Fluctuation-induced forces between rings threaded around a polymer chain under tension

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We characterize the fluctuation properties of a polymer chain under external tension and the fluctuation-induced forces between two ring molecules threaded around the chain. The problem is relevant in the context of fluctuation-induced forces in soft matter systems, features of liquid interfaces and to describe properties of polyrotaxanes and slide-ring materials. We perform molecular dynamics simulations of the Kremer-Grest bead-spring model for the polymer and a simple ring-molecule model, in the canonical ensemble. We study transverse fluctuations of the stretched chain, as a function of chain stretching and in the presence of ring-shaped threaded molecules. The fluctuation spectra of the chains are analyzed in equilibrium at constant temperature and the differences in presence of two ring molecules are compared. For the rings located at fixed distances, we find an attractive fluctuation-induced force between the rings, proportional to the temperature and decaying with the ring distance. We characterize this force as a function of ring distance, chain stretching, ring radius and measure the differences between the free chain spectrum and the fluctuations of the chain constrained by the rings. We also compare the dependence and range of the force found in the simulations with theoretical models coming from different fields.

I. INTRODUCTION

Fluctuation-induced forces have attracted enormous attention starting from the renowned Casimir effect, which was discovered in the context of quantum electrodynamics. However, the key elements for the existence of fluctuation-induced forces are present in a broad range of systems. Those elements are a fluctuating medium and an external object, whose presence inhibits or hinders the natural fluctuations of the medium. The first realm of study of fluctuation-induced forces was given by quantum fluctuations of the electromagnetic field with restrictions imposed by perfect parallel conducting plates, as in the seminal work by Casimir. However, forces arising from thermal fluctuations of the electromagnetic field have also been predicted and measured experimentally. A variety of physical systems were found to present effective forces of the same origin due to thermal fluctuations of material fields and molecules. For example, colloids located at liquid-liquid interfaces act as physical restrictions of interface fluctuations. Fisher and De Gennes noted that these interactions should appear in a film of a binary liquid mixture close to a wall at the critical point, where the correlation of concentration fluctuations diverges. The objects restricting fluctuations are in this case the interface with the wall and the gas-liquid film interface, which are affected by an attractive fluctuation-induced force. This force, known as critical Casimir effect, was measured recently using colloids and total reflection microscopy. Beyond being a fascinating physical effect, the fluctuation-induced forces became relevant in practice due to miniaturization and manipulation of matter at the nanoscale. This ranges from the development of micro and nano electromechanical systems (MEMS) and the behavior of colloids or proteins in interfaces and membranes. The range of the force is related to the characteristic length of correlation of fluctuations, which becomes comparable with mesoscopic distances between colloids, molecules or aggregates in many systems. Fluctuation-induced forces have been studied in superfluid films, liquid crystals, inclusions or proteins in membranes, and colloids confined in liquid interfaces. More recently, Casimir-like forces were studied in out-of-equilibrium diffusive systems and active matter.

Within the context of soft matter, we study the fluctuation-induced forces between ring molecules threaded around a polymer chain under tension at thermal equilibrium. The system is interesting from a basic point of view, but can be also synthesized in the form of supramolecular aggregates, the so-called polyrotaxanes. A polyrotaxane is formed by a varying number of ring molecules, usually cyclodextrin, threaded in a backbone linear polymer chain. The end-groups of the polymer are big enough such that the rings cannot get out of the chain, or they are called pseudo-rotaxanes, when the bulkier end beads are not
present. Novel materials called topological gels, have been produced with melts of polyrotaxanes, by cross-linking two α-cyclodextrin molecules belonging to different rotaxanes. These eight-shaped links are then movable through the backbone of the polymers, unlike the chemical gels, which have fixed cross-links. The topological gels refer usually to polymer melts in a solvent, but the polyrotaxanes aggregates with movable cross links can also be produced with a dry polymeric matrix, receiving the name of slide-ring materials.

In this work we study the properties of a fluctuating chain under tension with and without threaded rings fixed at given positions, which act as physical constraints of the fluctuation of the chains. The physical system we deal with is shown in Fig. 1 with a typical configuration of the chain-ring system. For the polymer chain without rings, we find a transversal fluctuation spectrum compatible with a dependence at high stretchings, and a deviation from it at shorter chain stretchings. We show how this spectrum is modified by the presence of two rings fixed in space, and the appearance of an attractive fluctuation-induced force between the rings. The details of the model and simulation techniques are explained in Section II and we present the results for the fluctuation properties of the chain as a function of chain extensions and temperatures in Section IIIA. We devote section IIIB to the characterization of the fluctuation-induced forces between the rings as a function of chain extension and temperature. We also compare the dependence of the force with the rings’ distance with models of different fields, such as classical electromagnetism and liquid-liquid interfaces. In Section IV we provide a final discussion and conclusions.

II. MODEL AND SIMULATION TECHNIQUES

We use the widely known and studied Kremer-Grest model for the polymer chain under tension. The interaction between neighboring beads along the polymer chain is modeled by a finitely extensible non-linear elastic (FENE) potential:

\[
U_{\text{FENE}} = \begin{cases} 
-\frac{1}{2} k R_0^2 \ln \left[ 1 - \left( \frac{r_{ij}}{R_0} \right)^2 \right] & \text{for } r_{ij} \leq R_0, \\
\infty & \text{for } r_{ij} > R_0
\end{cases},
\]

where the maximum allowed bond length is \( R_0 = 1.5\sigma \), the spring constant is \( k = 30\varepsilon/\sigma^2 \), and \( r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \) denotes the distance between neighboring monomers. Excluded volume interactions at short distances and van-der-Waals attractions between beads are described by a truncated and shifted Lennard-Jones (LJ) potential:

\[
U(r) = U_{\text{LJ}}(r) - U_{\text{LJ}}(r_c),
\]

with

\[
U_{\text{LJ}}(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^12 - \left( \frac{\sigma}{r} \right)^6 \right],
\]

where the LJ parameters, \( \varepsilon \) and \( \sigma \), define the units of energy and length, respectively. Temperature is given in units of \( \varepsilon/k_B \), with \( k_B \) being the Boltzmann constant. \( U_{\text{LJ}}(r_c) \) is the LJ potential evaluated at the cut-off radius. We used standard values for the LJ parameters and mass: \( \sigma = 1 \), \( \varepsilon = 1 \) and \( m = 1 \). The interaction cut-off is located at the minimum of the LJ potential, \( r_c = 2.5\sigma \), which gives effectively a fully repulsive potential and is typical of good solvent conditions when studying polymer melts. This model has been applied to a variety of thermodynamic conditions, chain lengths, and physical regimes such as glasses, melts, dilute solutions, etc. It has been also used for the study of single polymer chains under tension, in a similar physical situation as studied here, with focus in dynamical and relaxation properties. The polymer chain was maintained under tension by connecting the beads 1 and \( N \) through a FENE potential. Periodic boundary conditions were applied by computing the force on each of these beads with the periodic image of the other one. In this way, the length of the chain is set with the box dimension \( L_x \) in the \( x \) direction. In addition, the center of mass of the chain was kept fixed at the center of the MD box.

The ring molecules were generated at fixed positions within the boundaries of the simulation box, and the positions of their beads were not allowed to evolve in time. They were modeled by groups of 11 beads, arranged in two parallel circles. This number was chosen because we found it to be the minimal number of beads at which the rings did not unthread from the chain, for different chain stretchings and temperatures. We chose the beads of the rings to be the same size than the beads of the chain for simplicity. We do not aim at developing a detailed model of annular molecule. The ring molecules are meant to provide a consistent physical constraint for the transverse fluctuations of the polymer chain. Beads in the rings are connected by springs (see Fig. 1) with the
same FENE interactions that we used for the connectivity of the chains. In the model of the ring molecules it was necessary to use two interlocked groups of beads, because setting only one is prone to unthreading from the chain at high stretchings or temperatures (see Fig. 1). The excluded volume of beads was also described by a LJ potential, also with a cut-off of $r_c = 2 \pi \sigma$ which keeps only the repulsive part of the LJ potential. The interaction of the rings with the chain is therefore purely repulsive, as well as the interaction among beads of the rings. This rules out any direct attractive interaction between rings, which is important to isolate the effective interaction arising from the Casimir-like forces.

We used a Langevin thermostat to study the system at constant temperature. Dissipative and stochastic forces are added to the conservative forces, already present in the standard molecular dynamics equations of motions. The dissipative force on particle $i$ is given by $F_i^D = -\gamma \nu_i$, where $\gamma$ is the friction coefficient and $\nu_i$ the particle velocity. The random force, $F_i^R$, has zero mean value and its variance satisfies \cite{35, 36}

$$\langle F_i^R(t)F_{j\nu}^R(t') \rangle = 2\gamma T k_B \delta_{ij} \delta_{\mu\nu} \delta(t - t'),$$

where the indices $i$ and $j$ label particles, $\mu$ and $\nu$ Cartesian components, and $T$ is the temperature at which the system is simulated.

After a thermalization stage of $1 \times 10^6$ MD steps with a time step of $dt = 1 \times 10^{-5}\tau$, typical simulations were performed with trajectories of $1 \times 10^7$ MD steps each, with a time step of $dt = 2 \times 10^{-3}\tau$. The time unit in LJ parameters being $\tau = \sigma (\varepsilon/m)^{1/2}$. We took averages of physical quantities each 1000 time steps. The friction constant was set at $\gamma = 0.5\varepsilon\tau/\sigma^2$ for all the simulations, except for the initial thermalization stage in which the friction constant was set to $\gamma = 50.0\varepsilon\tau/\sigma^2$. The typical chain was composed of $N = 1024$ beads, but we also studied shorter and longer chains, when needed. These cases will be mentioned explicitly in the text. This choice allowed us to study ring distances in the range $3 - 60\sigma$, to obtain a fluctuation-induced force values with high enough signal-to-noise ratio.

### III. Results

#### A. Properties of the polymer chain under tension

We analyze firstly the structural and fluctuation properties of the chain under extensional force, without rings. We worked with simulations at constant length, giving rise to a mean constant stretching force. Fig. 2 shows typical configurations of the chains for different extensions. The chain length is given in units of the maximum extension of the FENE model chain $L_{max} = 1.5\sigma N$. For the smaller extensions the chain starts to show blob formation. There are local regions of beads arranged in configurations not very different from that of isolated chains (Fig. 2 $L^* = 0.4$). For larger extensions the chain is very stretched, with little freedom for transverse relative displacement among consecutive beads (Fig. 2 $L^* = 0.70$). In this regime the internal energy of the chain is very high, and dominant as compared to configurational entropy.

This behavior can be quantified with the mean bond length in units of the maximum allowed bond length for the FENE model ($R_{max} = 1.5\sigma$). This is shown in Fig. 3 as function of chain stretching, for different temperatures. For stretchings in the range $L^* < 0.65$, the mean bond is marginally dependent on chain length, and increases towards the limit $L^* \approx 0.65$. In this regime the blobs are dominant and bond length values are dominated by the thermal energy of the beads and the excluded volume which, given by the Lennard-Jones potential. In the case $L^* \gtrsim 0.65$, the bonds increase more pronouncedly with chain stretching. In this limit each bond is permanently stretched with respect to the equilibrium bond length and the excluded volume is not important for the mean bond. For very high $L^*$, the bonds converge to the maximum value for all the temperatures. The case $T = 0$ (athermal) is shown for comparison with a dashed line. This is the limiting case, in which there is only potential energy in the chain. It follows the tendency of the thermal case, indicating also the two distinctive behaviors. The value $r_{\min} \sim 0.65$ corresponds to a bond distance $d = 0.975\sigma$, where the Lennard-Jones and bond forces are equal. Fig. 1 shows the bond distance as a function of temperature for different chain extensions. The mean bond is more dependent on temperature at
compared with a free polymer chain. We define a discrete direction of the chain (i.e. those perpendicular to the stretching minor effect with increasing temperatures.

The fluctuation spectra, given by the square amplitude of the Fourier modes, are shown in Fig. 5, for some selected chain lengths. The inset shows the power spectra in logarithmic scale. The overall magnitude of fluctuations is, as expected, reduced with chain stretching. The wave amplitudes also decrease with q number or, equivalently, increase with wavelength λ.

In the limit of very high stretching, the harmonic approximation should fulfill, due to small amplitude oscillations of the beads, which are effectively trapped in very stiff potential wells. This can be thought as an effective Hamiltonian with quadratic degrees of freedom in coordinates and momenta. The chain is in a heat bath at constant temperature and therefore, equipartition theorem holds, giving a contribution of $\frac{1}{2}k_B T$ for each degree of freedom to the potential and kinetic energies. Each normal mode of the chain has the same mean potential energy of $\frac{1}{2}k_B T$ and, by using the relation between potential energy of a mode and amplitude $\Delta$, the harmonic model gives rise to a dependence of the squared mode amplitude $C^2 \sim 1/q^2$. The same conclusion can be reached in the realm of soft matter and interfaces for a capillary wave Hamiltonian. The fluctuating stretched chain projected in a plane, can be thought as a unidimensional interface between two immiscible liquids or a liquid-gas interface and the modes of the chain as the capillary waves of the interface. The energy cost of a non-flat surface in comparison to the flat case (of minimum area) can be written as an effective Hamiltonian of surface fluctuations. This so-called capillary wave Hamiltonian, describes the energy cost of surface undulations of thermal origin in terms of a function $h(x, y)$, which accounts for the local position of the interface. Expressing this Hamiltonian in Fourier space, leads to a quadratic form in the wave vectors $q$ of independent harmonic oscillators. The application of the equipartition theorem, leads to the dependence $C(q) \sim k_B T/q^2$ for the Fourier amplitudes of the Fourier modes of the surface.[38, 39] This analogy is very interesting, because simulations can test in which range of chain extensions is valid and allows the study of interface fluctuations by carefully simulating a stretched chain. The chain is, of course, much less demanding of computing power. The dashed line in the inset of Fig. 4 shows a curve $\sim 1/q^2$ for reference. For the higher extensions ($L^* = 0.90$ and $L^* = 0.70$) the chain fluctuations are very close to the harmonic model. The curves are parallel to $1/q^2$ for the whole range of q. Some differences show up for the smaller extension $L^* = 0.40$, which computing the mean position of the beads that belong to each bin. This binning procedure was used because for short chain lengths the beads are grouped in blobs and taking directly their positions would give a multivalued function at some x points. This type of discretization is usual in analysis of interface fluctuations.[30, 38]. $h_0$ is the horizontal along x direction, in which would lie the stretched chain at zero kinetic energy. For each time step the Fourier amplitudes are calculated and averaged over the chain configurations obtained in the simulations.

Figure 3: Mean bond length as a function of temperature for different chain extensions. A saturation at higher temperatures is observed in accordance with the fast increase of FENE bond energy.

Figure 4: Mean distance among beads as a function of temperature for different chain extensions. The dashed line represents beads distance in the limit of $k_B T = 0$ and no excitations in the chain (athermal limit). The vertical dotted line indicates the extension at which the bond length increases its rate of change with chain stretching shorter chain extensions and lower temperatures. The FENE contribution of the bond energy is, of course, nonlinear, and therefore the temperature has a progressively minor effect with increasing temperatures.

We also calculate the spectra of transverse fluctuations of the chain (i.e. those perpendicular to the stretching direction $\hat{x}$), to characterize the collective vibrations in the limit of high stretching. We point out that even the lowest stretching case ($L^* = 0.20$) is still very high, as compared with a free polymer chain. We define a discrete function $h(x_i) = h_{bin}(x_i) - h_0$, which accounts for the transverse fluctuations. $h_{bin}$ is obtained by dividing the space along the chain in bins of width $\Delta x = 2\sigma$ and then
increase appreciably for the lowest stretching $L^* = 0.20$. This is specially true for the high-$q$ part of the spectra, i.e. for the shorter-wavelength modes. Interestingly this is in line with the idea of the capillary wave Hamiltonian (also the Helfrich Hamiltonian, for membrane bilayers). These models are suitable for long-wavelength fluctuations\cite{38,39}. We recall that for the shorter chain lengths, the Lennard-Jones interaction, i.e. the excluded volume, has a role in the local dynamics of the beads.

Fig. 6 show the decaying exponent of the spectra for different chain stretchings and temperatures. We fitted the function $f(q) = A_0/q^\alpha$ in the log-form, where $A_0$ and $\alpha$ are the fitting parameters. A convergence towards $\alpha = 2$ is observed upon increase of chain stretching. For the range of shorter chain stretchings ($L^* < 0.5$) the exponent increases. This means a deeper decay of fluctuations for smaller wavelengths. For these shorter stretchings, the polymer chains are more intertwined and the vibrational behavior comes dominantly from groups of beads, more than from independent beads themselves. This could be thought as an effectively shorter chain (with fewer degrees of freedom and, therefore modes), which for the same $q$ range of the complete chain, it will have a faster decay.

\section{Effect of the rings on the chain and fluctuation-induced forces}

We analyze here the effect of the fixed rings in the natural fluctuations of the chain, to continue further to the fluctuation-induced or Casimir-like forces between rings. Fig. 7 shows the fluctuation spectra of the chain with the rings fixed at different distances. The decay range is similar for the chain with and without rings, but the modes whose wavelengths are higher than the distance between rings ($\lambda_{\text{mode}} > d$) are significantly reduced. The power spectrum of the chain without rings is shown also for comparison.

Fig. 8 shows the difference of the power spectrum with and without rings for different ring distances. The effect of the rings is clearly observed for the modes which are expected to be heavily hindered by the rings. The higher effect is observed for smaller distances in which modes of lower wavelengths are reduced, starting at $\lambda_{\text{min}} = d$. It is also observed that increasing the ring distance, changes the cut-off wave number from which the spectrum is significantly reduced, as compared to the stretched chain without rings.

In Fig. 9 the mean number density of the chain is presented. Panel (a) shows the chain without rings, while
for all the cases. First, there is a significant stretching of the outer zone for high ring distances (Panel B, the zone between rings, the bead distribution is similar to the case of the chain with rings). This is in line with the suppression of mode numbers. The outer zone however, presents monomers positioned at higher distances (see Panel B, in Fig. 9), compared to the case of rings located at distances 30σ and 6σ respectively. We obtained the histograms from a square binning in 2D with a bin lateral size of Δr = 0.25σ and a Bessel smoothing function was used for the color plots. The spatial zone at which the beads have access is significantly reduced by the presence of the rings. This is in line with the suppression of modes of higher amplitude in the presence of rings. For the zones between rings, the bead distribution is similar to the outer zone for high ring distances (Panel B, d = 30σ), but with reduced amplitudes. For rings very close (Panel C, d = 6σ), the inner zone presents beads only very close to the rings. The outer zone however, presents monomers in a slightly wider zone as compared to the case of rings located at higher distances (see Panel B, in Fig. 9), compatible with the fact that the outer zone of the chain can have modes of very high wavelength and amplitude (see Sec. IIIA) when the rings are very close to each other.

In addition to the fluctuation properties of the chain, we found other interesting aspect that changes in the presence of fixed ring molecules. We studied the mean bond length for all the chain bonds, considering separately the bonds lying between the rings and those in the outer region. Fig. 10 depicts the mean bond lengths obtained from the mean bond value over neighboring beads in the chain. The pair number is defined such that pair number i, indicates the bond between beads i + 1 and i. Fig. 10 provides an example of what we have observed for all the cases. First, there is a significant stretching of the bonds which are directly exposed to the fixed rings.

This can be expected: as the chain fluctuates the bond will scatter against the beads of the rings, producing a high stretching of these bonds. There is also a much more subtle and interesting effect, that we noticed for different stretchings and temperatures. Namely, the bond between rings are slightly stretched as average. This can be observed in the center points of Fig. 10 which are systematically above the dashed line which indicates the mean bond value for the bonds in the outer region of the chains (those in the regions of bond numbers 1-503 and 522-1023). The chain is more stretched between rings. From a mechanical viewpoint, we attribute this to action-reaction principle. As it will be shown next, the chain is effectively producing a mean force between rings and there should be a force equal in magnitude that the rings exert on the chain, giving rise to this slight increase of the bond length in the zone between rings. This interesting characteristic could be explored further, but this is outside the scope of the present work.

The nature and characteristics of effective forces between rings is one of the main results and motivations of our study. We compute the mean force on each bead of the rings, averaged over each MD step. This quantity is the mean force on the ring due to the interaction with the chain. We recall that ring-ring interaction is neglected because we used a cut-off for the ring-ring interaction of Rc = 1.12σ, among beads of same and different rings. We kept only the repulsive part of the Lennard-Jones potential, which means that only the excluded volume is considered. As rings were fixed at distances d ≥ 3σ, direct interaction between rings are disregarded by con-
helpful to analyze the fluctuation-induced force as a function of ring distance. We show in Fig. 11 one of the main results of this work, namely the existence of an effective force between rings that can only arise through interactions mediated by the chain. Furthermore, the rings are efficient to hinder transverse fluctuations of the chains, but not longitudinal waves, since the effective ring diameter is bigger than the bead diameter of the chain ($\sigma$). We conclude that this effective interaction is the expected fluctuation-induced force due to the disturbance of the natural fluctuations of the stretched unconstrained chain by the presence of the rings. They have a range clearly bigger than the bead diameter of the chain ($\sigma$). Another qualitatively important aspect is that the interaction is attractive for all the studied cases. We point out also that the nature of the system disregards other type of effective interactions, as for example, depletion interactions which are usually present together with fluctuation-induced forces in many systems [41]. From a thermodynamic viewpoint, the system minimizes free energy with the rings as close as possible to each other. This allows for modes with longer $\lambda$ in the outer region. However, as we have the chain in a thermal bath (canonical ensemble) the mean internal energy of the chain is the same for all the cases. Therefore the Casimir-like force arises in particular from the maximization of entropy, which is obtained when the rings are together. Entropy is maximized, when the maximum possible number of modes are active and specially those of higher amplitude ($\lambda > d$). As we showed, these modes are hindered when the rings are placed at higher distances.

The ring molecules, are of course physical constraints and not mathematical nodes imposed on the chain. It is helpful to analyze the fluctuation-induced force as a function of ring radius. This is done in Fig. 12 where we plot force versus ring distance for different ring radius. The force is present in all the cases, but greatly reduced for larger ring radii. The inset shows a zoom of the higher studied radius ($r_{\text{ring}} = 6\sigma$), which is barely noticeable in the scale of the main graph. As the ring radius increases, the rings are unable to hinder the fluctuations of middle to small wavelength, which are progressively of smaller amplitude as $\lambda$ decreases. The ring radius modifies significantly the strength of the fluctuation-induced force.

We present in Fig. 13 the force strength between rings for different chain stretchings and temperatures as a function of distance. Panel (a) presents the force intensity versus distance. The force is long range as compared to bead size. We resolve non-zero force values up to $d \simeq 48\sigma$ for a chain length of $L = 1076\sigma$ and 1024 beads. The force is non-negligible approximately for distances in a range of 5% of the chain length. For short ring distances, Fig. 13 shows that the strength of the force is highly influenced by the amplitude of the chain modes of higher wavelength. As it was showed for the fluctuations of the chain without rings (see Fig. 4), less stretching increases considerably the amplitude of the modes in the small $q$ range (longer wavelengths). On higher chain stretchings, for instance $L^* = 0.8$ in Fig. 13(a), it appears an oscillation of the force, noticeable at shorter ring distances. We will analyze this further in the next paragraphs.
to a contribution to the force of each normal mode of
ering harmonic modes, the equipartition limit gives rise
due to the restriction of modes in the cavity. Consid-
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= 1, which can be obtained analyti-
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modes [41, 42]. Boyer discusses the standard Casimir ef-
fect from zero point energy fluctuations of the electro-
magnetic field and thermal fluctuations of the classical
electromagnetic field in a unified way [41, 42]. The lat-
ter case is equivalent to the chain in a thermal bath.
The system is described as a one dimensional cavity at a
given temperature, with a partition inside the cavity at
position
x
. He calculates the total force on the partition
due to the restriction of modes in the cavity. Consi-
ering harmonic modes, the equipartition limit gives rise
to a contribution to the force of each normal mode of
f
mode
(ω, L, T ) = \frac{k_B T}{L}
, where
L
 is the length of the cavity.
Adding up over all the modes, the total force on the
partition at position
x
 is:

\[ f(x, L, T) = \frac{k_B T}{2\sigma} \left( \frac{1}{x} - \frac{1}{L - x} \right) \]

where the two terms indicate attractions to each one of
the wall cavities [42]. In our case the boundary con-
tion is periodic and the force between rings is mapped to
the force between the partition and one of the walls. If
the partition is close to one of the walls, the interaction
with the other one is negligible. This would be the limit

Comparison with theoretical models

To compare the force with analytical models, we pro-
vide a log-log plot of the force scaled with the temper-
ature in Fig. 13(b). Firstly we fitted force between
rings as a function of distance as a power law of the form:
F(d) = A(T)/d^\alpha. A log-log plot should present
a linear dependence, which is approximately the case in
Fig. 13(b). The exponent \alpha \text{ changes with chain stretch-
ing, growing for smaller } L^*. The dashed line repre-
sents the case \alpha = 1, which can be obtained analyti-
cally with a harmonic approximation of independent normal
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fect from zero point energy fluctuations of the electro-
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where the two terms indicate attractions to each one of
the wall cavities [42]. In our case the boundary con-
tion is periodic and the force between rings is mapped to
the force between the partition and one of the walls. If
the partition is close to one of the walls, the interaction
with the other one is negligible. This would be the limit
of two rings at short distance in comparison with chain
length \(d \ll L\), which we use in the simulations. The
ring distance varies in a range 2-60\(\sigma\) in a chain of typical
length \(L = 1076\sigma\). We also add a factor 2, due to two
independent fluctuation directions for the chain \((\hat{y} \text{ and } \hat{z})\),
which are locally constrained by the presence of the
rings. We end up therefore with a force dependence given
by:

\[ F_x(d) \equiv f_{\text{ring}}(d) = \frac{k_B T}{d} \]

which is plotted in Fig. 13 in dashed line.

Interestingly the theory agrees pretty well with our re-
results for relatively high chain stretchings \(L^* > 0.67\)
and for all the studied temperatures. At very high chain
stretching \(L^* > 0.7\), there are force oscillations at short
ring distances (considered later on), but we have again
good agreement with the theoretical model at longer ring
distances. It should be noted that the interactions of in-

Figure 12: Mean force between rings versus distance for dif-
erent ring radius
r
. The parameters were set
L^* = 0.70
and
T = 33.6\sigma/k_B
. The Inset shows a magnification of the case
r = 6\sigma
, for which the minimal restrictions imposed by this
big ring radius reduces significantly the fluctuation-induc-
ed force.

Figure 13: Upper panel: Mean force versus ring distance for
different chain stretchings and temperatures. The dashed line
represents the harmonic model for the force \(f \sim 1/d\). It
indicates only the power law decay. Lower panel: log-log plot
for the same cases. The dashed shows an idealized theoretica-
l model which is consistent for medium to high stretching (see
text).
individual bonds are non-harmonic elastic terms, given by the FENE potential (see Eq. 1). However, in the limit of high stretching we consider that the harmonic approximation is reasonable. We think that this is because each bead of the chain is trapped in a very stiff potential well, which for moderate temperatures, could be well approximated by a Taylor expansion of second order. This is in the same spirit of the small amplitude harmonic approximation of vibrational modes in a solid at relatively low temperature[43].

In the lower range of chain stretchings ($L^* < 0.65$) we do not observe a dependence $\sim 1/d$. We note that in this regime not all the degrees of freedom of the chain are taking part of vibrations. The low stretching produces local clusters of beads, closer to equilibrium than to bond stretched states (see Fig. 2(a)). We attribute to this effective reduction of vibrational modes a steeper decay of the interaction, as compared to the cases of higher stretchings, where the harmonic approximation holds. It is also interesting to note that in this region, the range of the fluctuation-induced force is reduced, but its absolute value at short ring distance increases. We assume that this happens because the amplitude of long-wavelength fluctuations is also increased. We assume that the fluctuation-induced force is reduced, but its absolute value at short ring distance increases. We assume that this happens because the amplitude of long-wavelength fluctuations is also increased.

$F_x(d) = -\frac{A}{d \ln(d/r_0)} + C_1 d^{-3} \ln(d)$

We fitted Eq. 5 with a multiplicative constant $A$ and $C_1 \equiv 1/r_0$ as fitting parameters, and found a very good agreement for the smaller chain stretchings ($L^* < 0.65$) at different temperatures. Two examples are provided in Fig. 14 for chain lengths of $L^* = 0.4$ (panel (a)) and $L^* = 0.5$ (panel (b)). The lateral extension of the rings, that can be regarded as the colloid radius $r_0$, is small as compared to typical ring distance in the simulations, fulfilling the conditions for these limiting case. The fitting parameter are around $A_0 \approx 4$ for the multiplicative constant of the force and $r_0 \approx 0.36$ (with $r_0 = 0.14$ and $r_0 = 0.55$ as the minimum and maximum values for all the fits). This mean value seems a bit smaller than the effective ring width (in its part exposed to the chain), but it is indeed in the order of magnitude of effective ring width.

We also studied the dependence of the fluctuation-induced force with the temperature. Fig. 15 shows the fluctuation-induced force between rings located at a distance $d \gg r_0$, pinned in the interface at distance $d$. For the limiting case $d \gg r_0$, they find the following expression for the fluctuation induced force (see Eq. (7) in Ref. [9]):

$$F_x(d) \sim -\frac{A}{\ln(d/r_0)} + C_1 d^{-3} \ln(d)$$

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i. e. for chains of higher low-amplitude modes (see also Fig. 5). These two facts may give rise to the smaller dependence with temperature of more stretched chains observed in Fig. 15. We recall that the maximum physical length that the FENE chain can have is \( L^* = 1 \), quite close to these cases. The beads are rather separated and the center of the bonds have a clearly reduced excluded volume, as compared to positions closer to the center of the beads.

In these conditions, for a given ring distance, it makes a significative difference if the rings are located very close to a bead (see inset (i) in Fig. 17) or in the central region of the bond (see inset (ii) in Fig. 17). In the second case, the chain can have fluctuations of higher amplitude inside the ring, giving rise to a lower fluctuation-induced force. This is also facilitated by the fact that the bond length lateral fluctuation is rather low due to the high stretching of the polymer and the high internal energy of the bond. We confirmed this by scaling the ring distance with the mean bond distance \( \langle \lambda_{bond} \rangle \) for each case. Plotting \( F_x \) vs \( d/\langle \lambda_{bond} \rangle \) we observe a period for the modulation of one bond length (not shown). The modulation smudges at longer ring distances, where lateral displacements of the beads close to the rings are much larger.

While these stretching values are rather extreme and might be not feasible experimentally, it draws the attention on the fact that the structure of the bond and the details of the polymer structure at the chemical level, could have a role in the modulation of fluctuation-induced forces in experiments.

**IV. DISCUSSION AND CONCLUSIONS**

In this work, we studied the fluctuation properties of a polymer chain under tension and the characteristics of the fluctuation-induced forces between two ring molecules threaded around the polymer and fixed in the space. In this way, the rings alter the natural fluctuations of a stretched chain giving rise to the observed Casimir-like forces. The system could be considered as a model of a pseudo-rotaxane under tension, which could be studied experimentally as an isolated entity, or as a component of a slide-ring material under tension.

The unconstrained chain under tension presents a fluctuation spectrum compatible with a \( \sim 1/q^2 \) law for a wide range of studied chain stretchings, which deviates from this behavior for lower chain lengths. Interestingly, the behavior at high stretching is similar to a capillary wave spectrum of a liquid-vapor interface or that of two immiscible liquids, in spite of the non-linearity of the chain connectivity.

We observed an attractive fluctuation-induced force

\[ F_x = \mu \Delta S / k_B T \]

The fluctuation-induced force versus distance at very high stretching observed in Fig. 13. In Fig. 17 we show the force versus ring distance for \( L^* = 0.8 \) for different chain lengths (Panel (a)) and different temperatures (Panel (b)). A clear modulation of the force shows up for short distances up to \( d \approx 16 \sigma \). This was observed in the high stretching limit \( L^* \gtrsim 0.8 \) for all the studied cases. We recall that the maximum physical length that the FENE chain can have is \( L^* = 1 \), quite close to these cases. The beads are rather separated and the center of the bonds have a clearly reduced excluded volume, as compared to positions closer to the center of the beads.

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While these stretching values are rather extreme and might be not feasible experimentally, it draws the attention on the fact that the structure of the bond and the details of the polymer structure at the chemical level, could have a role in the modulation of fluctuation-induced forces in experiments.

**Figure 15:** Force between rings \( F_x \) as a function of temperature for different chain lengths \( L^* \). In all the cases the rings were fixed at distance \( d = 6\sigma \). The lines come from a linear fit of the data point.

**Figure 16:** \( F_x \) versus temperature for different ring distances. All the cases correspond to \( L^* = 0.56 \) and the number of beads in the chain is \( N = 1024 \). The lines are linear fits of the data for each case.
between the rings for all the studied cases. We characterize these forces as function of chain stretching, temperature and ring radius, i.e. the properties of the physical constraint imposed to the chain. For higher stretching, we found a dependence of $\sim 1/d$ of the fluctuation-induced force, which is similar to that found in the context of a harmonic approximation for classical electromagnetic fields at thermal equilibrium\cite{41}, and 2D Ising model of a pinned magnetic interface\cite{45}. We observed a linear dependence of the force with the temperature, which is expected from an entropy-driven force of this type, if the entropy differences between constraint and unconstrained chains are not dependent on temperature.

At lower stretchings, in which not all the degrees of freedom of the chain are vibrating, we observe a deviation from this limiting behavior. In this case the force vs. distance is adjusted very well with a dependence $\sim 1/d\ln(c_1d)$. This behavior was also found theoretically in exact results for interfaces of 3D Ising systems\cite{45} and for colloids pinned in liquid-liquid interfaces\cite{9}. We also characterized fluctuations of the force at very high stretchings, coming from the discreteness of the beads and variations of the excluded volume of the chain along the bonds.

In addition to the results found for polymers under tension, we consider the system as a relatively simple model to study fluctuation-induced forces in different contexts. We are planning to continue this work, by studying the dynamics of rings allowed to move in the direction of the chain and also considering semi-flexible polymers with local flexural rigidity, reminiscent of biofilaments. For this case, there is an increment in the length of bond correlations, which could be very interesting. We are also planning to study aggregation of ring molecules threaded in the chain, in a system closer to a polyrotaxane. Finally, we think that the direct measurement of these forces with optical tweezers is plausible, or via a potential of mean force in fluorescence experiments\cite{46, 47}.

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