The probability distribution of the average relative distance between two points in a dynamical chain

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Subject of this letter is the dynamics of a chain obtained performing the continuous limit of a system of links and beads. In particular, the probability distribution of the relative position between two points of the chain averaged over a given interval of time is computed. The physical meaning of the obtained result is investigated in the limiting case of a stiff chain.

INTRODUCTION

We study in this letter the dynamics of a chain obtained performing the continuous limit of a system of links and beads. This kind of problems has been addressed in the seminal paper of Edwards and Goodyear [1] using an approach based on the Langevin equation. Related papers dedicated to the statistical mechanics of a freely jointed chain in the continuous limit are for example [2, 3, 4, 5]. In Ref. [6] it has been shown that it is possible to investigate the dynamics of such a chain in a path integral framework. The model which describes the fluctuations of the chain is a generalization of the nonlinear sigma model [7] called the generalized nonlinear sigma model or simply GNLSM. In [6] it has also been discussed the relation between the GNLSM and the Rouse model [8, 9]. Applications of the GNLSM have been the subject of Ref. [10], in which the dynamic structure factor of the chain has been computed in the semiclassical approximation.

The goal of the present work is to derive the probability distribution $Z(r_{12})$ which measures the probability that in a given interval of time $\Delta t$ the average distance between two
points of the chain \( P_1 \) and \( P_2 \) is \( r_{12} \). With respect to Ref. [10], we use to perform the calculation a totally different approximation, which linearizes the GNLSM. Moreover, a background field method is adopted, in which the effects of the thermal fluctuations are considered in the background of a fixed chain configuration chosen among the classical solutions of the linearized equations of motion. We find out that classical configurations are particularly stable against the changes due to fluctuations. The latter become relevant only if they act on the chain for a significant amount of time.

The material presented in this letter is divided as follows. The GNLSM is linearized exploiting a gaussian approximation of the functional Dirac delta function. Next, the probability distribution \( Z(r_{12}) \) is computed within this approximation. The asymptotic form of \( Z(r_{12}) \), which is valid in the case in which the chain is stiff, is derived. Finally, a discussion of the obtained result is presented.

**THE GENERALIZED NONLINEAR SIGMA MODEL IN THE GAUSSIAN APPROXIMATION**

Let us consider the partition function of the GNLSM:

\[
Z = \int \mathcal{D}R(t, \sigma) e^{-\tilde{c} \int_0^t \int_0^N d\sigma R^2(t, \sigma) \delta(|R'| - \ell)}
\]

with \( \dot{R} = \partial R / \partial t \) and \( R' = \partial R / \partial \sigma \). The boundary conditions at \( t = 0 \) and \( t = t_f \) of the field \( R \) are respectively given by \( R(0, \sigma) = R_0(\sigma) \) and \( R(t_f, \sigma) = R_f(\sigma) \), where \( R_0(\sigma) \) and \( R_f(\sigma) \) represent given static conformations of the chain. The boundary conditions with respect to \( \sigma \) are periodic: \( R(t, \sigma) = R(t, \sigma + N) \). It was shown in Refs. [6] and [10] that the above partition function describes the dynamics of a closed chain that is the continuous version of a freely jointed chain consisting of links and beads. The constant \( \tilde{c} \) appearing in Eq. (1) is given by:

\[
\tilde{c} = c \ell \quad \text{with} \quad c = \frac{M}{4k_B T \tau L}
\]

Here \( k_B \) denotes the Boltzmann constant, \( T \) is the temperature and \( \tau \) is the relaxation time which characterizes the ratio of the decay of the drift velocity of the beads. \( M \) and \( L \) represent the total mass and the total length of the chain respectively.

Let us note that in Eq. (1) the trajectory of the chain has been parametrized with the help of the dimensionless parameter \( \sigma \), which is related to the arc-length used in Refs. [6]
and \([10]\) by the relation \(s = \ell \sigma\). The scale of length \(\ell\) introduced with this parametrization is connected to the quantities \(L\) and \(N\) by the identity \(N = \frac{L}{\ell}\). We remark also that, with respect to Refs. \([6]\) and \([10]\), the constraint \(R'^2 = \ell^2\) has been replaced by the constraint \(\mid R' \mid = \ell\) exploiting the property of the functional Dirac delta function \(\delta(R'^2 - \ell^2) = \delta(\mid R' \mid - \ell)\). A proof of this equation can be found in Ref. \([6]\).

In order to deal with the delta function in Eq. (1) we use the following gaussian approximation \([6]\):

\[
\delta(\mid R' \mid - \ell) \sim \exp \left( \int_0^{t_f} dt \int_0^N d\sigma \frac{\nu^2}{2} R'^2 \right)
\]

which is valid when the parameter \(\nu\) is large, while \(\ell\) is small. As a consequence, the partition function \(Z\) becomes:

\[
Z = \int DR \exp \left[ - \int_0^{t_f} dt \int_0^N d\sigma \left( c\dot{R}^2 + \frac{\nu^2}{2} R'^2 \right) \right]
\]

After the approximation \([3]\) the chain may be regarded as a gaussian chain consisting in a set of \(N\) segments of average length \(\ell\).

**THE PROBABILITY DISTRIBUTION OF THE AVERAGE POSITION BETWEEN TWO POINTS OF THE CHAIN**

At this point we pick up two points \(P_1\) and \(P_2\) of the chain, for instance \(R(t, \sigma_1)\) and \(R(t, \sigma_2)\). We wish to study how the relative position between these two points changes due to thermal fluctuations. To this purpose, we introduce the following probability distribution:

\[
Z(r_{12}) = \int DR \exp \left[ - \int_0^{t_f} dt \int_0^N d\sigma \left( c\dot{R}^2 + \frac{\nu^2}{2} R'^2 \right) \right] \\
\times \delta \left( r_{12} - \int_{t_1}^{t_2} \frac{dt}{\Delta t} (R(t, \sigma_2) - R(t, \sigma_1)) \right)
\]

We suppose that \(0 \leq t_1 \leq t_2 \leq t_f\). To evaluate the path integral in Eq. \([5]\) it is convenient to perform the splitting: \(R(t, \sigma) = R_{cl}(t, \sigma) + r(t, \sigma)\). Here \(R_{cl}(t, \sigma)\) is a solution of the classical equations of motion \(\left( c\ddot{R}^2 + \frac{\nu^2}{2} \dot{R}^2 \right) R_{cl} = 0\). The fluctuations around the classical background \(R_{cl}(t, \sigma)\) are taken into account by \(r(t, \sigma)\). The boundary conditions for \(R_{cl}(t, \sigma)\) at the initial and final instants are: \(R_{cl}(t_f, \sigma) = R_f(\sigma)\) and \(R_{cl}(0, \sigma) = R_0(\sigma)\). With respect to \(\sigma\) periodic boundary conditions are assumed: \(R_{cl}(t_f, \sigma) = R_{cl}(t, \sigma + N)\). The solution of the classical equations of motion is complicated due the presence of the non-trivial boundary
conditions and will not be reported here. It can be found in standard books of mathematical methods in physics, like for instance [11]. The only important information related to the background fields that is needed in the probability distribution $Z(r_{cl})$ is the average relative position $r_{cl}$ of the points $P_1$ and $P_2$ for a given classical conformation $R_{cl}(t, \sigma)$:

$$r_{cl} = \int_{t_1}^{t_2} \frac{dt}{\Delta t} (R_{cl}(t, \sigma_2) - R_{cl}(t, \sigma_1))$$  \hspace{1cm} (6)$$

For the fluctuations $r(t, \sigma)$ we choose Dirichlet boundary conditions in time $r(t_f, 0) = 0$, $r(0, \sigma) = 0$. The boundary conditions with respect to $\sigma$ are instead periodic: $r(t, \sigma) = r(t, \sigma + N)$. After a few calculations, it is possible to rewrite $Z(r_{12})$ in the form:

$$Z(r_{12}) = \int_{-\infty}^{\infty} d^3k e^{ik(r_{12} - r_{cl})} e^{-A_{cl}} Z(k)$$  \hspace{1cm} (7)$$

where $r_{cl}$ and $A_{cl} = \int_0^{t_f} dt \int_0^N d\sigma \left( \hat{c} R_{cl}^2 + \frac{\nu}{2} r_{cl}^2 \right)$ take into account the contribution of the classical background, while the fluctuations appear in $Z(k)$:

$$Z(k) = \int D r \exp \left[ - \int_0^{t_f} dt \int_0^N d\sigma \left( \hat{c} r^2 + \frac{\nu}{2} r'^2 + iJ \cdot r \right) \right]$$  \hspace{1cm} (8)$$

In Eq. (8) the external current $J$ is given by:

$$J(t, \sigma) = \frac{k}{\Delta t} \left( \delta(\sigma - \sigma_2) - \delta(\sigma - \sigma_1) \right) \theta(t_2 - t) \theta(t - t_1)$$  \hspace{1cm} (9)$$

This current has been introduced to provide a convenient way of rewriting the integral $\int_{t_1}^{t_2} \frac{dt}{\Delta t} (r(t, \sigma_2) - r(t, \sigma_1))$.

Let’s now concentrate on the computation of the partition function of the fluctuations $Z(k)$. The gaussian integration over the fields $r(t, \sigma)$ may be easily carried out and gives as a result:

$$Z(k) = C e^{W(k)}$$  \hspace{1cm} (10)$$

where $C$ is a constant and

$$W(k) = \exp \left[ \frac{1}{2} \int_0^{t_f} dt dt' \int_0^N d\sigma d\sigma' G(t, \sigma; t', \sigma') J(t, \sigma) \cdot J(t', \sigma') \right]$$  \hspace{1cm} (11)$$

In the above equation $G(t, \sigma; t', \sigma')$ denotes the Green function satisfying the equation:

$$\left[ \hat{c} \frac{\partial^2}{\partial t^2} + \frac{\nu}{2} \frac{\partial^2}{\partial \sigma^2} \right] G(t, \sigma; t', \sigma') = \delta(t - t') \delta(\sigma - \sigma')$$  \hspace{1cm} (12)$$
According to our settings, we choose for \( G(t, \sigma; t', \sigma') \) Dirichlet boundary conditions at the instants \( t = t_f \) and \( t = 0 \) and periodic boundary conditions in \( \sigma \) and \( \sigma' \). To solve Eq. (12), we decompose \( G(t, \sigma; t', \sigma') \) in Fourier series as follows:

\[
G(t, \sigma; t', \sigma') = \sum_{n=-\infty}^{+\infty} g_n(t, t') e^{-2\pi i \frac{\ell}{L}(\sigma-\sigma')n}
\]

Substituting also the Fourier expansion of the periodic Dirac delta function \( \delta(\sigma - \sigma') = \sum_{n=-\infty}^{+\infty} \frac{\ell}{L} e^{-2\pi i \frac{\ell}{L}(\sigma-\sigma')n} \) in Eq. (12) and solving for \( g_n(t, t') \), we obtain for \( n = 0 \):

\[
g_0(t, t') = \frac{1}{Lc} \theta(t' - t) \left( t - t_f \right) + \frac{1}{Lc} \theta(t - t') \left( t' - t_f \right)
\]

and for \( n \neq 0 \):

\[
g_n(t, t') = A_n \theta(t' - t) \sinh \beta_n t' \sinh \beta_n (t - t_f) + A_n \theta(t' - t) \sinh \beta_n t \sinh \beta_n (t_f - t')
\]

with

\[
\beta_n = \frac{|n| \pi}{L} \sqrt{\frac{2\nu \ell}{c}}
\]

\[
A_n = -\frac{1}{\sqrt{2\nu l c}} \frac{1}{|n| \pi \sinh \beta_n t_f}
\]

In Eqs. (14) and (15) \( \theta(t) \) denotes the Heaviside \( \theta \)-function \( \theta(t) = 1 \) for \( t \geq 0 \) and \( \theta(t) = 0 \) for \( t < 0 \). To complete the calculation of \( Z(k) \) in Eq. (10) we rewrite \( W(k) \) as follows:

\[
W(k) = \frac{1}{2} \sum_{n=-\infty}^{+\infty} \int_0^{t_f} dt \int_0^N d\sigma d\sigma' \int_0^{t_f} g_n(t, t') e^{-2\pi i \frac{\ell}{L}(\sigma-\sigma')} J(t, \sigma) \cdot J(t', \sigma')
\]

It is easy to show that the only non-zero contributions to the above integral are those for which \( n \neq 0 \). After integrating over the variables \( \sigma, \sigma' \) and over one of the time variables, we obtain:

\[
W(k) = \frac{2k^2}{(\Delta t)^2} \sum_{n \neq 0} \frac{A_n}{\beta_n} \left[ 1 - \cos \left( \frac{\ell_2 - \ell_1}{L} \right) \right] \times \int_{t_1}^{t_2} dt \sinh \beta_n (t_f - t) (\cosh \beta_n t - \cosh \beta_n t_1)
\]

where we have put \( \ell_2 = \ell \sigma_2 \) and \( \ell_1 = \ell \sigma_1 \). Remembering that the coefficients \( A_n \) defined in Eq. (17) are all strictly negative, it is easy to realize that \( W(k) \) is negative too. This property of \( W(k) \) will be necessary in order to perform the remaining integration over \( k \) in the probability distribution \( Z(r_{12}) \) of Eq. (7).
A last integration over $dt$ in Eq. (19) delivers the following result:

$$W(k) = \frac{2k^2}{(\Delta t)^2} \sum_{n \neq 0} \frac{A_n}{\beta_n} \left[ 1 - \cos 2\pi n \left( \frac{t_2 - t_1}{L} \right) \right] \left[ \frac{1}{2}(t_2 - t_1) \sinh \beta_n t_f - \frac{\cosh \beta_n t_f}{2\beta_n} \right]$$

$$- \frac{1}{4\beta_n} (\cosh \beta_n(t_f - 2t_2) + \cosh \beta_n(t_f - 2t_1))$$

$$+ \frac{1}{2\beta_n} (\cosh \beta_n(t_f + t_1 - t_2) + \cosh \beta_n(t_f - (t_1 + t_2)))$$

(20)

Substituting Eq. (20) back in Eq. (10) we get an exact expression for $Z(k)$. To obtain the probability distribution $Z(r_{12})$ of Eq. (7) in closed form a gaussian integration over $k$ is sufficient.

**CALCULATION OF THE PROBABILITY DISTRIBUTION $Z(r_{12})$ IN THE LIMIT OF A STIFF CHAIN**

To simplify our calculations of the previous Section, we compute the infinite sum in Eq. (20) using an approximation. First of all, we give a physical meaning to the parameter $\nu$ by putting:

$$\nu = \frac{\alpha}{k_B T \tau \ell}$$

(21)

After performing the above substitution in the partition function of Eq. (4), the term proportional to $\nu$ appearing in the action of the fields $R$ becomes exactly the term introduced in the GNLSM in Ref. [10] in order to take into account the bending energy of the chain. This connection with the bending energy is confirmed by the fact that $\alpha$ has dimensions of an energy per unit of length, i.e. $[\alpha] = [\text{energy}] \cdot [\text{length}]^{-1}$.

As it was shown in Ref. [10], large values of $\alpha$ correspond to a stiff chain. Indeed, it is possible to check from Eq. (8) that in this case the corrections to the tangent vectors $R'_{cl}$ coming from the fluctuations $r'$ are strongly suppressed in $Z(k)$. In the following, we will work in the limit of a stiff chain, i.e.:

$$\alpha >> 1$$

(22)

implies that also From Eqs. (21) and (22) it turns out that the quantity $\nu \ell = \frac{\alpha}{k_B T \tau \ell}$ appearing in the coefficients $\beta_n$ and $A_n$ (see Eqs. (16) and (17)) is very large. As a consequence, within the approximation (22) the coefficients $\beta_n$ are large, while the coefficients $A_n$ are
exponentially small. Taking into account these facts, we may write the following asymptotic expression of $W(k)$:

$$W(k) = \frac{2k^2}{(\Delta t)^2} \frac{L}{2\pi^2 \nu \ell} \left[ -A \frac{(t_2 - t_1)}{2} + B \frac{L}{\pi} \sqrt{\frac{c}{2\nu \ell}} \right] + O \left( e^{-\frac{2\pi}{L} \sqrt{2\nu \ell} (t_2 - t_1)} \right)$$  \quad (23)

In Eq. (23) we have introduced the convenient notation:

$$A = \sum_{n \neq 0} \frac{1}{n^2} \left[ 1 - \cos 2\pi n \left( \frac{\ell_2 - \ell_1}{L} \right) \right]$$  \quad (24)

$$B = \frac{1}{2} \sum_{n \neq 0} \frac{1}{|n|^3} \left[ 1 - \cos 2\pi n \left( \frac{\ell_2 - \ell_1}{L} \right) \right]$$  \quad (25)

It is possible to check that the other contributions to $W(k)$, expressed in Eq. (23) with the symbol $O \left( e^{-\frac{2\pi}{L} \sqrt{2\nu \ell} (t_2 - t_1)} \right)$, decay at least as fast as $e^{-\frac{2\pi}{L} \sqrt{2\nu \ell} (t_2 - t_1)}$. These terms become negligibly small when $\nu \ell$ is large, provided of course that:

$$t_2 - t_1 >> \frac{1}{2} \frac{L}{\pi} \sqrt{\frac{c}{2\nu \ell}}$$  \quad (26)

Substituting Eq. (23) in Eq. (10), we obtain for $Z(k)$ the approximate expression:

$$Z(k) = Ce^{-\frac{\kappa k^2}{2}}$$  \quad (27)

where

$$\kappa = \frac{4}{(\Delta t)^2} \frac{L}{\pi^2 2\nu \ell} \left[ A \frac{t_2 - t_1}{2} - B \frac{L}{\pi} \sqrt{\frac{c}{2\nu \ell}} \right]$$  \quad (28)

The condition (26) guarantees that $\kappa > 0$. This is what is needed to compute the integral over $k$ in Eq. (7). After a few calculations we arrive at the final result:

$$Z(r_{12}) = Ce^{-A_{cl} \left( \frac{2\pi}{\kappa} \right)^{\frac{3}{2}}} \exp \left[ -\frac{1}{2} \frac{(r_{12} - r_{cl})^2}{\kappa} \right]$$  \quad (29)

Eq. (29) has a straightforward interpretation. The quantity $\kappa$ is inversely proportional to the product $\nu \ell$, which is supposed to be large. Thus $\kappa$ is very small. As a consequence, Eq. (29) implies that the relative positions of the two points $P_1$ and $P_2$ exhibits a sharp peak around the classical value, i.e. when $r_{12} = r_{cl}$. From Eq. (29) it turns also out that the changes of the classical background configuration $R_{cl}(t, \sigma)$ due to the fluctuations $r(t, \sigma)$ are relatively small. This is due to the fact that there is no contribution to the parameter $\kappa$ which is of zeroth order in $\nu \ell$. Potentially, a zeroth order contribution could come from the term proportional to $g_0(t, t')$ in Eq. (18), but we have seen that this term vanishes identically. This
suggests that the effects of thermal fluctuations are weak at short time-scales. Of course, with the increasing of the time interval $\Delta t = t_2 - t_1$ over which the average of the relative position of $P_1$ and $P_2$ is measured, the fluctuations have more and more time to act on the chain and their influence becomes more and more important. This intuitive prediction is confirmed by Eq. (29). Indeed, the coefficient $\kappa$ grows linearly with $\Delta t$ and, for larger values of $\kappa$, the peak around the classical point $r_{12} = r_{cl}$ in the probability distribution $Z(r_{12})$ becomes less sharp as expected.

CONCLUSIONS

In this work the GNLSM of Refs. [6] and [10] has been applied to compute the distribution function $Z(r_{12})$ of the relative position between two points of a chain with rigid constraints. The calculation has been performed using the approximation (3) of the functional Dirac delta function which is needed to impose the constraints. After this approximation, the finest details of the chain are lost, a fact that has already been noted in the case of a static chain [1].

A closed form of the probability distribution (29) may be obtained starting from the exact calculation of the contribution of the fluctuations to $Z(r_{12})$ given in Eq. (20). The final formula for $Z(r_{12})$ computed in this way is however complicated. For this reason the physical meaning of $Z(r_{12})$ has been investigated at the end of the previous Section in the case in which the energy needed for bending the chain is large. In this approximation the contributions of the fluctuations which decay exponentially when $\alpha$ becomes large are neglected.

Concluding, it would be interesting to explore the connections between the GNLSM and other models of the dynamics of a chain, in which instead of rigid constraints the addition of potentials is used in order to prevent the breaking of the chain [13].

ACKNOWLEDGEMENTS

This work has been financed by the Polish Ministry of Science and Higher Education, scientific project N202 156 31/2933. F. Ferrari gratefully acknowledges also the support of the action COST P12 financed by the European Union and the hospitality of C. Schick at
the University of Rostock. The authors would like to thank V. G. Rostiashvili for fruitful
discussions.

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