Double-folding of ring polymers in melt conditions: Conformational and dynamical signatures

Mattia Alberto Ubertini
Scuola Internazionale Superiore di Studi Avanzati (SISSA), Via Bonomea 265, 34136 Trieste, Italy

Jan Smrek
Faculty of Physics, University of Vienna, Boltzmanngasse 5, A-1090 Vienna, Austria

Angelo Rosa
Scuola Internazionale Superiore di Studi Avanzati (SISSA), Via Bonomea 265, 34136 Trieste, Italy
(Dated: July 21, 2022)

We present computer simulations for semi-flexible unknotted and unconcatenated ring polymers in melt conditions on the fcc lattice. By fine-tuning the bending stiffness of the chains and by carrying a systematic analysis of ring conformations in terms of chain size, shape, bending correlation and contact probabilities, we show that rings folding on the entanglement scale can be understood in terms of the once postulated double-folding of the polymer fiber around a tree-like backbone. Then, by considering the amount of polymers passing through the minimal surface of each ring as a measure of the interpenetration of the chains in the melt, we show that minimal surfaces are impacted by shallow threadings or piercings below the entanglement length which give rise to non-universal behavior. Finally we describe the consequences of double-folding for ring dynamics, in particular chains slowing-down and then quenching following the systematic freezing of a certain fraction of the overall polymer population.

I. INTRODUCTION

Topological constraints emerging from the mutual uncrossability between distinct chains dominate the viscoelastic behavior of polymer systems at high-density (melt) conditions [1–3]. In this context, of notable interest are those situations where polymers are prepared in a well-defined topological state which remains quenched for the entire course of the system. The simplest example in this respect is the case of melts of unknotted and unconcatenated (hereafter, untangled [4]) ring polymers: people have been now studying this particular class of polymer solutions since several decades, from the theoretical [5–26] as well as the experimental [27–31] point of view. Then, researchers have shown that there exist intriguing conceptual connections between melts of ring polymers and, for instance, chromosomes [32, 33], polymer glass dynamics [34, 35] and passive/active polymer mixtures [36]. On the other hand, in spite of these remarkable achievements, there are aspects concerning the physics of untangled ring polymers at melt conditions which await to be elucidated.

In a series of landmark papers [5, 6, 8] it was originally proposed that, in avoiding concatenation, rings minimize the mutual threadable surface they expose to each other while maximizing conformational entropy by double-folding on branched, tree-like conformations. As a consequence [13, 15, 23], rings form compact shapes whose mean linear size or gyration radius, \( \langle R_g \rangle \), scales with the chain contour length, \( L \), as:

\[
\langle R_g \rangle \sim L^{1/3},
\]

for \( L \) larger than the characteristic and material specific [37] contour length scale, \( L_e \), known as the entanglement length [1–3].

Many predictions of the lattice-tree model appear to be in agreement with dynamic simulations of melts of rings [7, 9–11, 14, 16, 20, 23], at the same time some inconsistencies in the model which have been recently pointed out [15, 19] indicate that the picture remains debated. Moreover, from a broader perspective it remains unclear if the length scale \( L_e \) is the only relevant one for melts of rings or, up to which extent, it is influenced by the local bending rigidity or Kuhn length \( \ell_K \) of the chain. In fact, the value of \( L_e \) is measured from a linear melt (e.g. by primitive path analysis [38]) and the length scale is only assumed to be applicable for rings (with the same polymer model) as well, although no direct method to find the value directly from the rings is known. Although some recent comparison of crazing in linear and ring glasses suggests that \( L_e/(\text{rings})/L_e/(\text{linear}) \approx 4 \) [39, 40], its role in ring melts, as well as its connection to \( \ell_K \), has not been thoroughly investigated.

Motivated by these considerations, in this work we perform a detailed analysis of extensive numerical simulations of melts of untangled ring polymers for different local bending rigidities with the goal of elucidating which, amongst the features of the polymer chains, can be understood as the consequence of the double folding of the contour length around a tree-like structure.
To this purpose, we describe here a modified version of the kinetic Monte Carlo algorithm introduced in Refs. [11,12] in order to achieve higher values of the polymer Kuhn length $\ell_{K}$: in doing so, we built on the numerically efficient strategy originally seen in Ref. [9] which allows to increase substantially the overlap between polymer chains by still resorting to relatively moderate chain sizes. Then, by employing “traditional” tools like the scaling of the polymer mean gyration radius and the polymer mean shape [43] alongside more recent and sophisticated methods like the ring minimal surface [17,44] or the dynamic behavior of the melt after the pinning [34] of a given fraction of the polymer population, we discuss the role of double-folding in ring conformations and the relevant length and time scales on which it is expected to play a significant role.

The paper is structured as the following. In Sec. II we introduce the essential notation employed in this work (Sec. II A) and summarize the structure (Sec. II B) and dynamics (Sec. II C) of melts of rings as predicted by the lattice-tree model. In Sec. III we present and discuss our lattice polymer model and derive the relevant length and time scales of the polymer melts. In Sec. IV we present the main results, for the structure (Sec. IV A) and the dynamics (Sec. IV B) of the rings. Finally, we discuss our results and outline some conclusions in Sec. V. Additional tables and figures are included in the Supplemental Material (SM).

II. RING POLYMERS IN MELT: THEORETICAL BACKGROUND

A. Entanglement length and time units: definitions and notation

Single polymers in melt are made of a linear sequence of monomer units with mean bond length $= \langle b \rangle$. The total number of monomers of each polymer chain is $= N$ and the polymer contour length is $L = N \langle b \rangle$, while we denote by $\ell (\leq L)$ the contour length of a polymer sub-chain made of $n = \ell / \langle b \rangle \leq N$ monomers.

Topological constraints affect polymer conformations in melt when the chain contour length $L$ exceeds the characteristic entanglement length scale $L_{e}$. In general $L_{e}$ is a non-trivial function of the chain bending stiffness or the Kuhn length, $\ell_{K}$, and the Kuhn segment density, $\rho_{K}$, of the melt (see Eq. [20] and Ref. [88]). Then, the mean gyration radius of the polymer chain of contour length $L = L_{e}$ and Kuhn length $\ell_{K}$,

$$d_{T} \equiv \sqrt{\frac{\ell_{K} L_{e}}{6}},$$  \hfill (2)

is of the order of the cross-sectional diameter of the tube-like region [13] where the polymer is confined to owing to the presence of topological constraints. Unless otherwise said, in the rest of the paper we will conveniently express polymer contour lengths $L$ in units of the entanglement length $L_{e}$ and polymer spatial distances in units of the tube diameter $d_{T}$. Thus, for brevity, we introduce the compact notations [11,14]:

$$Z \equiv \frac{L}{L_{e}} \equiv \frac{N}{N_{e}},$$  \hfill (3)

$$z \equiv \frac{\ell}{L_{e}} \equiv \frac{n}{N_{e}},$$  \hfill (4)

where $Z$ and $z$ are the number of entanglements of the polymer chain and the polymer sub-chain of contour lengths $L$ and $\ell$, respectively [15]. Similarly, entanglements produce detectable effects on chain dynamics on time scales $\tau$ larger than the characteristic time $\tau_{e}$, known as the entanglement time: accordingly, we adopt $\tau_{e}$ as our unit of time.

In Sec. III D we give a detailed derivation of these quantities for the polymer melts considered in this work.

B. Ring structure

According to the lattice-tree picture [5,6,8,13,14,16], ring conformations in melt are the result of the balance between compression to avoid linking with other rings and swelling to avoid self-knotting. At the same time, this size competition can be viewed as a balance between double-folding (which minimizes threadings between chains) and random branching (which maximizes polymer entropy). As a consequence, a melt of rings can be mapped [14] to an equivalent melt of randomly branching polymers or lattice trees with the same large scale behavior. In particular, this mapping can be employed [14,15] to formulate quantitative predictions concerning the scaling behaviors of the following observables, and the related exponents, for $L/L_{e} = Z \gtrsim 1$:

(i) The mean ring size or gyration radius (Eq. [1]) as a function of the ring mass:

$$\langle R_{g} \rangle \sim d_{T} Z^{\nu}, \ \nu = 1/3; \hfill (5)$$

(ii) The mean path length on the tree backbone as a function of the ring mass:

$$\langle L_{\text{tree}} \rangle \sim d_{T} Z^{\rho}, \ \rho = 5/9; \hfill (6)$$

(iii) The mean ring size as a function of the mean path length:

$$\langle R_{g} \rangle \sim d_{T}^{-\nu_{\text{path}}} \langle L_{\text{tree}} \rangle^{\nu_{\text{path}}}, \ \nu_{\text{path}} = 3/5. \hfill (7)$$

Eq. (5) means that rings (i.e., the equivalent trees) behave like compact, space-filling objects while Eq. (7) expresses the fact that linear paths follow self-avoiding walk statistics [13]. Notice also that Eq. (7) follows directly from Eqs. (5) and (6), hence $\nu_{\text{path}} = \nu / \rho$. 


C. Ring dynamics

Here, we recapitulate the general arguments for ring dynamics discussed in Refs. [8, 10].

In order to quantify chain dynamics we consider [10] the monomer mean-square displacement

\[ g_1(\tau) \equiv \left\langle \sum_{i=1}^{N} (\vec{r}_i(t + \tau) - \vec{r}_i(t))^2 \right\rangle, \quad (8) \]

and the mean-square displacement of the ring centre of mass

\[ g_3(\tau) \equiv \left\langle (\vec{r}_{cm}(t + \tau) - \vec{r}_{cm}(t))^2 \right\rangle. \quad (9) \]

as a function of time \( \tau \).

For time scales \( \tau \lesssim \tau_e \) and length scales \( \lesssim d_T \) monomer motion is not affected by entanglements and we expect the characteristic Rouse-like [3] behavior, \( g_1(\tau) \sim \tau^{1/2} \) and \( g_3(\tau) \sim \tau \). On larger time scales \( \tau \gtrsim \tau_e \), mass transport along the trunk is, by assumption, the dominant relaxation mode of the chain: in particular, each one of the \( \mathcal{O}(Z^p) \) branches (Eq. (6)) protruding from the trunk acts as a “reservoir” exchanging a single polymer mass of equivalent contour length \( \sim L_e \) on the time scale \( \sim \tau_e \) with its neighbors. The displacement associated to a single mass exchange, projected along the trunk, is of the order of \( \sim \frac{d_T}{Z} \); since each of them happens randomly the curvilinear mean-square displacement of the centre of mass of the chain after \( \tau_e \) is:

\[ \left\langle (\Delta L_{tree})^2 \right\rangle \sim \left( \frac{d_T}{Z} \right)^2 \rho = d_T^2 \rho Z^{-2}, \]

while the total relaxation time of the chain is given by

\[ \tau_r \sim \frac{\left\langle L_{tree}^2 \right\rangle}{\left\langle (\Delta L_{tree})^2 \right\rangle / \tau_e} \sim \tau_e \rho Z^{2+p}. \quad (10) \]

Per self-similarity of the branched structure, the mass \( z(\tau) \) of ring sections which have relaxed up to time \( \tau \) with \( \tau_e \lesssim \tau \lesssim \tau_r \) can be obtained by inverting Eq. (10), i.e.

\[ z(\tau) \sim \left( \frac{\tau}{\tau_e} \right)^{1/(p+2)}. \quad (11) \]

By using Eq. (5) this is equivalent to the mean-square displacement:

\[ g_1(\tau_e \lesssim \tau \lesssim \tau_r) \sim d_T^2 \left( \frac{\tau}{\tau_e} \right)^{2/(p+2)}. \quad (12) \]

Similarly, the mean-square displacement, \( g_3 \), of the centre of mass of the chain results from the sum of the (independent) random motions of the \( z(\tau) \) ring sections which have relaxed up to time \( \tau \), i.e.

\[ g_3(\tau_e \lesssim \tau \lesssim \tau_r) \sim \frac{g_1(\tau)}{Z/Z(\tau)} \sim d_T^2 \left( \frac{\tau}{\tau_e} \right)^{(2p+1)/(p+2)}. \quad (13) \]

At large times \( \tau \gtrsim \tau_r \), the whole chain is simply diffusing \( g_1(\tau) \sim g_3(\tau) \sim D_{ch} \tau \) with the chain diffusion coefficient given by \( D_{ch} \sim \left\langle R_0^2 \right\rangle / \tau_r \), with \( \left\langle R_0^2 \right\rangle \sim d_T Z^\nu \) (see Eq. (5)). By fixing the numerical coefficients for smooth crossovers and by neglecting all numerical prefactors, the complete time behaviors for \( g_1 \) and \( g_3 \) are then given by the respective expressions:

\[ g_1(\tau) \sim d_T^2 \times \begin{cases} \left( \frac{\tau}{\tau_e} \right)^{1/2}, & \tau \lesssim \tau_e \\ \left( \frac{\tau}{\tau_e} \right)^{2/(p+2)}, & \tau_e \lesssim \tau \lesssim \tau_r \end{cases}, \quad (14) \]

and

\[ g_3(\tau) \sim d_T^2 \times \begin{cases} \left( \frac{\tau}{\tau_e} \right)^{(2p+1)/(p+2)}, & \tau_e \lesssim \tau \lesssim \tau_r \\ \left( \frac{\tau}{\tau_e} \right)^{2p-2}, & \tau \gtrsim \tau_r \end{cases}. \quad (15) \]

Finally, we introduce the monomer mean-square displacement in the frame of the chain center of mass:

\[ g_2(\tau) \equiv \left\langle \sum_{i=1}^{N} (\vec{r}_i(t + \tau) - \vec{r}_{cm}(t + \tau) - \vec{r}_i(t) + \vec{r}_{cm}(t))^2 \right\rangle. \quad (16) \]

It is not difficult to see that \( g_2(\tau) \sim g_1(\tau) - g_3(\tau) \) and that \( g_2(\tau \rightarrow \infty) = 2\left\langle R_0^2 \right\rangle \) where \( \left\langle R_0^2 \right\rangle \) is the chain mean-square gyration radius (see definition, Eq. (21)). We adopt the appearance of a plateau in the large-time behavior of \( g_2 \) as the signature that our chains have attained complete structural relaxation (see Fig. S1 in SM).

III. POLYMER MODEL AND NUMERICAL METHODS

A. Melts of rings: the kinetic Monte Carlo algorithm

We model classical solutions of semi-flexible ring polymers with excluded volume interactions by adapting the kinetic Monte Carlo (kMC) algorithm for elastic lattice polymers on the three-dimensional face-centered-cubic (fcc) lattice introduced originally in [41, 42] and employed later in several studies on polymer melts [3, 47, 48]. In the following we provide the main features of the model, while we refer the reader to the mentioned literature for more details.

In the model, any two consecutive monomers along the chain sit either on nearest-neighbor lattice sites or on the same lattice site (with no more than two consecutive monomers occupying the same lattice site), while nonconsecutive monomers are never allowed to occupy...
the same lattice site due to excluded volume. By adopting the lattice distance $a$ between fcc nearest-neighbor sites as our unit distance, the bond length $b$ between nearest-neighbor monomers fluctuates between $a$ and 0 (the latter case corresponding to a unit of *stored length*): for an average bond length $= (b)$, a polymer chain with $N$ bonds has then a total contour length $L = N(b) < Na$. Thanks to this numerical trick, polymers are made effectively elastic [44].

In order to increase substantially the overlap between the polymer chains by maintaining, at the same time, moderate chain lengths and, hence, simulations feasible, we use the “trick” described in Ref. [9] and consider semi-flexible polymer chains, namely polymers whose *Kuhn length* $\ell_K$ [3] is significantly larger than the mean bond length $(b)$. To this purpose, we have complemented the chain Hamiltonian by introducing the bending energy term:

$$\frac{\mathcal{H}_{\text{bend}}}{k_B T} = -\kappa_{\text{bend}} \sum_{i=1}^{L/b} \cos \theta_i \equiv -\kappa_{\text{bend}} \sum_{i=1}^{L/b} \frac{\vec{r}_{i} \cdot \vec{r}_{i+1}}{||\vec{r}_{i+1}||},$$  \hspace{1cm} (17)

where $\kappa_{\text{bend}}$ represents the bending stiffness which determines $\ell_K$ (see Sec. [III.D] and $\ell_i \equiv \vec{r}_{i+1} - \vec{r}_{i}$ is the oriented bond vector between monomers $i$ and $i + 1$ [49] having spatial coordinates $\vec{r}_{i}$ and $\vec{r}_{i+1}$. Importantly, since bond vectors are obviously ill-defined when two monomers form a stored length, the sum in Eq. (17) is restricted to the effective bonds of the chains. By increasing $\kappa_{\text{bend}}$, the energy term Eq. (17) makes polymers stiffer.

Then, the dynamic evolution of the melts proceeds according to the following Metropolis-Hastings-like [20] criterion. One monomer is picked at random and displaced towards one of the nearest lattice sites. The move is accepted based on the energy term Eq. (17) and if, at the same time, *both* chain connectivity and excluded volume conditions are not violated: in particular, the latter condition is enforced by imposing that the destination lattice site is either empty or, at most, occupied by one and only one of the nearest-neighbor monomers along the chain. These two choices represent the lattice analogs, respectively, of the Rouse and the reptation relaxation modes [41,3] of polymer dynamics at dense conditions. As explained in detail in Ref. [12], the stored length “trick” ensures that the algorithm remains efficient even when it is applied to the equilibration of very dense systems. Specific values of acceptance rates as a function of the bending rigidity $\kappa_{\text{bend}}$ are summarized in Table I.

### B. Melts of rings: simulation details

We have studied bulk properties of dense solutions of $M$ closed (ring) semi-flexible polymer chains made of $N$ monomers or bonds per ring. By construction, rings are *unknotted and unconcatenated* or, for brevity [3], *untangled*. We simulate values $N \times M = [40 \times 1000, 80 \times 500, 160 \times 250, 320 \times 125, 640 \times 62]$, with fixed total number of monomers $= 40,000$ (for computational convenience, the total number of monomers for $N = 640$ is slightly less). All these systems have been studied for the bending stiffness parameters $\kappa_{\text{bend}} = 0, 1, 2$ (Eq. (17)). In addition, we have also simulated melts with $N \times M = [234 \times 171, 236 \times 58]$ for $\kappa_{\text{bend}} = 1$ and $N \times M = [104 \times 385, 104 \times 64]$ for $\kappa_{\text{bend}} = 2$: once rescaled in terms of the corresponding entanglement units (see Sec. [III.D] and Table I), these two set-up’s have the same number of entanglements per chain $Z \approx 8$ of $N = 640$ with $\kappa_{\text{bend}} = 0$.

Bulk conditions are implemented through the enforcement of periodic boundary conditions in a simulation box of total volume $V = L_{\text{box}}$. Similarly to previous works [31,32,38], melt conditions correspond to fix the monomer number per fcc lattice site to (i) $\rho_{\text{site}} = \frac{2}{3} = 1.25$ for $N \leq 320$ and (ii) $\rho_{\text{site}} = \frac{31}{25} = 1.24$ for $N = 640$: respectively, since the volume occupied by the fcc lattice site is $= \frac{a^3}{\sqrt{2}}$ [52], the monomer number per unit volume are given by (i) $\rho = \frac{3}{2} \sqrt{2} \approx 1.77 a^{-3}$ for $N \leq 320$ and (ii) $\rho = \frac{31}{25} \sqrt{2} \approx 1.75 a^{-3}$ for $N = 640$. Accordingly, we fix $L_{\text{box}} = 20 \sqrt{2} a$ for all $N$’s.

Finally, our typical runs amount to a minimum of $7 \times 10^6$ up to a maximum of $3 \times 10^8$ kMC time units where one kMC time unit $\tau_{\text{MC}}$ is $= N M$: these runs are long enough such that the considered polymers have attained proper structural relaxation (see Fig. S1 in SM).

### C. A closer look to the bending stiffness

It is worth discussing in more detail the consequences of the energy term, Eq. (17).

On the fcc lattice, the angle $\theta$ between consecutive chain bonds is restricted to the five values $= 0^\circ, 45^\circ, 90^\circ, 135^\circ, 180^\circ$. Otherwise, for ideal polymers (i.e. in the absence of the excluded volume interaction), the angles $\theta_i$ in Eq. (17) are obviously not correlated to each other. This implies that the distribution function $P_{\text{ideal}}(\kappa_{\text{bend}}; \cos \theta)$ of the variable $\cos \theta$ follows the simple Boltzmann form:

$$P_{\text{ideal}}(\kappa_{\text{bend}}; \cos \theta) = \frac{1}{Z} N(\cos \theta) e^{\kappa_{\text{bend}} \cos \theta},$$  \hspace{1cm} (18)

where $N(\cos \theta)$ is an entropy-like factor accounting for the total number of lattice conformations between two successive bonds at given $\cos \theta$ and $Z$ is the normalization factor.

In polymer melts, excluded volume interactions induce an effective long range coupling between bond vectors and the distribution function $P_{\text{melt}}(\kappa_{\text{bend}}; \theta)$ is expected to deviate from Eq. (18). For instance, one can immediately see that the angle $= 180^\circ$ (i.e. $\cos \theta = -1$) is possible for ideal polymers but strictly forbidden in the presence of excluded volume interactions. The distributions $P_{\text{melt}}(\kappa_{\text{bend}}; \theta)$ for the different $\kappa_{\text{bend}}$’s and in comparison to $P_{\text{ideal}}(\kappa_{\text{bend}}; \theta)$ are given in Fig. 4 (square-solid vs.
TABLE 1. Values of physical parameters characterizing the melts of polymers studied in this paper. \( a \) is the unit distance of the fcc lattice and the monomer number per unit volume is \( \rho a^3 \approx 1.77 \) (Sec. III B). (i) \( \kappa_{\text{bend}} \), bending stiffness parameter (Eq. (17)); (ii) acceptance rate of the kMC algorithm; (iii, iv) \( \langle \cos \theta \rangle^{\text{lin}} \), \( \langle \cos \theta \rangle^{\text{ring}} \), mean value of the cosine of the angle between two consecutive bonds along the linear/ring polymer (Eq. (17)); (v) \( \langle \cos \theta \rangle^{\text{lin}} / \langle \cos \theta \rangle^{\text{ring}} \), mean value of the cosines of the angles between two consecutive bonds along the linear/ring polymer (Eq. (17)); (vi) \( \ell_K / a \), mean bond length; (vii) \( \rho K \ell_K^2 \), number of Kuhn segments per Kuhn volume [51]; (viii) \( L_e / a \), entanglement length (Eq. (20)); (ix) \( N_e \equiv L_e / \langle \theta \rangle \), number of bonds per entanglement length; (x) \( d_T = \sqrt{\ell_K L_e / 6} \), tube diameter of untangled melts; (xi) \( \tau_e \), entanglement time.

| \( \kappa_{\text{bend}} \) | acc. rate | \( \langle \cos \theta \rangle^{\text{lin}} \) | \( \langle \cos \theta \rangle^{\text{ring}} \) | \( \langle b \rangle / a \) | \( \ell_K / a \) | \( \rho K \ell_K^2 \) | \( L_e / a \) | \( N_e \) | \( d_T / a \) | \( \tau_e / \tau_{\text{MC}} \) (\( \times 10^4 \)) |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 0.069 | 0.187 | 0.171 | 0.731 | 1.440 | 2.679 | 58.738 | 80.379 | 3.755 | 15.0 |
| 1 | 0.048 | 0.476 | 0.447 | 0.696 | 2.194 | 5.920 | 20.708 | 29.764 | 2.752 | 5.2 |
| 2 | 0.036 | 0.670 | 0.635 | 0.669 | 3.393 | 13.620 | 8.759 | 13.088 | 2.226 | 2.8 |

D. Polymer length and time scales

We provide here a detailed derivation of the relevant length and time scales characterizing our polymer melts (they are summarized in Table [1]). Since we work at fixed monomer density \( \rho \) (see Sec. III B), the values of these parameters depend only on the bending stiffness parameter \( \kappa_{\text{bend}} \).

**Average bond length, \( \langle b \rangle \)** – We observe that \( \langle b \rangle \) is a decreasing function of \( \kappa_{\text{bend}} \); arguably, this effect is due to the fact that the bending energy term Eq. (17) can be made effectively smaller (i.e. more negative) by simply letting the polymer to become less elastic through the reduction of the effective total contour length of the chain.

**Kuhn length, \( \ell_K \)** – By modulating the bending constant \( \kappa_{\text{bend}} \), we can fine-tune the flexibility of the polymers (Eq. (17)). The latter is quantified in terms of the Kuhn length \( \ell_K \), namely the unit of contour length beyond which the chain orientational order is lost [2, 3]. For linear chains, \( \ell_K \) is defined by the relation [2, 3],

\[
\ell_K \equiv \lim_{\ell \to \infty} \frac{\langle R^2(\ell) \rangle}{\ell},
\]

where \( \langle R^2(\ell) \rangle \) is the mean-square end-to-end distance between any two monomers along the chain at monomer number separation \( n \) or contour length separation \( \ell = n \langle b \rangle \). In order to determine the Kuhn length of our polymer chains, we have simulated melts of \( M = 125 \) linear chains with \( N = 320 \) monomers per chain at the same monomer density \( \rho \approx 2/\sqrt{2} \approx 1.77 a^{-3} \) (Sec. III B) and for \( \kappa_{\text{bend}} = 0, 1, 2 \) and, after equilibration, we have computed numerically Eq. (19). As shown in Fig. 2 (symbols), the chains become increasingly stiffer with \( \kappa_{\text{bend}} \) as expected by displaying, in particular, plateau-like regions for large \( \ell \)'s. In analogy to the procedure employed.
in Ref. [48], the heights of these plateaus, obtained by best fits to corresponding constants on the common interval \( t \in [150, 200] \) (Fig. 2(d), dashed lines), provide the values of the corresponding \( \ell_K \)'s which are used in this work (see Table I).

**Entanglement length, \( L_e \), and tube diameter, \( d_T \) — While predicting \( L_e \) in terms of the other parameters of the model is in general a difficult task [53–54], we use here the result by Uchida et al. [51] which expresses \( L_e \) as a function of \( \rho K \ell_K^2 \), the number of Kuhn segments per Kuhn volume at given density of Kuhn segments per unit volume \( \rho_K \):

\[
\frac{L_e}{\ell_K} = \left( \frac{1}{0.06 \rho K \ell_K^4} \right)^{2/5} + \left( \frac{1}{0.06 \rho K \ell_K^4} \right)^2.
\]  

(20)

By using Eq. (20), it is a simple exercise to extract \( L_e/\ell_K \) and the corresponding number of monomers per entanglement length, \( N_e \equiv L_e/(b) \). We observe (Table I) that \( N_e \) decreases by approximately an order of magnitude by the apt fine-tuning of \( \kappa_b \). This means that rings with the same contour length but stiffer will become increasingly entangled [9]. Finally, we use the definition Eq. (2):

\[
d_T = \sqrt{\frac{L_e \ell_K}{6}},
\]

for computing the tube diameters of polymers of different bending stiffnesses. Notice (Table I) that, by changing chain stiffness, \( d_T \) moves from smaller to comparable to \( \ell_K \) meaning that we cover the crossover from loosely to tightly entangled melts.

**Entanglement time, \( \tau_e \) — The entanglement time \( \tau_e \) marks the onset to entanglement-related effects in polymer dynamics. Here, we follow the definition introduced in [49], namely where the monomer time mean-square displacement (Eq. (8)) \( g_1(\tau = \tau_e) \approx 2d_T^2 \) (Eq. (2)). For consistency with the previous definitions, notice that \( g_1(\tau) \) has been calculated on the same dynamic simulations of melts of linear chains used for calculating \( \ell_K \).

**IV. RESULTS**

**A. Ring structure**

In order to characterize ring structure, we consider the chain mean-square “gyration” radius,

\[
\langle R_g^2 \rangle = \left\langle \frac{1}{N} \sum_{i=1}^{N} (\vec{r}_i - \vec{r}_{cm})^2 \right\rangle,
\]

(21)

where \( \vec{r}_i \) are the monomer coordinates and \( \vec{r}_{cm} = \frac{1}{N} \sum_{i=1}^{N} \vec{r}_i \) is the chain centre of mass, and the mean-square “magnetic” radius first introduced in Ref. [4] and defined as

\[
\langle R_m^2 \rangle = \frac{1}{\pi} \left\langle |\vec{A}| \right\rangle,
\]

(22)

where, inspired by the analogy to the classical electrodynamics of the magnetic far field generated by a loop carrying a constant electric current,

\[
\vec{A} \equiv \frac{1}{2} \sum_{i=1}^{N} \vec{r}_i \times (\vec{r}_{i+1} - \vec{r}_i) = \frac{1}{2} \sum_{i=1}^{N} \vec{r}_i \times \vec{r}_{i+1}
\]

(23)

is the (oriented) area enclosed by the ring. Both quantities are an expression of the average (square) ring size, yet they have different meaning: in particular, Eq. (22) was introduced to detect and quantify the presence of open loops inside the ring. Numerical values of \( \langle R_g^2 \rangle \) and \( \langle R_m^2 \rangle \) for melts of rings with different flexibilities are summarized in Table S1 in SM.

Fig. 3 shows these quantities, rescaled (filled symbols) by the corresponding tube diameters \( d_T \) and as a function of the total number of entanglements \( Z = L/L_e \), see Sec. H for details and Table I for specific values of \( d_T \) and \( L_e \). For further comparison, we have also included the results for \( \langle R_g^2 \rangle \) obtained from Monte Carlo simulations (bond-fluctuation model) of melts of rings by Müller et al. [9] (open symbols) and the universal curves (solid grey lines) from the “hierarchical crumpling” method by Schram et al. [4]. The excellent matching between these old data sets and the present new data validates our methodology: the average ring size covers the full crossover from Gaussian (\( \sim Z^1 \)) to compact (\( \sim Z^{2/3} \)) behavior. This is particularly evident for the stiffer rings (\( \kappa_b = 2 \)) whose reduced flexibility “helps”, in agreement with the results of Ref. [9], reaching the asymptotic behavior. The data for the mean-square magnetic radius \( \langle R_m^2 \rangle \) rescale equally well and, as noticed in [4], with
the same large-$Z$ behavior $\sqrt{\langle R_m^2 \rangle} \sim d_T Z^{1/3}$. However, a closer look to the ratio $\langle R_m^2 \rangle / \langle R_m^2 \rangle$ (see Fig. S2 in SM) reveals significant, albeit extremely slow ($O(Z^{-\gamma})$ with $\gamma \approx 0.07$), power-law corrections which were not noticed in the previous study \footnote{Ref. \text{[4]}}: instead, a similar result was already described in Ref. \text{[9]} where, however, the authors employed a different definition for the area spanned by a ring which was based on the $2d$ projection of the chain onto a random direction.

We examine next the average polymer shape, and we introduce the $3 \times 3$ symmetric gyration tensor $G$ whose elements are defined by:

$$G_{\alpha\beta} = \frac{1}{2N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} (r_{i,\alpha} - r_{j,\alpha})(r_{i,\beta} - r_{j,\beta}),$$ \hspace{1cm} (24)

where $r_{i,\alpha}$ with $\alpha = x, y, z$ are the Cartesian components of the spatial position of monomer $i$: the trace of the tensor $G$, $\text{Tr} G = \sum_{\alpha=1}^{3} \Lambda_{\alpha}^2$, is equal to $R_g^2$ and the three ordered eigenvalues, $\Lambda_1^2 \geq \Lambda_2^2 \geq \Lambda_3^2$, quantify the spatial variations of the polymer along the corresponding principal axes, i.e. the instantaneous shape of the chain. Polymers are ellipsoidal on average \footnote{Ref. \text{[33]}}, with mean values $\langle \Lambda_1^2 \rangle > \langle \Lambda_2^2 \rangle > \langle \Lambda_3^2 \rangle$ (see values in Table S1 in SM): similarly to $\langle R_g^2 \rangle$ (Fig. 3), we expect a scaling curve for each $\langle \Lambda_\alpha^2 \rangle$ in universal units $Z$ and $d_T$ and, for $Z \gg 1$, $\langle \Lambda_0^2 \rangle \sim \langle \Lambda_1^2 \rangle \sim \langle \Lambda_2^2 \rangle \sim d_T^2 N^{2\nu}$. In general our data (see Fig. S3 in SM) reflect well this trend, except for the smallest mean eigenvalue $\langle \Lambda_3^2 \rangle$ which displays consistent deviations from the asymptotic behavior for moderate chain sizes. Interestingly these deviations appear consistent with rings being double-folded on an underlying tree-like structure (Sec. \text{[1B]}): in fact, according to Fig. S3 in SM and Eq. \text{(4)} and for given mean path length $\langle L_{\text{tree}} \rangle$ on the “supporting” tree, we can write the expressions:

$$\langle \Lambda_{i=1,2}^2 \rangle \sim \langle L_{\text{tree}} \rangle^{2\nu_{\text{path}}},$$ \hspace{1cm} (25)

$$\langle \Lambda_3^2 \rangle \sim \langle L_{\text{tree}} \rangle^{2},$$ \hspace{1cm} (26)

where the latter is equivalent to assuming local stiff behavior at small contour lengths. Eqs. \text{(25)} and \text{(26)} are just equivalent to:

$$\langle \Lambda_{i=1,2}^2 \rangle \sim \langle L_{3} \rangle^{\nu_{\text{path}}},$$ \hspace{1cm} (27)

with $\nu_{\text{path}} = 3/5$ (Eq. \text{(7)}). Our data are well described by Eq. \text{(27)}, see Fig. 4 before the crossover to the asymptotic regime, $\langle \Lambda_{i=1,2}^2 \rangle \sim \langle \Lambda_3^2 \rangle$, takes finally place.

We look now for even more stringent signatures of an underlying branched structure for rings. As the first of these signatures, we consider the bond-vector correlation
function
\[
c(\ell) = \frac{\langle \hat{r}(\ell') \cdot \hat{r}(\ell' + \ell) \rangle}{\langle \hat{r}(\ell')^2 \rangle}.
\] (28)

Contrary to the known exponentially-decaying behavior typical of semi-flexible linear polymers (solid lines vs. long-dashed lines in the top panel of Fig. 5) \( c(\ell) \) is manifestly non-monotonic, showing an anti-correlation well whose minimum becomes more pronounced and locates around \( z = \ell/L_c \approx 1 \) with the increasing of the chain stiffness. By using the function \( \hat{r}(\ell) = (0, +1, 0) \) for \( 0 < \ell < L_c \) and \( \hat{r}(\ell) = (0, -1, 0) \) for \( L_c < \ell < 2L_c \) as a toy model for an exactly double-folded polymer filament of contour length \( = 2L_c \), it is easy to see that \( c(z = \ell/L_c) = (1 - 3/2z)/(1 - z/2) \) for \( 0 < z < 1 \) and \( c(z) = -1 \) for \( 1 \leq z < 2 \), i.e. \( c(\ell) \) displays an anti-correlation minimum at \( z = 1 \) or \( \ell = L_c \) (short-dashed line in the top panel of Fig. 5).

To corroborate further this conclusion, we introduce the mean contact probability, \( \langle p_c(\ell) \rangle \), between two monomers at given contour length separation \( \ell \) defined as:
\[
\langle p_c(\ell = n \langle b \rangle) \rangle = \left( \frac{2}{N(N-1)} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \Theta(r_c - |\vec{r}_i - \vec{r}_j|) \right),
\] (29)

where \( \Theta(x) \) is the usual Heaviside step function and the “contact distance” \( r_c \) between two monomers is taken equal to one lattice unit, \( a \). In terms of the “effective” ring contour length \( \zeta \equiv z(1 - z/Z) \), the data from the different rings (see Fig. 5 in SM) form three distinct curves according to their Kuhn length (Fig. 5 bottom panel). Notably these curves display the asymptotic power-law behavior \( \sim \zeta^{-\gamma} \) with scaling exponent \( \gamma \) close to 1, as variously reported in the past \([10, 14, 33]\). At the same time, the stiffer chains with \( k_{\text{bend}} = 2 \) display a short, yet quite evident, levelling of the contact probability curves around \( z \approx 1 \) which is clearly compatible with double-folding on the entanglement scale.

Arguably, double-folding should reduce the “exposed” area that each ring offers to its neighbors. To explore this possibility more quantitatively, we employ the concept of minimal surface of a ring \([17, 22, 44]\). The minimal surface (hereafter, \( \text{minS} \)) spanned on a ring polymer can be obtained by a suitable minimization algorithm as described in detail in Refs. \([17, 22]\). Essentially, the algorithm is based on successive iterations of triangulations evolving under surface tension by moving the free vertices: each triangle in the initial triangulation is made of two successive monomer positions and the center of the mass of the ring, then it is refined (by subdividing each edge into two edges, creating therefore four triangles out of one) and the surface area minimized by the surface tension flow with restructuring of the mesh. For the finer resolution that we use as well a two more refining steps are taken before the minimization. Finally, the algorithm stops when the relative surface area does not change by more than 0.1% over a few tens of additional steps of the minimization procedure. Similarly to the eye of a needle pierced by a rope, the single minimal surface of a given ring can be pierced or threaded by the other surrounding polymers in the melt: in particular, once the minimal surfaces of the rings in the melt are determined, by standard numerical tools (see details in Refs. \([17, 22]\)) it is possible to define in a precise and robust manner which amount of the total contour length of any given ring passes through the minimal surface of another ring.

Based on our results for the mean-square lengths like
\langle R_{2m}^0 \rangle \) and \( \langle R_{2m}^2 \rangle \) (Fig. [3]), it is natural to expect equal universal behavior for the mean minimal surface, \( \langle \text{minS} \rangle \) (see Table S1 in SM), as a function of \( Z \). Surprisingly, this is not the case (see Fig. [4]): in fact \( \langle \text{minS} \rangle \sim Z \) for the different flexibilities in agreement with previous results [17] for off-lattice simulations, but the three data sets do not collapse onto each other after rescaling in terms of entanglement units \( Z \) and \( d^2_0 \). Notice that this finding is robust and independent of the triangulation resolution employed to calculate the minimal surface of the rings ("o-symbols" vs. "x-symbols"). Similar lack of collapse is also observed in the mean number of threaded neighbors \( (n_t) \) of a ring (Fig. [7] circles), when we take all the threadings into account. However if we disregard the short threadings and we take the rings to be effectively threaded only if at least one threading length is longer than \( L_e \), we recover the collapse (triangles in Fig. [7] as was the case in [22]). This suggests that the minimal surface areas (Fig. [4]) are indeed impacted by the shallow threadings, which are nonuniversal and, therefore, the scaling of the area is nonuniversal too. Therefore, in the rest of the section we decide to disregard those threadings produced by ring segments of contour length \( Z < 1 \).

The decrease of \( \langle \text{minS} \rangle \) with \( \kappa_{\text{bend}} \) (Fig. [6]) takes us to ask to what extent rings rearrange the mutual overlap. By introducing the so called separation length [17] [22],

\[
L_{\text{sep}} = \min \left( \sum_{i: \text{seven}} L_{t_i}, \sum_{i: \text{odd}} L_{t_i} \right),
\]

where \( L_{t_i} \) is the (threading) contour length between the \( i \)-th and the \( i + 1 \)-th penetrations of the minimal surface (the penetrated ring splits each penetrating ring into two complementary portions of linear sizes \( L_{\text{sep}} \) and \( L - L_{\text{sep}} \)), and the associated quantity,

\[
Q \equiv \frac{L_{\text{sep}}}{L - L_{\text{sep}}},
\]

accounting for the relative amount of contour length on one ring side with respect to the other (\( Q = 1 \) means that the penetrating ring is half split by the penetrated surface), the mean value \( \langle Q \rangle \) decreases, i.e. less material enters the minimal surface of a ring (Fig. [8] top). Yet, the mean number of times, \( \langle n_p \rangle \), any ring penetrates the minimal surface of any other single ring increases (Fig. [8] bottom): notice that these two apparent contradictory features can be easily reconciled by supposing that while retracting from each other (i.e. decreasing \( Q \)), rings may at the same time pierce each other more frequently by the increased propensity to form branches at the entanglement scale. Accordingly, and in agreement with the off-lattice simulations presented in Ref. [22], both \( \langle Q \rangle \) and \( \langle n_p \rangle \) are universal functions in terms of \( Z \). In general this agrees with the results of previous [22] off-lattice dynamic simulations of melts of rings, yet with a warning caveat: while the current values for \( \langle n_p \rangle \) agree also quantitatively (Ref. [22], see Fig. 2(B) therein), the power-law decay measured here (\( \langle Q \rangle \sim Z^{-0.51} \), dashed line in the top panel of Fig. [8]) is definitely sharper than the quite softer behavior \( \langle Q \rangle \sim Z^{-0.31} \) reported in [22]. Interestingly, the latter power-law is found by reincluding in the analysis threading lengths of any size (see Fig. S5 in SM): however the scaling now is as a function of the total number of Kuhn segments \( L/\ell_K \) and not \( Z \), which may hint again at shallow threadings operating on length scales below \( L_e \). While beyond the scopes of the present work, understanding these quantitative discrepancies between the different polymer models is clearly an important issue which needs to be tackled in the future.

### B. Ring dynamics

As explained in Sec. [11C], the tree-lattice model gives very accurate predictions for the expected chain dynamics behavior which have been verified by off-lattice molecular dynamics simulations [11] and lattice mod-
FIG. 9. Monomer time mean-square displacement, $g_1(\tau)$ (Eq. (8)), and chain center of mass time mean-square displacement, $g_3(\tau)$ (Eq. (9)). Lines of the same color are for the same number of monomers $N$, and the corresponding number of entanglements $Z$ per chain is indicated in the legends. The dashed black lines correspond to the dynamic predictions of the lattice tree model, Eqs. (14) and (15) with $\nu = 1/3$ (Eq. (5)) and $\rho = 5/9$ (Eq. (6)).

els [26]. Similarly, here we quantify chain dynamics by means of the monomer mean-square displacement, $g_1(\tau)$ (Eq. (14)), and the center of mass mean-square displacement, $g_3(\tau)$ (Eq. (15)), and compare the results to the theoretical predictions for the dynamic behavior of tree-shaped rings, see Eqs. (14) and (15) with $\nu = 1/3$ (Eq. (5)) and $\rho = 5/9$ (Eq. (6)). Fig. 9 demonstrates the good agreement between simulations and theory, in particular for chains of large stiffness (i.e. high $Z$).

The establishment of topological links via threadings has been hold responsible of the unique rheological properties of melts of rings as, for instance, the unusually strong extension-rate thickening of the viscosity reported in extensional flows [25]. On the other hand, at equilibrium, double-folding was originally [5] [6] [8] proposed as a viable mechanism to minimize the threadable surface that nearby rings expose to each other. In the numerical experiments discussed here, double-folding is “enhanced” by the chain local stiffness and, intuitively, we expect that the corresponding reduction in the number of threadings should also produce visible dynamic effects.

Recently, Michieletto and others [34, 35] have demonstrated that by freezing or pinning a certain fraction $f_p$ of rings in the melt the dynamics of the remaining ones is considerably reduced if not frozen at all. In corresponding melts of linear chains this effect is not seen, so they attributed it to the presence of threadings present in rings but absent in linear chains. Based on that we expect that the reduction of threadings through double-folding should be visible through pinning, in particular where double-folding is more present the slowing-down by pinning should be less dramatic. To prove this we considered additional simulations of melts of rings for $\kappa_{\text{bend}} = 0, 1, 2$ with the same number of entanglements $Z = 8$ (to ensure the same large scale behavior, see Fig. 3) and for ring pinning fractions $f_p$ from 0 (i.e. no pinning) to 70%. Then we monitored the time mean-square displacement, $g_3(\tau)$, of the center of mass of the non-pinned rings. As shown in Fig. 10 our results are consistent with the proposed picture: more flexible rings ($\kappa_{\text{bend}} = 0$, left panel) which we have interpreted as more threaded are already completely frozen at $f_p \approx 30 - 40\%$ while the stiffer (and comparably less threaded, see “no-cutoff” data in Fig. 7) rings ($\kappa_{\text{bend}} = 2$, right panel) require $f_p \approx 60 - 70\%$. Importantly, these specific fractions do not seem to depend on the inevitably finite size of our systems: dynamic runs with smaller (and, arguably, more finite-size-dependent) systems give similar values for the freezing fractions (see Fig. S6 in SM).

V. DISCUSSION AND CONCLUSIONS

The conformational properties of unconcatenated and unknotted (untangled) ring polymers in dense melts represent one of the remaining unsolved challenge in polymer physics. In this work, in particular, we have focused on which properties of the rings can be interpreted as signatures of the hypothesis proposed long ago [5] [6] [8] that the polymer fiber double-folds around a branched
(lattice-tree) path.

In this respect, global observables like the polymer mean-size or the mean magnetic radius \((\langle R^2 \rangle_g \) and \(\langle R^2_m \rangle \), Fig. 3) are very useful for model validation but otherwise offer little insight.

On the contrary, robust evidence for double-folding comes by exploiting the mean polymer shape (Fig. 4). The 3 principal axes of the polymer are very different in size and, for relatively moderate polymer lengths, they are not at the same “point” of the crossover to asymptotic behavior: in particular, on the studied range where the largest and the smallest axes are not proportional to each other, we have shown that their functional relation is in quantitatively agreement with the lattice-tree model.

This argument is proposed here for the first time, and it could be useful to revise data relative to other polymer models at its light.

Additional signatures of double-folding on polymer contour lengths \(z = \ell / L_e \lesssim 1\) become manifested also in the characteristic negative well of the bond-vector orientation correlation function (Fig. 5, top panel) and in the “softer” slope of the mean contact probability \(\langle p_c(\ell) \rangle \) (Fig. 5, bottom panel) displayed before the asymptotic \(\sim \ell^{-1}\) power-law behavior takes effectively place. Intriguingly, the reported \(\langle p_c(\ell) \rangle \) for chromatin fibers measured in conformation capture experiments [56] displays the same systematic two-slope crossover [57] for \(\ell \lesssim 10^9\) basepairs, i.e. below the estimated [32] entanglement length of the chromatin fiber. Notice that, in this respect, the formulated hypothesis that such “shoulder” in the contact probability derives from active loop-extrusion [57] provides a dynamic explanation about how (double-folded) loops can form, otherwise it is not needed per se in order to explain the observed trend in the contact probabilities.

Overall it is worth stressing that these features, that we interpret as manifestations of double-folding, can be made explicit only by introducing some (even if only moderate) bending penalty to the polymer elasticity.

Interestingly, an analysis of ring conformations in terms of the so called minimal surfaces confirms (Fig. 6) that rings may reduce their threadable surfaces via double-folding on the entanglement scale, yet other features quantifying the piercing of the minimal surface of a ring from its neighbors (Fig. 7 and Fig. 8) evaluated on length scales larger than one entanglement length behave universally. The universal behavior shows the applicability and the relevance [39] of the (linear) entanglement scale to ring polymer melts.

From the point of view of ring dynamics, we have reported that single monomer and global chain motions are in good agreement (Fig. 9) with the theory stating that the dominant mode of relaxation is mass transport along the trunk of the underlying tree. Finally, the reduction of the ring threadable surface at high stiffnesses implies (Fig. 10) that the complete freezing of the melt is achieved by pinning [32] at a larger fraction of chains out of the whole population.

In conclusion, by tuning the mutual overlap between different chains through the local stiffness of the polymer fiber [9], we show that double-folding is a general feature of ring polymers in dense melt: yet it remains a feature whose detection proves to be a tricky task, essentially because double-folding manifests on relatively small spatial scales, typically of the order of the tube diameter.

Acknowledgements – JS and AR acknowledge networking support by the COST Action CA17139 (EUTOPIA). The computational results presented have been achieved in part using the Vienna Scientific Cluster (VSC).

[1] P.-G. De Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, 1979).
[2] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986).
[3] M. Rubinstein and R. H. Colby, *Polymer Physics* (Oxford University Press, New York, 2003).
Double-folding of ring polymers in melt conditions: Conformational and dynamical signatures
– Supplemental Material –

Mattia Alberto Ubertini, Jan Smrek, Angelo Rosa
| $N$ | $M$  | $(R_m^2)$ | $(R_m^2)$ | $\langle \text{minS} \rangle$ | $\langle \Lambda_1^3 \rangle$ | $\langle \Lambda_2^3 \rangle$ | $\langle \Lambda_3^3 \rangle$ |
|-----|-----|-----------|-----------|-----------------|-----------------|-----------------|-----------------|
| 40  | 1000| 3.3007 ± 0.0007 | 1.8937 ± 0.0008 | 11.60 ± 0.05 | 2.1160 ± 0.0007 | 0.8280 ± 0.0003 | 0.35669 ± 0.00008 |
| 80  | 500 | 6.304 ± 0.004 | 3.447 ± 0.004 | 25.6 ± 0.2 | 4.052 ± 0.004 | 1.560 ± 0.001 | 0.6912 ± 0.0003 |
| 160 | 250 | 11.76 ± 0.02 | 6.19 ± 0.02 | 55.6 ± 0.4 | 7.56 ± 0.02 | 2.891 ± 0.005 | 1.310 ± 0.001 |
| 320 | 125 | 21.48 ± 0.08 | 11.0 ± 0.1 | 119.7 ± 1.2 | 13.74 ± 0.07 | 5.29 ± 0.02 | 2.447 ± 0.005 |
| 640 | 62  | 38.6 ± 0.2 | 18.9 ± 0.2 | 256.2 ± 2.8 | 24.7 ± 0.2 | 9.37 ± 0.05 | 4.47 ± 0.01 |

$k_{\text{bend}} = 0$

| $N$ | $M$  | $(R_m^2)$ | $(R_m^2)$ | $\langle \text{minS} \rangle$ | $\langle \Lambda_1^3 \rangle$ | $\langle \Lambda_2^3 \rangle$ | $\langle \Lambda_3^3 \rangle$ |
|-----|-----|-----------|-----------|-----------------|-----------------|-----------------|-----------------|
| 40  | 1000| 4.133 ± 0.001 | 2.262 ± 0.002 | 12.82 ± 0.07 | 2.772 ± 0.001 | 0.9778 ± 0.0004 | 0.38363 ± 0.00008 |
| 80  | 500 | 7.915 ± 0.008 | 4.09 ± 0.01 | 28.6 ± 0.2 | 5.220 ± 0.006 | 1.893 ± 0.002 | 0.8028 ± 0.0004 |
| 160 | 250 | 14.52 ± 0.02 | 7.19 ± 0.05 | 61.9 ± 0.6 | 9.43 ± 0.02 | 3.506 ± 0.007 | 1.573 ± 0.002 |
| 234 | 171 | 19.97 ± 0.06 | 9.70 ± 0.04 | 94.3 ± 0.8 | 12.95 ± 0.03 | 4.834 ± 0.008 | 2.223 ± 0.002 |
| 320 | 125 | 25.8 ± 0.1 | 12.38 ± 0.07 | 132.3 ± 1.4 | 16.67 ± 0.08 | 6.28 ± 0.02 | 2.936 ± 0.006 |
| 640 | 62  | 44.3 ± 0.5 | 20.5 ± 0.3 | 279.7 ± 3.3 | 28.1 ± 0.4 | 10.73 ± 0.09 | 5.20 ± 0.03 |

$k_{\text{bend}} = 1$

| $N$ | $M$  | $(R_m^2)$ | $(R_m^2)$ | $\langle \text{minS} \rangle$ | $\langle \Lambda_1^3 \rangle$ | $\langle \Lambda_2^3 \rangle$ | $\langle \Lambda_3^3 \rangle$ |
|-----|-----|-----------|-----------|-----------------|-----------------|-----------------|-----------------|
| 40  | 1000| 5.600 ± 0.006 | 2.935 ± 0.005 | 14.8 ± 0.1 | 3.998 ± 0.004 | 1.199 ± 0.002 | 0.4030 ± 0.0003 |
| 80  | 500 | 10.82 ± 0.02 | 5.15 ± 0.03 | 33.6 ± 0.3 | 7.45 ± 0.02 | 2.426 ± 0.007 | 0.946 ± 0.002 |
| 104 | 385 | 13.56 ± 0.02 | 6.27 ± 0.02 | 44.1 ± 0.4 | 9.21 ± 0.01 | 3.092 ± 0.004 | 1.261 ± 0.001 |
| 160 | 250 | 19.4 ± 0.2 | 8.66 ± 0.06 | 70.7 ± 0.7 | 12.87 ± 0.07 | 4.50 ± 0.02 | 1.943 ± 0.006 |
| 320 | 125 | 33.2 ± 0.3 | 14.2 ± 0.1 | 148.7 ± 1.8 | 22.0 ± 0.3 | 7.90 ± 0.07 | 3.65 ± 0.02 |
| 640 | 62  | 54.9 ± 1.4 | 22.4 ± 0.4 | 308.8 ± 3.5 | 35.6 ± 1.3 | 12.9 ± 0.2 | 6.36 ± 0.06 |

$k_{\text{bend}} = 2$

TABLE S1. Conformational properties of melts of ring polymers with bending stiffness $k_{\text{bend}}$. $N$: number of monomers per chain; $M$: number of chains in the melt; $(R_m^2)$: mean-square gyration radius (Eq. 21 in the main paper); $(R_m^2)$: mean-square magnetic radius (Eq. 22 in the main paper); $\langle \text{minS} \rangle$: mean minimal surface; $\langle \Lambda_\alpha^3 \rangle$: mean value of the $\alpha$-th eigenvalue ($\alpha = 1, 2, 3$) of the gyration tensor $Q_{\alpha\beta}$ (Eq. 24 in the main paper). The reported values with the corresponding error bars have been rounded to the first decimal digit. The data for $\langle \text{minS} \rangle$ are for a coarse resolution of the triangulation procedure adopted to calculate the minimal surface of a ring polymer (see Ref. 17 for the technical details). A finer triangulation gives essentially the same values (“×-symbols” vs. “×-symbols” in Fig. 6 in the main paper) which we have not reported explicitly in this Table.
FIG. S1. Monomer time mean-square displacement, $g_2(\tau)$ (see Eq. (14) in the main paper), in the frame of the centre of mass of the corresponding chain. The horizontal lines are for the stationary values, $= 2\langle R_g^2(N)\rangle$ (see Sec. II C in the main paper), reported in Table S1. The dashed black lines correspond to the initial Rouse behavior where $g_2(\tau) \sim g_1(\tau)$ (see Eq. (14) in the main paper). Color code is as in Fig. 9 in the main paper.
FIG. S2. \( \langle R_g^2 \rangle / \langle R_m^2 \rangle \): ratio of the mean-square gyration radius (Eq. (21) in the main paper) to the mean-square magnetic radius (Eq. (22) in the main paper) as a function of the total number of entanglements, \( Z = L/L_e \), of the chain. Notice the weak increasing of the ratio with \( Z \) (the straight line is obtained by best fit of the data to a simple power-law).
FIG. S3. Scaling behavior of the mean-square eigenvalues \( \langle \Lambda_{2,3}^2 \rangle \) of the gyration tensor (Eq. (24) in the main paper) of untangled ring polymers as a function of the total number of entanglements, \( Z = L/L_e \), of the chain. Notice the large finite-size corrections to scaling for the smallest eigenvalue \( \langle \Lambda_3^2 \rangle \) and its behavior \( \sim Z^{2/\rho} \sim \langle L_{\text{tree}} \rangle^2 \) (see Eq. (6) in the main paper) for small to moderate number of entanglements per chain \( Z \). Error bars are smaller than the symbols size.
FIG. S4. Mean contact probabilities, $\langle p_c(\ell) \rangle$, as a function of the contour length separation in number of entanglements, $z \equiv \ell / L_e$. Lines in full colors are for the longest rings ($N = 640$) while lines in fainter colors are for chains of shorter contour lengths.
FIG. S5. \(\langle Q \rangle\): mean relative amount of contour length piercing one ring minimal surface side with respect to the other (Eq. (31) in the main paper) as a function of the total number of Kuhn segments, \(L/\ell_K\), of the chain. The dashed (black) line corresponds to the best fit to the data. Contrary to the data displayed in the top panel of Fig. 8 in the main paper, here we have included threading segments of any contour length.
FIG. S6. Effects of random pinning on chain dynamics. Same as in Fig. 10 in the main paper, but for melts containing fewer chains (for implementation details, see Sec. III B in the main paper).