathcal{A}_0 = \frac{M}{2L} \int_{t_i}^{t_f} dt \int_0^L ds \frac{\partial \bar{\Phi}(t, s)}{\partial t} \frac{\partial \Phi(t, s)}{\partial t}\] (37)

In the rest of this Section we study the classical equations of motion corresponding to the action \(\mathcal{A}_0\):
\[\frac{\partial^2 \Phi(t, s)}{\partial t^2} = \frac{\partial^2 \bar{\Phi}(t, s)}{\partial t^2} = 0\] (38)

and the constraint (28):
\[\left| \frac{\partial \Phi(t, s)}{\partial s} \right|^2 = 1\] (39)
The solutions of Eqs. (38) are of the form:

$$\Phi_{cl}(t, s) = a(s) + tb(s) \quad \bar{\Phi}_{cl}(t, s) = \bar{a}(s) + t\bar{b}(s)$$  \hspace{1cm} (40)$$

$a$ and $b$ are complex functions of $s$ and $\bar{a}, \bar{b}$ are their complex conjugates. If we put

$$a(s) = \frac{t_f\Phi_i(s) - t_i\Phi_f(s)}{t_f - t_i} \quad b(s) = \frac{1}{t_f - t_i}(\Phi_f(s) - \Phi_i(s))$$  \hspace{1cm} (41)$$

then Eq. (40) represents the evolution of a chain which during the time $t_f - t_i$ passes from an initial conformation $\Phi_i(s)$ to a final conformation $\Phi_f(s)$ for $0 \leq s \leq L$. The constraint (28) requires additionally that $b$ and $\bar{b}$ are constants independent of $s$ and that:

$$\partial_s a(s) = e^{i\tilde{\varphi}(s)} \quad \partial_s \bar{a}(s) = e^{-i\tilde{\varphi}(s)}$$  \hspace{1cm} (42)$$

where $\tilde{\varphi}(s)$ describes the angles of a given static conformation of the chain. Going to the real coordinates $x(t, s)$ and $y(t, s)$ of Eq. (30), this implies that:

$$x_{cl}(t, s) \equiv x_{cl}(s) = \int_0^s du \cos \tilde{\varphi}(u) + l_1 \cos \varphi_1$$  \hspace{1cm} (43)$$

$$y_{cl}(t, s) \equiv y_{cl}(s) = \int_0^s du \sin \tilde{\varphi}(u) + l_1 \sin \varphi_1$$  \hspace{1cm} (44)$$

We note that in the above equation we have put $b = \bar{b} = 0$, so that there is no dependence on the time. This is required by condition (35), which demands that the beginning of the chain is fixed at the point $(l_1 \cos \varphi_1, l_1 \sin \varphi_1)$. In other words, in the absence of interactions, the conformation of the chain does not change in time. This is not surprising. In fact, we note that, in the passage from the discrete kinetic energy $K^{2d}_{disc}$ to its continuous counterpart, the term $\sum_{n=1}^N \sum_{k=1}^{n-1} \frac{l_2}{r_{n-k+1}^2} \frac{m_n}{m} \dot{r}_{n-k+1}^2$ which was present in $K^{2d}_{disc}$ disappeared after performing the limit $a \rightarrow 0$. This fact, together with the conditions (21), which fix one of the ends of the chain, make the classical dynamics of the ideal chain trivial.

As anticipated in the previous Section, it is now easy to add the interactions. For example, let us suppose that the segments of the chain are immersed in an external potential $V_{ext}(r)$ and that there are also internal interactions associated to a two-body potential $V_{int}(r_1, r_2)$. In this case, Eq. (27) generalizes to:

$$\mathcal{A} = \mathcal{A}_0 + \mathcal{A}_{ext} + \mathcal{A}_{int}$$  \hspace{1cm} (45)$$

where $\mathcal{A}_0$ has been defined in Eq. (37), while

$$\mathcal{A}_{ext} = \int_{t_i}^{t_f} dt \int_0^L ds V_{ext}(\mathbf{R}(t, s))$$  \hspace{1cm} (46)$$
and
\[ A_{\text{int}} = \int_{t_i}^{t_f} dt_1 \int_0^L ds_1 \int_{t_i}^{t_f} dt_2 \int_0^L ds_2 V_{\text{int}}(R(t_1, s_1), R(t_2, s_2)) \] (47)

Alternatively, if one wishes to express \( A_{\text{ext}} \) and \( A_{\text{int}} \) as functionals of \( \Phi(t, s) \) and \( \bar{\Phi}(t, s) \) it is possible to exploit Eqs. (46).

IV. DYNAMICS OF A CHAIN IMMERSED IN A THERMAL BATH

At this point we are ready to study the dynamics of a chain fluctuating in a solution at fixed temperature \( T \). Once the action of the system is known, it is possible to introduce the dynamics using a path integral approach. To this purpose, we consider the following probability distribution:

\[ \Psi^{2d} = \int_{\Phi(t_f, s) = \Phi_f(s)} D\Phi(t, s) D\bar{\Phi}(t, s) \exp \left( -\frac{A}{k_B T} \right) \delta(|\partial_s \Phi(t, s)|^2 - 1) \] (48)

where \( A \) is the action of Eqs. (45)–(47). The boundary conditions for the complex conjugated field \( \bar{\Phi} \) do not appear in Eq. (48), because they are fixed by the boundary conditions of the field \( \Phi \) due the constraint (28), which is imposed in Eq. (48) by means of the Dirac \( \delta \)–function. Let us also note that due to that constraint the action \( A \) may be written in a form which resembles more that of a two dimensional field theory:

\[ A = \frac{M}{2L} \int_{t_i}^{t_f} dt \int_0^L ds |\nabla \Phi(t, s)|^2 + A_{\text{ext}} + A_{\text{int}} \] (49)

with \( \nabla = (\partial_t, \partial_s) \). The actions \( A_{\text{ext}} \) and \( A_{\text{int}} \) are useful in order to describe the interactions of the chain with itself and with the surrounding environment. The distribution \( \Psi^{2d} \) gives the probability that a chain of length \( L \) starting from an initial conformation \( \Phi_i(s) \) at time \( t = t_i \) arrives to a final conformation \( \Phi_f(s) \) at the instant \( t = t_f \) after fluctuating in a thermal bath held at constant temperature \( T \). To understand how this probability is computed by means of the path integral appearing in the right hand side of Eq. (48) it is helpful to look at Fig. 2 [18]. During its motion in the time interval \([t_i, t_f]\) the chain spans a surface \( \Sigma \). In Eq. (48) it is performed a sum over all possible surfaces of this type. If the temperature \( T \) is zero, the chain moves according to the classical equations of motion. In that case, the conformations of minimal energy are favored and the energy is conserved along the motion at each instant. If however the temperature is different from zero, the energy does not need to be conserved in time, because of the thermal fluctuations. The conformations for
FIG. 2: In its motion from the initial conformation $\Phi_i(s)$ to the final conformation $\Phi_f(s)$ the chain spans a two dimensional surface in the space.

which the energy is not minimal are suppressed in the exponential $\exp\left(-\frac{\mathcal{A}}{k_BT}\right)$ appearing in Eq. (48), but may still give a relevant contribution to the whole path integral if their number is overwhelming with respect to the conformations of minimal energy.

Let us now discuss the boundary conditions which appear in the path integrals of Eq. (48). Since the interactions are not relevant in the present context, we will consider just ideal chains. It is also convenient to reformulate Eq. (48) in terms of the real variables $x(t, s)$ and $y(t, s)$:

$$
\Psi^{2d} = \int_{R(t_i, s) = R_i(s)} \int_{R(t_f, s) = R_f(s)} \mathcal{D}x(t, s) \mathcal{D}y(t, s) e^{-\frac{\mathcal{A}_0}{M} \int ds \delta \left( \left( \partial_s x \right)^2 + \left( \partial_s y \right)^2 - 1 \right)}
$$

where

$$
\mathcal{A}_0 = \frac{M}{2L} \int_{t_i}^{t_f} \int_0^L ds \dot{R}^2(t, s)
$$

Apart from the boundary conditions:

$$
R(t_f, s) = R_f(s)
$$

$$
R(t_i, s) = R_i(s)
$$

and

$$
R(t, 0) = (l_1 \cos \varphi_1, l_1 \sin \varphi_1)
$$

one could also add the requirement that the chain forms a closed loop. This further condition is implemented by the constraint:

$$
R(t, 0) = R(t, L)
$$
Eq. (55) constrains the two ends of the chain, occurring when \( s = 0 \) and \( s = L \), to coincide with the fixed point \((l_1 \cos \varphi_1, l_1 \sin \varphi_1)\) at any instant \( t \). It is cumbersome to keep track of all these boundary conditions within the path integral, so that it becomes preferable to expand the fields \( \mathbf{R}(t, s) \) around a classical background:

\[
\mathbf{R}(t, s) = \mathbf{R}_{cl}(t, s) + \mathbf{R}_q(t, s)
\]  

We first concentrate ourselves on the background. Due to the fact that there we assumed that the chain is ideal, the classical fields \( \mathbf{R}_{cl}(t, s) \) can be chosen among those which obey the free equations of motion associated to the action \( A_0 \) of Eq. (51):

\[
\ddot{\mathbf{R}}_{cl}(t, s) = 0
\]  

The above equation should be solved in such a way that its solutions satisfy the boundary conditions (52) – (54), but not the constraint (28), because this is taken into account separately by the \( \delta \) functions appearing Eq. (50). Explicitly, one may write the general expression of \( \mathbf{R}_{cl}(t, s) \) as follows:

\[
\mathbf{R}_{cl}(t, s) = \frac{t_f \mathbf{R}_i(s) - t_i \mathbf{R}_f(s)}{t_f - t_i} + \frac{t}{t_f - t_i} (\mathbf{R}_f(s) - \mathbf{R}_i(s))
\]

The boundary condition (54) is fulfilled by requiring that \( \mathbf{R}_i(0) = \mathbf{R}_f(0) = (l_1 \cos \varphi_1, l_1 \sin \varphi_1) \). If one wishes to add closed loop condition (55), one has to ask additionally that:

\[
\mathbf{R}_r(0) = \mathbf{R}_r(L) = \mathbf{R}_0(0) = \mathbf{R}_0(L) = (l_1 \cos \varphi_1, l_1 \sin \varphi_1)
\]

Let’s now discuss the component \( \mathbf{R}_q(t, s) \) appearing in Eq. (56). It describes the statistical fluctuations around the classical background \( \mathbf{R}_{cl}(t, s) \). Since the non-trivial boundary conditions are already taken into account by the background, \( \mathbf{R}_q(t, s) \) has a trivial behavior at the boundary:

\[
\mathbf{R}_q(t_i, s) = \mathbf{R}_q(t_f, s) = 0
\]

After having split the fields \( \mathbf{R}(t, s) \) as in Eq. (56), the probability distribution (50) becomes:

\[
\Psi^{2d} = \exp \left( -\frac{A_0(\mathbf{R}_{cl})}{k_B T} \right) \\
\times \int \mathcal{D}\mathbf{R}_q(t, s) \exp \left( -\frac{A_0(\mathbf{R}_q)}{k_B T} \right) \delta \left( (\partial_s \mathbf{R}_{cl}^2) + (\partial_s \mathbf{R}_q^2) + 2\partial_s \mathbf{R}_{cl} \cdot \partial_s \mathbf{R}_q - 1 \right)
\]  

(61)
where $A_0(R_{cl})$ contains just the classical field conformations:

$$A_0(R_{cl}) = \frac{M}{L(t_f - t_i)} \int_0^L ds \left( R_f(s) - R_i(s) \right)^2 \quad (62)$$

while the statistical fluctuations are in $A_0(R_q)$:

$$A_0(R_q) = \frac{M}{2L} \int_{t_i}^{t_f} dt \int_0^L ds \dot{R}_q^2 \quad (63)$$

After introducing a Lagrange multiplier $\lambda(t, s)$, it is possible to write in Eq. (61) as follows:

$$\Psi^{2d} = \exp \left[ -\frac{A_0(R_{cl})}{k_B T} \right] \times \int DR_q(t, s) \exp \left[ -\frac{A_0(R_q)}{k_B T} \right] \times \exp \int_{t_i}^{t_f} dt \int_0^L ds \left[ -\lambda(t, s) \left( (\partial_s R_{cl})^2 + (\partial_s R_q)^2 + 2 \partial_s R_{cl} \cdot \partial_s R_q - 1 \right) \right] \quad (64)$$

After the field splitting of Eq. (56), one has to deal only with the statistical fluctuations $R_q$, whose boundary conditions are trivial. In this way it becomes in principle possible to eliminate the $R_q$'s from the path integral (63) by performing a gaussian integration. Finally, let us discuss when it is convenient to split the fields as in Eq. (56). We know already from Section II that the constraint (28) forces the identity $R_f(s) - R_i(s) = 0$ in Eq. (58) as in the case of the classical solutions (43) and (44). For this reason, if the final and initial conformations $R_f(s)$ and $R_i(s)$ are chosen to be very different, it is licit to expect that the statistical fluctuations $R_q(t, s)$ will not be small, since they are needed to restore the constraint (28). Thus, from a perturbative point of view, it is possible to consider the fluctuations $R_q(t, s)$ as small perturbations only if $R_f(s) \sim R_i(s)$, i.e.

$$|R_f(s) - R_i(s)| < \epsilon \quad (65)$$

with $\epsilon$ being a small constant parameter.

V. THE THREE DIMENSIONAL CASE

In this Section we consider a chain of $N$ segments $P_i P_{i-1}$ of fixed lengths $l_i$, $i = 2, \ldots, N$, in three dimensions. Using spherical coordinates, the positions of the end points of the segments $P_i(t) = (x_i(t), y_i(t), z_i(t))$ are given by:

$$x_n(t) = \sum_{i=1}^N l_i \cos \varphi_i(t) \sin \theta_i(t)$$
$$y_n(t) = \sum_{i=1}^N l_i \sin \varphi_i(t) \sin \theta_i(t) \quad n = 1, \ldots, N$$
$$z_n(t) = \sum_{i=1}^N l_i \cos \theta_i(t) \quad (66)$$
For simplicity, the kinetic energy $K^3_{\text{disc}}$ of the system will be computed in the particular case in which the chain is attached at the origin of the coordinates, i.e.

$$P_1 = (0, 0, 0) \quad l_1 = \dot{l}_1 = 0$$

(67)

After a long but straightforward calculation, the result is:

$$K^3_{\text{disc}} = \sum_{n=1}^{N} \sum_{k=1}^{N-1} \frac{m_n l^2}{2} \beta_{n-k+1} \sin^2 \theta_{n-k+1} + \sum_{n=1}^{N} \sum_{k=1}^{N-1} \frac{m_n l^2}{2} \beta_{n-k+1}^2$$

$$+ \sum_{n=1}^{N} \sum_{k=1}^{N-1} \sum_{i=2}^{n-k} m_n l_i l_{n-k+1} \left[ \dot{\beta}_i \dot{\beta}_{n-k+1} \sin \theta_i \sin \theta_{n-k+1} \cos (\varphi_{n-k+1} - \varphi_i) \right]$$

(68)

It is now possible to pass to the limit of a continuous chain $a \rightarrow 0$ and $N \rightarrow +\infty$. Making the same assumptions of uniform length and mass distributions as in Eqs. (19) and (20), we get after some algebra:

$$K^3 = \frac{M}{L} \int_0^L ds (L - s) \int_0^s dv \left[ \dot{\beta}(t, v) \dot{\beta}(t, s) \sin \theta(t, v) \sin \theta(t, s) \cos (\varphi(t, s) - \varphi(t, v)) \right]$$

$$+ \dot{\beta}(t, v) \dot{\beta}(t, s) \sin \theta(t, v) \sin \theta(t, s) \sin (\varphi(t, v) - \varphi(t, s))$$

$$+ \dot{\beta}(t, s) \dot{\beta}(t, v) \sin \theta(t, v) \sin \theta(t, s) \cos (\varphi(t, s) - \varphi(t, v))$$

$$+ \dot{\beta}(t, v) \dot{\beta}(t, s) \cos \theta(t, v) \cos \theta(t, s) \cos (\varphi(t, s) - \varphi(t, v)) + \sin \theta(t, v) \sin \theta(t, s)) \right]$$

(69)

This is the three dimensional analog of Eq. (22).

The kinetic energy of (69) is complicated, but from the lesson of the two dimensional case we know how to simplify it. First of all, we note that the kinetic energy of the discrete chain may be written in terms of the cartesian coordinates (66) as follows:

$$K^3_{\text{disc}} = \sum_{n=2}^{N} \frac{m_n}{2} (\dot{x}_n^2 + \dot{y}_n^2 + \dot{z}_n^2)$$

(70)

where $x_n$, $y_n$ and $z_n$ have been defined in Eq. (66). The sum over $n$ starts from 2 because one end of the chain coincides with the origin of the axes, so that $l_1 = 0$. Of course, due to the condition that each segment has a fixed length $l_i$, Eq. (70) must be completed by the following constraints:

$$(x_n - x_{n-1})^2 + (y_n - y_{n-1})^2 + (z_n - z_{n-1})^2 = l_i^2 \quad n = 2, \ldots, N$$

(71)
At this point we have two choices. Either we keep the kinetic energy in the simple form of Eq. (70) at the price of having to deal with the constraints (71), or we solve those constraints using spherical coordinates $l_i, \theta_i, \phi_i$, as it has been done in Eq. (66). In the latter case, we have the complicated expression of the kinetic energy of Eq. (69) and there is the problem of defining a path integration over spherical coordinates. In the continuous limit, the situation does not change substantially. After performing the continuous limit following the prescriptions of Section II, the kinetic energy of Eq. (70) and the constraints (71) are respectively replaced by:

$$K^{3d} = \frac{M}{2L} \int_0^L ds \left[ (\partial_t x(t, s))^2 + (\partial_t y(t, s))^2 + (\partial_t z(t, s))^2 \right]$$  \hspace{1cm} (72)

and

$$(\partial_s x(t, s))^2 + (\partial_s y(t, s))^2 + (\partial_s z(t, s))^2 = 1$$  \hspace{1cm} (73)

The constraint (73) can be eliminated by introducing spherical coordinates $\theta(t, s), \varphi(t, s)$:

$$x(t, s) = \int_0^s du \cos \varphi(t, u) \sin \theta(t, u)$$  \hspace{1cm} (74)

$$y(t, s) = \int_0^s du \sin \varphi(t, u) \sin \theta(t, u)$$  \hspace{1cm} (75)

$$z(t, s) = \int_0^s du \cos \theta(t, u)$$  \hspace{1cm} (76)

If one makes the coordinate substitutions of Eqs. (74–76) in the kinetic energy (72) and applies the formula (17), one arrives exactly at the expression of the kinetic energy (69). Thus, Eq. (69) and Eq. (72) together with the constraint (73) are equivalent.

To construct of the probability distribution $\Psi^{3d}$ in three dimensions we choose the approach in which the the coordinates $x(t, s), y(t, s)$ and $z(t, s)$ are independent and the right number of degrees of freedom is restored by the condition (73). The result is similar to that of the two dimensional case:

$$\Psi^{3d} = \int_{R(t_i, s) = R_f(s)} DR(t, s) \exp \left\{ -\frac{A_0^{3d}}{k_B T} \right\} \delta((\partial_s R)^2 - 1)$$  \hspace{1cm} (77)

where

$$A_0^{3d} = \frac{M}{2L} \int_{t_i}^{t_f} dt \int_0^L ds \left[ (\partial_t x(t, s))^2 + (\partial_t y(t, s))^2 + (\partial_t z(t, s))^2 \right] = \frac{M}{2L} \int_{t_i}^{t_f} dt \int_0^L ds \hat{R}^2$$  \hspace{1cm} (78)

The above expression of the probability distribution has been obtained assuming that one end of the chain is attached at the origin according to the condition of Eq. (67). However,
using translational invariance, it is easy to check that Eqs. (77) and (78) remain valid also if the chain has one of its ends fixed at any other given point $R_{\text{fixed}}$, so that to complete the set of boundary conditions of Eq. (77) we may add the following requirement:

$$R(t, 0) = R_i(0) = R_{\text{fixed}}(0)$$  \hspace{1cm} (79)

$R_{\text{fixed}}(0)$ being a fixed point.

VI. CHAINS WITH CONSTANT ANGLE OF BENDING

The approach presented above in order to treat the dynamics of random chains has some interesting variants which we would like to discuss in this Section. To this purpose, we choose the formulation in which the positions of the ends of the segments composing the chain are given in cartesian coordinates. As we have already seen, in this way the expression of the kinetic energy $K_{\text{disc}}^{3d}$ is simply:

$$K_{\text{disc}}^{3d} = \frac{1}{2} \sum_{n=1}^{N} m_n (\dot{x}_n^2 + \dot{y}_n^2 + \dot{z}_n^2)$$  \hspace{1cm} (80)

However, one has to take into account also the constraints:

$$(x_n - x_{n-1})^2 + (y_n - y_{n-1})^2 + (z_n - z_{n-1})^2 = l_n^2 \quad n = 2, \ldots, N$$  \hspace{1cm} (81)

We assume as before that all segments have the same fixed length $l_n = a$, but additionally we require that:

$$(z_n - z_{n-1})^2 = b^2 \leq a^2$$  \hspace{1cm} (82)

This implies that the projection of each segment onto the $z$–axis has length $\pm b$, so that the segments are bound to form with the $z$–axis the fixed angles $\alpha_1 = \alpha$ or $\alpha_2 = (\pi - \alpha)$ defined by the relations:

$$\cos \alpha_1 = \frac{b}{a} \quad \cos \alpha_2 = -\frac{b}{a}$$  \hspace{1cm} (83)

Clearly, in both cases the constraints (81) and (82) may be rewritten as follows:

$$\frac{(x_n - x_{n-1})^2}{b^2} + \frac{(y_n - y_{n-1})^2}{b^2} = \frac{1}{\cos^2 \alpha} - 1 \quad n = 2, \ldots, N$$  \hspace{1cm} (84)

We suppose now that only the angle $\alpha_1$ is allowed, so that the chain cannot make turns in the $z$ direction. An example of a conformation of a chain satisfying these assumptions is
FIG. 3: Example of motion of a chain whose segments are constrained to form a fixed angle $\alpha$ with the $z-$axis. In the figure $\alpha = 30^\circ$

given in Fig 3. The constraints (84) are solved by choosing spherical coordinates, in which however the angles $\theta_n$ formed by the segments with the $z-$axis are always equal to $\alpha$:

$$x_n(t) = \sum_{i=1}^{n} l_i \cos \varphi_i(t) \sin \alpha$$  \hspace{1cm} (85)$$

$$y_n(t) = \sum_{i=1}^{n} l_i \sin \varphi_i(t) \sin \alpha$$  \hspace{1cm} (86)$$

$$z_n(t) = \sum_{i=1}^{n} l_i \cos \alpha = n \cos \alpha$$  \hspace{1cm} (87)$$

As we see from the above equation, each segment is left only with the freedom of rotations around the $z-$direction, corresponding to the angles $\varphi_i(t)$. Moreover, the total length of the chain is always $L = Na$, but now also the total height $h$ of the trajectory along the $z-$axis is fixed:

$$h = Nb$$  \hspace{1cm} (88)$$

At this point, we pass to the continuous limit, this time taking as parameter describing the trajectory of the chain the variable $z$ instead of the arc-length $s$. Due to the last of Eqs. (87), the $z-$components of the velocities are always zero:

$$\dot{z}_n(t) = 0$$  \hspace{1cm} (89)$$
As a consequence, we are left with a two dimensional problem, which may be treated in exactly the same way as we treated the two dimensional chain of Section II. The only difference is that Eqs. (2) should be replaced by Eqs. (85) and (86) and the constraints have a slightly different form. Following the same procedure presented in Section II we find after a few calculation the expression of the kinetic energy:

$$K^{3d}_\alpha = \tan^2 \alpha \int_0^h dz \int_0^z dz_1 \int_0^{z_2} dz_2 \rho_m(t, z) \rho_l(t, z - z_1) \rho_l(z_2)$$

$$\times \dot{\varphi}(t, z - z_1) \dot{\varphi}(t, z_2) \cos(\varphi(t, z - z_1) - \varphi(t, z_2))$$  \hspace{1cm} (90)

and of the constraint (84):

$$\left(\frac{\partial z}{\partial x}\right)^2 + \left(\frac{\partial z}{\partial y}\right)^2 = \tan^2 \alpha$$ \hspace{1cm} (91)

Apart from the appearance of the factor $\tan^2 \alpha$ and the choice of the height $z$ instead of the arc-length $s$, Eqs. (90) and (91) are identical to Eqs. (14) and (71) in the limit $l(t) = \dot{l}(t) = 0$.

It is now not difficult to show that the probability distribution $\Psi^{3d}_\alpha$ is given by:

$$\Psi^{3d}_\alpha = \int Dx(t, z) Dy(t, z) \exp \left\{ -\frac{A_{0,\alpha}}{k_BT} \right\} \delta((\partial_z x)^2 + (\partial_z y)^2 - \tan^2 \alpha)$$ \hspace{1cm} (92)

where

$$A_{0,\alpha} = \tan^2 \alpha \int_{t_i}^{t_f} dt \int_0^h dz \left[ \dot{x}^2 + \dot{y}^2 \right]$$ \hspace{1cm} (93)

At this point we discuss briefly the case in which both angles $\pi - \alpha$ and $\alpha$ are allowed. In this situation, the trajectory of the chain may have turns. An example of motion of this kind is given in Fig 4. The constraints (81) and (82) remain unchanged, but the coordinate $z$ cannot be chosen as a valid parameter of the trajectory of the chain and one has to come back to the arc-length $s$. The most serious problem occurs due to the fact that the variables $z_n(t)$ are not continuous functions of the time, since each $z_n(t)$ is allowed to jump discretely between the two discrete values $+b$ and $-b$, corresponding to the angles $\alpha$ and $\pi - \alpha$ respectively. It is therefore difficult to define the components $\dot{z}_n$ of the velocities of the ends of the segments and thus their contribution to the kinetic energy. Let us note that this problem affects only the $z$ degrees of freedom. The degrees of freedom $x_n(t)$ and $y_n(t)$ of the chain remain continuous functions of $t$ despite the jumps of the $z_n$’s. This fact can be easily verified looking at the definition of $x_n(t)$ and $y_n(t)$ in Eqs. (85) and (86). Since $\sin(\pi - \alpha) = \sin \alpha$, both the $x_n(t)$’s and $y_n(t)$’s are not affected by the jumps of the angle $\alpha \leftrightarrow \pi - \alpha$. The situation simplifies only if the chain has no interactions in which the $z$
FIG. 4: Example of motion of a chain whose segments are constrained to form fixed angles \( \alpha \) or \( \pi - \alpha \) with the \( z \)-axis. In the figure \( \alpha = 30^\circ \). Turning points are emphasized by means of black points.

A variable is involved. The reason is that in the kinetic energy and in the constraints given by Eqs. (80–82) the degrees of freedom connected to the motion along the \( z \)-directions are decoupled from the other degrees of freedom and may be ignored. As a consequence, in absence of \( z \)-dependent interactions, the difficulties related to the motion along the \( z \)-direction disappear and once again the problem reduces to that the two dimensional chain treated in Section II. Since the constraints are always those of Eqs. (80–82) one may proceed as in the case of fixed angle \( \alpha \). As a result, one finds that the final probability distribution is of the form:

\[
\Psi_{3d,\pi-\alpha} = C \int \mathcal{D}x(t, s) \mathcal{D}y(t, s) \exp \left\{ -\frac{A_{0,\alpha,\pi-\alpha}}{k_B T} \right\} \delta((\dot{x})^2 + (\dot{y})^2 - \tan^2 \alpha) \tag{94}
\]

where

\[
A_{0,\alpha,\pi-\alpha} = \sin^2 \alpha \int_{t_i}^{t_f} dt \int_0^L ds \left[ \dot{x}^2 + \dot{y}^2 \right] \tag{95}
\]

and \( C \) is a constant containing the result of the integration over the decoupled \( z \) degrees of freedom. Let us note in Eqs. (94) and (95) the appearance of the factor \( \sin^2 \alpha \) in the action instead of \( \tan^2 \alpha \) and the replacement of \( z \) with the arc-length \( s \) as the parameter of the trajectory of the chain.
VII. CONCLUSIONS

The dynamics of a random chain has been discussed both from the classical and statistical point of view. The classical energy of the chain has been derived in two and three dimensions. We have mainly concentrated ourselves on the computation of the kinetic energy because the addition of the contribution of the interactions to the total energy is straightforward, see Eqs. (46) and (47). The kinetic energy on the contrary has a complicated and non-Markoffian expression as shown by Eq. (9) in two-dimensions and by Eq. (68) in three dimensions. After passing to the continuous limit discussed in Section II, one term disappears from the kinetic energy. This is the reason for which in the continuous case the classical equations of motion have simple solutions of the form given in Eqs. (13)–(14). Let us note that the passage to the continuous limit is straightforward and does not need mathematical subtleties as the analogous limit by which the Edwards model is obtained in the statistical mechanics of random chains.

The stringy approach to the dynamics of random chains is formulated in Section IV. One would naively expect that the final model is related with non-relativistic string theories, such as those derived in Refs. [13], but this is not the case. In two and three dimensions the probability distributions $\Psi^{2d}$ and $\Psi^{3d}$ are respectively given in Eqs. (48) and (77)–(78). As it is possible to see from these equations, the path integral sums which provide the expressions of $\Psi^{2d}$ and $\Psi^{3d}$ have the form of a $O(n)$ nonlinear sigma model on a two dimensional world-sheet, where $n = 2, 3$ depending on the dimensionality of the physical space in which the chains fluctuate. The difference with respect to the nonlinear sigma model is that here the derivatives of the fields with respect to the arc-length $s$ are subjected to the condition $(\partial_s R)^2 = 1$. In standard nonlinear sigma models it is instead the modulus of the fields themselves to be constrained. The presence of a complicated constraint and the absence of a small parameter which could be used to start a perturbative expansion complicate the computation of the probability functions. For this reason, in Section IV it has been proposed the field splitting (56). This splitting provides a convenient way to deal with the boundary conditions satisfied by the fields $R(t, s)$ and also allows a perturbative treatment provided the initial and final conformations $R_i(s)$ and $R_f(s)$ do not differ very much in the sense of Eq. (65). Alternatively, the statistical fluctuations $R_q(t, s)$ may be eliminated from the partition function of Eq. (64) with a Gaussian integration [19], but then one ends up with
a complicated two dimensional field theory in which the Lagrange multipliers $\lambda(t, s)$ are coupled together with the classical background $\mathbf{R}_{cl}(t, s)$. Another possibility in order to simplify the model consists in relaxing the constraint $(\partial_s \mathbf{R})^2 = 1$, imposing for instance the weaker condition $\frac{1}{T_L} \int_{t_i}^{t_f} dt \int_0^L ds (\partial_s \mathbf{R})^2 = 1$. This constraint requires that the average length of the chain in the interval of time $t_i \leq t \leq t_f$ is $L$. In this case the Lagrange multiplier $\lambda$ does no longer depend on $t$ and $s$ and calculations become easier. It would also be interesting to study the probability functions $\Psi^{2d}$ and $\Psi^{3d}$ in the limit $t_f \rightarrow +\infty$ and $t_i \rightarrow -\infty$ or to sum them over all possible values of the initial and final conformations $\mathbf{R}_i(s), \mathbf{R}_f(s)$.

Finally, chains with fixed angles have been discussed in Section VI. Our approach is valid only if the chain has no turning points. If there are turning points the kinetic energy is not well defined, because the variable $z(t, s)$ is no longer a continuous function and thus its time derivative becomes a distribution. One way for adding to our treatment turning points as those of Fig. [4] is to replace the variable $z$ with a stochastic variable which is allowed to take only discrete values. Another way is to look at turning points as points in which the chain bounces against an invisible obstacle. A field theory describing a one-dimensional chain with such kind of non-holonomic constraints has been already derived in Refs. [14]. The problem of turning points is currently work in progress, as well as the possibility of imposing topological constraints on the trajectory of the chain.

[1] M. Doi and S.F. Edwards, The Theory of Polymer Dynamics (Clarendon Press, Oxford, 1986).
[2] P. E. Rouse, J. Chem. Phys. 21 (1953), 1272.
[3] B. H. Zimm, J. Chem. Phys. 24 (1956), 269.
[4] H. Yamakawa, Ann. Rev. Phys. Chem. 35, 23, 1984
[5] P.H. Verdier and W.H. Stockmayer, J. Chem. Phys, 36, 227, 1962
[6] A. Dua and T.A. Vilgis, Phys. Rev E, 71, 021801, 2005
[7] J. Zinn - Justin, Quantum Field Theory and Critical Phenomena, Clarendon Press, Oxford, 2002,
[8] H. Kleinert, Path Integrals in Quantum Mechanics, Statistics, Polymer Physics, and Financial Markets, (World Scientific Publishing, 3nd Ed., Singapore, 2003).
[9] M. Gell-Mann and M. Lévy, Nuovo Cim. 16 (1965), 705; B. W. Lee, Chiral Dynamics, Gordon
and Breach, 1972.

[10] S. Edwards, *Proc. Phys. Soc.* 91 (1967), 513; *J. Phys. A1* (1968), 15.

[11] W. Tomaszewski and P. Pieranski, *New Jour. Phys.* 7 (2005), 45. H. Kleinert, *Gauge Fields in Condensed Matter*, Vol 1, (World Scientific, 1990).

[12] H. Kleinert, *Gauge Fields in Condensed Matter*, Vol 1, (World Scientific, 1990).

[13] J. Gomis and H. Ooguri, *J. Math. Phys.* 42 (2001), 3127 [arXiv: hep-th/0009181]; U. H. Danielsson, A. Guijosa and M. Kruczenski, *JHEP* 0010 (2000), 020 [arXiv: hep-th/0009181].

[14] H. Arodź, P. Klimas and T. Tyranowski, *Acta Phys. Pol. B* 36 (2005). 3861; H. Arodź, *Acta Phys. Pol. B* 33 (2002). 1241; H. Arodź, *Acta Phys. Pol. B* 35 (2004). 625.

[15] Our result agrees with that of Ref. [11], where a similar calculation has been recently reported. Our expression of the kinetic energy of the chain is slightly more general, since both ends of the chain are free to move.

[16] An exhaustive discussion about the passage from discrete to continuous random chain systems may be found in [12].

[17] Let us note that in Eq. (28) and from now on we will use the following notations to denote partial derivatives in $t$ and $s$:

$$
\frac{\partial f(t,s)}{\partial t} = \partial_t f(t,s) = \dot{f}(t,s) \quad \frac{\partial f(t,s)}{\partial s} = \partial_s f(t,s) = f'(t,s)
$$

[18] For simplicity, in Fig. 2 it has been described a chain in which both ends are allowed to move. We should however remember that, from our construction, one end of the chain remains always fixed according to Eq. (36).

[19] F. Ferrari would like to thank L. Cugliandolo for suggesting this possibility.