

Dynamics of Nanoparticles in Solutions of Semiflexible Ring Polymers

Published as part of *The Journal of Physical Chemistry B* special issue “Athanasios Z. Panagiotopoulos Festschrift”.

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Cite This: *J. Phys. Chem. B* 2024, 128, 12586–12596



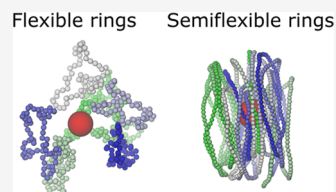
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ABSTRACT: We use hybrid molecular dynamics–multiparticle collision dynamics (MD–MPCD) simulations to investigate the influence of chain stiffness on the transport of nanoparticles (NPs) through solutions of semiflexible ring polymers. The NPs exhibit subdiffusive dynamics on short time scales before transitioning to normal diffusion at longer times. The terminal NP diffusivity decreases with increasing ring stiffness, similar to the behavior observed in solutions of semiflexible linear chains. The NP subdiffusive exponent is found to be strongly correlated with that of the polymer center of mass (COM) for the range of chain stiffnesses examined, which is at odds with the pronounced decoupling of the NP and polymer COM motions previously observed upon increasing the stiffness of linear chains. Our analysis indicates that these marked differences in the intermediate dynamics are rooted in distinct structural changes that emerge with increasing bending stiffness: Stiffer ring polymers adopt increasingly circular conformations and stack into transient tubes. The void space created near the ring centers is occupied by NPs and other polymers, resulting in strong dynamic coupling on short time scales.



1. INTRODUCTION

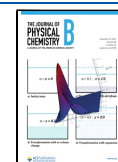
The transport of nanoparticles (NPs) through polymer solutions is encountered in applications ranging from hydrocarbon exploration¹ to drug delivery^{2–7} to nanocomposite processing.^{8–13} Transport through Newtonian fluids is well described by the Stokes–Einstein relation (SER), which predicts that the NP diffusivity is inversely proportional to the zero-shear solution viscosity. The SER can be generalized to complex fluids by incorporating a frequency-dependent solution viscosity.^{14,15} Both the SER and the generalized SER, however, assume that the transported NPs are larger than the characteristic length scales associated with heterogeneities in the background fluid. In complex fluids, this assumption breaks down when the NP size is comparable to the polymer radius of gyration or mesh size, resulting in measured dynamics that are faster than predicted from the solution’s zero-shear viscosity.^{16–21}

The factors governing NP transport in this size regime have been investigated in several computational^{22–29} and theoretical^{30–35} studies. Although most of these studies have focused on flexible linear chains, polymers found in many settings often have other architectures and different degrees of flexibility. Circular or ring-like architectures, for example, are commonly used to model chromatin^{36–39} and are observed to form in semiflexible biopolymers such as DNA.^{40–42} Ring polymers exhibit distinct structural and dynamical properties due to their

closed conformations.^{36,37,41–50} Examples include the faster relaxation of ring polymers compared to linear chains of the same molecular weight⁴⁴ due to the absence of free ends, which allows ring polymers to avoid or delay entanglements.⁵¹ Additionally, inter-ring threadings, or penetrations, can also lead to a topological glass transition in concentrated solutions and melts, which has not been reported to occur for linear chains.⁵²

The distinct properties of ring polymers and their effects on NP transport remain incompletely understood. Simulation studies have investigated NP transport in entangled ring polymer systems,^{39,53} finding faster NP motions in melts of ring polymers than in similar systems of linear chains due to the absence of long-lived entanglement tubes in the former. The effects of chain flexibility on the NP dynamics have also been compared in polymer melts with linear and circular architectures. NP dynamics were found to be faster in melts of stiff linear chains compared to rings with the same stiffness, but the opposite behavior was observed for flexible systems.⁵⁴

Received: August 22, 2024
Revised: November 11, 2024
Accepted: November 25, 2024
Published: December 6, 2024



Langevin dynamics (LD) simulations have also been performed to investigate the influence of NP size on transport in weakly entangled solutions of ring and linear polymers.⁵⁵ NPs were found to diffuse faster in solutions of ring polymers than in solutions of linear polymers when the NP size was larger than the tube diameter. For smaller NPs, however, the diffusivities were found to be comparable in ring and linear polymer solutions, which was posited to be due to the similarity of the Rouse dynamics on these length scales.⁵⁵ Finally, increasing the concentration of NPs in ring polymer melts was found to lead to a slowing of the dynamics of the ring polymers; further, the dynamics decreased sharply at high NP concentrations as more monomers come into contact with multiple NPs.⁵⁶

These prior studies provide insight into how polymer architecture and stiffness influence NP dynamics in concentrated or entangled systems. However, much less is known about their effects on NP transport in unentangled (semi)-dilute solutions, which is the characteristic of many biological systems.^{57–59} At such concentrations, long-range hydrodynamic interactions (HI) may also influence the dynamics, necessitating careful modeling of these effects.^{60–62} In our recent studies, we used a hybrid molecular dynamics–multiparticle collision dynamics (MD–MPCD) scheme to perform hydrodynamic simulations of NP transport in unentangled, semidilute solutions of polymers.^{26–28,63} NP dynamics were found to be remarkably insensitive to the polymer architecture when compared in solutions of flexible linear chains and rings with similar monomer concentrations.²⁸ For both systems, the scaling behavior of the long-time NP diffusivity was well described by a recently developed polymer coupling theory (PCT),³⁰ which assumes that NP motions fully couple to the segmental Rouse dynamics of the polymers. The short-time subdiffusive NP dynamics, by contrast, were found to be faster than predicted by PCT. This finding was attributed to the NPs coupling to polymer center-of-mass (COM) motions on short time scales, which is an additional coupling mechanism that is not accounted for by PCT.²⁸

Although the architecture of flexible polymers was not found to strongly influence NP dynamics, our previous MD–MPCD study of semiflexible linear chains demonstrated that polymer stiffness has an appreciable effect.²⁷ As chain stiffness was increased, the long-time NP diffusivity exhibited increasing deviations from PCT, which was developed for fully flexible chains. The short-term subdiffusive NP dynamics also became increasingly decorrelated with the polymer COM motions. These effects were hypothesized to arise from changes in the segmental mobility as the stiffness of the chains increased.

To understand the combined effects of ring-shaped polymer topology and bending stiffness, we performed a complementary study of NP dynamics in solutions of semiflexible ring polymers using MD–MPCD simulations. Similar to the behavior observed for semiflexible linear chains, the NP diffusivity decreases as the polymer stiffness increases. In contrast with the behavior observed for semiflexible linear chains, however, the NP and polymer COM subdiffusive dynamics remain strongly correlated across the range of chain stiffnesses examined. Our analysis indicates that structural changes in the ring polymer solutions allow the NP and polymer COM subdiffusive motions to remain highly coupled, even as the segmental motions change upon stiffening.

2. METHODS

Hybrid MD–MPCD^{62,64,65} simulations of spherical NPs in solutions of semiflexible ring polymers were performed using LAMMPS (ver. 22Aug18).⁶⁶ For simplicity, we describe the model parameters of the system using fundamental units σ , m , and ϵ for length, mass, and energy, respectively. The corresponding unit of time is expressed in these fundamental units as $\tau = \sqrt{m\sigma^2/\epsilon}$. All of the model parameters and physical quantities derived from the simulations are reported in these units.

The model is similar to the one used in our prior study of NP dynamics in solutions of flexible ring polymers.²⁸ The ring polymers consist of N_m monomer beads, each with a diameter of σ_m , whereas the NPs are modeled as single large beads with a diameter of σ_{NP} . Excluded volume interactions between particles are modeled with a shifted Weeks–Chandler–Andersen (sWCA)⁶⁷ potential:

$$U_{\text{sWCA}}(r_{ij}) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma_{ij}}{r_{ij} - \Delta_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij} - \Delta_{ij}} \right)^6 \right] + \epsilon, & r_{ij} \leq r_{ij}^c \\ 0, & r_{ij} > r_{ij}^c \end{cases} \quad (1)$$

where r_{ij} is the distance between particles i and j , Δ_{ij} is the shift parameter that accounts for size differences between particles of different types, and $r_{ij}^c = 2^{1/6}\sigma_{ij} + \Delta_{ij}$ is the cutoff distance. For monomer–monomer and NP–NP interactions, $\{\sigma_{ij}, \Delta_{ij}\} = \{\sigma_m, 0\}$ and $\{\sigma_{ij}, \Delta_{ij}\} = \{\sigma_{NP}, 0\}$, respectively. For NP–monomer interactions, $\sigma_{ij} = \sigma_m$ and $\Delta_{ij} = (\sigma_{NP} - \sigma_m)/2$.

Bonds between neighboring monomers are modeled using the finitely extensible nonlinear elastic (FENE) potential:⁶⁸

$$U_{\text{FENE}}(r_{ij}) = \begin{cases} -\frac{1}{2}kr_0^2 \ln \left[1 - \left(\frac{r_{ij}}{r_0} \right)^2 \right], & r_{ij} < r_0 \\ \infty, & r_{ij} \geq r_0 \end{cases} \quad (2)$$

where $k = 30$ and $r_0 = 1.5$ are the spring constant and maximum bond extension length, respectively. The equilibrium bond length with these parameters is $b \approx 0.97$. The stiffness of rings is controlled by incorporating the bending potential,

$$U_{\text{bend}}(\Theta_{ijk}) = \kappa(1 - \cos \Theta_{ijk}) \quad (3)$$

where Θ_{ijk} is the angle between the bond vectors connecting adjacent monomers $\{i, j\}$ and $\{j, k\}$ and κ is the stiffness parameter.

We examined systems with $N_m = 70$, $\sigma_m = 1$, and $\sigma_{NP} = 5$. These choices ensure that $\sigma_{NP} \approx R_{g,0}$ for highly flexible rings ($\kappa \leq 2$), where $R_{g,0}$ is the radius of gyration at infinite dilution (Table 1). To study the influence of ring flexibility, we varied the stiffness parameter, $\kappa = 0–70$. The NP–polymer solutions were simulated in a cubic cell with an edge length of $L = 64$, and periodic boundary conditions were applied in all directions. The number of ring polymers N_p in the simulation cell was varied from 93 to 1497, yielding solutions with monomer concentrations $c = N_m N_p L^{-3}$ ranging from 0.025 to 0.4 (Table 1). This range of monomer concentrations is well below the typical value $c \approx 0.9$ found in the melts of similar polymer models^{36,37,39,53} and thus corresponds to solution-like

Table 1. Properties of Semiflexible Ring Polymer Solutions

κ	$R_{g,0}$	c_{\min}	c_{\max}
0	4.4	0.025 (0.13 c^*)	0.40 (2.07 c^*)
1.5	5.0	0.025 (0.19 c^*)	0.40 (2.97 c^*)
5	6.8	0.025 (0.46 c^*)	0.40 (7.39 c^*)
10	8.5	0.025 (0.91 c^*)	0.30 (10.95 c^*)
20	9.7	0.025 (1.37 c^*)	0.15 (8.22 c^*)
32	10.1	0.025 (1.56 c^*)	0.10 (6.22 c^*)
70	10.5	0.025 (1.74 c^*)	0.10 (6.95 c^*)

Notes: c_{\min} and c_{\max} are the minimum and maximum monomer concentrations investigated in this study, and $c^* = 3N_p(4\pi R_{g,0}^3)^{-1}$ is the overlap concentration.

conditions. At sufficiently high bending stiffness κ , ring polymers can exhibit transitions from isotropic to (discotic) nematic or smectic phases, depending on, for example, the concentration and ring stiffness.⁶⁹ Since we are primarily interested in the transport properties in the isotropic phase, we restrict the maximum monomer concentration (at each investigated κ value) to stay below this phase transition (Table 1). To model dilute NP conditions, only 20 NPs were simulated in each ring polymer solution, corresponding to an NP volume fraction of approximately 0.005. Using cluster analysis, we confirmed that these conditions are sufficiently dilute to minimize NP–NP interactions and to avoid NP aggregation.

All simulations were performed at a reduced temperature of $T = 1.0$, using a velocity-Verlet scheme with a time step of 0.005 to integrate the equations of motion. The systems were first equilibrated for $\approx 10^6$ time units using Langevin thermostats with LAMMPS “damp” parameters of 3.0 and 0.9 for the NPs and monomers, respectively. This duration is approximately 10 times longer than the relaxation time of the system at the highest κ and c examined, which exhibits the most sluggish dynamics. Next, the systems were simulated using a hybrid MD–MPCD technique to incorporate solvent-mediated HI.^{26–28,62} The MPCD parameters and implementation are identical to those employed in our previous studies^{26–28} and result in a coarse-grained solvent with dynamic viscosity $\eta_s \approx 4.0$ and Schmidt number $Sc \approx 12$. The NP–polymer solutions were briefly equilibrated for $\approx 5 \times 10^4$ time units with the MD–MPCD scheme to allow the MPCD solvent to thermalize and then simulated for a production period of $\approx 2 \times 10^6$ time units, during which data are collected to compute ensemble averages. Three independent simulations were performed to generate a total of 60 NP trajectories for each set of conditions examined. Static and dynamic properties were calculated by averaging over independent simulations. Complementary LD simulations were also performed for select systems using the Langevin thermostats described above to investigate the behavior of the solutions in the absence of many-body HI.

Following our previous study of NP transport in solutions of flexible rings,²⁸ the polymer mesh size ξ was computed using the geometric pore size distribution defined in ref 70. In this method, ξ is calculated as the spatial average of the local pore size $h(\mathbf{r})$, which is defined as the diameter of the largest spherical test probe that can be placed in the polymer system such that it encompasses point \mathbf{r} without overlapping the surrounding monomers (points within a distance of 0.5 of a monomer center were considered overlapping). $h(\mathbf{r})$ was evaluated via the nonlinear optimization approach described in

refs 71,72. The resulting ξ provides an unambiguous geometric definition of mesh size that is consistent with intuition for regular polymer networks⁷² and is universally applicable regardless of network topology, monomer concentration, or polymer architecture.²⁸

3. RESULTS AND DISCUSSIONS

To investigate the dynamics of the NP–polymer solutions, we calculated the mean-squared displacement (MSD) $\langle \Delta r^2 \rangle$ for the monomers in the polymer COM reference frame, for the polymer COM, and for the NPs as a function of stiffness parameter κ . At short times ($\Delta t < 10^3$), the segmental dynamics of the fully flexible rings ($\kappa = 0$) are hydrodynamically coupled and exhibit $\langle \Delta r^2 \rangle \sim t^{2/3}$ scaling behavior, as predicted by the Zimm model (Figure 1a).⁷³ Although this scaling behavior is observed for all κ , the magnitude of $\langle \Delta r^2 \rangle$ at a given lag time Δt within this intermediate regime decreases

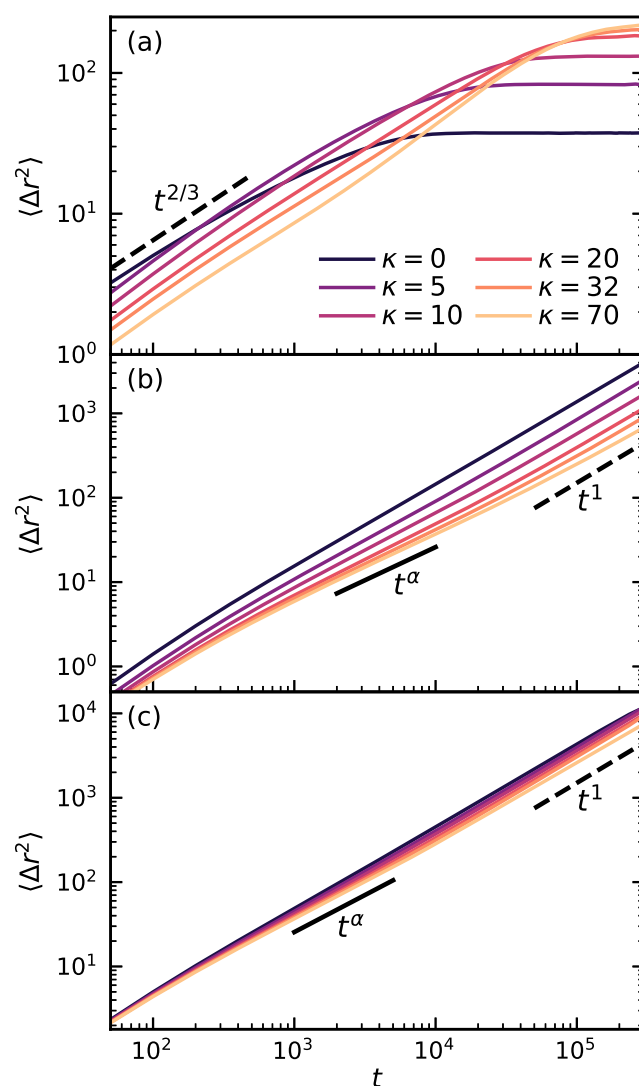


Figure 1. Mean-squared displacements $\langle \Delta r^2 \rangle$ for (a) monomers in the polymer COM reference frame, (b) polymer COM, and (c) NPs in ring polymer solutions with monomer concentration $c = 0.05$ and different values of the stiffness parameter κ . Dashed line in (a) indicates Zimm ($\sim t^{2/3}$) scaling. Solid and dashed lines in (b) and (c) indicate subdiffusive ($\sim t^\alpha$, $\alpha < 1$) and diffusive ($\sim t^1$) scaling, respectively.

as stiffness increases, indicating a decrease in segmental mobility. This behavior is in agreement with that observed in previous studies of semiflexible linear polymers in solution.^{27,74,75} On long times ($\Delta t > 10^4$), the MSD exhibits a terminal plateau $\langle \Delta r^2 \rangle \approx 2R_{g,0}^2$ that arises from the constraints imposed on the monomer motions by their connectivity (Figure 1a). The height of the terminal plateau increases with κ , consistent with stiffer rings exhibiting more expanded conformations and larger $R_{g,0}$ values (Table 1).

The polymer COM and NP dynamics are also influenced by the ring stiffness. The MSDs for the polymer COM and NPs exhibit subdiffusive behavior on short time scales in which $\langle \Delta r^2 \rangle \sim t^\alpha$ with exponent $\alpha < 1$ but crossover to diffusive dynamics ($\alpha = 1$) on longer time scales. The magnitudes of the MSDs decrease across all time scales with increasing κ , mirroring the slowing of the segmental dynamics. This behavior is consistent with recent simulations of semiflexible ring melts, where a dramatic increase in the zero-shear viscosity was found with increasing bending stiffness κ .⁷⁶ Due to the increase in ring size (i.e., R_g) with κ , the dynamical slowing is more pronounced for the polymer COM than for the NPs, as expected from the SER. These trends are similar to those reported for NPs in solutions of semiflexible linear chains.²⁷

3.1. Short-Time Dynamics. To characterize the effects of ring stiffness on the short-time dynamics, we extracted the subdiffusive exponents α_{NP} and α_p for the NPs and polymer COM from their respective MSDs (Figure 2). We restrict our range of c and κ to stay in the isotropic phase.⁶⁹ The values of α_{NP} and α_p can depend on the range of Δt selected for the analysis. Thus, to avoid ambiguity, we follow ref 39 and report the minimum values of α_{NP} and α_p attained in the subdiffusive regime. At a low monomer concentration (e.g., $c = 0.025$), α_{NP} gradually decreases with increasing ring stiffness. As the

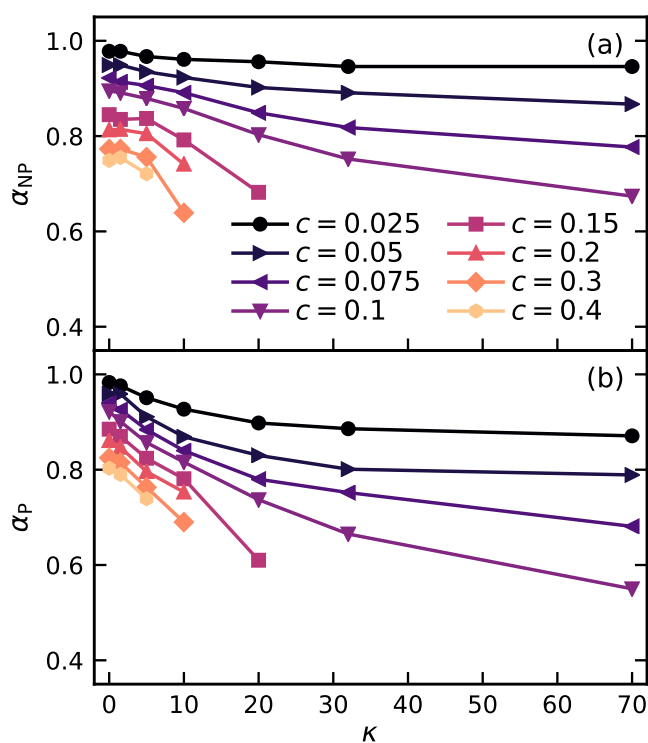


Figure 2. Subdiffusive exponents of (a) NPs (α_{NP}) and (b) polymer COM (α_p) as functions of stiffness parameter κ for different values of the monomer concentration c .

monomer concentration increases, however, the rate of decrease becomes significantly more pronounced. Although subdiffusion can arise from a variety of physical mechanisms including transient caging in glassy colloidal suspensions,^{77–80} it is most commonly attributed to a coupling of probe dynamics to viscoelastic relaxations in polymer solutions.^{20,30} These relaxations arise from a combination of segmental fluctuations and COM translation of the polymer.²⁶ Thus, the decrease in α_{NP} with increasing κ and c values indicates an enhancement in the strength of the dynamic coupling between particle and polymer dynamics. Indeed, the subdiffusive exponent of the polymer COM α_p exhibits qualitative behavior similar to that of α_{NP} (Figure 2b). A similar decay of α_p with increasing bending stiffness was also observed in previous simulations of pure solutions of semiflexible chains in the semidilute regime.⁷⁵

According to PCT,³⁰ the dynamics of the NPs depend on the ratio of the NP diameter to polymer mesh size σ_{NP}/ξ . When the NPs are smaller than the mesh size ($\sigma_{NP}/\xi < 1$), their short-time motions are not constrained by the surrounding polymers. As a result, NPs are freely diffusive on all time scales, so the exponent is $\alpha_{NP} = 1$. By contrast, when the NPs are larger than the mesh size ($\sigma_{NP}/\xi > 1$), they become caged by nearby polymer segments and fully coupled to their relaxations. On length scales larger than ξ , (semi)-flexible polymers in semidilute solutions can be regarded as Rouse chains of correlation blobs; the MSD of the polymer segments scales as $\langle \Delta r^2 \rangle \sim t^{1/2}$ at time scales below the Rouse relaxation time,^{73,74} leading to an expectation of $\alpha_{NP} = 0.5$.³⁰ This prediction has been confirmed experimentally for systems in which the NP–polymer dynamics are fully coupled by chemically bonding the NPs to the polymer network.⁸¹ Previous simulations also showed that the NP dynamics are purely diffusive in solutions of free (unpolymerized) monomers at similar values of c .²⁸ These studies confirm that the NP subdiffusive dynamics, as predicted by PCT, arise from coupling with polymer segmental relaxations with $\alpha_{NP} = 0.5$ in the limit of full coupling.

For the (semi)flexible ring polymer solutions, however, the short-time NP dynamics deviate from the PCT predictions (Figure 3). Rather than abruptly dropping from 1.0 to 0.5 at $\sigma_{NP}/\xi \approx 1$, as predicted by PCT, α_{NP} gradually decreases as σ_{NP}/ξ increases. Similar deviations from PCT have been reported in experiments on NPs in solutions of linear polymers.²⁰ They have also been observed in our previous computational work on systems with (semi)flexible linear chains^{26,27} and flexible ring polymers.²⁸ In those previous studies, the faster-than-expected subdiffusive NP dynamics suggested the presence of an additional mode of NP–polymer coupling that is not accounted for in PCT. Indeed, the strong correlation observed between the subdiffusive exponents α_{NP} and α_p indicated that the translational COM motions of the NPs and polymers were coupled on short time scales. Thus, these studies suggest that the NP subdiffusive dynamics in solutions of (semi)flexible linear chains and flexible rings are coupled to both the polymer segmental relaxations and their COM motions, whereas only the former coupling mode is described by PCT.

Interestingly, for the semiflexible ring polymer solutions studied here, we observe that α_{NP} and α_p are strongly correlated for all values of κ examined (Figure 4). Results from complementary LD simulations reveal these correlations are observed even when HI are neglected (Figure 4). This

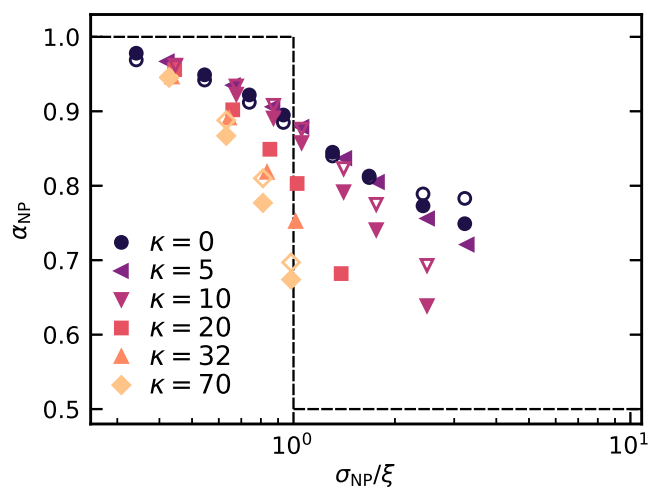


Figure 3. Subdiffusive exponents of NPs α_{NP} as a function of the ratio of the NP diameter to polymer mesh size σ_{NP}/ξ . Dashed line indicates the prediction from PCT.³⁰ Closed and open symbols indicate data from hybrid MD–MPCD simulations (with HI) and LD simulations (without HI), respectively.

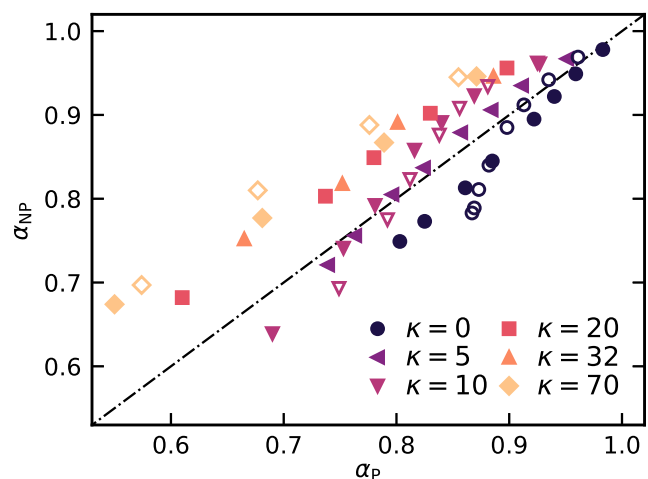


Figure 4. Correlation of NP and polymer COM subdiffusive exponents (α_{NP} and α_{p} , respectively) for different values of stiffness parameter κ . Dashed-dotted line indicates $\alpha_{\text{NP}} = \alpha_{\text{p}}$. Closed and open symbols indicate data from hybrid MD–MPCD simulations (with HI) and LD simulations (without HI), respectively.

behavior indicates that the COM motions of the NPs and ring polymers remain coupled even as the rings expand and their segmental dynamics slow as chain stiffness is increased. This finding is in sharp contrast with the behavior observed in our analogous study of semiflexible *linear* chains, where it was found that α_{NP} and α_{p} became increasingly decoupled as κ was increased.²⁷ The decoupling for the linear chains was attributed to them becoming more rod-shaped, leading to increasingly anisotropic polymer COM motions that alter the way the NPs and polymers dynamically couple on short time scales. The nature of the NP–ring correlations, however, depends on stiffness, with the NPs being more subdiffusive than polymers at low κ but less subdiffusive at high κ . As discussed below, we attribute this dependence to contributions from structural changes in the polymer solutions.

3.2. Long-Time Dynamics. On longer time scales, both NPs and polymer COMs crossover to diffusive motion with diffusivities (D and D_{p} , respectively) that decrease monotonically

with increasing κ and c (Figure 5). These trends match those observed for the subdiffusive exponents (Figure 2),

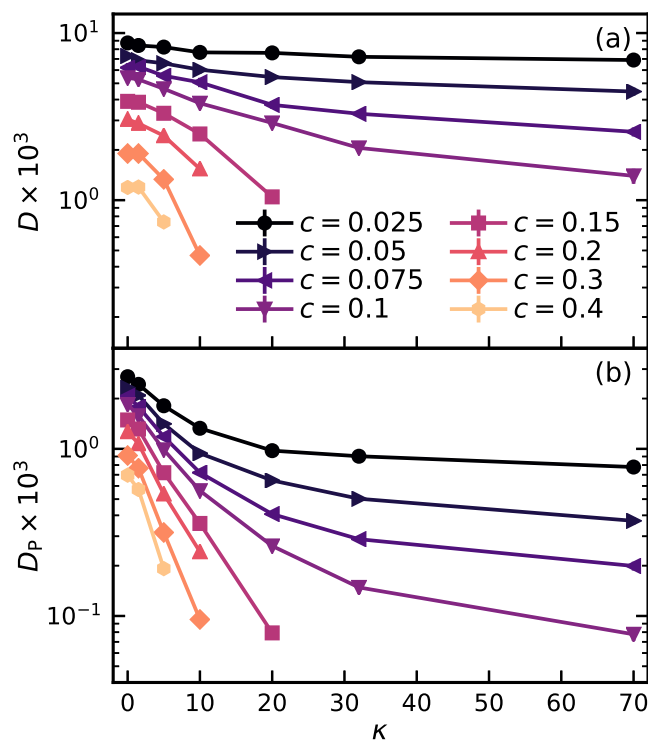


Figure 5. Diffusion coefficients of (a) NPs (D) and (b) polymer COM (D_{p}) as functions of stiffness parameter κ for various monomer concentrations c .

indicating that the slowing of the segmental dynamics and changes in ring conformations upon increasing bending stiffness (see Section 3.3) affect both the short- and long-time translational dynamics of the NPs and polymer COM. Indeed, PCT assumes that the polymer segments surrounding the NPs present an infinite energy barrier to diffusion and that the segments must relax before the NPs can escape their local cages. Specifically, PCT asserts that the segments must relax over length scales comparable to the NP diameter, resulting in the scaling prediction $D/D_0 \sim (\sigma_{\text{NP}}/\xi)^\gamma$ with exponent $\gamma = -2$ for $\sigma_{\text{NP}}/\xi \geq 1$, where D_0 is the NP diffusivity in the background solvent.

The PCT scaling predicting for D/D_0 has been confirmed in experimental²⁰ and computational studies²⁶ of NP diffusion in solutions of flexible linear chains; it has also been found to be approximately consistent with results from simulations of flexible ring polymers.²⁸ We observe that D/D_0 decreases with σ_{NP}/ξ for $\sigma_{\text{NP}}/\xi \geq 1$ (Figure 6). Although this decreasing trend is generally consistent with PCT, it is not possible to determine whether the decay follows power-law behavior with the predicted scaling exponent of $\gamma = -2$ due to the limited range of σ_{NP}/ξ accessible for these systems. The decrease in NP diffusivity starts at a smaller σ_{NP}/ξ with increasing κ , indicating that the NPs more readily experience local heterogeneities for stiffer rings. As κ increases, the segmental dynamics become slow, and the time scale for the polymer segments to relax over the NP surfaces increases. Hence, we posit that this slowing results in a sharper decrease in D/D_0 as the mesh size decreases, and the NPs become more confined by the surrounding polymers. Langevin dynamics simulations

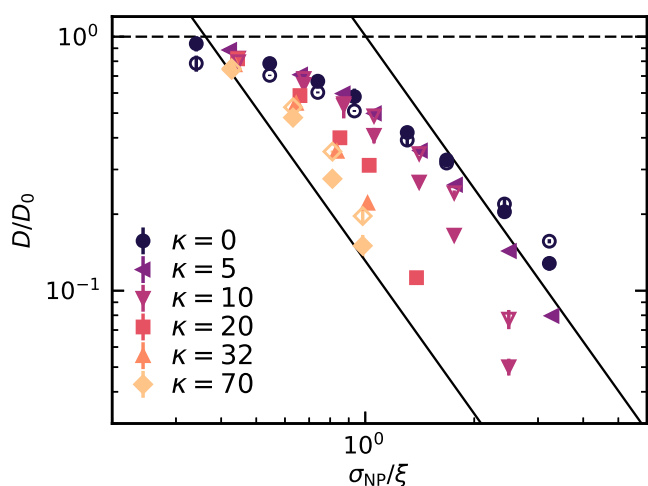


Figure 6. Normalized diffusivity of NPs D/D_0 as a function of the ratio of NP size and polymer mesh size σ_{NP}/ξ . The solid lines denote the $D/D_0 \sim (\sigma_{\text{NP}}/\xi)^{-2}$ scaling behavior predicted by PCT.³⁰ Closed and open symbols indicate data from hybrid MD–MPCD simulations (with HI) and LD simulations (without HI), respectively.

show that these qualitative trends are largely insensitive to the inclusion of many-body HI, which is consistent with our previous computational study of NPs in solutions of flexible linear chains.²⁶ Lastly, we observe that the terminal NP and polymer COM diffusivities are approximately linearly correlated for all of the κ examined (Figure 7). The linear

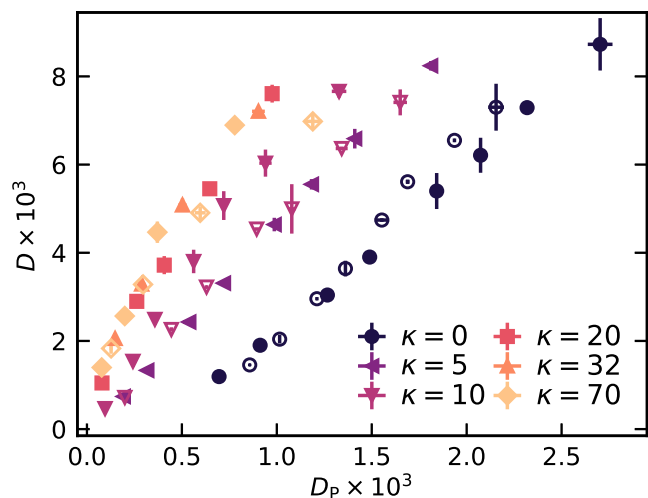


Figure 7. Correlation of terminal NP and polymer COM diffusivities (D and D_p , respectively) for different values of stiffness parameter κ . Closed and open symbols indicate data from hybrid MD–MPCD simulations (with HI) and LD simulations (without HI), respectively.

correlation is consistent with the terminal NP and polymer COM motions being strongly coupled to the bulk solution viscosity. In the limit of full coupling, the SER would predict that $D/D_p \sim R_g/\sigma_{\text{NP}}$. Accordingly, we find that the slope of D versus D_p increases as κ increases due to the concomitant increase in ring size (i.e., increase in R_g).

3.3. Structural Effects. The observed changes in NP dynamics over short and long time scales indicate a unique coupling to local heterogeneities in solutions of stiff rings. We therefore characterized the structural properties of the solutions to understand their potential influence on the NP

and polymer dynamics. To this end, we first analyzed the shape of the individual polymers by computing the gyration tensor

$$G_{\alpha\beta} = \frac{1}{N_m} \sum_i (\Delta r_{i,\alpha} \Delta r_{i,\beta}) \quad (4)$$

where $\Delta r_{i,\alpha}$ is the position of monomer i relative to the polymer COM and α and β denote components along the Cartesian x , y , and z directions. Several descriptors can be calculated from the gyration tensor, including the radius of gyration

$$R_g = (\lambda_1 + \lambda_2 + \lambda_3)^{1/2} \quad (5)$$

where $\lambda_1 > \lambda_2 > \lambda_3$ are the eigenvalues of the gyration tensor. The polymer shape can be characterized via the asphericity,

$$a = \frac{(\lambda_1 - \lambda_2)^2 + (\lambda_2 - \lambda_3)^2 + (\lambda_3 - \lambda_1)^2}{2(\lambda_1 + \lambda_2 + \lambda_3)^2} \quad (6)$$

which has limiting values of 0 and 1 for perfectly spherical ($\lambda_1 = \lambda_2 = \lambda_3$) and one-dimensional objects ($\lambda_2 = \lambda_3 = 0$), respectively. For a three-dimensional random walk with $N_m \rightarrow \infty$, numerical calculations have found $a = 0.039$.⁸² For polymers with $a > 0$, the nature of their asphericity can further be characterized using the prolateness,

$$p = \frac{(2\lambda_1 - \lambda_2 - \lambda_3)(2\lambda_2 - \lambda_3 - \lambda_1)(2\lambda_3 - \lambda_1 - \lambda_2)}{2(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - \lambda_1\lambda_2 - \lambda_2\lambda_3 - \lambda_3\lambda_1)^{3/2}} \quad (7)$$

which has limiting values of 1 and -1 for perfectly prolate (rod-like) and oblate (disk-like) objects, respectively.

The shape descriptors R_g , a , and p exhibit weak variations with the monomer concentration c (Figure 8). Specifically, the R_g of rings with $\kappa \leq 5$ decreases by about 15% as the concentration increases from $c = 0.025$ to $c = 0.4$. This behavior aligns with the expected transition from good solvent conditions in dilute solutions to theta-like conditions above the overlap concentration (Table 1).^{83,84} This effect becomes much weaker with increasing κ , however, because the conformations of stiff rings are primarily dictated by the intramolecular bending energy and packing entropy.^{85–88} The radius of gyration R_g increases monotonically with κ , exhibiting an initial sharp rise over the range $0 \leq \kappa \leq 10$ followed by a much smaller growth for $\kappa \gtrsim 20$. The expansion of the rings is accompanied by nonmonotonic changes in the shape descriptors a and p , which both initially increase and then decrease for $\kappa \geq 10$. The sign of p changes from positive to negative at $\kappa \approx 20$, indicating that rings transition from prolate to oblate-like objects as κ increases. Although the probability density distributions for R_g and a exhibit well-defined maxima for all κ , $P(p)$ becomes almost flat at $\kappa = 20$ (Figure 9). This behavior reveals that fluctuations in p are maximized near $\kappa = 20$ and that the mean value of $p \approx 0$ results from averaging over the nearly uniform $P(p)$ distribution at this critical value of the stiffness parameter.

The changes in the ring structure with κ also affect the structural correlations between the NP–polymer and polymer–polymer COM, as measured by the respective radial distribution functions (RDFs) $g_{\text{NP-p}}(r)$ and $g_{\text{p-p}}(r)$ (Figure 10). The RDFs for the solutions with fully flexible rings ($\kappa = 0$) are approximately zero for $r \leq 5$ and exhibit single maxima in the range of $r \approx 8–10 \approx 2R_g$ before decaying toward unity at larger r . The compact and isotropic nature of the flexible rings

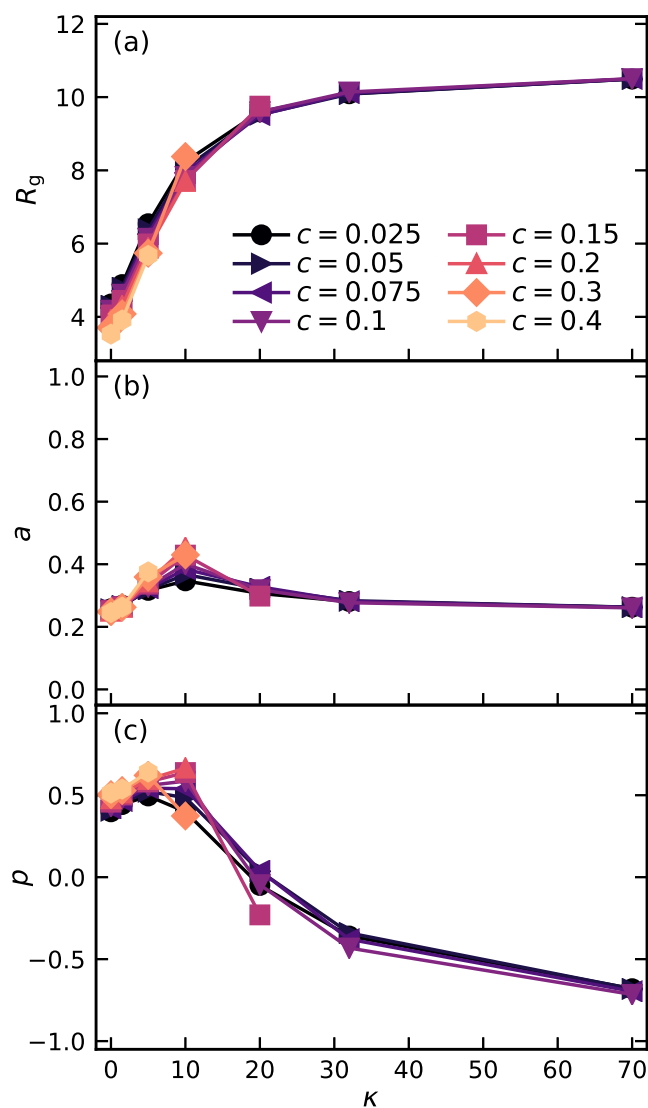


Figure 8. (a) Radius of gyration R_g , (b) asphericity a , and (c) prolateness p of the ring polymers as a function of stiffness parameter κ for different monomer concentrations c .

results in effective short-ranged excluded volume interactions between the NP–polymer and polymer–polymer COM, which prevent them from coming into close proximity and lead to the formation of well-defined neighbor contact peaks in $g_{\text{NP-P}}(r)$ and $g_{\text{P-P}}(r)$ at intermediate $r \approx \sigma_{\text{NP}} + R_g$ and $r \approx 2R_g$, respectively. The RDF $g_{\text{NP-P}}(r)$ for semiflexible rings with $\kappa = 10$, by contrast, is nearly flat except for a slight upturn near $r = 0$. This behavior suggests that the effective excluded volume interaction between the NP and polymer COM vanishes, allowing a small fraction of the NPs to penetrate the center of the rings, such that the positions of their COM coincide. A similar interpenetration or “threading” of the rings explains the increase in $g_{\text{P-P}}(r)$ at $r = 0$.^{85–88} Interestingly, $g_{\text{NP-P}}$ and $g_{\text{P-P}}(r)$ both flatten at $\kappa = 10$, where the distributions of the ring shape descriptors R_g , a , and p are also relatively broad (Figure 9). This behavior suggests that large fluctuations in ring shape allow interpenetration to occur, reducing excluded volume effects such that the NP–polymer and polymer–polymer interactions become nearly ideal under these conditions.

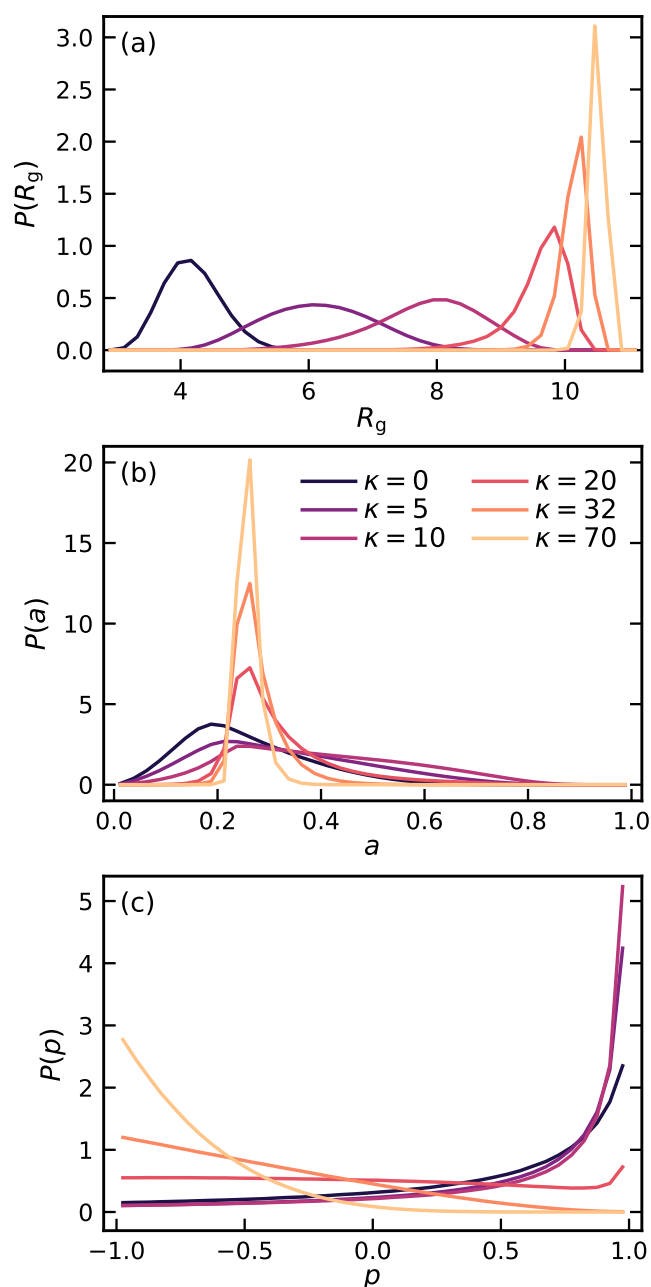


Figure 9. Probability density distributions of the (a) radius of gyration R_g , (b) asphericity a , and (c) prolateness p of the ring polymers at monomer concentration $c = 0.1$ for different values of the stiffness parameter κ .

As κ increases further, the rings continue to expand and become increasingly oblate. These conformational changes coincide with $g_{\text{NP-P}}(r)$ increasing in magnitude at low r and developing a strong peak at $r = 0$. Similar trends are observed in $g_{\text{P-P}}(r)$ along with the formation of a second peak at $r \approx 3$. Inspection of configurations from the simulations confirms that the peaks at $r = 0$ signify an increased propensity for NPs and polymers to occupy the “holes” created in the centers of the rings as they stiffen and expand (Figures 10b and 11). They also reveal that the second peak observed in $g_{\text{P-P}}(r)$ at $r \approx 3$ arises from the local ordering of neighboring rings into stacked arrangements (Figure 10b).^{76,85,87}

We posit that the ring conformational changes observed upon varying κ directly influence the caging of the NPs.

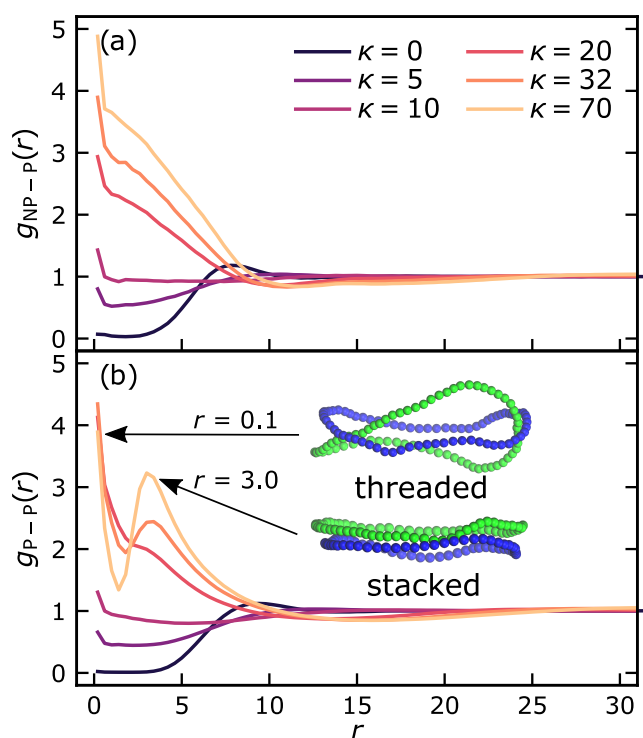


Figure 10. Radial distribution functions for (a) NP–polymer COM and (b) polymer–polymer COM at monomer concentration $c = 0.1$ for different values of the stiffness parameter κ . The inset in (b) shows the threaded and stacked ring arrangements observed for $\kappa = 70$ at $r \approx 0.1$ and $r \approx 3.0$, respectively.

Specifically, the compact conformations of flexible rings have characteristic dimensions similar to those of the NPs, allowing the rings to behave as soft crowders that transiently cage the NPs. Consequently, the short-time NP dynamics are coupled to the ring segmental relaxations and translational COM motions. As κ increases, the polymers expand and the segmental relaxations become slow. In the case of semiflexible linear chains, chain stiffening causes the polymer COM motions to become increasingly anisotropic and decoupled from the NP dynamics. For semiflexible rings, by contrast, the short-time NP and polymer COM dynamics remain strongly coupled due to transient caging of the NPs inside the “holes” near the ring centers, as they adopt more expanded conformations. Thus, although the NPs experience distinct local environments when caged by flexible rings with compact conformations or within semiflexible rings with expanded conformations, both types of cages lead to strong coupling of the NP and polymer COM dynamics on short time scales. As a result, the coupling of NP and polymer subdiffusive dynamics is observed across the full range of κ examined.

4. CONCLUSIONS

We used hybrid MD–MPCD simulations to investigate the diffusion of NPs in solutions of ring polymers with tunable stiffness. The NPs exhibit subdiffusive dynamics on short time scales before transitioning to normal diffusion at longer times. The NP diffusivity decreases as the ratio of the NP diameter to polymer mesh size, σ_{NP}/ξ , becomes sufficiently large. Although this decreasing trend is generally consistent with PCT, it is not possible to determine whether the decay follows the predicted power-law behavior due to the limited range of σ_{NP}/ξ

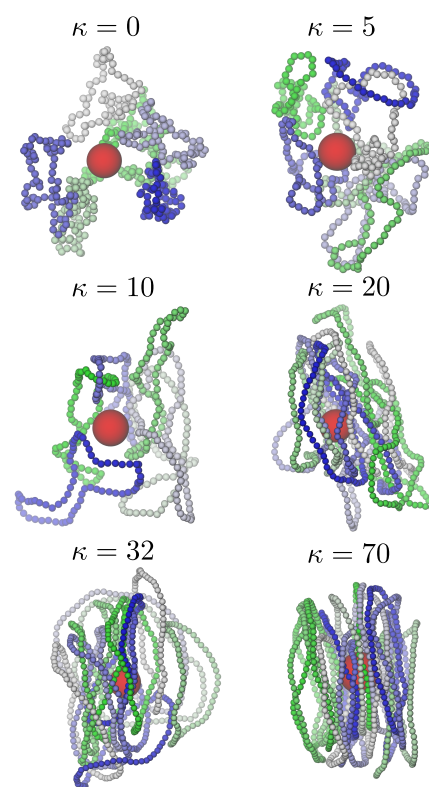


Figure 11. Ring polymers (chains of small spheres) around a central NP (large red sphere) at monomer concentration $c = 0.1$ for different values of the stiffness parameter κ . Only rings whose COM are within a separation distance of $r = 10$ from that of the central NP are shown. Snapshots are rendered using Visual Molecular Dynamics 1.9.3.⁸⁹

accessible for these systems. The NP subdiffusive exponent in solutions of flexible rings is larger than that predicted by PCT and strongly correlated with that of the polymer COM. These findings mirror those reported for NPs in solutions of flexible linear chains,²⁶ which exhibit similar dynamics to solutions of flexible ring polymers when compared at the same monomer concentration.²⁸ The faster-than-predicted subdiffusive dynamics in both cases arise from coupling between the NP and polymer COM motions on short time scales, which is not accounted for by PCT.

As the rings become stiffer, the terminal NP diffusivity decreases. The short-time dynamics of the NPs also become slower, as evidenced by the decrease in their subdiffusive exponent. These trends are reminiscent of those reported for solutions of semiflexible linear chains and are attributed to the reduced segmental mobility of stiff polymers.²⁷ Interestingly, the NP and ring polymer COM subdiffusive exponents remain strongly correlated for all of the examined semiflexible ring polymer solutions. This behavior is at odds with the pronounced decoupling of the NP and polymer COM motions previously observed upon increasing the stiffness of linear chains.²⁷ Our analysis indicates that stiffer ring polymers adopt increasingly circular conformations, accompanied by distinct stacking into transient tubes. The void space created near the ring centers is occupied by NPs and other polymers, resulting in strong coupling on short time scales between the dynamics of NPs and those of the polymer centers of mass. These insights identify the unique transport properties of NPs in semidilute solutions of ring polymers and serve as a starting model by which to predict transport in (bio)macromolecule

suspensions^{36–42} and, in future work, uncover the microstructural origins of the coupling across broad ranges of particle and polymer size.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Welch Foundation (Grants E-1882, E-1869, and the Welch Center for Advanced Bioactive Materials Crystallization, Award V-E-0001), the National Science Foundation (CBET-2004652, CBET-1803728, and CBET-2223084), the ACS Petroleum Research Fund (65826-DNI9), and the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation, Project No. 470113688). Computational resources were provided by the Hewlett-Packard Enterprise Data Science Institute at the University of Houston and the Texas Advanced Computing Center at the University of Texas at Austin.

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