

Structure Controlled Dynamics of Particles and Polymers in Aqueous Polyelectrolyte Solutions

by

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Abstract

Complex fluids of particles and polymers can be found a wide range of industrial applications including enhanced oil recovery, drug delivery, and consumer goods. Polyelectrolytes are polymers with charged functional groups on their backbone. The charged groups allow polyelectrolytes to maintain high stability and good biocompatibility in aqueous solutions. The induced electrostatic repulsion, however, result in highly extended directed random walk conformations inside their correlation volumes. The size, strength, and recurrence of these charged groups between the monomers leads to conformations ranging from rigid rod to semiflexible chain. These unique electrostatically-induced structural properties likely affect the transport of objects within their geometries as well as their chain relaxations in solutions. In this work, we investigated the dynamics of particles and polyelectrolyte chains in semidilute aqueous polyelectrolyte solutions. First, we explored the effect of chain conformation on the transport of spherical particles across an order of magnitude in size using fluorescence microscopy. We tuned the chain conformation by varying solution ionic strength. We found that large particles follow predictions according to bulk viscoelasticity. Smaller particles on the order of magnitude of chains, however, experience non-monotonic deviations from predictions. These deviations arise from the structural properties of polyelectrolytes in the form of confinements despite the absence of entanglements. We then studied the effects of chain flexibility on the dynamics of nanoparticles using dynamic x-ray scattering. The chain flexibility was altered by changing the degree of polymerization of the chains. We observed three unique behaviors at each chain size. In solutions with small chains, particles couple to the predictions according to the bulk viscoelasticity. Intermediate size polymer solutions showed signs of confinement effects with signature non-monotonic deviations from expectations. Solutions with largest chains, however, linearly deviated from Stokes-Einstein predictions at all concentrations. These observations confirmed the important role of chain flexibility on the dynamics of nanoparticles in solutions. Next, we studied the segmental dynamics of charged chains in

solutions using neutron scattering techniques. We independently vary the geometry and electrostatics by changing polymer concentration and chain ionic strength. We found that the relaxations are slower than predictions with signatures of de Gennes' narrowing phenomenon. Moreover, the structure factor of the chains tracks the observed dynamics. These observations suggested that we have a direct correlation between the structure and dynamics in these systems. Finally, we explore the structure, rheology, and dynamics of colloid-polymer suspensions using in situ x-ray scattering, rheo-XPCS, that allows rheological and scattering measurements simultaneously. We find that suspensions without and with small and dispersed depletants remain as fluids whereas particles in the presence of large depletants experience gelation. This observation suggests that suspensions with smaller size depletants require a stronger attraction potential compared to suspensions with larger ones.

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Chapter 1

Introduction

Complex fluids of nanoparticles and polymers experience both thermal energy^{1,2} and hydrodynamics.^{3,4} Understanding the interactions between particles and polymers is key to understanding their transport properties in solutions. There are three regimes of interest according to particle to polymer size ratios for framing particle transport in polymer solutions. When particles are much smaller than polymer chains, particles hardly interact with surrounding chains and diffuse according to the solvent viscosity. In the opposite regime when particles are much larger than surround chains, the heterogeneities average out across the particle surface and their transport couples to the bulk viscoelasticity of solutions. In the intermediate regime, the nature of interactions between particles and polymer chains become much more important as both components are on similar length scales. Dynamics of polymer chains in unentangled solutions, however, are governed by two pictures depending on the length scales of interest. Inside the correlation blob of chains, hydrodynamic interactions persist and chains move in a Zimm nondraining behavior.³ At length scales beyond the correlation volume, frictional interactions dominate over hydrodynamics and collective chain dynamics follow a free draining behavior according to the Rouse model.⁵ All existing theories focus on understanding the dynamics of particles and polymers in a simple Gaussian chain system. The effects of chain structure on the dynamics of particles and polymers remains an open question.

1.1 Particle dynamics in polymer solutions

Nanoparticles diffuse according to Brownian motion due to thermal vibrations. These vibrations result in collisions between the fluid molecules and nanoparticles which are seen as random displacements. The random nature of such collisions allows us to predict that any displacement of one particle will simultaneously occur with another's displacement in an opposite direction. This makes the overall displacement of particles equal to zero.⁶ The probability distribution function of particle displacements is expressed as a Gaussian distribution

$$P(\Delta x, \Delta t) = \frac{1}{\sqrt{4\pi D \Delta t}} \exp\left[-\frac{\Delta x^2}{4D \Delta t}\right], \quad (1.1)$$

where D is diffusivity, Δt is time, and Δx is displacement. This distribution widens as a function of time and diffusivity could be expressed as the second moment of the displacement. Mean-squared displacement is always positive and greater than zero and evolves linearly with time in one dimensional analysis

$$\langle \Delta x^2(\Delta t) \rangle = 2D(\Delta t). \quad (1.2)$$

By tracking the particle displacements, we can get a mean-squared displacement and extract a diffusivity from it.⁷ This empirical diffusivity can be compared to theoretical predictions of particle diffusivity known as the Stokes-Einstein (SE) equation.

Einstein showed that diffusivity in homogeneous solutions is proportional to the ratio of thermal fluctuations expressed by Boltzmann constant and temperature, $k_B T$, and the viscous dissipation ζ . In Stokes regime where the Reynolds number $Re \ll 1$, the viscous drag on the particle could be expressed as $\zeta = 6\pi\eta R_{NP}$, where η is the solvent viscosity, and R_{NP} is the nanoparticle hydrodynamic radius. As a result, one can predict the diffusivity of the particle when viscosity and size of the particle are known as follows

$$D = \frac{k_B T}{\zeta} = \frac{k_B T}{6\pi\eta R_{NP}}. \quad (1.3)$$

The main assumption underlying the Stokes-Einstein behavior is the particle experiencing constant fluid properties across its surface. While this is true in homogeneous solutions, it is not the case for complex fluids which exhibit local physical structures that introduce heterogeneities across the solution. In polymer solutions, these physical structures are in the form of polymer coils of which their characteristic size represents the inhomogeneity.⁸ In dilute solutions, the random coil is characterized by radius of gyration R_g . As concentration increases, these coils will start to overlap one another. The concentration at which the coils become space-filling is known as the overlap concentration

$$c^* = \frac{M_w}{\frac{4}{3}\pi R_g^3 N_A}, \quad (1.4)$$

where M_w is the polymer molecular weight, and N_A is the avogadro's number. The overlap concentration marks the boundary between dilute and semidilute regimes. As concentration further increases, polymer coils further pack and overlap. This packing behavior introduces another length scale at which heterogeneities occur known as correlation length ξ which is a measure of the distance between polymer chains. At length scales much greater than ξ , each coil can be treated as independent and assumed to only be surrounded by solvent. On the opposite regime, where the length scale is much smaller than ξ , the fluid can be treated as homogeneous.

Multiple models have attempted to describe how particle diffusivity changes as a function of polymer concentrations. Generally, these models fall within two categories. The first one is referred to as the obstruction model.^{9,10,11,12,13,14} Obstruction models treat polymer coils as rigid and static objects that form a polymer mesh similar to the geometry of an air filter. As polymer concentration increases, the volume occupied by the polymer mesh increases resulting in a decrease in accessible space for particle to diffuse through. The

available medium will require particles to move through a tortuous path. The path tortuosity is then predicted to be the reason for the reduction in particle diffusivity. Since the model assumes no interaction between particles and polymer chains, the particle diffusivity should only be related to polymer concentration. A variety of recently studies have focused on using hydrodynamic models,^{15,16,17,18,19,20,21} the second broad category of diffusivity models. These models assume that the dominant effect of polymer solutions is seen as an increase in viscous drag on the particle surface. Since hydrodynamic drag does not only depend on solution properties but also on particle size, these models have been successful in describing diffusivities of specific particle sizes in various concentrated solutions of neutral polymers.

1.2 Polyelectrolytes

Polyelectrolytes are polymer chains with charged functional groups on their backbone. The presence of long range electrostatic interactions results in these systems being highly correlation.^{22,23,24,25} The size and recurrence of charged groups within monomers modifies the structure and chain flexibility. Electrostatic repulsion in charged polymers results in a highly extended conformation of electrostatic blobs inside the correlation volume.^{26,27,23,28,29} On length scales beyond the correlation blob, polyelectrolytes transition to a random walk conformation of correlation blobs as the repulsive interactions are screened.^{27,23,28} As a result of these structural differences, polyelectrolytes exhibit different disentanglement, relaxations, and rheological properties than neutral chains. Moreover, polyelectrolytes exhibit unique ionic strength-dependent viscoelasticity compared to their neutral counterparts.^{30,31} As ionic strength increases, charges on the polymer backbone are screened and the chain retains more flexibility until approaching a Gaussian conformation at the fully screened limit. The pronounced charge-induced differences in structure and relaxations in polyelectrolytes likely affect their dynamics and the transport of nanoparticles

within their matrices.

1.3 Objective and organization of dissertation

Despite studies of nanoparticle diffusion in charged polymers and polyelectrolyte properties in solutions, the effects of electrostatically-induced structural differences have not been thoroughly investigated. In this work, we systematically study the effects of chain structure on the dynamics of polyelectrolytes and nanoparticles in aqueous solutions.

First, we investigate the effects of chain conformation on the long time dynamics of nanoparticles in semidilute polyelectrolyte solutions using fluorescence microscopy (Chapter 2). We alter the chain conformation by changing the ionic strength of solutions. We discuss the unique deviations of nanoparticle dynamics from predictions and their origins in charged polymer solutions. This study shows that structure of polyelectrolytes modifies the interaction between particles and polymers in semidilute solutions.

Second, we study the dynamics of nanoparticles in polyelectrolyte solutions with different chain flexibility using x-ray scattering (Chapter 3). We tune the chain flexibility by changing the number of repeat units on the backbone, while keeping the same chemistry. We report different trends in particle dynamics at each chain flexibility. This study emphasizes how flexibility changes the nature of particle-polymer physical interactions.

Next, we examine the effects of chain geometry and electrostatics on the segmental relaxations of polymer chains using neutron scattering (Chapter 4). We tune these parameters using polymer concentration and solution ionic strength. We discuss the coupling mechanism between structure and dynamics in polyelectrolyte systems. This study emphasizes on the importance of incorporating structure for understanding the behavior of polyelectrolyte systems.

Then, we use in situ x-ray scattering to explore the structure, rheology, and dynamics of colloid-polymer suspensions (Chapter 5). We vary the attraction potential in the suspen-

sions by changing the size of the depletants. We find that large depletants induce gelation whereas suspensions without or with small and dispersed depletants remain as fluids. This study shows the importance of considering depletant size to tune the interaction properties in colloid-polymer suspensions.

Finally, chapter 6 provides a summary of this work and discusses open questions for future directions.

Chapter 2

Local Confinement Controls Diffusive

Nanoparticle Dynamics in Semidilute

Polyelectrolyte Solutions

2.1 Introduction

Nanoparticle transport in concentrated complex fluids is important for enhanced oil recovery^{32,33,34}, nanocomposite materials^{35,36,37}, and targeted drug delivery.^{38,39} Understanding the mechanisms controlling particle diffusion is necessary to enhance the efficacy of particle transport in these applications. The diffusion of a particle of radius R_{NP} in a homogeneous medium with viscosity η is given by the Stokes-Einstein (SE) equation, $D_{\text{SE}} = k_{\text{B}}T/6\pi\eta R_{\text{NP}}$. The assumptions underlying the SE model do not hold as the particle size becomes comparable to the length scales of inhomogeneities in the medium, and deviations from SE predictions appear^{40,41,42,17}. In this size regime, particle dynamics depend on length scales present in solution.

In entangled solutions, the length scale controlling particle dynamics is the tube diameter a , the distance between entanglement strands. The entanglement mesh cages large particles until the time scale of reptation, after which SE behavior is recovered^{43,44,45,46}. Conversely, particles that are much smaller than the entanglement mesh diffuse through the mesh and are unaffected by the polymer network. In *unentangled* polymer solutions, however, particle dynamics are controlled by the correlation length ξ , the distance between neighboring chains. Hydrodynamic models assume polymer solutions to be a homoge-

neous medium in which hydrodynamic interactions decay over $\xi^{17,15,16}$ and in which particle dynamics are dictated by polymer length scales, such as radius of gyration R_g and correlation length $\xi^{45,47,48}$. These pictures have been developed for neutral polymers. In charged polymers, by contrast, electrostatic repulsion between monomers alters structure and chain flexibility^{49,50}. The size of the charged group and its recurrence within the monomers results in conformations ranging from rigid rod to semiflexible chain. In turn, the local conformation determines the mesh geometry. As a result of these structural differences, the onset of entanglements in charged polymers is shifted to much higher concentrations than for neutral chains^{51,26}. The pronounced differences in structure and relaxations in charged polymers likely affect the length scales controlling diffusive transport of nanoparticles. Despite recent studies of nanoparticle diffusion in charged polymer solutions and melts^{52,53}, the effect of charge-induced conformation on nanoparticle transport remains incompletely understood.

Here, we probe the dynamics of nanoparticles in dilute and semidilute unentangled solutions of a model polyelectrolyte. The polymer conformation is tuned by varying the solution ionic strength. The particle dynamics are diffusive across all experimental time scales. We find that the diffusivity of large particles ($R_{\text{NP}}/R_g > 1$) follows bulk predictions at all ionic strengths. For smaller particles ($R_{\text{NP}}/R_g < 1$), however, we observe surprising dynamics with non-monotonic deviations from SE within the unentangled semidilute regime. The size-dependent dynamics do not collapse onto a master curve according to physical arguments derived for Gaussian chains. We find that the non-Gaussian parameter maps onto the same concentration dependence as scaled particle diffusivity D/D_{SE} , suggesting the rise of confinement effects despite the absence of entanglements.

2.2 Materials and methods

2.2.1 Solution Preparation

Glass vials were cleaned overnight in a solution of 6.5 wt% potassium hydroxide in isopropanol, ensuring near salt-free conditions. Vials were thoroughly rinsed 10 times using Millipore water to remove any residual salt, then dried in an oven at 105°C degrees for 2 hours. Fluorescent polystyrene particles with diameters d_{NP} ranging from 100 to 790 nm (Fluoro-Max, Thermo Fisher Scientific) were dispersed in aqueous solutions of NaPSS with a weight-averaged molecular weight $M_w = 2\,200\,000$ Da (Scientific Polymer Products) at three different ionic strengths. A constant particle volume fraction $\phi = 1.5 \times 10^{-6}$ was used across all samples to minimize interparticle interactions and avoid aggregation (observed for $\phi \geq 5 \times 10^{-5}$) while maintaining good statistics for particle tracking. Deionized water was assumed to have an ionic strength of 10^{-6} M⁵⁴, whereas the other two sets of samples were prepared using sodium chloride to achieve ionic strengths of 10^{-3} M and 10^{-1} M. The overlap concentration c^* of NaPSS was estimated at each ionic strength from intrinsic viscosity measurements, and the radius of gyration $R_{g,0}$ in each ionic strength solution was determined via $R_{g,0} = (M_w[\eta]/(4/3\pi N_{\text{av}}))^{1/355,56}$. The resulting $R_{g,0}$ in dilute solutions were 190, 130, and 75 nm at ionic strengths of 10^{-6} , 10^{-3} , and 10^{-1} M, respectively.

2.2.2 Rheology

Steady-shear measurements of the rate-dependent viscosity were performed on Discovery Hybrid Rheometer (TA Instruments, HR-2). Polymer solutions were loaded into a single gap Couette cell with a cup diameter of 15 mm, a bob diameter of 14 mm, and a bob length of 42 mm. The inertia and torque of the instrument were calibrated prior to measurements. Samples were pre-sheared for one minute to reach equilibrium, after which the viscosity was determined as the average value over one minute. Dynamic frequency sweep measurements were collected using a single-gap Couette cell on a Discovery Hybrid

Rheometer (TA Instruments, HR-2). The cell has a diameter of 15 mm, a bob diameter of 14 mm, and a bob length of 42 mm. We performed a dynamic strain sweep at angular frequencies $\omega = 1, 10, \text{ and } 100 \text{ rad/s}$. The linear viscoelastic regime extended up to strains $\gamma = 20\%$. Storage (G') and loss (G'') moduli were measured at 10% strain as a function of angular frequency for NaPSS solutions. We eliminate any data points with generated torque values below $0.1 \mu\text{N}\cdot\text{m}$ or raw phase angle values above 175° to meet the instrument's minimum criterion while minimizing the contribution of inertia to data collection.

2.2.3 Imaging Sample Preparation

To create a sample chamber for imaging, two cover slips ($22 \text{ mm} \times 22 \text{ mm} \times 0.2 \text{ mm}$, Fisherbrand cover glass) were adhered on Gold Seal cover glass ($48 \text{ mm} \times 65 \text{ mm} \times 0.15 \text{ mm}$) using UV epoxy-based adhesive to form two sides of a chamber. Another cover slip was attached on top of the two cover glass slips using UV epoxy. The particle-polymer solutions were then pipetted through one of the two open sides. Finally, the two remaining open sides were sealed with UV epoxy.

2.2.4 Imaging and Particle Tracking

A Leica DM4000 inverted fluorescent microscope equipped with 63x and 100x oil immersion lenses was used to acquire series of images of quiescent samples over time. For each image series, 4100 images were captured at a frame rate of 32 fps. At least five image series per sample were recorded at different locations. Particle centroids were located with a spatial resolution 25 and 35 nm for 200 and 790 nm particles, respectively, and tracked over time using particle-tracking algorithms⁷. From the particle trajectories, we calculated the one-dimensional ensemble-averaged mean-squared displacement (MSD) $\langle \Delta x^2(\Delta t) \rangle$ as a function of lag time Δt . At least 10^4 time steps were averaged for each MSD data point. To extract the diffusivity D , we fitted each MSD to $\langle \Delta x^2(\Delta t) \rangle = 2D(\Delta t)$.

2.3 Results and discussion

2.3.1 Intrinsic Viscosity

Dilute aqueous sodium polystyrene sulfonate (NaPSS) solutions were prepared by diluting a concentrated stock solution. Samples were introduced into a glass capillary viscometer (Cannon Instrument Company, OC), which was submerged into a water bath for better temperature control. Although the capillary viscometer operates at a high shear rate of approximately 300 s^{-1} , we observe excellent agreement between the viscosities determined using the viscometer and the rheometer (Figure 1 in manuscript), as evident by the consistent crossover between dilute and semidilute regimes at the overlap concentration calculated using capillary viscometer. These observations suggest that the viscometer accurately captures NaPSS contribution in dilute solutions. Figure 2.1 shows the sample viscosity as a function of NaPSS concentration. We fitted the data to the two term virial expansion of viscosity $\eta = \eta_0(1 + [\eta]C_{\text{NaPSS}})$, where $[\eta]$ is the intrinsic viscosity, and η_0 is the solvent viscosity. Using the fitting equation, we determined the intrinsic viscosity $[\eta]$. We then calculated the overlap concentration ($c^* = 1/[\eta]$) 0.13, 0.41, and 2.1 g/L and determined the radius of gyration ($R_{g,0} = (M_w/(4/3\pi N_{\text{av}}c^*))^{1/3}$) 190, 130, and 75 nm for 2200 kDa polymer at 10^{-6} , 10^{-3} , 10^{-1} M ionic strength, respectively. Flory exponent ν at each ionic strength was determined from the scaling of polymer size as a function of molecular weight (Figure 2.2) according to the Flory theory of fractal chains⁵⁷.

2.3.2 Rheology

We examine the oscillatory rheology of the polyelectrolyte solutions at all ionic strengths. We find that terminal crossover is not reached within the experimented angular frequency range for all samples, suggesting that relaxations occur at very short time scales $< 10 \text{ ms}$ and an absence of entanglements in our solutions. In Figure 2.4, we present the viscosity as a function of shear rate for NaPSS solutions at 10^{-3} and 10^{-1} M ionic strength. The vis-

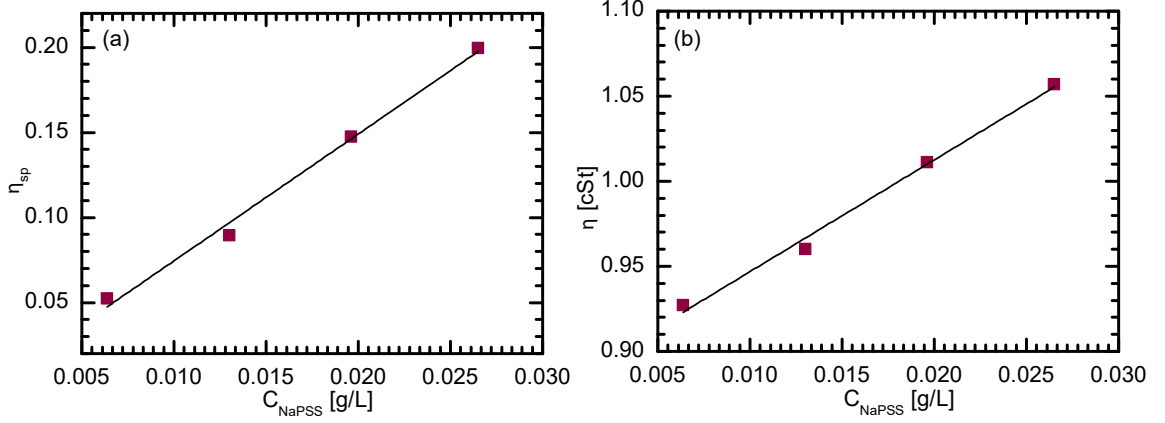


Figure 2.1: Specific η_{sp} (a) and solution viscosity η (b) as a function of NaPSS concentration C_{NaPSS} for 2200 kDa NaPSS in 10^{-6} M solutions.

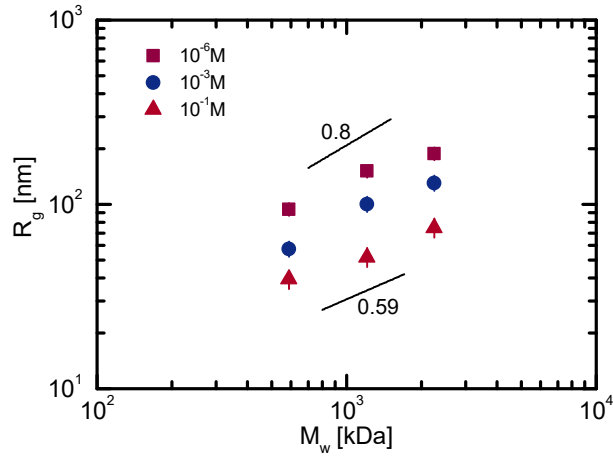


Figure 2.2: Radius of gyration R_g as a function of polymer molecular weight M_w . Solid lines represent scaling at the low and high salt limits for polyelectrolytes.

cosity is independent of shear rate, indicating that chains relax quickly in solutions. These results are consistent with the 10^{-6} M solutions.

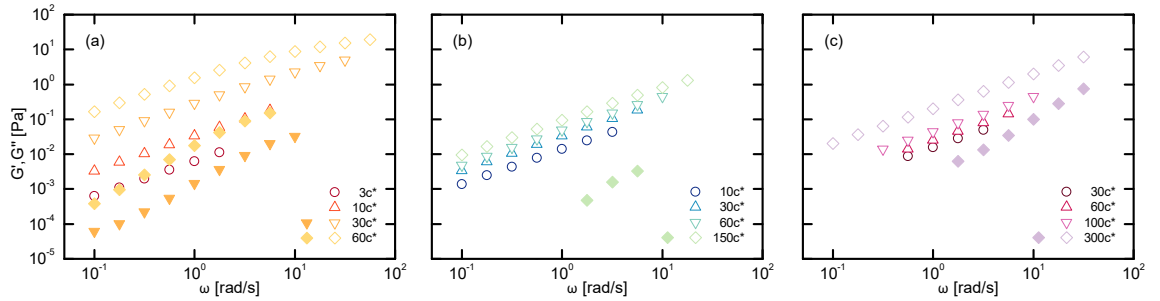


Figure 2.3: Storage G' (closed) and loss G'' (open) moduli as a function of angular frequency ω for (a) 10^{-1} , (b) 10^{-3} , and (c) 10^{-6} M ionic strength solutions.

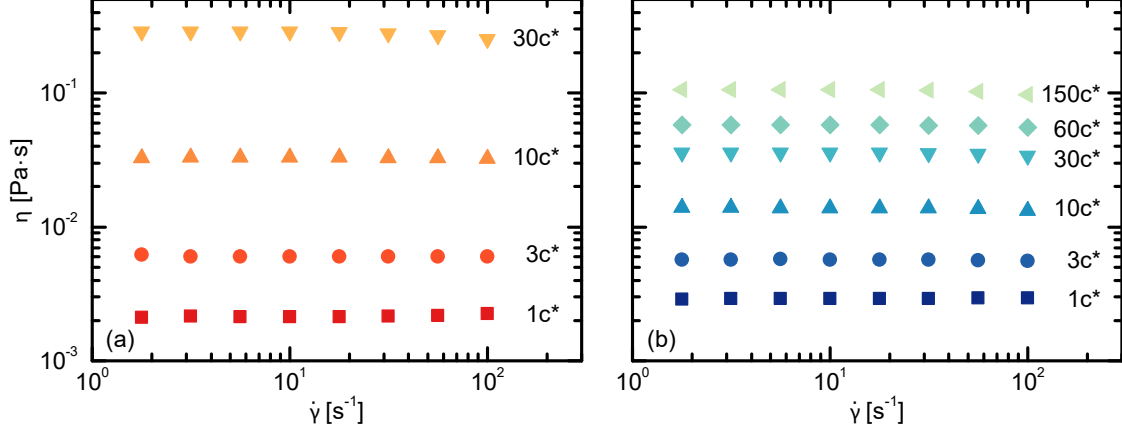


Figure 2.4: Viscosity η for (a) 10^{-1} and (b) 10^{-3} M ionic strength NaPSS solutions as a function of shear rate $\dot{\gamma}$.

We characterize the rheological properties of the polyelectrolyte solutions at three solution ionic strengths. The viscosity increases concomitant with polymer concentration c/c^* and is approximately independent of shear rate across two orders of magnitude in concentration (inset to Figure 2.5), indicating that the chains relax quickly in solution.

The viscosity of charged polymer solutions exhibits a dependence on ionic strength that is not observed for their neutral counterparts^{26,58}. We examine the changes in specific viscosity $\eta_{\text{sp}} = (\eta - \eta_0)/\eta_0$ because it offers a direct measurement of the polymer contribution to solution viscosity. The specific viscosity of the polyelectrolyte solutions increases as a function of both polymer and ionic strength. In the dilute regime, the specific viscosity scales with concentration as $\eta_{\text{sp}} \sim (c/c^*)^1$ following the theoretical prediction²³. The specific viscosity is independent of ionic strength for concentrations $c/c^* < 1$ due to the dominance of hydrodynamic interactions^{3,4}. In the semidilute regime ($c/c^* > 1$), the specific viscosity scales according to predictions²³ for polyelectrolyte solutions at low ($\eta_{\text{sp}} \sim (c/c^*)^{1/2}$) and high ($\eta_{\text{sp}} \sim (c/c^*)^{5/4}$) ionic strength^{23,51,26}. When the ionic strength is intermediate between these limits, however, the specific viscosity in the semidilute regime scales with concentration as $\eta_{\text{sp}} \sim (c/c^*)^\alpha$ with $\alpha = 0.8 \pm 0.1$. The specific viscosity increases with ionic strength for constant c/c^* in the semidilute regime,

consistent with an increase in chain-chain interactions as the salt screens monomeric repulsion²⁶. We observe a sharp upturn in η_{sp} at high polymer concentrations only in solutions of high ionic strength, suggesting that these solutions are entangled. Such a crossover, however, is not observed at low and intermediate ionic strength, suggesting the absence of chain entanglements. These observations are consistent with the expectations for entanglements in charged polymer solutions occurring at high concentrations that are $\gg 10c^*$. Thus, these polyelectrolyte solutions have rheological properties that agree well with existing theories^{51,23,54} and serve as a model system to investigate how particle dynamics depend on polymer conformations.

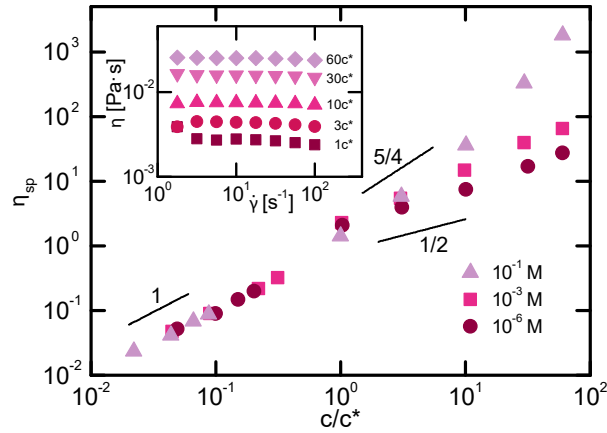


Figure 2.5: Specific viscosity $\eta_{sp} = (\eta - \eta_0)/\eta_0$ as a function of normalized NaPSS concentration c/c^* for solutions of various ionic strength. *Inset:* Viscosity η for 10^{-6} M ionic strength solutions as a function of shear rate $\dot{\gamma}$.

2.3.3 Dynamic Light Scattering

Dynamic light scattering measurements were conducted using a Brookhaven Instruments goniometer (BI-200SM, Brookhaven Instruments Corporation) equipped with an Avalanche photodiode detector (Brookhaven, BI-APD) and a digital correlator (Brookhaven, TurboCarr) and a laser (Mini-L30 Laser Source) with an excitation wavelength $\lambda = 637.6$ nm. Glass vials were cleaned using acetone, water, and lens paper to minimize the scattering from contaminants on the surface. Dilute polymer solutions were prepared with a

particle volume fraction of 10^{-5} for all samples. Scattered light was collected at angles $\theta = 60^\circ, 75^\circ, 90^\circ, 105^\circ$, and 120° , corresponding to wavevectors q from 14 to $23 \mu\text{m}^{-1}$, and for 60 seconds at 200 delay times ranging from $1 \mu\text{s}$ to 20 s. From this data, the intensity-intensity autocorrelation $g_{(2)}(\tau, q) = \langle I(t+\tau)I(t) \rangle / \langle I(t) \rangle^2$ functions were calculated. The field-field autocorrelation function $g_{(1)}(\tau, q)$ was obtained from the intensity-intensity autocorrelation function using the Siegert relation $g_{(2)}(\tau, q) = 1 + \beta[g_{(1)}(\tau, q)]^2 + \varepsilon$, where ε is noise, $g_{(1)}(\tau, q) = \exp(-t/\tau)$, and τ is the decay rate that represents the characteristic relaxation time of the system.

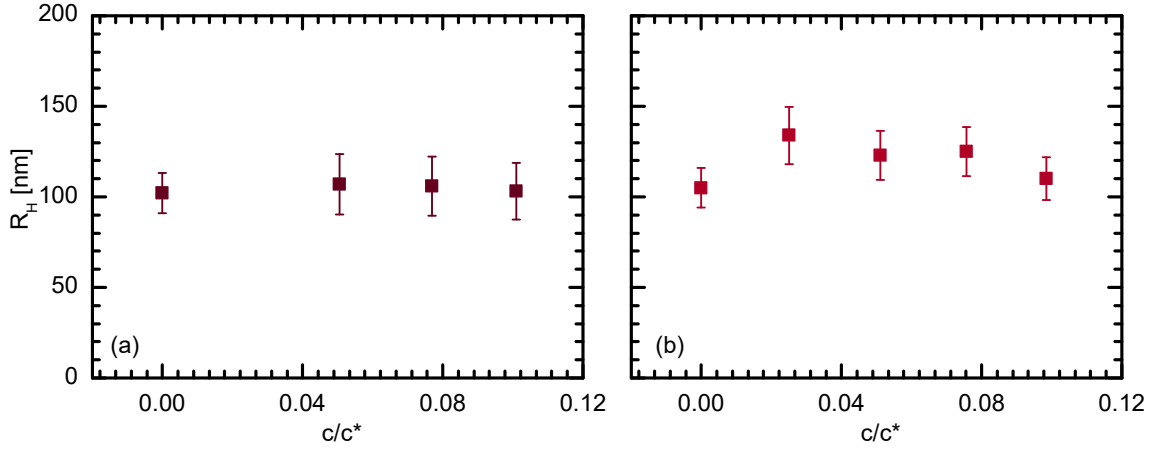


Figure 2.6: Hydrodynamic radius R_H as a function of normalized polymer concentration c/c^* for 200 nm particles in solutions with (a) 10^{-6} and (b) 10^{-1} M ionic strength.

Nanoparticle diffusivity was calculated using the relation $D = 1/\tau q^2$ and hydrodynamic radii of particles was estimated using Stokes-Einstein relationship $D_{SE} = k_B T / 6\pi\eta R_{NP}$, where the viscosity η for each polymer concentration was determined using a capillary viscometer. We find that hydrodynamic radius of particles remains constant as polymer concentration increases (Figure 2.6), suggesting no adsorption of chains onto particle surfaces.

2.3.4 Particle Dynamics

The mobility of nanoparticles in polyelectrolyte solutions decreases with increasing nanoparticle size (Figure 2.7(a)) and polymer concentration (Figure 2.7(b)). The mean-

square displacement (MSD) scales linearly with lag time $\langle \Delta x^2 \rangle = 2D\Delta t$ across all time scales, indicating diffusive dynamics with a diffusivity D as expected for Newtonian solutions with fast relaxations. We remove explicit size dependence by normalizing D by the diffusivity of the particle in pure solvent D_0 .

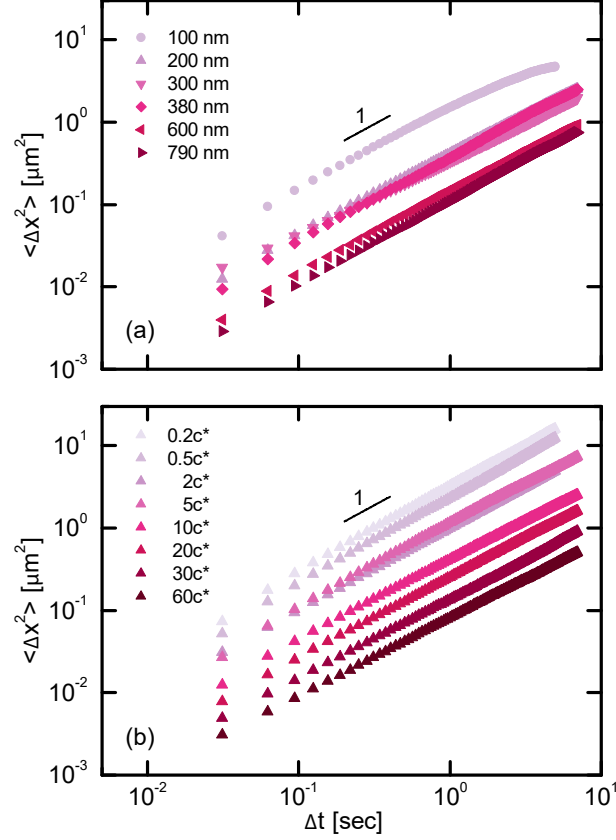


Figure 2.7: Mean-square displacement $\langle \Delta x^2 \rangle$ as a function of lag time Δt for (a) particles of various sizes in a solution of polymer concentration $10c^*$ and (b) for 200 nm particles in 10^{-6} M ionic strength solutions of various polymer concentrations.

Particles diffuse according to solvent viscosity at low polymer concentrations across all ionic strengths $D/D_0 = 1$ (Figure 2.8). The dynamics slow as concentration increases into the semidilute regime. At a given concentration c/c^* within the semidilute regime, the particle dynamics are faster as ionic strength decreases, consistent with the lower viscosity of the solutions (Fig. 2.5). The normalized diffusivities are approximately independent of particle size in solutions of ionic strength 10^{-1} M and 10^{-3} M, consistent with the idea that

the particle diffusion probes the bulk solution viscosity. In solutions with the lowest ionic strength (10^{-6} M), however, the dynamics of small particles deviate from those of large particles, indicating that the dynamics of small particles decouple from the bulk solution viscosity.

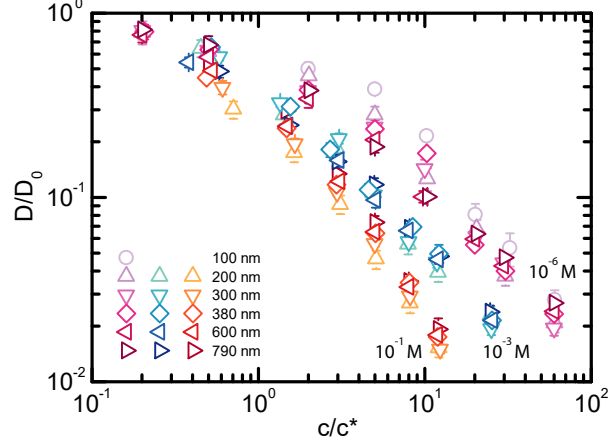


Figure 2.8: Normalized particle diffusivity D/D_0 as a function of polymer concentration c/c^* in solutions of different ionic strength. Error bars represent the standard deviation of five measurements per sample.

To quantify the extent to which dynamics deviate from the predictions using bulk solution viscosity, we examine the particle diffusivity normalized by the Stokes-Einstein diffusivity D/D_{SE} as a function of polymer concentration. We use the dynamics of the large particles to quantify bulk solution viscosity so that $D_{SE}/D_0 = D_{790}/D_{790,0}$ to overcome torque limitations of the rheometer at low solution viscosity. Particles in solutions of high (10^{-1} M) and intermediate (10^{-3} M) ionic strength exhibit diffusivities that approximately conform to the Stokes-Einstein prediction using the measured bulk viscosities (Figures 2.9 a and b). We attribute systematic deviations in D/D_{SE} from the predicted value of 1 to the use of the largest particles as bulk probes. In these solutions, the particles are larger than the radii of gyration of the polymers at infinite dilution, which we calculate to be 130 and 75 nm for solutions of intermediate (10^{-3} M) and high (10^{-1} M) ionic strength. Thus the near-Stokes-Einstein diffusivities measured for these systems, for which $R_{NP} > R_g$, are consistent with earlier studies that show that the dynamics of large particles ($R_{NP} > R_g$)

couple to bulk viscosity behavior according to the SE prediction⁵⁹.

By contrast, the dynamics in solutions at low ionic strengths (10^{-6} M) depend on particle size. The diffusivities of 600 nm particles follow the predicted SE behavior at all polymer concentrations (Fig. 2.9(c)). The dynamics of smaller particles, however, agree with SE predictions at low polymer concentrations ($c/c^* < 1$) but exhibit a striking departure from SE predictions at higher polymer concentrations. This deviation increases with increasing polymer concentration until $c/c^* \approx 10$, at which point the particle dynamics begin to approach SE predictions again. In these low ionic strength solutions, the particles are comparable in size to the radius of gyration of the polymer ($R_{NP} \sim R_g$) and hence the solutions cannot be treated as homogeneous continua. In this limit, interactions between particles and polymer chains become more important and lead to deviations from predictions based on the bulk solution rheology.^{45,20}

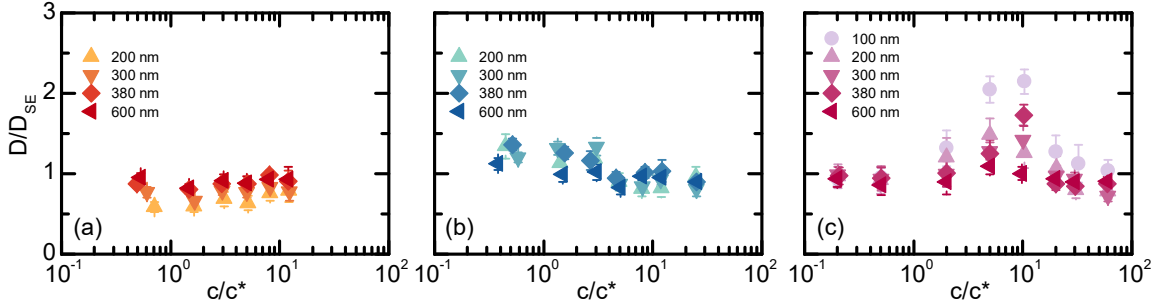


Figure 2.9: Diffusivity normalized to SE predictions D/D_{SE} as a function of polymer concentration c/c^* at (a) 10^{-1} M, (b) 10^{-3} M, and (c) 10^{-6} M ionic strength. Error bars represent the standard deviation of five measurements per sample.

2.3.5 Particle Dynamics Models

A number of models and scaling theories attempt to explain particle dynamics in polymer solutions.

Empirical Models

Empirical models generally fall into one of two categories: obstruction^{9,10,11,12,13,14} or hydrodynamic^{15,16,17,18,19,20,21}. Obstruction models assume that the polymer mesh is effectively immobile on time scales of particle diffusion and serve as geometric barriers to particle diffusion, but this assumption does not hold in our system because chains relax on time scales of the same order of magnitude as those characterizing the particle dynamics. We examined the normalized diffusivities D/D_0 for 10^{-6} M ionic strength solutions according to the proposed scaling for obstruction pictures^{9,10,11}. Here, we plot the data only for those particles for which the assumption for an immobile mesh is valid (i.e. $\tau_R > \tau_D$). We find that the model is not able to capture the observed dynamics.

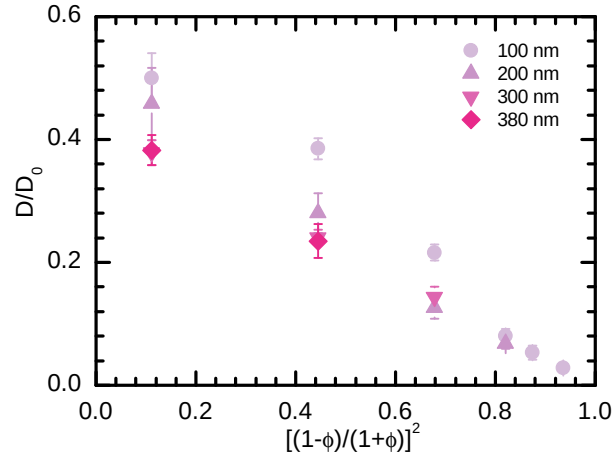


Figure 2.10: Relative diffusivity D/D_0 as a function of $(\frac{1-\phi}{1+\phi})^2$.

Hydrodynamic models assume that hydrodynamic interactions are screened over ξ so that viscous drag increases as ξ decreases. Hydrodynamic models, however, predict monotonic deviations from Stokes-Einstein behavior because ξ decreases monotonically with increasing polymer concentration. We examined the scaled diffusivities D/D_0 or D_0/D for 10^{-6} M ionic strength samples as a function of the proposed length scales of various hydrodynamic models^{17,18,19,21}, particle-polymer coupling theory⁴⁵, and depletion layer theory²⁰. None of the models cleanly collapse the dynamics across all particle sizes or polymer concentrations.

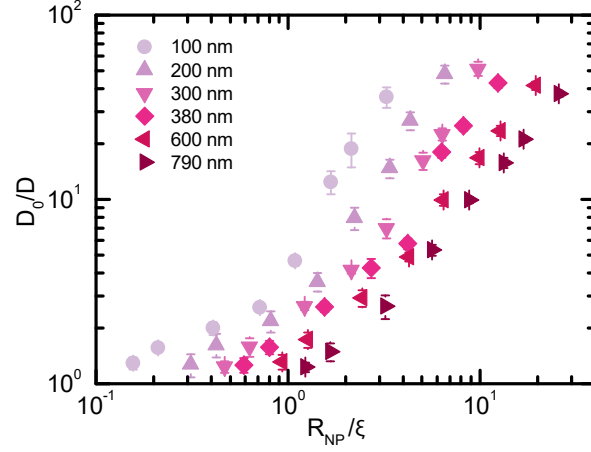


Figure 2.11: Relative diffusivity D_0/D as a function of R_{Cheng}/ξ , where $R_{\text{Cheng}} = R_{\text{NP}}$. This model does not collapse the data at any particle or polymer size.¹⁷

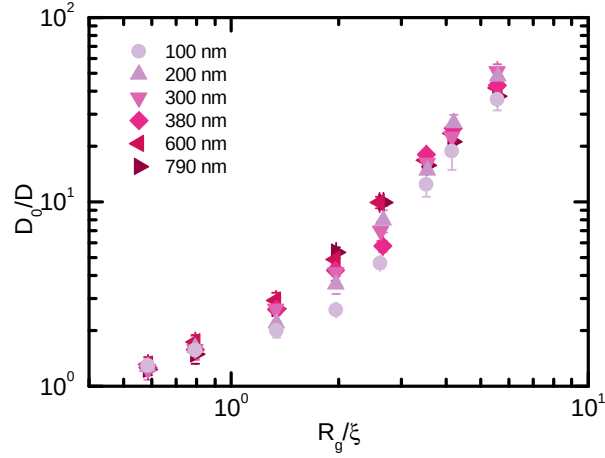


Figure 2.12: Relative diffusivity D_0/D as a function of R_g/ξ . The success of this model decreases as particles become smaller. The model successfully collapsed large ($R_{\text{NP}} > R_g$) particles data that follow SE behavior.¹⁸

Importantly, these empirical models cannot describe the non-monotonic behavior of D/D_{SE} in our system.

Particle-Polymer Interactions Models

A second category of models incorporate how the particle interacts with the polymer. For neutral polymer systems, the polymer may develop a depletion layer around the particle, whereas for attractive polymer systems, the surrounding polymer will form a bound

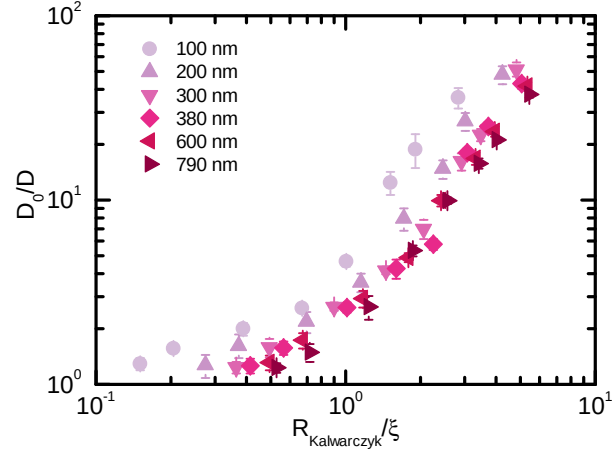


Figure 2.13: Relative diffusivity D_0/D as a function of R_K/ξ . The effective radius R_K is defined as $R_K^{-2} = R_{NP}^{-2} + R_g^{-2}$. This model is successful for large particles but fails to collapse the dynamics of small particles onto the same curve.¹⁹

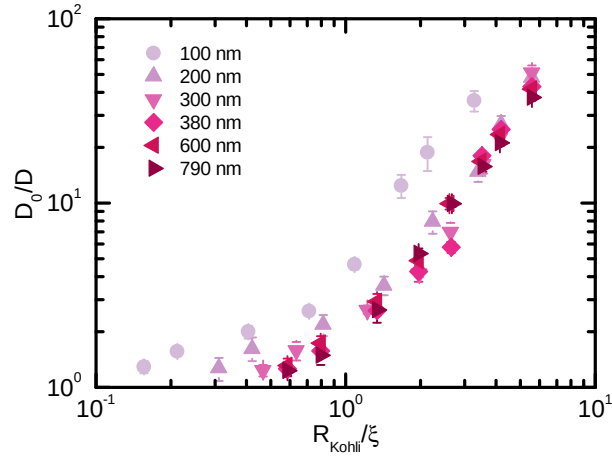


Figure 2.14: Relative diffusivity D_0/D as a function of R_{Kohli} . The effective radius R_{Kohli} is defined as $R_{Kohli} = R_{NP}$ if $R_{NP} < R_g$ and $R_{Kohli} = R_g$ if $R_{NP} > R_g$. The model does not capture the behavior of the 100 nm particles.²¹

layer covering the particle. In the depletion layer picture, the particle diffuses quickly through the depletion layer and then slowly through the polymer mesh²⁰. Our data, however, does not collapse according to the scaling suggested by this picture, suggesting the absence of a depletion layer surrounding the particles. In the bound-layer picture, the polymer binds to the surface of the particle and increases the viscous drag acting on the particle so that the particle diffusion is slower than expected⁶⁰. Dynamic light scattering (DLS) on our particles in NaPSS solutions in the low and high ionic strength limits and in dilute

conditions reveal that polymer chains do not significantly adsorb on the particle. Moreover, we expect that particles with a bound layer would exhibit slower-than-expected diffusion, whereas in our experiments D/D_{SE} approaches 1 for solutions with high polymer concentrations and low ionic strength.

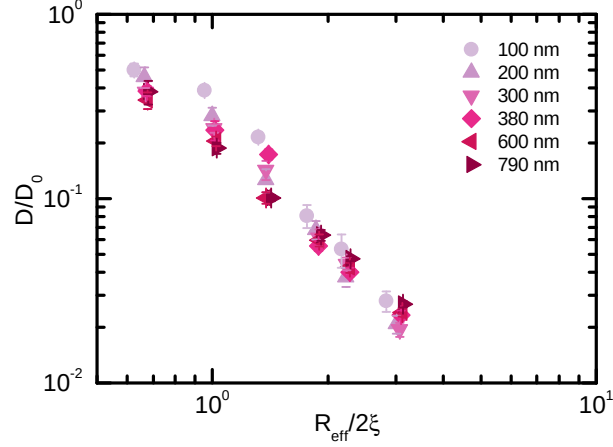


Figure 2.15: Relative diffusivity D/D_0 as a function of $2R_{\text{eff}}/2\xi$. The effective radius R_{eff} is defined as $R_{\text{eff}} = \sqrt{\frac{R_g^2(2R+2d)^2}{R_g^2 + (2R+2d)^2}}$, where d is the depletion layer thickness.²⁰

Electric Double Layer Model

A third class of pictures, developed for particles in dielectric media, predict a non-monotonic decrease in the diffusion coefficient when a particle is surrounded by an electric double layer of comparable size⁶¹ or when the particle dielectric constant increases⁶². The former case⁶¹ results in slowing of particle diffusion when the particle size is on the order of the inverse of the Debye length (i.e. $d_{\text{NP}}\kappa = 1$, where κ^{-1} is the Debye length). Our experiments, however, span size ratios that are orders of magnitude larger than $2R_{\text{NP}}\kappa = 1$. Furthermore, this picture predicts that particle dynamics are slower at intermediate electrolyte concentrations ($-2 < \log(2R_{\text{NP}}\kappa) < 1$) before recovering SE behavior at higher electrolyte concentrations ($\log(2R_{\text{NP}}\kappa) > 1$) and hence trend in the opposite direction of our data. Finally, the predicted deviations from SE behavior are of order $\sim 10\%$ ⁶¹, which are much smaller than our observed deviations (Figure 2.9). The latter picture⁶² predicts an

enhanced polymer-particle affinity as chain length or nanoparticle size increases when the dielectric constant of the particle increases beyond that of the surrounding medium. The polystyrene particles in our experiments, however, have a dielectric constant ($\epsilon = 2.5$) that is significantly lower than the solvent, water ($\epsilon = 80$). Additionally, we expect the negatively charged polystyrene particles and polyelectrolyte chains to further reduce the affinity of chains to adsorb on the particle surface. Thus, these models are also not able to describe the non-monotonic deviations from SE dynamics in our low-ionic-strength samples.

Particle-Polymer Coupling

A final model predicts that, within certain size ranges, the particle dynamics are coupled to the relaxations of polymer segments of similar size.⁴⁵ In this theory, particle-polymer coupling results in diffusion according to an effective solution viscosity that is lower than the bulk viscosity⁴⁵. In our earlier experiments on partially hydrolyzed polyacrylamide, the coupling theory scaling prediction $D/D_0 \sim (R_{\text{NP}}/\xi)^{-2}$ was able to collapse the diffusivities of systems with similar particle-polymer size ratios (R_{NP}/R_g)⁶³. This scaling, however, is not able to collapse the diffusivities measured in NaPSS solutions onto a master curve. This result suggests that different physics must control particle dynamics in these solutions as compared to solution of fully flexible Gaussian chains, likely arising from effects due to the charge on the polymers in the semidilute regime.

2.3.6 Polymer Length Scales

Sodium polystyrene sulfonate is a polyelectrolyte with one charged functional group per repeat unit. Charge repulsion leads to persistence length values larger than those of neutral polymers. The chains, however, remain flexible at length scales larger than persistence length due to their large length. This causes chains to adopt a semiflexible conformation. Therefore, the scaling behavior of the physical properties of sodium polystyrene sulfonate in salt free conditions is between neutral polymers in good solvent and polyelec-

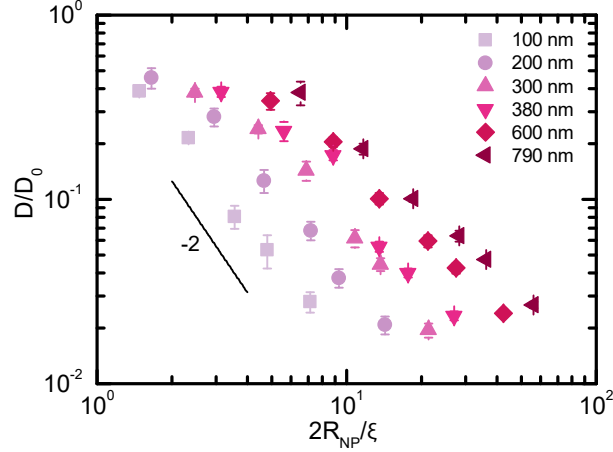


Figure 2.16: Relative diffusivity D/D_0 as a function of $2R_{NP}/\xi$. The coupling theory picture predicts intermediate size particles ($\xi < R_{NP} < a$) should collapse according with a scaling exponent of -2 .⁴⁵

trolytes with no salt. We calculated the contour length $l = Na$, where N is the number of repeat units, and a is the length of a carbon bond (1.54 Å). Polymer end-to-end distance was determined using $R_e = \sqrt{N}a$. Persistence length l_p was estimated to be equal to the Debye screening length $k_D = 1/\sqrt{4\pi i}$, where i is the ion density. We calculated the Kuhn length to be twice the persistence length. Correlation length ξ and polymer size R_g beyond the dilute regime were calculated via $\xi = R_{g,0}(c/c^*)^{-\frac{\nu}{3\nu-1}}$ and $R_g = R_{g,0}(c/c^*)^{-\frac{\nu-0.5}{3\nu-1}}$.

Table 2.1: Estimations of relevant length scales for 2200 kDa NaPSS in dilute solutions.

Polymer Property	10^{-6} M Solution	10^{-3} M Solution	10^{-1} M Solution
Radius of gyration R_g	190 nm	130 nm	75 nm
Contour length l	1890 nm	1890 nm	1890 nm
End-to-end distance R_e	170 nm	170 nm	170 nm
Persistence length l_p	21 nm	4 nm	1 nm
Kuhn length $2l_p$	42 nm	8 nm	2 nm

To identify the controlling physics, we examine the differences between polyelectrolytes and uncharged polymers. Both the radius of gyration $R_g \sim c^{-1/4}$ and the correlation length $\xi \sim c^{-1/2}$ of polyelectrolytes decrease as concentration is increased (Table 2.2), similar to those for neutral chains but with different scaling exponents.^{23,26,4} Surprisingly, we observe non-monotonic behavior in D/D_{SE} when $R_{NP}/R_g < 1$ for all polymer

concentrations (100, 200 nm diameter particles), when $R_{\text{NP}}/R_g > 1$ for all polymer concentrations (380 nm), and when R_{NP}/R_g transitions from > 1 to < 1 as concentration is increased (300 nm). Likewise, we observe non-monotonic behavior when $R_{\text{NP}}/\xi > 1$ for all concentrations (380 nm) and when R_{NP}/ξ transitions from > 1 to < 1 as concentration is increased (100, 200, 300 nm). Thus structural length scales do not directly control the non-monotonic behavior of D/D_{SE} in the semidilute regime.

Table 2.2: Calculated correlation length ξ and radius of gyration R_g as a function of polymer concentration for solutions of varying ionic strength using scaling theory^{26,51,23}

c/c^*		1.5	2	5	10	20	30
10^{-6} M	ξ [nm]	164	121	68	44	28	22
	R_g [nm]	174	165	140	123	108	101
10^{-3} M	ξ [nm]	98	80	43	26	16	12
	R_g [nm]	122	117	102	91	82	77
10^{-1} M	ξ [nm]	94	43	21	12	7	-
	R_g [nm]	72	70	63	59	55	-

2.3.7 Polymer Time Scales

In semidilute unentangled solutions, polymer chains undergo a crossover between two dynamic modes that occur at different time scales. The relaxations at length scales shorter than the correlation length ξ are well-described by the Zimm model, up to the relaxation time of correlation blobs $\tau_\xi \sim \eta_s \xi^3 / k_B T$ ^{26,3,4}. At time scales larger than the relaxation time of a correlation blob ($t > \tau_\xi$), polymers relax according to the Rouse model as a chain of correlation blobs. Chains move subdiffusively until the terminal relaxation time $\tau_R \sim \tau_\xi (N/g)^{2\nu+14,26}$, where N/g represents the number of correlation blobs per chain and ν is the Flory exponent. We calculated particle diffusion times $\tau_D = R_{\text{NP}}^2 / D$, where D is the particle diffusivity at a given polymer concentration. Here, we summarize the characteristic relaxation time of a correlation blob, terminal relaxation time (Table 2.3), and particle diffusion times (Table 2.4).

Table 2.3: Estimations of correlation blob and terminal relaxation times for 2200 kDa NaPSS solutions at 10^{-6} M ionic strength.

Polymer conc. c/c^*	τ_ξ [ms]	τ_R [sec]
1.5	0.957	0.342
3	0.178	0.246
5	0.067	0.203
8	0.028	0.170
12	0.013	0.146
25	0.003	0.111
60	0.001	0.080

Table 2.4: Estimations of particle diffusion times for various particle sizes as a function of 2200 kDa sodium polystyrene sulfonate concentrations at 10^{-6} M ionic strength.

Polymer conc. c/c^*	τ_D [sec]					
	100 nm	200 nm	300 nm	380 nm	600 nm	790 nm
2	0.001	0.011	0.043	0.088	0.354	0.757
5	0.002	0.018	0.067	0.144	0.592	1.53
10	0.003	0.040	0.113	0.194	1.20	2.84
20	0.008	0.075	0.262	0.612	2.05	4.59
30	0.013	0.137	0.363	0.840	2.90	6.00
60	0.025	0.244	0.833	1.44	5.00	11.1

Prior studies on NaPSS revealed that chain relaxation times exhibit a local maximum at the overlap concentration⁵¹, first increasing with concentration in the dilute regime and subsequently decreasing with concentration in the semidilute regime^{58,64}. The non-monotonic deviations from SE in our study do not occur at the crossover between dilute and semidilute regimes, but rather well-within the semidilute regime $c/c^* \sim 10$. This result suggests that the non-monotonic behavior in D/D_{SE} in the semidilute regime does not arise from non-monotonicity in the chain relaxation time.

2.3.8 Confinement Effects

We hypothesize that the non-monotonic dynamics may be associated with particles experiencing local heterogeneity in solution. The distributions of particle displacements $G_s(\Delta x, \Delta t) = \frac{1}{N} \left\langle \sum_{i=1}^N \delta(x_i(t) - x_i(t + \Delta t) - \Delta x) \right\rangle$ are Gaussian on all accessible

time scales for some particle sizes and polymer concentrations (e.g., 100 nm particles and $2c/c^*$ Figure 2.17 (a), all data is at 10^{-6} M ionic strength.). For 100 nm particles at $20c^*$, however, $G_s(\Delta x, \Delta t)$ is non-Gaussian for all accessible lag times (Figure 2.17 (b), all data is at 10^{-6} M ionic strength.). For all samples, the non-Gaussian parameter $\alpha_2 = \frac{\langle \Delta r^4 \rangle}{3\langle \Delta r^2 \rangle^2} - 1$, which characterizes the extent to which the distributions deviate from the Gaussian prediction for Fickian diffusion, is approximately independent of time. Surprisingly, we find that α_2 for the 100 nm particles is also a non-monotonic function of c/c^* and exhibits a local maximum (Fig. 2.17(c), all data is at 10^{-6} M ionic strength.). Moreover, the concentration at which it attains its local maximum, $20c/c^*$, is close to that at which D/D_{SE} attains its local maximum, providing additional evidence that the non-monotonic deviations from SE may be related to particles experiencing different heterogeneous environments.

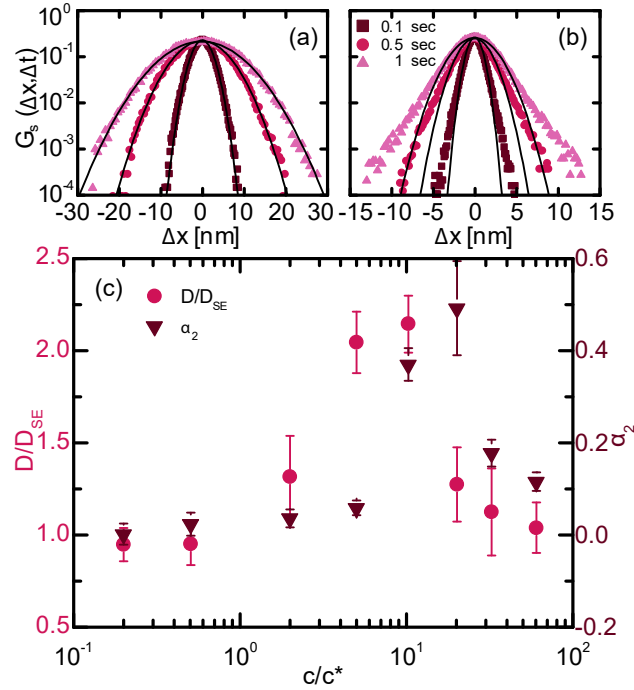


Figure 2.17: Normalized distribution of displacements G_s for 100 nm particles in (a) $2c^*$ and (b) $20c^*$ solutions. (c) Scaled diffusivity D/D_{SE} and non-Gaussian parameter α_2 as a function of concentration c/c^* for 100 nm particles.

Non-Gaussian distributions of particle displacements can arise from temporal^{65,66} or

spatial^{67,68} heterogeneities in the environment or from multiple dynamic modes^{69,70}. In these solutions, chain relaxations occur on time scales faster than those characterizing particle diffusion (inset to Figure 2.5), indicating that the solution dynamics are not temporally heterogeneous on timescales relevant for particle diffusion. Anomalously large displacements are often attributed to hopping of particles between cages in a mesh or network^{71,72,73}. A recent theory proposes that particles whose size is comparable to or slightly larger than ξ in entangled solutions experience intermittent hopping within the mesh at long time scales.^{45,48} Recent experiments attribute the non-Gaussian behavior in entangled solutions to a competition between three time scales: the short-time relaxation of an entanglement strand, the time scale for activated hopping of nanoparticles, and the long-time reptation of the polymers.^{72,74} In our experiments, however, the solutions are not entangled. Instead, we propose that the return to SE diffusion arises due to increasing confinement from the polymers. These confinements behave similarly to a tube diameter in an entangled system and become more prominent as the polymer concentration is increased. Because the non-monotonic deviations from SE are not observed in the salted solutions, our results suggest that the anomalous diffusion in Fig. 2.9 arises from the distinctive structural properties of polyelectrolytes.

Displacement Autocorrelation

To explore the confinement picture, we calculate displacement autocorrelation functions $C_d(t) = \langle \Delta x(t + \tau) \Delta x(t) \rangle$ at all polymer concentrations in 10^{-6} M solutions. The displacements of 100 nm particles become anticorrelated at $t = 32$ ms, which corresponds to the first time interval in our movies, in solutions with $c > 10c^*$ (Figure 2.18 & 2.19(a)). The degree of anticorrelation increases with increasing polymer concentration but decreases for larger particles. The larger anticorrelation in 100 nm particles suggests that they experience caging-like effects, in which the particle rebounds after encountering an elastic polymer network as polymer concentration increases. Additionally, the appear-

ance of anticorrelated displacements occurs close to the onset of non-Gaussian particle displacements and the maximum in the D/D_{SE} deviation. Together, these factors suggest that the observed anomalous diffusion is a result from the unique structural properties of polyelectrolytes.

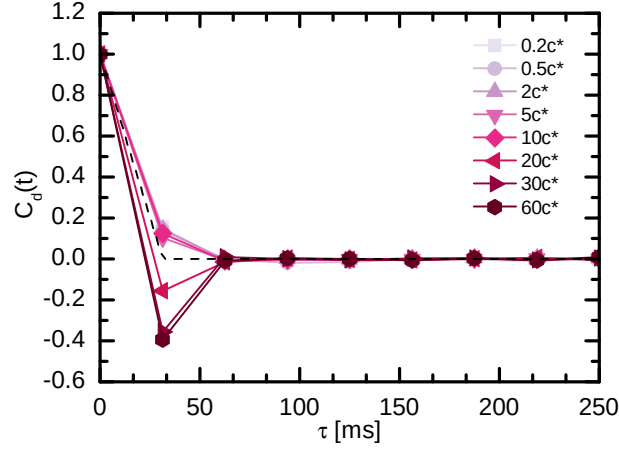


Figure 2.18: Normalized coefficient of displacement autocorrelation $C_d(t)$ as a function of elapsed time τ for 100 nm particles in 10^{-6} M ionic strength solutions. Dashed line represents the displacement autocorrelation of a Gaussian process.

We calculate displacement autocorrelation functions to quantify the correlation between two successive displacements. The calculations are conducted according to

$$\Delta x(t) = x(t + \Delta t_{\text{int}}) - x(t) \quad (2.1)$$

and

$$C_d^*(\tau) = \langle \Delta x(t + \tau) \Delta x(t) \rangle, \quad (2.2)$$

where $x(t)$ represents the particle position at a time t , Δt_{int} is the real time step for change of displacement, and τ is the correlation displacement step. Angular brackets denote the ensemble-average at multiple time origins. To compare sample to sample data more easily, we normalize the autocorrelation coefficient via

$$C_d(\tau) = \frac{C_d^*(\tau)}{C_d^*(0)}, \quad (2.3)$$

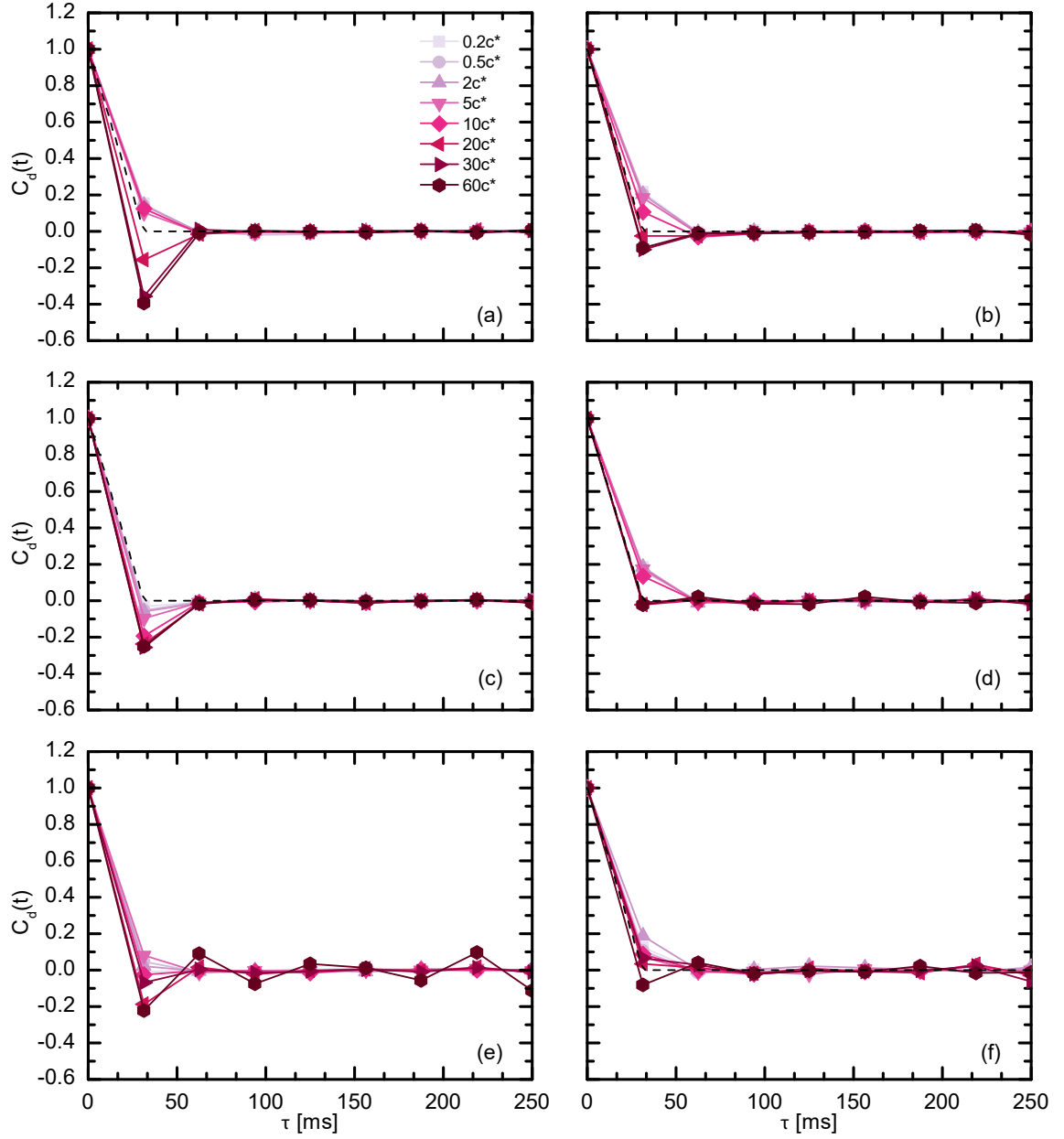


Figure 2.19: Normalized coefficient of displacement autocorrelation $C_d(t)$ as a function of elapsed time τ for (a) 100, (b) 200, (c) 300, (d) 380, (e) 600, and (f) 790 nm particles in NaPSS solutions at 10^{-6} M ionic strength. Dashed line represents a Gaussian process.

where $C_d^*(0)$ represents the displacement autocorrelation value of the first displacement step. This choice normalizes the function such that at $t = 0$ it has the value 1 for all samples. We observe more pronounced anticorrelation for small particles compared to large ones, suggesting that small particles experience caging-like effects with increasing

polymer concentrations (Figure 2.19).

2.4 Conclusions

We probe the mobility of nanoparticles of diameter 100 – 790 nm in dilute and semidilute solutions of a model flexible polyelectrolyte, sodium polystyrene sulfonate, at three different ionic strengths (10^{-6} , 10^{-3} , and 10^{-1} M). We find that nanoparticles exhibit Fickian diffusion on experimental time scales with dynamics that become slower as particle size and polymer concentration are increased. Large particles ($R_{\text{NP}} > R_g$) diffuse according to Stokes-Einstein predictions at all ionic strengths. The diffusivities of small particles ($R_{\text{NP}} < R_g$) in polyelectrolyte solutions of low ionic strength, however, exhibit a non-monotonic deviation from the SE prediction that depends on polymer concentration, including a return to SE behavior at high polymer concentrations. Available models for diffusion of particles in solutions of fully flexible Gaussian chains are unable to explain the observed dynamics. In analogy with a physical picture developed for particle diffusion in entangled systems, we suggest that increasing constraints on particle motion due to confinement by the polyelectrolyte chains are responsible for the return to SE diffusion at high concentrations.

The length scale driving this confinement is still unknown. Polymer structure on short length scales may need to be considered to develop models that are capable of capturing particle dynamics in charged polymer solutions. To probe the dynamics of different size particles at the relevant size limit ($R_{\text{NP}} \ll R_g$), different dynamic techniques (such as but not limited to X-ray photon correlation spectroscopy, XPCS, or superresolution microscopy) are required to extend the dynamic range beyond the resolution limit of optical microscopy ($d_{\text{NP}} \sim 100$ nm). A better understanding of the length scales controlling particle dynamics has interesting implications for a wide range of applications requiring diffusion in complex media, including rigid rods⁷⁵, emulsions⁷⁶, and cellular cytoplasm¹⁹.

Chapter 3

Chain Flexibility Effects on Nanoparticle

Dynamics in Semidilute Polyelectrolyte Solutions

3.1 Introduction

Nanoparticle transport through complex media is ubiquitous in various applications including targeted drug delivery,^{38,39} enhanced oil recovery,^{32,33} and nanocomposite materials.^{35,36} Understanding the transport of particles in complex fluids is key to effectively utilize them in applications. The Stokes-Einstein (SE) model gives an accurate description of the diffusion of a nanoparticle with radius R_{NP} through a homogeneous medium according to the equation $D_{SE} = k_B T / 6\pi\eta R_{NP}$. When inhomogeneities in the medium are comparably sized as particles, however, the underlying assumptions from SE theory do not hold and particles deviate from predicted dynamics.^{40,41,42,17} In these solutions, the interactions between the particles and heterogeneities define the relevant length scales for particle transport.

In neutral polymer solutions, the length scales are defined according to the properties of the polymer mesh. The length scale in entangled solutions is the tube diameter a , the distance between entanglement strands. Large particles are locally caged within the entanglement mesh until the reptation time scale, after which SE behavior is recovered.^{43,44,45,46} Conversely, smaller particles ($R_{NP} \ll a$) diffuse within the entanglement mesh. While particle dynamics in entangled solutions are well understood, a complete physical picture for the transport of particles in charged unentangled solutions is still lacking.

In unentangled neutral polymer solutions, the distance between the two nearest neigh-

boring chains, correlation length ξ , represents the important length scale in unentangled solutions. In these systems, particle dynamics depend on hydrodynamic interactions, which decay over ξ . Empirical models assume a homogeneous medium where particle dynamics depend on polymer length scales including ξ and radius of gyration R_g . Studies probing the diffusion of particles and tracers in polymer solutions show that particle dynamics can be predicted using the particle and polymer length scales.^{21,59,63,52,53} In charged unentangled polymer solutions, however, recent studies show that the unique structural properties, in the form of highly extended conformation within correlation volumes,^{26,27,23,28,29} introduce confinement effects resulting in non-monotonic deviations from SE.⁷⁷ Polyelectrolytes exhibit higher backbone stiffness (i.e. persistence length l_B),⁴⁹ compared to their neutral counterparts due to the electrostatic repulsion on their backbones.^{22,23,24,25} The larger l_B values allow polyelectrolytes to acquire a multitude of conformations ranging from rigid rod to semiflexible chain depending on the chain size or degree of polymerization. Despite recent studies exploring tracer transport and chain structure on particle dynamics in polymer solutions,^{52,53,77,78} chain flexibility effects remain incompletely understood.

In this chapter, we examine the dynamics of spherical nanoparticles in unentangled semidilute polyelectrolyte solutions using dynamic x-ray scattering. We tune the chain flexibility by changing the molecular weight of the polyelectrolyte chains, effectively varying the size of the chain with respect to its persistence length. The particle relaxation rates scale diffusively as a function of wavevector $\Gamma \sim Q^2$ in all solutions examined. We find that particles in stiffest chain solutions follow the predictions according to SE, consistent with the relative particle to polymer size regime. In solutions of intermediate chain stiffness, particles exhibit non-monotonic deviations from predictions with signatures of confinement effects. Particles in solutions of least stiff chains, however, linearly deviate from bulk predictions as concentration increases. The observed dynamics do not scale according to predictions of existing models. Together, these observations suggest that chain flexibility and stiffness plays a significant role on the dynamics of particles in polyelectrolyte systems.

3.2 Materials and methods

3.2.1 Solutions preparation

Glass vials were cleaned overnight in a solution of 6.5 wt% potassium hydroxide in isopropanol, ensuring near salt-free conditions. Residual salt was removed by rinsing vials ten times using Millipore water. The vials were then dried in an oven for two hours at 105 °C. Silica particles with diameter $d_{\text{NP}} = 60$ nm (Polydispersity $< 12\%$ and zeta potential -25 to -80 mV, nanoComposix) and silanol surface modification were dispersed in separate aqueous solutions of NaPSS with a weight-averaged molecular weights $M_w = 22000, 200, 68$ kDa (Scientific Polymer Products) at salt free conditions. Deionized water was assumed to have an ionic strength of 10^{-6} M.⁵⁴ A constant particle volume fraction $\phi = 0.4 \times 10^{-2}$ was used across all samples to ensure enough scattering intensity signal while minimizing interparticle interactions and avoid aggregation. The overlap concentration c^* of NaPSS was estimated at each ionic strength from intrinsic viscosity measurements, and the radius of gyration $R_{g,0}$ in each ionic strength solution was determined via $R_{g,0} = (M_w[\eta]/(4/3\pi N_{\text{av}}))^{1/3}$.^{55,56} The resulting $R_{g,0}$ in dilute solutions were 190, 41, and 13 nm at M_w values of 2200, 200, and 68 kDa, respectively.

3.2.2 Rheology

Steady-shear measurements of the rate-dependent viscosity and dynamic frequency sweep measurements were performed on Discovery Hybrid Rheometer (TA Instruments, HR-2). Polymer solutions were loaded into a single gap Couette cell with a cup diameter of 15 mm, a bob diameter of 14 mm, and a bob length of 42 mm. The inertia and torque of the instrument were calibrated prior to measurements. Samples were pre-sheared for one minute to reach equilibrium, after which the viscosity was determined as the average value over one minute. All data points with a generated torque value below $0.1 \mu\text{N}\cdot\text{m}$ or raw phase angle values above 175° were eliminated to ensure torque was above instrument

sensitivity and to avoid effects of inertia, respectively.

3.2.3 X-ray photon correlation spectroscopy

Experiments were carried out at the x-ray photon correlation spectroscopy (XPCS) setup at sector 8-ID of the Advanced Photon Source at Argonne National Laboratory. We estimated the scattering length densities (SLDs) in $10^{-6} \text{ \AA}^{-2}$ to be 18.831 for particles, 7.131 for NaPSS, and 9.469 for water. Solutions were pipetted into thin-walled quartz capillary tubes (2 mm thickness, Charles Supper), which was then sealed to prevent any evaporation. Finally, the samples were attached to a copper block with an attached Peltier plate to control the temperature. An area detector (X-spectrum LAMBDA 750 K)^{79,80} was located 8 m away from the sample, allowing the capture of scattering intensity across a wavevector range $0.001 \text{ \AA}^{-1} < Q < 0.051 \text{ \AA}^{-1}$ that is equivalent to a length scale range $0.21 < L/d_{\text{NP}} < 10.5$. All measurements were carried out at 25 °C. We measured autocorrelation curves at five different positions across the sample then averaged the data together while propagating error throughout the fitting protocol. All rheo-XPCS data was analyzed using the Gui Matlab scripts provided by sector 8-ID.

3.3 Results and discussion

3.3.1 Rheology

We confirm that the rheology of these solutions follows established predictions for polyelectrolyte solutions (Figure 3.2).^{23,51,54,26,77} The specific viscosity of the polyelectrolyte solutions increases as a function of polymer concentration (Figure 3.1). We examine the changes in specific viscosity $\eta_{\text{SP}} = (\eta - \eta_0)/\eta_0$ (Figure 3.2), where η and η_s are the solution and solvent viscosities, respectively, because it offers a direct measurement of the polymer contribution to solution viscosity. At dilute concentrations ($c/c^* < 1$), the specific

viscosity η_{sp} of solutions at all molecular weights collapse onto a single curve due to the dominance of hydrodynamic interactions^{81,3,4} with a concentration scaling $\eta_{\text{sp}} \sim (c/c^*)^1$. In the semidilute regime ($c/c^* > 1$), the specific viscosity scales according to predictions for polyelectrolyte solutions at low ($\eta_{\text{sp}} \sim (c/c^*)^{1/2}$).^{23,51,26} We report the shear-dependent viscosity for aqueous NaPSS solutions at all ionic strengths and find that viscosity remains constant at all shear rates for all solutions (Figure 3.1). This observation suggests that chains relax at time scales < 10 ms and are not entangled in our solutions. Thus, these solutions serve as a model system to investigate the effects of chain flexibility on particle dynamics.

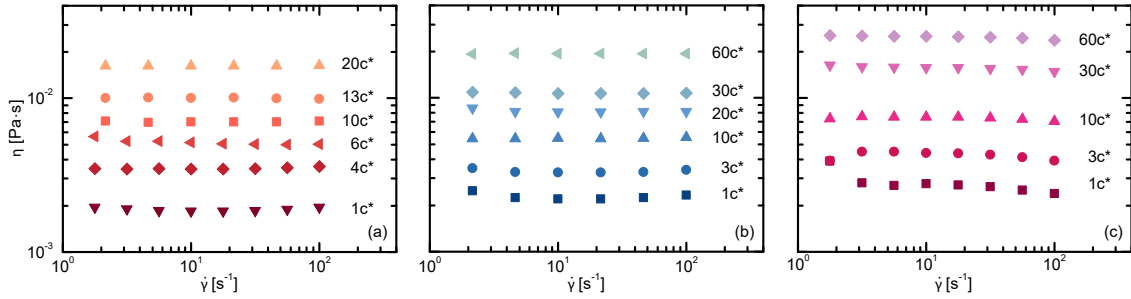


Figure 3.1: Viscosity η for (a) 68, (b) 200, and 2200 kDa NaPSS solutions as a function of shear rate $\dot{\gamma}$.

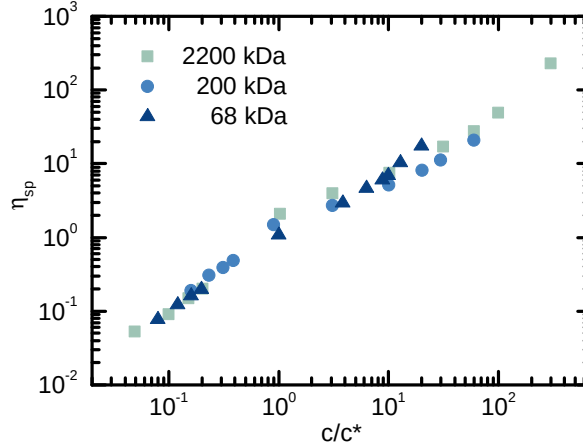


Figure 3.2: Specific viscosity $\eta_{\text{sp}} = (\eta - \eta_0)/\eta_0$ as a function of normalized NaPSS concentration c/c^* for solutions with different chain molecular weights.

3.3.2 Polymer Length Scales

NaPSS is a model polyelectrolyte that exhibits a unique structural dependence on solution ionic strength. The electrostatic interactions along its backbone results in a larger persistence length l_B compared to its neutral counterparts. As molecular weight increases, the chain becomes larger than l_B and chains retain more flexibility. We calculate contour length $l = Na$, where N is the number of monomers and a represents the length of a carbon bond (1.54 Å). Polymer end-to-end distance was determined using $R_e = \sqrt{N}a$. Kuhn length is estimated as $b = \sqrt{6R_{g,0}^2/N}$. We calculated correlation length ξ and polymer size R_g within the semidilute regime via $\xi = R_{g,0}(c/c^*)^{-\nu/(3\nu-1)}$ and $R_g = R_{g,0}(c/c^*)^{-(\nu-0.5)/(3\nu-1)}$, where ν is the Flory exponent.

Table 3.1: Estimations of relevant length scales for 68, 200, and 2200 kDa NaPSS in dilute aqueous solutions.

Polymer Property	68 kDa	200 kDa	2200 kDa
Number of monomers N	373	1283	12251
Contour length l [nm]	58	198	1890
Radius of gyration R_g [nm]	13	41	190
End-to-end distance R_e [nm]	32	55	170
Kuhn length b [nm]	1.7	2.8	4.2

3.3.3 Particle Dynamics

After confirming that our solutions follow expected polyelectrolyte rheology in the dilute and semidilute regimes, we investigate the dynamics of silica particles in polyelectrolyte solutions using XPCS. The probed dynamics represent the center of mass dynamics of silica particles since x-ray scattering is dominated by the silica particles. The intensity autocorrelation curves G_2 decay faster with time at smaller wavevectors Q . We fit the autocorrelation curves using a stretched exponential function $G_2(Q, \Delta t) = 1 + B \exp \left[-(\Gamma \Delta t)^\beta \right]^2 + \varepsilon$ where B is the Siegert factor that depends on experimental geometry, and $\beta \approx 0.93$ is a stretching exponent that is globally fit, and ε represents the residual

noise (Figure 3.3). Relaxation rates of silica particles scale diffusively as $\Gamma = DQ^2$, where D is the particle diffusivity (Figure 3.4), consistent with the observed stretching exponent values $\beta \approx 0.93$. The particle diffusivity slows down with polymer concentration c/c^* , reflecting the increase in bulk viscosity of the solutions. To quantify the particle dynamics with respect to their size, we normalize the measured diffusivities D by the diffusivity of the silica particles in pure solvent D_0 .

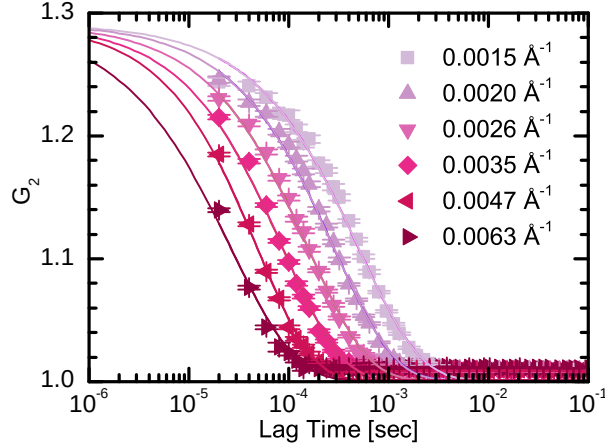


Figure 3.3: Intensity autocorrelation function G_2 as a function of lag time for $0.0015 \text{ \AA}^{-1} \leq Q \leq 0.0063 \text{ \AA}^{-1}$ for a $60c^*$ solution of 2200 kDa NaPSS chains. Solid curves are stretched exponential fits.

Particles diffuse according to solvent viscosity (i.e. $D/D_0 \approx 1$) at low polymer concentrations across all molecular weights (Figure 3.5), with an outlier at the lowest concentration sample in 68 kDa NaPSS. The dynamics slow as concentration increases into the semidilute regime in low and intermediate M_w samples. In the highest ionic strength samples, however, the particle dynamics remain coupled to the solvent viscosity until reaching intermediate polymer concentrations within the semidilute regime $10c^*$, after which particle diffusivity decreases with increasing concentration. At a given concentration c/c^* within the semidilute regime, the particle dynamics are faster as chain flexibility increases, consistent with the lower viscosity of the solutions (Figure 3.2). The different concentration dependencies of particle dynamics at different chain flexibilities suggests that these systems decouple differently from bulk solution viscosity.

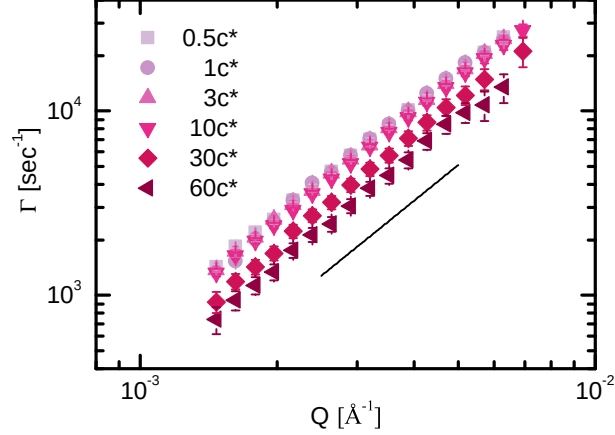


Figure 3.4: Relaxation rate Γ as a function of wavevector Q for 2200 kDa NaPSS solutions at various concentrations. Solid lines indicate Q^2 scaling.

We analyze the dynamics of silica particles in the different NaPSS solutions in comparison to the predictions based on the bulk viscosity to investigate the difference between nanoscale dynamics of particles and microrheological predictions. Specifically, we examine the particle diffusivity normalized by the SE diffusivity D/D_{SE} as a function of polymer concentration. We use the viscosities from shear rheology measurements to estimate SE diffusivities.

Instead, the discrepancy in D/D_{SE} must originate from interactions between silica particles and the surrounding polymer solution on the nano- or microscale.

Particles in solutions of lowest M_w exhibit diffusivities that approximately conform to the Stokes-Einstein prediction using the measured bulk viscosities (Figure 3.6). For intermediate and high M_w samples, the dynamics of particles follow predictions from SE then systematically deviate with polymer concentration. The trend and extent to which the dynamics deviate, however, depends on the chain size. In intermediate M_w samples, D/D_{SE} increases with concentration until reaching a global maximum at intermediate concentrations $\sim 6c^*$ after which dynamics slow down. The observed dynamics in intermediate size samples suggests that deviations are non-monotonic in nature, consistent with earlier studies of particle dynamics at similar length scales as chains in semidilute polyelectrolyte

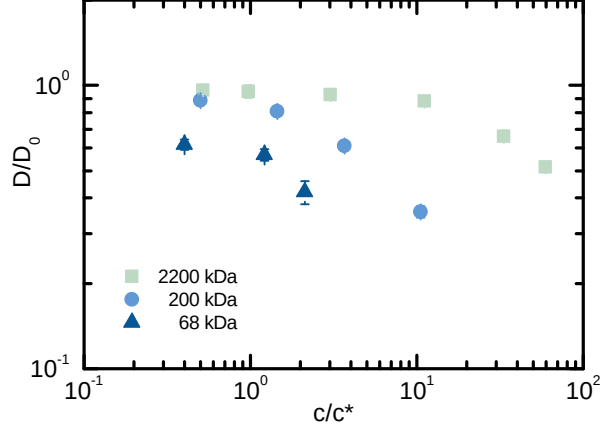


Figure 3.5: Normalized particle diffusivity D/D_0 as a function of NaPSS concentration c/c^* for various chain flexibility samples. Error bars represent a 95% confidence interval.

solutions.⁷⁷ The non-monotonic deviations are attributed to the unique structural properties of polyelectrolytes that give rise to confinement effects despite the absence of entanglements.

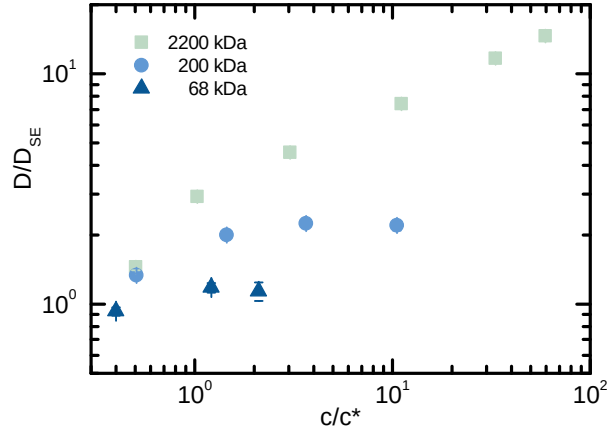


Figure 3.6: Normalized particle diffusivity D/D_{SE} as a function of NaPSS concentration c/c^* for various chain flexibility samples. Error bars represent a 95% confidence interval.

Particle dynamics in the largest chains, however, linearly deviate from SE predictions as concentration increases. The systematic deviations are quantitatively similar to earlier studies examining particle dynamics in partially functionalized polymer solutions.⁶³ In these systems, the dynamics of intermediate size particles ($\xi < R_{NP} < a$) couple to the

segmental relaxation of polymer chains resulting in a collapse of the observed dynamics onto a master curve according to the particle to polymer size ratio ξ/R_{NP} with a scaling exponent of -2 .⁴⁵ When we examine our dynamics with respect to this model, however, we find that the scaling behavior does not capture our observed dynamics (Figure 4.7), suggesting that the particles do not couple to polymer relaxations as predicted for neutral polymers.

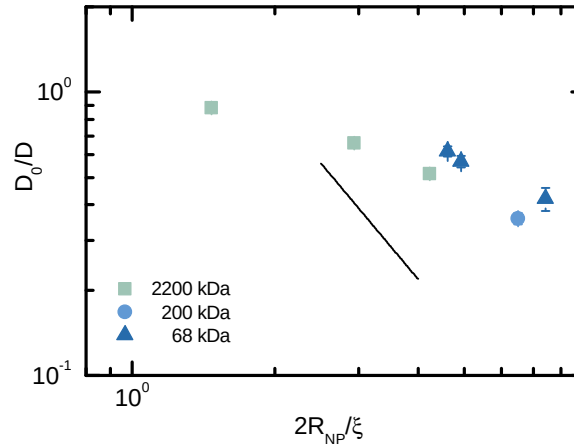


Figure 3.7: Relative diffusivity D_0/D as a function of $2R_{NP}/\xi$ for NaPSS solutions at different molecular weights. Solid line represents a scaling exponent of -2 .⁴⁵

The differences in particle dynamics in polymer solutions can be examined according to the relative particle to polymer size regimes. In our solutions, the particles are twice the size of the lowest molecular weight chains $R_{NP} \approx 2R_{g,0}$. Because the dynamics in these samples couple to the bulk viscoelasticity according to SE, we confirm that particles probe an effectively homogeneous medium with heterogeneities from chains averaging out across the particle surface. For intermediate and large molecular weight chains, particles are smaller than the size of chains and fall within the regime where deviations from SE are previously observed.⁷⁷ Despite finding that particles experience deviations within the semidilute regime, these deviations trend differently at each molecular weight. These observations suggest that chain flexibility plays a significant role in influencing particle dynamics in polyelectrolyte solutions.

3.4 Conclusions

We show that the dynamics of particles in polyelectrolyte solutions are influenced by the structural properties and size of the background chains. Specifically, we use dynamics x-ray scattering to demonstrate how chain flexibility affects particle dynamics. We tune chain flexibility molecular weight. Particles follow predictions according to their size relative to polymer chains in lowest molecular weight samples. The intermediate and highest molecular weight samples exhibit deviations from SE predictions. The deviations, however, are non-monotonic for intermediate size samples and monotonic in the highest molecular weight solutions. We attribute the different deviations to changes in the interactions between the particles and the polymer chains as chain flexibility is altered. These observations emphasize the importance of chain structural properties to understand the underlying physics controlling particle dynamics in solutions. This work has implications for a wide range of applications requiring diffusion in complex media, including rigid rods⁷⁵, emulsions⁷⁶, and cellular cytoplasm¹⁹.

Chapter 4

Electrostatic Repulsion Slows Relaxations of Polyelectrolytes in Semidilute Solutions

4.1 Introduction

The mechanical response of polyelectrolytes is primarily determined by the chain dynamics,⁸² which in turn is dictated by the configuration of polyelectrolyte chains. Electrostatic interactions on the polyelectrolyte backbone affect the chain conformation. Additionally, these interactions underpin the favorable properties (stability and compatibility) that make polyelectrolytes an essential component of biological systems such as cartilage tissues^{83,84,85} and good lubricants for muscle joints,⁸⁶ and as thickening agents and rheological modifiers in cosmetics,^{87,88} food products,^{89,90} and paints.⁹¹ Hence, understanding the effects of structure on the dynamics of polyelectrolyte solutions is key to identify and control the distinct physical processes governing the mechanics of polyelectrolyte solutions.

The structure of polyelectrolytes deviates strongly from predictions for neutral chains^{58,27} because of the electrostatic repulsions along the polymer backbone.^{22,23,24,25} These interactions result in a highly extended conformation of electrostatic blobs inside the correlation blob.^{26,27,23,28,29} On length scales beyond the correlation volume, polyelectrolytes transition to a random walk conformation of correlation blobs as the repulsive interactions are screened.^{27,23,28} Alternatively, these interactions can be screened at high ionic strengths so that polyelectrolytes approach fully flexible chain conformations. These unique structural properties have significant effects on chain dynamics, as reported by studies exploring the effects of counterion valence,⁹² electrostatic screening length scaling,⁹³ and entanglement

crossover and density.⁵⁴ The segmental relaxations of neutral chains are described by the Zimm model in dilute solutions,³ by the Rouse model in semidilute solutions,⁵ and by the reptation model in entangled solutions.⁹⁴ Experimental measurements of viscosity, relaxation times, and disentanglement,^{95,51,96,97,98,99,100,54,101,102} however, show poor agreement with scaling model predictions for polyelectrolytes. We expect these discrepancies are caused by the extended structure of the polyelectrolyte chains. Therefore, there is a critical need to independently measure polyelectrolyte conformation and segmental relaxations to elucidate the relationship between structure and dynamics in semidilute polyelectrolyte solutions.

In this study, we show that the segmental relaxations of polyelectrolytes follow de Gennes narrowing in which the local chain structure perturbs standard Zimm relaxations. We independently tune geometric and electrostatic length scales, measured with small-angle neutron scattering (SANS), by varying polymer and salt concentration, respectively, to understand the dynamic behavior of polyelectrolytes, measured with neutron spin echo (NSE) spectroscopy. The SANS profiles of these solutions at all ionic strengths resemble the profile expected for chains with highly extended random walk conformation and can be fit using a model combining the form factor of a semiflexible chain with excluded volume interactions and a PRISM structure factor. Chain dynamics across the correlation length ξ , however, deviate from the standard Zimm model. Specifically, the polymer dynamics are suppressed around the structure peak induced by the electrostatic interactions between chains. Approximating the structure factor of the polyelectrolyte chains as a perturbation from neutral Gaussian chains, we demonstrate that these slow relaxations are wholly described by the structure of polyelectrolytes and follow the theoretical prediction of de Gennes narrowing, in which dynamics are inversely related to structure due to the presence of a free energy minimum over a characteristic structural length scale.^{103,104} Our findings indicate that the unique structural properties of charged chains underpin the deviation of polyelectrolyte dynamics from theoretical predictions.

4.2 Materials and methods

Our experimental system consists of sodium polystyrene sulfonate (NaPSS) chains ($M_w = 68$ kDa) dissolved in Millipore water or deuterium oxide for rheology and neutron scattering experiments, respectively.⁷⁷ The ionic strength of the solutions was tuned by adding appropriate amounts of sodium chloride. The radius of gyration was determined from intrinsic viscosity experiments to be $R_{g,0} = (13, 12, \text{ and } 9.5)$ nm at ionic strengths of $I = (10^{-6}, 10^{-2}, \text{ and } 10^{-1})$ M (M = mol/L, moles per liters of solution), respectively. The polymer concentrations were chosen to obtain similar correlation lengths for samples at different ionic strengths according to de Gennes' scaling predictions $\xi = R_{g,0}(c/c^*)^{-\nu/(3\nu-1)}$ (Table 4.2). Steady-shear rheology measurements were performed on a Discovery Hybrid Rheometer (TA Instrument, HR-2) using a Couette geometry. We collected small-angle neutron scattering (SANS) and neutron spin-echo (NSE) data on the NGB30 and NSE instruments, respectively, at the Center for Neutron Research, National Institute of Standards and Technology (NIST).^{105,106} The raw SANS and NSE data were reduced using IgorPro¹⁰⁷ and DAVE¹⁰⁸ software package, respectively. All experiments were performed at room temperature.

4.2.1 Solution preparation

Glass vials were soaked overnight in a base bath solution of 6.5% mass fraction potassium hydroxide in isopropanol to ensure near salt-free conditions. Residual salt was removed by rinsing vials ten times using Millipore water. The vials were then dried in an oven for two hours at 105 °C. Sodium polystyrene sulfonate (NaPSS) with a weight-averaged molecular weight $M_w = 68,000$ Da (Scientific Polymer Products) was dissolved in deuterium oxide (Sigma-Aldrich) or Millipore water at three different ionic strengths. The ionic strength of deuterium oxide and deionized water was assumed to be 10^{-6} M (M = mol/L, moles per liter of solution).⁵⁴ The ionic strength of the other two sets of solutions

was adjusted by adding sodium chloride to achieve (10^{-2} and 10^{-1}) M.

4.2.2 Rheology

A single-gap Couette cell (15 mm in diameter), equipped with a bob (14 mm in diameter, and 42 mm in length) was used to collect dynamic frequency sweep measurements on a Discovery Hybrid Rheometer (TA Instruments, HR-2). Dynamic strain sweep measurements were performed at angular frequency frequencies $\omega = (1, 10, \text{ and } 100)$ rad/s. We observe linear viscoelastic behavior up to strain values of $\gamma = 20\%$. We measured storage (G') and loss (G'') moduli of aqueous NaPSS solutions as a function of angular frequency at a fixed strain value of 10%. All data points with a generated torque value below $0.1 \mu\text{N}\cdot\text{m}$ or raw phase angle values above 175° were eliminated to ensure torque was above instrument sensitivity and to avoid effects of inertia, respectively.

4.2.3 Neutron Scattering

We prepared three sets of NaPSS solutions in deuterium oxide at three different ionic strengths. Deuterium oxide was used as the solvent to minimize incoherent scattering contribution to total scattering and enhance contrast. The polymer concentrations were chosen to obtain similar chain structural properties (i.e., correlation length) for samples at different ionic strengths according to de Gennes' scaling predictions. We estimated the scattering length densities (SLDs) in $10^{-6} \text{ \AA}^{-2}$ to be 1.140 for NaPSS, and 6.393 for deuterium oxide, which provided sufficient contrast to isolate the scattering signal from polyelectrolyte chains. Samples were loaded into 4 mm thick titanium demountable cells to ensure a transmission of 60% to 70%. We collected small-angle neutron scattering (SANS) and neutron spin-echo (NSE) on the NGB30 and NSE instruments, respectively, at the Center for Neutron Research, National Institute of Standards and Technology (NIST).^{105,106} SANS was performed at all available configurations including lenses and sample to detector distances (1, 4, and 13) m to achieve a wavevector range of $(0.001 \text{ to } 0.5) \text{ \AA}^{-1}$, corresponding to

length scales of (1.3 to 630) nm. The raw SANS data was reduced to an absolute intensity by correcting for the blocked beam scattering, empty cell scattering, and detector sensitivity and normalizing to the incoming beam intensity using IgorPro.¹⁰⁷ NSE was collected at two incident wavelengths (6 and 8) Å to acquire data across a wavevector range of (0.05 to 0.26) Å⁻¹, corresponding to length scales of (2.4 to 12.6) nm. The data were scaled to account for the solvent dynamics and instrument resolution by measuring the echoes of pure deuterium oxide and a charcoal standard, respectively. The DAVE software package was used to reduce NSE data.¹⁰⁸ All measurements were performed at room temperature.

4.3 Results and discussion

4.3.1 Intrinsic viscosity

Dilute aqueous NaPSS solutions were introduced into a glass capillary viscometer (Cannon Instrument Company, 0C). The consistent observed crossover between the dilute (viscometer) and semidilute (rheometer) regimes at the estimated overlap concentration suggests that the viscometer accurately captures the polymer contribution to viscosity despite operating at a high shear rate of $\approx 300 \text{ s}^{-1}$. We determined intrinsic viscosity $[\eta]$ by fitting the data to the first order virial expansion of viscosity $\eta = \eta_0(1 + [\eta]C_{\text{NaPSS}})$, where η_0 is the solvent viscosity, and $[\eta]$ is the intrinsic viscosity. The overlap concentration ($c^* = 1/[\eta]$) was then estimated to be (12.3, 15.7, and 31.9) g/L and radius of gyration ($R_{g,0} = (M_w/(4/3\pi N_{\text{av}}c^*))^{1/3}$) was calculated to be (13, 12, and 9.5) nm for 68 kDa polymer at (10^{-6} , 10^{-3} , 10^{-1}) M ionic strength, respectively. We determined the Flory exponent ν at each ionic strength from the scaling of polymer size with molecular weight (Figure 4.1(b)) using the Flory theory of fractal chains.⁵⁷

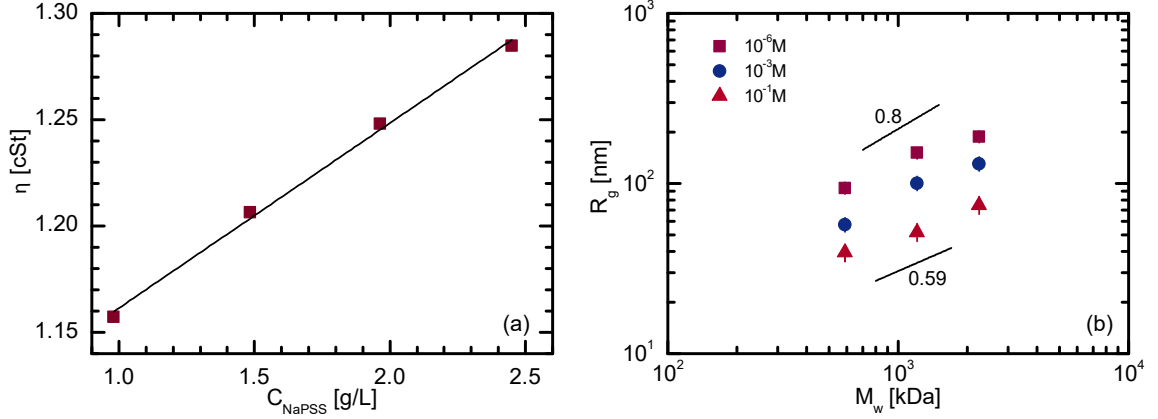


Figure 4.1: (a) Solution viscosity η as a function of NaPSS concentration C_{NaPSS} for 68 kDa NaPSS in 10^{-6} M solutions. (b) Radius of gyration R_g as a function of polymer molecular weight M_w . Solid lines represent theoretical scaling.

4.3.2 Rheology

We confirm that the rheology of these solutions follows established predictions for polyelectrolyte solutions (Figure 4.2).^{23,51,54,26,77} Polymer solutions viscosity remains constant at all shear rates. At dilute concentrations ($c/c^* < 1$), the specific viscosity $\eta_{\text{sp}} = (\eta - \eta_s)/\eta_s$, where η and η_s are the solution and solvent viscosities, respectively, of solutions at all ionic strengths collapse onto a single curve due to the dominance of hydrodynamic interactions^{81,3,4} with a concentration scaling $\eta_{\text{sp}} \sim (c/c^*)^1$. In the semidilute regime ($c/c^* > 1$), η_{sp} increases as a power-law with normalized polymer concentration ($\eta_{\text{sp}} \sim (c/c^*)^\alpha$) and conforms with the scaling predictions in the limits of low ($\alpha = 1/2$) and high ($\alpha = 5/4$) ionic strength. For solutions of intermediate ionic strength, however, $\alpha = 0.9 \pm 0.1$ is intermediate between the low and high salt limits. The storage modulus of these samples was not detected within our angular frequency range and instrument criteria. As a result, we were not able to observe a crossover between G' and G'' , suggesting the absence of entanglements and that chains relax quickly in our solutions. We report the shear-dependent viscosity for aqueous NaPSS solutions at all ionic strengths and find that viscosity remains constant at all experimented shear rates for all solutions (Figure 4.4). This observation suggests that chains relax at time scales < 10 ms, consistent with

the measured oscillatory rheology (Figure 4.3).

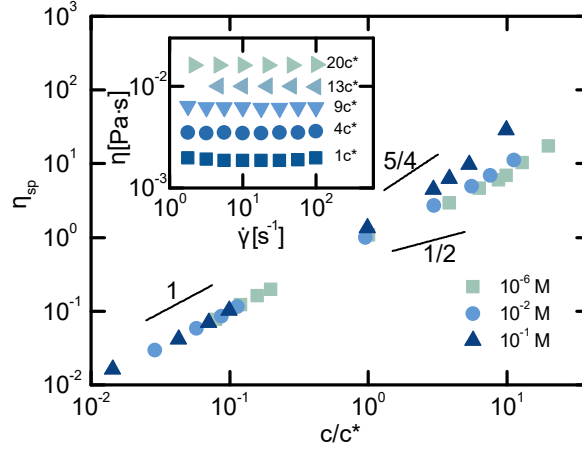


Figure 4.2: Specific viscosity $\eta_{sp} = (\eta - \eta_0)/\eta_0$ as a function of normalized NaPSS concentration c/c^* for solutions of various ionic strength. *Inset:* Viscosity η for 10^{-6} M ionic strength solutions as a function of shear rate $\dot{\gamma}$.

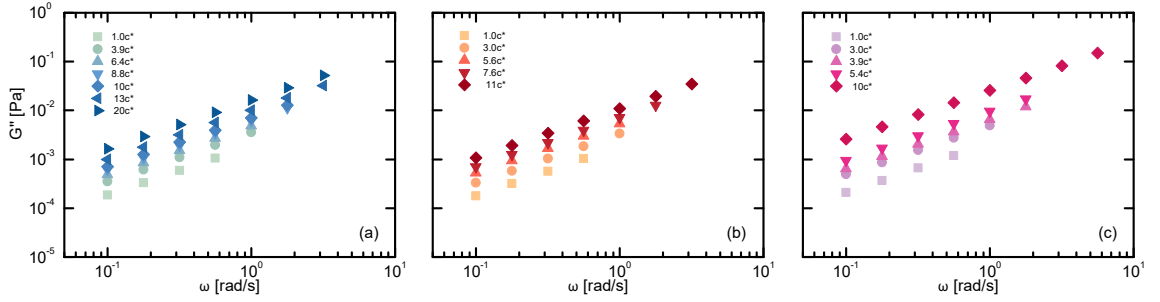


Figure 4.3: Loss modulus G'' as a function of angular frequency ω for (a) 10^{-6} M, (b) 10^{-2} M, and (c) 10^{-1} M ionic strength NaPSS aqueous solutions. Error bars are smaller than symbols and represent a standard deviation of two measurements.

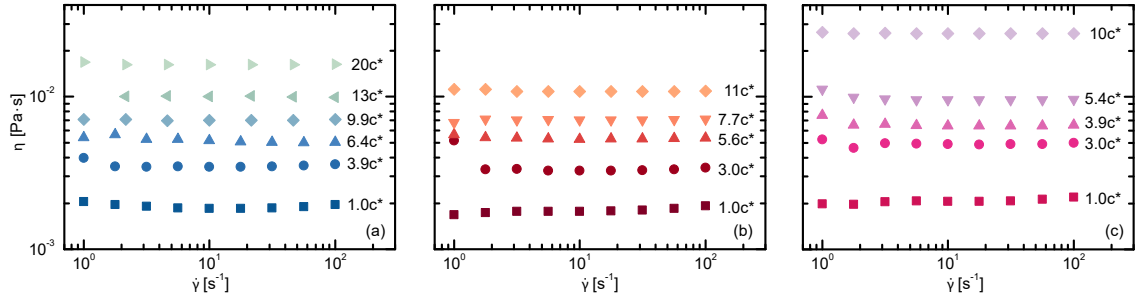


Figure 4.4: Viscosity η for (a) 10^{-6} M, (b) 10^{-2} M, (c) 10^{-1} M ionic strength NaPSS aqueous solutions as a function of shear rate $\dot{\gamma}$. Error bars are smaller than symbols and represent the standard deviation of two separate measurements.

4.3.3 Polymer Length Scales

NaPSS is a model polyelectrolyte that exhibits a unique structural dependence on solution ionic strength. The electrostatic interactions along its backbone results in a larger persistence length compared to its neutral counterparts. As ionic strength increases, the charges on the backbone are screened and chains retain more flexibility. We calculate contour length $l = Na$, where N is the number of monomers and a represents the length of a carbon bond (1.54 Å). Electrostatic blob size is estimated $D_e^* = b(uf_*^2)^{-1/3}$ at the effective charge fraction f_* , where $u = l_B/b$ is the interaction parameter, l_B is the Bjerrum length, and $b = \sqrt{6R_{g,0}^2/N}$ is the Kuhn length. We calculate the number of monomers $n_b = D_e^*/a$ in an electrostatic blob. The stretching parameter B is determined according to $B = Na/R_{g,0}$. We calculated correlation length ξ and polymer size R_g within the semidilute regime via $\xi = R_{g,0}(c/c^*)^{-\nu/(3\nu-1)}$ and $R_g = R_{g,0}(c/c^*)^{-(\nu-0.5)/(3\nu-1)}$.

Table 4.1: Estimations of relevant length scales for 68 kDa NaPSS in dilute solutions at different solution ionic strength. Error bars are estimated according to a 95% confidence interval.

Polymer Property	10^{-6} M Solution	10^{-3} M Solution	10^{-1} M Solution
Radius of gyration R_g [nm]	13 ± 0.5	12 ± 0.3	9.5 ± 0.4
Contour length l [nm]	58 ± 0.3	58 ± 0.3	58 ± 0.3
Kuhn length b [nm]	1.7 ± 0.1	1.5 ± 0.1	1.2 ± 0.1
Electrostatic blob D_e^* [nm]	2.2 ± 0.1	2.0 ± 0.1	1.4 ± 0.1
Monomers per blob n_b	14 ± 1.0	13 ± 1.0	9.0 ± 1.0
Stretching Parameter B	4.5 ± 0.2	4.8 ± 0.1	6.1 ± 0.3

4.3.4 Polyelectrolyte Chain Structure

The rheology measurements show that the properties of polyelectrolyte systems can be tuned by screening the electrostatic interactions, which modify the polymer conformations. To characterize these conformations, we capture the scattering profile of our solutions using SANS to quantify their structural properties within the correlation blob. The SANS scattering profiles of NaPSS solutions display a local maximum at Q^* between (0.08 and 0.14)

$\text{\AA}^{-1}$ (Figure 4.5(a)). The peak is the characteristic structural signature of polyelectrolyte solutions and results from the high osmotic pressure due to counterion entropy, which prevents the overlap of correlation volumes.^{23,27}

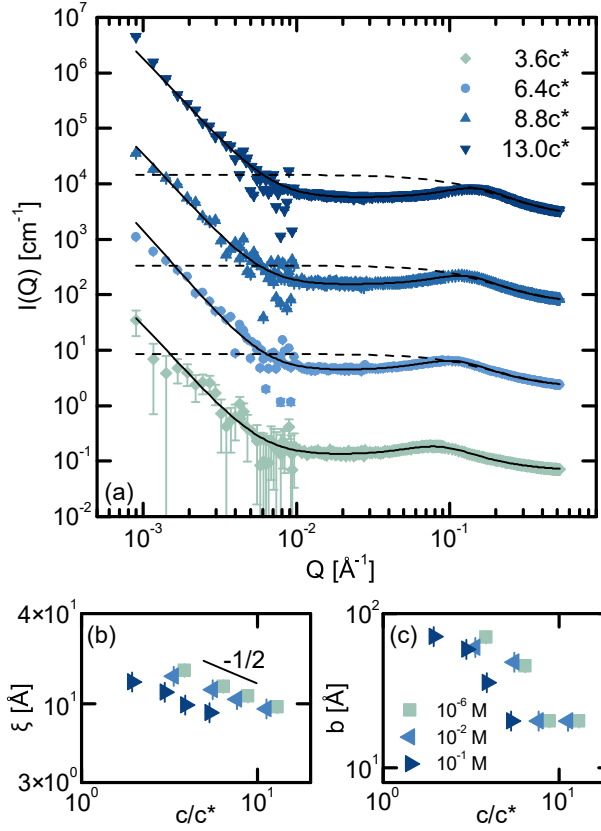


Figure 4.5: (a) SANS intensity $I(Q)$ as a function of wavevector Q for various NaPSS concentrations at $I = 10^{-6}$ M. (b) Correlation length ξ and (c) Kuhn length b from fits to eqn. 4.1 as a function of concentration c/c^* at various I values.

Small-Angle Neutron Scattering Fitting

The scattering profiles are well fit using an established model that combines the form factor of a semiflexible chain with excluded volume interactions and a PRISM-based structure factor (Solid lines in Figures 4.5(a) & 4.6. Data are shifted vertically for clarity).^{109,110,111} The form factor assumes that chains are semiflexible on length scales greater than the persistence length ($l_p = 0.5b$, where b is the Kuhn length) and rod-like at length scales below l_p without accounting for electrostatic contributions. The effects of electrostatic interac-

tions are incorporated by adding the form factor into the PRISM theory expression for the scattering intensity^{112,113,114,115,116} to obtain an equation for the scattering intensity. We add an empirical power law term to capture the upturn at low Q , due to large scale inhomogeneities.²⁵ SANS data were fitted using the following equation

$$I(Q) = k \frac{P(Q, L, b)}{1 + \alpha c(Q, \xi) P(Q, L, b)} + Q^{-m} + I_{inc}, \quad (4.1)$$

where $c(Q, \xi)$ represents the Fourier transform of the direct correlation function of spheres on chains to simulate excluded volume interactions,¹¹³ and m is the slope of $I(Q)$ at low Q . The components of equation 4.1 are defined as follows

$$c(Q, \xi) = e^{-Q^2 \xi^2}, \quad (4.2)$$

$$P(Q, L, b) = \begin{cases} P_1(Q, L, b), & Qb < 3.1 \\ P_2(Q, L, b), & Qb \geq 3.1 \end{cases}, \quad (4.3)$$

$$\begin{aligned} P_1(Q, L, b) = & (1 - w(QR_g)) \frac{2}{u_1^2} (e^{-u_1} + u_1 - 1) + f_{corr}(Q) w(QR_g) \\ & [1.22(QR_g)^{-\frac{1}{0.585}} + 0.4288(QR_g)^{-\frac{2}{0.585}} - 1.651(QR_g)^{-\frac{3}{0.585}}] \\ & + \frac{C(n_b)}{n_b} \left[\frac{4}{15} + \frac{7}{15u_2} - \left(\frac{11}{15} + \frac{7}{15u_2} e^{-u_2} \right) \right] \end{aligned} \quad (4.4)$$

where

$$w(x) = 0.5(1 + \tanh \frac{x - 1.523}{0.1477}), \quad (4.5)$$

$$u_1 = \frac{Lb}{6} \left(1 - \frac{3}{2n_b} + \frac{3}{2n_b^2} - \frac{3}{4n_b^3} (1 - e^{-2n_b}) \right) Q^2, \quad (4.6)$$

$$R_g^2 = (\epsilon(n_b))^2 \frac{Lb}{6}, \quad (4.7)$$

$$u_2 = (\epsilon(n_b))^2 \frac{Q^2 Lb}{6}, \quad (4.8)$$

$$\epsilon(x) = \left(1 + \left(\frac{x}{3.12} \right)^2 + \left(\frac{x}{8.67} \right)^3 \right)^{\frac{0.176}{6}}, \quad (4.9)$$

$$n_b = \frac{L}{b}, \quad (4.10)$$

$$C(n_b) = \begin{cases} 3.06n_b^{-0.44}, & L > 10b \\ 1, & L \leq 10b \end{cases}, \quad (4.11)$$

$$f_{corr}(Q) = \begin{cases} 1, & \frac{dP_1}{dQ} \leq 0 \\ 0, & \frac{dP_1}{dQ} > 0 \end{cases}, \quad (4.12)$$

and

$$P_2(Q, L, b) = \frac{a_1(Q, L, b)}{(Qb)^{4.95}} + \frac{a_2(Q, L, b)}{(Qb)^{5.29}} + \frac{\pi}{QL}. \quad (4.13)$$

Here, b and L are the Kuhn and contour lengths of the chain, respectively. Contour length $L = Na$ is fixed across all fitting protocols. The functions $a_1(Q, L, b)$ and $a_2(Q, L, b)$ are determined by imposing the differentiability and continuity condition at $Qb = 3.1$. An additional background I_{inc} and power law Q^{-m} terms are added to the function to capture incoherent scattering contribution and the low- Q upturn, respectively. The model cleanly represents the scattering profiles at all ionic strengths and concentrations (Figure 4.6, data are shifted vertically for clarity.).

The structural parameters obtained from SANS fits follow the expectations for polyelectrolyte solutions (Figure 4.5(b) & Table 4.2). With increasing polymer concentration, the electrostatic screening of backbone functional groups by counterions increases, resulting in a power-law decrease of $\xi \sim (c/c^*)^{-1/2}$, consistent with theoretical predictions.^{51,23} At all polymer and salt concentrations, the effective Kuhn length is larger than or equal to the Kuhn length of uncharged polystyrene $b \approx 50 \text{ \AA} \geq 16 \text{ \AA}$ due to the contribution of intrachain electrostatic interactions.¹¹⁷ Moreover, b decreases with concentration and approaches the bare Kuhn length value of a fully flexible chain.^{118,100} As intended by our experimental design, we achieve comparable correlation length values for solutions at different ionic strengths. Moreover, solutions with similar ξ have substantially different values of b , indicating that the electrostatic interactions in these solutions are significantly differ-

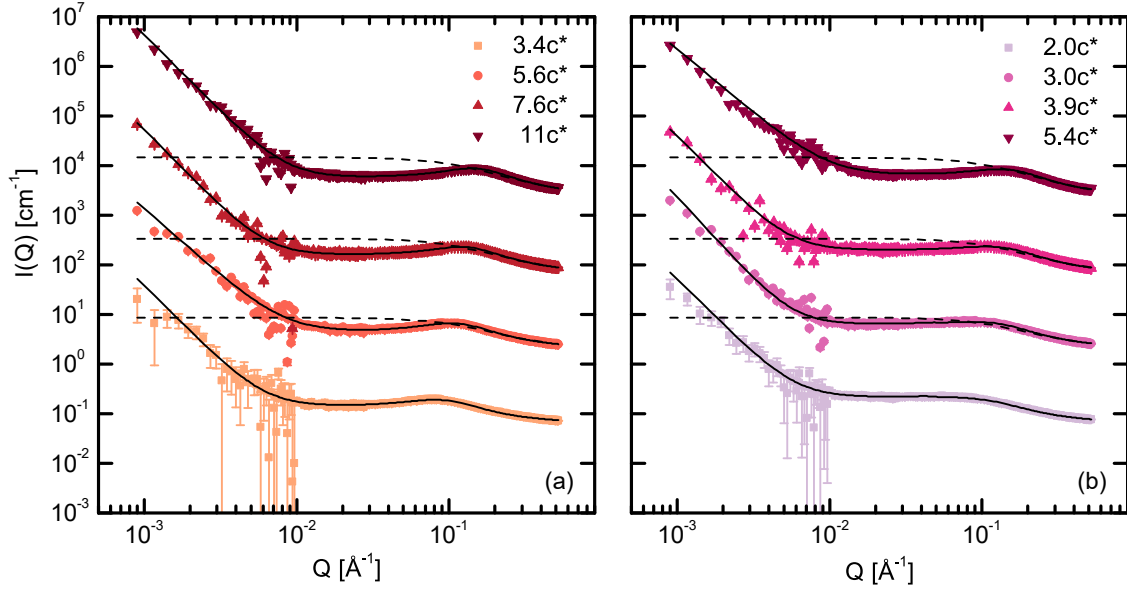


Figure 4.6: SANS intensity $I(Q)$ as a function of wavevector Q for different concentrations of NaPSS solutions at (a) 10^{-2} M and (b) 10^{-1} M ionic strength. Solid and dashed lines represent fits from eqns. 4.1 and 4.14, respectively.

ent. From these structural measurements, we conclude that we have successfully produced a library of solutions in which geometric and electrostatic length scales are independently varied.

Table 4.2: Measured chain properties as a function of polymer concentration for solutions at varying ionic strength.

Ionic Strength [M]	10^{-6}		10^{-2}		10^{-1}	
c/c^*	3.6	13	3.4	11	2.0	5.4
$\xi \pm 3$ [$\text{\AA}$]	77	47	81	45	77	47
$b \pm 2$ [$\text{\AA}$]	71	20	60	20	71	20

4.3.5 Polyelectrolyte Chain Dynamics

We now use these solutions to explicitly test how segmental relaxations depend on geometric and electrostatic length scales using NSE. Dynamic measurements are performed across a wide range of time scales $0.1 \text{ ns} < t < 45 \text{ ns}$ and wavevectors $0.051 \text{ \AA}^{-1} < Q < 0.26 \text{ \AA}^{-1}$, equivalent to $0.45 < Q\xi < 4.36$. The normalized intermediate scat-

tering functions are well-represented by a stretched exponential decay $I(Q, t)/I(Q, 0) = A \exp[(-\Gamma t)^\beta]$ (Figures 4.7(a) & 4.8), where the prefactor $A = 1$ represents fully correlated dynamics at short time scales, β is the stretching exponent, and Γ is the relaxation rate characterizing segmental relaxations. The stretching exponent remains constant across the experimental wavevectors with an average value $\beta \approx 0.83 \pm 0.02$, indicating that the polymer chains follow Zimm-like relaxations. Although the limiting Zimm relaxations predict $\beta = 2/3$, over the range of interest for these experiments, it has been found that $\beta \approx 0.85$.^{119,120}

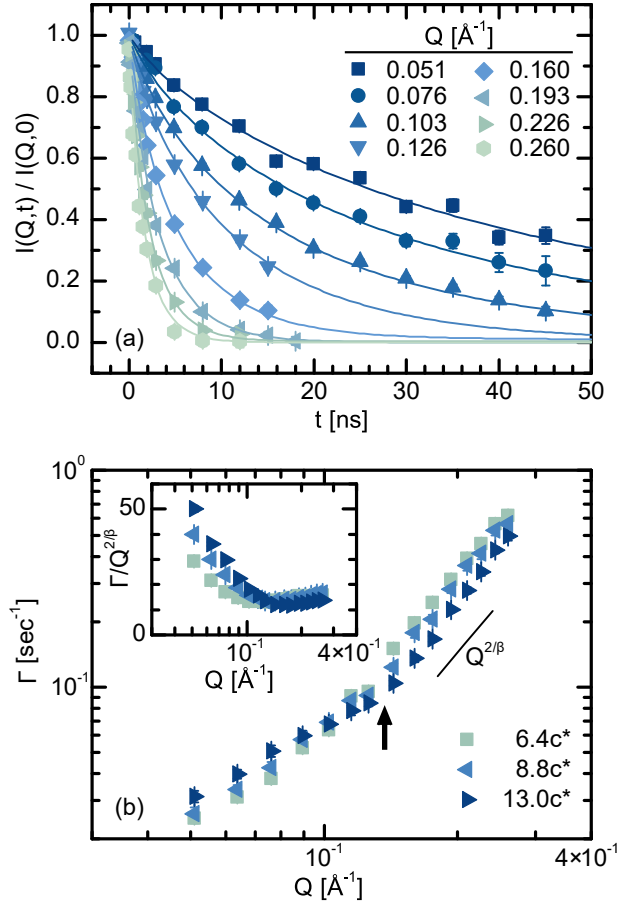


Figure 4.7: (a) Scaled correlation curves $I(Q, t)/I(Q, 0)$ as a function of time t at different wavevectors Q for $6.4c^*$ NaPSS solution. (b) Relaxation rate Γ as a function of Q . *Inset*: Ratio of relaxation rate to length scales $\Gamma/Q^{2/\beta}$ as a function of Q .

For neutral polymers that relax according to the Zimm model, the relaxation rate should scale with wavevector according to $\Gamma \sim Q^3$. For these polyelectrolyte systems, how-

ever, there are two distinct scaling regions. At small length scales, the relaxation rates scale close to predictions (Figure 4.7(b)), but over longer length scales (i.e., small Q) the relaxation rates follow a weaker power law. The scaling behavior of the relaxation rate is qualitatively similar across all samples. The transition between these two scaling regimes occurs at length scales comparable to Q^* , suggesting that the dynamic changes may arise from the structure of the solution. The different dynamic regimes are further emphasized when the relaxation rates are normalized according to their expected Q -dependence. Fundamentally, the correlation curves from NSE are related to the relative mean-squared displacement between polymer monomers according to a Gaussian approximation $I(Q, t)/I(Q, 0) = \exp[-\langle \Delta r^2(t) \rangle Q^2/6]$.¹²¹ Following established methods,^{46,122} we set this expression equal to the stretched exponential decays observed in our experiments, leading to $(\Gamma t)^\beta = -\langle \Delta r^2(t) \rangle Q^2/6$. Because polymer monomers move subdiffusively on these time scales (i.e. $\langle \Delta r^2(t) \rangle \sim t^\beta$), the relaxation rate must scale as $\Gamma \sim Q^{2/\beta}$.

When normalized by $Q^{2/\beta}$, Γ decreases as a function of Q until it reaches a minimum at $Q \approx Q^*$, after which it increases to a constant value at large wavevector (inset of Figure 4.7(b) and Figure 4.9). This minimum shifts to higher Q with increasing polymer concentration, consistent with the shift in structure factor peak measured in SANS (Figure 4.5). These observations suggest that the structure of polyelectrolytes, mediated by the electrostatic repulsion between charged monomers, plays a significant role in dictating the chain dynamics.

Previous studies have reported suppressed dynamics across Q^* in multiarm polymers,^{123,124} colloidal suspensions,^{125,126,127,128,129} and particle-polymer composites.¹²² In these systems, the dynamics can be interpreted through the phenomenon of de Gennes narrowing¹⁰³ in which a peak in the structure factor $S(Q)$ exists at Q^* due to the presence of a free energy minimum that slows relaxations. Under this framework, dynamics are inversely related to structure through $D(Q) \sim 1/S(Q)$, where $D(Q)$ is the wavevector-dependent diffusivity. An earlier study found that the diffusion coefficient of polyelectrolyte chains is inversely

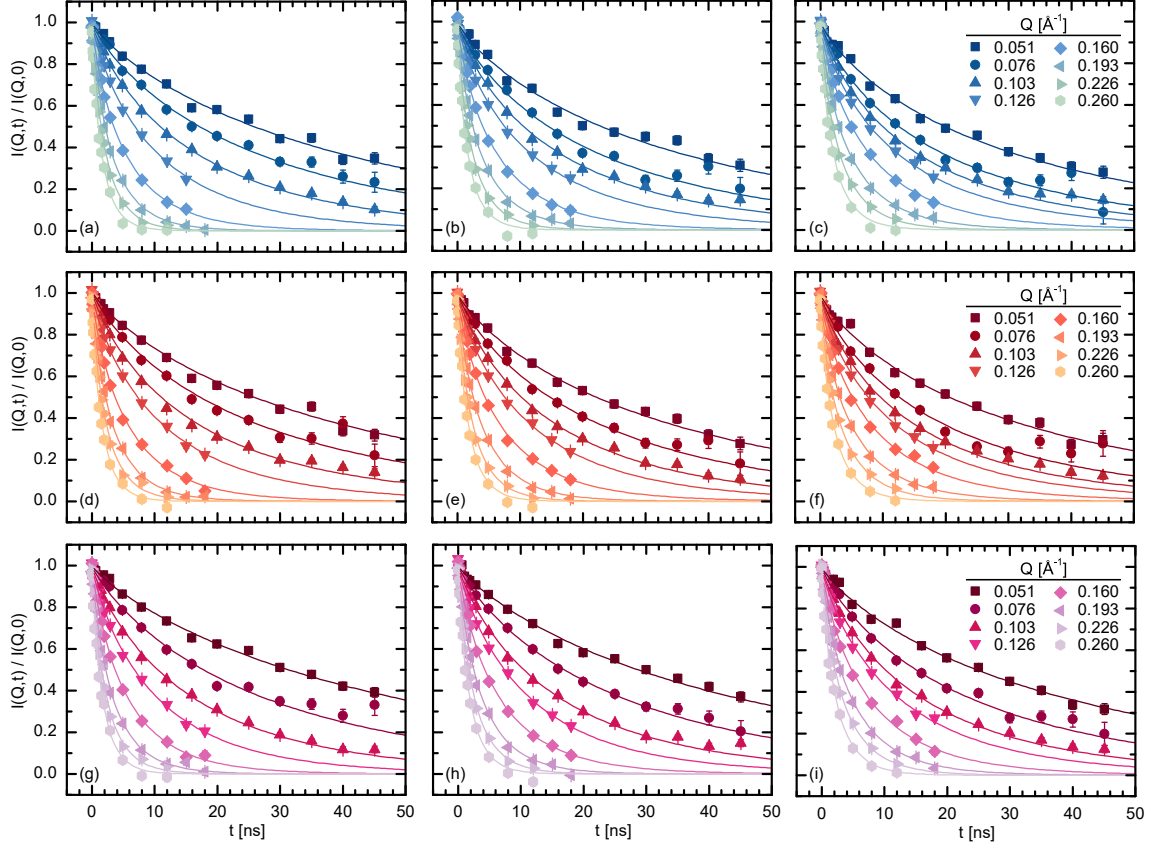


Figure 4.8: Scaled correlation curves $I(Q, t)/I(Q, 0)$ as a function of time t at different Q for (a) $6.4c^*$, (b) $8.8c^*$, and (c) $13c^*$ at $I = 10^{-6}$ M, (d) $5.6c^*$, (e) $7.6c^*$, and (f) $11c^*$ at $I = 10^{-2}$ M, (g) $3.0c^*$, (h) $3.9c^*$, and (i) $5.4c^*$ at $I = 10^{-1}$ M.

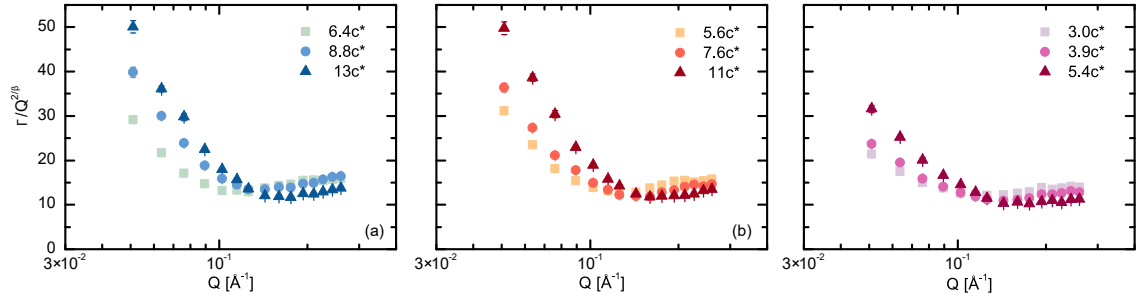


Figure 4.9: Relaxation rate normalized to length scales $\Gamma/Q^{2/\beta}$ as a function of wavevector Q for (a) 10^{-6} M, (b) 10^{-2} M, (c) 10^{-1} M ionic strength solutions. Error bars are estimated according to a 95% confidence interval.

related to structure.¹³⁰ In our solutions, however, we measure the segmental relaxations, which relax subdiffusively. Thus, we define an analogous subdiffusion coefficient that satisfies $\Gamma = KQ^{2/\beta}$ where K is a kinetic parameter that characterizes the subdiffusive Zimm

relaxations in the system.

Lorentzian Fitting

To compare this kinetic parameter K to the structure of the solution, we must extract a structure factor $S(Q)$ from the measured scattering profiles. Typically, the scattering intensity can be decomposed according to $I(Q) = P(Q)S(Q)$, where $P(Q)$ is the form factor that captures the scattering from an individual component and $S(Q)$ is the structure factor that captures the scattering intensity between components. Without a closed-form theoretical expression for $S(Q)$ in a polyelectrolyte solution, we make a simplifying assumption that the polyelectrolyte chain structure can be represented as a perturbation from an ideal Gaussian chain.^{109,131} To explore this picture, we fit the SANS scattering profile to a Lorentzian (Dashed lines in Figures 4.5(a) & 4.6) at high wavevectors ($Q \geq 0.3 \text{ \AA}^{-1}$), where $S(Q)$ is expected to be 1, to represent $P(Q)$ of Gaussian chains^{132,133} according to

$$P(Q) = \frac{I_{\text{poly}}}{1 + (Q\xi_0)^2}. \quad (4.14)$$

In this expression, I_{poly} is the scattering intensity of the polyelectrolyte chains and ξ_0 is the effective correlation length of the ideal, unperturbed chain. Because the monomer density is similar between solutions with the same correlation length ξ , we globally fit I_{poly} and ξ_0 across these samples. We then calculate $S(Q)$ of our NaPSS chains by dividing the total scattering $I(Q)$ from SANS by $P(Q)$ from eqn. 4.14. To evaluate the relationship between structure and dynamics in these semidilute polyelectrolyte solutions, we then compare these extracted $S(Q)$ to the normalized kinetic parameters $K_0/K(Q)$, where K_0 represents the dynamics in the absence of structural contributions. Following the procedure established in our earlier work¹²², K_0 is defined per sample at the wavevector at which $S(Q)$ is first equal to 1 after the peak. The $S(Q)$ curves capture the peak positions of $K_0/K(Q)$ at all NaPSS concentrations and ionic strengths (Figure 4.10(a) and (b)). Data and $S(Q)$ s shifted

for clarity). Moreover, $S(Q)$ accurately predicts the trends of the dynamics before and after the structural peak. The weaker electrostatic repulsion at high ionic strength results in a shallower structural peak and less suppressed dynamics as the perturbation from a Gaussian chain becomes weaker (Figure 4.10(b)). Furthermore, $S(Q)$ still accurately captures the shape and decay of the dynamics as ionic strength changes. The excellent agreement between $S(Q)$ and K_0/K demonstrates that the segmental dynamics of polyelectrolytes are controlled in large part by their underlying structure. Furthermore, the electrostatic repulsions that dictate the local structure in semidilute polyelectrolyte solutions also act to perturb the expected Zimm relaxations.

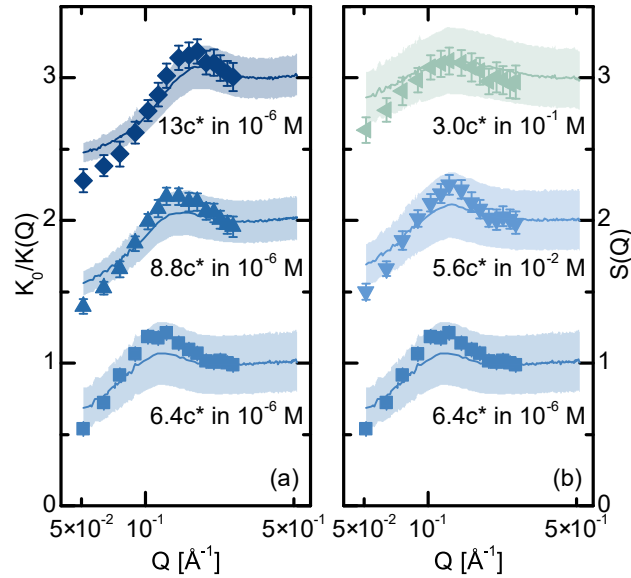


Figure 4.10: Normalized dynamic factor $K_0/K(Q)$ as a function of Q for solutions (a) with different concentrations at $I = 10^{-6} \text{ M}$ and (b) with similar correlation length $\xi \sim 79 \text{ \AA}$ at different I . Solid lines represent the structure factor $S(Q)$.

The success of our approach in relating the structure and dynamics of polyelectrolyte chains relies on the assumption that electrostatic interactions act as perturbations to a neutral chain. To implement this approach, we use the simplest model of an ideal Gaussian chain. This implementation is necessary due to the extremely limited Q -range ($Q \geq 0.3 \text{ \AA}^{-1}$) over which we can fit $P(Q)$ in the absence of structural effects. As a result, the pa-

rameters from the fits to eqn. 4.14 do not fully describe the physics of our system. Whereas I_{poly} increases with polymer concentration as physically expected, the values of the effective correlation length ξ_0 converge to a constant irrespective of polymer concentration. We attribute this behavior to the inability of such a simple representation of the Laplacian form factor $P(Q)$ to capture subtle changes to polymer structure. An improved description of the relationship between structure and dynamics in these systems would require the development of a separable polyelectrolyte structure factor similar to those derived for colloidal suspensions.^{134,135,136} Nevertheless, the excellent agreement between the observed dynamics and the calculated $S(Q)$ conclusively demonstrates that electrostatic repulsions suppress Zimm-like relaxations across the structural peak in semidilute polyelectrolyte solutions.

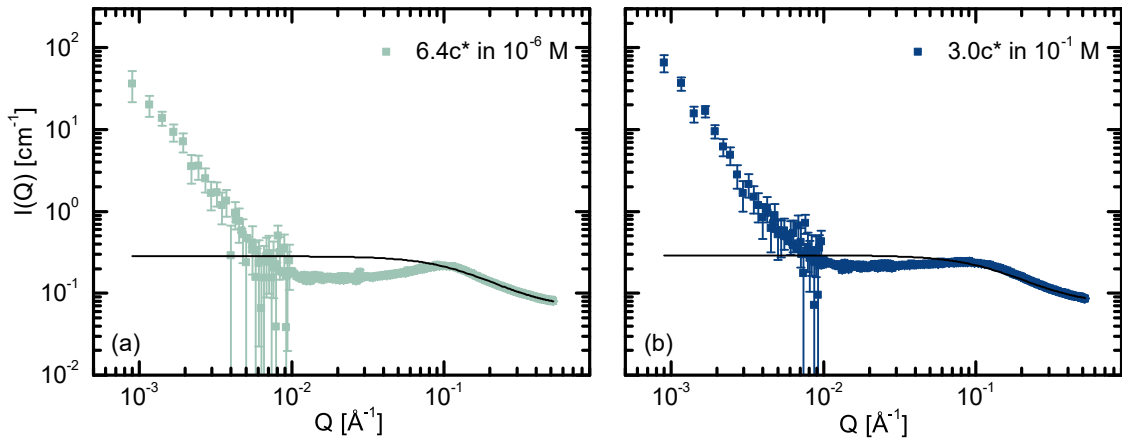


Figure 4.11: SANS intensity $I(Q)$ as a function of wavevector Q for (a) $6.4c^*$ and (b) $3.0c^*$ NaPSS in (10^{-6} and 10^{-1}) M solutions, respectively. Solid lines represent fits from eqn. 4.14. Error bars represent a 95% confidence interval.

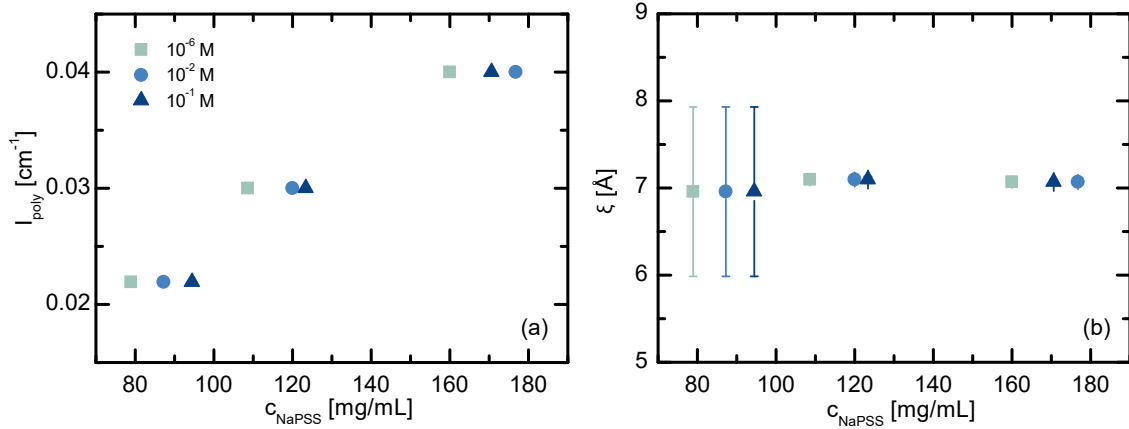


Figure 4.12: (a) Scattering intensity of NaPSS chains I_{poly} and (b) fitted correlation length ξ_0 as a function of NaPSS concentration c_{NaPSS} at different ionic strength extracted from fits to eqn. 4.14. All errors represent a 95% confidence interval.

4.4 Conclusions

By independently varying the electrostatic and geometric length scales in semidilute solutions, we show that the dynamics of polyelectrolytes are strongly coupled to their structural properties in solutions. The polymer dynamics follow Zimm-like relaxations that are suppressed across the structure factor peak according to de Gennes narrowing. Although our approach of determining the structure factor of polyelectrolytes uses the simplest model of Gaussian chains, we still observe remarkable agreement between structure and dynamics. Our work illustrates the importance of incorporating the coupling between structure and dynamics to further understand polyelectrolyte chain properties. Developing structure-dynamics relationships is essential to accurately describe the properties of polyelectrolyte materials.

Chapter 5

Effects of Depletant Size on the Recovery of Colloid-Polymer Mixtures

5.1 Introduction

Suspensions of submicron particles with attractive interparticle interactions are consumed as cheeses, jellies, and thick sauces, and found in common industrial products such as agrochemicals, paints and coatings, and personal care formulations.^{137,138} Programming the performance and appeal of these materials requires understanding how the interactions between the particles determines the suspension's structure and mechanics. Mixtures of colloids and non-adsorbing polymers serve as a convenient model system for probing the role of attractive interactions on suspension phase behavior and mechanics. In these systems, the Asakura-Oosawa (A-O) model¹³⁹ provides a straightforward estimate of the attraction induced by the polymers. In the A-O model, the depletant polymers are treated as ideal spheres that generate an effective attraction via an unbalanced osmotic pressure.¹⁴⁰ The strength and range of the resultant effective attraction are controlled by the concentration c_p and size of the polymer.^{141,142} the latter is typically parametrized by $\xi = R_g/a$, where R_g is the polymer radius of gyration R_g and a is the colloid radius.

Exploiting this tunability, depletion mixtures have been widely employed to investigate the phase behavior of attractive suspensions, revealing cluster fluids, gels, and attractive glasses.^{139,143,141,142,144,145,146,147,148,149,150} At low to medium particle volume fractions ϕ , Depletion mixtures undergo a fluid-to-solid transition as c_p is increased.¹⁵¹ Gels become less structurally heterogeneous as the strength of the attraction is increased.^{152,153} Likewise,

clusters become increasingly tenuous as the range of the attraction is decreased¹⁵¹. Similarly, these mixtures have been used to probe the effects of attractions on flow properties, including linear and nonlinear rheology as well as recovery and aging.^{152,147,154} For example, bulk rheological measurements have revealed that concentrated depletion gels exhibit multiple yielding processes, corresponding to the breaking of bonds and the fragmentation and/or erosion of clusters.^{155,156,157} Dynamically, yielded depletion gels with weak attractions (low c_p) exhibit fast and slow subpopulations.¹⁵⁸

Scattering methods are convenient for probing the dynamics at the single particle scale.^{159,160} Scattering experiments have revealed that concentrated depletion gels form clusters¹⁶¹ that are thought to control the mechanics¹⁶². They have also been used to show that the relaxation time of a colloidal gel increases linearly with sample age and scales inversely with wave vector,¹⁶³ consistent with elastic deformation of a strained network.¹⁶⁴ Finally, they have been used to detect and characterize irreversible particle rearrangements in gels under oscillatory strain.¹⁵⁹ What remains less explored is the role of the depletant size (i.e. attraction range) and size distribution on microscopic dynamics. While known to affect the phase behavior^{165,166} and flow behavior¹⁶⁷ of colloid-polymer mixtures, its role on recovery after shear has not yet been studied.

In this paper, we use x-ray scattering to characterize the short-time recovery of colloidal gels after cessation of shear. We formulate suspensions of colloids using three depletants at a fixed normalized polymer concentration relative to overlap. Static x-ray scattering measurements show that the structure of the gel near the single-particle length scale is not strongly perturbed by shearing. Dynamic x-ray scattering measurements using x-ray correlation spectroscopy reveal that the relaxation time increases with recovery time, and depends both on the shear rate applied prior to recovery and on the depletant size distribution.

5.2 Materials and methods

5.2.1 Sample preparation

2,2,2-trifluoro ethyl methacrylate (TFEMA) particles [$D_H = 423$ nm (PDI 0.04)] were synthesized¹⁶⁸ to be density and refractive index matched to 80 (w/w)% glycerol/water solvent. The density of suspensions was estimated to be $\rho = 1.34$ kg m⁻³. Electrostatic interactions between particles were screened by adding 5 mM NaCl. Solutions of polyacrylamide (PAM) in 80 (w/w)% glycerol/water were added to particle suspensions to induce depletion interactions.¹⁶⁹ Three polyacrylamide depletants of different weight-averaged molecular weight M_w and dispersity $\mathcal{D}$ were used to induce attractions between the particles: $M_w = 186$ kDa and $\mathcal{D} = 1.4$ (Polymer Source, USP), $M_w = 1.14$ MDa and $\mathcal{D} = 1.8$ (PolySciTech, ULP), and $M_w = 1.97$ MDa and $\mathcal{D} = 21$ (Sigma-Aldrich, DP). Four suspensions were prepared at constant particle fraction $\phi = 0.40$: $0c^*$, $1.2c^*$ USP, $1.2c^*$ ULP, and $1.2c^*$ DP. The range of attraction for the suspensions containing polymer was $\xi/a \approx 0.10$ (USP) and 0.23 (ULP).

5.2.2 Flow curves

Prior to the in situ scattering experiments, steady-shear rheology data were collected on a DHR-2 hybrid rheometer (TA Instruments, New Castle, DE) operated in stress-controlled mode using a cone and plate geometry, which consisted of a 2° cone with hard-anodized aluminum 40-mm diameter, and a matching 40-mm bottom plate. All measurements were carried out at 20 °C and temperature was maintained via a Peltier controller. Samples were pipetted onto the bottom plate then the cone was slowly lowered to a trim gap 62 μm at a rate 5 $\mu\text{m/s}$, while maintaining an axial force $F_N < 0.5$ N.¹⁷⁰ The cone was lowered further to a truncation gap 59 μm at a rate 5 $\mu\text{m/s}$ to start the preshear protocol.

A consistent preshear protocol was performed on all samples following a previously established protocol.¹⁶⁹ The shear rate $\dot{\gamma}$ was increased from 0.5 to 50 s⁻¹ over 30 s then shear

rate was held at 50 s^{-1} for 30 s. After preshear, all samples were sheared at rates between 0.1 and 2000 s^{-1} , while splitting each decade into 6 different shear rates. At all shear rates below 100 s^{-1} , samples were equilibrated for 30 s and measurements were averaged for an additional 10 s. For higher shear rate values ($> 100 \text{ s}^{-1}$), samples were equilibrated for 10 s and data was averaged over another 5 s. The equilibration and averaging times were reduced to avoid a transient decrease in viscosity due to particle migration.^{171,172}

5.2.3 Rheo-XPCS

Experiments were carried out at the rheo-XPCS setup at sector 8-ID of the Advanced Photon Source at Argonne National Laboratory. We estimated the scattering length densities (SLDs) in $10^{-6} \text{ \AA}^{-2}$ to be 11.659 for glycerol, 10.828 for PAM, 10.306 for particles, and 9.469 for water. Suspensions were slowly pipetted into a polycarbonate Couette cell (inner diameter $D_{\text{in}} = 11 \text{ mm}$ and outer diameter $D_{\text{out}} = 11.4 \text{ mm}$) of a stress-controlled rheometer (Anton Paar MCR 301), which was mounted on the beamline. The Couette cell was oriented vertically and perpendicularly to the incident beam, which was directed through the center of the cell and thus oriented parallel to the shear-gradient direction. This setup allows x-ray scattering and rheological measurements to be concurrently performed.

Prior to scattering measurements, samples were presheared following a consistent protocol. The shear rate $\dot{\gamma}$ was increased from 0.5 to 50 s^{-1} over 30 s and subsequently held constant for 30 s. Samples were then left to rest without shear for approximately 120 seconds. This protocol was repeated five times per sample. Following the preshear protocol, suspensions were sheared for 60 s at eleven different shear rates $\dot{\gamma} = 1, 5, 10, 50, 100, 150, 200, 250, 300, 350,$ and 400 s^{-1} . After each shear interval, data were captured for 450 s using 30 s intervals, which consisted of 15,000 frames at 500 frames per second.

An area detector (X-spectrum LAMBDA 750 K)^{79,80} was located 8 m away from the sample, allowing the capture of scattering intensity across a wavevector range $0.001 \text{ \AA}^{-1} < q < 0.051 \text{ \AA}^{-1}$ that is equivalent to a length scale range $0.03 < L/D_{\text{H}} < 1.5$. We measured

autocorrelation curves at five different positions across the sample then averaged the data together while propagating error throughout the fitting protocol. All rheo-XPCS data was analyzed using the Gui Matlab scripts provided by sector 8-ID.

5.3 Results and discussion

5.3.1 Sample rheology

Three polyacrylamide (PAM) solutions were prepared by dissolving appropriate amounts of powder polymer stocks in 80 (w/w)% glycerol/water to achieve a scaled concentration $1.2c^*$. The viscosity of pure 80 (w/w)% glycerol/water solvent was measured to estimate the background viscosity of suspensions without depletants. Samples were introduced into a 2° cone with hard-anodized aluminum 40-mm diameter, and a matching 40-mm bottom plate. A consistent pre-shear protocol consisting of two steps was followed across all solutions. First, an initial shear ramp between 0.5 to 50s^{-1} across 30s. Then, samples were sheared for an additional 30s at a shear rate 50s^{-1} followed by a 300s rest period. Data was collected between 0.1 and 1000s^{-1} with 5 and 6 points per decade for samples without and with depletants, respectively. Samples were left to equilibrate for 30s at each shear rate followed by an averaging time of 10s for each viscosity calculation. All measurements were carried out at 20°C and temperature was maintained via a Peltier controller. Figure 5.1 shows the sample viscosity η as a function of shear rate $\dot{\gamma}$. We find that the addition of depletants at the same scaled concentration c/c^* causes the same increase in viscosity from $\sim 0.06\text{ Pa}\cdot\text{s}$ for pure solvent to $\sim 0.13\text{ Pa}\cdot\text{s}$ due to chain contribution, resulting in a collapse of the viscosity flow curves of all solutions with depletants.

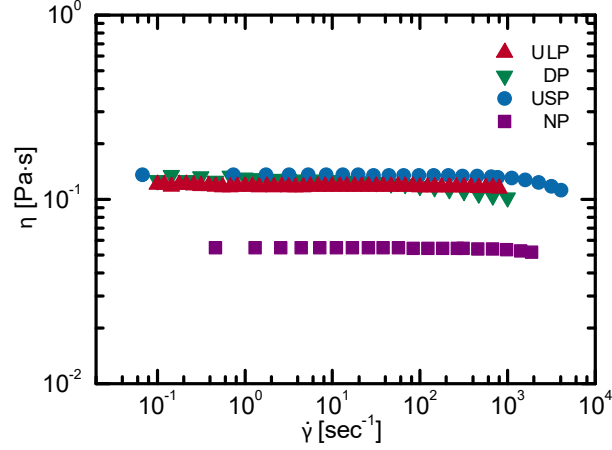


Figure 5.1: Viscosity η as a function of shear rate $\dot{\gamma}$ for different solutions in 80 (w/w)% glycerol/water.

5.3.2 Flow curves

We characterize the bulk rheology of colloid-polymer suspensions by measuring the apparent viscosity as a function of shear rate. In the absence of depletants, a colloidal suspension formulated at a volume fraction of $\phi = 0.40$ exhibits weak shear thinning behavior at shear rates $\dot{\gamma} < 10^1$ and a constant viscosity $\eta_{NP} \approx 0.2$ Pa·s at higher shear rates (Figure 5.2). Over the accessible range of shear rates, this suspension shows no signs of continuous shear thickening, consistent with the behavior anticipated for a moderately concentrated suspension of nearly hard spheres.^{170,173,174}

In the presence of depletant polymers at a normalized concentration of $1.2c^*$, the viscosity increases by less than an order of magnitude at a given shear rate. Addition of USP leads to a modest increase in viscosity at high shear rates ($\eta_{USP} \approx 4$ Pa·s). The strength of the shear-thinning is slightly reduced, as indicated by a small decrease in the shear-thinning exponent n ($\eta \sim \dot{\gamma}^{-n}$) from 0.18 (NP) to 0.09 (USP), and the onset of near-constant viscosity occurs at $\dot{\gamma} \approx 10^{-1}$ s⁻¹. Addition of DP leads to rheological behavior that is very similar to that of the sample containing USP. Finally, addition of ULP leads to a somewhat higher increase in viscosity at all shear rates and a high-shear viscosity $\eta_{ULP} \approx 5$ Pa·s. The shear-thinning behavior in ULP ($n \approx 0.30$), observed for $\dot{\gamma} < 10^2$, is enhanced relative

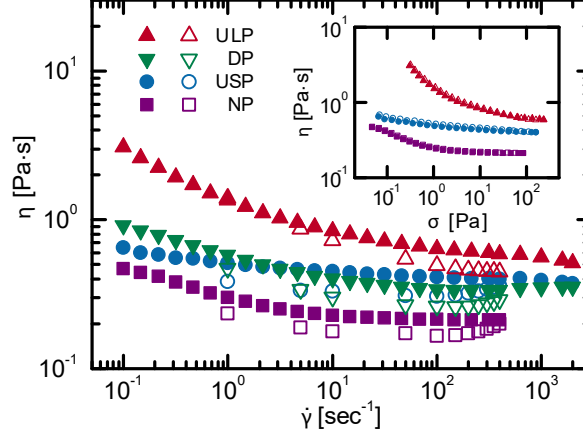


Figure 5.2: Viscosity η as a function of shear rate $\dot{\gamma}$ for suspensions at volume fraction $\phi = 0.40$. *Inset:* Viscosity η as a function of shear stress σ . Closed and open symbols are measurements from the DHR-2 and MCR 301, respectively.

to NP and USP. Thus, the rheological measurements indicate that the polymer size distribution alters the steady-shear rheological properties. This observation is in accord with previous measurements of depletion systems.^{163,154,162,161}

5.3.3 Structure during and after shear

We characterize the structural properties of the TFEMA suspensions at 30 s intervals after shear cessation for all shear rates using static x-ray scattering. Over the accessible range of wavevectors $10^{-3} \text{ \AA}^{-1} < q < 10^{-2} \text{ \AA}^{-1}$ the scattering intensity $I(q)$ resembles a spherical form factor and is comparable to the predicted scattering intensity of spheres of size $2R_{\text{NP}} = 390 \text{ nm}$ (Figure 5.4, all data are shifted vertically for clarity). The solvent trap around the rheometer geometry contributes to the scattering intensity at $q > 10^{-2} \text{ \AA}^{-1}$, resulting in excess scattering at the higher q . The characteristic structure peak at $q^* \sim 0.0016 \text{ \AA}^{-1}$ represents the particle diameter $2R_{\text{NP}} = 2\pi/q^* \sim 390 \text{ nm}$ (Figure 5.3), confirming that scattering intensity is dominated by TFEMA particles.

To extract the spherical form factor, we estimate the predicted scattering intensity according to $I(q) = AS(q)P(q)$, where A is a scaling factor relating to the volume of scatterers and SLDs, $P(q)$ represents the spherical form factor, and $S(q)$ is the structure factor of

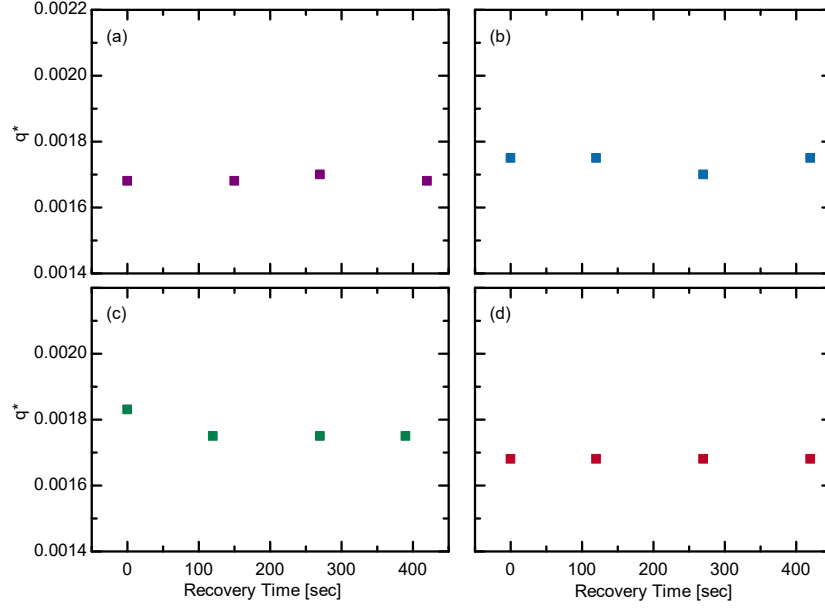


Figure 5.3: Structure peak value q^* as a function of recovery time after 400 s^{-1} shear cessation for suspensions (a) without polymer, (b) in $1.2c^*$ USP, (c) in $1.2c^*$ DP, and (d) in $1.2c^*$ ULP.

charged spheres. After calculating the ideal $P(q)$ using particle size and volume fraction, we then extract $S(q)$ as the ratio of $I(q)$ to $P(q)$.

5.3.4 Dynamics

We first characterize the microscopic dynamics on length scales comparable to the particle size using XPCS at the lowest accessible $q = 0.0012 \text{ \AA}^{-1}$, corresponding to a length scale $L \approx 524 \text{ nm} \approx 1.24D_H$ ($qa = 5.08$), through the wave-vector-dependent instantaneous intensity autocorrelation function

$$G_2(q, t_1, t_2) = \frac{\langle I(q, t_1)I(q, t_2) \rangle}{\langle I(q, t_1) \rangle \langle I(q, t_2) \rangle}, \quad (5.1)$$

where $I(q, t)$ represents the scattering intensity at time t and wave vector q , and the brackets indicate averages of a single measurement over a range of detector pixels centered on q . In the two-time autocorrelation function, which represents the low- q plateau behavior, a consistent scattering intensity along the main diagonal ($x = y$) indicates fully correlated

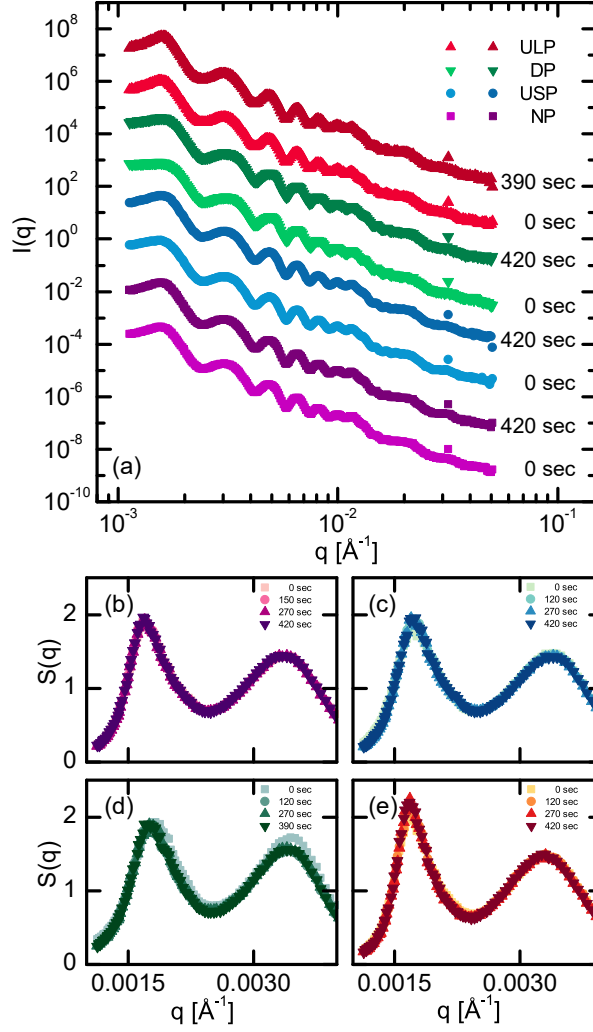


Figure 5.4: (a) Scattering intensity $I(q)$ as a function of q for suspensions at time intervals after 400 s^{-1} shear cessation. (b-e) Structure factor $S(q)$ as a function of q at four $\dot{\gamma}$ for suspensions (b) NP, in $1.2c^*$ (c) USP, (d) DP, and (e) ULP.

dynamic behavior. We calculate the two-time autocorrelation function at $q = 0.0012 \text{ \AA}^{-1}$, where our measurements have the best statistics and least noise (Figure 5.5). The black parallelogram indicates a representative region used to calculate the partial autocorrelation functions at $t = 7 \text{ s}$. Arrows indicate the size of the region between $6.1 \text{ s} < t_{1,2} < 7.89 \text{ s}$. Across all time scales, the maximum in the two-time signal intensity follows the main diagonal (Figure 5.5b&c). Moreover; the two-time signal increases as lag-time increases. This observation along with the slight broadening at long time scales suggests the onset of a non-equilibrium process that could be a result of dynamic heterogeneity.

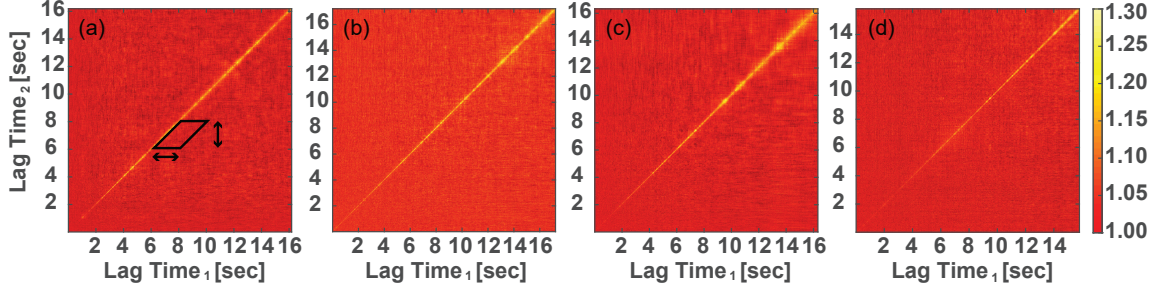


Figure 5.5: Instantaneous correlation function after 400 s^{-1} shear cessation at a wavevector value $q = 0.0012 \text{ \AA}^{-1}$ for suspensions (a) without polymer, in (b) $1.2c^*$ USP, (c) $1.2c^*$ DP, and (d) $1.2c^*$ ULP.

To characterize the microscopic dynamics after shear cessation, we subdivide the dynamic range Δt into nine equal subintervals, each representing a time interval of 1.67 s. This protocol results in nine partial autocorrelation functions $G_2(q, \Delta t)$, each calculated at $t_{1,2} = (t_1 + t_2)/2$ with $\Delta t = t_2 - t_1 = 1.67 \text{ s}$. For all samples, the $G_2(q, \Delta t)$ s initially evolve with lag time and converge after $\sim 30 \text{ s}$ (Figure 5.6), suggesting that their dynamics at the single-particle length scale fully recover over this time scales. The $G_2(q, \Delta t)$ s do not appear to evolve at longer recovery times (Figure 5.7, 5.9, & 5.11). Hence, we focus on the evolution of the dynamics on time scales shorter than 30 s.

In mixtures of colloids and non-adsorbing polymers, bonds between particles driven by depletion attractions form rapidly after mixing. Thus, the decorrelation in the dynamics at the particle-scale arises from thermal fluctuations in the reforming network.^{175,176} To model the decay, we fit the the partial intensity autocorrelation functions to a stretched exponential function, which can be written using the Siegert relation as

$$G_2(q, \Delta t) = 1 + B \exp \left[-(\Delta t / \tau)^\beta \right] + \varepsilon, \quad (5.2)$$

where $\Delta t = t_2 - t_1$ represents lag time, B is the Siegert factor, and ε captures any residual noise from fits. From the fits to eqn. 5.2, we extract two parameters: the exponent β , which characterizes the shape of the distribution of relaxation timescales, and the relaxation time τ , which characterizes the timescale of thermal fluctuations at the single-particle length

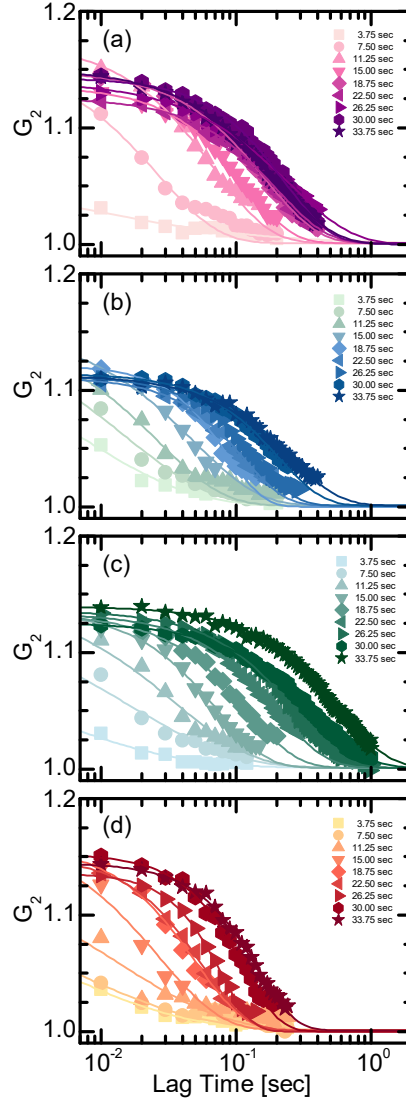


Figure 5.6: Evolution of the intensity partial autocorrelation function G_2 as a function of lag time after 400 s^{-1} shear cessation for suspensions (a) without polymer, (b) in $1.2c^*$ USP, (c) in $1.2c^*$ DP, and (d) in $1.2c^*$ ULP.

scale.

We first examine the exponents and relaxation times (eqn 5.2) as a function of the recovery time. In the absence of polymer (sample NP), $\beta \approx 0.75$ after shear at $1 - 200 \text{ s}^{-1}$, independent of recovery time (Figure 5.8(a)). By contrast, after shear at 400 s^{-1} β first increases rapidly over 10 s and then is approximately 1 thereafter in NP. In samples containing polymer (USP, DP, ULP), β remains approximately constant as the recovery time increases after shear at 1 s^{-1} (Figure 5.8(b) – (d)). For larger initial shear rates, β first

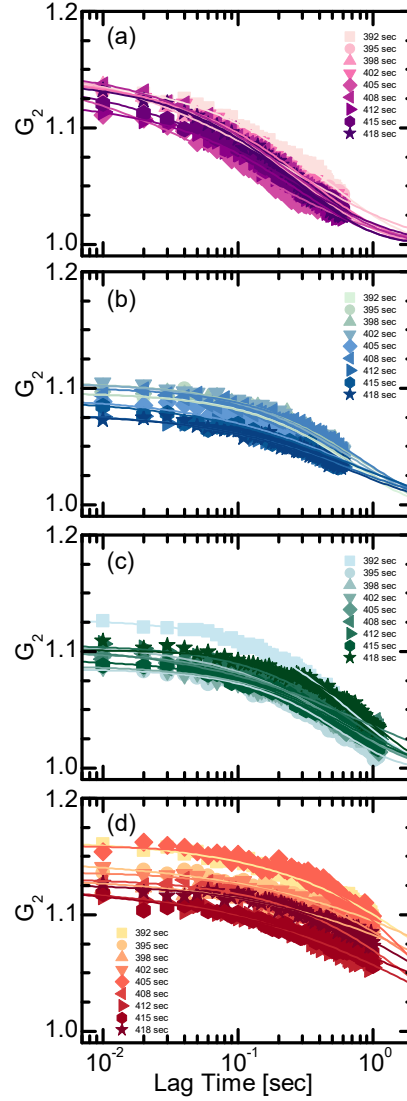


Figure 5.7: Intensity partial autocorrelation function G_2 as a function of lag time after 400 s^{-1} shear cessation for suspensions (a) without polymer, (b) in $1.2c^*$ USP, (c) in $1.2c^*$ DP, and (d) in $1.2c^*$ ULP.

increases with recovery time and then attains a plateau on longer time scales. The plateau value is close to 1 for USP and DP. In ULP, however, $\beta > 1$ at longer recovery times, consistent with compressed exponential dynamics often observed in aging soft solids^{177,178} and attributed in these studies to superdiffusive, ballistic motion.

For samples sheared at 1 s^{-1} , β is constant as recovery time increases (Figure 5.8). In samples sheared at higher rates, however, β evolves with recovery time. At short recovery times, the partial autocorrelation function exhibits a stretched exponential decay with $\beta <$

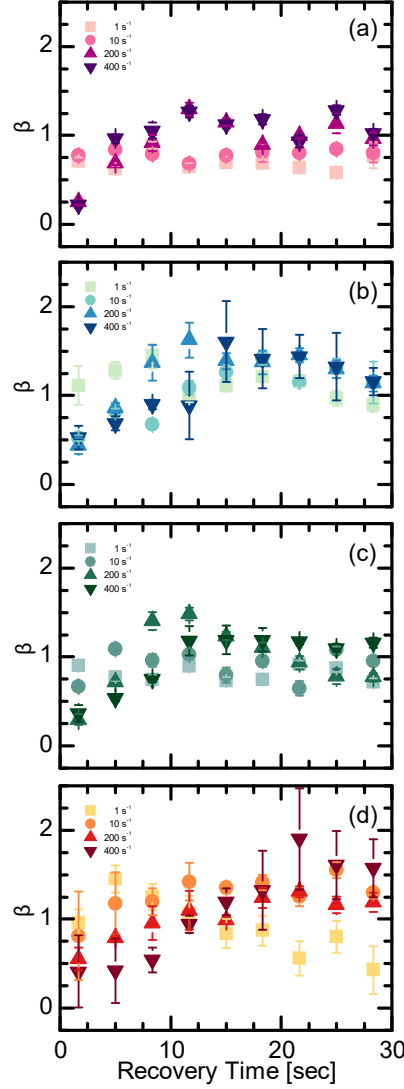


Figure 5.8: Stretching exponent β as a function of recovery time after shear cessation for suspensions (a) NP, (b) in $1.2c^*$ USP, (c) in $1.2c^*$ DP, and (d) in $1.2c^*$ ULP at four $\dot{\gamma}$. This data represents times immediately after shear cessation.

1. The exponent steadily increases as recovery time increases and reaches $\beta \sim 1.5$ at a recovery time ~ 10 s. Compressed exponential decays with $\beta \sim 1.5$ have been previously reported in various dense colloidal systems and have been attributed to ballistic dynamics with a broad distribution of velocities^{164,163} or to intermittent rearrangements.^{179,178} On time scales longer than 10 s β gradually decreases to a plateau value of 1.

For comparisons across the samples during recovery, we scale the relaxation times according to the bulk relaxation time τ_0 predicted from the Stokes-Einstein (SE) relationship

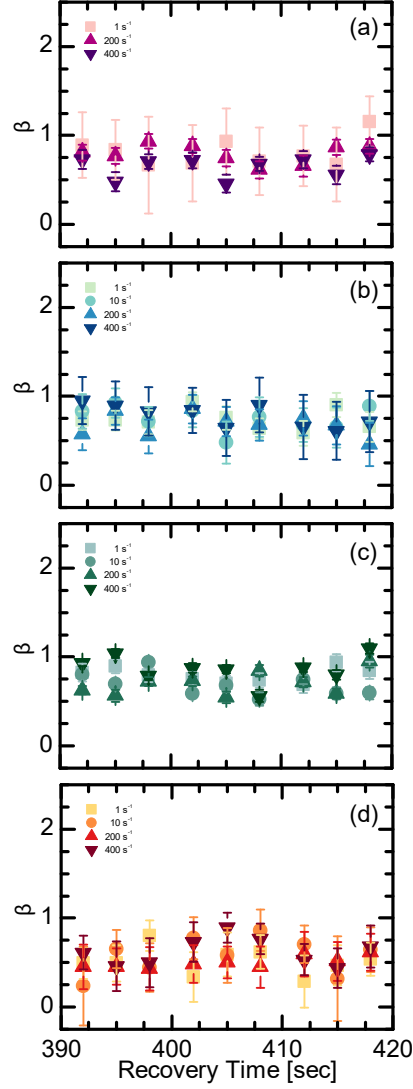


Figure 5.9: Stretching exponent β as a function of recovery time after shear cessation for suspensions (a) without polymer, (b) in $1.2c^*$ USP, (c) in $1.2c^*$ DP, and (d) in $1.2c^*$ ULP at four different shear rates.

using the measured solution or solvent viscosities (Figure 5.1) for samples with or without depletants, respectively, via

$$\frac{1}{\tau_0} = \frac{k_B T q^2}{6\pi\eta R_{\text{NP}}}, \quad (5.3)$$

where k_B is the Boltzmann constant, T is the temperature, η is the solution viscosity (Figure 5.1), and R_{NP} is the nanoparticle radius. Large particles (i.e. those for which $2R_{\text{NP}} \gg 2R_g$) in semidilute ($c_p > c^*$) polymer solutions couple to the bulk solution viscoelasticity.¹⁸

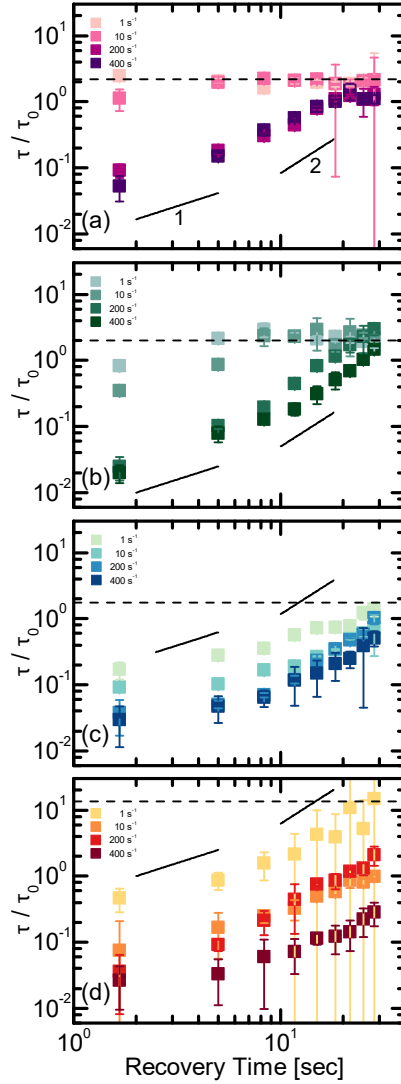


Figure 5.10: Scaled relaxation time τ/τ_0 as a function of recovery time for suspensions (a) NP, in (b) $1.2c^*$ USP, (c) $1.2c^*$ DP, and (d) $1.2c^*$ ULP at four $\dot{\gamma}$ immediately after shear cessation. Dashed line is the average long time relaxation.

Thus, this scaling allows us to remove any explicit depletant size contribution.

The evolution of suspension dynamics depends on the shear rate prior to cessation. Particle suspensions that do not contain depletants show no sign of dynamic recovery at low shear rates ($\leq 10 \text{ s}^{-1}$) (Figure 5.10a), suggesting that samples quickly evolve and exhibit long-time dynamics at all accessible time scales. Suspensions with depletants, however, display recovery-like behavior at all experimented shear rates (Figure 5.10b,c,&d). Nevertheless, the dynamic evolution becomes more pronounced as shear rate increases for all

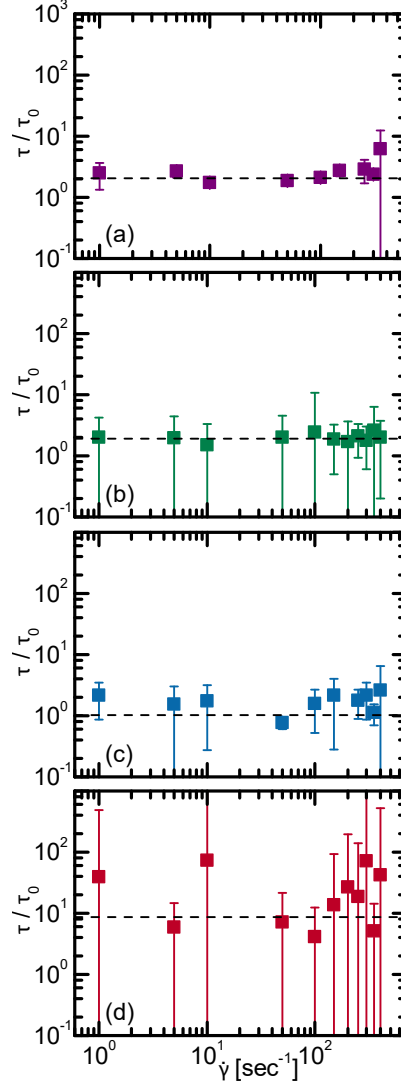


Figure 5.11: Scaled relaxation time τ/τ_0 as a function of $\dot{\gamma}$ for different suspensions (a) NP, in (b) $1.2c^*$ USP, (c) $1.2c^*$, and (d) $1.2c^*$ ULP at a time interval equivalent to 422 s after shear cessation. Dashed line is the average of represented data.

samples. At short time scales, the scaled relaxation rate τ/τ_0 consistently increases as shear rate increases for all four suspensions, indicating faster dynamics than bulk predictions. As recovery time increases, particle dynamics become slower until long-time behavior is achieved. The onset on which dynamics fully recover increases in the presence of depletants or as they increase in size (~ 18 s without depletants, ~ 30 s with small and disperse depletants, and ~ 35 s with large depletants). This mechanism of slow-down in dynamics is comparable to dynamics in concentrated colloidal suspensions near glass

transition.^{180,181,182}

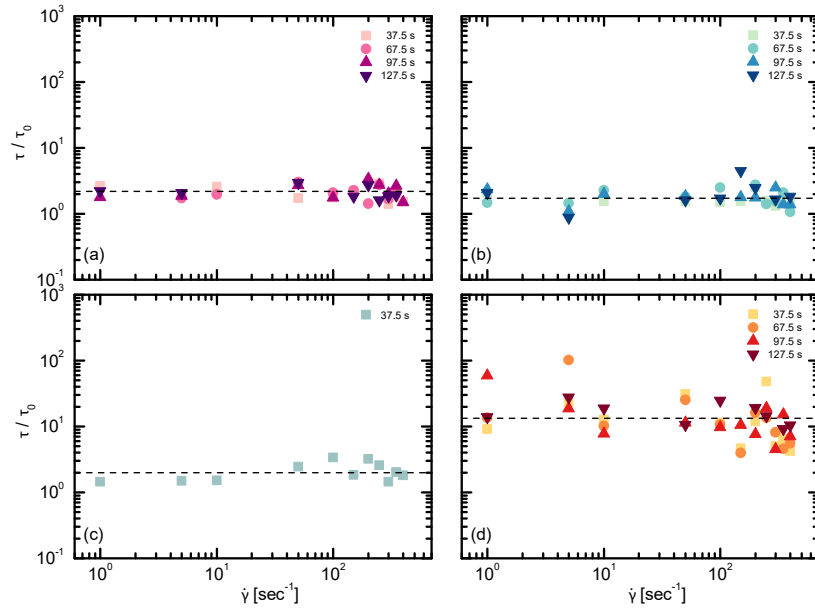


Figure 5.12: Scaled relaxation time τ/τ_0 as a function of $\dot{\gamma}$ at different recovery times for suspensions (a) NP, (b) in $1.2c^*$ USP, (c) in $1.2c^*$ DP, and (d) in $1.2c^*$ ULP. Dashed line represents average relaxation time value of the plotted data.

The intensity partial autocorrelation functions G_2 trend similarly without signatures of evolution across all measurements beyond 35 s at all shear rates (Figure 5.6), suggesting that dynamic equilibrium is achieved and long-time dynamics are maintained. To explore the effects of depletants and their size on the particle dynamics, we compare the long-time ($\gg 35$ s) exponents and relaxation times (Figure 5.11) of all four suspensions at long recovery times and all shear rates, respectively. The exponent β stays constant, within error, at the longest experimented recovery times (> 390 s) for all four samples (Figure 5.8) with a value ~ 1 , suggesting that the dynamics remain diffusive at long time scales. Suspensions without (NP) depletants exhibit relaxation times that approximately conform onto bulk prediction from SE, suggesting that particle dynamics are highly controlled by the background elasticity from introduced polymer chains above c^* rather than depletion attraction. These dynamics persist as small (USP) and dispersed (DP) depletants are introduced to the colloidal suspensions with similar relaxation times as the sample without depletants. These observations suggest that suspensions are behaving like fluids and the small and dispersed

polymer concentration used does not provide a large enough attraction potential to induce gelation, consistent with the idea that stronger attraction is necessary to obtain gels in small depletant mixtures.¹⁸³ In the presence of large (ULP) depletants, however, particle dynamics are slower than predicted by bulk behavior with a characteristic relaxation time ~ 10 times larger than SE predictions. We propose that the attraction potential in large depletant samples is significantly larger than the other suspensions,¹⁸³ resulting in gelation. These observations are consistent with the flow curves from rheology (Figure 5.2).

5.4 Conclusions

By probing the dynamics of colloidal particles in colloid-polymer suspensions, we confirm that gelation differs depending on the depletant size. Specifically, we show that suspensions with smaller depletant sizes require a stronger attraction potential compared to suspensions with large depletants. We utilize an in situ x-ray scattering technique, rheo-XPCS, to simultaneously probe the structure, rheology, and dynamics of colloid-polymer suspensions. We find that suspensions without or with small size depletants exhibit relaxation times according to the predictions for bulk behavior, suggesting that these systems behave like fluids. Suspensions with large depletants, however, exhibit relaxation times that are ~ 10 times slower than SE behavior. This observation suggests the presence of larger clusters of particles due to enhanced depletion. This work illustrates the importance of tuning the depletant size according to the colloids to control the interactions in colloid-polymer suspensions.

Chapter 6

Summary and future work

This work focused on understanding how the structure differences in polyelectrolytes affects the dynamics of nanoparticles and polymer chains. By systematically tuning the properties of our systems and utilizing various experimental techniques, we were able to probe the dynamics of particles and polymers in aqueous solutions and open further questions to further understand transport of complex fluids in the future.

6.1 Summary

Complex fluids of polymers and particles are ubiquitous in a wide range of applications. We first probed the dynamics of nanoparticles in semidilute polyelectrolyte solutions. We tuned the conformation of polyelectrolyte chains by changing the solution ionic strength through the addition of sodium chloride. In the presence of salt, the dynamics of particles followed theoretical predictions according to the Stokes-Einstein equation. In the absence of salt, large probe particles diffused according to predictions within their size limit and coupled to bulk viscoelasticity. As particle size decreased, however, we observed non-monotonic deviations from theory. The deviations systematically increased with polymer concentration until reaching a maximum at intermediate ones, after which the particle dynamics coupled back to predictions. By examining the displacement autocorrelation functions of our particles, we found that particles experience confinement effects on length scales relevant to chain size despite the absence of entanglements. These results highlighted the importance of accounting for chain conformation to better understand transport of particles in complex fluids.

To measure the effect of flexibility on particle dynamics, we developed a system of nanoparticles and polyelectrolytes for x-ray scattering experiments. We altered the chain flexibility by changing the degree of polymerization or molecular weight of chains. We determine the diffusivity of particles according to relaxation rates and their corresponding wavevectors. In solutions with smallest chains, particles diffused according to Stokes-Einstein theoretical predictions. We observed non-monotonic deviations in intermediate polymer size solutions, suggesting the presence of confinement effects despite the absence of entanglement in these solutions. The solution with the largest chain size, however, linearly deviated from predictions according to the bulk viscoelasticity. The systematic deviation from theory was not captured by the coupling theory of particle and polymer segmental dynamics despite being qualitatively similar. The presence of three different regimes of dynamics emphasized need to incorporate chain flexibility into the understanding of particle dynamics to better utilize them in applications.

Then, we studied the effects of geometry and electrostatics on the segmental dynamics of polyelectrolyte chains in unentangled solutions. We independently tuned the geometry and electrostatics by varying polymer concentration and solution ionic strength, respectively. We characterized the chain structure using a model that combines the form factor of a semiflexible chain with excluded volume interactions and a PRISM based structure factor; and confirmed that geometry and electrostatics are independently changed in our solutions. The segmental chain dynamics displayed two distinct scaling behaviors with wavevector. At small length scales, the relaxation rates scaled consistent with predictions for Zimm-like dynamics. As length scales increased, however, we observed deviations from theory with relaxation times that are smaller than predictions. The onset for the change in scaling behaviors occurred at length scales equivalent to the structure peak, signature of polyelectrolyte systems. We interpreted this observation using the de Gennes' narrowing phenomenon, which proposes the presence of a free energy minimum at characteristic length scales that makes relaxations out of it unfavorable. As a result, the picture suggests

a coupling between the structure and dynamics. To test this hypothesis and found excellent agreement between the observed dynamics and the structure factor of our chains as both polymer concentration and ionic strength changes. This observation suggested that we have a direct correlation between structure and dynamics in polyelectrolyte systems.

Finally, we characterize the structure and dynamics of colloid-polymer suspensions. We tune the attraction potential between the two components by changing the depletant size. We utilize an in situ x-ray scattering technique, rheo-XPCS, that allows rheological and dynamic measurements simultaneously. We find that suspensions with large depletants relax up to ~ 10 times slower than ones without or with small depletants, which in return relax according to the bulk predictions from Stokes-Einstein. These observations suggest that the suspensions with large depletant chains form gels, whereas the rest of the suspensions behave like fluids. This study confirms that the attraction potential required for gelation depends on the depletant size in colloid-polymer mixtures.

6.2 Future work

Through this work, we showed that changing the presence of electrostatic interactions on the polymer backbone in a complex fluid of particles and polymers brings forth a complex set of interactions that alter both the dynamics of the particles and polymer chains. As such, there still remain a series of open questions to be further studied in the future:

6.2.1 Dynamics of anisotropic particles in polyelectrolyte solutions

This work focused on exploring the underlying physical phenomenon that control the dynamics of spherical particles in semidilute polyelectrolyte solutions. For spherical particles, the controlling length scale is the particle's radius and translational diffusion is the major long time transport process. Anisotropic particles, however, possess multiple important length scales that influence both translational and rotational motion at long times.

A systematic study of the dynamics of anisotropic particles in polyelectrolyte solutions would give further insight into the specific controlling parameters to decouple the underlying physics in these systems. A combination of fluorescence or confocal microscopy with a dynamic scattering technique including fluorescence correlation spectroscopy or polarized dynamic light scattering would provide sufficient displacement and dynamic information to understand the transport of anisotropic particles.

6.2.2 Dynamics of nanoparticles in pH-responsive polymer solutions

Similar to polyelectrolytes, pH-responsive polymers can exhibit a rich array of tunable properties including conformation and flexibility. Although not explored in this work, we expect pH to play a significant role in the extent to which the polymer backbone is charged.¹⁸⁴ Using a polymer with an appropriate pKa value, we can explore the dynamics of nanoparticles at different functionalization rates. With changing pH conditions, particle stability can become a challenging factor due to enhanced aggregation. Finding a suitable particle chemistry that is compatible with the changing pHs would be key for this project's success. Microscopy or scattering techniques can both be used to study the dynamics of these systems. The results of this project would advance the understanding of particle transport for applications in biomedical applications and drug delivery.^{185,186}

6.2.3 Counterion size effects on polyelectrolyte dynamics

In this work, we demonstrated how the unique structural properties of polyelectrolytes due to the presence of electrostatic interactions result in deviations from theoretical predictions. Furthermore, we showed how chain conformation can be tuned by changing ionic strength through the addition of a monovalent salt. The counterion dissociation and density, however, differs between mono, di, and trivalent salts, and thus differently alter the structural properties of chains.^{187,188} There remains a lack of understanding of how the different counterion sizes impact the relaxations of polyelectrolyte chains in solutions. By fixing

ionic strength of a set of model polyelectrolyte solutions using different size counterions, we would be able to elucidate the effects of counterion size effects on the relaxations of polyelectrolyte systems. This project requires dynamic neutron scattering experiments to probe the dynamics at the time and length scales of interest.

6.2.4 Particle dynamics in sodium polystyrene sulfonate solutions with different sulfonation levels

Controlling the degree of sulfonation of the backbone monomers can be used as an approach to alter the chain flexibility, conformation, and stiffness. The structural properties can be tuned using the reaction time, which in return controls the sulfonation level. By fixing the chain radius of gyration and changing degree of sulfonation, we can isolate the contribution of chain stiffness to particle transport. The dynamics of particles in these systems can be studied using dynamic x-ray scattering techniques or microscopy depending on the length scales of interest. This project will illustrate the physical mechanism governing the dynamics of particles in solutions and elucidate the role of chain stiffness in these systems.

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