Entropic elasticity of dilated and contorted idealized circular chains

Martin Bertrand, Martin Forget, and Béla Joós*
Institut de physique Ottawa-Carleton, Campus de l'Université d'Ottawa, Ottawa, Ontario, Canada K1N 6N5
(Received 18 November 2009; revised manuscript received 20 April 2010; published 28 June 2010)

Thermal energy provides random motion to particles that leads to the well-known entropic force, which favors the clumping of linear and circular molecules. We evaluate the entropic force which resists the radial dilation and subsequent twisting out of plane of circular polymers by developing mechanical models and performing molecular dynamics simulations. We find that dilating a circular chain is analogous to stretching its linear counterpart. We also find that the torque applied to an already dilated ring and the resulting twist out of plane are related by a linear relationship for a wide range of deformed configurations and, using this result, we are able to predict the angular fluctuations of such a macromolecule.

DOI: 10.1103/PhysRevE.81.061803 PACS number(s): 82.35.Lr, 87.15.H−, 87.15.La, 87.14.E−

I. INTRODUCTION

Entropic forces play an important role in both soft and condensed matter physics, and biological physics. Indeed, whether it be the elasticity of rubber or the self-assembly of lipid bilayers, many materials often owe their unique properties to forces that are entropic in nature. Anytime thermal motion, or Brownian motion, is observed, one cannot neglect entropy as part of the free energy for the system under study. A classical problem involving entropic forces is the linear polymer in solution under stretch. Its entropic elastic response has been widely studied (see the review by Slater *et al.* [1]) and is a great subject matter for physics courses. A short description of the phenomenology goes as follows: thermal motion pushes the unconstrained linear chain in solution toward its most probable state, the random coil. Stretching the chain moves it into a lower entropy configuration. The thermal motion of the monomers fights this tendency creating the entropic recoil force. There are well-established expressions which relate this force to the chain's deformation and are unique for both freely jointed chains (FJC) and wormlike chains (WLC) when excluded volume interactions (EVI) are neglected [1]. But when EVI are included, one has to use scaling arguments that lead to different expressions for all force regimes. The entropic forces associated with circular chains have not received such an attention. In this paper, we present simple expressions that describe the entropic elastic response to applied external forces for prototypical circular polymers modeled as Gaussian chains with EVI (bead-spring model).

Circular polymers are of particular interest in soft matter [2–5] and biological physics. For example, we find circular DNA strands in many organisms [6], circular chains in the structure of macromolecules such as proteins, and cyclic peptides are often used in the pharmaceutical industry [7]. Of all circular molecules, DNA loops have been the most extensively studied and modeled as wormlike chains with both bending and twist rigidities [8,9]. A circular chain can be deformed by external forces in many different ways: it can be stretched, dilated, bent, and contorted. Entropic and mechanical elastic responses should be observed for all types of deformations. In the case of elastic rings modeling DNA loops dominated by mechanical forces, Panyukov and Rabin [8] provide a nice framework to describe shape changes due to external forces.

We focus on isolated simple idealized circular chains subjected to *dilation*, such as would result from a circular chain wrapped around a bulk object. A *twisting out of plane* is applied to the circular chain, which can be seen as a forced writhe and will be referred to as a *torsion* to avoid any ambiguity with an axial twist [10]. We develop simple relations for such deformations and compare them with molecular dynamics simulations on the bead-spring model. The next section introduces some useful theory. In Sec. III, the models are developed. Section IV presents the MD simulations and discusses the results in the light of our predictions.

II. ENTROPIC ELASTICITY

An isolated system connected to a heat bath of constant temperature T will always try to minimize its free energy A given by the following:

$$A = U - TS, \tag{2.1}$$

where we find the internal energy of the system U, a result of the interactions between the particles, and the entropy S, a measure of how probable the current conformation of the system is. In order to minimize the free-energy, it is clear that the entropy has to be maximized and thus the system will always tend toward its most probable conformation, driven to reconfigure by thermal motion. For a FJC made of N segments of length b in a thermal bath ($U=0$), under no constraint, this means it will clump in a shape that we call a random coil, with an average square end-to-end distance $\langle h^2\rangle = Nb^2$ [11] (more generally we find $\langle h^2\rangle = N^{2\nu}b^2$ where ν is the Flory exponent and is equal to 1/2 for a FJC [11]). It follows that it will resist any change of shape imposed by a constraint applied on a given coordinate x with an entropic recoil force, much like a spring:

*bjoos@uottawa.ca

$$f_{\text{recoil}} = -\frac{\partial A}{\partial x} = -\frac{\partial U}{\partial x} + T\frac{\partial S}{\partial x}. \tag{2.2}$$

Here, the derivative of the potential energy U should vanish leaving us with a force of entropic origin only. For example, if one pulls on both ends of a linear FJC (stress ensemble) with a force f in opposite directions (equivalently one can pull on one end with the other pinned in place), the chain develops an entropic recoil force equal to f and the mean end-to-end distance as a function of the force $\langle h(f)\rangle$ is given by the well-known relation [1]:

$$H = \frac{\langle h(F)\rangle}{h_{\max}} = \coth(F) - \frac{1}{F}, \tag{2.3}$$

where $h_{\max}=Nb$ is the maximal extension of the chain and $F=fb/k_bT$ is the scaled force or rather a ratio of a "stretching energy" over the thermal energy. The inversion of the series expansion of the above expression and subsequent interpolation of the solution produce an approximation of the entropic force in terms of the chains deformation [1]:

$$F(H) \cong \frac{3H - H^3}{1 - H^2}, \tag{2.4}$$

For very small deformations ($H \ll 1$) Eq. (2.4) can be reduced to Hooke's law $f \cong k\langle h\rangle$, where the spring constant is $k=3k_bT/Nb^2$. The entropic rigidity of the linear chain is directly proportional to temperature: the "warmer" it is, the stiffer it becomes.

For a real chain with EVI one observes a deviation from Eq. (2.3) for all but forces $F>1$. In the small forces regime ($F<N^{-\nu}$), scaling arguments still lead to Hooke's law:

$$\langle h\rangle \cong N^{2\nu}bF, \tag{2.5}$$

whereas in the intermediate forces regime ($N^{-\nu}<F<1$), they lead to a power law relationship [1]:

$$\langle h\rangle \cong NbF^{1/\nu-1} \tag{2.6}$$

If the chain is in a good solvent the Flory exponent is $\nu=0.588$.

III. MODELS

A. Dilating a circular chain

We here wish to calculate the entropic elastic response of a dilated circular chain as shown in Fig. 1. The system here studied resembles the two-dimensional (2D) planar polymeric loops studied by Camacho *et al.* in [12]. Like its linear counterpart, a circular chain will also clump in the entropically favorable coil conformation with a radius of gyration $R_{g,0} \propto bN^{\nu}$ (the proportionality constant is 0.29 for a Gaussian chain with $\nu=1/2$ [11]). Thus, if it is deformed in any given way, it will resist. In particular, if a force f_r is exerted on every components of a loop in a radial direction from the center of mass as shown in Fig. 1, we expect it will reach an equilibrium ring conformation with a radius of gyration $R_g(f_r)$ up to a maximum $R_{g,\max}=h_{\max}/2\pi=Nb/2\pi$. At equilibrium, we will assume that the entropic recoil force can be

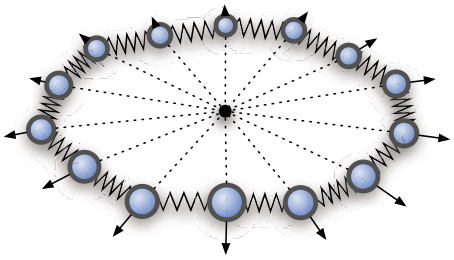

FIG. 1. (Color online) Dilating a polymer ring: a force f is exerted on the constituents of the chain in a chosen plane and in a radial direction from the center of mass.

assimilated to a uniform linear tension in the ring λ while a radial force per unit length $\tilde{f}_r=Nf_r/2\pi r$ is acting on it, where r is the radius of the ring ($r \approx R_g$). If a loop of circumference $l=2\pi r$ is stretched by an amount dl beyond equilibrium, the work done by the radial force $W_r=\tilde{f}_r dA=\tilde{f}_r 2\pi r dr$ has to be equal to the work done by the entropic force $W_e=\lambda dl=\lambda 2\pi dr$ such that we get a Laplace relation:

$$\lambda = \frac{Nf_r}{2\pi}. \tag{3.1}$$

As we go toward maximal extension, we propose the average circumference of the loop $\langle l\rangle$ approaches the end-to-end distance $\langle h\rangle$ of a linear chain pulled with a force f equivalent to the linear tension λ in the loop. In this regime, Eq. (2.3) would apply with a ratio on the left hand side of,

$$R = R_g(\Lambda)/R_{g,\max}, \tag{3.2}$$

and a scaled tension,

$$\Lambda = \lambda b/k_bT = Nf_r b/2\pi k_bT. \tag{3.3}$$

The analogy to a linear chain being stretched should still hold for intermediate extensions, with the relation between R and Λ being described by a power law:

$$R(\Lambda) \propto \Lambda^{\alpha}, \tag{3.4}$$

where the exponent α can be determined by experiment or simulation. However, it is clear that as we approach minimal extension the analogy does not apply. As the force decreases toward zero, the radius of the ring tends toward its undeformed radius of gyration $R_{g,0}(R_{g,0}/R_{g,\max} \sim N^{\nu-1})$. Of the functional form of the relation $R_g(\Lambda)/R_{g,\max}$ vs Λ for the weaker forces not much can be predicted, although one might observe a Hooke's type of relation analogous to the one introduced for the extension of a linear chain for $F \ll 1$. We will not focus on this regime for which the deformation is hard to separate from thermal fluctuations.

B. Twisting a dilated circular chain out of plane

What happens now if a chain dilated as in Fig. 1 is subject to a subsequent torsion, e.g., what is the entropic response to this additional deformation? To answer this question, let us imagine a circular chain dilated by a radial pressure $\tilde{f}_r$ that we twist out of plane as we would a towel as shown in Fig.

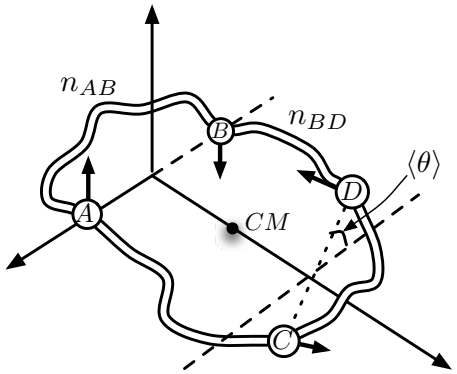

FIG. 2. Polymer loop under torsion: the pair AB is conveniently positioned on an axis such that one can clearly see what average angular displacement $\langle\theta\rangle$ is measured. If A and B are distant by d_A and d_B from their center of mass, and we find corresponding distance d_C and d_D for C and D, then the following is true about external torsion forces applied to the pairs and the resulting torque τ. $\tau=f_A d_A+f_B d_B=f_C d_C+f_D d_D$.

2: upon a ring of N elements, beads in our case, we select four of these ($i=\{A,B,C,D\}$), two pairs, AB and CD, on which we want to apply a torque of equal magnitude τ, with $n=n_{AB}$ beads between A and $B(n_{CD}=n_{AB})$ and n_{AC} beads between A and $C(n_{AC}=n_{BD})$. Vectors $\vec{d}_A$ and $\vec{d}_B$ run from the middle of the pair AB to A and B, respectively, while vectors $\vec{d}_C$ and $\vec{d}_D$ do the same for the pair CD. Vectors $\vec{s}_{AB}$ and $\vec{s}_{CD}$ run from the center of mass to the middle of opposite pairs. The direction of the force $\vec{f}_A$ is given by the cross product $\vec{d}_A\times\vec{s}_{AB}$ and its magnitude is equal to $\tau/2d_A$. All other forces are determined similarly thus setting the following equalities: $f_A d_A=f_B d_B$, $f_C d_C=f_D d_D$, and $\tau=f_A d_A+f_B d_B=f_C d_C+f_D d_D$.

The average angle $\langle\theta\rangle$ as depicted in Fig. 2 is then a measure of the amount of torsion (angular deformation) and can be plotted against the applied torque τ for a given set of parameters (n,f_r,N,k_bT) where n is short for n_{AB}. In the small angle limit, we predict the ring will contort until the entropic tension λ in the chain produces a torque equal to the one applied. The challenge is in evaluating the value of λ and its component along the direction of the forces producing the torque $\lambda_\parallel$, for a given angular displacement θ.

We refer the reader to Fig. 2 for the following discussion. Let us take point A since it is clear that all four points (A,B,C,D) are equivalent. The ring is dilated by a linear pressure $\tilde{f}_r$ that triggers the response of a uniform entropic tension λ we assume to be tangential to the curve at all points and normal to the force from which originates the pressure. Thus, A is pulled along an arc toward B and C by a force λ for both. As the ring is contorted, the tension pulling toward B does not produce any torque on A since it is by definition perpendicular to the twisting force f_A at all times. So is the dilation force f_r acting on A. We are thus left with the tension vector $\vec{\lambda}$ tangential to the arc that leads from A to C as the only candidate to produce a force $\lambda_\parallel$ that will oppose f_A. To evaluate $\vec{\lambda}$ and the component $\lambda_\parallel$ we place ourselves in the referential of C and first define the following:

$$d=d_A=d_C=R_g\sin\left(\frac{n}{N}\pi\right), \tag{3.5}$$

$$l=2R_g\cos\left(\frac{n}{N}\pi\right), \tag{3.6}$$

where d is half the length of the chords AB and CD, and l is the length of the chord AC (also BD) when the ring is at rest with a radius of gyration R_g. We assume here that this radius stays roughly constant as the loop gets twisted. These lengths so defined allow to write the following three vectors:

$$\vec{CA}=[d(1-\cos\theta),d\sin\theta,l], \tag{3.7}$$

$$\vec{CMA}=(-d\cos\theta,d\sin\theta,l/2), \tag{3.8}$$

$$\hat{f}_A=(-\sin\theta,-\cos\theta,0), \tag{3.9}$$

where $\vec{CA}$ is the vector going from C to A, $\vec{CMA}$ is the vector going from the center of mass to A, and $\hat{f}_A$ is the unit vector giving the direction of f_A. These vectors are defined in terms of an angular displacement θ. The cross product of $\vec{CA}$ and $\vec{CMA}$ gives a vector $\vec{p}_A$ normal to the twisting plane in A: $\vec{p}_A=\vec{CA}\times\vec{CMA}$. Another cross product of this new vector with $\vec{CMA}$ yields a vector $\vec{t}_A$ tangent to the curvature of the chain in A, following the arc going from A to C: $\vec{t}_A=\vec{p}_A\times\vec{CMA}$. This last vector allows to determine the tension vector we are hunting for: $\vec{\lambda}=\lambda\hat{t}_A$. We then can calculate $\lambda_\parallel$, the component of interest here, with the dot product $\lambda_\parallel=-\lambda\hat{t}_A\cdot\hat{f}_A$ which gives:

$$\lambda_\parallel=\frac{\lambda\sin\theta}{\left[\cos^2\left(\frac{n}{N}\pi\right)(2\cos\theta+1+\cos^2\theta)+\sin^2\theta\right]^{1/2}}, \tag{3.10}$$

where values for d and l were replaced by their definitions given in Eqs. (3.5) and (3.6). This component of the tension opposes and matches the force f_A acting on A at equilibrium. In the small angular displacement approximation ($\theta\ll1$), the second order Taylor series of the above expression gives the following polynomial approximation:

$$\lambda_\parallel\cong\frac{1}{2}\lambda\sec\left(\frac{n}{N}\pi\right)\theta. \tag{3.11}$$

Since the torque τ on the pairs AB and CD is equal to $2f_A d_A$, the preceding statement and Eq. (3.5) and (3.11) allow to write:

$$\tau\cong\kappa\theta=\lambda R_g\tan\left(\frac{n}{N}\pi\right)\theta. \tag{3.12}$$

The above equation is in the form Hooke's law for torsional elasticity where the elastic constant κ depends on three factors: size, entropic tension, and the points where torsional forces are applied. The third term in κ is a tangent function of the ratio n/N, which makes the entropic torque minimal as $n\to0$ and tend to infinity as $n\to N/2$: the entropic tension

induced in the arcs AC and BD of the ring grows as $n \to N/2$ until one reaches a point when the bonds between the beads making up the chain start to be stretched and the purely entropic response vanishes.

We know that the size of the ring R_g increases with the dilation force and the number of elements in the chain which leads to a dependence in λ and N. Thus we can rewrite Eq. (3.12) in a more practical form with the following substitutions, $R_g = \frac{Nb}{2\pi} R(\Lambda)$ and $\lambda = \frac{k_b T}{b}\Lambda$:

$$\tau \cong \kappa\theta = \frac{N}{2\pi} k_b T \Lambda R(\Lambda) \tan\left(\frac{n}{N}\pi\right)\theta, \tag{3.13}$$

where the product $\Lambda R(\Lambda)$ can be determined from the study of ring dilation (Sec. III A).

With Eq. (3.13), one can estimate the twist fluctuations when no torque is applied on the polymer ring. Using the equipartition of energy, one can argue that the twist is an actual degree of freedom and that the elastic energy of twist is related to the thermal energy as follows:

$$E_{\text{twist}} = \frac{1}{2}\kappa\langle\theta^2\rangle \cong \frac{1}{2}k_b T. \tag{3.14}$$

This equality then leads to an estimate of the root-mean-square value of the angular deviation:

$$\theta_{\text{rms}} \cong \sqrt{\frac{k_b T}{\kappa}} = \left[\frac{N}{2\pi}\Lambda R(\Lambda)\tan\left(\frac{n}{N}\pi\right)\right]^{-1/2}. \tag{3.15}$$

It is worth noting that throughout this last section, λ is assumed to be unchanging for a given dilation force. The fact that part of the entropic tension in the chain counteracts an additional applied torque on the points A,B,C,D implies that the tension itself needs to change as the ring is twisted for it to reach a new equilibrium configuration. The local lost of tension to counteract the dilation will be compensated by a redistribution of the load in segments AC and BD which is bound to change the physics of our problem and render the above model useless once a certain torsion angle is attained.

IV. MOLECULAR DYNAMICS SIMULATIONS OF DILATED AND CONTORTED LOOPS

This article presents data obtained from molecular dynamics (MD) simulations of single polymer chains either in a linear or circular configuration, all executed with ESPRESSO [13]. We use the Kremer-Grest approach [14], which consists in modeling the chains like beads connected by springs. In our simulations springs are modeled using a finitely extensible non-linear (FENE) potential of the form $U_{\text{FENE}}(r_{ij}) = 0.5kR_0^2 \log[1-(r_{ij}/R_0)]$, where $k = 30\epsilon_{\text{LJ}}/\sigma^2$ and $R_0 = 1.5\sigma$. Additionally, all beads interact through the repulsive part of a truncated and shifted Lennard-Jones (LJ) potential of the form $U_{\text{LJ}}(r_{ij}) = 4\epsilon_{\text{LJ}}[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6 + shift]$ so that EVI are recuperated ($r_{cut} = 2^{1/6}\sigma$, $shift = 0.25$). The equilibrium distance between two adjacent beads on a chain is observed to be $b \cong 0.97\sigma$. The equations are integrated using a Langevin thermostat so that the system appears to be connected to a heat bath of temperature T (thermal energy $k_B T$). All numerical values are in MD units, σ being the unit of length (LJ range), ϵ, of energy (LJ energy), and m, of mass. Thus time has units of $\sqrt{m\sigma^2/\epsilon}$, and force, ϵ/σ.

Stretching experiments on linear chains were preformed with one end fixed in space and the other being pulled by a constant force f, while dilation and twisting out of plane experiments were performed as described in Secs. III A and III B. It is worth mentioning that using springs to model bonds leads to a longitudinal elasticity of the chain and thus a mechanical elastic response will appear for large applied loads ($F \gg 1$). However, this response has been shown to be negligible in our simulations, the overall contour length increase of both linear and ring polymers being at maximum close to 1%.

A. Dilated loops compared to stretched chains

We simulated the dilation of a circular chain and compared the results to the extension of a linear chain with the same number of segments for a wide range of parameters: $N = [40, 200]$, $k_B T = [0.4, 1.2]$, and $\{F, \Lambda\} = [0, 10]$. It is interesting to note that our results are very much similar to what Camacho *et al.* get in [12] where the linear pressure is replaced by an intrinsic bending stiffness in the ring.

We calculated, for undisturbed chain configurations ($F = 0$), Flory exponents for the radius of gyration of undeformed linear chains and rings resulting in values of $\nu = 0.60 \pm 0.02$ and $\nu = 0.623 \pm 0.005$, respectively. These values are within each other's confidence interval and are only slightly different than the one obtained from mean-field calculations for linear polymers with EVI ($\nu = 0.588$ [11]). The discrepancies are probably due to the model used for simulating our polymers (Kremer-Grest MD) and have been documented for linear chains [15]. We also found a ratio of $R_g/\langle h\rangle = 0.29$ for the ring's radius of gyration over the linear chain's end-to-end distance which, interestingly, corresponds to the theoretical prediction for ideal Gaussian chains, $R_{g,0}/bN^{1/2} = 0.29$.

We computed the entropic component of the recoil force ($T\frac{\partial S}{\partial x}$) by plotting f vs T [see Eq. (2.2)] at fixed values of the deformation ratio for both circular and linear chains of length $N = 100$. Figure 3 shows that the entropic force matches almost exactly the recoil force itself, showing that the increase of potential energy for high loads as seen in the inset of Fig. 3 (maximum of 0.5%) is of negligible incidence on the total force, and demonstrating that the entropic force is linearly dependent upon temperature.

Figure 3 also clearly shows that there is a good match between the elastic response of a polymer loop being dilated and a linear chain being stretched. In fact, the two response curves really start to diverge only when the load becomes smaller than the thermal force ($\{F, \Lambda\} < 1$). The intermediate loads regime for ring dilation (region between the vertical dotted lines in Fig. 3) was fitted with a power law, and although the parameters slightly vary with chain size N, the following fit formula is an approximation that covers well the range of sizes we are studying in here:

$$R(\Lambda) \cong 0.52\Lambda^{0.29}, \quad \text{for } 1 < \Lambda \leq 4. \tag{4.1}$$

In the high-loads regime ($\{F, \Lambda\} > 4$), Eq. (2.3) makes a good fit of the data and can be used to finish the construction of a piecewise function of $R(\Lambda)$ for $\Lambda > 1$:

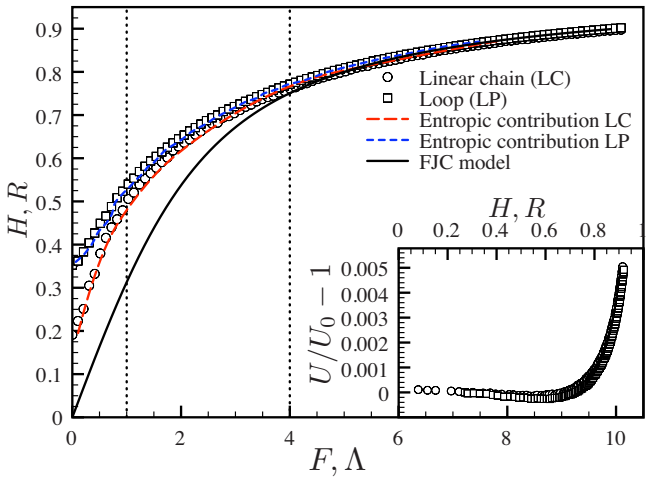

FIG. 3. (Color online) Comparison of a linear chain being stretched to a ring being dilated ($N=100$). The amount of *Stretch* (H,R respectively) in function of the scaled force F or tension Λ is shown in the main view along with entropic contributions and the theoretical curve for a FJC. The inset shows the increase in potential energy as the chains are deformed.

$$R(\Lambda) \cong \coth(\Lambda) - \frac{1}{\Lambda}, \quad \text{for } \Lambda > 4. \tag{4.2}$$

The function made of Eqs. (4.1) and (4.2) should prove to be a good tool to estimate the entropic component of the rigidity of mildly to strongly dilated polymer rings and be highly useful to complete the model for twisting rings out of plane [see Eq. (3.13)].

B. Circular chains under torsion

1. Angular displacement vs applied torque

Torsion experiments were performed as described in Sec. III B. We explored the following parameter space: $N=[20,200]$, $n=[5,35]$, $\Lambda=[1,8]b$, $k_bT=[0.4,1.2]$. The results obtained are quite remarkable, the hallmark of which is probably the presence of a linear relationship between the angular displacement and the applied torque over a rather wide range of values for $\langle\theta\rangle$ (see Fig. 4 for an example). It, thus, seem that the approximate formula we proposed to describe this same relationship in Eq. (3.13), used in conjunction with the fits given in 4.1 and 4.2, applies to a greater extent than we initially thought. In fact, in Fig. 4 one can observe how close the prediction is to the actual data from simulations, a deviation of 8.7% being observed in this particular case. In fact, a thorough comparison between the predicted slope κ^{-1} in this linear regime and the simulation results, throughout our parameter space, revealed deviations around or lower than 10% as long as the ring dilation corresponds to the intermediate or high-loads regimes ($\Lambda \gtrsim 1.5$). It is then clear that the counteracting torque originates from the entropic tension in the ring. Given a polymer ring dilated by an intermediate or high load, one can use Eq. (3.13) to either predict how much the molecule can contort if the applied forces are known or find the magnitude of those forces for a given contorted configuration.

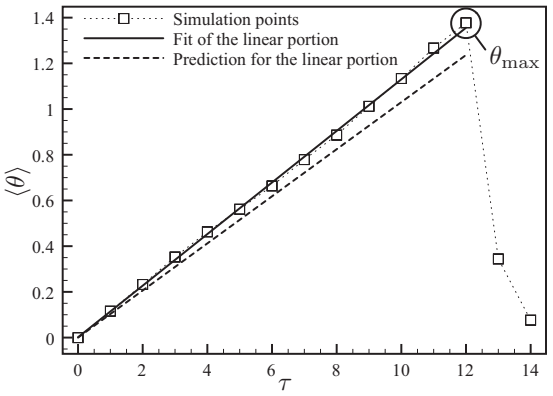

FIG. 4. Characteristic curve of the relationship between the average angular displacement $\langle\theta\rangle$ and the applied torque τ on both the pairs of beads AB and CD. Here it is shown for $N=100$, $n=5$, $\Lambda=5.0b$, and $k_bT=1$. The slope κ^{-1} of the linear portion is 0.113 while Eq. (3.13) predicts 0.103, a value that deviates by 8.7%. The maximum twist angle $\theta_{\max}$ beyond which the ring enters an overtwisted regime is pointed out.

2. Maximum contortion

Figure 4 shows that there is a maximum angular displacement $\theta_{\max}$ that can be achieved in our simulations, to which corresponds an applied torque $\tau_{\max}$. Beyond this limit, the ring enters a regime of over-contortion leading to a shape of writhe equal to 1, which is out of the scope of this study. We cannot provide any quantitative prediction for the values of $\theta_{\max}$ due to limitations in our simple model. However, we'd like to propose an explanation as to why we observe that the most influential parameter is the ratio n/N, i.e., the position of the twisting points in proportion to the chain length. Indeed, as this ratio increases, the overall trend is to see the maximum angular displacement decrease. We suppose this is mostly due to the stretching of chain segments AC and BD in Fig. 2: as the ring is contorted, the entropic tension in those same segments increases, and the inhomogeneity this introduces in the tension along the circumference of the ring brings on its collapse. Let us use expressions 3.5, 3.6, and 3.7 to write down an approximation for the stretch ratio l'/l:

$$\frac{l'}{l} = \sqrt{\frac{1}{2}\tan^2\left(\frac{n}{N}\pi\right)(1-\cos\,\theta) - 1}. \tag{4.3}$$

We then assume that passed a "stretch" threshold, the ring collapses. For the sake of this argument, we fix this threshold as low as 1% and assume it is uniform for all n/N. The above equation can then be solved for θ which should give a trend for $\theta_{\max}$ vs n/N. This is confirmed in Fig. 5 where we see qualitative agreement between values obtained from simulations and the predicted trend.

3. Angular fluctuations with no net angular displacement

Equation (3.15) at the end of Sec. III B approximates $\theta_{\rm rms}$ for rings upon which no torque is applied. It so happens that in such a conformation the mean angular displacement $\langle\theta\rangle$ is zero and that $\theta_{\rm rms}$ is equal to σ_θ, the standard deviation of θ. We, therefore, compared $\theta_{\rm rms}$ to σ_θ obtained from simula-

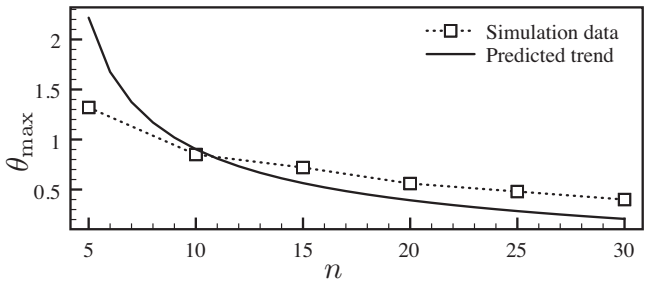

FIG. 5. Qualitative agreement of the maximum twist angle from simulations with the predicted trend as a function of n. The size of the loop is $N=100$ and the thermal energy is $k_bT=1$.

tions for various permutations of the parameters n, N, and k_bT, through all dilation regimes ($\Lambda=[1.0b,8.0b]$). For any given dilation value with n and N fixed, our model predicts angular fluctuations independent of temperature, a behavior that simulation data confirms. We then fixed the temperature, scaled the data and the model by the appropriate asymptotic values for very high loads $\Lambda \gg 1$, $\sigma_{\theta,\min}$ and $\theta_{\mathrm{rms},\min}$ respectively, and found that they are thus in excellent agreement in both the intermediate and high-loads regimes. Hence, for a given dilation load, the model is able to predict values obtained from simulations within a prefactor $\theta_{\mathrm{rms},\min}/\sigma_{\theta,\min}$, which has a strong dependence on the ratio n/N, and a weak one on N alone that we will neglect here. We plotted the prefactor in function of n/N and found the relationship to be approximately linear. We fitted the curve and used the resulting coefficients to adjust our model:

$$\theta'_{\mathrm{rms}} = \left(0.55\frac{n}{N} + 0.72\right)^{-1} \theta_{\mathrm{rms}}. \tag{4.4}$$

The angular fluctuations thus approximated are consistent with what we measure from simulations as shown in Fig. 6. We believe that the prefactor in Eq. (4.4) is due to the approximations made in our model, in particular to the reduced number of degrees of freedom since we only consider the four A,B,C,D beads and not the entire chain. Nonetheless, Eq. (4.4) is a valuable tool to get a very good estimate of the angular fluctuations in a dilated ring.

V. CONCLUSION

We presented a study on circular chain dilation with subsequent twisting out of plane of which the two highlights are: (1) the dilation of a ring is analogous to stretching a linear chain of the same size; (2) when twisting out of plane a dilated ring, a linear relationship is found between the entropic response torque and the angular displacement. We proposed simple mechanical models for both types of deformation. Our analysis suggests that the entropic response to both dilation and contortion originates from an entropic tension along the contour of the polymer loop. The models provide a surprisingly good approximation to the results from simulations of bead-spring chains. Aside from its intrinsic interest as a thermally driven force, our study complements our understanding of the entropic spring so prevalent whenever polymers are present. Entropic rings may be less prevalent. But they may provide some insight into the rigidity of certain folded proteins where loops are present resulting from hydrogen-like bonds, for instance, linking different segments together [16,17].

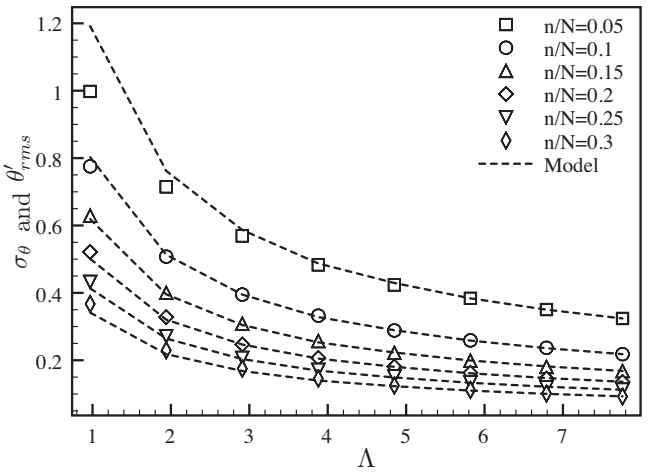

FIG. 6. Comparison of the twist fluctuations θ'_{rms} derived from our model (dotted lines) to the standard deviation of the twist σ_θ obtained from simulations (symbols) when no torque is applied on the dilated ring: the model accurately predicts the observed behavior for a large interval of the ratio n/N across all dilation load Λ regimes except for the lowest values of the load and ratio.

ACKNOWLEDGMENTS

BJ would like to thank Michael F. Thorpe for a useful discussion. The work has been funded in part by the Natural Sciences and Engineering Reserach Council (Canada) and "Le fonds québécois de la recherche sur la nature et les technologies" (FQRNT).

[1] G. W. Slater, Y. Gratton, M. Kenward, L. McCormick, and F. Tessier, Soft Matter **1**, 365 (2003).
[2] S. P. Obukhov, M. Rubinstein, and T. Duke, Phys. Rev. Lett. **73**, 1263 (1994).
[3] M. Müller, J. P. Wittmer, and M. E. Cates, Phys. Rev. E **53**, 5063 (1996).
[4] S. Brown and G. Szamel, J. Chem. Phys. **108**, 4705 (1998).
[5] G. Zifferer and W. Preusser, Macromol. Theory Simul. **10**, 397 (2001).
[6] D. Helinski and D. Clewell, Annu. Rev. Biochem. **40**, 899 (1971).
[7] J. Mulvenna, C. Wang, and D. Craik, Nucleic Acids Res. **34**, D192 (2006).
[8] S. Panyukov and Y. Rabin, Phys. Rev. E **64**, 011909 (2001).

[9] S. Medalion, S. Rappaport, and Y. Rabin, J. Chem. Phys. **132**, 045101 (2010).
[10] J. Marko and E. Siggia, Macromolecules **27**, 981 (1994).
[11] I. Teraoka, *Polymer Solutions: an Introduction to Physical Properties* (Wiley, New York, 2002).
[12] C. Camacho, M. Fisher, and R. Singh, J. Chem. Phys. **94**, 5693 (1991).
[13] H. Limbach, A. Arnold, B. Mann, and C. Holm, Comput. Phys. Commun. **174**, 704 (2006).
[14] G. S. Grest and K. Kremer, Phys. Rev. A **33**, 3628 (1986).
[15] D. Rapaport, J. Phys. A **11**, L213 (1978).
[16] D. J. Jacobs, L. A. Kuhn, and M. F. Thorpe, in *Rigidity Theory and Applications*, edited by M. F. Thorpe and P. M. Duxbury (Kluwer Academic/Plenum, New York, 1999).
[17] D. J. Jacobs and S. Dallakyan, Biophys. J. **88**, 903 (2005).