Path-integral approach to the dynamics of a random chain with rigid constraints

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In this work the dynamics of a chain consisting of a set of beads attached to the ends of segments of fixed lengths is investigated. The chain fluctuates at constant temperature in a viscous medium. For simplicity, all interactions among the beads have been switched off and the number of spatial dimensions has been limited to two. In the limit in which the chain becomes a continuous system, its behavior may be described by a path integral, in which the rigid constraints coming from the infinitesimally small segments are imposed by means of a functional δ function. In this way a model of the dynamics of the chain is obtained, which closely resembles a two-dimensional nonlinear σ model. The partition function of this generalized nonlinear σ model is computed explicitly for a ring-shaped chain in the semiclassical approximation. The behavior of the chain at both long and short scales of time and distances is investigated. The connection between the generalized nonlinear σ model presented here and the Rouse model is discussed.

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I. INTRODUCTION

Subject of this work is a study of the dynamics of a continuous chain which is subjected to thermodynamic fluctuations at constant temperature T. The chain is represented as the limit of a system of beads and links of fixed length, in which the number N of beads becomes infinite, while the length a of the links goes to zero in such a way that the total length of the chain $L=Na$ remains a finite constant. Problems of this kind are encountered, for example, in polymer physics, because with some approximation long flexible polymers may be regarded as continuous chains [1]. It is thus spontaneous to consider an isolated polymer fluctuating in some viscous environment as a concrete realization of the system investigated here. A few applications in which the dynamics of a chain turns out to be relevant are mentioned in Ref. [2]. In particular, in Ref. [2] six regimes of the chain dynamics are distinguished, which apply not only to the well-known case of a polymer in a solution, but also to other cases, like for instance those of an isolated cold chain and of a hot polymer in the vapor phase.

From polymer physics, one may borrow the standard approach to the dynamics of a chain. It consists of considering the fluctuations of the chain as a stochastic process, which is usually described with the help of the Langevin equations or, alternatively, of the Fokker-Planck-Smoluchowski equations [1]. This approach leads to the well-known models of Rouse [3] and Zimm [4] which allow a satisfactory understanding of the main properties of polymers in solutions. One major drawback of these coarse-grained models is that they do not take into account the rigid constraints which are necessary in order to keep constant the length of the links connecting the beads. The Rouse and Rouse-Zimm equation consider instead beads joined together by springs, where the local spring is infinitely extensible. In this way the length of the chain is not fixed and is allowed to become infinite. Moreover, in the continuous limit the Rouse equation is nothing but the stochastic equation (Langevin equation) for the classical Wiener measure, which yields paths without well-defined tangent vectors [1]. These problems have been tackled by various attempts, see, e.g., [5,6]. However, the correct use of rigid constraints in (stochastic) dynamics requires some mathematical effort [7,8], in contrast to the static cases where rigid constraints can be implemented by Dirac δ functions in the partition functions. For instance, the probability distribution of N ideal closed chains topologically linked together may be represented as a path integral of N noninteracting particles with the insertion of Dirac δ functions which enforce the topological constraints on their trajectories [9–12].

Here a strategy similar to that used for static chains will be applied to dynamics. We consider the distribution Ψ_{disc} of the probability that a fluctuating chain passes from a initial discrete spatial conformation Γ_i to a final one Γ_f in a given interval of time $\Delta t=t_f-t_i$. The idea behind our approach is based on the fact that the beads of the chain may be regarded as a set of N Brownian particles with constrained trajectories. The constraints arise due to the presence of the $N-1$ links of fixed lengths connecting the beads. As a consequence, it is possible to write the probability distribution Ψ_{disc} in the form of a path integral describing the fluctuations of N Brownian particles with the insertion of Dirac δ functions. The latter are needed in order to impose the necessary conditions on the trajectories of the particles. For simplicity, possible interactions among the beads have been switched off, including hydrodynamic interactions and only the two-dimensional case has been discussed.

The limit in which the chain becomes continuous is not entirely trivial. It involves the vanishing of three crucial quantities, the mass of the beads, their mobility and their size. After performing this limit very carefully, we obtain as a final result the probability distribution Ψ of the continuous chain. It is found that Ψ consists of a path integral which closely resembles the partition function of a two-dimensional

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nonlinear σ model [13]. For this reason the obtained model will be called the generalized nonlinear σ model (GNLSM). The main difference from the nonlinear σ model is that the holonomic constraint is replaced in the GNLSM by a nonholonomic constraint, which requires that the tangent at every point of the trajectory of the chain is a unit vector. The Lagrange multiplier that imposes this nonholonomic constraint plays the same role of pressure in the hydrodynamics of incompressible fluids, a fact already noted in Ref. [2]. The "incompressibility" is related to the fact that it is not possible to "compress" the lengths of the links joining the beads. The GNLSM is well suited to study all situations in which it is possible to assume that the thermodynamic fluctuations and the conformational changes are small and slow. Systems satisfying these requirements are for instance cold chains or chains in a very viscous medium.

In principle, the GNLSM is exactly solvable after performing two Gaussian integrations, but the presence of nontrivial boundary conditions complicates the calculation of the probability distribution Ψ. Even the method of the effective potential, which is useful to investigate phase transitions in nonlinear σ models, cannot be easily applied. As a matter of fact, in the nonlinear σ model the effective potential is computed assuming that the field configurations which minimize the action are constants. However, in the GNLSM, configurations of this kind correspond to the situation in which the chain has collapsed to a point and are thus unphysical. Despite these difficulties, it is possible to compute the probability distribution Ψ and the associated generating functional of the correlation functions of the bond vectors $\Psi[J]$ using a background field approximation, in which small Gaussian fluctuations are considered in the background of a dominating classical conformation. The initial and final conformations of the chain are picked up by choosing in a suitable way the background classical solution and by tuning the boundary conditions of the Gaussian fluctuations. The semiclassical approximation is valid in the case of low temperatures or of highly viscous media, exactly the regimes in which the GNLSM can be applied. The explicit formulas of Ψ and $\Psi[J]$ derived here show that the fluctuations which deform the chain along directions which are tangent to the trajectory of the classical background conformation propagate differently from the normal fluctuations. This fact is a direct consequence of the presence of rigid constraints and could be relevant, for example, in the theory of formation of single polymer crystals [14].

The material presented in this paper is organized as follows. In Sec. II the form of the Lagrangian of a classical discrete chain in two dimensions has been derived in polar and in Cartesian coordinates. No restrictions are posed to the motion of the discrete chain. The limit to a continuous chain is however performed assuming that one of the ends of the chain is fixed. The calculation in polar coordinates shows that one crucial term in the Lagrangian disappears in the continuous limit. This fact simplifies the classical equations of motion of the chain. The probability distribution Ψ of the fluctuating chain is computed in Sec. III using a path-integral approach. Some subtleties arising when taking the continuous limit in the probability distribution of the discrete chain are discussed. Section IV is dedicated to the study of the classical solutions of the GNLSM. It is shown that the only possible classical solutions are time independent, apart from rigid translations with constant velocity of the whole chain. The computation of the probability distribution Ψ and of the generating functional $\Psi[J]$ for a ring-shaped chain is performed in the semiclassical approximation in Sec. V. The physical interpretation of the results obtained in the preceding sections is presented in Sec. VI. The equilibrium limit of the GNLSM and its connection with the Rouse model are studied in Sec. VII. Finally, in Sec. VIII the conclusions are drawn and possible future developments are discussed.

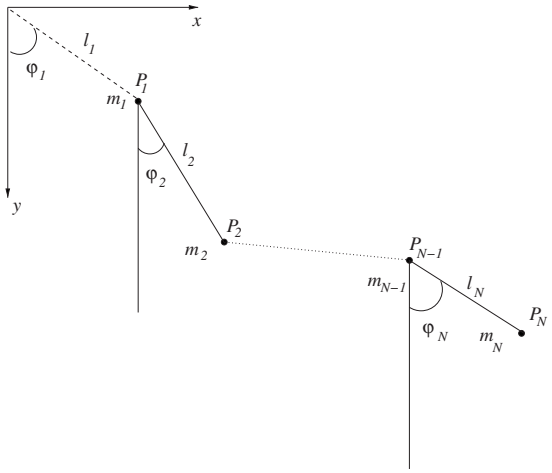

FIG. 1. A chain with N segments. Let us note that the end point P_1 is not bound to stay at a fixed distance with respect to the origin of the Cartesian reference system.

II. CLASSICAL DYNAMICS OF A CONTINUOUS CHAIN

Let us consider a discrete chain of $N-1$ 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

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

The segments are joined together at the points P_i, where $2 \leq i \leq N-1$, 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.

At this point we compute the kinetic energy of the above system,

$$K_{\text{disc}} = \sum_{i=1}^{N} \frac{m_i}{2}(\dot{x}_i^2 + \dot{y}_i^2). \tag{2}$$

The subscript "disc" on the left-hand side of Eq. (2) is to recall that we are considering at the moment a discrete chain with $N-1$ segments. For future purposes, it will be convenient to introduce the kinetic energy of point P_i,

$$K_i = \frac{m_i}{2}(\dot{x}_i^2 + \dot{y}_i^2). \tag{3}$$

Of course, to Eq. (2) one should also add the constraints

$$(x_i - x_{i-1})^2 + (y_i - y_{i-1})^2 = l_i^2, \quad i = 2, \ldots, N \tag{4}$$

in order to enforce the requirement that the segments have fixed length l_i. It is possible to eliminate these constraints passing to polar coordinates,

$$x_i = \sum_{j=1}^{i} l_j \cos\varphi_j, \quad y_i = \sum_{k=1}^{i} l_j \sin\varphi_j, \quad i = 1, \ldots, N. \tag{5}$$

φ_j is the angle formed by segment j with the y axis, see Fig. 1. According to our settings, the radial coordinates l_j are constants for $j=2,\ldots,N$. The length l_1, which denotes the distance of the end point x_1, y_1 from the origin, is not fixed, so that $l_1 = l_1(t)$ is allowed to vary with the time t. From Eq. (5) the velocity components of the ith segment may be written as follows:

$$\dot{x}_i = -\sum_{j=1}^{i-1} l_j\dot{\varphi}_j \sin\varphi_j - l_i\dot{\varphi}_i \sin\varphi_i + \dot{l}_1 \cos\varphi_1, \quad i = 2, \ldots, N, \tag{6}$$

$$\dot{y}_i = \sum_{j=1}^{i-1} l_j\dot{\varphi}_j \cos\varphi_j + l_i\dot{\varphi}_i \cos\varphi_i + \dot{l}_1 \sin\varphi_1, \quad i = 2, \ldots, N, \tag{7}$$

$$\dot{x}_1 = -l_1\dot{\varphi}_1 \sin\varphi_1 + \dot{l}_1 \cos\varphi_1, \tag{8}$$

$$\dot{y}_1 = l_1\dot{\varphi}_1 \cos\varphi_1 + \dot{l}_1 \sin\varphi_1. \tag{9}$$

Separating the contribution coming from the first $i-1$ variables as shown in Eqs. (6) and (7), the kinetic energy K_i of the ith point can be expressed in terms of the kinetic energy K_{i-1} of the $(i-1)$th segment,

$$K_i = \frac{m_i}{m_{i-1}}K_{i-1} + \frac{m_i}{2}l_i^2\dot{\varphi}_i^2 + m_i\sum_{j=1}^{i-1} l_i l_j \dot{\varphi}_i\dot{\varphi}_j \cos(\varphi_j - \varphi_i) + m_i l_i \dot{\varphi}_i \dot{l}_1 \sin(\varphi_1 - \varphi_i). \tag{10}$$

It is possible to solve the above recursion relation and to find a closed expression of K_i in polar coordinates. If we do that, at the end, the total kinetic energy of the discrete chain becomes

$$K_{\text{disc}} = \frac{M}{2}(l_1^2\dot{\varphi}_1^2 + \dot{l}_1^2) + l_1\dot{\varphi}_1 \sum_{i=1}^{N}\sum_{j=1}^{i-1} m_i l_{i-j+1}\dot{\varphi}_{i-j+1} \times \cos(\varphi_{i-j+1} - \varphi_1) + \dot{l}_1 \sum_{i=1}^{N}\sum_{j=1}^{i-1} m_i l_{i-j+1}\dot{\varphi}_{i-j+1} \times \sin(\varphi_1 - \varphi_{i-j+1}) + \sum_{i=1}^{N}\sum_{j=1}^{i-1} l_{i-j+1}^2 \frac{m_i}{2}\dot{\varphi}_{i-j+1}^2 + \sum_{i=1}^{N}\sum_{j=1}^{i-1}\sum_{k=2}^{i-j} m_i l_{i-j+1} l_k \dot{\varphi}_{i-j+1}\dot{\varphi}_k \times \cos(\varphi_{i-j+1} - \varphi_k), \tag{11}$$

where $M = \Sigma_{i=1}^{N} m_i$ is the total mass of the chain [23,15].

We wish now to perform the limit in which the chain of $N-1$ segments becomes a continuous system [24,16]. To this purpose, it is convenient to consider the indices $i, j, k, \ldots$ appearing in Eq. (11) as discrete variables taking values in a one-dimensional lattice with N points. Quantities f_i carrying the index i may be interpreted as discrete functions of i. Their variations Δf_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 $i \to s_i$, $f_i \to f(s_i)$, 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. (11) in the limit

$$N \to \infty, \quad a \to 0, \quad Na = L, \tag{12}$$

in which the product Na remains finite and is equal to the total length of the chain L. Clearly, in the limit (12), the right-hand side of Eq. (11) 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

$$l_i \to l(s_i) = a\sigma(s_i), \quad m_i \to m(s_i) = a\rho(s_i), \tag{13}$$

where $\sigma(s_i)$ and $\rho(s_i)$ are, respectively, the distribution of length and of mass along the chain. To be consistent with our settings, the distributions $\sigma(s_i)$ and $\rho(s_i)$ must be normalized as follows:

$$\sum_{i=1}^{N} \sigma(s_i)\Delta s_i = L, \quad \sum_{i=1}^{N} \rho(s_i)\Delta s_i = M. \tag{14}$$

While it would be interesting to study chains in which the segments are allowed to have different lengths and the points have different masses, for simplicity we will suppose from now on that the length and mass distributions in the chains are uniform, i.e.,

$$\sigma(s_i) = 1 \quad \text{for} \quad i = 2, \ldots, N \quad \text{and} \quad \rho(s_i) = \frac{M}{L} \quad \text{for} \quad i = 1, \ldots, N. \tag{15}$$

In the discrete case [compare with Eq. (13)] this implies that all segments of the chain and the masses m_i are equal,

$$l_i = a \quad \text{for} \quad i = 2, \ldots, N \quad \text{and} \quad m_i = \frac{M}{L}a \quad \text{for} \quad i = 1, \ldots, N. \tag{16}$$

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:

$$f(s_i) \to f(s), \quad \sum_{i=1}^{N} \Delta s_i \to \int_0^L ds. \tag{17}$$

After a few calculations one finds the following:

$$K_{\text{disc}}(t) \to K(t), \tag{18}$$

where

$$\begin{aligned} K(t) = {} & \frac{M}{2}[l_1^2(t)\dot{\varphi}_1^2(t) + \dot{l}_1^2(t)] + \dot{\varphi}_1(t) l_1(t) \frac{M}{L} \int_0^L ds \int_0^s du \dot{\varphi} \\ & \times (t, s-u) \cos[\varphi(t, s-u) - \varphi_1(t)] \\ & + \dot{l}_1(t) \frac{M}{L} \int_0^L ds \int_0^s du \dot{\varphi}(t, s-u) \sin[\varphi_1(t) - \varphi(t, s-u)] \\ & + \frac{M}{L} \int_0^L ds \int_0^s du \int_0^{s-u} dv \dot{\varphi}(t, s-u) \dot{\varphi}(t, v) \\ & \times \cos[\varphi(t, s-u) - \varphi(t, v)]. \end{aligned} \tag{19}$$

Let us note that the right-hand side of Eq. (19) contains four terms, while the original discrete version of the kinetic energy in Eq. (11) contained five terms. In fact, the contributions proportional to $\dot{\varphi}_{i-j+1}^2$ of Eq. (11) disappear in the continuous limit.

Equation (19) may be simplified by performing the following change of variables:

$$u' = s - u, \quad du' = -du. \tag{20}$$

Using also the formula

$$\int_0^L ds \int_0^s du' f(u') = \int_0^L ds (L-s) f(s), \tag{21}$$

which is valid for any integrable function $f(s)$, we obtain

$$\begin{aligned} K(t) = {} & \frac{M}{2}[l_1^2(t)\dot{\varphi}_1^2(t) + \dot{l}_1^2(t)] + \dot{\varphi}_1(t) l_1(t) \frac{M}{L} \\ & \times \int_0^L ds (L-s) \dot{\varphi}(t,s) \cos[\varphi(t,s) - \varphi_1(t)] + \dot{l}_1(t) \frac{M}{L} \\ & \times \int_0^L ds (L-s) \dot{\varphi}(t,s) \sin[\varphi_1(t) - \varphi(t,s)] + \frac{M}{L} \\ & \times \int_0^L ds (L-s) \int_0^s du \dot{\varphi}(t,s) \dot{\varphi}(t,u) \cos[\varphi(t,s) - \varphi(t,u)]. \end{aligned} \tag{22}$$

As a further simplification, one could fix the point P_1 in some location, so that

$$\dot{l}_1 = \dot{\varphi}_1 = 0. \tag{23}$$

Exploiting the above assumptions in Eq. (22), we find that the Lagrangian $\mathcal{L}_0(t) = K(t)$ of the ideal chain is given by

$$\begin{aligned} \mathcal{L}_0(t) = {} & \frac{M}{L} \int_0^L ds (L-s) \int_0^s du \dot{\varphi}(t,s) \dot{\varphi}(t,u) \cos[\varphi(t,s) \\ & - \varphi(t,u)]. \end{aligned} \tag{24}$$

What happens if, instead of polar coordinates, we choose Cartesian coordinates in order to compute the continuous limit of the kinetic energy (2)? With the help of the prescriptions given in Eqs. (12)–(17) and related comments, it is easy to show that the Lagrangian of the ideal chain $\mathcal{L}_{0,\text{disc}} = K_{\text{disc}}$ becomes in Cartesian coordinates

$$\mathcal{L}_0(t) = \frac{M}{2L} \int_0^L ds [\dot{x}^2(t,s) + \dot{y}^2(t,s)]. \tag{25}$$

Of course, the fields $x(t,s)$ and $y(t,s)$ are not independent, because they satisfy the relationship

$$[x'(t,s)]^2 + [y'(t,s)]^2 = 1, \tag{26}$$

where $x' = \frac{\partial x}{\partial s}$ and $y' = \frac{\partial y}{\partial s}$. Equation (26) is the continuous version of the constraints (4). As we see, the form of the kinetic energy is much simpler than that of its analog in polar coordinates, but the price to be paid is the cumbersome presence of the constraints (26). If l_1 and φ_1 are constants, according to the assumption of Eq. (23), one should also add to Eqs. (25) and (26) the boundary conditions

$$x(t,0) = l_1 \cos \varphi_1, \quad y(t,0) = l_1 \sin \varphi_1. \tag{27}$$

In this way one end of the chain is fixed at the given point $[x(t,0), y(t,0)] = (l_1 \cos \varphi_1, l_1 \sin \varphi_1)$. It is possible to implement other boundary conditions. For instance, one could ask that the chain forms a closed loop,

$$x(t,0) = x(t,L), \quad y(t,0) = y(t,L). \tag{28}$$

To show that the Lagrangian in Cartesian coordinates (25) and the Lagrangian in polar coordinates (24) are equivalent, it is possible to perform in Eq. (25) the field transformations

$$\begin{aligned} x(t,s) = {} & \int_0^s du \cos \varphi(t,u) + l_1 \cos \varphi_1, \\ y(t,s) = {} & \int_0^s du \sin \varphi(t,u) + l_1 \sin \varphi_1. \end{aligned} \tag{29}$$

These are analogous to the discrete changes of variables of Eqs. (6) and (7) in the case in which one end of the chain is kept fixed. It is easy to check that, after the substitutions (29) in Eq. (25), one obtains exactly Eq. (24) as desired.

For future convenience we introduce also the vector notation

$$\mathbf{R}(t,s) = [x(t,s), y(t,s)]. \tag{30}$$

In this way we get for the functional $\mathcal{L}_0$ and the constraint (26) the more compact expressions

$$\mathcal{L}_0(t) = \frac{M}{2L} \int_0^L ds \dot{\mathbf{R}}^2(t,s) \tag{31}$$

and

$$[\mathbf{R}'(t,s)]^2 = 1. \tag{32}$$

Finally, Eqs. (27) and (28) become, respectively,

$$\mathbf{R}(t,0) = (l_1 \cos \varphi_1, l_1 \sin \varphi_1), \tag{33}$$

$$\mathbf{R}(t,0) = \mathbf{R}(t,L). \tag{34}$$

It is now easy to add the interactions. For example, let us suppose that the segments of the chain are immersed in an potential $V_1(\mathbf{r})$ and that there are also internal interactions associated to a two-body potential $V_2(\mathbf{r}_1,\mathbf{r}_2)$. In this case, the Lagrangian $\mathcal{L}_0$ of Eq. (31) generalizes to

$$\mathcal{L} = \mathcal{L}_0 + \mathcal{L}_1 + \mathcal{L}_2, \tag{35}$$

where

$$\mathcal{L}_1 = -\int_0^L ds V_1[\mathbf{R}(t,s)] \tag{36}$$

and

$$\mathcal{L}_2 = -\int_0^L ds_1 \int_0^L ds_2 V_{\text{int}}[\mathbf{R}(t,s_1),\mathbf{R}(t,s_2)]. \tag{37}$$

III. DYNAMICS OF A CHAIN IMMERSED IN A THERMAL BATH

In this section we address the problem of describing the dynamics of a random chain subjected to thermodynamic fluctuations and immersed in an environment held at constant temperature T.

The strategy in order to treat this problem is to consider the discrete chain as a set of N particles of mass m performing a random walk while subjected to the discrete constraints (4), which we rewrite here for convenience as follows:

$$\frac{|\mathbf{R}_n(t) - \mathbf{R}_{n-1}(t)|^2}{a^2} = 1, \quad n = 2, \ldots, N. \tag{38}$$

It is additionally required that at the instants $t=t_i,t_f$ the nth particle is located, respectively, at the initial point $\mathbf{R}_{i,n}$ and at the final point $\mathbf{R}_{f,n}$ for $n=1,\ldots,N$. For simplicity, the interactions among the particles are switched off including hydrodynamic forces [25].

If one could ignore the constraints, the probability distribution Ψ_N of the system of N particles would be

$$\Psi_N = \prod_{n=1}^{N} \psi_n(t_f - t_i, \mathbf{R}_{f,n}, \mathbf{R}_{i,n}), \tag{39}$$

where ψ_n is the probability distribution describing the free random walk of the nth particle. As it is well known, ψ_n satisfies the Fokker-Planck-Smoluchowski equation

$$\frac{\partial \psi_n}{\partial (t_f - t_i)} = D \frac{\partial^2 \psi_n}{\partial \mathbf{R}_n^2}, \tag{40}$$

D represents the diffusion constant. Equation (40) is completed by the boundary condition

$$\psi_n(0, \mathbf{R}_{f,n}, \mathbf{R}_{i,n}) = \delta(\mathbf{R}_{f,n} - \mathbf{R}_{i,n}). \tag{41}$$

The solution of Eq. (40) can be written up to an irrelevant normalization factor A in the form of a path integral,

$$\psi_n = A \int_{\substack{\mathbf{R}_n(t_f)=\mathbf{R}_{f,n} \\ \mathbf{R}_n(t_i)=\mathbf{R}_{i,n}}} d\mathbf{R}_n(t) e^{-\int_{t_i}^{t_f} (\dot{\mathbf{R}}_n^2/4D) dt}. \tag{42}$$

Substituting Eq. (42) in Eq. (39), the probability distribution Ψ_N becomes

$$\Psi_N = A^N \int_{\substack{\mathbf{R}_1(t_f)=\mathbf{R}_{f,1} \\ \mathbf{R}_1(t_i)=\mathbf{R}_{i,1}}} d\mathbf{R}_1(t) \cdots \int_{\substack{\mathbf{R}_N(t_f)=\mathbf{R}_{f,N} \\ \mathbf{R}_N(t_i)=\mathbf{R}_{i,N}}} d\mathbf{R}_n(t) \times \exp\left(- \sum_{n=1}^{N} \int_{t_i}^{t_f} \frac{\dot{\mathbf{R}}_n^2(t)}{4D} dt \right). \tag{43}$$

Now we must add to the above free random walks the constraints (38). This will be done by inserting in the probability distribution of Eq. (43) a product of Dirac δ functions which enforce exactly these constraints,

$$\Psi_{\text{disc}} = C \int_{\substack{\mathbf{R}_1(t_f)=\mathbf{R}_{f,1} \\ \mathbf{R}_1(t_i)=\mathbf{R}_{i,1}}} d\mathbf{R}_1(t) \cdots \int_{\substack{\mathbf{R}_N(t_f)=\mathbf{R}_{f,N} \\ \mathbf{R}_N(t_i)=\mathbf{R}_{i,N}}} d\mathbf{R}_n(t) e^{-\mathcal{A}_{0,\text{disc}}} \times \prod_{n=2}^{N} \delta\left(\frac{|\mathbf{R}_n(t) - \mathbf{R}_{n-1}(t)|^2}{a^2} - 1 \right). \tag{44}$$

In the above equation C denotes a normalization constant. Moreover, we have introduced the functional $\mathcal{A}_{0,\text{disc}}$ defined as follows:

$$\mathcal{A}_{0,\text{disc}} = \sum_{n=1}^{N} \int_{t_i}^{t_f} \frac{\dot{\mathbf{R}}_n^2(t)}{4D} dt. \tag{45}$$

The distribution Ψ_{disc} measures the probability that a chain starting from the initial configuration $\{\mathbf{R}_{i,1},\ldots,\mathbf{R}_{i,N}\}$ of its segments ends up after a time $t_f - t_i$ in the configuration $\{\mathbf{R}_{f,1},\ldots,\mathbf{R}_{f,N}\}$. We note that the diffusion constant D appearing in (45) satisfies the relation

$$D = \mu k T, \tag{46}$$

where μ is the mobility of the particle, k is the Boltzmann constant, and T is the temperature. This fact allows us to rewrite the quantity $\mathcal{A}_{0,\text{disc}}$ in a form which reflects the analogy of the present problem with a quantum mechanical problem,

$$\mathcal{A}_{0,\text{disc}} = \frac{1}{2kT\tau} \sum_{n=1}^{N} \int_{t_i}^{t_f} \frac{m}{2} \dot{\mathbf{R}}_n^2(t) dt. \tag{47}$$

In the above equation we have set

$$\tau = \mu m. \tag{48}$$

The parameter τ has the dimension of a time. Indeed, τ is the relaxation time that characterizes the rate of the decay of the drift velocity of the particles composing the chain. The quantity $\mathcal{A}_{0,\text{disc}}$ appears now as a real action of a set of N quantum particles of mass m in complex time, with the constant factor

$$\kappa = 2kT\tau \tag{49}$$

replacing the Planck constant $\hbar$. This is not a surprise, because the connections between quantum mechanics and Brownian motion are well known. Indeed, one may show that the uncertainties in the position and momentum of a Brownian particle are related to the constant $2mD=\kappa$ [17].

At this point we are ready to take in the probability distribution (44) the continuous limit (12). By introducing the rescaled variables s_n as we did in Sec. II, the probability distribution (44) becomes

$$\Psi_{\text{disc}} = C\prod_{n=1}^{N} \int_{\substack{\mathbf{R}(t_f,s_n)=\mathbf{R}_f(s_n)\\ \mathbf{R}(t_i,s_n)=\mathbf{R}_i(s_n)}} d\mathbf{R}(t,s_n) e^{-1/2kT\tau\int_{t_i}^{t_f} M/2L\Sigma_{n=1}^{N}\dot{\mathbf{R}}^2(t,s_n)\Delta s_n} \times\prod_{n=2}^{N} \delta\left(\frac{|\mathbf{R}(t,s_n)-\mathbf{R}(t,s_{n-1})|^2}{a^2}-1\right). \tag{50}$$

In the limit $N\to\infty$, $a\to 0$, $Na=L$ we obtain from Ψ_{disc} the probability distribution Ψ of the continuous chain,

$$\Psi = C\int_{\substack{\mathbf{R}(t_f,s)=\mathbf{R}_f(s)\\ \mathbf{R}(t_i,s)=\mathbf{R}_i(s)}} \mathcal{D}\mathbf{R}(t,s) e^{-\mathcal{A}_0}\delta\left(\left|\frac{\partial\mathbf{R}(t,s)}{\partial s}\right|^2-1\right), \tag{51}$$

where

$$\mathcal{A}_0 = \frac{1}{2kT\tau}\int_{t_i}^{t_f} dt\int_0^L ds\frac{M}{2L}\dot{\mathbf{R}}^2(t,s). \tag{52}$$

This is the desired result. Formally, the normalization constant C may be written as a path integral over the initial and final configurations,

$$C^{-1} = \int \mathcal{D}\mathbf{R}_i(s)\mathcal{D}\mathbf{R}_f(s)\int_{\substack{\mathbf{R}(t_f,s)=\mathbf{R}_f(s)\\ \mathbf{R}(t_i,s)=\mathbf{R}_i(s)}} \mathcal{D}\mathbf{R}(t,s) \times e^{-\mathcal{A}_0}\delta\left(\left|\frac{\partial\mathbf{R}(t,s)}{\partial s}\right|^2-1\right). \tag{53}$$

The model described by Eqs. (51) and (52) will be called here the generalized nonlinear σ model due to its close resemblance to a two-dimensional nonlinear σ model. The most striking difference is that the constraint $\mathbf{R}^2=1$ of the nonlinear σ model has been replaced by the condition (32), which contains the derivatives of the bond vectors $\mathbf{R}$ and it is thus nonholonomic.

Before concluding this section, we would like to complete the derivation of the probability distribution of Eqs. (51) and (52) by discussing the continuous limit of the relaxation time τ. This parameter has been defined in Eq. (48) as the product of the mobility μ with the mass m of the beads. When the distance a between the beads goes to zero, m goes to zero as well according to Eq. (16). On the other side, with decreasing values of a, two contiguous beads will become closer and closer until they will eventually merge one into another. To avoid this unphysical situation, one should add to the continuous limit (12) the requirement that the dimensions of the beads vanish together with a. Supposing for instance that the beads are circles of radius ρ, for dimensional reasons one is lead to set $\rho=ca$, where c is a dimensionless proportionality factor. As it is intuitive, when the size of a bead decreases, its mobility μ increases. The increasing of μ compensates the vanishing of m, so that the product $\tau=\mu m$ remains finite. This fact can be verified rigorously in three dimensions using the well-known Stokes formula of the mobility.

IV. CLASSICAL SOLUTIONS OF THE GENERALIZED NONLINEAR σ MODEL

To get rid of the δ function appearing in the formulation of the generalized σ model of Eqs. (51) and (52), it will be convenient to introduce a Lagrange multiplier $\lambda=\lambda(t,s)$ and to use the Fourier representation of the Dirac δ function. Moreover, we add a coupling of the bond vectors $\mathbf{R}(t,s)$ with an external source $\mathbf{J}(t,s)$. In this way the generating functional $\Psi[J]$ of the correlation functions of the bond vectors may be written in the form

$$\Psi[J] = \int \mathcal{D}\mathbf{R}\mathcal{D}\lambda \exp\left[-\int_{t_i}^{t_f} dt\int_0^L ds\left(\frac{M}{2L\kappa}\dot{\mathbf{R}}^2 + i\lambda(\mathbf{R}'^2-1) + \frac{1}{\kappa}\mathbf{J}\cdot\mathbf{R}\right)\right]. \tag{54}$$

Let us note that, for the sake of generality, in Eq. (54) no boundary conditions for the relevant fields have been specified. As it stands, Eq. (54) could be applied both to open or closed chains. Moreover, in the case of open chains both possibilities of free or fixed end points are allowed. It turns out that the degree of complexity of the computation of $\Psi[J]$ strongly depends on the choice of boundary conditions.

Let us now derive the solutions $\mathbf{R}_{\text{cl}}$ and λ_{cl} of the classical equations of motion associated with the generating functional $\Psi[J]$ of Eq. (54),

$$\frac{M}{L}\frac{\partial^2\mathbf{R}}{\partial t^2} = \mathbf{J}, \tag{55}$$

$$\frac{\partial\lambda}{\partial s}\frac{\partial\mathbf{R}}{\partial s} + \lambda\frac{\partial^2\mathbf{R}}{\partial s^2} = 0, \tag{56}$$

$$\left|\frac{\partial\mathbf{R}}{\partial s}\right|^2 = 1. \tag{57}$$

It is easy to see that, due to the constraint (57), the current $\mathbf{J}$ must depend only on the variable t, i.e., $\mathbf{J}(t,s)=\mathbf{J}(t)$. Always for the same reason, it is possible to check that Eq. (56) is inconsistent unless $\lambda_{\text{cl}}=\text{const}\neq 0$ or $\lambda_{\text{cl}}=0$. Depending on the fact that λ_{cl} is zero or not, one finds that the relevant solutions of Eqs. (55)–(57) may be divided into two groups, which we call here solutions of type A and of type B. The solutions of type A are characterized by the condition $\lambda_{\text{cl}}=0$ and may be summarized as follows:

Type A solutions:

$$\lambda_{\text{cl}} = 0, \tag{58}$$

$$\mathbf{R}_{\mathrm{cl}}(t,s) = \mathbf{R}_{0,A} + \mathbf{V}t + \mathbf{R}_{1,A}(t) + \mathbf{R}_{2,A}(s), \tag{59}$$

where $\mathbf{R}_{0,A}$ and $\mathbf{V}$ are constant vectors,

$$\mathbf{R}_{1,A}(t) = \int_{t_i}^{t_f} dt' G(t,t')\mathbf{J}(t') \tag{60}$$

and

$$\mathbf{R}_{2,A}(s) = \int_0^s du[\cos\,\varphi(u), \sin\,\varphi(u)]. \tag{61}$$

Here $\varphi(u)$ is an arbitrary function of u, while in Eq. (60) $G(t,t')$ denotes the Green function which solves the differential equation

$$\frac{M}{L}\frac{\partial^2 G(t,t')}{\partial t^2} = -\delta(t-t'). \tag{62}$$

Type A solutions admit closed chain configurations. In that case, the functions $\varphi(s)$ must satisfy the additional periodicity condition

$$\varphi(s+L) = \varphi(s). \tag{63}$$

Besides the classical solutions of type A, there are also the solutions of type B listed below:

Type B solutions:

$$\lambda_{\mathrm{cl}} = \mathrm{const} \neq 0, \tag{64}$$

$$\mathbf{R}_{\mathrm{cl}}(t,s) = \mathbf{R}_{0,B} + \mathbf{V}t + \mathbf{R}_{1,B}(t) + \mathbf{R}_{2,B}(s), \tag{65}$$

where $\mathbf{R}_{0,B}$ and $\mathbf{V}$ are constants vectors,

$$\mathbf{R}_{1,B}(t) = \int_{t_i}^{t_f} dt' G(t,t')\mathbf{J}(t') \tag{66}$$

and

$$\mathbf{R}_{2,B}(s) = (0,s). \tag{67}$$

In the absence of the external source $\mathbf{J}(t)$, this type of solution corresponds to a configuration in which the chain is stretched along the y axis with one end in the point $\mathbf{R}_{0,B}$ and the other end in the point $\mathbf{R}_{0,B}+(0,L)$. No closed loop configuration is allowed. Of course, the stretched chain may be oriented in a different way by means of a rotation.

We would like to stress the fact that, if there are no external currents, both type A and type B of classical solutions are static, i.e., they do not depend on time apart from the rigid translations of the whole chain with constant velocity $\mathbf{V}$. This result is confirmed if one studies the equations of motion corresponding to the Lagrangian (24) obtained using polar coordinates. The only allowed classical solutions for the field $\varphi(t,s)$ are in fact time independent.

V. COMPUTATION OF THE GENERATING FUNCTIONAL $\Psi[J]$ IN THE SEMICLASSICAL APPROXIMATION

The exact computation of $\Psi[J]$ is a formidable problem despite the simplicity of the action of the generalized nonlinear σ model. One of the main difficulties is the presence of the nonholonomic constraint $|\mathbf{R}'|^2=1$ in the path integral (51). In principle, this cumbersome condition may be easily eliminated by introducing a scalar field $\varphi(t,s)$ and performing the formal substitutions of Eq. (29),

$$\mathbf{R}(t,s) = \int_0^s du[\cos\,\varphi(t,u), \sin\,\varphi(t,u)]. \tag{68}$$

Here we have assumed for simplicity that the chain has one fixed end in the origin of the coordinates, so that $\mathbf{R}(t,0)=(0,0)$ in agreement with Eq. (68). To show that after the field transformation (68) the constraint disappears from the path integral (51), we use the following relation which will be proved in Appendix A for a generic functional $f[\mathbf{R}(t,s)]$:

$$\int \mathcal{D}\mathbf{R}(t,s) f[\mathbf{R}(t,s)]\delta(|\mathbf{R}'|^2 - 1) = \mathcal{N}\int \mathcal{D}\varphi(t,s) f\left(\int_0^s du[\cos\,\varphi(t,u), \sin\,\varphi(t,u)]\right), \tag{69}$$

where $\mathcal{N}$ is an irrelevant constant. In our particular case, in which

$$f[\mathbf{R}(t,s)] = \exp\left(-\int_{t_i}^{t_f} dt \int_0^L ds \frac{M}{2\kappa L}\dot{\mathbf{R}}^2\right), \tag{70}$$

one obtains from Eq. (69),

$$\Psi = \mathcal{N}\int \mathcal{D}\varphi(t,s) e^{-(1/\kappa)\int_{t_i}^{t_f} dt \mathcal{L}_0} \tag{71}$$

with $\mathcal{L}_0$ being the Lagrangian defined in Eq. (24). As we see, the Dirac δ function with the constraint is no longer present in the path integral (71), but the Lagrangian of Eq. (24) is both nonlocal and nonlinear.

In the following, we will stick to Cartesian coordinates limiting ourselves to study small Gaussian fluctuations of the field $\mathbf{R}(t,s)$ around the classical solutions derived in the preceding section. To this purpose, in Eq. (54) we split both fields $\mathbf{R}(t,s)$ and $\lambda(t,s)$ into classical contributions $\mathbf{R}_{\mathrm{cl}}, \lambda_{\mathrm{cl}}$ and statistical corrections $\delta\mathbf{R}, \delta\lambda$,

$$\mathbf{R}(t,s) = \mathbf{R}_{\mathrm{cl}}(t,s) + \kappa^{1/2}\delta\mathbf{R}(t,s), \tag{72}$$

$$\lambda(t,s) = \lambda_{\mathrm{cl}} + \kappa^{1/2}\delta\lambda(t,s). \tag{73}$$

Moreover, it will also be convenient to split the external source $\mathbf{J}$ in an analogous way,

$$\mathbf{J}(t,s) = \mathbf{J}_{\mathrm{cl}}(t) + \kappa^{1/2}\delta\mathbf{J}(t,s), \tag{74}$$

where $\mathbf{J}_{\mathrm{cl}}(t)$ denotes the current depending only on the time t appearing in Eqs. (60) and (66). Due to the fact that the Lagrange multiplier λ is just an auxiliary field, it is possible to choose for its variation $\delta\lambda$ trivial boundary conditions at the initial and final instants,

$$\delta\lambda(t_i,s) = \delta\lambda(t_f,s) = 0. \tag{75}$$

The boundary conditions of $\delta\mathbf{R}(t,s)$ will be fixed later.

At this point, we expand the action

$$\mathcal{A} = \int_{t_i}^{t_f} dt \int_0^L ds \left(\frac{M}{2L\kappa} \dot{\mathbf{R}}^2 + i\lambda(\mathbf{R}'^2 - 1) + \frac{1}{\kappa} \mathbf{J} \cdot \mathbf{R} \right) \quad (76)$$

appearing in the path integral (54) with respect to the quantities $\delta\mathbf{R}, \delta\lambda$, and $\delta\mathbf{J}$. Since the latter are supposed to be small corrections of the dominating classical solutions, we stop the expansion at the second order,

$$\mathcal{A} = \mathcal{A}_{\mathrm{cl}} + \delta\mathcal{A}^{(1)} + \delta\mathcal{A}^{(2)}. \quad (77)$$

At the zeroth order we have

$$\mathcal{A}_{\mathrm{cl}} = \frac{1}{\kappa} \int_{t_i}^{t_f} dt \int_0^L ds \left(\frac{M}{2L} \dot{\mathbf{R}}_{\mathrm{cl}}^2 + \mathbf{J}_{\mathrm{cl}} \cdot \mathbf{R}_{\mathrm{cl}} \right). \quad (78)$$

This is just the action $\mathcal{A}$ in which the fields have been replaced by their classical configurations, which may be either of type A or of type B. In both cases, the term $\lambda_{\mathrm{cl}}(\mathbf{R}'^2 - 1)$, which in principle should be present in Eq. (78), has been omitted because Eq. (57) forces it to vanish identically. Let us now compute the first-order contribution $\delta\mathcal{A}^{(1)}$. Usually, first-order contributions vanish after exploiting the classical equations of motion. In our case this is in general not true. The reason is that, due to the nontrivial boundary conditions satisfied by $\mathbf{R}(t,s)$, nonzero boundary terms may still appear in $\delta\mathcal{A}^{(1)}$. Despite this fact, it is possible to show that $\delta\mathcal{A}^{(1)}$ vanishes at least in the following two situations:

(1) Closed chains satisfying the boundary conditions (34).

(2) Open chains in which both ends are fixed, so that besides the condition (33) also the following one is valid: $\mathbf{R}(t,L) = (x_{0,L}, y_{0,L})$, where $x_{0,L}$ and $y_{0,L}$ are constants.

Assuming that one of the above two conditions is verified, it is possible to set

$$\delta\mathcal{A}^{(1)} = 0. \quad (79)$$

Thus, we are left only with the computation of the second-order corrections $\delta\mathcal{A}^{(2)}$. After simple calculations, one finds

$$\delta\mathcal{A}^{(2)} = \int_{t_i}^{t_f} dt \int_0^L ds \left(\frac{M}{2L} \delta\dot{\mathbf{R}} \cdot \delta\dot{\mathbf{R}} + i\kappa\lambda_{\mathrm{cl}} (\delta\mathbf{R}')^2 + 2i\kappa(\mathbf{R}'_{\mathrm{cl}} \cdot \delta\mathbf{R}')\delta\lambda + \delta\mathbf{J} \cdot \delta\mathbf{R} \right). \quad (80)$$

Putting together all the above results, it is possible to conclude that, within the present Gaussian approximation, the expression of $\Psi[J]$ reduces to

$$\Psi[J] = e^{\mathcal{A}_{\mathrm{cl}}} Z[J], \quad (81)$$

where

$$Z[J] = \int \mathcal{D}\delta\mathbf{R} \mathcal{D}\delta\lambda e^{-\delta\mathcal{A}^{(2)}} \quad (82)$$

and $\mathcal{A}_{\mathrm{cl}}$ and $\delta\mathcal{A}^{(2)}$ are, respectively, given in Eqs. (78) and (80).

From this point on we will consider only chain configurations which are closed, so that both classical configurations $\mathbf{R}_{\mathrm{cl}}$ and their statistical corrections $\delta\mathbf{R}$ must satisfy the boundary conditions in s of Eq. (34). In the Lagrange multiplier sector, besides the trivial boundary conditions in time of Eq. (75), we require also the following ones with respect to the variable s:

$$\delta\lambda(t,0) = \delta\lambda(t,L). \quad (83)$$

The case of closed chains is particularly interesting because under this assumption the path integral appearing on the right-hand side of Eq. (82) may be rewritten in such a way that it closely resembles the generating functional of a field theory of a one-dimensional system at finite temperature. In this field theory the coordinate s plays the role of time while the real time t becomes the spatial coordinate of the one-dimensional space. We still need to specify the boundary conditions with respect to the time for the fields $\delta\mathbf{R}$. We fix them in such a way that the Gaussian path integration over these fields in the generating functional of Eq. (82) will be as simple as possible. To this purpose, reasonable choices are the following.

The Dirichlet-Dirichlet boundary conditions are

$$\delta\mathbf{R}(t_i,s) = 0, \quad \delta\mathbf{R}(t_f,s) = 0. \quad (84)$$

The Dirichlet-Neumann boundary conditions are

$$\delta\mathbf{R}(t_i,s) = 0, \quad \left. \frac{\partial\mathbf{R}(t,s)}{\partial t} \right|_{t=t_f} = 0. \quad (85)$$

The Neumann-Dirichlet boundary conditions are

$$\left. \frac{\partial\delta\mathbf{R}(t,s)}{\partial t} \right|_{t=t_i} = 0, \quad \delta\mathbf{R}(t_f,s) = 0. \quad (86)$$

The Neumann-Neumann boundary conditions are

$$\left. \frac{\partial\delta\mathbf{R}(t,s)}{\partial t} \right|_{t=t_i} = 0, \quad \left. \frac{\partial\delta\mathbf{R}(t,s)}{\partial t} \right|_{t=t_f} = 0. \quad (87)$$

At this point we are ready to perform the Gaussian integrations over the fields $\delta\mathbf{R}$ in the generating functional $Z[J]$ given in Eq. (82). After some integrations by parts, which do not produce boundary terms thanks to the boundary conditions (34) and (83), one finds

$$Z[J] = C_1 \int \mathcal{D}\delta\lambda e^{-S(\delta\lambda)} \quad (88)$$

with

$$S(\delta\lambda) = \frac{1}{2} \int_0^L ds \int_{t_i}^{t_f} dt dt' G(t,t') \times \left[-4\kappa^2 \delta\lambda(t,s) \frac{\partial\mathbf{R}_{\mathrm{cl}}(s)}{\partial s} \cdot \frac{\partial^2}{\partial s^2} \left(\delta\lambda(t',s) \frac{\partial\mathbf{R}_{\mathrm{cl}}(s)}{\partial s} \right) - 2i\kappa\delta\lambda(t,s) \frac{\partial\mathbf{R}_{\mathrm{cl}}(s)}{\partial s} \cdot \frac{\partial\delta\mathbf{J}(t',s)}{\partial s} - 2i\kappa\delta\lambda(t',s) \times \frac{\partial\mathbf{R}_{\mathrm{cl}}(s)}{\partial s} \cdot \frac{\partial\delta\mathbf{J}(t,s)}{\partial s} + \delta\mathbf{J}(t,s) \cdot \delta\mathbf{J}(t',s) \right] \quad (89)$$

and

$$C_1 = \int \mathcal{D}\delta\mathbf{R} e^{-(M/2L)\int_0^L ds \int_{t_i}^{t_f} dt (\partial \delta\mathbf{R}/\partial t)^2}. \tag{90}$$

The symbol $G(t,t')$ denotes the propagator (62) computed taking into account one of the boundary conditions defined in Eqs. (84)–(87) [18]. We have thus four possibilities.

The Dirichlet-Dirichlet boundary condition is

$$G(t,t') = -\frac{L}{M}\theta(t'-t)(t-t_i)\frac{(t'-t_f)}{t_f-t_i} - \frac{L}{M}\theta(t-t')(t'-t_i)\frac{t-t_f}{t_f-t_i}. \tag{91}$$

The Dirichlet-Neumann boundary condition is

$$G(t,t') = -\frac{L}{M}(t_i-t')\,\theta(t-t') - \frac{L}{M}(t_i-t)\,\theta(t'-t). \tag{92}$$

The Neumann-Dirichlet boundary condition is

$$G(t,t') = \frac{L}{M}(t_f-t')\,\theta(t'-t) + \frac{L}{M}(t_f-t)\,\theta(t-t'). \tag{93}$$

The Neumann-Neumann boundary condition is

$$G(t,t') = \frac{L}{M}[t\,\theta(t'-t) + t'\,\theta(t-t')] + \frac{L}{M}\frac{[(t-t_f)^2+(t'-t_f)^2]}{2(t_f-t_i)}. \tag{94}$$

In Eqs. (91)–(94) the function $\theta(t)$ is the usual θ function of Heaviside. Let us note that the function $G(t,t')$ of Eq. (94) is actually a pseudo-Green function, which satisfies the equation

$$\frac{M}{L}\frac{\partial^2 G(t,t')}{\partial t^2} = -\delta(t-t') + \frac{1}{t_f-t_i} \tag{95}$$

instead of Eq. (62). This is due to the fact that, in the case of Neumann-Neumann boundary conditions, one should project out the constant solution of the eigenvalue equation associated to the operator $\frac{M}{L}\frac{\partial^2}{\partial t^2}$.

We remark that in the action (89) the classical conformations appear only in the derivatives $\frac{\partial \mathbf{R}_{\mathrm{cl}}}{\partial s}$, which coincide with the derivatives of the vectors $\mathbf{R}_{2,A}(s)$ defined in Eq. (61). In components,

$$\frac{\partial \mathbf{R}_{\mathrm{cl}}}{\partial s} = [\cos\varphi(s), \sin\varphi(s)]. \tag{96}$$

From Eq. (96) it is clear that the vector $\frac{\partial \mathbf{R}_{\mathrm{cl}}}{\partial s}$ has the meaning of the unitary vector which is tangent to the classical trajectories. It is therefore convenient to decompose all vectors appearing in the action $S(\delta\lambda)$ in components which are normal or tangent to $\mathbf{R}_{\mathrm{cl}}(s)$. After some algebra, one obtains in this way an expression of $Z[J]$ in which now $S(\delta\lambda)$ takes the simplified form

$$S(\delta\lambda) = \frac{1}{2}\int_0^L ds \int_{t_i}^{t_f} dt dt' G(t,t') \Bigg[-4\kappa^2 \delta\lambda(t,s) \times \left(\frac{\partial^2}{\partial s^2} - [\varphi'(s)]^2\right)\delta\lambda(t',s) + 2i\kappa\delta\lambda(t,s)\,\delta J_T(t',s) + 2i\kappa\delta\lambda(t',s)\,\delta J_T(t,s) + \delta\mathbf{J}(t,s)\cdot\delta\mathbf{J}(t',s)\Bigg]. \tag{97}$$

Here we have introduced the tangential component $\delta J_T(t,s)$ of the current $\delta\mathbf{J}(t,s)$,

$$\delta J_T(t,s) = \partial_s \mathbf{R}_{\mathrm{cl}}(s)\cdot\partial_s\delta\mathbf{J}(t,s). \tag{98}$$

At this point we are ready to eliminate the auxiliary field $\delta\lambda$ from the functional of Eq. (88), where now the action $S(\delta\lambda)$ is defined in Eq. (97). To this purpose, one needs to perform a Gaussian integration, which produces the result

$$Z[J] = C_1 C_2 e^{-(1/2)\int_0^L ds ds' \int_{t_i}^{t_f} dt dt' G(t,t')[K(s,s')\delta J_T(t,s)\delta J_T(t',s') + (1/L)\delta\mathbf{J}(t,s)\cdot\mathbf{J}(t',s)]}. \tag{99}$$

In the above equation $K(s,s')$ denotes the Green function which satisfies the relation

$$\left(\frac{\partial^2}{\partial s^2} - [\varphi'(s)]^2\right)K(s,s') = -\delta(s,s'), \tag{100}$$

while

$$C_2 = \int \mathcal{D}\delta\lambda e^{\int_0^L ds \int_{t_i}^{t_f} dt dt' G(t,t')(2\kappa^2\delta\lambda(t,s)\{(\partial^2/\partial s^2) - [\varphi'(s)]^2\}\delta\lambda(t',s))}. \tag{101}$$

Setting this all together we obtain the expression of the generating functional $\Psi[J]$ in its final form,

$$\Psi[J] = e^{\mathcal{A}_{\rm cl}} C_1 C_2 \times \exp\left[-\frac{1}{L}\int_0^L ds \int_{t_i}^{t_f} dt dt' G(t,t') \delta \mathbf{J}(t,s) \cdot \delta \mathbf{J}(t',s) \right] \times \exp\left[-\frac{1}{2}\int_0^L ds ds' \int_{t_i}^{t_f} dt dt' G(t,t') K(s,s') \times \delta J_T(t',s') \delta J_T(t,s) \right]. \quad (102)$$

The right-hand side of Eq. (102) displays the asymmetry in the propagation of transverse and longitudinal modes.

The differential equation satisfied by the Green function $K(s,s')$ of Eq. (100) cannot be solved analytically for any given function $\varphi(s)$. Here we discuss just the case in which the background classical solution corresponds to a chain with the configuration of a circle, i.e.,

$$\mathbf{R}_{\rm cl}^{\rm circle}(s) = \frac{L}{2\pi}\left(\cos\frac{2\pi s}{L}, \sin\frac{2\pi s}{L} \right). \quad (103)$$

The radius of the circle is $\frac{L}{2\pi}$, so that the total length of the chain is L as desired. Comparing Eq. (103) with Eq. (61), it is clear that for this conformation $\varphi(s) = \frac{2\pi}{L} s$. Substituting this expression of $\varphi(s)$ in Eq. (100), it turns out that the Green function $K(s,s')$ satisfies the relation

$$\left(\frac{\partial^2}{\partial s^2} - \frac{4\pi^2}{L^2} \right) K(s,s') = -\delta(s-s'). \quad (104)$$

The solution of the above equation corresponding to the boundary conditions (83) is

$$K(s,s') = \frac{\sinh\left(\frac{2\pi}{L}(L-s') \right) \sinh\frac{2\pi}{L} s}{\frac{2\pi}{L}\sinh 2\pi} \theta(s'-s) + \frac{\sinh\left(\frac{2\pi}{L}(L-s) \right) \sinh\frac{2\pi}{L} s'}{\frac{2\pi}{L}\sinh 2\pi} \theta(s-s'). \quad (105)$$

In the limit $\mathbf{J}(t,s)=0$, we obtain from the generating functional of Eq. (102) the expression of the probability distribution Ψ of Eqs. (51) and (52) in the semiclassical approximation

$$\Psi = e^{\mathcal{A}_{\rm cl}(\mathbf{J}_{\rm cl}=0)} C_1 C_2. \quad (106)$$

Remembering the respective definitions of the constants C_1 and C_2 of Eqs. (90) and (101), together with the form (78) of the classical action, Ψ may be explicitly written as follows:

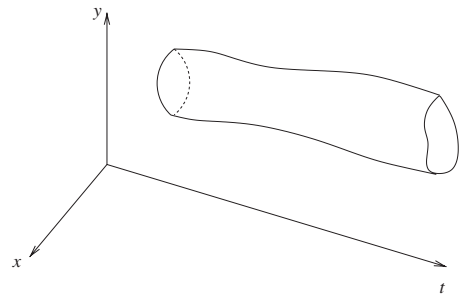

FIG. 2. During its motion, a closed chain spans in the x,y,t a surface which has the topology of a cylinder.

$$\Psi = \exp\left[-\frac{1}{\kappa}\int_{t_i}^{t_f} dt \int_0^L ds \left(\frac{M}{2L}\dot{\mathbf{R}}_{\rm cl}^2 \right) \right] \int \mathcal{D}\delta\mathbf{R} \times \exp\left(-\frac{M}{2L}\int_{t_i}^{t_f} dt \int_0^L ds (\delta\dot{\mathbf{R}})^2 \right) \int \mathcal{D}\delta\lambda \times \exp\left\{ \int_{t_i}^{t_f} dt dt' \int_0^L ds G(t,t') \left[2\kappa^2 \delta\lambda(t,s) \times \left(\frac{\partial^2}{\partial s^2} - [\varphi'(s)]^2 \right) \delta\lambda(t',s) \right] \right\}. \quad (107)$$

VI. PHYSICAL INTERPRETATION OF THE OBTAINED RESULTS

The classical equations of motion (55)–(57) admit only static solutions in which the conformation of the chain is fixed. Only rigid translations of the chain as a whole with constant velocity $\mathbf{V}$ are allowed. Apart from these rigid translations, the time dependence of the classical solutions $\mathbf{R}_{\rm cl}(t,s)$ in Eqs. (59) and (65) is just an artifact of the presence of the classical current $\mathbf{J}(t) \equiv \mathbf{J}_{\rm cl}(t)$ which is fictitious and may thus be set to zero without any loss of generality. In the following discussion, it will be assumed that both $\mathbf{J}_{\rm cl}(t)$ and $\mathbf{V}$ are zero. The absence of any relevant dynamics in the classical solutions is somewhat surprising. We can only suggest that this absence could be related to the fact that, after performing the continuous limit, the fourth term appearing in the left-hand side of Eq. (11) vanishes identically. This term is important for the chain dynamics since it contains second time derivatives of the angles $\varphi(t,s)$. In some sense, the continuous chain is simpler than its discrete counterpart, in which this term is present.

Less trivial is the treatment of the fluctuations of the chain at constant temperature T. The nonlinear σ model given in Eq. (54) or, alternatively, its formulation without the Lagrange multiplier of Eqs. (51) and (52), describe the fluctuations of a chain of N segments of constant length a in the continuous limit (12). During its motion in the time interval $[t_i, t_f]$ the chain spans a two-dimensional surface which, in the case of a closed conformation, has the topology of a cylinder in the x,y,t space, see Fig. 2. If the chain is open, instead, the topology of the cylinder should be replaced with that of a strip.

We recall that in deriving the GNLSM of Eqs. (51) and (52) the contribution of the hydrodynamic interactions has been neglected. This limits the validity of this model to the following cases:

(a) The viscosity of the fluid is large, so that the motion of the particles composing the chain is slow. Thus, the velocity field created by each particle is too weak to influence the motion of other particles.

(b) The temperature is low, so that once again the motion of the chain is slow.

(c) The conformation of the chain is relatively straight because there is some energy cost when the chain is being bent. To this purpose, however, one should introduce the stiffness at the joints between the segments.

On the other side, the semiclassical approximation used in order to derive the generating functional $\Psi[J]$ of Eq. (107) is valid in the case in which the parameter κ defined in Eq. (49) is small. This parameter depends essentially on the temperature T and on the relaxation time τ. Since τ is inversely proportional to the viscosity in the limit of low Reynolds number, it is reasonable to assume that the semiclassical approach can be applied to a cold isolated chain or to an isolated chain in a very viscous solution. These situations correspond, respectively, to the points (b) and (a) mentioned above.

Both the generating functional $\Psi[J]$ of Eq. (102) and the probability distribution of Eq. (107) have been computed in the case of closed chains, whose conformations are subjected to the boundary conditions (84)–(87). The physical meaning of these boundary conditions may be summarized as follows.

Dirichlet-Dirichlet boundary conditions. In this case $\mathbf{R}_i(s)=\mathbf{R}_f(s)=\mathbf{R}_{\mathrm{cl}}(s)$, where $\mathbf{R}_{\mathrm{cl}}(s)$ is a given static solution of the classical equations of motion. The probability that, starting from the conformation $\mathbf{R}_i(s)$, the fluctuating chain ends up at the time t_f in the same conformation, is proportional up to a normalization constant to the probability distribution Ψ of Eq. (107), in which the Green function $G(t,t')$ is that of Eq. (91).

Dirichlet-Neumann boundary conditions. In this case the probability distribution Ψ of Eq. (107) is proportional to the probability that a closed chain starting from a classical static conformation $\mathbf{R}_i(s)=\mathbf{R}_{\mathrm{cl}}(s)$ at the time t_i ends up at the instant t_f in an arbitrary conformation characterized by the fact that the velocities of each segment composing the chain is zero. Ψ must be computed choosing the Green function $G(t,t')$ defined in Eq. (92).

Neumann-Dirichlet boundary conditions. Here the segments of the chain have zero velocity at the beginning, but the conformation of the chain is otherwise arbitrary. At the time t_f the chain is found in a given static classical conformation, i.e., $\mathbf{R}_f(s)=\mathbf{R}_{\mathrm{cl}}(s)$. The probability for this to happen is obtained after substituting in Eq. (107) the Green function $G(t,t')$ of Eq. (93).

Neumann-Neumann boundary conditions. This is the situation in which the conformation of the chain at the initial and final times t_i and t_f are not specified, but the velocities of all the segments composing the chains must be zero. The relevant Green function $G(t,t')$ to be inserted in the probability distribution Ψ is that of Eq. (94).

By choosing Neumann-Dirichlet boundary conditions one may check for instance if, starting from any static conformation, there is a particular conformation in which it is very likely that the chain will be found after a certain time t_f-t_i. The stability of a given conformation with respect to the thermodynamic fluctuations which attempt to reshape the chain can be tested by choosing Dirichlet-Dirichlet boundary conditions. In principle, it is also possible to study other types of boundary conditions than those considered here, provided they do not give rise to unwanted boundary terms in the action of the generating functional $\Psi[J]$.

To conclude this section, it is interesting to see how the original constraint (32) is realized in the semiclassical approximation. In Eq. (81), which gives the second-order corrections to the classical action $\mathcal{A}_{\mathrm{cl}}$, there are two Lagrange multipliers, $\delta\lambda$ and λ_{cl}. The most relevant condition is that imposed by $\delta\lambda$,

$$\mathbf{R}'_{\mathrm{cl}}\cdot\delta\mathbf{R}'=0. \tag{108}$$

Let us note that the above relation is at the origin of the asymmetry in the generating functional (102) between modes which are tangent or normal to the classical background conformation $\mathbf{R}_{\mathrm{cl}}$. Equation (108) is just the approximated version of the full constraint (32). As a matter of fact, remembering the splitting into classical solutions and statistical corrections of Eqs. (72) and (73), we may rewrite Eq. (32) as follows:

$$(\mathbf{R}')^2_{\mathrm{cl}}+2\mathbf{R}'_{\mathrm{cl}}\cdot\delta\mathbf{R}'+(\delta\mathbf{R}')^2-1=0. \tag{109}$$

Due to the fact that $(\mathbf{R}'_{\mathrm{cl}})^2=1$ and neglecting the second-order term $(\delta\mathbf{R}')^2$, we obtain from Eq. (109),

$$2\mathbf{R}'_{\mathrm{cl}}\cdot\delta\mathbf{R}'=0, \tag{110}$$

which coincides exactly with Eq. (108). In the case of solutions of type B there is an additional constraint, which is associated to the nonzero constant Lagrange multiplier λ_{cl}. This constraint requires that the average over the time t and over the chain length s of the quadratic term $(\delta\mathbf{R}')^2$ is zero,

$$\int_{t_i}^{t_f}\frac{dt}{t_f-t_i}dt\int_0^L\frac{ds}{L}(\delta\mathbf{R}')^2=0. \tag{111}$$

In the solutions of type A the above condition is not present because in that case $\lambda_{\mathrm{cl}}=0$.

VII. EQUILIBRIUM LIMIT OF THE GNLSM AND ITS CONNECTION WITH THE ROUSE MODEL

First, we study the equilibrium limit of the GNLSM. We use the formulation of the model given in Eqs. (51) and (52). For simplicity, we set $t_i=0$. Thus,

$$\Psi=\int\mathcal{D}\mathbf{R}(t,s)e^{-(M/2L\kappa)\int_0^{t_f}dt\int_0^L ds\dot{\mathbf{R}}^2(t,s)}\delta[|\mathbf{R}'(t,s)|^2-1]. \tag{112}$$

At this point, we rescale the time variable by setting $\sigma=\frac{t}{t_f}$, so that the above equation becomes

$$\Psi = \int \mathcal{D}\mathbf{R}(t_f\sigma,s)e^{-(M/2L\kappa t_f)\int_0^1 d\sigma\int_0^L ds(\partial\mathbf{R}/\partial\sigma)^2}\delta[|\mathbf{R}'(t_f\sigma,s)|^2-1]. \tag{113}$$

In the equilibrium limit $t_f\to\infty$ we obtain

$$\Psi_{\rm eq} = \int \mathcal{D}\mathbf{R}_{\rm eq}(s)\,\delta[|\mathbf{R}'_{\rm eq}(s)|^2-1], \tag{114}$$

where $\mathbf{R}_{\rm eq}(s)=\mathbf{R}(\infty,s)$. Equation (114) is exactly what one should expect in the case of the statistical mechanics of a discrete chain subjected to the constraints

$$|\mathbf{R}_n-\mathbf{R}_{n-1}|^2 = a^2. \tag{115}$$

The discrete probability function of the conformation of such a chain is given by

$$\Psi_{\rm eq,disc} = \prod_{n=1}^{N}\int d\mathbf{R}_n \prod_{n=2}^{N}\delta\left(\frac{|\mathbf{R}_n-\mathbf{R}_{n-1}|^2}{a^2}-1\right). \tag{116}$$

In the continuous limit this becomes exactly the distribution of Eq. (114). This result is in agreement with the analogous probability function given in [2].

While the purpose of this work is to provide a path-integral formulation of the dynamics of a freely jointed chain without having in mind concrete applications to polymer physics, it is interesting to explore possible connections between the GNLSM of Eqs. (51) and (52) and the Rouse model. A direct attempt to set the Rouse model in the path-integral form via the Martin-Siggia-Rose formalism leads to a probability distribution for the Rouse chain which differs profoundly from the GNLSM obtained in this work. Indeed, let us start from the Langevin equation,

$$\zeta\frac{\partial\mathbf{R}}{\partial t} = \xi\frac{\partial^2\mathbf{R}}{\partial n^2}+\mathbf{f}. \tag{117}$$

Here we have used instead of the arc length s the dimensionless variable n defined as follows: $s_0 n=s$. Moreover, $\mathbf{f}=\mathbf{f}(t,n)$ is a stochastic force with a Gaussian distribution of width α given by $e^{-\int_0^{t_f}dt\int_0^{L/s_o}dn(\mathbf{f}^2/2\alpha)}$. ζ and ξ are constant parameters which will be specified later. After the application of the Martin-Siggia-Rose method, one finds the Rouse probability distribution

$$\Psi_{\rm Rouse} = \int \mathcal{D}\mathbf{R}e^{-(1/2\alpha)\int_0^{t_f}dt\int_0^{L/s_0}dn[\zeta^2(\partial\mathbf{R}/\partial t)^2+\xi^2(\partial^2\mathbf{R}/\partial n^2)^2]}. \tag{118}$$

In principle, in the exponent of the above equation there should be the additional term

$$I = -\frac{\zeta\xi}{\alpha}\int_0^{t_f}dt\int_0^{L/s_0}dn\frac{\partial\mathbf{R}}{\partial t}\cdot\frac{\partial^2\mathbf{R}}{\partial n^2}. \tag{119}$$

However, due to the fact that $\frac{\partial\mathbf{R}}{\partial t}\cdot\frac{\partial^2\mathbf{R}}{\partial n^2}=\frac{\partial}{\partial n}\left(\frac{\partial\mathbf{R}}{\partial n}\cdot\frac{\partial\mathbf{R}}{\partial t}\right)-\frac{\partial\mathbf{R}}{\partial n}\cdot\frac{\partial^2\mathbf{R}}{\partial t\partial n}$ and remembering the identity $\frac{\partial\mathbf{R}}{\partial n}\cdot\frac{\partial^2\mathbf{R}}{\partial t\partial n}=\frac{1}{2}\frac{\partial}{\partial t}\left[\left(\frac{\partial\mathbf{R}}{\partial n}\right)^2\right]$, it is easy to realize that I amounts to total derivative terms, which can be neglected.

Coming back to Eq. (118), we see that, while the GNLSM is nonlinear and contains just second derivatives of the bond vector $\mathbf{R}$, the Rouse model is linear and contains derivatives of $\mathbf{R}$ up to the fourth order. As an upshot, while it is possible to investigate the Rouse model by decomposing $\mathbf{R}(t,s)$ into normal coordinates as explained in [1], that kind of Fourier analysis cannot be easily applied to the nonlinear GNLSM. We show at this point that, indeed, the two models are quite different and that it is not possible starting from one of them to recover the probability function of the other and vice versa, because they correspond to regimes which do not overlap. To this purpose, instead of the constraint $\mathbf{R}'^2=1$ of the GNLSM, we introduce the more general condition

$$\mathcal{R} = \left|\frac{1}{s_0}\int_{-s_0}^{s_0}ds'A(s')[\mathbf{R}(t,s+s')-\mathbf{R}(t,s)]\right|^2-a^2=0, \tag{120}$$

where s_0 is a new length scale such that

$$a \ll s_0 \ll L \tag{121}$$

and $A(s')$ is a function of s' normalized in such a way that

$$\frac{1}{s_0}\int_{-s_0}^{s_0}A(s')ds' = 1. \tag{122}$$

Let us note that a is the smallest length at our disposal: Any segment of the chain of contour length shorter than a may be regarded as rigid. At this point, following the same strategy used in Sec. III, we build the new distribution function

$$\Psi_{\rm int} = \int \mathcal{D}\mathbf{R}e^{-c\int_0^{t_f}dt\int_0^L ds\dot{\mathbf{R}}^2}\delta(\mathcal{R}) \tag{123}$$

with $c=\frac{M}{4kT\tau L}$. The index "int" means that the distribution probability $\Psi_{\rm int}$ describes a model which, as we will see, interpolates between the GNLSM and the Rouse model.

We remark that the insertion of the δ function $\delta(\mathcal{R})$ in the path integral (123) has a double meaning. On one side, it may be seen as a condition on the length of the averaged vector

$$\mathbf{S} = \frac{1}{s_0}\int_{-s_0}^{s_0}ds'A(s')[\mathbf{R}(t,s+s')-\mathbf{R}(t,s)]. \tag{124}$$

In the above equation the distance between points of the chain has been averaged over arc segments of length $2s_0$. On the other side, the introduction of the δ function $\delta(\mathcal{R})$ may also be related to the internal forces among the beads composing the chain, which appear due to the presence of constraints. For example, in the case of the GNLSM the presence of these forces is evident in the formulation of Eq. (54), in which the free action is corrected by the addition of the interacting term $\lambda(\mathbf{R}'^2-1)$.

It is easy to realize that the GNLSM is a special case of the model described by Eq. (123). We must remember that in the GNLSM the motion of the chain is observed at the smallest available scale of distances, i.e., the segment length a. Thus, we choose the form of the function $A(s')$ as follows:

$$A(s') = s_0 \delta(s' - a). \tag{125}$$

As a consequence, the constraint (120) becomes $|\mathbf{R}(t,s+a) - \mathbf{R}(t,s)|^2 - a^2 = 0$. Dividing both members of the above equation by a^2 and supposing that a is very small, we obtain up to higher-order terms in a the relation

$$|\mathbf{R}'|^2 - 1 = 0. \tag{126}$$

In the limit $a=0$, this is exactly the condition which has been imposed to the chain in the GNLSM, see Eq. (32). Using the property of the δ function, $\delta[a^2(|\mathbf{R}'|^2-1)] = \frac{1}{a^2}\delta(|\mathbf{R}'|^2-1)$, it is possible to check that also the probability distribution Ψ_{int} becomes that of the GNLSM.

To obtain the Rouse model from the interpolating probability distribution Ψ_{int}, we need first to decrease the resolution with which the segments of the chain are observed. Accordingly, we require that the function $A(s')$ appearing in the constraint (120) is constant over the whole interval $[-s_0, s_0]$,

$$A(s') = \tfrac{1}{2}. \tag{127}$$

In this way, the finest details of the chain are not taken into account, because the chain conformations are averaged over the scale of distance $2s_0$, which is by hypothesis much larger than the smallest available scale a. To pass to the Rouse model, we must also restrict ourselves to the long-time-scale behavior of the chain. This is achieved by assuming, following Ref. [1] (Sec. 4.1, p. 93), that, for long-time scales, $\mathbf{R}(t,s)$ varies slowly with s. This hypothesis allows us to stop the expansion of $\mathbf{R}(t,s+s')$ with respect to s' at the first few orders,

$$\mathbf{R}(t,s+s') = \mathbf{R}(t,s) + \mathbf{R}'(t,s)s' + \frac{\mathbf{R}''(t,s)}{2}s'^2 + \cdots. \tag{128}$$

Substituting the above truncated expansion in Eq. (120) and performing the trivial integrations over s' we obtain the condition

$$\frac{|\mathbf{R}''(t,s)|^2 s_0^4}{6^2} - a^2 = 0. \tag{129}$$

Setting in the above constraint in Eq. (123), we obtain the following approximated expression of Ψ_{int}:

$$\Psi_{\text{int}} \sim \int \mathcal{D}\mathbf{R} e^{-c\int_0^{t_f} dt \int_0^L ds \dot{\mathbf{R}}^2} \delta(|\mathbf{R}''|^2 s_0^4 - a^2), \tag{130}$$

where the factor 6^2 has been absorbed by a rescaling of the length s_0. At this point we use the fact that, apart from an irrelevant infinite constant, the functional δ function present in Eq. (130) may be simplified as follows:

$$\delta(|\mathbf{R}''|^2 s_0^4 - a^2) = \delta(|\mathbf{R}''|s_0^2 - a). \tag{131}$$

A proof of this identity, which is valid up to an irrelevant constant, will be given in Appendix B. Exploiting Eq. (131), the probability distribution Ψ_{int} of Eq. (130) becomes

$$\Psi_{\text{int}} \sim \int \mathcal{D}\mathbf{R} e^{-c\int_0^{t_f} dt \int_0^L ds \dot{\mathbf{R}}^2} \delta(|\mathbf{R}''|s_0^2 - a). \tag{132}$$

We may still simplify the above equation by applying the following slightly modified version of the Gaussian approximation of the δ function:

$$\delta(|\mathbf{R}''|s_0^2 - a) \sim \int \mathcal{D}\lambda e^{-i\int_0^{t_f} dt \int_0^L ds \lambda (|\mathbf{R}''|s_0^2 - a)} \times e^{-\int_0^{t_f} dt \int_0^L ds [(\lambda^2/2\nu) + i(\beta/\nu)\lambda]}, \tag{133}$$

where we have supposed that the parameter ν is very large while the ratio β/ν is very small. Clearly, the usual Fourier representation of the functional Dirac δ function is recovered in the limit $\nu \to \infty$ and $\beta/\nu \to 0$. Up to now β is an arbitrary parameter. We choose it in a such a way that

$$\frac{\beta}{\nu} = a. \tag{134}$$

This choice is compatible with our requirement for β, since a is the smallest scale of lengths at our disposal, so that β/ν is a very small quantity. Using Eq. (134) in order to eliminate ν from Eq. (133), we obtain the relation

$$\delta(|\mathbf{R}''|s_0^2 - a) \sim \int \mathcal{D}\lambda e^{-i\int_0^{t_f} dt \int_0^L ds \lambda |\mathbf{R}''|s_0^2} e^{-\int_0^{t_f} dt \int_0^L ds (a/2\beta)\lambda^2}. \tag{135}$$

After performing the Gaussian integration over λ in Eq. (135), we obtain

$$\delta(|\mathbf{R}''|s_0^2 - a) \sim e^{-\int_0^{t_f} dt \int_0^L ds (\beta/2a)|\mathbf{R}''|^2 s_0^4}. \tag{136}$$

We may now set in the above expression of the δ function in the distribution probability Ψ_{int} of Eq. (132). The result is

$$\Psi_{\text{int}} \sim \int \mathcal{D}\mathbf{R} e^{-\int_0^{t_f} dt \int_0^L ds [c\dot{\mathbf{R}}^2 + (\beta/2a)|\mathbf{R}''|^2 s_0^4]}. \tag{137}$$

This approximated probability distribution has the same structure of that coming from the Rouse model given in Eq. (118).

To make the comparison with the Rouse model more explicit, we perform in Eq. (137) the substitution $ns_0 = s$,

$$\Psi_{\text{int}} \sim \int \mathcal{D}\mathbf{R} e^{-\int_0^{t_f} dt \int_0^{L/s_0} dn s_0 [c\dot{\mathbf{R}}^2 + (\beta/2a)|\partial^2 \mathbf{R}/\partial n^2|^2]}. \tag{138}$$

Let us now identify the coefficients appearing in Eq. (138) with those of Eq. (118). We recall the fact that in the case of the Rouse model,

$$\zeta = \frac{1}{\mu}, \quad \xi = \frac{3kT}{s_0^2}, \quad \alpha = \frac{4kT}{\mu}. \tag{139}$$

On the other side, the parameter c in the exponent of Eq. (138) may be written as follows: $c = \frac{1}{4D}$. It is now easy to verify that the probability function Ψ_{Rouse} of Eq. (118) and that of Eq. (138) coincide if we make the following choice for β: $\beta = \frac{9}{4}\frac{\mu a}{s_0^2} kT$.

VIII. CONCLUSIONS

This work may be considered as the ideal continuation of the seminal paper of Edwards and Goodyear of Ref. [2], in which the problem of a chain subjected to the constraints (38) has been investigated using an approach based on the Langevin equation. With respect to Ref. [2], our approach based on the Fokker-Planck-Smoluchowski equation provides a path-integral and field theoretical formulation of the dynamics of a freely jointed chain in the continuous limit. The GNLSM obtained here makes possible the application of field theoretical techniques to the study of the fluctuations of a freely jointed chain. As an example, we have derived in the semiclassical approximation the probability function of the chain and the associated generating functional. The approximation used in the computation of the generating functional is valid, for instance, in the cases of a cold isolated chain or of a chain fluctuating in a very viscous medium.

Most of the results obtained in this paper have been discussed in the preceding two sections, so that we provide only a short summary here.

(1) Derivation of the GNLSM, which provides a path-integral formalism to the freely jointed chain.

(2) Computation of the partition function and of the generating functional of the GNLSM in the semiclassical approximation.

(3) The behavior of a chain at scales of length and time which are very long has been compared with the behavior at short scales of length and time in Sec. VII. It is shown in this way that it is not possible to compare directly the Rouse model and models describing a freely jointed chain, such as the GNLSM, because the regimes and the assumptions of these two models do not overlap. In particular, the Rouse model considers only the long-time behavior of the chain and long scales of distances, while in the case of the freely jointed chain the short-time behavior is taken into account and the chain is observed at a short scale of distance.

(4) A chain model which encompasses both the regimes of the Rouse model and of the GNLSM has been proposed in Eq. (123).

(5) The equilibrium limit of the GNLSM has been recovered. It gives the expected result in agreement with Ref. [2].

(6) Last, the dynamics of a random chain has been investigated also from the classical point of view. The equivalence of the expressions of the classical Lagrangian of the chain computed starting from Cartesian and polar coordinates has been verified.

To conclude, we would like to mention the problems which are still open and possible further developments of our work. For simplicity, we have restricted our analysis to a two-dimensional chain. However, its extension to any dimensions is not difficult. Preliminary work in three dimensions can be found in Ref. [19]. It turns out that more dimensions allow the possibility of performing the continuous limit in different ways, so that one could end up with a flexible chain or with a rigid chain which privileges only certain directions along a fixed axis. There should be also no problem in switching on the interactions among the beads composing the chain. To this purpose, one may use the path-integral methods applied to stochastic differential equations explained in Ref. [8]. Only the inclusion of the hydrodynamic interactions requires still some work. It is not simple to provide for these interactions a Lagrangian based formulation as that developed here for a continuous chain. However, hydrodynamic interactions have been already implemented in the path-integral formalism in Ref. [20] using the Martin-Siggia-Rose formalism. Work is in progress in order to extend the results of [20] to the freely jointed chain discussed in this work. Another open question is how the chain behaves in the short time regime when it is stretching under the action of a force. This could be interesting in the biophysics of DNA [21]. Finally, work is in progress in order to linearize the GNLSM applying the same approach used in the case of the standard nonlinear σ model. In this way it would be possible to study the GNLSM as the strong coupling limit of its linear version with the help of the techniques of Ref. [22].

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APPENDIX A: PROOF OF EQ. (69)

In this appendix we wish to prove Eq. (69). To this purpose, we start from the path integral

$$I = \int \mathcal{D}x(t,s)\mathcal{D}y(t,s) f[x(t,s),y(t,s)]\delta[(\partial_s x)^2 + (\partial_s y)^2 - 1]. \tag{A1}$$

Upon the transformation

$$x_s(t,s) = \partial_s x(t,s), \quad y_s(t,s) = \partial_s y(t,s), \tag{A2}$$

we obtain

$$I = \int \mathcal{D}x_s(t,s)\mathcal{D}y_s(t,s) \times (\det{}^{-1}\ \partial_s)^2 f\left(\int_0^s du x_u(t,u), \int_0^s du y_u(t,u)\right)\delta(x_s^2 + y_s^2 - 1), \tag{A3}$$

where we have made use of the fact that

$$\det\left(\frac{\delta x}{\delta x_s}\right)\det\left(\frac{\delta y}{\delta y_s}\right) = (\det\ \partial_s^{-1})^2 = (\det{}^{-1}\ \partial_s)^2. \tag{A4}$$

Now it is possible to eliminate the variable y_s by performing in I the substitution

$$\chi = x_s^2 + y_s^2 - 1. \tag{A5}$$

As a consequence, the path integration over y_s appearing in (A3) may be replaced by a path integration over the new variable χ,

$$\int \mathcal{D}y_s \delta(x_s^2 + y_s^2 - 1) f\left(\int_0^s x_u du, \int_0^s y_u du\right) = \int_{\chi \geq x_s^2 - 1} \mathcal{D}\chi \delta(\chi) \det\left|\frac{\delta y_s}{\delta \chi}\right| \times f\left(\int_0^s x_u du, \int_0^s y_u du\right)\Bigg|_{y_s = \pm\sqrt{1+\chi-x_s^2}}. \tag{A6}$$

In the above equation the determinant $\det|\frac{\delta y_s}{\delta \chi}|$ is the functional determinant giving the Jacobian of the transformation (A5), so that

$$\det\left|\frac{\delta y_s}{\delta \chi}\right| = \det\left(\frac{1}{2\sqrt{1+\chi-x_s^2}}\right). \tag{A7}$$

Applying Eqs. (A4) and (A6) in (A1) we obtain

$$I = \int_{x_s^2 - 1 \leq 0} \mathcal{D}x_s \det{}^{-1}|\partial_s|^2 \det{}^{-1}(2\sqrt{1-x_s^2}) \times f\left(\int_0^s x_u(t,u) du, \pm \int_0^s \sqrt{1 - x_u^2(t,u)}\right). \tag{A8}$$

Finally, we perform in Eq. (A8) the substitution $x_s = \cos\varphi$. In this way I may be rewritten as a path integral over φ,

$$I = \int \mathcal{D}\varphi \det\left|\frac{\delta x_s}{\delta \varphi}\right| \det{}^{-1}|\partial_s^2| \det{}^{-1}(2\sin\varphi) \times f\left(\int_0^s \cos\varphi(t,u) du, \int_0^s \sin\varphi(t,u) du\right). \tag{A9}$$

Noting that $\det|\frac{\delta x_s}{\delta \varphi}| = -\sin\varphi$, we obtain, apart from an irrelevant constant $\mathcal{N} = \det^{-1}|\partial_s^2| \det^{-1} 2$, the final result

$$I = \mathcal{N} \int \mathcal{D}\varphi f\left(\int_0^s \cos\varphi(t,u) du, \int_0^s \sin\varphi(t,u) du\right). \tag{A10}$$

APPENDIX B: FUNCTIONAL IDENTITY

To prove the identity (131), we write the functional δ function on the right-hand side of Eq. (131) with the help of its Fourier representation

$$\delta(|\mathbf{R}''|^2 s_0^4 - a^2) = \int \mathcal{D}\tilde{\lambda} e^{-i\int_0^t du \int_0^L ds \tilde{\lambda}(|\mathbf{R}''|^2 s_0^4 - a^2)}. \tag{B1}$$

Since $|\mathbf{R}''|^2 s_0^4 - a^2 = (|\mathbf{R}''| s_0^2 - a)(|\mathbf{R}''| s_0^2 + a)$, Eq. (B1) becomes

$$\delta(|\mathbf{R}''|^2 s_0^4 - a^2) = \int \mathcal{D}\tilde{\lambda} e^{-i\int_0^t du \int_0^L ds \tilde{\lambda}(|\mathbf{R}''| s_0^2 - a)(|\mathbf{R}''| s_0^2 + a)}. \tag{B2}$$

Due to the fact that $|\mathbf{R}''| s_0^2 + a$ is always different from zero, one may perform the change of variables,

$$\tilde{\Lambda} = \tilde{\lambda}(|\mathbf{R}''| s_0^2 + a). \tag{B3}$$

Applying the substitution (B3) in (B2) we obtain

$$\delta(|\mathbf{R}''|^2 s_0^4 - a^2) = \det{}^{-1}(2a) \delta(R''| s_0^2 - a) \tag{B4}$$

which coincides with Eq. (131) up to the irrelevant constant $\det^{-1}(2a)$.

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[23] Our result agrees with that of Ref. [15], 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.
[24] An exhaustive discussion about the passage from discrete to continuous random chain systems may be found in [16].
[25] Here and in the following the interactions among particles of mass m mediated by the motion of the fluid are called hydrodynamic interactions, according to the definition of hydrodynamic interactions given in Ref. [1], Sec. 3.6, p. 66.