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SIMULATING NANOPARTICLE AND POLYMER DYNAMICS IN SOLUTION

A Dissertation

Presented to

the Faculty of the Department of Chemical and Biomolecular Engineering

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

in Chemical Engineering

by

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Abstract

The dynamics of nanoparticles in complex fluids are of great interest for applications in drug delivery, oil recovery, and materials processing. Particle mobility is well described by the generalized Stokes-Einstein (GSE) relation when the nanoparticles are much larger than the polymers. Violations of GSE predictions are observed, however, when the size of nanoparticles is comparable to or smaller than length scales in polymer solutions. We investigate the microscopic origin of this anomalous behaviour using multi-particle collision dynamics (MPCD), an advanced algorithm for rigorously modelling solvent-mediated hydrodynamic interactions in coarse-grained, mesoscale simulations. We apply MPCD to study transport in nanoparticle-polymer systems and the effects of many-body hydrodynamic interactions on this behaviour. We demonstrate that the translational center-of-mass motions of both nanoparticles and polymers are sub-diffusive on short times before transitioning into a diffusive regime on longer time scales. In solutions of flexible, linear polymer chains, the long-time diffusivities of nanoparticles collapse according to scaling predictions, in accord with recent experiments. The sub-diffusive behavior predicted by MPCD simulations, by contrast, agrees with experiments, but significantly deviates from theoretical predictions. We show that this disagreement is due to a hitherto unreported transport mechanism characterized by the tight coupling of the translational motions of the nanoparticle and polymer centers-of-masses, which is not accounted for in current theories. We explore the consequences of this new coupling mechanism and perform extensive MPCD studies to investigate how it is influenced by hydrodynamic interactions and polymer concentration, stiffness, and morphology.

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Chapter 1: Introduction

Nanoparticles suspended in complex fluids have attracted significant interest due to a variety of applications in science and industry, such as nanocomposite materials, drug delivery, and oil recovery. Incorporation of nanoparticles into polymer matrices produces nanocomposites with exceptional functional properties.^{1–3} Nanoparticles also serve as drug delivery vehicles, providing controlled release of therapeutic agents.^{4–7} Polymer-coated nanoparticles are usually superior to bare nanoparticles when acting as surfactants in enhanced oil recovery processes due to their improved solubility and stability.⁸ In many of these situations, nanoparticles are transported through a complex fluid to reach an intended target or to achieve a desired dispersity. Understanding nanoparticle mobility and dispersion in polymer matrices is therefore of fundamental importance for developing rational strategies for designing nanoparticle-polymer systems to achieved improved performance in such applications.

Considerable theoretical and experimental efforts have been devoted to studying nanocomposite systems. Although experimental methods have provided significant insight into the behavior of nanoparticles and polymers in solutions and melts, existing techniques cannot probe physical mechanisms that dictate short-time and length-scale coupling between dynamics of particles and polymers in solution due to their limited spatiotemporal resolution. Modern mesoscale simulation methods are powerful modeling techniques that enable the structure and dynamics of soft matter systems to be probed simultaneously. These methods are widely used to study polymers and colloids because they can comfortably probe effective length ($\sim 10^{-1} - 10^4$ nm) and time scales ($\sim 10^{-9} - 10^0$ s) that complement those accessible with experiment. These methods provide the spatiotemporal resolution necessary to quantify

structure and dynamics of multiple components in solution and hence resolve complex coupling behavior. Consequently, we have used molecular simulation techniques to investigate the diffusion of nanoparticles in semidilute polymer solutions. Specifically, we employ a mesoscale simulation technique called multi-particle collision dynamics (MPCD),^{9–12} which provides an accurate description of the solvent-mediated hydrodynamic interactions that are assumed to strongly influence polymer dynamics in the semidilute regime. Whereas the MPCD method is used to treat particle-solvent interactions, standard molecular dynamics (MD) algorithms are employed to propagate the motions of the nanoparticles and polymers. We briefly describe these algorithms below along with relevant theoretical background information needed to understand polymer dynamics in solution.

1.1 Background

1.1.1 Polymer dynamics: Rouse and Zimm model

The main features of polymer dynamics come from the long-chain connectivity. The first model that successfully captured polymer dynamics was developed by Rouse.¹³ The Rouse model describes a polymer as a linear chain of N monomer beads connected by spring-like bonds. Assuming that the solvent is freely draining and that the viscous drag force experienced by each monomer bead is independent, the total friction felt by a Rouse chain with N beads is given by

$$\zeta_{\text{R}} = N\zeta, \quad (1.1)$$

where ζ is the friction coefficient for a single monomer bead.

Inserting this expression into the Einstein relation¹⁴ yields the diffusivity of a single Rouse chain,

$$D_{\text{R}} = \frac{k_{\text{B}}T}{\zeta_{\text{R}}} = \frac{k_{\text{B}}T}{N\zeta}, \quad (1.2)$$

where k_B is Boltzmann's constant and T is temperature.

The Rouse time is defined as the characteristic time in which a Rouse chain moves a distance comparable to its size R and is given by

$$\tau_R \approx \frac{R^2}{D_R} \approx \frac{\zeta}{k_B T} N R^2. \quad (1.3)$$

Similarly, using the Einstein relation, one can define a characteristic time scale for bead motion, or Kuhn relaxation time, as

$$\tau_0 \approx \frac{\zeta b^2}{k_B T}, \quad (1.4)$$

where b is the mean-square root of the size of the springs connecting adjacent beads in the Rouse chain.

On intermediate times t between the Kuhn relaxation time τ_0 and the Rouse time τ_R , the mean-square monomer displacement scales as

$$\langle [\mathbf{r}_j(t) - \mathbf{r}_j(0)]^2 \rangle \approx b^2 \left(\frac{t}{\tau_0} \right)^{1/2}, \quad \tau_0 < t < \tau_R. \quad (1.5)$$

In dilute environments, however, the viscous resistance experienced by each bead is not independent. The motion of each bead perturbs the surrounding solvent, which in turn influences the effective drag experienced by other beads. These solvent-mediated hydrodynamic interactions are approximately captured by the Zimm model,¹⁵ which treats the polymer chain as a solid moving object of size R that drags solvent within its pervaded volume. The friction on the polymer chain is thus given by

$$\zeta_Z \approx \eta_s R, \quad (1.6)$$

where η_s is the solvent viscosity. The diffusion coefficient of a Zimm chain is then

$$D_Z = \frac{k_B T}{\zeta_Z} \approx \frac{k_B T}{\eta_s R}. \quad (1.7)$$

Analogously to the Rouse relaxation time, the Zimm relaxation time is defined by

$$\tau_Z \approx \frac{R^2}{D_Z} \approx \frac{\eta_s}{k_B T} R^3. \quad (1.8)$$

Finally, on intermediate times between the Kuhn relaxation time τ_0 and the Zimm time τ_Z , the mean-square monomer displacement is predicted to scale as¹⁶

$$\langle [\mathbf{r}_j(t) - \mathbf{r}_j(0)]^2 \rangle \approx b^2 \left(\frac{t}{\tau_0} \right)^{2/3}, \quad \tau_0 < t < \tau_Z. \quad (1.9)$$

1.1.2 Nanoparticle dynamics in polymer solutions

Semidilute polymer solutions are non-Newtonian fluids that are commonly used as ideal models for complex heterogeneous materials. They are well-suited for fundamental studies because the characteristic length scales associated with their structural heterogeneities, such as the polymer radius of gyration R_g , which is a measure of the size of the polymer coil, and the correlation length ξ , a measure of separation between polymer chains, are well-defined and easily tuned by changing the polymer molecular weight and concentration.¹⁶

Nanoparticle transport is best understood in the limit of a large particle diffusing through a continuous medium. In this limit, the diffusion coefficient of a Brownian particle is described by Einstein's theory,

$$D_0 = \frac{k_B T}{\zeta} = \frac{k_B T}{z\pi\eta_0\sigma_{\text{NP}}}, \quad (1.10)$$

where σ_{NP} is the nanoparticle's diameter, η_0 is the zero-shear viscosity of the back-

ground solvent, $k_B T$ is the thermal energy scale, and $z = 2$ or 3 for slip or no-slip boundary conditions at the particle surface, respectively.

Upon addition of polymer, the medium becomes viscoelastic. This relationship can be extended for complex fluids by incorporating a complex (frequency-dependent) solution viscosity $\tilde{\eta}$ according to the generalized Stokes-Einstein relation (GSER).^{17,18} GSER assumes that the suspended particle is large enough that any heterogeneity of the fluid is negligible over the particle surface.

However, when the polymer radius of gyration R_g exceeds the nanoparticle diameter, local heterogeneity can no longer be ignored and particles transport faster than expected. In this case, SER fails to capture the particle dynamics and significantly underestimates the diffusion coefficients,^{19–26} indicating that complex viscosity $\tilde{\eta}$ alone is insufficient to predict the motion of particles in heterogeneous polymer solutions.

In addition to the relative size, nanoparticle mobility is also affected by the concentration of polymer in solutions. When the solution is sufficiently dilute, the nanoparticles do not experience any inhomogeneities arising from interactions with the polymer and the background solvent can be considered uniform. When the concentration exceeds the overlap concentration c^* (the concentration at which polymer coils start to overlap), a large particle cannot transport through the medium without interacting with the polymer barriers. The overlap concentration is given by²⁷

$$c^* = \frac{M}{\frac{4}{3}\pi R_g^3 N_A}, \quad (1.11)$$

where M is the molecular weight of the polymer and N_A is Avogadro's number.

Early theories attempting to describe the diffusion of nanoparticles through polymer meshes use obstruction models,^{28,29} hydrodynamic models,^{30–33} and free volume³⁴ approaches. Obstruction theories treat the polymers as barriers through

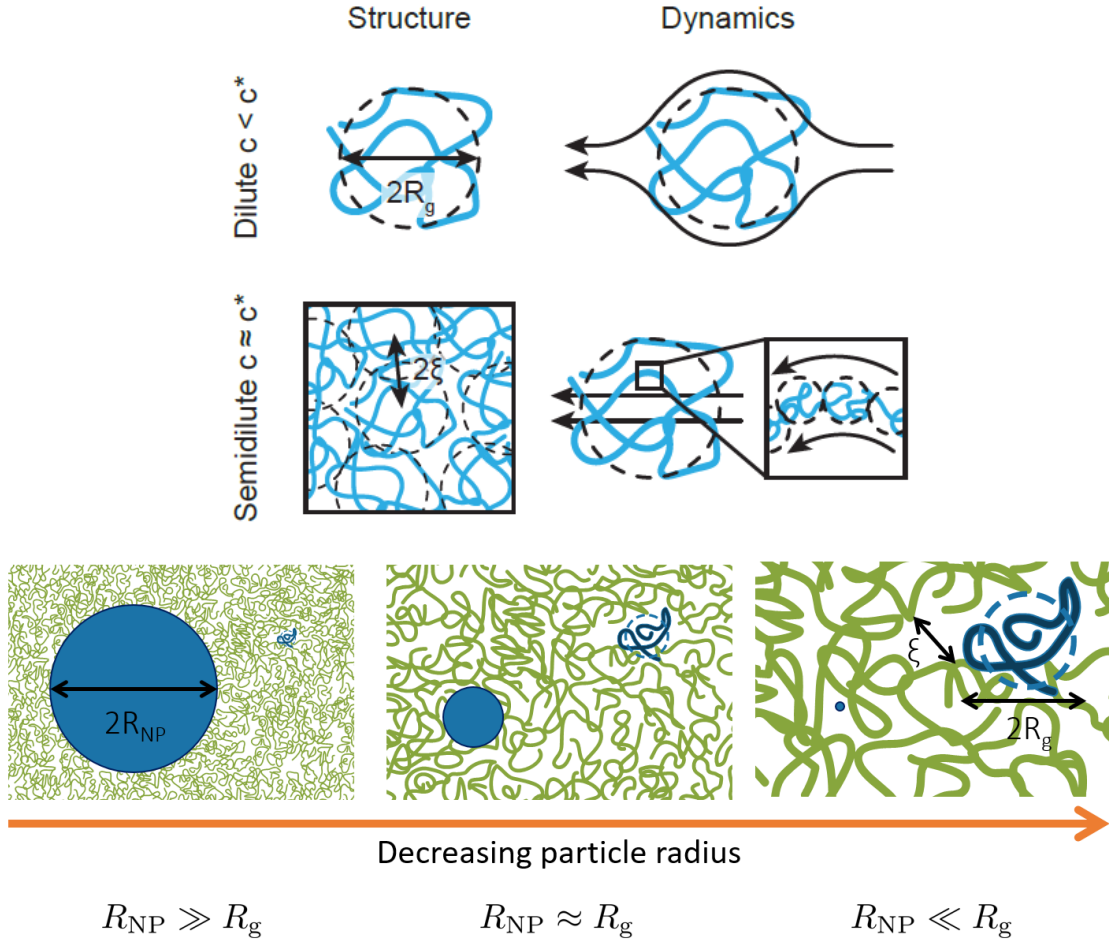


Figure 1.1: A schematic diagram of characteristic size scales of nanoparticles and polymer solutions adapted from Ref. 27 with permission.

which the particles must transport, and the motion of particles is continuous and stochastic. The hydrodynamic models treat the polymers as a porous network that impedes solvent motion via hydrodynamic interactions.²⁸ The hydrodynamic interactions become increasingly screened as the concentration of polymers is increased. Finally, the free volume approach assumes that the diffusivity of particles is controlled by rearrangement of volume not occupied by the polymers, which creates “holes” for particles to pass through. These models are largely empirical.

More recent theories, by contrast, attempt to connect particle diffusivity to microscopic physical phenomena. Mode-coupling theory (MCT)^{35,36} describes nanoparti-

cle diffusion as a combination of contributions from binary collision, solvent density mode, and the solvent transverse mode. Self-consistent Langevin equations³⁷ have been used to relate the fluctuations in the polymer matrix to the particle dynamics.

These theories largely focus on terminal diffusion of nanoparticles and do not account for the relaxation of polymer chains. More recently, Cai, Panyukov, and Rubinstein³⁸ argued that it is the polymer dynamics that control the dynamics of nanoparticles. This theory assumes that the nanoparticles are fully coupled to the polymer segmental relaxations, and that the energy barrier presented by the polymers is infinite. Particle dynamics are then predicted to exhibit subdiffusive dynamics on short time scales and diffusive dynamics on long time scales. Furthermore, the subdiffusive exponent of the nanoparticle α_{NP} is predicted to exhibit a step-like decay from 1 to 0.5 (according to Rouse relaxation) when particle size exceeds the correlation length ξ . This fully coupling theory also suggests that the terminal diffusivity of nanoparticles should be controlled by the relaxation of polymer matrix, and scales as a power-law function with size ratio as

$$D/D_0 \sim (D_{\text{NP}}/\xi)^{-2}, \quad (1.12)$$

where D_0 represents diffusion in solvent (absent of polymers). This prediction deviates from the previous models, which describe the long-time diffusivity as an exponential scaling with concentration.

1.2 Simulation methodology

1.2.1 Molecular dynamics (MD)

Molecular dynamics (MD) is a computational technique for simulating the motions of model particle systems that allows for calculation of both equilibrium and non-equilibrium properties.³⁹ The main idea behind MD is that we numerically solve Newton’s equations of motion for the particle system to follow its time evolution. Af-

ter the system reaches equilibrium, we collect statistics to estimate thermodynamic (e.g., energies), structural (e.g., particle-particle distribution functions), and dynamical (e.g., diffusion coefficients) properties of the system.⁴⁰ The system's relaxation towards equilibrium can also be monitored to investigate non-equilibrium behavior.

To build a model system, we put N particles into a simulation box, and assign each particle a random initial momentum. Interactions among particles are described using a classical force field that can, in general, capture both bonded and non-bonded terms. Although one-body and many-body terms can be modeled, pair-wise interactions are usually sufficient for modeling the simple nanoparticle-polymer systems described herein. In the case of pair-wise interactions, the potential energy of the system is calculated via

$$U(\mathbf{r}^N) = \sum_j \sum_{j>i} u(r_{ij}), \quad (1.13)$$

where $\mathbf{r}^N$ is a $3N$ -dimensional vector specifying the Cartesian coordinates of the particles, $u(r_{ij})$ is the inter-particle pair potential, and r_{ij} is the separation distance between particles i and j . One of the simplest models for non-bonded pair interactions is the commonly used Lennard-Jones

$$u^{\text{LJ}}(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], \quad (1.14)$$

where σ is the particle diameter and ϵ is the interaction well depth. The simplest bonded interaction, which is commonly used for modeling freely-jointed polymer chains, is the harmonic potential

$$u^{\text{bond}}(r_{ij}) = \kappa(r_{ij} - r_0)^2, \quad (1.15)$$

where κ is the spring constant and r_0 is the equilibrium bond distance.

Newton's equations of motion are solved to obtain the time evolution of the particles in the system. Solving the equations of motion requires evaluating the net force acting on each particle via

$$\mathbf{F}_i = m_i \frac{d^2 \mathbf{r}_i(t)}{dt^2} = - \frac{\partial}{\partial \mathbf{r}_i} U, \quad (1.16)$$

where $\mathbf{r}_i(t) = (x_i(t), y_i(t), z_i(t))$ is the coordinate vector for particle i at time t , $\mathbf{F}_i$ is the net force acting on the particle, and m_i is the particle's mass. The resulting set of second-order differential equations for the N -particle system is solved using a finite difference scheme. In the widely-used leapfrog integration scheme, for instance, the equations for updating position and velocity are

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t)\Delta t + \frac{1}{2} \frac{\mathbf{F}_i}{m_i} \Delta t^2 \quad (1.17)$$

and

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + \frac{1}{2} \left(\frac{\mathbf{F}_i(t)}{m_i} + \frac{\mathbf{F}_i(t + \Delta t)}{m_i} \right) \Delta t, \quad (1.18)$$

which allow the position and momentum of each particle at time $t + \Delta t$ to be obtained from those at time t .

Periodic boundary conditions (Fig. 1.2) are commonly used in simulation to mimic an infinite domain and thus minimize spurious surface effects that would otherwise arise from modeling small systems. These boundary conditions are equivalent to having identical replicas of the system surrounding the main simulation cell. In this paradigm, when a particle moves out of the main cell, for example, it is replaced by an equivalent particle from a periodic image. In practice, however, the replicas are not modeled explicitly, and the position vector of the exiting particle is simply wrapped back into the main cell at the appropriate location. Because the artificial periodicity imposed by periodic boundary conditions can introduce spurious long-range corre-

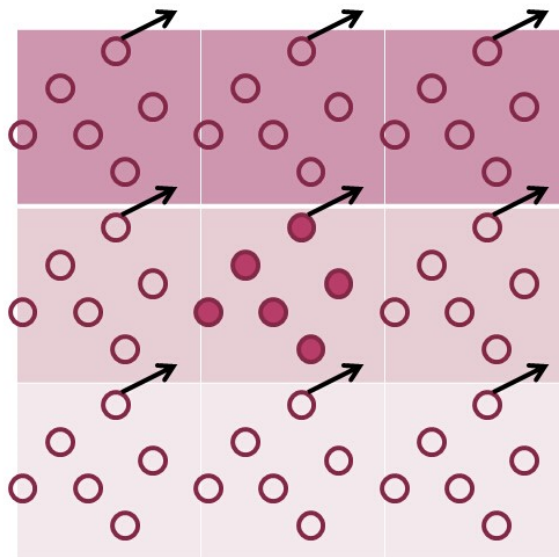


Figure 1.2: A unit cell and its periodic images.

lations, special care must be taken in computing certain physical properties (e.g., diffusivities) and in treating long-range interactions (e.g., Coulomb forces).

1.2.2 Multiparticle collision dynamics (MPCD)

Computer simulation can in principle provide the spatiotemporal resolution necessary to investigate coupling between nanoparticle and polymer dynamics in solution. Modeling a dilute dispersion of neutrally buoyant 10 nm particles at 10% volume fraction in water with rigorous methods such as molecular dynamics, however, requires simulating $\sim 10^8$ water molecules per particle, far beyond current computational capabilities. One approach to address this issue is to use a simplified solvent model to reduce the computational cost of the simulations. This strategy underpins the multi-particle collision dynamics (MPCD)^{9–12} method. The MPCD method, also known as stochastic rotation dynamics (SRD), is a simulation technique in which the background solvent is modeled as a collection of ideal-gas-like point particles. Although the solvent particles do not interact through pair-wise forces, they are allowed to exchange momentum periodically to ensure that the correct hydrodynamic behavior naturally appears on large length scales in the system.¹⁰

Figure 1.3 illustrates basic aspects of the MPCD algorithm. The positions and velocities of the solvent particles are propagated in time through streaming and collision steps.^{10,41} In the streaming step, the motions of solvent particles are propagated over a time interval Δt using Newton's equations,

$$\mathbf{r}_i(r + \Delta t) = \mathbf{r}_i(t) + \Delta t \mathbf{v}_i(t). \quad (1.19)$$

The collision steps can be handled using a number of different schemes. In the original SRD scheme, for example, the particles are first sorted into cubic cells. The velocities of particles are then rotated (with respect to the center-of-mass velocity of the assigned collision cell, $\mathbf{v}_{cm}$) around a randomly chosen axis by a fixed angle α ,

$$\mathbf{v}'_i(t) = \mathbf{v}_{cm} + \mathbf{R}(\alpha)[\mathbf{v}_i(t) - \mathbf{v}_{cm}], \quad (1.20)$$

where $\mathbf{R}(\alpha)$ is the rotation matrix. The center-of-mass velocity of the collision cell is calculated using

$$\mathbf{v}_{cm} = \frac{\sum m_i \mathbf{v}_i}{\sum m_i}, \quad (1.21)$$

where sums run over the number of particles in the collision cell.

Both the streaming and collision steps conserve the mass and linear momentum of the system, thereby allowing hydrodynamic correlations to build up in the system. The use of collisions cells, however, can lead to artifacts associated with loss of Galilean invariance. This issue is typically addressed by randomly shifting the origin of the MPCD cell grid before each collision step to restore Galilean invariance.^{10,43}

The MPCD algorithm can be coupled with standard MD to study the dynamics of solutes embedded in the MPCD solvent.^{9–12,42} In these MD-MPCD hybrid schemes, solute trajectories are propagated using conventional MD techniques, while also exchanging momentum with the solvent during the streaming and/or collision steps of

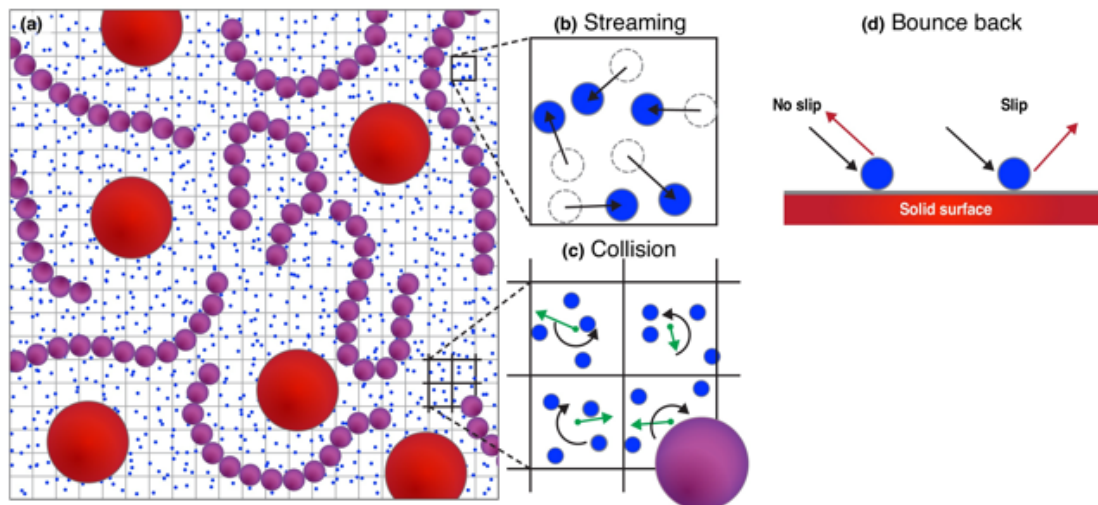


Figure 1.3: MPCD modeling, adapted from Ref. 42 with permission.

the MPCD. Small solutes such as polymer beads are typically treated similarly to solvent particles and included directly into the MPCD collision step.^{10,41,42} Momentum exchange with larger solutes such as nanoparticles, by contrast, is typically handled using bounce-back schemes, in which solvent particles interact with the solute's surface during the streaming step.^{10,41,42} Additional technical details of the MPCD and hybrid MD-MPCD schemes can be found in Ref. 42.

The following chapters describe how these techniques are used to model nanoparticle and polymer dynamics: Chap. 2 focuses on nanoparticle dynamics in solutions of fully flexible polymers, with and without hydrodynamic interactions; Chap. 3 addresses the effect of polymer flexibility by tuning stiffness of polymers; and Chap. 4 highlights the effect of polymer morphology by replacing linear polymers with ring polymers.

Chapter 2: Coupling of nanoparticle dynamics to polymer center-of-mass motion in semidilute polymer solutions

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2.1 Introduction

The Brownian dynamics of colloids suspended in a purely viscous fluid are traditionally described by the Stokes-Einstein (SE) equation, which relates the diffusivity D to the ratio of thermal energy of the colloid to the viscous drag over the particle surface. In complex fluids, *e.g.*, polymer solutions, the colloid dynamics are in addition affected by viscoelastic contributions, which can be incorporated into the generalized Stokes-Einstein (GSE) expression through a complex viscosity $\tilde{\eta}$.^{17,18} An underlying assumption of both the SE and GSE expressions is that the fluid can be regarded as an effective continuum over the particle surface. When this continuum approximation is broken by a particle that is comparably sized to a characteristic length scale of the material, however, the particle dynamics deviate from these expressions and a description based solely on the zero-shear viscosity of the material becomes insufficient.^{19,21,33,44–48}

Semidilute polymer solutions are non-Newtonian fluids used commonly during polymer composite processing,² as sweep fluids in enhanced oil recovery methods,⁴⁹ and to produce hydrogels.⁵⁰ They serve as ideal models for complex heterogeneous materials because their characteristic length scales, such as the polymer radius of gy-

ration R_g and the correlation length ξ , are well-defined and easily tuned by changing the molecular weight and concentration of the polymer.¹⁶

As introduced in more detail in Chap. 1, transport of particles or molecules through polymer solutions has traditionally been explained using geometric obstruction models,^{28,29} in which the diffusivity decreases with an increase in polymer concentration due to a higher frequency of collisions between the particles and polymer chains, or using hydrodynamic models,^{30–33,51} in which the polymer chains increase the solution viscosity and screen hydrodynamic interactions. The success of these models, however, is typically limited to a narrow range of particle sizes, polymer molecular weights, or polymer concentrations; furthermore, these models do not specifically address the deviations of nanoparticle dynamics from SE predictions. Recent theoretical treatments have employed modified mode-coupling theory³⁵ or self-consistent Langevin equations³⁷ to relate the nanoparticle dynamics to local fluctuations in the polymer mesh. Such treatments accurately reproduce the long-time dynamics of the nanoparticles but have largely not investigated dynamics on shorter time and length scales due to the sensitivity of the analytical calculations to the dynamic propagator of the polymer fluctuations. To model nanoparticle dynamics over a wide range of time and length scales, Rubinstein coupling theory³⁸ proposes that the nanoparticle dynamics directly couple to the segmental relaxations of the surrounding polymer chains. Under this assumption, nanoparticles are locally trapped by the polymer chains, leading to subdiffusive motion on short time scales. As the polymer chains relax over the particle surface, the nanoparticle can break out of its local cage and begin to freely diffuse through the solution with a size-dependent diffusivity, which scales as σ_{NP}/ξ , where σ_{NP} is the nanoparticle diameter. Previous experimental work found excellent agreement between coupling theory and long-time particle diffusivities, and for the short-time particle dynamics in the limit of small or large nanoparticles relative to the characteristic length scales of the polymer solution (*i.e.*,

$\sigma_{\text{NP}} < \xi$ and $\sigma_{\text{NP}} \gtrsim 10\xi$, respectively).²⁶

Substantial deviations from the predicted behavior, however, were observed at short times for particles of size comparable to the correlation length. Across a broad range of polymer concentrations, the nanoparticle subdiffusive exponents α_{NP} were much larger than predicted, and varied with both particle size and polymer concentration. Additionally, we found that long-range interparticle interactions affected the subdiffusive motion of the particles.⁵² This result suggests that the energy barrier for particle motion through the polymer mesh on short time and length scales is finite, in contrast to the infinite barrier required for full coupling of the particle and polymer dynamics. Thus, despite the notable success of coupling theory in describing the long-time dynamics in experiments^{22,26} and simulations,⁵³ the physics underlying the subdiffusive particle dynamics on short time scales in polymer solutions remains incompletely understood. Critical open questions are what causes the short-time subdiffusive dynamics and what controls the crossover to long-time diffusion. This understanding is essential for predicting particle transport and dispersion during composite² and hydrogel⁵⁰ processing and in oil production and exploration.⁴⁹ Simulations are an ideal method to probe short-time dynamics and have been extensively used to investigate nanoparticle dynamics in polymer melts.^{53–55} Extending these methods to investigate dynamics in polymer solutions, however, remains challenging due to the computationally demanding nature of accurately modeling solvent-mediated interactions. These interactions are strongly screened in melts, but influence short-time dynamics in polymer solutions.

Here, we simulate the dynamics of nanoparticles in semidilute solutions of comparably sized polymers, using multiparticle collision dynamics (MPCD) to account for solvent-mediated hydrodynamic interactions (HI).^{9–12,41,56–61} Complementary Langevin dynamics (LD) simulations, which remove HI between particles, are also performed. The friction coefficients employed in the LD simulations are chosen to

reproduce the long-time nanoparticle and polymer center-of-mass (COM) diffusion coefficients calculated from the MPCD simulations in the dilute regime, allowing us to study short and intermediate time dynamics in the absence of HI while approximately preserving the long-time relaxation behavior observed in the MPCD simulations. The MPCD simulations reveal trends that are qualitatively similar to previous experiments – the nanoparticle dynamics are subdiffusive on short time scales and diffusive on long time scales, with diffusivities that scale as predicted by coupling theory. The subdiffusive exponents, however, are larger than the predicted value of 0.5 and smoothly decrease with increasing polymer concentration, similarly to what is observed experimentally. Moreover, the subdiffusive exponents of the particle are strongly correlated to those of the polymer COM, suggesting that coupling to the motion of the polymer COM may provide an additional mechanism by which the nanoparticles can move through a polymer solution. This coupling mechanism appears in both MPCD and LD simulations, indicating that many-body hydrodynamic interactions are not required when the long-time dynamics are preserved.

2.2 Simulation methodology

Following recent studies,^{41,57–60} we model the polymers in solution as bead-spring chains composed of N_m monomer beads with diameter σ_p . Polymer bonds are described by the finitely extensible nonlinear elastic (FENE) potential:⁶²

$$U_{\text{FENE}}(r) = \begin{cases} -\frac{1}{2}kr_0^2 \ln \left[1 - \frac{r^2}{r_0^2} \right], & r \leq r_0 \\ \infty, & r > r_0 \end{cases}, \quad (2.1)$$

where r is the scalar separation distance between two bonded beads. Excluded volume interactions are modeled using the purely repulsive, shifted Weeks-Chandler-

Andersen (sWCA) potential to simulate good solvent conditions:⁶³

$$U_{\text{sWCA}}(r) = \begin{cases} 4\varepsilon \left[\left(\frac{\sigma_{ij}}{r - \Delta_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r - \Delta_{ij}} \right)^6 \right] + \varepsilon, & r \leq 2^{1/6}\sigma_{ij} + \Delta_{ij} \\ 0, & r > 2^{1/6}\sigma_{ij} + \Delta_{ij} \end{cases}, \quad (2.2)$$

where ε controls the strength of the repulsion. For monomer-monomer interactions, we set $\Delta_{ij} = 0$ and $\sigma_{ij} = \sigma_P$. Similarly, for nanoparticle-nanoparticle interactions, $\Delta_{ij} = 0$ and $\sigma_{ij} = \sigma_{\text{NP}}$. To account for the size asymmetry of the polymer monomers and nanoparticles, however, we use $\Delta_{ij} = (\sigma_{\text{NP}} - \sigma_P)/2$ and $\sigma_{ij} = \sigma_P$ for the cross interactions.

All simulations were performed in a cubic box with a $40\sigma_P$ edge length and periodic boundary conditions in all directions. We used LAMMPS⁶⁴ to conduct our simulations. A value of $\varepsilon = k_B T$ was used for all particle interactions, where k_B is Boltzmann's constant and T is temperature. The polymers were modeled using $N_m = 50$ beads and the standard Kremer-Grest parameters for the bonded interactions,⁶⁵ *i.e.*, $\kappa = 30k_B T \sigma_P^{-2}$ and $r_0 = 1.5\sigma_P$. Simulations using larger simulation cells ($60\sigma_P$) or longer polymer chains (up to $N_m = 250$) revealed no qualitative differences in the scaling behavior of the nanoparticle dynamics. The radius of gyration at infinite dilution for this model is $R_{g,0} = 4.9\sigma_P$, leading to an overlap concentration of $c^* = N_m \times \left(4\pi R_{g,0}^3 / 3 \right)^{-1} = 0.1\sigma_P^{-3}$. Hence, for the range of concentrations investigated here ($0.2 - 8.0c/c^*$), the simulated systems contain between 25 and 1000 polymer chains. We use 5 nanoparticles in each simulation and set $\sigma_{\text{NP}} = 6\sigma_P$, such that they are similar in size to the polymer coils. Figure 2.1 shows a typical simulation snapshot for $c/c^* = 0.5$.

Many-body HI interactions in the nanoparticle-polymer solutions were simulated using the MPCD algorithm.⁹⁻¹² In MPCD, mesoparticles (polymers and nanoparticles) are immersed in an background solvent, which is modeled explicitly through

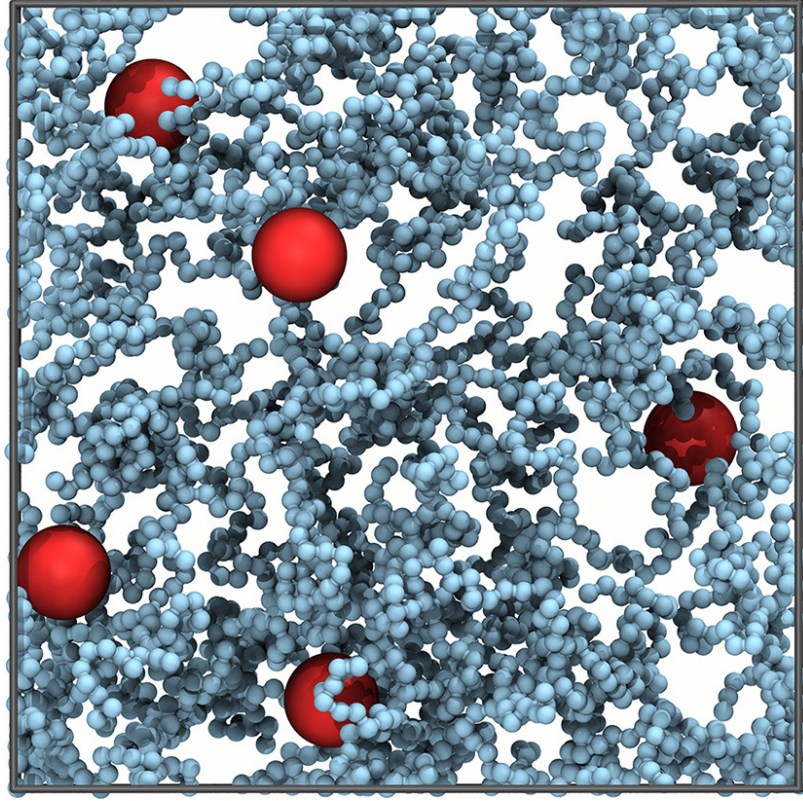


Figure 2.1: Rendering of nanoparticles (red) dispersed in a solution of polymers (blue) at $c/c^* = 0.5$ simulated in our study.

an ensemble of point particles. These solvent particles exchange momentum with nearby solvent and mesoparticles through stochastic collisions, which are designed to ensure that hydrodynamic correlations emerge over sufficiently large length scales.¹¹ The MPCD simulations for our model were conducted using a momentum conserving version of the Andersen thermostat^{66,67} that we implemented into LAMMPS' existing stochastic rotation dynamics (SRD) module.⁶⁸ This scheme, which is often referred to as MPCD-AT, is described in detail elsewhere.^{66,67,69} The MPCD routines for LAMMPS used in our study are available online,⁷⁰ along with example scripts for simulating solutions of polymers and nanoparticles.

The edge length, a , of the cubic MPCD collision cells dictates the spatial resolution of the HI,⁷¹ and we chose $a = \sigma_P$ for our simulations. We assigned unit mass $m = 1$ to each solvent particle and used an average MPCD solvent density $\rho = 5m/\sigma_P^3$. The collision time step was set to $\Delta t = 0.09\tau$, where $\tau = \sqrt{m\sigma_P^2/(k_B T)}$ is the unit of

time in the simulations. The reference positions of the cell were also randomly shifted before each collision step to ensure Galilean invariance.⁴³ These typical parameters give rise to an MPCD solvent with Schmidt number $Sc \approx 12.0$ and dynamic viscosity $\eta_0 \approx 4.0\tau k_B T/\sigma_p^3$. The motions of the polymers and nanoparticles in the MPCD simulations were integrated using a velocity-Verlet scheme with a 0.002τ time step. Momentum transfer between solvent particles and polymers during the collision steps was handled using the scheme described in Ref. 41, whereas solvent collisions with the nanoparticles were treated using the stochastic boundary algorithm discussed in Ref. 68 with slip conditions. The masses of the monomers ($M_P = \rho\sigma_p^3$) and nanoparticles ($M_{NP} = \rho\pi\sigma_{NP}^3/6$) were set to achieve neutral buoyancy in the background solvent. Dynamic properties reported for the nanoparticles were obtained by averaging over at least 30 trajectories.

We also performed a complementary set of LD simulations to investigate the behavior of the solutions in the absence of many-body HI. The LD friction coefficients⁷² for the nanoparticles and polymer monomers were adjusted independently to match the long-time nanoparticle diffusivity in pure MPCD solvent. Similarly, the friction coefficient for the monomers was chosen in such a way that the long-time polymer COM diffusion coefficients from MPCD and LD simulations matched in the absence of nanoparticles at $c/c^* = 0.2$.

2.3 Results and discussions

Coupling theory³⁸ predicts that the nanoparticle dynamics are subdiffusive on short time scales with a mean-squared displacement (MSD) that scales as a power-law in time, $\langle \Delta r^2 \rangle \sim t^{\alpha_{NP}}$. Nanoparticles smaller than the polymer correlation length (e.g., $\sigma_{NP} < \xi$) are predicted to pass freely through the polymer mesh, so that $\alpha_{NP} = 1$. Once $\sigma_{NP} > \xi$, the particles are predicted to be locally trapped by the polymer and can only move according to the segmental Rouse relaxations of the surrounding chains, so that $\alpha_{NP} = 0.5$. Indeed, this sharp transition has been observed in previous ex-

periments where the dispersed nanoparticles were chemically bound to transient polymer networks.⁷³ In our MPCD simulations of athermal nanoparticle-polymer solutions, however, we observe a smooth, monotonic decay in α_{NP} rather than the predicted step function from $\alpha_{\text{NP}} = 1$ to 0.5 at $\sigma_{\text{NP}}/\xi = 1$ (Fig. 2.2). A similar trend was observed in our previous experiments,²⁶ recovering $\alpha_{\text{NP}} = 0.5$ only for large particles at high polymer concentrations. The MPCD simulations and experiments therefore collectively demonstrate that coupling theory correctly captures the dynamic behavior in the limits $\sigma_{\text{NP}} < \xi$ and $\sigma_{\text{NP}} \gtrsim 10\xi$. However, they also reveal a surprisingly broad crossover regime, where the subdiffusive exponent is significantly larger than expected from coupling theory.

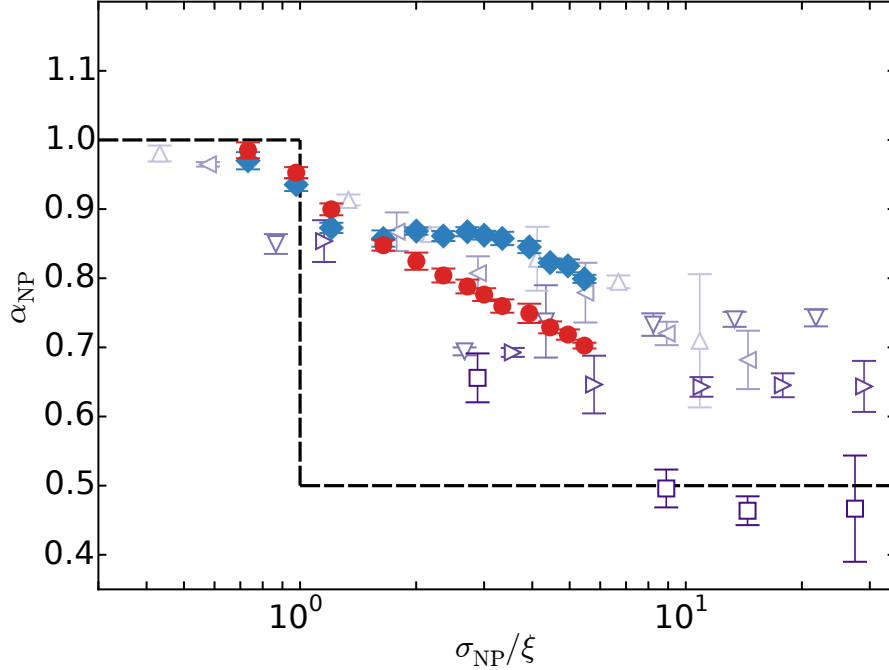


Figure 2.2: Subdiffusive exponent α_{NP} as a function of the ratio σ_{NP} to ξ for MPCD (red circles) and LD (blue diamonds) simulations.

Comparison of the LD and MPCD simulations also suggests that HI influence the short-time nanoparticle dynamics. In the dilute limit (i.e., $c/c^* \rightarrow 0$), both LD and MPCD predict that $\alpha_{\text{NP}} \rightarrow 1$, in accord with experiment (Fig. 2.2, $\sigma_{\text{NP}}/2R_{\text{g},0} = 0.61$ for simulations). Open symbols are experimental data from Ref. 26 for particles with

$\sigma_{\text{NP}}/2R_{g,0} = 0.56$ ($\triangle$), 0.74 ($\triangleleft$), 1.1 (∇), 1.5 ($\triangleright$), and 3.7 ($\square$). Dashed line is prediction from coupling theory in Ref. 38). This behavior indicates that the nanoparticle dynamics become purely diffusive after transitioning from a ballistic regime on much shorter time scales. Agreement between the two simulation methods is expected in this regime because the LD friction coefficients are matched to explicitly reproduce the long-time diffusive relaxations from MPCD. Progressively larger deviations between LD and MPCD are observed, however, as σ_{NP}/ξ (and c/c^*) increase. For $1 \lesssim \sigma_{\text{NP}}/\xi \lesssim 4$, α_{NP} in LD is approximately constant and deviates from the steady decay with concentration observed in the MPCD simulations, suggesting that many-body HI strongly affect the dynamics in this regime. Finally, for $\alpha_{\text{NP}} \gtrsim 4$, α_{NP} from LD and MPCD scale similarly with polymer concentration. This behavior is consistent with the expectation that many-body HI are screened in concentrated polymer solutions.^{41,74–76}

To investigate these short-time dynamics, it is instructive to examine the behavior of both nanoparticles and polymer chains in the MPCD simulations. Qualitatively, the MSD $\langle \Delta r^2 \rangle$ of the nanoparticles (Fig. 2.3(a), dashed and solid lines indicate diffusive and subdiffusive dynamics, arrow indicates the observed diffusive crossover time τ_c for the $8c^*$ solution) exhibits the predicted features³⁸ that have been observed in experiments^{24,26} and simulations.⁷⁷ On short time scales, the particles move subdiffusively with $\alpha_{\text{NP}} < 1$. On long time scales, the particle motion becomes diffusive (i.e., $\alpha_{\text{NP}} = 1$) with a diffusivity D that decreases with increasing polymer concentration. As an additional verification of the simulations, the MSD for the monomer beads in the COM reference frame (Fig. 2.3(b), dashed and solid lines indicate Zimm and Rouse dynamics, the Zimm time $\tau_\xi \approx \eta_0 \xi^3/k_B T$ is estimated to be $\tau_\xi \sim 10\tau$ for $8c^*$ and hence is not shown) exhibits the expected Zimm scaling ($\langle \Delta r^2 \rangle \sim t^{2/3}$) at low polymer concentrations and Rouse scaling ($\langle \Delta r^2 \rangle \sim t^{1/2}$) at higher polymer concentrations. The transition from Zimm to Rouse relaxations confirms that HI are screened

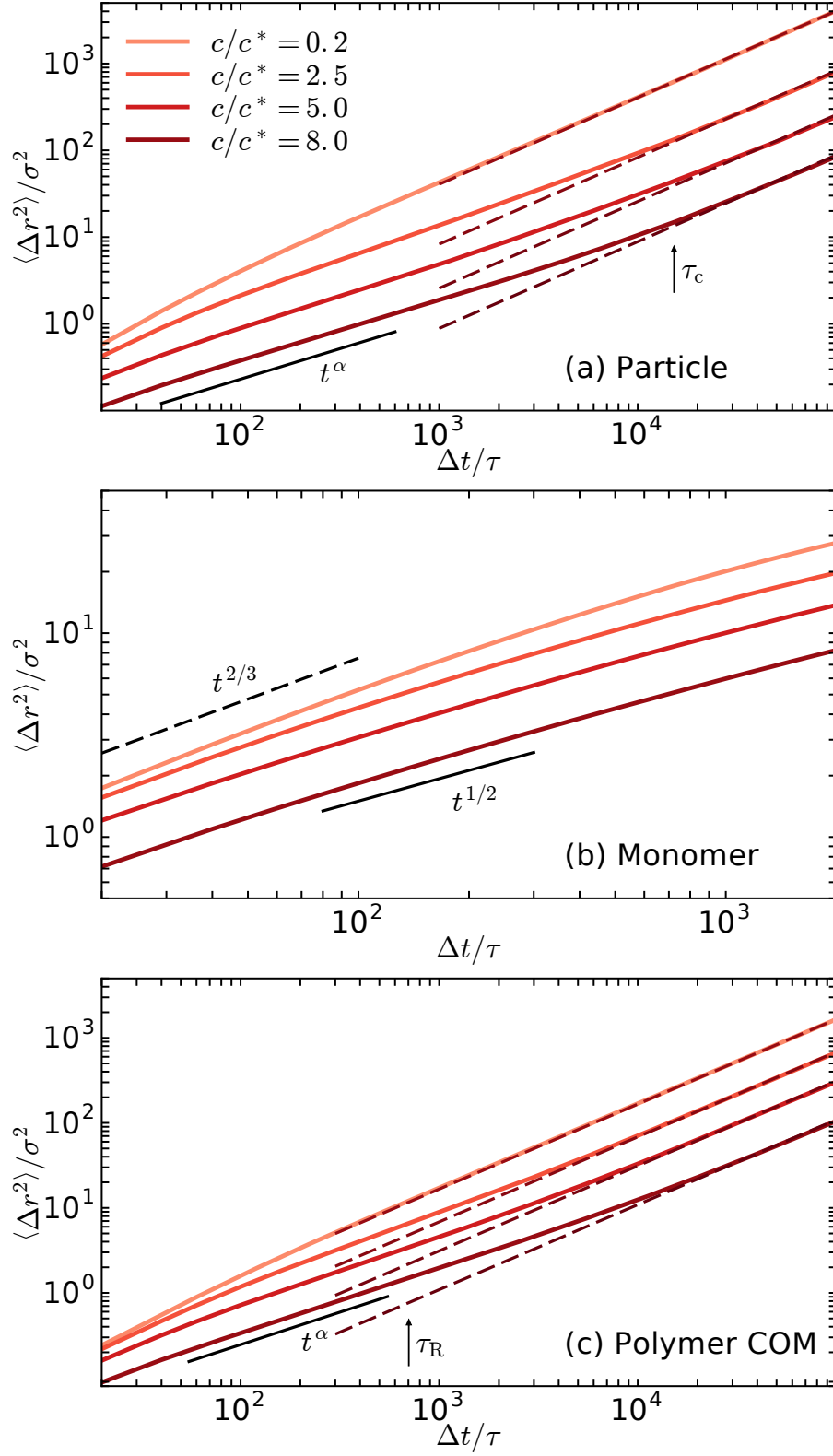


Figure 2.3: Mean-squared displacement $\langle \Delta r^2 \rangle$ normalized by bead diameter σ_P as a function of lag time $\Delta t / \tau$.

at high polymer concentrations, in agreement with polymer scaling predictions.⁷⁴ Finally, the MSD for the polymer chain COM (Fig. 2.3(c), dashed and solid lines indicate diffusive and subdiffusive dynamics, arrow indicates the estimated Rouse relaxation time $\tau_R = \tau_\xi(R_g/\xi)^4$ for the $8c^*$ solution) exhibits qualitatively similar behavior to that of the nanoparticles. On short time scales, the polymer COM motion is subdiffusive with an exponent $\alpha_P < 1$, similar to what has been observed previously in molecular dynamics simulations⁷⁸ and experiments⁷⁹ for polymer chains in unentangled melts. On long time scales, the polymer relaxations are dominated by the longest Rouse mode, so that the COM moves diffusively. Additionally, comparison of the nanoparticle and polymer COM MSDs at the same polymer concentration indicates that both nanoparticles and polymer chains are mobile over similar time and length scales.

Confirming that the MPCD simulations accurately capture the polymer relaxations, we now analyze the change in long-time particle diffusivity with increasing polymer concentration (Fig. 2.4, closed symbols are MPCD (red circles) and LD (blue diamonds) simulations with $\sigma_{NP}/2R_{g,0} = 0.61$, open symbols are experimental data from Ref. 26 for particles with $\sigma_{NP}/2R_{g,0} = 0.56$ (Δ), 0.74 ($\triangleleft$), 1.1 (∇), 1.5 ($\triangleright$), and 3.7 ($\square$), solid lines show coupling theory predictions from Ref. 38). At low polymer concentrations where $\sigma_{NP}/\xi < 1$, the particle diffusivities are almost unchanged from that of a pure solvent so that $D/D_0 \approx 1$, where $D_0 \sim k_B T/\eta_0 \sigma_{NP}$ is the diffusivity of the particle in the absence of polymer and η_0 is the solvent viscosity. For $\sigma_{NP}/\xi > 1$, the particle diffusivities scale as $D/D_0 \sim (\sigma_{NP}/\xi)^{-2}$, as predicted from coupling theory,³⁸ where $\xi = R_{g,0}(c/c^*)^{-\nu/(3\nu-1)}$ is the polymer correlation length¹⁶ and ν is the inverse of the polymer fractal dimension. For the bead-spring polymer model considered here $\nu = 0.61$, which is in good agreement with previous computational studies,⁴¹ with the estimated value of 0.62 for the partially hydrolyzed polyacrylamide used in experiment,²⁶ and with the theoretically predicted value of 0.59 for flexible chains in a

good solvent.⁴¹

The scaling of the nanoparticle diffusivities with σ_{NP}/ξ for MPCD simulations agrees with that observed in our recent experiments.²⁶ The offset between the simulated and experimental data is attributable in large part to the difference in shear viscosities (inset to Fig. 2.4(b), dashed line indicates predicted scaling behavior for an ideal polymer solution). In both experiments and simulations, the solution viscosity η was determined through shear measurements in the linear response regime.⁸⁰ Whereas the simulations use a generic monodisperse polymer model in a good solvent, the polymers used in experiment were highly polydisperse polyelectrolytes with a charge functionality of $\approx 30\%$. It is well established that the viscosity of solutions of charged polymers scales differently with concentration than that of neutral polymer solutions,^{81,82} resulting in the order of magnitude difference between the viscosities of the experimental and simulated solutions (inset to Fig. 2.4(b)). Specifically, the shear viscosity of the experimental solution is approximately 60 times higher for $c/c^* = 3$. Hence, the fact that the normalized diffusivities D/D_0 for the experiments are lower than those computed from simulation is expected. Nevertheless, both data sets exhibit the same qualitative trends.

To assess the changes in particle diffusivity relative to bulk solution properties, we compare the diffusivities from simulation and experiment to the Stokes-Einstein predictions $D_{\text{SE}} \sim k_{\text{B}}T/\eta\sigma_{\text{NP}}$, where η is the zero-shear solution viscosity. For $c/c^* \lesssim 5$, the diffusivities obtained from simulations are in statistical agreement with the Stokes-Einstein predictions (Fig. 2.4(b), Stokes-Einstein prediction D_{SE} calculated from zero-shear solution viscosity as a function of polymer concentration c/c^*). At higher concentrations, however, the diffusivities begin to increasingly surpass D_{SE} , in accord with experiments. Thus, the MPCD simulations accurately capture the change in the long-time nanoparticle dynamics with increasing polymer concentration and semiquantitatively describe the deviations from Stokes-Einstein

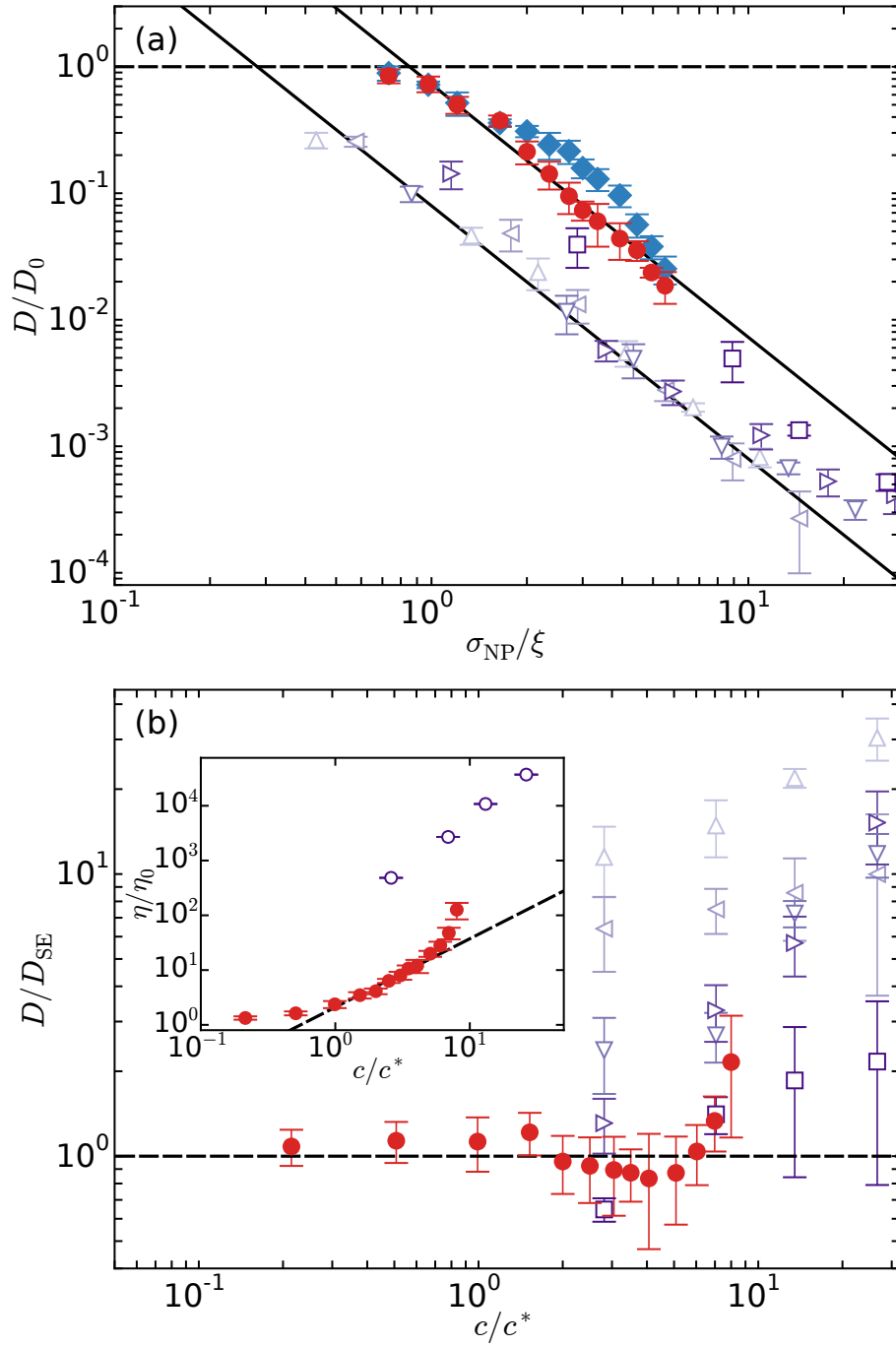


Figure 2.4: (a) Normalized nanoparticle diffusivity D/D_0 as a function of σ_{NP}/ξ . (b) Ratio of diffusivities to SER predictions. *Inset*: Zero-shear viscosity of MPCD and experimental solutions.

predictions at high concentrations.

Finally, we assess the effects of HI by comparing the diffusivities extracted from the MPCD simulations to those from the LD simulations (Fig. 2.4(a)). LD is an implicit-solvent simulation method that captures only the viscous drag on the individual particles but no short- or long-range HI. The friction coefficients for the dispersed nanoparticles and monomers were chosen in such a way to match the long-time diffusivity computed from the MPCD simulations under dilute conditions. Hence, as expected, we observe agreement between the diffusivities extracted from LD and from MPCD simulations in the dilute regime for $\sigma_{\text{NP}} \lesssim 1$, where the dynamics were matched by construction. For $\sigma_{\text{NP}} \gtrsim 5$, where HI are strongly screened,^{41,74–76} the diffusivities from LD and MPCD also exhibit similar scaling behavior. However, deviations between LD and MPCD, similar to those observed for the subdiffusive exponent (Fig. 2.2), occur in the intermediate regime. Thus, our results suggest that HI influence the long-time particle diffusivities for $\sigma_{\text{NP}} \lesssim 5$.⁸³

In addition to the long-time nanoparticle dynamics, the MPCD and LD simulations provide crucial insights on the coupling between nanoparticles and polymer chains on short time and length scales, which are difficult to experimentally measure. Coupling theory assumes that the longest relaxation time of the polymer $\tau_{\text{R}} = \tau_{\xi}(R_{\text{g}}/\xi)^4$ is much larger than the crossover time τ_{c} at which the nanoparticle dynamics transition from subdiffusive to diffusive,³⁸ so that the particle dynamics are fully coupled to the polymer segmental relaxations. Under this assumption, nanoparticle dynamics become diffusive once the polymer segments relax over the particle surface. For the simulated polymer chains, the calculated Rouse time ranges from $10^2\tau$ to $10^3\tau$ depending on polymer concentration, in good agreement with when the polymer COM begins moving diffusively (Fig. 2.3(c)). Whereas coupling theory assumes a separation of time scales, this Rouse time scale is comparable to the crossover time of the particles ($\tau_{\text{c}} \approx \tau_{\text{R}}$), indicating that the polymer COM motion

cannot be neglected. Comparable time scales were also observed in previous experiments.²⁶ On the basis of the similarities of the MSDs (Fig. 2.3), we compare the subdiffusive exponents for the nanoparticles and the polymer COM (Fig. 2.5(a,b)). At low polymer concentrations, both particles and polymer chains move diffusively (i.e., $\alpha_{\text{NP}}, \alpha_{\text{P}} \approx 1$). As the polymer concentration increases, the particles and polymer chains become subdiffusive with monotonically decreasing subdiffusive exponents. Furthermore, the change in nanoparticle and polymer subdiffusive exponents are similar in magnitude and shape, indicating that the particle and polymer dynamics on short time scales are positively correlated. The subdiffusive exponents of the nanoparticles are slightly lower than those of the polymers but are highly correlated over the entire concentration range (Fig. 2.5(c)). Comparison of MPCD and LD simulations reveals differences in the scaling of the subdiffusive exponents and long-time diffusion coefficients at low to intermediate polymer concentrations due to HI (Fig. 2.2 and 2.4). Nonetheless, both methods find strong correlation between the nanoparticle and polymer COM subdiffusive exponents. This key finding suggests that the coupling is due to the comparable relaxation time scales of the nanoparticles and polymers and not explicitly due to manybody HI. The high degree of correlation between nanoparticle and polymer dynamics within the subdiffusive regime indicates that the COM polymer motion may indeed play a role in controlling the nanoparticle dynamics.

The fact that the short-time nanoparticle dynamics are consistently more subdiffusive than those of the polymer COM ($\alpha_{\text{NP}} \lesssim \alpha_{\text{P}}$, Fig. 2.5(a,b)) suggests that the nanoparticle dynamics may be coupled to additional relaxation modes beyond the polymer COM dynamics. Because polymer chains are fractal in structure, there is a distribution of relaxation mechanisms that control polymer dynamics. Moving over similar time scales as the polymer, the nanoparticles likely couple to this distribution – from segmental Rouse motions to COM diffusion. Indeed, coupling theory³⁸

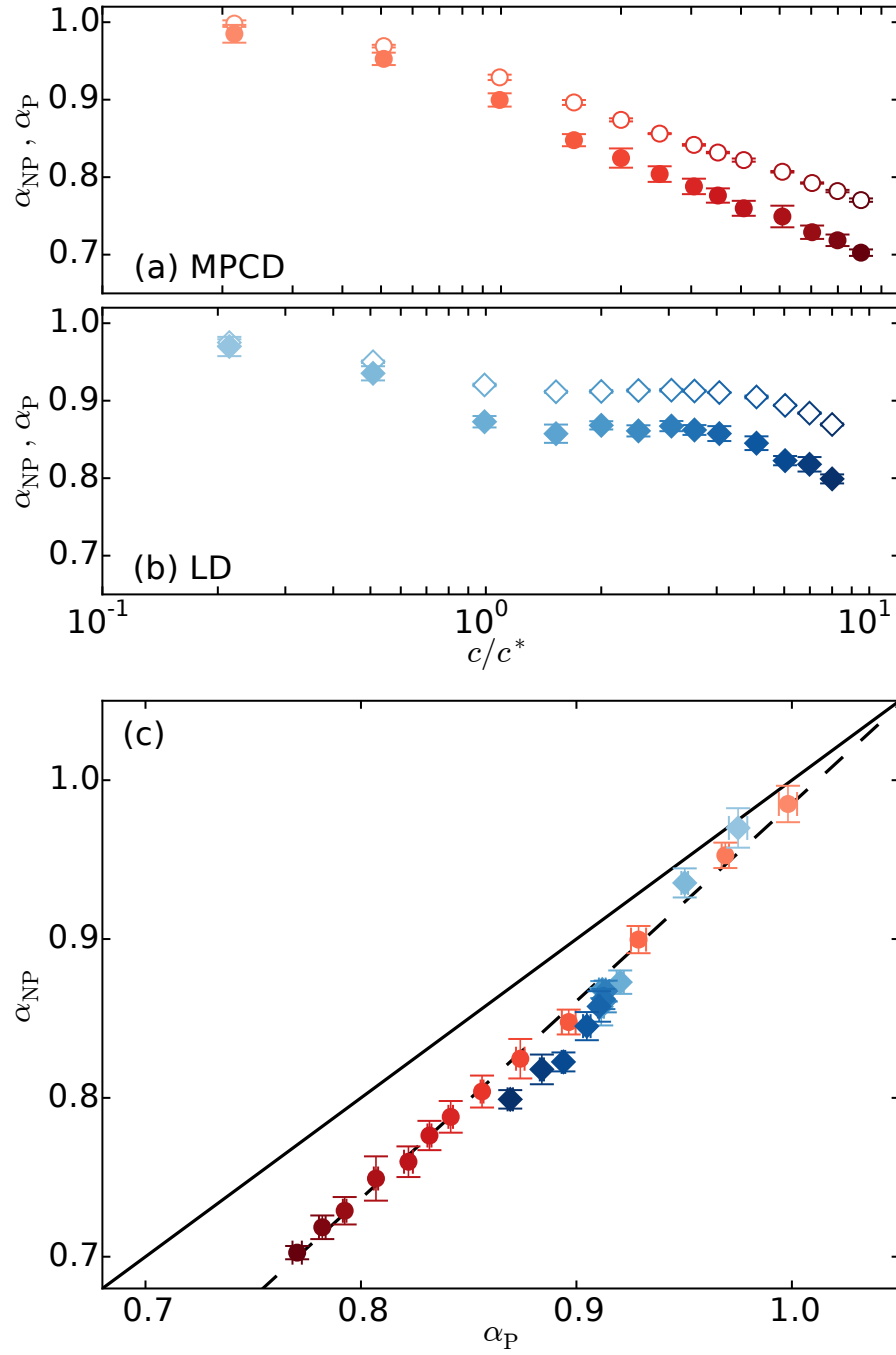


Figure 2.5: Subdiffusive exponents α_{NP} (closed) and α_P (open) for MPCD (red circles) and LD (blue diamonds). Identity line drawn in black.

predicts that the segmental motions should play a role in controlling the subdiffusive nanoparticle dynamics. Moreover, from this work and previous experiments, we observe that nanoparticle coupling to segmental relaxations accurately predicts the long-time nanoparticle diffusion across orders of magnitude in polymer concentration and particle size, while the subdiffusive exponents of the nanoparticles and polymer COM are highly correlated over an order of magnitude in polymer concentration. To combine these contributions into a unified picture, the data suggest that the nanoparticles generally move through polymer solutions via two mechanisms – coupling to segmental relaxations to move *relative* to the polymer COM and coupling to the COM motion to move with the polymer COM (Fig. 2.6). The combination of these two mechanisms may lead to the long-time diffusivity of nanoparticles that scales according to the length-scale ratio σ_{NP}/ξ and deviates from the zero-shear solution viscoelasticity and to the short-time subdiffusive dynamics with subdiffusive exponents $0.5 \leq \alpha_{\text{NP}} \lesssim \alpha_{\text{P}} \leq 1$ and crossover times $\tau_c \approx \tau_R$.

While finalizing our article, Chen et al.⁸³ published an MPCD study in which they observed similar subdiffusive behavior for nanoparticles in semidilute polymer solutions. Our findings are in good agreement with the results from their MPCD simulations performed with HI. Although they used a different interpretive framework based on the empirical model of Holyst and collaborators,^{84,85} the long-time diffusion coefficients and subdiffusive exponents from their simulations can be collapsed on the same scaling plots shown here and thus support our conclusions. The empirical Holyst model^{84,85} was not used in this study because, as we previously documented in the Supporting Information of Ref. 26, it does not collapse the experimental data as well as the coupling theory of Ref. 38.

Chen et al.⁸³ also performed simulations without HI in their study. Rather than using LD, however, they destroyed HI within the MPCD framework by randomizing the solvent positions and velocities. Interestingly, in contrast with our findings,

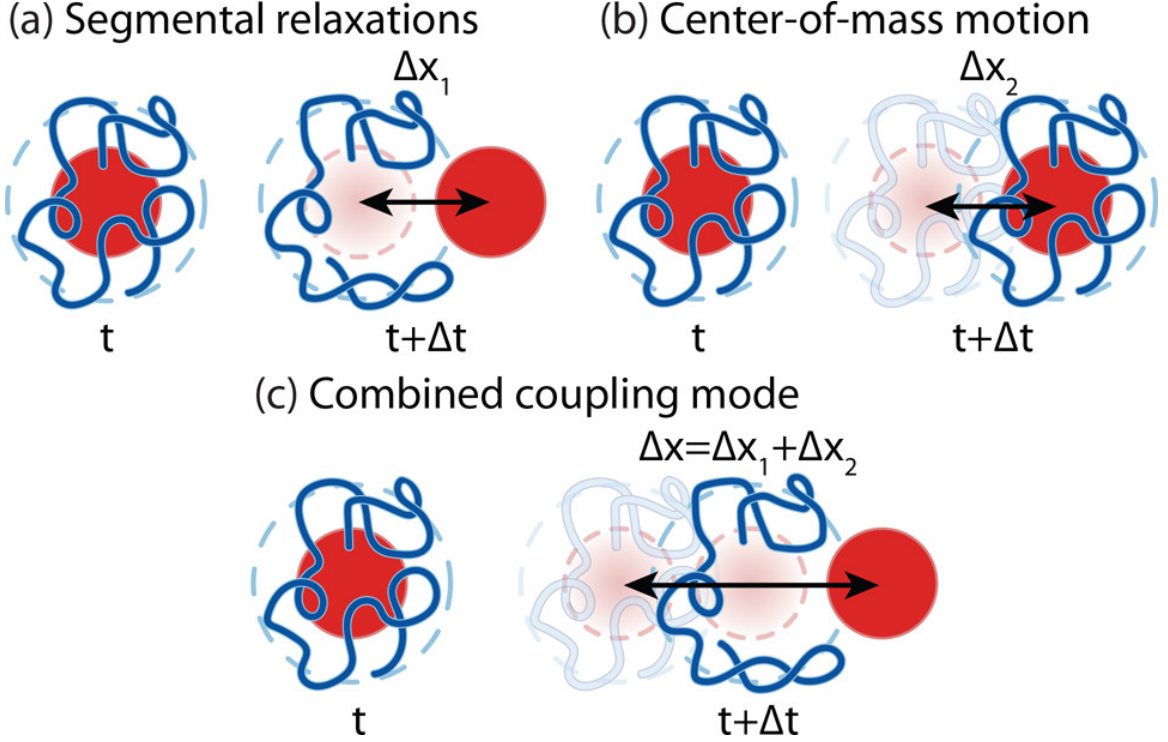


Figure 2.6: Schematic illustrating the physical processes controlling nanoparticle dynamics. (a) Segmental relaxation, described in Ref. 38. (b) Center-of-mass (COM) motion of the polymer. (c) Combined coupling mode.

their simulations predict that the nanoparticle and polymer COM subdiffusive behavior decouples in the absence of HI. We hypothesize that this discrepancy arises because their approach for destroying HI does not preserve the long-time nanoparticle and polymer COM diffusive behavior, and thus it also likely distorts the relative time scales associated with other relaxation processes in the system. Hydrodynamic interactions influence various aspects of solution dynamics. Unfortunately, there is no unique approach for removing HI from simulations that would allow an unambiguous characterization of its contributions at all time scales. The approach that we have adopted preserves the long-time particle and polymer relaxation time scales under dilute conditions. These relaxations are influenced by drag from the solvent but, by definition, not by many-body contributions arising from momentum transfer between nanoparticles and polymers. Even though these additional contributions may influence relaxations at finite solute concentrations, this does not imply that

they dictate the physical mechanisms controlling nanoparticle – polymer coupling. Indeed, our results demonstrate that when the long-time relaxations of the system are preserved, the nanoparticle and polymer COM subdiffusive behavior remains strongly coupled even in the absence of many-body nanoparticle – polymer hydrodynamic correlations.

2.4 Conclusions

We simulated the dynamics of nanoparticles in semidilute polymer solutions with and without long-range hydrodynamic interactions. The long-time nanoparticle dynamics were well described by recent theoretical predictions based on coupling to segmental relaxations; this coupling theory also captures the short-time dynamics for particles smaller than or much larger than the polymer correlation length. In agreement with experiments, however, the simulations revealed a surprisingly broad crossover regime where the subdiffusive exponent was larger than predicted. Analysis of the simulation trajectories suggests that the nanoparticles couple to the subdiffusive dynamics of the polymer COM on short time scales, which provides an additional mechanism by which nanoparticles can move through the solution. Analogous physical pictures have been proposed to explain tracer dynamics in colloidal glasses⁸⁶ and crowded biological material,⁸⁷ in which the coupling between tracer and crowder dynamics leads to subdiffusive dynamics.

Chapter 3: Influence of polymer flexibility on nanoparticle dynamics in semidilute solutions

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3.1 Introduction

As described in the pervious chapters, the recent polymer coupling theory (PCT),³⁸ based on scaling arguments for polymer dynamics,^{74,88} assumes that the nanoparticle (NP) dynamics fully couple to segmental relaxations of the polymers on comparable length scales. This model, which predicts that the dynamics are controlled by the ratio of σ_{NP} to the polymer correlation length ξ , correctly captures the change in long-time diffusivity as the particle size or polymer concentration is changed.²⁶ On short length and time scales, however, experiments and simulations suggest that the particle dynamics are incompletely coupled to the segmental dynamics of flexible polymers and additionally couple to the center-of-mass (COM) relaxations of the polymers.^{26,52,83,89}

For semiflexible polymers, theoretical descriptions based on simple scaling laws are expected to be even less fruitful because stiff macromolecules cannot be described by a self-similar fractal structure. Instead, semiflexible chains are characterized by several crossover length scales, such as the persistence and contour lengths, which introduce a large number of disparate time and length scales that are relevant to describing their dynamics. Accordingly, it has been shown that even modest stiffness affects both static^{90–93} and dynamic^{59,60,94} properties of polymer liquids. This scenario is relevant for understanding transport through the intracellular space, crowded by

actin, microtubules, and other semiflexible biopolymers.^{95,96} On short time scales the motion of microscale particles (larger than the mesh size or correlation length) is subdiffusive, scaling with time with an exponent of $3/4$ ^{97,98} as predicted from the microscopic relaxations of semiflexible polymers.^{99,100} Surprisingly, how smaller particles couple to the dynamics of semiflexible chains has not been systematically explored and is the focus of this study.

In this work, we use a combination of simulation and theory to probe NP dynamics in solutions of semiflexible polymers, whose stiffnesses are characterized by the persistence length l_p . The colloidal suspensions are simulated using a hybrid molecular dynamics–multi-particle collision dynamics (MD–MPCD) scheme, which accounts for hydrodynamic interactions through the use of an explicit coarse-grained solvent. The simulation results are also compared with predictions from MCT³⁵ for concentrated polymer solutions. The NP dynamics are subdiffusive on short time scales and diffusive on long time scales. The long-time diffusivities scale with the polymer correlation length at low polymer concentrations in agreement with PCT, but depend on polymer stiffness at higher concentrations. Good agreement is also observed with the long-time diffusivities calculated from MCT at high polymer concentrations, where the theory is expected to be most accurate. The short-time subdiffusive dynamics, by contrast, vary strikingly with the flexibility of the polymers. For fully flexible polymers whose characteristic length scales are comparable to the NP size, we observe that the subdiffusive behavior of the NPs is coupled to the polymer COM motion, in accord with our previous study.⁸⁹ As l_p is increased such that the polymer chains become more rigid, however, the dynamics of the NPs become more subdiffusive and decouple from the dynamics of the polymer chain COM. These effects likely arise from changes in the segmental relaxations as the chain stiffness is increased.

3.2 Methods

Molecular dynamics simulations of the NP–polymer systems were performed with LAMMPS.⁶⁴ For convenience in describing the model system, we define σ , m , and ε as the fundamental base units for length, mass, and energy, respectively. The corresponding unit of time is $\tau = \sqrt{m\sigma^2/\varepsilon}$. All physical quantities are reduced using these fundamental base units and reported in dimensionless form.

We adopted similar models to those used in our previous study of NP dynamics in solutions of fully flexible polymer chains.⁸⁹ Nanoparticles were modeled as large spheres with diameter $\sigma_{\text{NP}} = 5$. Polymers were represented by the Kremer-Grest (KG) model¹⁰¹ as linear chains composed of $N_{\text{m}} = 32$ smaller beads with diameter $\sigma_{\text{P}} = 1$. Excluded volume interactions were modeled using the shifted Weeks-Chandler-Andersen (sWCA) potential⁶³

$$U_{\text{sWCA}}(r_{ij}) = \begin{cases} 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij} - \Delta_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij} - \Delta_{ij}} \right)^6 \right] + \varepsilon_{ij}, & r_{ij} \leq r_{ij}^c, \\ 0, & r_{ij} > r_{ij}^c \end{cases}, \quad (3.1)$$

where r_{ij} is the scalar separation distance between particles i and j , $\varepsilon_{ij} = 1$ is the parameter controlling the strength of the repulsion, and the potential is truncated and shifted at $r_{ij}^c = 2^{1/6}\sigma_{ij} + \Delta_{ij}$. For NP–NP and monomer–monomer interactions we used $\sigma_{ij} = \sigma_{\text{NP}}$ and $\sigma_{ij} = \sigma_{\text{P}}$, respectively, and set $\Delta_{ij} = 0$. For NP–monomer interactions, we chose $\sigma_{ij} = \sigma_{\text{P}}$ and $\Delta_{ij} = (\sigma_{\text{NP}} - \sigma_{\text{P}})/2$ to account for their size asymmetry.

Adjacent beads on each polymer chain were connected by springs described using the finitely extensible nonlinear elastic (FENE) potential,⁶²

$$U_{\text{FENE}}(r_{ij}) = \begin{cases} -\frac{1}{2}kr_0^2 \ln \left[1 - \frac{r_{ij}^2}{r_0^2} \right], & r_{ij} \leq r_0, \\ \infty, & r_{ij} > r_0 \end{cases}, \quad (3.2)$$

with spring constant $k = 30$ and a maximum bond extension $r_0 = 1.5$. Chain stiffness was incorporated into the KG model using the bending potential^{59,60,102–104}

$$U_{\text{bend}}(\Theta_{ijk}) = \kappa(1 - \cos \Theta_{ijk}), \quad (3.3)$$

where Θ_{ijk} is the angle between the bonds connecting consecutive beads i to j and j to k (an angle of $\Theta_{ijk} = 0^\circ$ corresponds to three beads in a line). The parameter κ modulates the strength of the potential and stiffness of the chains. For sufficiently stiff polymers ($\kappa > 2$), it is related to the chain persistence length via $l_p \approx b\kappa$,⁵⁹ where b is the equilibrium bond length ($b \approx 0.97$ for the standard parameterization of the KG model). The contour length of the chain is given by $L_c = (N_m - 1)b \approx 30$.

To study the influence of chain flexibility on NP dynamics, we performed simulations using different values of κ ranging from 0 (fully flexible) to 32 ($l_p/L_c \approx 1$) (Table 3.1; Fig. 3.1). The edge length of the box ($L = 64$) was chosen to be approximately eight times the radius of gyration $R_{g,0}$ of the stiffest polymer ($\kappa = 32$) at infinite dilution to minimize finite-size effects. All simulations were conducted in a cubic box with periodic boundary conditions in each direction. For highly flexible polymers ($\kappa \leq 2$), the number of polymer chains N_c was varied from 200 to 4900, to achieve monomer concentrations $c = N_c N_m L^{-3}$ ranging from 0.025 to 0.5. At higher values of κ , however, the maximum value of c was further limited to avoid the well-characterized isotropic-nematic transition in this system⁹² and stay within the isotropic phase (Table 3.1). The number of NPs was fixed at 20 in each simulation (volume fraction ≈ 0.005) to improve sampling while keeping NP–NP interactions negligible.

Molecular dynamics trajectories were propagated using a velocity-Verlet integrator with time step 0.005. Each simulation was equilibrated for $\approx 10^5 \tau$ followed by a production period of $\approx 10^6 \tau$ during which trajectories were saved for subsequent analysis. Ensemble averages were computed from three independent simulations

Table 3.1: Properties of the polymer systems investigated in this study.

κ	l_p/L_c	$R_{g,0}$	ν	$c_{\min}$	$c_{\max}$
0	0.03	3.63	0.61	0.025 (0.16 c^*)	0.50 (3.13 c^*)
2	0.06	4.37	0.62	0.025 (0.27 c^*)	0.40 (4.37 c^*)
5	0.15	5.62	0.62	0.025 (0.58 c^*)	0.40 (9.29 c^*)
10	0.31	6.82	0.66	0.025 (1.04 c^*)	0.40 (16.61 c^*)
20	0.63	7.73	0.74	0.025 (1.51 c^*)	0.25 (15.12 c^*)
32	1.01	8.15	0.81	0.025 (1.77 c^*)	0.25 (17.72 c^*)

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

(60 NP trajectories), and statistical uncertainties were estimated from the standard error. Hydrodynamic interactions (HI) were incorporated by coupling the MD particles to a coarse-grained solvent modeled using the multi-particle collision dynamics (MPCD) method.^{9–12} Implementation details of the hybrid MD–MPCD algorithm are identical to those reported in our previous study.⁸⁹ Briefly, the MD–MPCD simulations were performed using a collision cell edge length $a = 1$, a solvent particle mass $m_s = 1$, an average solvent density $\rho = 5$ (5 solvent particles per collision cell), and a collision time step 0.09. Solvent collisions were handled using a momentum-conserving version of the Andersen thermostat^{66,67} with a set temperature $T = 1$. Further, the reference positions of the cells were randomly shifted before each collision step to ensure Galilean invariance.⁴³ These choices lead to an MPCD solvent with Schmidt number $Sc \approx 12.0$ and dynamic viscosity $\eta_s \approx 4.0$. Solvent–polymer collisions were handled using the scheme discussed in Ref. 41, whereas momentum transfer between the solvent and NPs was treated using the stochastic boundary algorithm described in Ref. 68 with slip conditions. To achieve neutral buoyancy in the background solvent, the masses of the polymer beads and NPs were set to $m_P = \rho\sigma_P^3$ and $m_{NP} = \rho\pi\sigma_{NP}^3/6$, respectively.

To compare the simulated NP diffusivities to the SER and MCT, in both cases the zero-shear viscosities η_0 of the polymer solutions from simulation were used as input parameters, the shear viscosities were determined through reverse nonequilibrium molecular dynamics (RNEMD) simulations^{60,106} using HOOMD-blue with

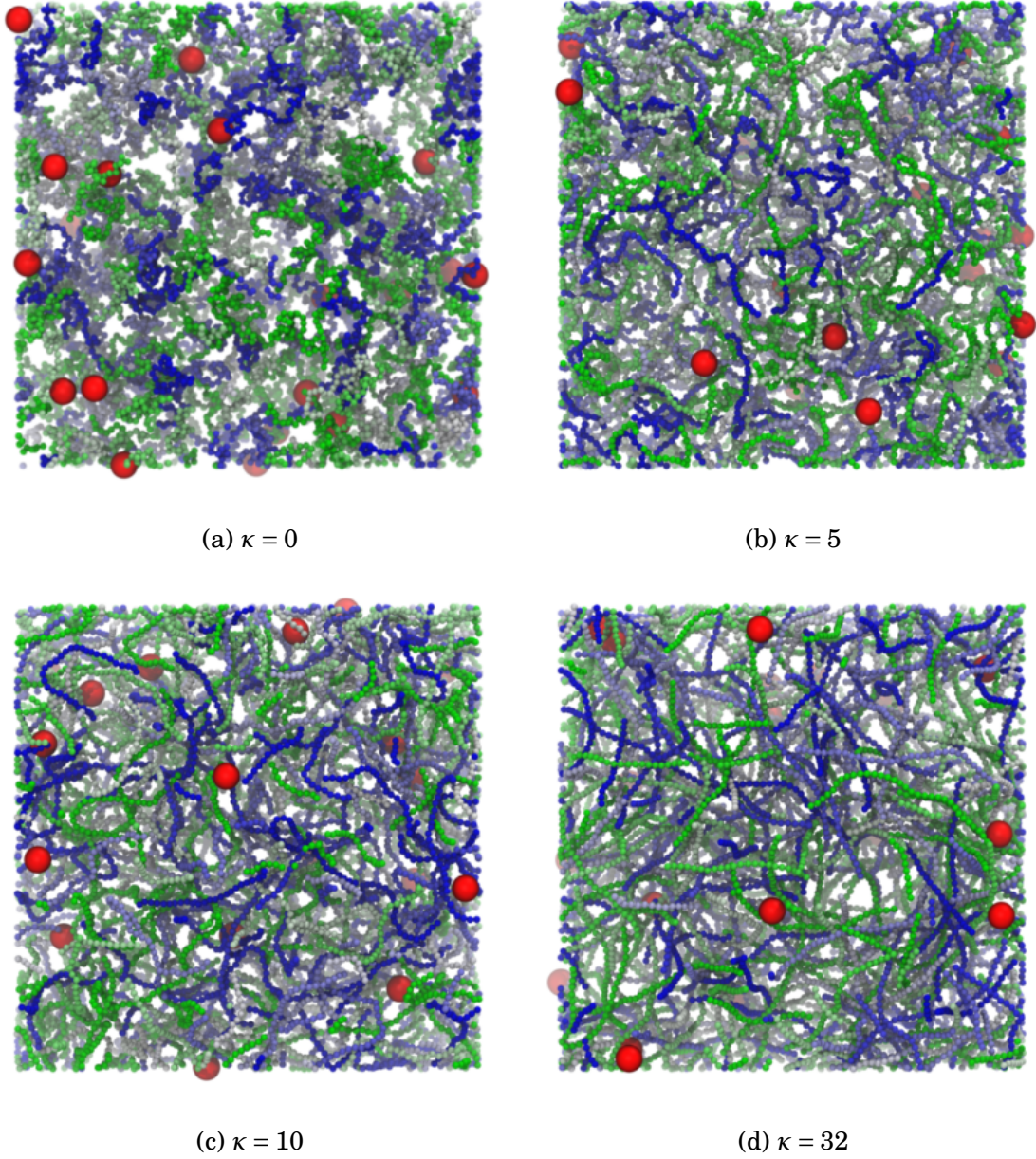


Figure 3.1: Nanoparticles (red) in solutions of (a) fully flexible (b,c,d) semiflexible chains. Snapshots rendered using Visual Molecular Dynamics 1.9.3.¹⁰⁵

MD^{107–109} and MPCD¹¹⁰ accelerated on graphics processing units. Stress was imposed on the solutions by generating a momentum flux, and the shear rate $\dot{\gamma}$ was extracted from the emerging flow profile, as described in Ref. 106. For the fully flexible chains ($\kappa = 0$) we were able to directly access the linear response regime and measure the zero-shear viscosity η_0 . As the stiffness was increased, however, the

polymer relaxation slowed down significantly, making a direct measurement of η_0 computationally infeasible. In these cases, we extracted the zero-shear viscosity by fitting our data to the Cross model.^{60,111,112}

$$\eta(\dot{\gamma}) = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (\tau_s \dot{\gamma})^m}, \quad (3.4)$$

where η_∞ is the asymptotic viscosity as $\dot{\gamma} \rightarrow \infty$, τ_s is the characteristic time for the onset of shear thinning, and m is a parameter sensitive to the degree of shear thinning ($m = 0$ for Newtonian liquids; $m \rightarrow 1$ for increasingly shear thinning fluids).

3.3 Results and discussions

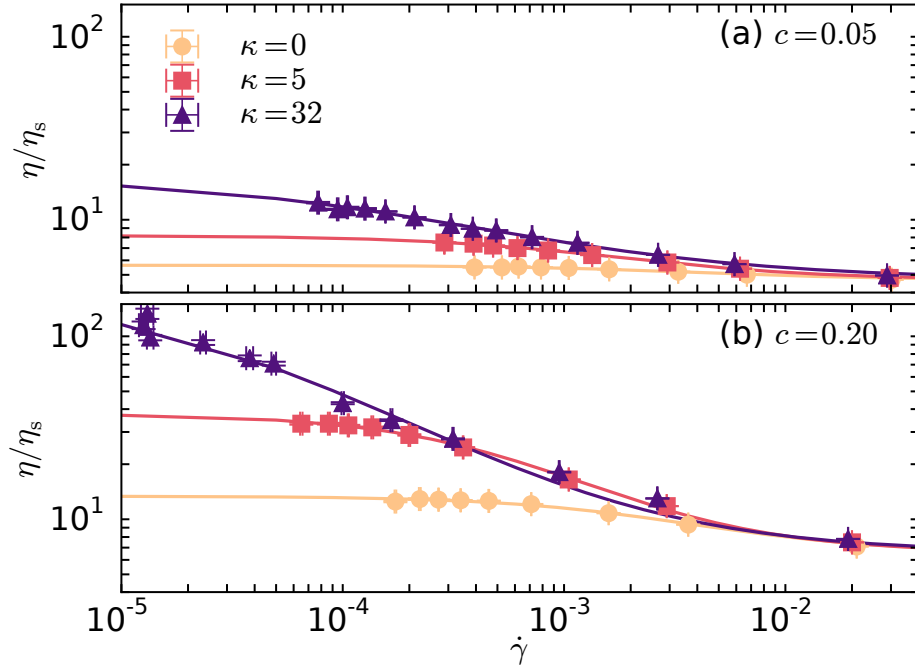


Figure 3.2: Reduced viscosity η/η_s as a function of shear rate $\dot{\gamma}$ with stiffness $\kappa = 0$ ($\circ$), 5 ($\square$), and 32 ($\triangle$), solid lines are fittings using the Cross model (eqn. 3.4).

The Cross model provided excellent fits to the RNEMD simulation data in each case, independent of the polymer stiffness and concentration (Fig. 3.2). Further, for fully flexible polymers ($\kappa = 0$), the values of η_0 extracted using eqn. 3.4 were found

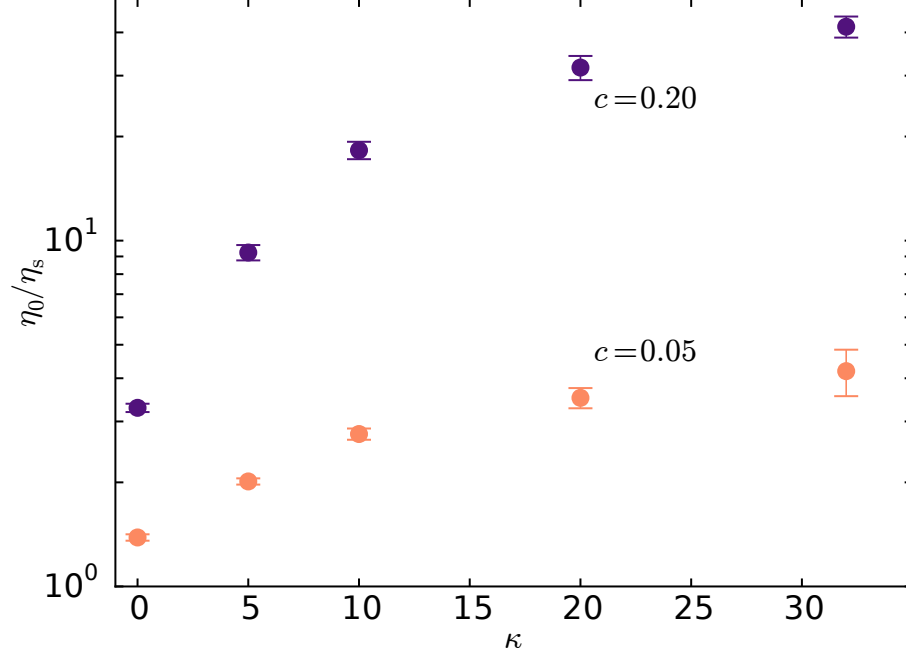


Figure 3.3: Reduced zero-shear viscosity η_0/η_s as function of stiffness κ , η_0 was estimated by fitting RNEMD simulation data to the Cross model (eqn. 3.4).

to be in excellent agreement with estimates obtained from standard linear response analysis. Analysis of η_0 reveals that it is a strong function of polymer stiffness and concentration, varying by as much as an order of magnitude over the range of conditions and parameters examined in our study (Fig. 3.3). These findings are consistent with our recent simulation study examining the dynamics and shear rheology of semiflexible polymers in solution using similar polymer models and computational methods;⁶⁰ we refer interested readers to this study for in-depth discussion of the influence of polymer stiffness and concentration on these solution properties.

We then characterized the structure of the polymer chains as the stiffness κ was varied. Polymer chains are fractal, and their radius of gyration in dilute solution $R_{g,0}$ scales with the number of monomer beads N_m as $R_{g,0} \sim N_m^\nu$, where ν is the excluded volume exponent. For fully flexible chains (i.e., $\kappa = 0$), we found $\nu \approx 0.61$ (Fig. 3.4; Table 3.1), which is in good agreement with theoretical predictions and previous simulation results of self-avoiding chains in a good solvent.^{16,89} As the chain

stiffness increased, the polymer chains became more rod-like, which is reflected by the increasing excluded volume exponent ν . However, ν remained below the physical limit for hard rods ($\nu = 1$) and reached a value of $\nu \approx 0.81$ for the largest investigated stiffness of $\kappa = 32$ (Fig. 3.4; Table 3.1).

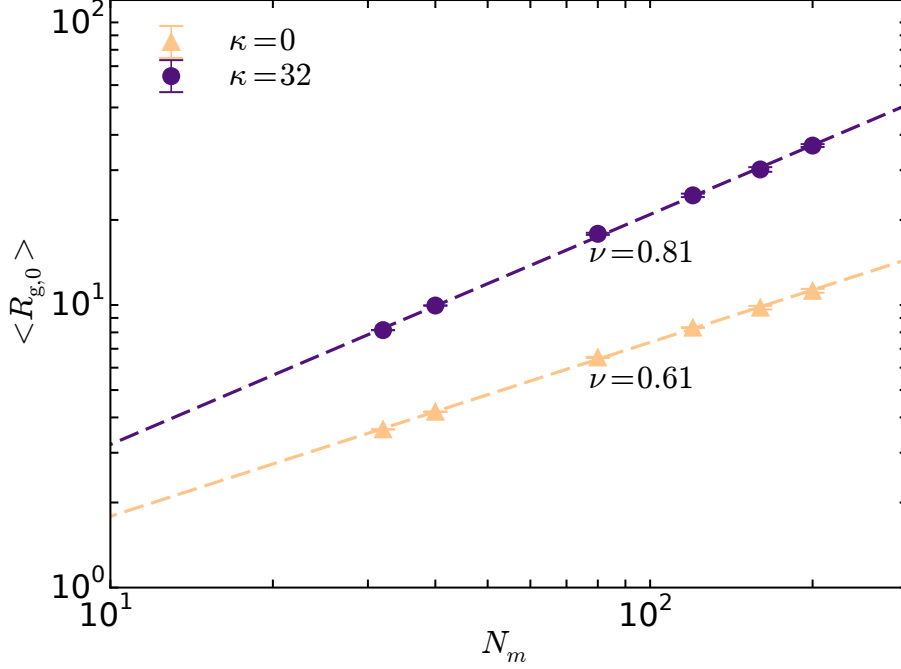


Figure 3.4: Scaling of $R_{g,0}$ as a function of the number of monomer beads N_m with stiffness $\kappa = 0$ (Δ) and 32 ($\circ$). Dashed lines are power law fits.

After confirming that the simulated polymer structure agrees with theoretical predictions, we analyzed the dynamics of the constituents of the suspensions. From the MPCD simulations, we calculated the mean-squared displacement $\langle \Delta r^2 \rangle$ of the monomers in the reference frame of the polymer centers-of-mass (COM), for the polymer COM, and for the dispersed NPs as functions of chain stiffness κ (Fig. 3.5), dashed and solid lines indicate diffusive ($\sim t^1$) and subdiffusive ($\sim t^\alpha, \alpha < 1$) scaling, respectively. For fully flexible chains (i.e., $\kappa = 0$), monomers are hydrodynamically coupled and move according to Zimm dynamics on short time scales with $\langle \Delta r^2 \rangle \sim t^{2/3}$, as expected.¹⁶ As κ increases, the monomers remain hydrodynamically coupled, but the chains become stiffer and their segmental mobility decreases (Fig. 3.5(a)).

The chain stiffness also affects the motion of the polymer COM (Fig. 3.5(b)). On short time scales, the mean-squared displacement of the polymer COM develops a subdiffusive region as κ increases, in which $\langle \Delta r^2 \rangle \sim t^\alpha$ and $\alpha < 1$ is the subdiffusive exponent. On long time scales, the MSD of the polymer COM recovers diffusive scaling $\alpha = 1$ with the diffusivity decreasing with κ due to lower segmental mobility and larger size of the stiffer chains. The motion of the NPs (Fig. 3.5(c)) is qualitatively similar to that of the polymer COM with a pronounced subdiffusive region when dispersed in solutions of stiff chains.

3.3.1 Long-time nanoparticle diffusivity

The effect of polymer stiffness on the dynamics of NPs was further characterized by calculating their long-time diffusivity D and short-time subdiffusive exponent α_{NP} . To facilitate quantitative comparisons with theory, the NP diffusivities measured in the simulations, $D(L)$, were corrected for finite-size effects using¹¹³

$$D = \left(1 - \frac{\zeta \sigma_{\text{NP}}}{3L} \right)^{-1} \times D(L) \approx 1.08 \times D(L), \quad (3.5)$$

where $\zeta = 2.837297$. Eqn. 3.5 corrects for finite-size effects associated with long-range hydrodynamic interactions between periodic images of the simulation box, which vanish as $L \rightarrow \infty$ and are thus not present in infinite systems. This expression is valid for NPs with a slip boundary condition at their surface, but analogous expressions have also been derived for no-slip boundary conditions.¹¹³ For the system considered here ($L = 64$, $\sigma_{\text{NP}} = 5$), the correction is relatively small and increases the diffusivity by $\approx 8\%$.

The values of D from simulation are significantly larger than the diffusivities predicted by the SER (Fig. 3.6, closed symbols in (a) and (b) indicate diffusivities and open symbols in (c) and (d) indicate ratios of diffusivities. Dashed lines in (c) and (d) indicate a diffusivity ratio of unity), indicating that the motions of the NPs are

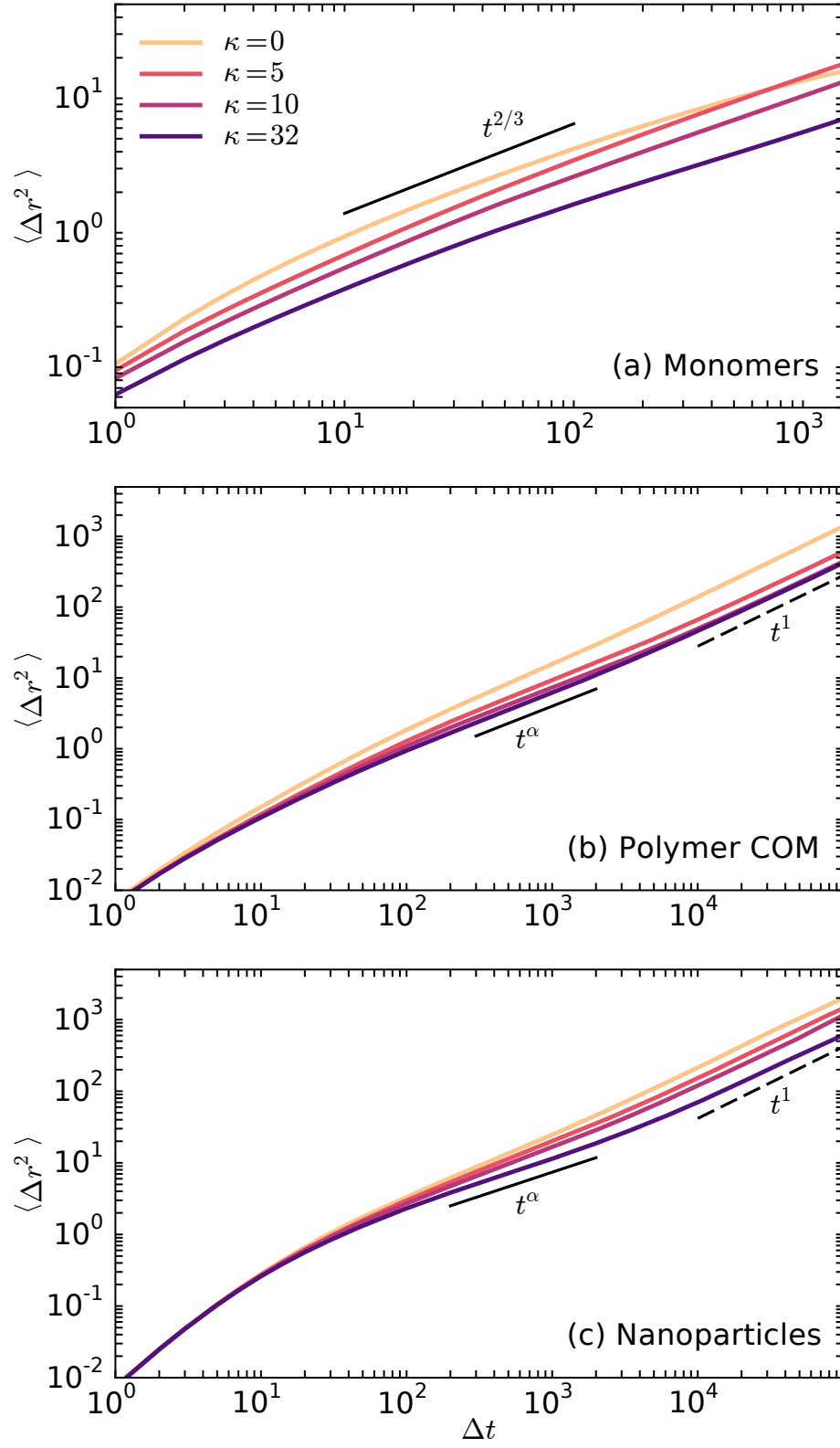


Figure 3.5: Mean-squared displacement $\langle \Delta r^2 \rangle$ as a function of lag time Δt at multiple polymer stiffnesses and monomer concentration $c = 0.20$.

incompletely coupled to the bulk viscosity of the background polymer solutions. Deviations from SER predictions have also been observed in experimental studies performed on NPs in solutions of similarly sized polymers,^{23,26} ranging from $D/D_{\text{SER}} \approx 2$ when $\sigma_{\text{NP}}/2R_{\text{g},0} \approx 0.9$ to $D/D_{\text{SER}} \approx 30$ when $\sigma_{\text{NP}}/2R_{\text{g},0} \approx 0.6$. They arise because the NPs are comparably sized to the polymer chains, which violates the homogeneity assumption underlying the SER.²¹ The deviations from SER predictions become more pronounced as the chains become stiffer, indicating that the NPs become increasingly decoupled from the bulk solution viscosity. For simulations of NPs in solutions of infinitely rigid rods, these deviations were posited to develop because of constraint release mechanisms in the rod matrix.¹¹⁴

We also compared our simulation results to calculations performed using a variant of MCT developed for dense polymer solutions.^{35,36} Details of the MCT calculations follow those in Ref. 35 and are thus not repeated here. Within MCT, the overall NP diffusion coefficient D_{MCT} is written as a sum of hydrodynamic and non-hydrodynamic (microscopic) terms.^{35,36} The former is given by D_{SER} , whereas the latter contribution, D_{micro} , arises due to the coupling of the NP motion to polymer collective density modes.^{35,36} Calculation of D_{micro} requires several structural (NP–monomer and monomer–monomer radial distribution functions and $R_{\text{g},0}$) and dynamical (monomer diffusion coefficient) quantities as input.³⁵ These quantities can be calculated directly from theory,³⁵ but here we use input from the MD–MPCD simulation, as our main interest is to test the approximations inherent in MCT. In computing D_{micro} , we also include the contribution arising from the coupling to the self-transverse current mode given in Ref. 115, which affects the dynamic shear viscosity and has been shown to play an important role in treating diffusion in low-density fluids.¹¹⁵ Although this additional contribution is negligible in dense systems, we nonetheless include it in all MCT calculations and evaluate it using input from the MD–MPCD simulation.

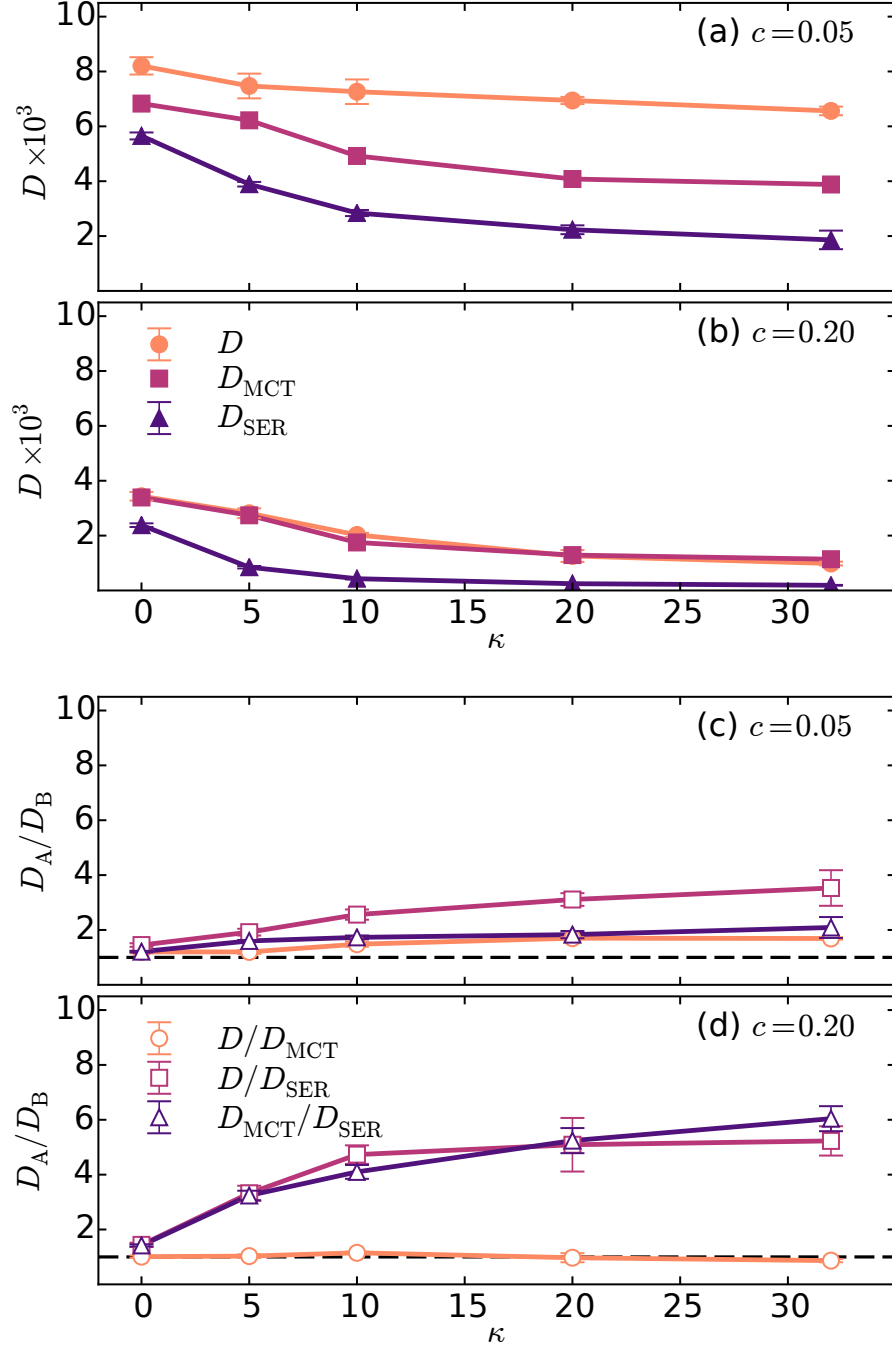


Figure 3.6: NP diffusivity obtained from MD–MPCD simulations with finite size correction following Ref. 113 (D), from MCT calculations (D_{MCT}), and from the SER (D_{SER}).

The relative contributions of D_{SER} and D_{micro} to D_{MCT} depend on polymer concentration for the small particles examined here; D_{SER} is comparable to D_{micro} at low polymer concentrations ($c = 0.05$, Fig. 3.7(a)) but much smaller than D_{micro} at

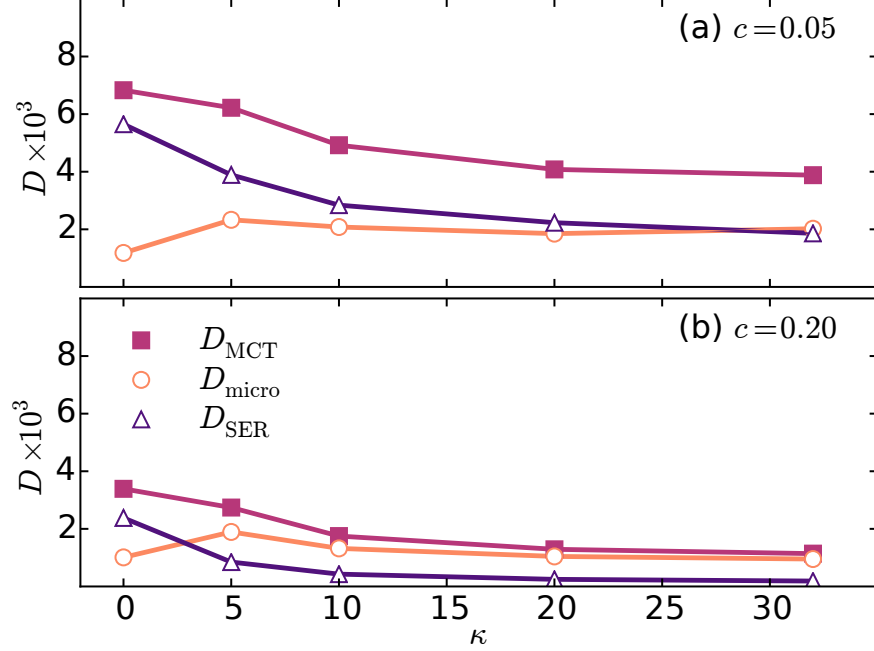


Figure 3.7: NP diffusivity obtained from the MCT calculations broken down into hydrodynamic (D_{SER}) and non-hydrodynamic (D_{micro}) contributions.

high polymer concentrations ($c = 0.20$, Fig. 3.7(b)), as also seen in an earlier MCT study.³⁵ The overall diffusivities D_{MCT} predicted by MCT are in excellent agreement with those calculated from the MD-MPCD simulations (Fig. 3.6) at polymer concentration $c = 0.20$ for all values of κ examined.

For lower concentration $c = 0.05$, however, deviations between MCT and simulation are observed. Even with incorporation of the contribution from the coupling to the self-transverse current mode, MCT systematically underestimates the NP diffusivity at $c = 0.05$. This discrepancy is presumably due to the fact that additional collective modes, which have not been taken into account, are important at these conditions. Nevertheless, the overall agreement with simulation is reasonable, and MCT correctly captures the increasingly significant deviations from SER as the polymers become stiffer.

Lastly, we compared the behavior of the NP diffusivity with predictions from the PCT developed in Ref. 38 for fully flexible polymers to explain deviations from the

SER. This theory assumes that the NPs are locally caged by polymers until the surrounding chains relax over the particle surface. Accordingly, the long-time NP diffusivity is predicted to depend on the length-scale ratio of NP diameter to polymer correlation length σ_{NP}/ξ and to scale as $D/D_0 \sim (\sigma_{\text{NP}}/\xi)^{-2}$, where D_0 is the nanoparticle diffusivity in pure solvent. For $c/c^* > 1$ we used $\xi = R_{g,0}(c/c^*)^{-\nu/(3\nu-1)}$ from scaling theory,¹⁶ where $c^* = 3N_m(4\pi R_{g,0}^3)^{-1}$ is the overlap concentration (Table 3.1). For $c/c^* \leq 1$, we calculated ξ according to the mean geometric separation distance $R_{g,0}(c/c^*)^{-1/3}$. We verified this PCT prediction experimentally²⁶ and with simulations⁸⁹ in previous work for fully flexible chains. By contrast, tests of PCT in computational studies of nanoparticle-polymer composites modeled using flexible chains have yielded inconclusive results.¹¹⁶ Here, we extend tests of this scaling relation to semiflexible polymer systems (Fig. 3.8).

At very low polymer concentrations, the NP diffusivities remain mostly unaffected by the polymers so that $D/D_0 \approx 1$. The diffusivities decrease with increasing polymer concentration solely as a function of length-scale ratio σ_{NP}/ξ . In solutions of flexible chains ($\kappa \approx 0$), the NP diffusivities eventually cross over and scale according to $D/D_0 \sim (\sigma_{\text{NP}}/\xi)^{-2}$ at large σ_{NP}/ξ , in agreement with the PCT predictions of Ref. 38. Similar behavior for flexible chains was also observed in our previous study,⁸⁹ where the agreement with PCT was even more clear due to the use of longer polymer chains ($N_m = 50$), which provided access to larger σ_{NP}/ξ . Slightly shorter chains ($N_m = 32$) were used in this study to avoid approaching the isotropic-nematic transition in systems with stiff chains.⁹¹ For stiffer chains (large κ), however, the NP diffusivities decrease more rapidly and deviate from the predicted scaling. According to PCT, the long-time dynamics depend on the segmental relaxations of the polymer chains. Thus, the different diffusivity dependences likely arise from the slower monomer dynamics of the stiffer chains (Fig. 3.5(a)). As the monomer dynamics slow down with increasing κ , the time required for the polymer mesh to relax over the particle

surface increases. This longer relaxation thereby slows the long-time NP motion.

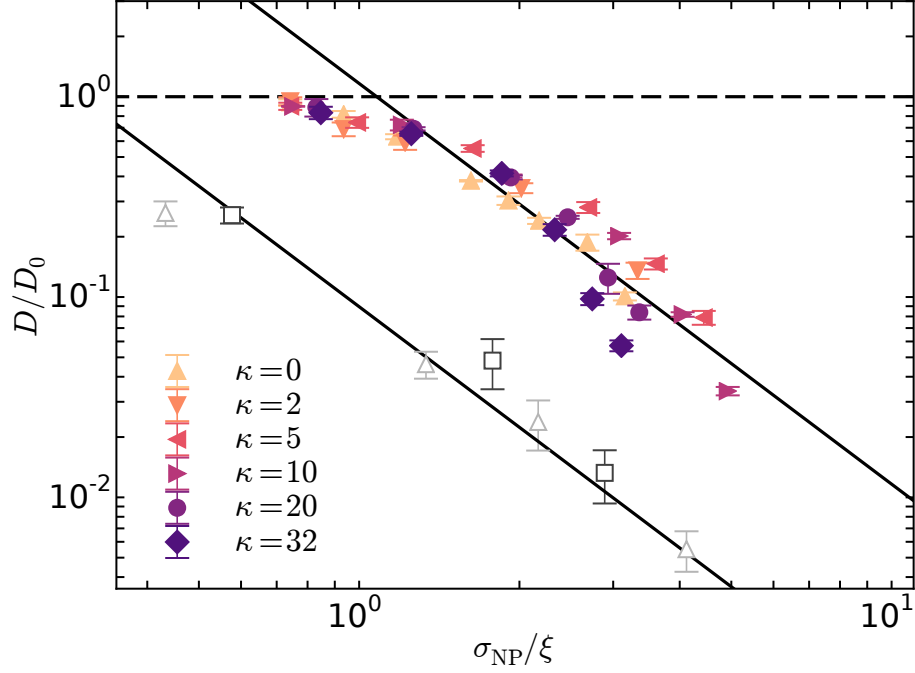


Figure 3.8: Normalized NP diffusivity D/D_0 as a function of size ratio σ_{NP}/ξ . Open symbols are experimental data from Ref. 26 with $\sigma_{\text{NP}}/2R_{g,0} = 0.56$ (Δ), 0.74 ($\square$). Solid lines are scaling predictions (Ref. 38) $D/D_0 \sim (\sigma_{\text{NP}}/\xi)^{-2}$.

3.3.2 Short-time subdiffusion

Beyond segmental mobility, the dynamics of the polymer COM also play an important role in controlling the subdiffusive motion of dispersed NPs.⁸⁹ For flexible chains, both Rouse and Zimm theories assume that the COM of polymer chains move diffusively on all time scales.¹⁶ Experimentally, however, the COM dynamics of polymers deviate from this diffusive assumption and move subdiffusively on short time scales.⁷⁵ Our simulations reveal that the subdiffusive dynamics of the polymer COM depend on both polymer concentration and chain stiffness (Fig. 3.9). For both concentrations, the subdiffusive exponent α_P for the polymer COM initially decays with increasing κ before reaching a plateau. Higher polymer concentrations lead to lower values of α_P for all κ . The NP subdiffusive exponent α_{NP} also decreases as the polymer concentration and κ are increased, similar to α_P . It does not, however, reach a

plateau at high κ for the higher polymer concentration ($c = 0.20$), unlike α_P .

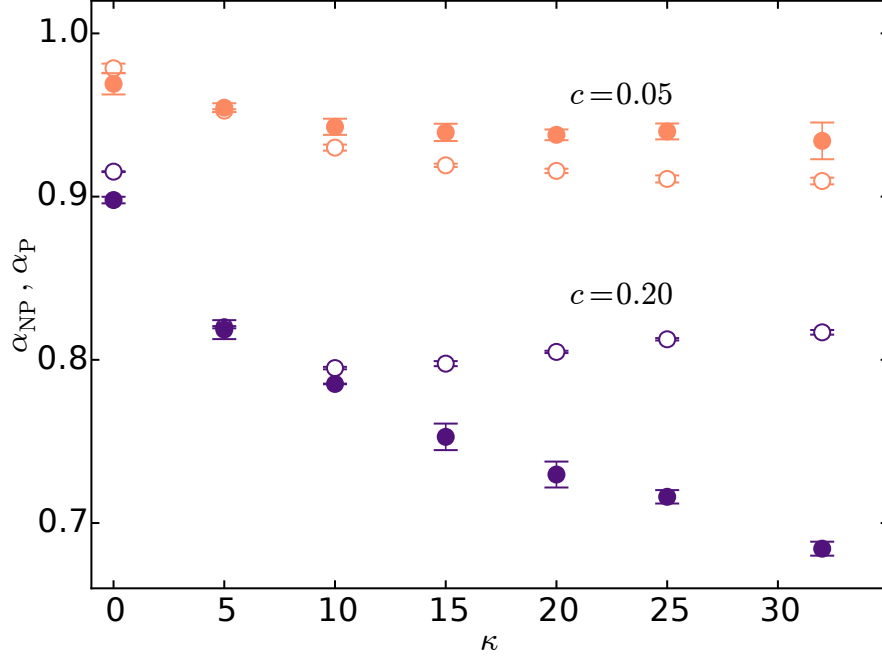


Figure 3.9: Subdiffusive exponent of NPs α_{NP} (closed) and polymer centers-of-mass α_P (open) as a function of bending constant κ , for monomer concentrations of $c = 0.05$ (orange) and $c = 0.20$ (purple).

When particles are much larger than characteristic length scales in the polymer, ($\sigma_{NP} \gg 2R_{g,0}$), their short-time dynamics directly follow the segmental relaxations of the free polymer. This coupling results in subdiffusive particle dynamics in the microrheological limit, with $\alpha_{NP} = 0.5$ in solutions of flexible polymer^{26,38,73} and $\alpha_{NP} = 3/4$ in solutions of semiflexible chains.^{97,98} The PCT developed for smaller (nano)particles in Ref. 38 still assumes direct coupling of the NP to segmental relaxations of the surrounding polymer chains on short time scales, so that α_{NP} exhibits a step change and abruptly decreases from 1 to 0.5 at $\sigma_{NP}/\xi = 1$ (Fig. 3.10, open symbols are experimental data from Ref. 26 with $\sigma_{NP}/2R_{g,0} = 0.56$ (Δ), 0.74 ($\square$), dashed lines are predictions from PCT in solutions of flexible polymer chains.³⁸). For flexible chains, such a step change is not observed in experiments²⁶ or simulations.⁸⁹ Instead, α_{NP} smoothly decreases as the size ratio σ_{NP}/ξ increases. For stiff chains,

the shape of this decay changes (Fig. 3.10). At low polymer concentrations, α_{NP} decreases with increasing polymer concentration independent of κ . At higher polymer concentrations (i.e., larger σ_{NP}/ξ), the NP dynamics become increasingly subdiffusive with increasing polymer stiffness. The steeper decays suggest that the NP dynamics couple differently to the segmental mobility of stiffer chains.

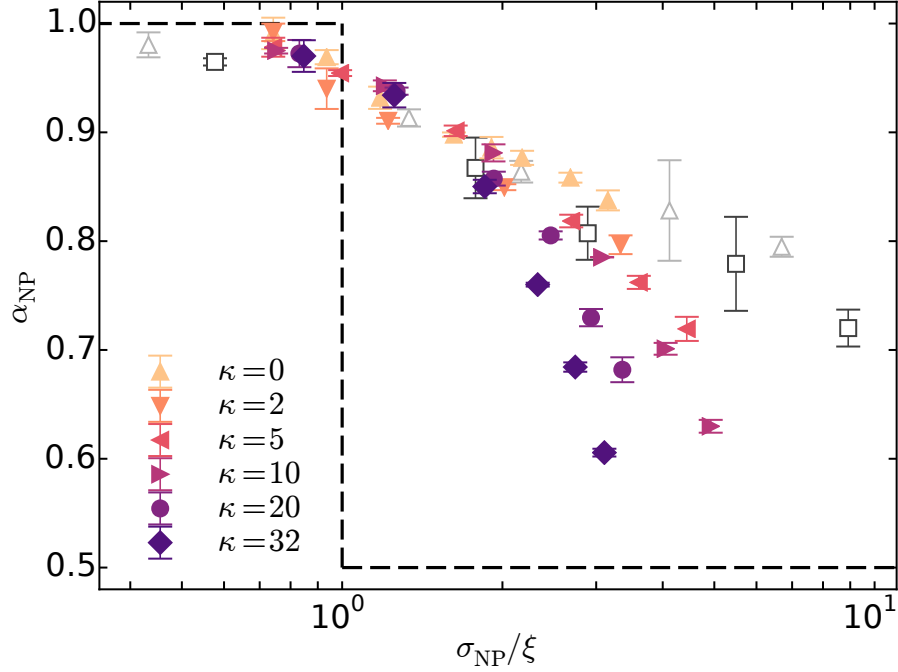


Figure 3.10: Subdiffusive exponent of NPs α_{NP} as a function of particle diameter σ_{NP} to polymer correlation length ξ size ratio for chains with varying stiffness κ .

In previous work,⁸⁹ we attributed the deviation from scaling predictions on short time scales to the coupling of the NP dynamics to both the segmental relaxations of the polymer chains and to the dynamics of the polymer COM. To assess the degree to which NP dynamics couple to segmental relaxations and the dynamics of polymer COM in solutions of semiflexible chains, we analyze the correlation between α_{NP} and α_{P} (Fig. 3.11). At low polymer concentrations, the dynamics of the NPs and polymer COM are largely diffusive for all κ with $\alpha_{\text{NP}} = \alpha_{\text{P}} \approx 1$. As the polymer concentration increases, α_{NP} decreases concomitant with α_{P} for all κ , indicating that the NP

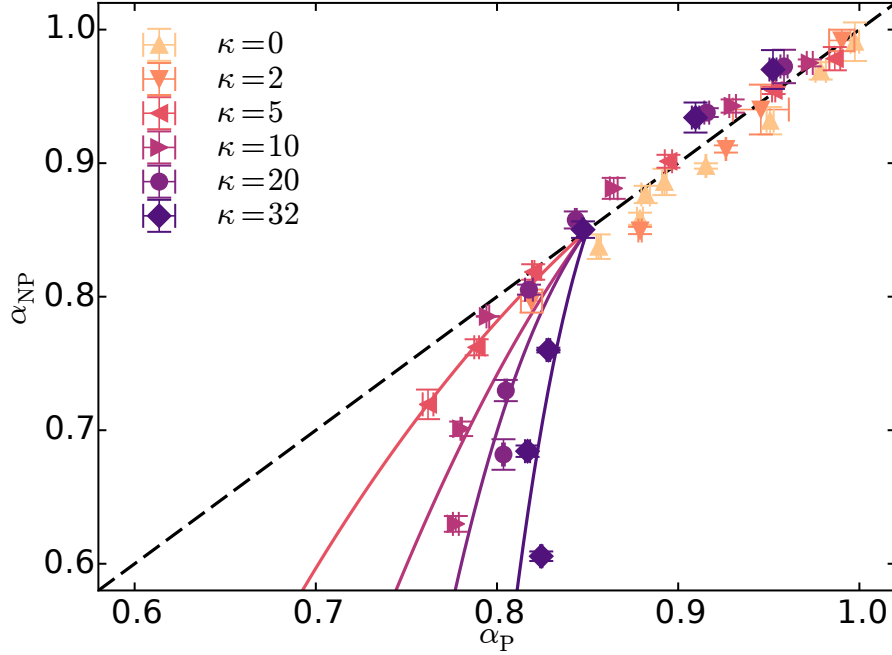


Figure 3.11: Correlations between subdiffusive exponent of NPs α_{NP} and polymer centers-of-mass α_{P} for polymers with varying stiffness κ . Dashed line indicates $\alpha_{\text{NP}} = \alpha_{\text{P}}$.

and polymer COM dynamics are correlated in these solutions. At higher polymer concentrations, however, α_{NP} decouples from α_{P} and decreases more rapidly with increasing chain stiffness. The stronger subdiffusion of NPs in solutions of stiff chains is a marked difference from the predicted microrheological behavior of micron-sized particles in solutions of semiflexible chains in which $\alpha_{\text{NP}} = 3/4$.^{97,98} The decorrelation of the short-time dynamics of nanoparticles and polymer COM suggests that the NPs couple more strongly to the decreased monomer dynamics of the surrounding chains in solutions of semiflexible chains. This hypothesis is consistent with the steeper decay of α_{NP} with polymer concentration shown in Fig. 3.10.

3.4 Conclusions

Understanding the effects of polymer stiffness on NP transport is critical to improving the efficacy of composite processing and drug delivery. Here, we performed hybrid MD-MPCD simulations of semidilute solutions of polymers with tunable stiff-

ness to investigate the influence of polymer flexibility on the dynamics of NPs of comparable size. The NPs exhibit subdiffusive dynamics on short time scales and diffusive dynamics on long time scales. With increasing polymer stiffness the long-time diffusivities of the NPs more markedly deviate from the SER, consistent with decoupling from the bulk polymer solution viscosity, and from PCT, which was developed for flexible polymers. The long-time diffusivities are adequately predicted by MCT, however, especially at high concentrations of the polymers where the theory is expected to be most accurate. On short time scales, the dynamics of the NPs become progressively more subdiffusive and decouple from the dynamics of the polymer chain COM as the stiffness of the polymer chains is increased. These changes in dynamics likely arise from differences in the segmental relaxations of the semiflexible chains. We anticipate that these predictions can be tested experimentally using, e.g., nematic elastomers,^{117,118} dendronized polymers,¹¹⁹ or the well-characterized biopolymers ds-DNA or actin. Finally, the results from our computational study may aid in extending existing theories for describing NP transport in systems of flexible chains (e.g., PCT) to solutions of stiff and semiflexible polymers.

Chapter 4: Effect of polymer morphology: nanoparticle dynamics in ring polymer solutions

4.1 Introduction

As discussed in the previous chapters, the study of nanoparticle (NP) transport in polymer solutions is an active research field with relevance to a variety of problems^{1–8} in science and industry. Our previous simulation study revealed a hitherto unreported dynamic coupling mechanism in which the short-time motions of NPs couple to the center-of-mass (COM) motions of fully flexible polymers in semidilute solutions.⁸⁹ We subsequently observed a breakdown of this coupling mechanism in solutions of semiflexible polymers – the COM motions of NPs and polymers were found to gradually decouple as the polymer backbone stiffness increased and the chain morphology shifted from coil-like to more elongated, rod-like conformations.¹²⁰ This key result suggests that polymer morphology may strongly influence NP-polymer coupling in semidilute solutions. Indeed, polymers with a wide variety of chain architectures, ranging from linear to star-shaped morphologies, can be synthesized. Ring polymers are a particularly intriguing system that have received considerable attention because similar circular morphologies have been observed in biologically relevant macromolecules such as DNA.^{121–123} Studies show that the closed conformations of ring polymers lead to structural and dynamical properties that differ from those of systems with linear chains.^{122–127} Free chain ends play an important role in polymer behavior and in development of theoretical models for polymers, such as the reptation model for linear polymers¹²⁸ and the back-folding model for branched polymers.¹²⁹ The absence of free ends poses unique challenges in developing theoretical models for ring polymers. As a result, many aspects of ring polymers

remain poorly understood from a theoretical perspective.

It has been suggested that statics and dynamics of ring polymers are self-similar,¹³⁰ that is, similar conformations and motions are observed in any part of the chain due to the circular symmetry along the contour length of the ring. Early theories^{131–133} for describing the conformations and motions of a ring polymer were inspired by the de Gennes¹²⁸ reptation model of a linear polymer, which describes motions of the entire molecule in terms of motions of “diffusing kinks” along the chain. Deviating from the Gaussian-like linear chains, relatively compact structure¹²⁵ is observed for ring polymers and interpenetration is not entropically preferred. Cates and Deutsch¹³¹ presented a Flory-like theory suggesting that the radius of the ring scales as $R \sim N^{2/5}$. Grosberg¹³⁴ described the ring as a crumpled globule with a fractal dimension of 3. Theories for ring polymer dynamics have been proposed based on the “diffusing kinks” picture¹³⁵ and Rouse dynamics.¹³⁶ Although the diffusion coefficient of a ring polymer scales with contour length in a similar way to that of a linear chain,^{131–133,135} the relaxation mode is quite different due to the absence of free ends. A subsection of the ring relaxes immediately once any of the segments relaxes, whereas only those segments close to the chain ends relax as rapidly for linear and branched polymers.

Knotting behavior is a second unique feature of ring polymers. Concatenated rings that are irreversibly linked never relax over each other due to their permanent topological constraints. For nonconcatenated rings, by contrast, no permanent constraints exist,¹³⁷ and deviations from linear chain behavior arise solely from their closed conformations. Nonconcatenated ring polymers in a melt or solution are better understood as they are considered good models of chromatin and thus have been widely investigated.^{125,126,130,138} Although not as widely studied, the effects of interlinking and knot concentration have also been explored.^{139,140}

Despite these efforts, however, a clear description of both the statics and dynam-

ics of ring polymers remains elusive. This knowledge gap is due in part to the difficulty in precisely controlling inter-linking between rings in experimental systems and difficulty in simulating sufficient long chains in computational studies. Nonetheless, recent attempts have been made to understand NP transport in ring polymer systems. Ge and Rubinstein¹³⁸ used simulation to study the motions of NPs in entangled melts of nonconcatenated ring polymers. They found that NP motions are not as strongly suppressed as in melts of linear chains. They attributed the faster NP dynamics to the absence of long-lived entanglement tubes in ring polymers, which restrict polymer relaxations in linear melts. Here, we perform an analogous computational study, but in unentangled semidilute solutions, where solvent-mediated hydrodynamic interactions are expected to play a role in dictating how chain morphology influences dynamic coupling between NPs and polymers.

4.2 Simulation methodology

Similar to our previous studies,^{89,120} we performed simulations of NP-polymer solutions using our LAMMPS-based⁶⁴ implementation of the hybrid of molecular dynamics (MD) and multi-particle collision dynamics (MPCD) algorithm. Following our recent studies, NPs are modeled as soft spheres with diameter $\sigma_{\text{NP}} = 5$ and polymers are described using the Kremer-Grest (KG) bead-spring model.¹⁰¹ Excluded volume interactions are modeled using the shifted Weeks-Chandler-Andersen (sWCA) potential⁶³

$$U_{\text{sWCA}}(r_{ij}) = \begin{cases} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij} - \Delta_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij} - \Delta_{ij}} \right)^6 \right] + \epsilon_{ij}, & r_{ij} \leq r_{ij}^c, \\ 0, & r_{ij} > r_{ij}^c \end{cases}, \quad (4.1)$$

where r_{ij} is the separation distance between particles i and j and $\epsilon_{ij} = 1$ is the energy scale that sets the strength of the interactions. The cutoff distance $r_{ij}^c = 2^{1/6}\sigma_{ij}$ ensure that the interactions are purely repulsive. Parameters $\sigma_{ij} = \sigma_{\text{NP}}$, $\sigma_{ij} = \sigma_{\text{P}}$ and $\Delta_{ij} = 0$ are used for NP–NP and polymer (P) monomer–monomer interactions,

whereas $\sigma_{ij} = \sigma_P$ and $\Delta_{ij} = (\sigma_{NP} - \sigma_P)/2$ are used for the NP–monomer interactions.

Spring-like bonds between adjacent monomers on the polymer chains are modeled using the finitely extensible nonlinear elastic (FENE) potential,⁶²

$$U_{\text{FENE}}(r_{ij}) = \begin{cases} -\frac{1}{2}kr_0^2 \ln \left[1 - \frac{r_{ij}^2}{r_0^2} \right], & r_{ij} \leq r_0 \\ \infty, & r_{ij} > r_0 \end{cases}, \quad (4.2)$$

with $k = 30$ and $r_0 = 1.5$ as the maximum bond extension length.

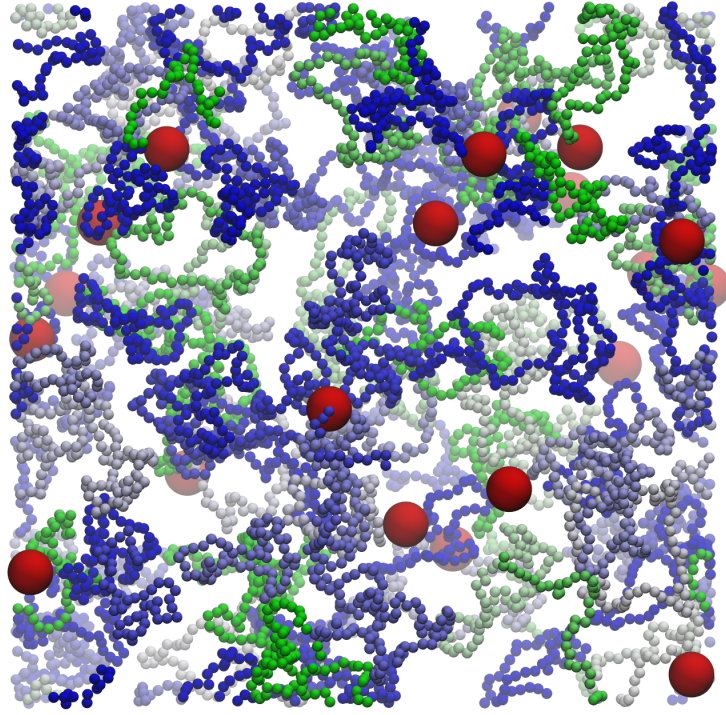


Figure 4.1: Nanoparticles (red) in ring polymer solutions (colored by index), rendered with Visual Molecular Dynamics 1.9.3.¹⁰⁵

Models of nonconcatenated ring polymers are built by simply adding a bond between the first and last monomer beads of linear polymer chains (Fig. 4.1). Following refs. 125 and 126, a weak constraint is applied to the bond angles with the bending potential^{59,60,102–104}

$$U_{\text{bend}}(\Theta_{ijk}) = \kappa(1 - \cos \Theta_{ijk}), \quad (4.3)$$

where parameter κ , which is related to the persistence length,⁵⁹ is set to 1.5 to introduce a small degree of chain stiffness.

To facilitate comparison between NP dynamics in solutions filled with ring and linear polymers, we set the number of monomer beads per chain to $N_m = 70$ for ring polymers and $N_m = 42$ for linear chains. These choices yield ring and linear chains with approximately the same radius of gyration $R_{g,0} \sim 5.0\sigma_P$ at infinite dilution, which is equivalent to the diameters of the NPs used in our simulations. Additional parameters used to model the NP-polymer systems in our study are listed in Table 4.1.

Table 4.1: Parameters for the model ring and linear polymer solutions simulated in this study.

System	N_m	L_{box}	c/c^*	ξ
Ring	70	64.0	0.2 (min)	10.66
Ring	70	64.0	4.0 (max)	2.38
Linear	42	64.0	0.2 (min)	13.97
Linear	42	64.0	6.0 (max)	2.55

Notes: $c^* = 3N_m(4\pi R_{g,0}^3)^{-1}$ is the overlap concentration; L_{box} is the edge length of the cubic simulation cell; $\xi = \sqrt{3/(vL)}$ is the mesh size of the polymer network (where v is the number of chains per unit volume and L is the contour polymer length).

Initial configurations for the ring polymer systems were built to avoid ring concatenation. The NP-polymer systems were first equilibrated by running Langevin dynamics for a period of $\approx 3 \times 10^5 \tau$. Final configurations from the Langevin dynamics simulation were subsequently used to initialize the MPCD simulations, which were run for an additional $\approx 3 \times 10^5 \tau$. Integration time steps of $dt = 0.005\tau$ were used in both the Langevin dynamics and MPCD simulations. Three independent MPCD simulations (each with 20 NPs) were run for each polymer solution examined. Thus, statistical quantities were computed by averaging over 60 NP trajectories for each system. The remaining simulation parameters are identical to those reported in Chap. 3.

4.3 Results and discussions

From the MPCD trajectories, we calculated mean-squared displacements (MSDs) for the NPs, for the ring polymer monomers in the chain COM reference frame, and for the COM of rings (Fig. 4.2). The segmental dynamics are Zimm-like at short time scales, as indicated by the $t^{2/3}$ scaling of the monomer MSDs at early times. The eventual crossover to $t^{1/2}$ scaling indicates the Rouse dynamics are recovered at longer times as hydrodynamic correlations decay. Remarkably, no significant qualitative differences are observed between the MSDs computed in solutions of ring and linear polymers (Fig. 4.3). Although qualitatively similar, the dynamics in the ring polymer solution are slower than those in the system with linear polymer chains. The slow relaxations in the ring polymer solutions are due to the high monomer concentration in these systems. Despite having the same $R_{g,0}$, the ring polymers contain more monomers per chain than the linear polymers and hence yield solutions with higher monomer densities at the same reduced concentration c/c^* . The higher monomer densities frustrate relaxation, leading to slower dynamics in the ring polymer solutions.

As discussed in the previous chapters, polymer coupling theory³⁸ (PCT) assumes that nearby polymer chains present an infinite energy barrier to NP diffusion. As a result, NPs have to wait until the polymer chains relax to be able to escape the local cage created by the surrounding polymers. According to this picture, the terminal diffusivities of NPs depend on the relaxation of polymer matrix, and scale as a power-law function of the NP diameter to polymer matrix mesh size ratio $D/D_0 \sim (\sigma_{\text{NP}}/\xi)^{-2}$, where D_0 is the diffusivity in the absence of polymers. To test this prediction, we estimate the mesh size using $\xi = \sqrt{3/\nu L}$, where ν is the number of chains per unit volume and L is the contour length. This definition of mesh size is derived purely from geometric considerations and it is independent of polymer morphology. Thus it provides a consistent definition of ξ for analyzing solutions of ring and linear poly-

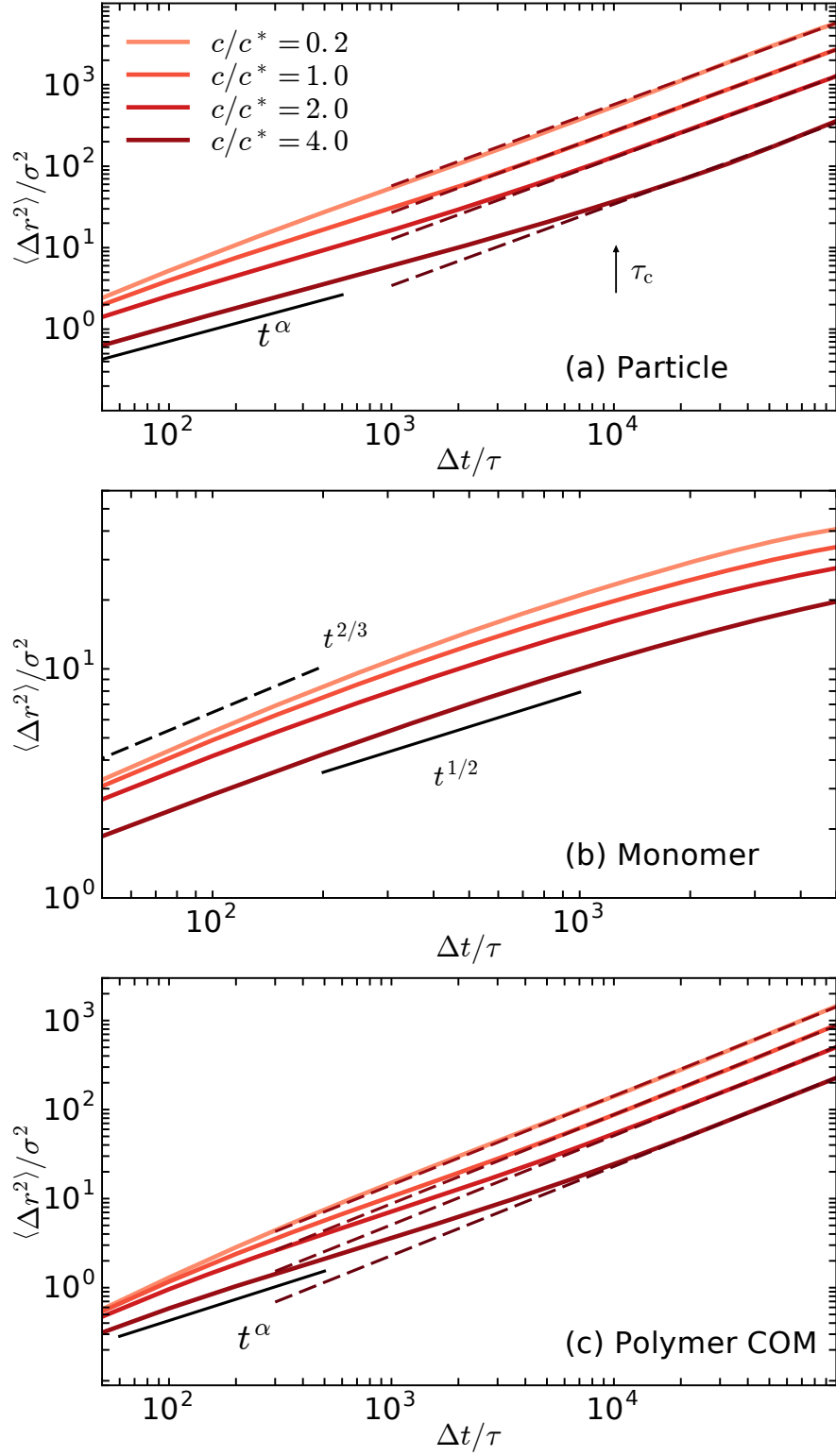


Figure 4.2: Mean-squared displacement $\langle \Delta r^2 \rangle$ for (a) nanoparticles, (b) monomers in the polymer COM reference frame, and (c) polymer COM in ring polymer solutions.

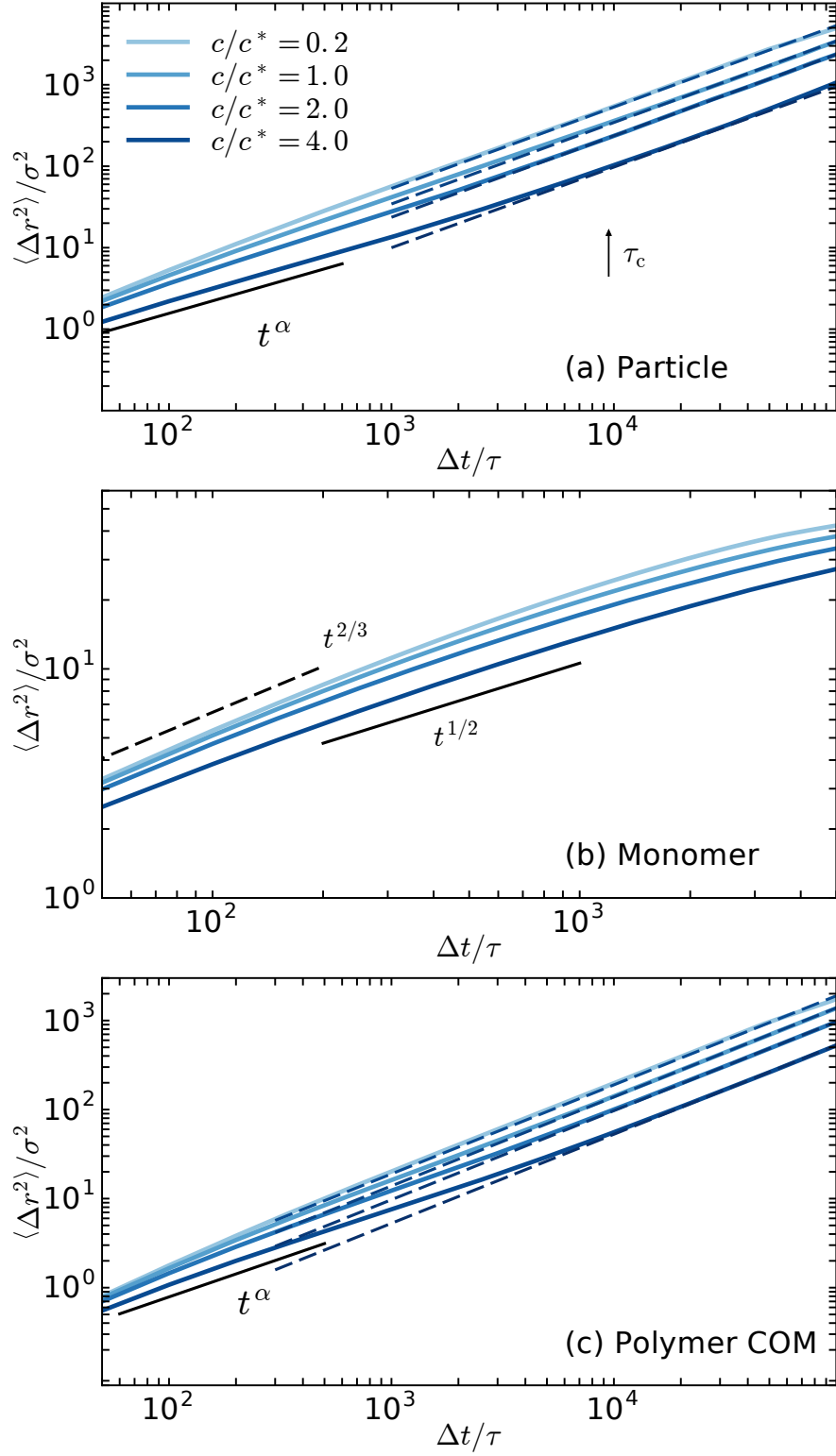


Figure 4.3: Mean-squared displacement $\langle \Delta r^2 \rangle$ for (a) nanoparticles, (b) monomers in the polymer COM reference frame, and (c) polymer COM in linear polymer solutions.

mers. Because all of the calculations are performed using NPs of the same size, the ratio σ_{NP}/ξ is varied across different simulations by changing the polymer concentration and hence ξ .

In our previous studies,^{89,120} we found that the PCT scaling prediction for D/D_0 is obeyed in solution of fully flexible polymers for $\sigma_{\text{NP}}/\xi \geq 1$. Increasing violations of this scaling law were observed, however, as polymer stiffness was increased, indicating that the NPs moved slower than predicted¹²⁰ for large σ_{NP}/ξ . This behavior was not entirely surprising because polymer segmental relaxations become slower with increasing chain stiffness. Hence, if long-time NP dynamics are coupled to these segmental relaxations, they should also become increasingly sluggish as chain stiffness increases.

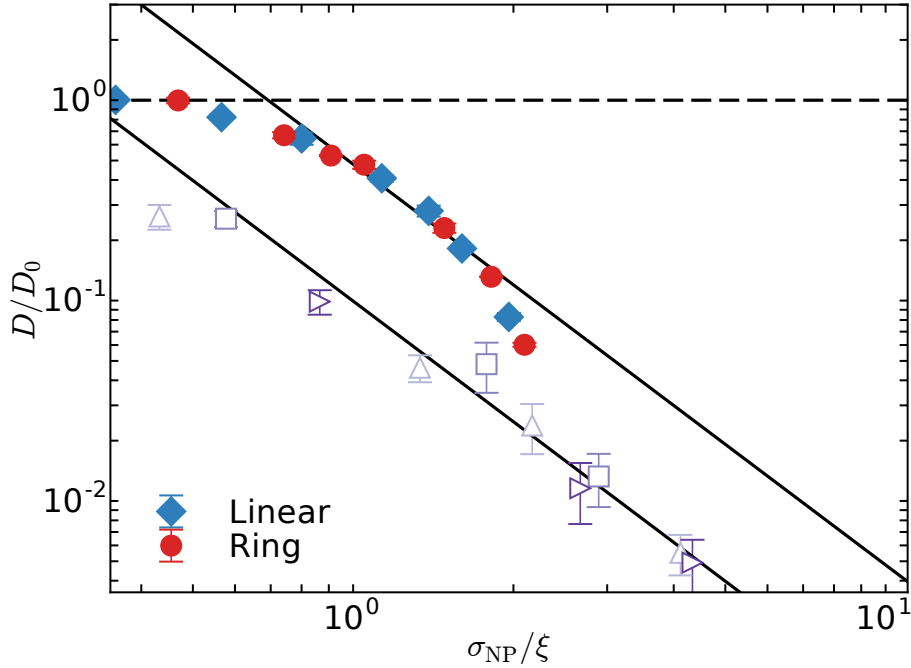


Figure 4.4: Normalized nanoparticle diffusivity D/D_0 in ring (red circles) and linear (blue diamonds) polymer solutions.

Figure 4.4 shows the long-time NP diffusivities in solutions of ring and linear polymers. For comparison, experimental data from Ref. 26 are shown (open symbols with $\sigma_{\text{NP}}/2R_{g,0} = 0.56$ ($\triangle$), 1.5 ($\triangleright$), and 3.7 ($\square$)) along with the PCT scaling predic-

tion³⁸ $D/D_0 \sim (\sigma_{\text{NP}}/\xi)^{-2}$ (solid lines). The results reveal that the long-time NP diffusivities obey the predicted scaling behavior for $\sigma_{\text{NP}}/\xi \geq 1$, independent of polymer morphology. Even more surprising is the fact that, for a given size ratio σ_{NP}/ξ , the values of the long-time diffusivities are similar in both types of solutions. For a given σ_{NP}/ξ , the ring and linear polymer solutions have the same monomer density. Under such conditions, the ring polymers are expected to relax faster than linear polymers with the same contour length (same number of monomers, N_m) due to the absence of free chain ends. The relaxation time, however, is also a function of the chain contour length, and in our simulations the ring polymers contain more monomers than the linear chains (N_m is 70 and 42 for the ring and linear polymers, respectively). Hence, we posit that these two competing effects (i.e., polymer morphology and chain length) may offset each other, resulting in comparable relaxations times for ring and linear polymers in solutions with similar monomer densities.

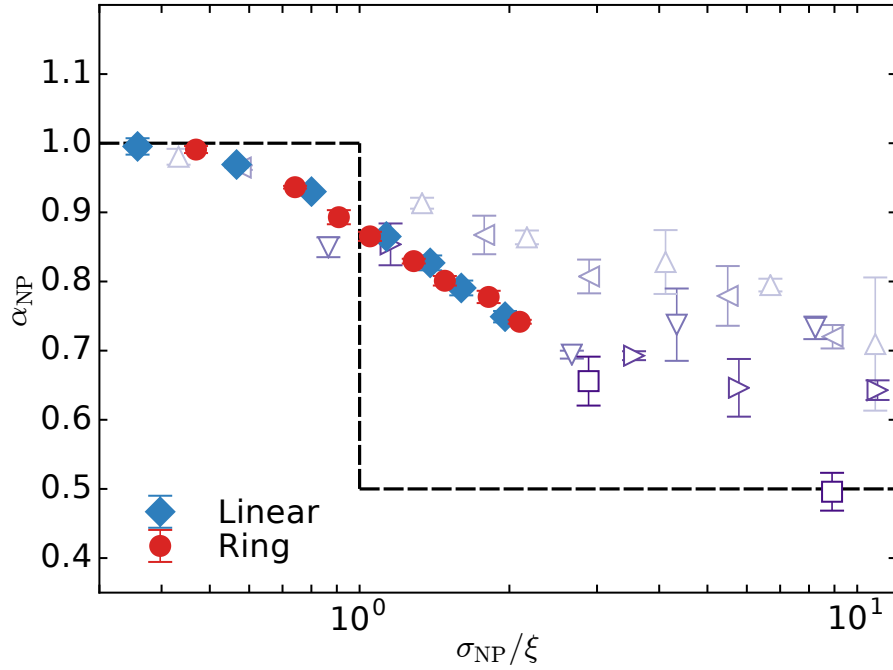


Figure 4.5: Subdiffusive exponents α_{NP} for nanoparticle as function of size ratio σ_{NP}/ξ in ring (red) and linear (blue) polymer solutions.

Figure 4.5 shows the subdiffusive exponents for the NPs in the ring and linear

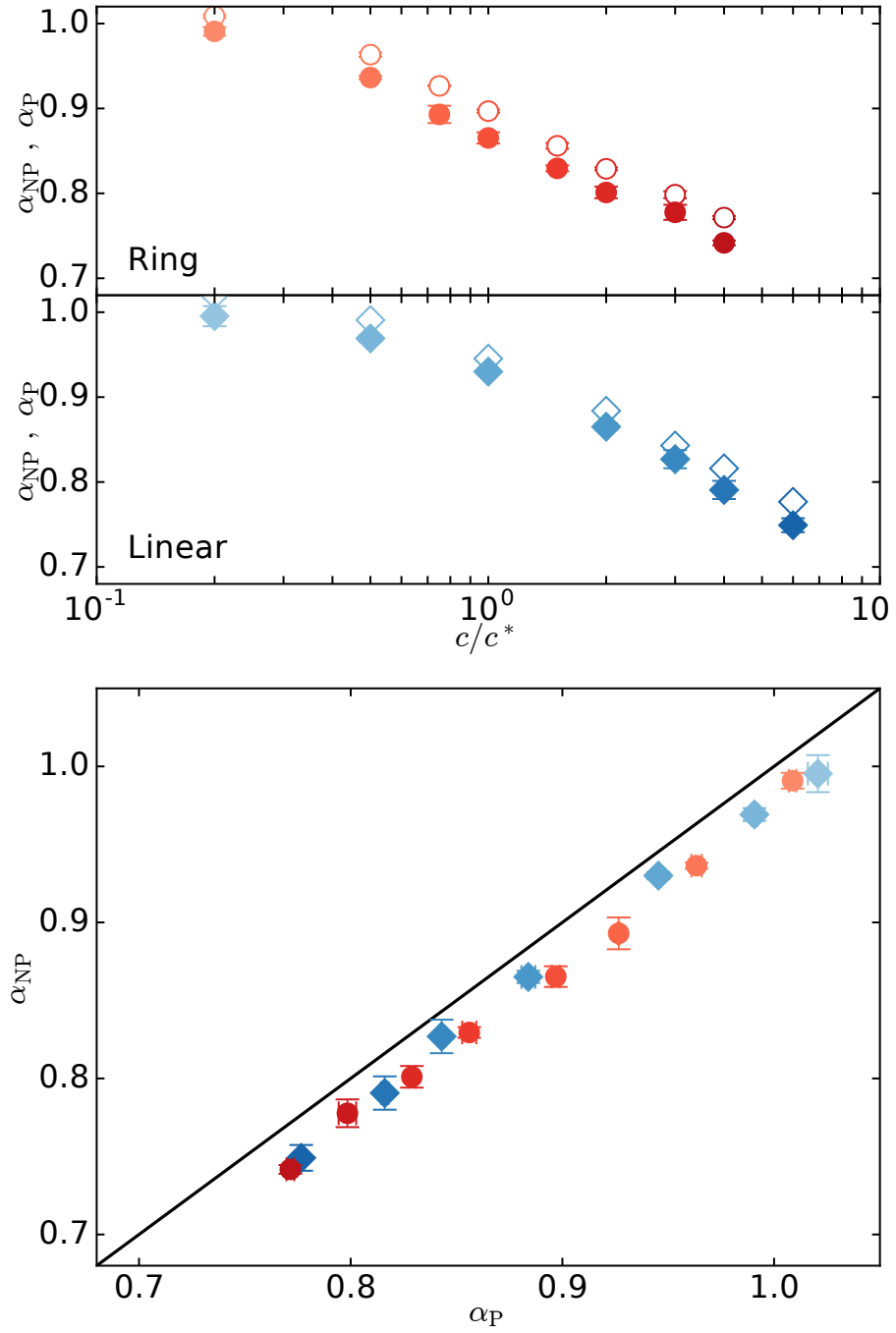


Figure 4.6: Subdiffusive exponents α_{NP} for nanoparticle as function of polymer concentration (top), α_{NP} and α_P correlation (bottom).

polymer solutions as a function of the size ratio σ_{NP}/ξ . Open symbols in Fig. 4.5 are experimental data from Ref. 26 for particles with $\sigma_{\text{NP}}/2R_{\text{g},0} = 0.56$ (Δ), 0.74 ($\triangleleft$), 1.1 (∇), 1.5 ($\triangleright$), and 3.7 ($\square$). The dashed line is the prediction from the PCT,³⁸ which posits that α_{NP} should abruptly decrease from 1 to 0.5 at $\sigma_{\text{NP}}/\xi = 1$ due to complete coupling of the NPs with the polymer segmental relaxations. In accord with our previous studies^{89,120} and experiment,²⁶ however, we observe that the short-time NP dynamics in both the ring and linear polymer solutions deviate from PCT predictions. Rather than abruptly changing, the subdiffusive exponents gradually decay as the size ratio σ_{NP}/ξ increases. Moreover, as with the long-time diffusivities, the close numerical agreement between the NP subdiffusive exponents in the ring and linear polymer solutions suggests that this behavior is insensitive to polymer morphology for the chain sizes and range of σ_{NP}/ξ examined in this study.

Finally, Fig. 4.6 shows the subdiffusive exponents for the NPs (α_{NP} , closed symbols) and polymer COM (α_{P} , open symbols). We find that α_{NP} and α_{P} exhibit a very similar concentration dependence (top panel), suggesting a tight coupling between the subdiffusive dynamics of the NPs and polymers, which is consistent with our previous study on solutions of flexible polymers.⁸⁹ Evidence of coupling can be seen more clearly by examining the dependence of α_{NP} on α_{P} (bottom panel). The data for both the ring and linear polymer solutions fall onto the same straight line, indicating that the degree of NP–polymer coupling on short time scales is similar in both systems and remarkably insensitive to polymer morphology. In our analogous study of semiflexible linear chains, by contrast, we observed a decoupling of α_{NP} and α_{P} as chain stiffness was increased. While this could be due to the change in morphology of the polymers from coil-like to rod-like as stiffness is increased, the data here suggest that size (i.e., radius of gyration) rather than morphology may be the dominant factor. Indeed, as the stiffness of linear chains is increased, their radius of gyration also increases, which could provide an explanation for the decoupling between the

NP and polymer subdiffusive exponents observed in those systems. When the radius of gyration is controlled, by contrast, as is the case of the similarly-sized ring and linear polymer solutions examined here, polymer morphology does not seem to strongly influence NP–polymer coupling on subdiffusive time scales. The hypothesis that the polymer radius of gyration is the dominant factor controlling NP–polymer coupling on short-time is speculative at this point, but it is an interesting avenue for potential future investigation.

4.4 Conclusions

To understand the effect of polymer morphology on NP dynamics in polymer solutions, we performed simulations with nonconcatenated ring polymers and linear chains of the same coil size. No significant difference is observed for both NP and polymer dynamics in linear or ring polymer solutions on either short or long time scales. Both NP and polymer COM exhibit a transition from subdiffusive to diffusive dynamics, and the transition happens approximately on the same time scale in solutions of linear and ring polymers. As we previously observed for linear flexible polymers,⁸⁹ the short-time dynamics of NPs and polymer COM are coupled for ring polymers. We hypothesize that the striking similarity between the concentration dependence of α_{NP} and α_{P} in solutions of linear and ring polymers indicates that the size of polymer chains plays a dominant role in controlling the coupling between nanoparticle and polymer dynamics. Additional studies of the dynamics of nanoparticles in polymers of various sizes and monomer densities are needed to fully elucidate the role of polymer morphology on nanoparticle dynamics.

Chapter 5: Conclusions and future work

5.1 Conclusions

The work presented in this thesis was motivated by the challenges faced in understanding nanoparticle transport through complex fluids, a scenario that is encountered in a wide variety of scientific and applied settings. To develop fundamental understanding, we performed hybrid MD-MPCD simulations to study nanoparticle diffusion in polymer solutions. Our analysis focused on investigating how the dynamic coupling between nanoparticles and polymer chains influences transport behavior under quiescent conditions. In agreement with experiment, we found that the nanoparticles exhibit subdiffusive dynamics on short time scales and normal Fickian diffusion on long time scales. The long-time Fickian diffusivities collapse onto the power-law relationship predicted by a recent coupling theory,³⁸ which assumes that the nanoparticle dynamics fully couple to polymer segmental relaxations. As also observed in experiment,²⁶ however, coupling theory fails to accurately predict the short-time dynamics of the nanoparticles in simulation. Our analysis suggests that this discrepancy arises from an extra nanoparticle-polymer coupling mechanism that is not accounted for in the theory. In addition to coupling to polymer segmental relaxations, our simulations suggest that nanoparticle motions also couple to the center-of-mass dynamics of the polymers on short time scales. This hitherto unreported coupling mechanism is not accounted for in current theories and thus it explains the breakdown of their predictive capabilities in describing the short-time dynamics of nanoparticles in polymer solutions. Moreover, we found this new coupling mechanism is enhanced by many-body hydrodynamic interactions, suggesting that it is necessary to model these interactions using advanced methods such as MPCD when

studying nanoparticle transport in these systems.

We also extended our initial study on fully flexible polymers to investigate the effects of chain stiffness on the dynamics of nanoparticles suspended in polymer solutions. We observed that the long-time diffusivities of nanoparticles begin to deviate from the predictions of coupling theory, which was developed for fully flexible chains, as polymer stiffness increases. This observation suggests that the nature of the segmental relaxations are fundamentally different for flexible and stiff chains. Alternatively, it may suggest that the nanoparticles decouple from the segmental relaxations of stiff polymers. A combination of both mechanisms is also possible. Independent of chain flexibility, however, the long-time diffusivities were found to be accurately predicted by mode-coupling theory, demonstrating the utility of this theory for describing nanoparticle transport in different polymer systems with disparate chain properties. We also observe that short-time center-of-mass motions of the nanoparticles and polymers also decouple as chain stiffness is increased. We posit that this decoupling may be due to the change in chain morphology, which transitions from coil-like to rod-like, as stiffness is increased.

Finally, while our investigation of chain stiffness suggested that polymer morphology may influence nanoparticle-polymer coupling, we observed no substantial differences in nanoparticle dynamics on either short or long time scales upon replacing flexible linear chains with nonconcatenated ring polymers with similar radius of gyration. This key result suggests that the radius of gyration, which sets the effective nanoparticle-polymer collision diameter, may be the critical length scale responsible for controlling the short time dynamic coupling between nanoparticle and polymer center-of-mass motions observed in our computational studies. Future work will be required, however, to fully test this hypothesis.

5.2 Future work

5.2.1 Effects of ring concatenation on nanoparticle dynamics in ring polymer solutions.

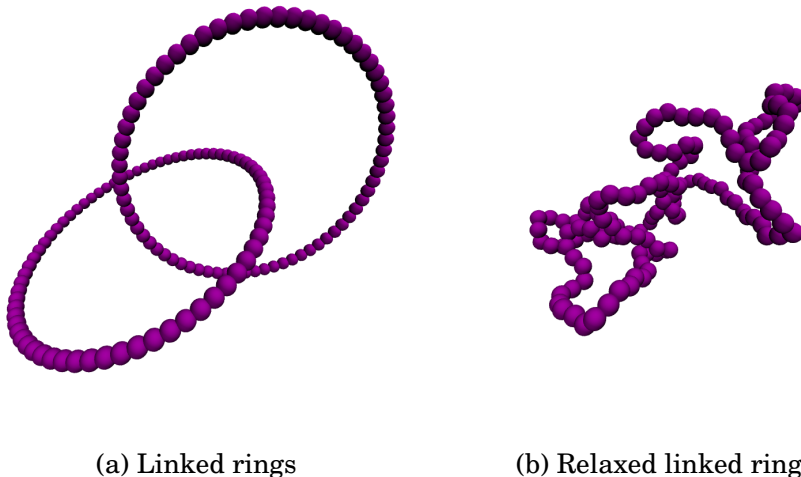


Figure 5.1: A pair of linked ring polymers (a) and the relaxed configuration (b). Snapshots rendered using Visual Molecular Dynamics 1.9.3.¹⁰⁵

In our simulation of ring polymers, we only considered systems of nonconcatenated rings. An interesting future direction may be to introduce knots between the rings (e.g., self-knots, ring inter-penetration, and ring concatenation) to examine their effects on solution properties and nanoparticle transport. Understanding the effects of knots is of interest because they are prevalent in experimentally synthesized ring polymer systems and in natural systems such as DNA.^{141,142} The presence of concatenations in particular is expected to drastically change the polymer relaxation modes, as linked rings are permanently coupled (Fig. 5.1). This coupling is expected to lead to long-range correlations that may influence solution properties and also the dynamics of suspended nanoparticles. We anticipate that the relaxation dynamics of the solutions will dramatically slow as the fraction of concatenated rings increases, which is also likely to suppress the motions of nanoparticles. Additionally, we expect that there may be some non-trivial effects, particularly on short time scales because

concatenations effectively increase the polymer size. We anticipate that this size increase will influence the center-of-mass motions of the polymers and how they couple with the nanoparticle dynamics.

5.2.2 Effects of nanoparticle-polymer attractions on transport through semidilute solutions.

Both experimental and simulation studies have been performed to investigate the effects of attractive nanoparticle-polymer interactions on nanoparticle transport in concentrated melts.^{73,143,144} These studies demonstrate that simulations can provide significant information on how short-time nanoparticle dynamics, which are difficult to resolve in experiment, are influenced by these attractive interactions. To our knowledge, however, similar studies have not been performed in semidilute polymer solutions, where hydrodynamic interactions are also important. We posit that the presence of strong attractions between particles and polymer chains will enhance dynamic coupling between these species. Attractive forces will also likely slow down polymer relaxation near the particle surface.⁵⁴ These two effects may significantly alter nanoparticle dynamics and lead to significant deviations from the transport behaviors observed in solutions where only excluded volume interactions are present. These effects could be investigated by performing computational studies in which the strength of the attractions are systematically tuned to study their influence on nanoparticle dynamics. The insights gained from such a study are expected to be useful for understanding nanoparticle transport in many applied settings where similar attractions between diffusing nanoparticles and components of the background medium likely exist.

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