Depletion layer dynamics of polyelectrolyte solutions under Poiseuille flow

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Results

Steady-State Fluorescence Anisotropy of Aqueous Polyelectrolyte Solutions. STED-anisotropy imaging developed for this study relies on imaging polymer concentration profiles in solution by contrasting spatially heterogeneous changes in the rotational dynamics of a small-molecule chromophore dispersed in the solution. By leveraging the interaction between AlexaFluor488 (water-soluble, net negative charge) and an anionic polymer (30, 31), local concentrations of the polymer can be estimated by steady-state anisotropy values (γ). To calibrate the imaging protocol, we first measure bulk steady-state fluorescence anisotropy of deionized

Significance

The interfacial physics of complex liquids under flow remains a long-standing problem in fluid mechanics that is important for fields ranging from lubrication to nanofluidics. Liquids containing small amounts of high-molecular weight polymers are found to flow through channels faster than expected, a phenomenon attributed to the formation of boundary depletion layers that relaxes the no-slip boundary condition and allows the bulk of the fluid to slip past the walls. This work provides the most direct measurement to date of the dimension and composition of depletion layers of a polymer solution under flow. We anticipate extending this approach to help understand fluid dynamics in different regimes, such as flow in nanofluidics and turbulence.

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(DI) water solutions containing PSS and AlexaFluor488. PSS concentrations ranging from 0 to 40% wt/wt were used. Note that the maximum concentration tested for polymer solutions was $c^*$, where $c^*$ is the overlap concentration of the polymer solution, so polymer chain entanglements are not expected to physically hinder chromophore rotation. The anisotropy value at each PSS concentration was calculated using

$$a = \frac{\text{Int}_1 - G \cdot \text{Int}_\perp}{\text{Int}_\parallel + 2G \cdot \text{Int}_\perp}$$

where $\text{Int}_1$ and $\text{Int}_\perp$ are the fluorescence intensities parallel and perpendicular to the excitation polarization, respectively, and $G$ is a correction factor that accounts for depolarization induced by the optics of the instrument (32). $G$ was calculated using AlexaFluor488 in DI water, assuming complete depolarization ($a = 0$).

The steady-state anisotropy values measured for AlexaFluor488 in PSS solutions (DI water) increase with increasing PSS concentration (Fig. 1, blue). This indicates a significant slowdown in the ensemble averaged rotational time constant of the chromophore. To further characterize the AlexaFluor488–PSS interactions, we perform dynamic anisotropy measurements (SI Appendix, section 1) which reveal 3 chromophore subpopulations: 1) free chromophores (unhindered rotation), 2) chromophores reversibly complexed with the polyelectrolyte (partially hindered rotation), and 3) chromophores irreversibly complexed with the polyelectrolyte (fully hindered rotation within the experimental timescales) (SI Appendix, Fig. S1). The contribution of each subpopulation to the steady-state anisotropy signal is dependent on the polyelectrolyte concentration (SI Appendix, Fig. S1 C–E). In addition, the fluorescence emission spectrum of AlexaFluor488 in PSS solution shows a red shift, the magnitude of the shift being dependent on PSS concentration (SI Appendix, section 2).

The interaction between AlexaFluor488 and PSS can be attributed to short-range attraction between the anionic side group of the polymer and electron-depleted regions of the aromatic ring (33). These short-range interactions facilitate π-stacking of the chromophores (30, 31) that are independent of the solution ionic strength (34). Indeed, in both a Tris-EDTA buffer (buffer strength = 25 mM, ionic strength tuned to $I = 25$ mM using NaCl) and DI water, the steady-state anisotropy values increase comparably with increasing PSS concentration (Fig. 1 B, blue and cyan). Consistently, we find that the anisotropy values of the AlexaFluor532, a chromophore with steric side groups that disrupt short-range intermolecular stacking interactions between chromophores (31), are only weakly dependent on PSS concentration (Fig. 1 B, purple and light pink). Furthermore, in a control experiment with AlexaFluor488 in solutions of polyethylene glycol (PEG, $N = 1,590$) the anisotropy values are independent of PEG concentration (Fig. 1 A, red), as expected for noninteracting chromophore and polymer. Taken together, these results show that short-range interactions between the chromophore and the anionic side groups of the polyelectrolyte lead to hindered chromophore rotation resulting in an increase in the ensemble anisotropy values (30, 31).

**Equilibrium Depletion Layer at a Nonadsorbing Wall.** At equilibrium, a polymer solution forms a depletion layer driven by repulsions arising from a reduction in the configurational entropy (entropic repulsions) of the polymer as it approaches a nonadsorbing wall (35–37). As such, the thickness of the depletion layer ($d$) approximates $\left(r_s^2\right)^{1/2}$ of the polymer (37). The polymer concentration profile in the depletion layer, as a function of distance from the wall ($x$) (Fig. 2), follows the analytical function (28, 38)

$$\phi\left(x, \frac{d}{a}\right) = \phi_s \tanh\left(\frac{x}{d}\right) + \phi_p,$$

where $\phi_s$ and $\phi_p$ are the bulk and surface concentration, respectively.

To probe the depletion layer of PSS at a nonadsorbing wall, we used a fused silica microfluidic channel (30 $\mu$m × 100 $\mu$m × 100 mm). A 10% solution of PSS in DI water (1 $\mu$M AlexaFluor488) was allowed to equilibrate for 30 min after injection into the channel. The PSS concentration is well below the overlap concentration ($c^*/6$); therefore, the solution is in an unentangled semifluid regime (39). Using a home-built STED-anisotropy microscope (SI Appendix, section 3) we image the anisotropy profiles extending from the wall to $\approx 150$ $\mu$m into the bulk (Fig. 24). Differences in fluorescence anisotropy values reflect differences in local polymer concentration (Fig. 2 B and C). A 2D STED-anisotropy image shows a pronounced decrease in average fluorescence anisotropy within a distance of few hundred nanometers from the wall (Fig. 2 C, Top). Averaging over the $y$ dimension gives a 1D anisotropy profile characterized by the depletion layer thickness $d$, the anisotropy value at the wall ($\phi_s$), and the anisotropy value in the bulk solution ($\phi_p$) (Fig. 2 C, Bottom).

For PSS in DI water, the anisotropy value at the wall is smaller than that in bulk solution, which indicates depletion of polymer concentration near the wall (Fig. 2 C and D). The thickness of the depletion layer is measured to be $310 \pm 42$ nm (Fig. 2 D, gray). The PSS concentration at the wall is estimated to be $\approx 8$% PSS wt/wt, which is only slightly lower than the bulk concentration ($\approx 10%$ PSS wt/wt). The anisotropy profiles are well captured by Eq. 2 and hence provide a good estimate of polymer concentrations in the depletion layer. Note that the fluorescence intensity profile, which reflects only the spatial distribution of probe molecules, shows uniform signal near the wall (Fig. 2 D, Inset), indicating that the spatial profiles shown in Fig. 2D do not depend on the spatial distribution of the chromophore. Under the experimental conditions, the silica surface is expected to be
negatively charged (40), although the electrostatic interaction length is estimated to be significantly less than 300 nm (SI Appendix, section 4).

Comparing the experimentally measured depletion layer thickness to \(\langle r^2 \rangle^{1/2} \) of PSS in DI water is difficult as the highly charged nature of the PSS prevents direct calculation of the polymer size. However, the scaling of \(\langle r^2 \rangle^{1/2} \) for a polyelectrolyte in solution as a function of ionic strength can be estimated using an appropriate model for polymer conformation and electrostatic persistence length. The wormlike chain (WLC) model is typically applied to semiflexible polyelectrolytes (41), such as PSS (42) and nucleic acids (43–45). We find that the experimental data are best captured by a WLC with an electrostatic persistence length given by Odijk–Skolnick–Fixman (OSF) theory (46, 47) (SI Appendix, section 5, for model comparisons). The \(\langle r^2 \rangle^{1/2} \) can be estimated as

\[
\langle r^2 \rangle^{1/2} \propto \left[ \frac{2L_p}{l} + \frac{2l_i}{l} \left( 1 - \epsilon / \epsilon_p \right) \right]^{1/2},
\]

where \(l = Nb \) is the contour length, \(N \) is the number of monomers, \(b \) is the monomer length, and \(L_p \) is the persistence length of the polymer. According to OSF theory, the polyelectrolyte persistence length scales inversely with ionic strength. Therefore, with increasing solution ionic strength, due to reduced \(\langle r^2 \rangle^{1/2} \), \(d \) is expected to narrow.

To characterize \(d \) with respect to \(\langle r^2 \rangle^{1/2} \), we measured the depletion layer of PSS in Tris-EDTA buffer solutions at different ionic strengths. The buffer strength was varied from 25 to 0.25 mM. NaCl was added to the solution to tune the ionic strength of the buffer to the desired values (25.0, 2.50, and 0.25 mM final ionic strength of solution). We find that with increasing ionic strength, the depletion layer thickness decreases significantly (from 50 to 25 nm) (48). Accounting for the point spread function (PSF) of the microscope, the experimentally measured value of \(d \) at highest ionic strength approaches the calculated \(\langle r^2 \rangle^{1/2} \) with ionic strength calculated using Eq. 3 (Fig. 2 E, gray box). The \(d_{\text{cal}} \) values are found to increase with increasing ionic strength (Fig. 2 F), indicating increased polymer concentration in the depletion layer. This is expected as \(\langle r^2 \rangle^{1/2} \) of
the polymer decreases with increasing ionic strength due to chain collapse.

**Depletion Layer Dynamics under Poiseuille Flow.** Under Poiseuille flow, a shear force arises near the wall due to the no-slip boundary condition (Fig. 2B) (17). For polymer solutions, the shear elongates the chains in a direction parallel to the flow (10, 11, 13, 26, 49). While the dynamics of depletion layers under flow have been extensively studied via theory/modeling, the complete picture has not been confirmed experimentally. The most direct experimental study was by Ausserré et al. (50), who reported thickening of depletion layers in an aqueous solution of xanthan under flow at high shear rates. However, narrowing of depletion layers at low to intermediate shear rates, which has been theoretically predicted (11), has not been experimentally observed to date.

We probe depletion layers of PSS (10% wt/wt solution in DI water, 1 μM AlexaFluor488) under flow at intermediate shear rates (0 to 4 × 10^3 s⁻¹) (Fig. 3A). The Reynolds number under these conditions is < 1 (SI Appendix, section 6), indicating that the flow is laminar (51). To compute Wi, we first calculate the relaxation time of PSS in DI water. For a polyelectrolyte solution in the unentangled semidilute regime the dynamics are expected to be Rouse-like (39),

$$\tau = \frac{\zeta b^2 N^2}{6\pi k_B T p^2} \text{ for } p = 1, 2, \ldots, N,$$

where \(p = 1\) gives the longest relaxation time. The friction coefficient (\(\zeta\)) is given by Stokes’ law (\(\zeta = 6\pi n\eta R_c\)). The longest relaxation time for PSS in DI water is calculated to be 1.4 × 10⁻⁶ s at room temperature, which yields a range of \(Wi\) from 0 to 10 (Fig. 4) for the shear rates employed in this study.

The depletion layer concentration profiles imaged by STED-anisotropy were fit to Eq. 2 (Fig. 3A). With increasing shear rate, pronounced effects are observed: 1) depletion layer narrowing (decrease in depletion layer thickness as polymer center of mass approaches the wall) and 2) depletion layer sharpening (polymer concentration in the depletion layer approaches pure solvent) (Fig. 4). Note that in absence of polymer, no change in the anisotropy profile is observed with flow (SI Appendix, section 7).

Modeling studies suggest that depletion layer narrowing occurs due to shear-induced elongation and alignment of the polymer along the direction of flow (11, 52). Such deformation allows the center of mass of the polymer to approach the wall without incurring an entropic penalty. This mechanism is valid in the low to intermediate \(Wi\) regime (\(Wi = 1 - 10\)), where the average rotational time of the polymer is slower than the relaxation time of the deformation (11). At high \(Wi\), where the average rotational time of the polymer is faster than its relaxation time (29), the depletion layers thicken as the effective time-averaged polymer size increases (11, 50).

The anisotropy profile as a function of distance from the wall sharpens with increasing shear (Fig. 4B). This observation, which reflects drifting of polymer segmental density away from the wall, can be attributed to the hydrodynamic lift generated by tension in the polymer chain induced by shear (13, 53–56). At the highest shear rate (\(\gamma \sim 7 \cdot 10^4 s^{-1}\)) studied here, the polymer concentration measured at the wall approaches that of pure solvent (up to an order of magnitude lower than the bulk solution, <1% wt/wt).

![Fig. 3. Depletion layer dynamics under Poiseuille flow at nonadsorbing wall probed by STED-anisotropy imaging. Anisotropy profiles of PSS solutions in (A) DI water, (B) \(I = 0.25\) mM, and (C) \(I = 2.5\) mM at shear rates ranging from 0 to 3.6 \(10^3\) s⁻¹. The anisotropy profiles are fit to Eq. 2 to obtain \(d\) and \(a_{\perp 0}\) values.](image)

![Fig. 4. Narrowing and sharpening of depletion layers at nonadsorbing wall under Poiseuille flow. (A) Depletion layer thickness (\(d\)) as a function of Weissenberg number (\(Wi\)) for PSS solutions in DI water. \(d\) narrows from ~310 to ~112 nm over a range of \(Wi\) from 0 to 10. (B) Polymer concentration at the wall (\(a_{\perp 0}\)) as a function of \(Wi\) for PSS solutions in DI water. At the highest shear rate studied here (\(Wi \sim 10\)), the polymer concentration in the depletion layer approaches pure solvent (~1 order of magnitude lower than that in bulk solution). Such depletion layer sharpening with increasing \(Wi\) is attributed to hydrodynamic lift pulling polymer segmental density away from the wall.](image)
Depletion Layer Dynamics at High Ionic Strength. In the previous sections, we show that the equilibrium depletion layer thickness approximates the \((\rho^2)^{1/2}\) of a polyelectrolyte chain and decreases significantly with increasing solution ionic strength. We also report narrowing and sharpening of depletion layers at low to intermediate shear rates. In this section, we discuss the effect of flow on the polyelectrolyte depletion layers at high ionic strength.

PSS (10% wt/wt) in high-ionic strength buffer solutions \((I = 0.25\) and \(I = 2.5\) mM, \(1\) μM AlexaFluor488) was subjected to shear rates of \(0-4 \times 10^3\) s\(^{-1}\) (Fig. 3 B and C). The depletion layer concentration profiles imaged by STED-anisotropy were fit to Eq. 2 (Fig. 3 B and C). The presence of ions increases the internal relaxation time of the polymer, and therefore, \(Wi\) for each experimental condition must be calculated. For high-ionic strength solutions, the relaxation time was first estimated as \(\tau = (1 + 2Ac_i/c)^{-3/4}\) \(\left[5\right]\)

assuming that the solvent viscosity and Flory–Huggins interaction parameter are similar to the values in DI water. Here \(\tau\) is the longest relaxation time in DI water, \(A\) is the average number of units between charges (based on 80% residues charged), \(c_i\) is the salt concentration, and \(c\) is the polymer concentration. The longest relaxation times of PSS at \(I = 0.25\) mM and \(I = 2.5\) mM are calculated to be \(8 \times 10^{-5}\) and \(2 \times 10^{-5}\) s, respectively.

Fig. 5 shows master plots of \(d\) and \(d_{eq}\) as a function of \(Wi\) (for PSS in DI water, \(I = 0.25\) mM, and \(I = 2.5\) mM), which fit to a power law with scaling factors of \(-0.40\) and \(-0.25\), respectively. The \(Wi\) numbers span 4 orders of magnitude from \(\sim 10^{-2}\) to \(\sim 10^{3}\) across all ionic strength conditions used in this study. Below the critical \(Wi\) value \((Wi = 1)\), no change in \(d\) is observed (Fig. 5A). However, significant narrowing of the depletion layer thickness sets in at the critical \(Wi\). Over the range of \(Wi\) studied, \(d\) decreases from \(\sim 310\) to \(\sim 112\) nm. Note that at high \(Wi\) \((>10)\), the depletion layer thickness deviates from the power law fit, likely due to the turnover from depletion layer narrowing to thickening (11, 50).

Interestingly, depletion layer sharpening for the PSS solutions is observed below the critical \(Wi\) (Fig. 5B). This could arise from small perturbations to the polymer structure (57). While these perturbations are too weak to modulate center of mass of the polymer, they could be sufficient to generate hydrodynamic lift at the wall (13, 53). This is reminiscent of Boger fluids (elastic polymer solutions that are engineered to prevent shear-induced elongation of the polymers), which show significant reductions in drag coefficients at \(Wi \ll 1\) that plateau at the critical \(Wi\) (58).

Discussion

Superresolution anisotropy imaging employed in this study reveals depletion layer dynamics of polymer solutions, measured with a nonperturbative approach, at length scales previously inaccessible to traditional imaging techniques. We image depletion layers with thicknesses approximating the \((\rho^2)^{1/2}\) of the polymer, in agreement with theoretical predictions for entropically driven depletion of polymer solutions at nonadsorbing walls (24, 28). We also report depletion layer narrowing under Poiseuille flow at low to intermediate shear rates. This drifting of the center of mass of the polymer in the depletion layer toward the wall is observed only above the critical \(Wi\), where significant chain extension sets in. At higher \(Wi\) \((>10)\), the depletion layer thickness deviates from the observed trend, likely indicating a turnover to depletion layer thickening that has been predicted (11) and experimentally observed (24) at high \(Wi\). Furthermore, measurements of concentration at the wall reveal significant segmental drift away from the wall (depletion layer sharpening) attributed to hydrodynamic lift. Unexpectedly, depletion layer sharpening is observed well below the critical \(Wi\). This suggests that small perturbations to the polymer conformation can lead to sufficient chain tension to generate lift forces. Through real-space nanoscopic measurements, this work provides insights into the long-standing problem of enhanced flow of complex liquids.

Methods

Materials. Poly(styrene sulfonate) (M\(_w\) = 334,400, M\(_n\)/M\(_w\) = 1.04, \(N = 1,827, 80\%\) charged) and poly(ethylene glycol) (M\(_w\) = 70,000, M\(_n\)/M\(_w\) = 1.28, \(N = 1,590,\) neutral) were purchased from Polymer Source. AlexaFluor488 and fluorescent polystyrene beads (100 nm) were purchased from Invitrogen, ThermoFisher. Fused silica microfluidic channels were purchased from Darwin Microfluidics.

Bulk Anisotropy Measurements. A steady-state spectrophotometer (Photon Technology International) equipped with linear polarizers (Thorlabs) in the excitation and emission pathways was employed for bulk anisotropy measurements. The excitation wavelength was set to 488 nm, and the detection wavelength was set to 510 nm.

STED-Anisotropy Imaging. A home-built setup was used for STED-anisotropy measurements. CW laser at 488 nm, generated by an OBIS LX 120 mW CW laser (Coherent), was passed through Glan–Taylor polarizer (Thorlabs) to obtain highly pure (100,000:1) linearly polarized excitation beam. CW laser at 592 nm (VFL-P-1000 592; MPB Communications Inc.) was passed through a vortex phase plate (VPP-1a; RPC Photonics) to generate a depletion with a doughnut profile. The excitation and depletion beams were focused on the sample using a 100×, 1.49 NA oil immersion objective (Nikon). Excitation modulation and synchronous detection were carried out according to SI Appendix, section 3.

The emitted fluorescence was collected by the same objective lens. The parallel and orthogonal components of the emitted fluorescence were separated by a polarizing cube (CCM1-PBS251; Thorlabs) and steered to 2 single-photon counters (SPCM-AQRH; EXCELITAS) for anisotropy measurements. The TTL signal from SPC was acquired with a DAQ card (PCIe-6353; National Instruments). Data acquisition and analysis was automated by custom LabVIEW software (National Instruments).

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