Density effects in entangled solutions of linear and ring polymers

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Abstract
In this paper, we employ molecular dynamics computer simulations to study and compare the statics and dynamics of linear and circular (ring) polymer chains in entangled solutions of different densities. While we confirm that linear chain conformations obey Gaussian statistics at all densities, rings tend to crumple becoming more and more compact as the density increases. Conversely, contact frequencies between chain monomers are shown to depend on solution density for both chain topologies. The relaxation of chains at equilibrium is also shown to depend on topology, with ring polymers relaxing faster than their linear counterparts. Finally, we discuss the local viscoelastic properties of the solutions by showing that the diffusion of dispersed colloid-like particles is markedly faster in the rings case.

Keywords: polymer solutions, linear and ring polymers, entanglements, molecular dynamics simulations

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(Some figures may appear in colour only in the online journal)

1. Introduction
Since the pioneering works of Flory [1], De Gennes [2] and Edwards [3], excluded volume effects and topological constraints have been recognised as playing a fundamental role in the comprehension of the structural and dynamical properties of polymers in semi-dilute solutions and melts. Topological constraints (or entanglements) hinder the thermal motion of polymers in a way akin to the process of threading a rope out of a pool: polymer chains cannot pass through each other, while they are allowed to slide past each other. This fundamental mechanism is recognised as being responsible for the unique properties of polymer solutions and melts [1–4]. Since the very early days of polymer physics, theoretical speculation and experimental investigation have mainly dealt with the solutions and melts of linear polymer chains [1–4].

More recently a new class of systems has emerged and started receiving similar systematic attention: the entangled solutions and melts of unconcatenated and unknotted circular (ring) polymers [5–24]. Why are ring polymers so special and, as we will shortly see, challenging? According to current theoretical understanding, linear polymers in entangled solutions follow (quasi) ideal statistics because of the screening of excluded volume [3] at large scales, while ring polymers do not display such an analogous ‘compensation’ mechanism and tend to crumple into compact configurations [9, 10, 12–14, 16, 20]. At odds with their linear counterparts then, topological constraints affect not only the dynamical properties of rings in solution but they also have consequences on their properties at equilibrium. Last but not least, the physical behaviour of ring polymers in solution has revealed intriguing connections to the experimentally observed behaviour of chromosomes inside the nuclei of the cells [18, 20]. In spite of the considerable theoretical and experimental work which has already been dedicated to the subject, there are still several features of ring polymers in solution which wait to be examined in more detail.

In this article, we present a systematic numerical investigation concerning the equilibrium and dynamical properties of ring polymers in solution, either as a function of ring size or solution density. The latter aspect in particular has received
less attention in the past and this work intends primarily to start filling this gap. For comparison, we also discuss the same properties for the corresponding entangled solutions of linear chains. As a result, we confirm that while linear chains statistics remains nearly Gaussian in the long-chain limit at all densities, rings tend to crumple becoming more and more compact as the density increases. Nonetheless, and interestingly, we prove that increasing the density has also non-negligible, measurable effects for contact frequencies in linear chains. We discuss polymer dynamics, showing that chains and rings of the same size have different relaxation times, with rings relaxing faster. Then we conclude this work by addressing the issue of how chain structure affects the diffusion of non-sticky colloid particles.

This paper is structured as follows: in section 2 we describe the details of the computational methods employed in this work. In section 3 we present and discuss the results of our work. Finally, in section 4 we outline the conclusions.

2. Model and methods

2.1. The model

2.1.1. Polymer model. Linear and ring polymers in solution are described according to the Kremer and Grest [25] polymer model. Excluded volume interactions between beads (including consecutive ones along the contour of the chains) are modelled by the shifted and truncated Lennard-Jones (LJ) potential:

$$U_{LJ}(r) = \begin{cases} 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} + \frac{1}{4} \right] & r \leq r_c, \\ 0 & r > r_c, \end{cases} \quad (1)$$

where $r$ denotes the spatial separation between the bead centres. The cutoff distance $r_c = 2^{1/6}\sigma$ is chosen so that only the repulsive part of the Lennard-Jones is used. The energy scale is set by $\epsilon = k_BT$ and the length scale by $\sigma$, both of which are set to unity in our simulations. Consistent with that, in this work all quantities will be reported in these reduced LJ units.

Nearest-neighbour monomers along the contour of the chains are connected by the finitely extensible nonlinear elastic (FENE) potential, given by:

$$U_{FENE}(r) = \begin{cases} -0.5kR_0^2 \ln(1-(r/R_0)^2) & r \leq R_0, \\ \infty & r > R_0, \end{cases} \quad (2)$$

where $k = 30\epsilon/\sigma^2$ is the spring constant and $R_0 = 1.5\sigma$ is the maximum extension of the elastic FENE bond.

In order to maximise mutual chain interpenetration at a relatively moderate chain length [10] and hence reduce the computational effort, we have introduced an additional bending energy penalty between consecutive triplets of neighbouring beads along the chain in order to control the polymer stiffness:

$$U_{\text{bend}}(\theta) = k_b(1 - \cos \theta). \quad (3)$$

Here, $\theta$ is the angle formed between adjacent bonds and $k_b = 5k_BT$ is the bending constant. With this choice, the polymer is equivalent to a worm-like chain with Kuhn length $l_K$ equal to $10\sigma$ [26].

2.1.2. Model for colloid particles. Colloid-monomer and colloid–colloid interactions are described by the model potentials introduced by Everaers and Ejtehadi [27].

The total interaction energy between colloid particles at centre-to-centre distance $r$ can be represented as the sum of two functions:

$$U_{cc}(r) = \begin{cases} U^{A}_{cc}(r) + U^{R}_{cc}(r) & r \leq r_c, \\ 0 & r > r_c. \end{cases} \quad (4)$$

$U^{A}_{cc}(r)$ is the attractive component and is given by:

$$U^{A}_{cc}(r) = -\frac{A_{cc}}{6} \left( \frac{2a^2}{r^2} - \frac{2a^2}{r^2} + \ln \left( \frac{r^2 - 4a^2}{r^2} \right) \right). \quad (5)$$

The repulsive component of the interaction, $U^{R}_{cc}(r)$, is:

$$U^{R}_{cc}(r) = \frac{A_{cc}}{37800} \frac{\sigma^6}{r^7} \left( \frac{r^2 - 14ar + 54a^2}{(r - 2a)^2} - \frac{r^2 + 14ar + 54a^2}{(r + 2a)^2} - 2 \frac{r^2 - 30a^2}{r^7} \right). \quad (6)$$

In previous formulas, $a = 2.5\sigma$ is the colloid particle radius and the constant $A_{cc} = 39.478 k_BT$ [27]. As we are interested in modelling hard-sphere colloids, the interaction is truncated at its minimum value of $5.595\sigma$.

Finally, the interaction energy, $U_{mc}$, between a single monomer and a colloid particle with centre-to-centre distance $r$ is given by:

$$U_{mc}(r) = \begin{cases} 2a^6/\sigma A_{mc} \left[ 1 - \frac{(5a^6 + 45a^4r^2 + 63a^2r^4 + 15\sigma^6\sigma^6)}{15(a - r)(a + r)^6} \right] & r \leq r_{mc}, \\ 0 & r > r_{mc}. \end{cases} \quad (7)$$

where $A_{mc} = 75.358 k_BT$ [27]. Again, since we model non-sticky particles, the potential is cut off at its minimum, $r_{mc} = 3.363\sigma$.

2.2. Simulation details

Here, we consider polymer solutions consisting of $M = 160$, 80 and 40 circular (ring) or linear chains made of, respectively, $N = 250$, 500 and 1000 beads each. The total number of monomers is then fixed to 40,000 units. Each polymer solution also includes 100 colloid particles of diameter $= 5\sigma$. The volume of the simulation box accessible to chain monomers
has been chosen in order to fix the monomer density $\rho$ to the values $\rho^3 = 0.1, 0.2, 0.3$ and 0.4.

The static and kinetic properties of the chains and colloids are studied using molecular dynamics (MD) computer simulations in the fixed-volume/constant-temperature (NVT) ensemble with implicit solvent and periodic boundary conditions. The MD simulations are performed using the LAMMPS package [28]. The equations of motion are integrated using a velocity Verlet algorithm, in which all the beads are weakly coupled to a Langevin heat bath with a local damping constant $\Gamma = 0.5\tau_{\text{MD}}^{-1}$, where $\tau_{\text{MD}} = \sigma (m/\varepsilon)^{1/2}$ is the Lennard-Jones time and $m = 1$ is the conventional mass unit for the monomer and colloid particles. The integration time step is set to $\Delta t = 0.012\tau_{\text{MD}}$.

2.3. Preparation of initial configurations

Linear polymers—the solutions of linear chains and colloid particles were prepared first at $\rho^3 = 0.1$. Linear chains were arranged as random walks in space and placed at random positions inside the simulation box. Random positions were also chosen for colloid particles. In order to remove possible overlaps between the chain monomers and between those and the colloid particles, a short (of the order of a few $\tau_{\text{MD}}$) MD run with capped, soft (i.e. non-diverging) repulsive interactions between the monomers and between the monomers and the colloids was used.

Ring polymers—this first setup is not suitable for ring polymers, which needs to satisfy the supplementary constraint of avoiding mutual concatenation. Hence, the ring polymers were initially arranged in a very large simulation box, i.e. in very dilute conditions. In order to reach the correct monomer density of $\rho^3 = 0.1$ we then performed a short (about $400\tau_{\text{MD}}$ MD steps) simulation by putting external pressure on the system, which shrinks the simulation box until it reaches the desired value.

For both systems of linear and circular chains, higher densities were obtained by compressing the solutions by means of higher external pressures. Of course, during this preparatory phase the complete set of interaction terms described in section 2.1 was employed.

2.4. Equilibration

Once the system was prepared at the chosen density, we switched to the NVT ensemble. Polymer solutions with chain sizes of $N = 250$, $N = 500$ and $N = 1000$ beads were simulated for run times of $12 \times 10^6\text{MD}$, $24 \times 10^6\text{MD}$ and $48 \times 10^6\text{MD}$, respectively. Unless otherwise stated, the chain properties at equilibrium were always calculated on the last tenth of the corresponding trajectory.

In order to check for system equilibration, we monitored [25] the mean-square displacement of the chain monomers in the absolute frame ($g_2(\tau)$) and in the frame relative to the chain centre of mass ($g_3(\tau)$), and the mean-square displacement of the chain centre of mass ($g_3(\tau)$) at lag-time $\tau$. They are defined, respectively, as:

$$g_2(\tau) = \langle (\vec{r}(t + \tau) - \vec{r}(t))^2 \rangle,$$
$$g_3(\tau) = \langle (\vec{r}(t + \tau) - \vec{r}_m(t) + \vec{r}(t) - \vec{r}_m(t))^2 \rangle,$$
$$g_3(\tau) = \langle (\vec{r}_m(t + \tau) - \vec{r}_m(t))^2 \rangle.$$

where the brackets ‘$\langle \ldots \rangle$’ mean average over the MD trajectory, the further average over monomer position $i$ along the chain is implicitly assumed. After complete chain relaxation, i.e. for long enough simulations, $g_2(\tau) \sim g_3(\tau) \sim \tau$ and $g_3(\tau) \approx 2\langle R^2(N) \rangle$ [25], where $\langle R^2(N) \rangle$ is the chain square gyration radius at equilibrium. As shown in figures S1 and S2 (stacks.iop.org/JPhyCM/28/065101/mmedia), these conditions are met for polymer solutions of chain lengths with $N = 250$ and $N = 500$, while they hold less well for the largest chain size of $N = 1000$, see figure S3 (stacks.iop.org/JPhyCM/28/065101/mmedia). Nonetheless, we decided to include data for $N = 1000$ in our analysis.

3. Results and discussion

Here, we will analyse and discuss our results on the statics and dynamics of entangled polymer chains in solution, and how the entanglements affect the diffusion of large colloid particles. For the sake of notation, in the rest of the paper we will denote by $L = N\sigma$ (respectively, $l = n\sigma$) the total contour length of the chain made by $N$ monomers (respectively, the contour length of a subchain made of $n$ monomers).

We first need to provide a justification for why our polymers can effectively be considered as ‘entangled’. Consistent with previous work [20, 29], we adopt here the formalism by Uchida et al [30] showing that the entanglement length of the polymer solution, $L_e$, can be expressed as a simple function of the polymer Kuhn length, $l_k$, and the solution density, $\rho$: $L_e/l_k = (0.06(\rho l_k^3)^{2/5} + 0.06(\rho l_k^3)^{2})$. With solution densities $\rho^3 = 0.1, 0.2, 0.3, 0.4$ and chain Kuhn length $l_k/\sigma = 10$, the corresponding entanglement lengths are given by $L_e/l_k \approx 4.00, 1.62, 1.10, 0.89$. At the highest density then, our longest chains have a contour length $L/L_e \approx 100$.

3.1. Chain statics

We first computed the mean-square spatial distance $\langle R^2(l) \rangle$ between the monomers located at contour length separation $l$ along the chain. It is interesting to compare the numerical results for linear and ring polymers to, respectively, the exact worm-like chain (WLC) expression [4] for semi-flexible linear polymers with Kuhn length $l_k$:

$$\langle R^2(l) \rangle^{\text{WLC}} = \frac{2l}{l_k} \left( \frac{l}{l_k} + e^{-2l/l_k} - 1 \right).$$

and the approximate formula for ideal semi-flexible rings:
which gives an accurate description provided $L \gg l_k^1$. The numerical results and analytical expressions for $\langle R^2(l) \rangle$ are summarised in figure 1 as symbols and black solid lines, respectively. We note the striking difference between the linear chains and rings: as expected based on the theoretical scenario [3] predicting the screening of the excluded volume interactions, the numerical results for $\langle R^2(l) \rangle$ of linear chains (figure 1, left-hand panels) show little or no dependence on density and agree well with the WLC prediction, equation (9). Conversely, in solutions of ring polymers where screening is absent [9, 10, 12–14, 16, 20] the numerical predictions for $\langle R^2(l) \rangle$ markedly deviate from equation (10) (the right-hand panels in figure 1). In particular, the rings show a tendency to become more and more compact as the density increases. Alternatively [20], the same data can be recast in terms of the so-called overlap parameter $\Omega(l) \equiv \rho \langle R^2(l) \rangle^{3/2} l$, which gives the total number of sub-chains of contour length $l$ contained inside the corresponding occupied volume. The results are shown as insets in figure 1, highlighting the important difference between the chains and rings: in fact, for the latter $\Omega(l)$ tends to plateau on increasing the chain size (i.e. $\langle R^2(l) \rangle \sim l^{3\nu}$ with critical exponent [4] $\nu = 1/3$), the

\[ \langle R^2(l) \rangle^{\text{WLR}} = \left( \frac{1}{\langle R^2(l) \rangle^{\text{WLC}}} + \frac{1}{\langle R^2(L-l) \rangle^{\text{WLC}}} \right)^{-1} \]
value of the plateau slightly increases from \( \approx 12 \) for \( \rho = 0.1 \) to \( \approx 28 \) for \( \rho = 0.4 \).

Next, we considered the full distribution functions \( p(R/l) \) of end-to-end distances \( R = R(l) \) as a function of \( l = 15, 30, 60, 120 \) and density \( \rho \), see figure 2. Both the linear and ring polymers show the expected shift from the non-universal short chain behaviour \( (l = 15) \), where fiber stiffness plays the dominant role to the universal, entropy-governed long chain behaviour. Again, there are important noticeable differences between the linear and ring polymers: for linear
chains, the progressive screening of excluded volume effects [3] on increasing $\rho$ is well exemplified by the fact that $p(R/l)$ super-imposes on the semi-empirical formula of ideal worm-like chains given in [31] (left-hand panels in figure 2, black lines):

$$p(R/l)_{\text{WLC}} = J(l) \left( \frac{1 - c R^2}{1 - R^2} \right)^{5/2} \frac{\sum_{i=0}^{\infty} c_i (\frac{R}{l})^i}{1 - R^2}$$

$$\times e^{-d \frac{R}{l} (1 + b) R^2} I_0 \left( -d \frac{R}{l} a (1 + b) R \right)$$

$$= \frac{1 - c R^2}{1 - R^2} \left( \frac{1}{1 - R^2} \right)^{5/2} \sum_{i=0}^{\infty} c_i (\frac{R}{l})^i$$

$$\times e^{-d \frac{R}{l} (1 + b) R^2} I_0 \left( -d \frac{R}{l} a (1 + b) R \right)$$

with numerical constants $a = 7.027$, $b = 0.473$, and $c_i = \begin{pmatrix} -3/4 & 23/64 & -7/64 \\ -1/2 & 17/16 & -9/16 \end{pmatrix}$. $I_0$ the modified Bessel function of the first kind and

$$1 - c = \left( 1 + \left( \frac{k_e}{l} \right)^{-0.95} \right)^{-5}$$

$$1 - d = \begin{cases} 0, & \frac{k_e}{l} < \frac{1}{4} \\ 1 - \frac{0.354}{k_e l} - 0.222, & \frac{1}{4} \leq \frac{k_e}{l} < 0.95 \\ 28.01 (\frac{k_e}{l})^2 e^{0.492 \frac{k_e}{l} - \frac{k_e}{l}^2} - 15 \frac{k_e}{l}, & \frac{k_e}{l} \geq 0.95 \end{cases}$$

In particular, for large $l$s $p(R/l)$ becomes nearly Gaussian (figure 2, last panel on the left). In striking contrast, the large-$l$
behaviour of $p(R|l)$ for the ring polymers is markedly non-Gaussian. In particular, $p(R|l = 120)$ for well-equilibrated rings with $N = 500$ are well described (solid lines, last panel on the right of figure 2) by the classical Redner-des Cloizeaux (RdC) function [32–35]:

$$p(R|l)^{\text{RdC}} = \frac{1}{(R^2(l))^{3/2}} \left( \frac{R(l)}{\sqrt{(R^2(l))}} \right),$$

$$q(\vec{x}) = C x^\theta \exp(-Kx^t),$$

(13)

where the two constants $C$ and $K$ are determined by the conditions (1) that the distribution is normalised ($\int q(x) 4\pi x^2 \, dx \equiv 1$) and (2) that the second moment was chosen as the scaling length ($\int x^2 q(x) 4\pi x^2 \, dx \equiv 1$): $C = t \frac{1}{3^{\theta/2} \Gamma(\frac{3\theta}{2})}$ and $K^2 = \frac{1}{\Gamma(\frac{3\theta}{2})}$. fit of data with $l = 120$ to the two-parameter RdC function gives the following estimates\(^*\) for $\theta$ and $t$

$$\rho_s^3 = 0.1: \quad \theta = 0.5 \pm 0.1, \quad t = 1.6 \pm 0.1$$

$$\rho_s^3 = 0.2: \quad \theta = 0.4 \pm 0.2, \quad t = 1.5 \pm 0.2$$

$$\rho_s^3 = 0.3: \quad \theta = 0.3 \pm 0.2, \quad t = 1.5 \pm 0.2$$

$$\rho_s^3 = 0.4: \quad \theta = 0.1 \pm 0.2, \quad t = 1.5 \pm 0.2$$

(14)

Interestingly, $t$ appears compatible with $3/2$, a result which is consistent with the Fisher–Pincus [36, 37] relationship $t = 1/(1 - \nu)$ with $\nu = 1/3$. On the other hand, the excluded-volume exponent [33] $\theta$ tends to become small as the density increases, finally suggesting for the asymptotic high-density limit the simple and elegant stretched-exponential form:

$$q(\vec{x}) \sim \exp(-Kx^{3/2})$$

with $K = \sqrt{10/3} \approx 1.667$.

We continue our analysis of chain structure by studying (figure 3) the probability distribution functions $p(\delta r)$ of monomer spatial distances from the chain centre of mass $\delta r \equiv \vec{r} - \vec{r}_m$, whose second moment corresponds to the mean-square gyration radius $\langle R_g^2(L) \rangle$. Again, linear chains and rings have different behaviour. Consistent with the generic result for worm-like chains [38], linear chains deviate from the Gaussian function (black solid lines):

$$p(\delta r)^G = \left( \frac{3}{2\pi \langle R_g^2(L) \rangle} \right)^{3/2} \exp\left(-\frac{3(\delta r)^2}{2\langle R_g^2(L) \rangle}\right),$$

(15)

\(^*\) Final estimates of exponents $\theta$ and $t$ are obtained by averaging the results of two fits to the RdC function, equation (13). In the first fit, we consider the complete set of points for $p(R|l)$, while in the second one we exclude a few points close to $R = 0$. The two procedures give very similar results for $t$ (which describes the large-$R$ behaviour of $P(R|l)$), while estimates for $\theta$ are typically noisier due to large fluctuations of $P(R|l)$ around $R = 0$. The outcomes of the two fits are combined together as (average value) $\pm$ (statistical error) $\pm$ (systematic error), where the ‘statistical error’ is the combination of the two statistical errors from the two fitting procedures while the ‘systematic error’ is the spread between the single estimates, respectively. Final error bars reported in equation (14) are given by $\sqrt{(\text{statistical error})^2 + (\text{systematic error})^2}$. 

and agree well with the exact analytical prediction by Debye and Bueche [38] (black dashed lines):

$$p(\delta r)^{\text{DB}} = \frac{1}{L} \int_0^L \frac{3}{2\pi (\langle \delta r \rangle^2)} \exp\left(-\frac{3(\delta r)^2}{2\langle \delta r \rangle^2}\right).$$

(16)

where $\langle (\delta r)^2 \rangle = 2\langle R_g^2(L) \rangle \left(1 - \frac{1}{2} (1 - \frac{1}{4})\right)$, with $\langle R_g^2(L) \rangle = k_B/L$. Interestingly, the distribution functions for the ring polymers are closer to the Gaussian distribution, although with some noticeable deviations.

We next studied the effects of topological constraints on the average contact frequencies, $\langle \rho(l) \rangle$, between the chain monomers at contour length separation $l$ defined as:

$$\langle \rho(l) \rangle \equiv \int_0^{l_{\text{ev}}} p(R|l) 4\pi R^2 dR \int_0^l p(R|l) 4\pi R^2 dR,$$

(17)

where $r_{\text{ev}}$ is the distance of closest approach due to the intra-monomer excluded volume effects, and $r_c = 2\sigma$ is the chosen contact cutoff distance (figure 4). For both the linear and ring polymers ($\rho(l)$) increases as a function of density, figure 5. For linear chains, this is arguably due to the progressive screening of excluded volume effects. In particular, by using equation (17) with the WLC expression equation (9) the long-$l$ behaviour of $\langle \rho(l) \rangle$ can be well reproduced (solid lines in the left-hand panels of figure 5) by the following values for $r_{\text{ev}}$: $r_{\text{ev}}/\sigma = 1.6, 1.4, 1.2, 1.0$ for, respectively, $\rho = 0.1, 0.2, 0.3, 0.4$. Then, $\langle \rho(l) \rangle \sim l^{-3/2}$ at all densities. Conversely, the observed tendency of $\langle \rho(l) \rangle$ to shift towards higher values is the consequence of the rings becoming more and more compact as the density increases (figure 2, right-hand panels). Furthermore, now the observed scaling law is different, $\langle \rho(l) \rangle \sim l^{-1}$, and in particular

![Figure 4](image-url)
compatible with the predictions of crumpled globules [14, 20, 39]. This analysis is complemented by considering separately the two contributions to the average number of contacts of each monomer of the chain: the first arising from contacts between the monomers inside the same chain, \( \rho_{\text{intra}} \), and the second arising from contacts between the monomers belonging to different chains, \( \rho_{\text{inter}} \). The results are shown in figure 6. As expected, \( \rho_{\text{intra}} \) for linear chains, show almost no variation with solution density or chain length, in agreement with the picture that the chains remain nearly ideal. On the other hand, \( \rho_{\text{intra}} \) for rings increases significantly with the density. This effect cannot be ascribed to local contacts along the chain (otherwise we should have seen a similar effect for linear chains, too), while it can be easily understood in terms of the crumpling of the rings, which constrains distal monomers along the chain to move close in space. The second contribution, \( \rho_{\text{inter}} \), increases in a similar manner for both linear and ring polymers, demonstrating in particular that crumpling does not prevent a single ring from maintaining substantial interactions with its neighbours.

3.2. Chain and colloid dynamics

Chain dynamics can be appropriately characterised by considering the following three quantities [3, 25, 40]: the mean-square displacement of single monomers in the absolute frame \( \langle \chi^2 \rangle \) and in the frame of the chain centre of mass \( \langle \rho^2 \rangle \), and the mean-square displacement of the chain centre of mass \( \langle \delta^2 \rangle \) at lag-time \( \tau \) (equation (8) for definitions), see

![Figure 5. Average-square contact frequencies \( \langle \rho \rangle \) between monomers at contour length separation, \( l \). The solid lines in the left-hand panels correspond to the numerical integration of equation (17) with \( \rho(R/l) \) given by the semi-empirical WLC formula, equation (11).](image-url)
figures S1–S3 (stacks.iop.org/JPhyCM/28/065101/mmedia).
In the long-time limit, \( g_1(\tau) \sim g_3(\tau) \sim \tau \) and \( g_2(\tau) \sim 2\langle R_2^2(L) \rangle \) [25], where \( \langle R_2^2(L) \rangle \) is the mean-square gyration radius of the chains. We notice that, for all the cases considered the ring polymers relax faster than the linear ones. Particularly striking is the example of \( g_2(\tau) \) for \( N = 1000 \) linear chains at \( \rho \sigma^3 = 0.1 \).
Nahali and A Rosa showing that the present simulations are still too short to guarantee the complete relaxation of the linear chains, but long enough to equilibrate their circular counterparts. These results are in agreement with the theoretical arguments by Rubinstein and coworkers [7] related to the different ways entanglements affect the relaxation of linear chains and rings. Linear chains obey the classical mechanism of ‘reptation’ [3, 41]: hindered by topological constraints they reduce to sliding past each others in a ‘snake-like’ fashion, the total relaxation time being \( \sim L^3 \). Pointing out on the analogy between entangled ring polymers and branched trees, Rubinstein and coworkers suggested [7] that ring polymers relax instead owing to the mass flowing along the ring contour length, a mechanism leading to the faster relaxation time \( \sim L^{2.5} \).

We now discuss the micro-rheological properties of polymer solutions by studying the diffusive motion of hard-sphere colloid particles [42, 43] of diameter \( d = 5\sigma \). This size was specifically chosen because, being at the crossover between the solution mesh size of \( \approx 8\sigma \) for \( \rho\sigma^3 = 0.1 \) and \( \approx 4\sigma \) for \( \rho\sigma^3 = 0.4 \), it ought to be relevant to characterise how the entanglements affect the local viscosity of the solutions of linear and ring polymers. Figure 7 shows our final results for the mean-square displacement \( \langle \delta r^2(\tau) \rangle \equiv \langle (\bar{r}(t + \tau) - \bar{r}(t))^2 \rangle \) of colloid position \( \bar{r}(t) \) at lag-time \( \tau \). At the lowest density, the colloid diffusion does not depend on the chain topology. Conversely, as the highest density is attained the colloids diffuse manifestly faster in the solution of ring polymers. In either cases, \( \langle \delta r^2(\tau) \rangle \sim \tau \) at long-times. We then characterise this density-dependent long-time regime by defining the corresponding diffusion coefficients \( D_{\infty}(\rho) \equiv \lim_{\tau \to \infty} \langle \delta r^2(\tau) \rangle / 6\tau \).

\footnote{The mesh size of the solution is taken of the order of the tube diameter [3] \( \sim \sqrt{(R_e^2 L_s)} = \sqrt{R_e L_s} / \delta \), where \( L_s \) is the entanglement length of the solution (see the discussion in section 3).}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.png}
\caption{Mean-square displacement, \( \langle \delta r^2(\tau) \rangle \), of the dispersed colloid particles of diameter \( d = 5\sigma \).}
\end{figure}
and viscosities $\eta_\infty$ as given by the classical Stokes–Einstein relationship [3] $\eta_\infty = \frac{kT}{6\pi\eta Id + \sigma d^2}$. The values for $D_\infty(\rho)$ obtained by the best fits of the data and the corresponding $\eta_\infty(\rho)$ (which are $N$-independent!) are reported in table 1. We thus see that solutions of ring polymers are up to $\approx 3$ times less viscous than their corresponding linear counterparts.

4. Conclusion

In this article, we have presented the results of molecular dynamics computer simulations for the characterisation of the statics and dynamics of semi-flexible linear and ring polymers in semi-dilute solutions. Chains of different sizes and at different solution densities were considered.

In agreement with the well-known picture invoking the screening [3] of excluded volume effects, we confirm that linear chains behave as quasi-ideal at all the considered densities (figure 1, left). Conversely (figure 1, right), ring polymers in the same physical conditions tend to become increasingly more compact. These results prompted us to consider the full chain statistics given by the distribution function $p(R|l)$ of spatial distances between the ends of a subchain of linear size $l$ (figure 2): at high densities the screening effects in linear chains extend down to small scales and $p(R|l)$ is well described by the worm-like chain statistics. In particular, at large $l$s the chain statistics is almost Gaussian. On the other hand, chain compaction in rings induces deviations from the ideal statistics at all $l$s. Interestingly, by describing the large-$l$ behaviour of $p(R|l)$ by the classical Redner-des Cloizeaux [32, 33] statistics we suggest that $p(R|l)$ ought to obey the universal stretched exponential form $\sim \exp \left[-1.667 \left(\frac{R|l}{R(l)}\right)^{3/2}\right]$ which satisfies the Fisher–Pincus relationship [36, 37]. We formalised the description of chain statistics by measuring the frequencies of monomer–monomer interactions inside the same chain (figure 5) and between different chains (figure 6). In particular, we explain the observed increase in contact frequencies with the solution density (at fixed chain length $l$) by taking into account the progressive screening of the excluded volume effects (for linear polymers) and chain compaction (for ring polymers).

Finally, we investigated chain relaxation at equilibrium (figures S1–S3), confirming the general tendency [7, 40] of rings to relax faster than linear chains of the same size. At the same time, we provide previously unreported evidence that dispersed colloid particles of linear size exceeding the nominal mesh size of the solution show a tendency to diffuse more rapidly in ring polymer solutions than in linear polymers ones. Intriguingly, it was recently pointed out [18, 29] that the experimentally observed chromosome organisation in eukaryotes should resemble a solution of ring polymers.

The reader may notice that the effective cross-diameter of the colloid particle is given by the sum of its nominal diameter $d$ and the monomer diameter $\sigma$. Moreover, due to pure repulsion between colloid particles and monomer particles the traditional [3] geometric factor $3\pi r^2$ valid for sticky boundary conditions is substituted by the more correct $2\pi r^2$ valid for slip boundary conditions [45] which apply here.

In this respect, then, enzymes and other functional macromolecular complexes which need to run and bind to specific target sequences along the genome might have greatly benefited from the enhanced mobility stemming from the peculiar organisation of the genome [44].

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