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# Langevin dynamics prediction of polymer-particle adsorption and saturation processes in shear flows

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**Abstract** – Polymer-particle interactions, adsorption and subsequent polymer saturation in shear flows is studied using Langevin dynamics and a potential-based interaction modelling technique. The polymeric phase is modelled as macromolecular chains of interacting beads (monomers), with the effects of bead-bead and bead-particle steric interactions incorporated through a truncated Lennard-Jones potential and the Kratky-Porod bending rigidity accounted for. Simulations of multi-polymer particle adsorption events are performed, with the effects of bending rigidity studied. It is found that for low bending rigidities, polymers fully adsorb onto the particle, with conformities tightly bound and flattened to the spherical surface. Increased rigidities cause polymer chains to hang away from the particle surface. Around 75% adsorption is achieved for low rigidity polymers whereas for high rigidity, just over half of the monomers remain bound. Furthermore, it is demonstrated that increasing the rigidity leads to more monomers present in the surrounding area adsorption zone, constituting an increase in effective radius.

## 1. Introduction

Optimized filtration and thickening stands as an industrial challenge across many applications, such as water treatment, chemical manufacture and nuclear waste processing (Lockwood et al. 2021). Various techniques are in development to aid these processes. For instance, low concentrations of high molecular weight polymers are often added to aqueous particle-laden suspensions in order to separate the non-settling solid phase. Though having demonstrated their efficacy in laboratory scale rigs, polymer additives and their particle adsorption dynamics are complex to predict and so optimization of these systems is difficult with present knowledge. Furthermore, to use polymer flocculation in sensitive systems such as nuclear waste settling tanks and flows, the effectiveness and resultant behaviour must be fully proven, demonstrated and understood. One key challenge lies in predicting the process of steric stabilization, which occurs at high adsorption densities, wherein adsorbed nonionic polymers inhibit further flocculation by producing a strong repulsion between the particles. This reduces the effectiveness of bridging, wherein polymers span the gap between nearby particles (leading to flocculation) by shielding available adsorption sites on the particle surface.

In this study, we aim to determine the extent to which key parameters are capable of encouraging the bridging mechanism in the steric stabilization regime. Natural flocculants can be combined with synthetic polymers tailored to ideal conditions, improving efficiency of flocculation processes. With knowledge surrounding the flocculation dynamics on the particle scale, these optimizations can be improved. Here, nonequilibrium Langevin dynamics is used to predict polymer-particle interaction and adsorption in shear flow conditions, as applied in various other studies (Li et al. 2016; Brackley et al. 2020; Mortimer et al. 2023). We explore the methods by which adsorption saturation and steric stabilization occurs and determine how the polymeric phase parameters can offer various conformities as the adsorption density increases.

## 2. Methodology

The present work uses Langevin dynamics as well as the finitely extensible nonlinear elastic (FENE) polymer model to predict the motion of polymer chains in a shear flow in the presence of a spherical particle. Polymers themselves are represented as macromolecular chains of interacting monomer beads, with each bead's trajectory calculated using the Newtonian equation of motion:

$$m_b \frac{d^2\boldsymbol{r}_i}{dt^2} = -\boldsymbol{\nabla} V_i - \xi\left(\frac{d(\boldsymbol{r}_i)}{dt} - \boldsymbol{u}_{F,i}\right) + \sqrt{2k_B T\xi}\boldsymbol{\eta}_i(t) \tag{1}$$

Here, $\boldsymbol{r}_i$ is the position vector of bead $i$ in the chain, $m_b$ is the mass of the bead, $\xi$ is the drag coefficient, $\boldsymbol{u}_{F,i}$ is the fluid velocity interpolated at the bead position, $k_B$ is Boltzmann's constant and $\boldsymbol{\eta}_i(t)$ is a Brownian noise term which satisfies $\langle \eta_{ia}(t) \rangle = 0$ and $\langle \eta_{ia}(t)\eta_{ib}(t') \rangle = \delta_{a,b}\delta(t-t')$. This equation is solved in non-dimensional form, with the space timescale using the bead diameter, $\sigma_b$, and time using the Brownian bead timescale, $\tau_b = \sqrt{m_b\sigma_b/k_B T}$. Then, the non-dimensional potential field $V_i$ is assembled as:

$$V_i^* = V_{i,F}^* + V_{i,B}^* + V_{i,W}^* + V_{i,P}^*, \tag{2}$$

which accounts for the FENE spring force, the Kratky-Porod bending rigidity potential, the steric interactions Weeks-Chandler-Anderson (WCA) potential and the polymer-particle truncated Lennard-Jones (LJT) potential, respectively.

The equations above are solved for each monomer bead using a Verlet-velocity integration scheme and constant timestep $\delta t^* = 0.005$. To study multi-polymer adsorption onto a stationary particle within a flow, the domain is a $60 \times 30 \times 30$ computational channel cell in all cases. Periodic conditions are enforced in the streamwise ($x^*$) and spanwise ($z^*$) directions, while the wall-normal ($y^*$) direction extents use a wall potential, $V_{i,W}^*(\delta y^*) = 10\delta {y^*}^2$, for wall peneration depth $\delta y^*$. The velocity of the lower wall is kept constant, $u_x^* = 0$, while the top wall moves with velocity $u_x^* = L_y We$, with $L_y$ the vertical length and $We = 0.3$ the Weissenberg number. The velocity gradient is constant across the channel. Before the first timestep, 15 polymer chains are injected into the upstream region $x^* < 20$, with the particle of diameter $d_P^* = 10$ fixed stationary at $x^* = 30$. The computational domain at injection is illustrated in Fig. 1.

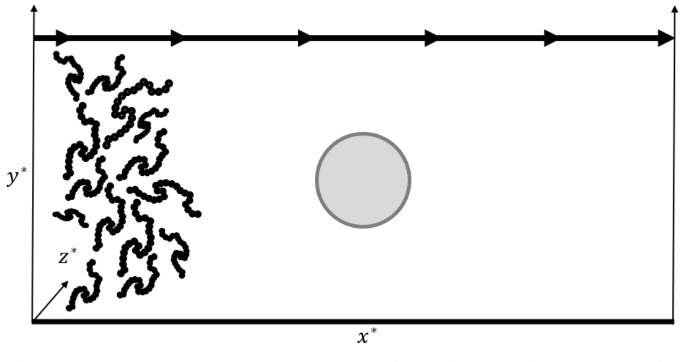

Figure 1: Schematic illustrating the injection condition for an instance of multi polymer-particle adsorption interaction events.

## 3. Results and discussion

The Kratky-Porod bending rigidity potential, given by $V_{i,B}^{*}(\theta_i) = K_B^{*}(1+\cos(\theta_i))$, has been demonstrated to influence the conformity of the polymer chain when adsorption takes place (Mortimer et al. 2013). Here, we consider the effect of the strength of this potential, which acts to restrict the bead chains from adopting acute angles. Figure 2 illustrates the result of such interactions while varying the potential strength, $K_B^{*}$. At low bending rigidity, the result is that polymers are able to adsorb onto the particle with ease, flattening and spreading out across its surface. From the instantaneous snapshot, we observe that the surface coverage is high, with only a few loops and tails formed travelling away from the particle. As the rigidity is increased, the inability to flatten out onto the particle leads to more cluster-like polymer conformities forming on the particle, and longer structures leading to longer tails. These also tend to form parallel to the streamwise direction. Similar results are observed for $K_B^{*} = 5$ with most structures tending to be more train like, encircling the particle diameter in some cases.

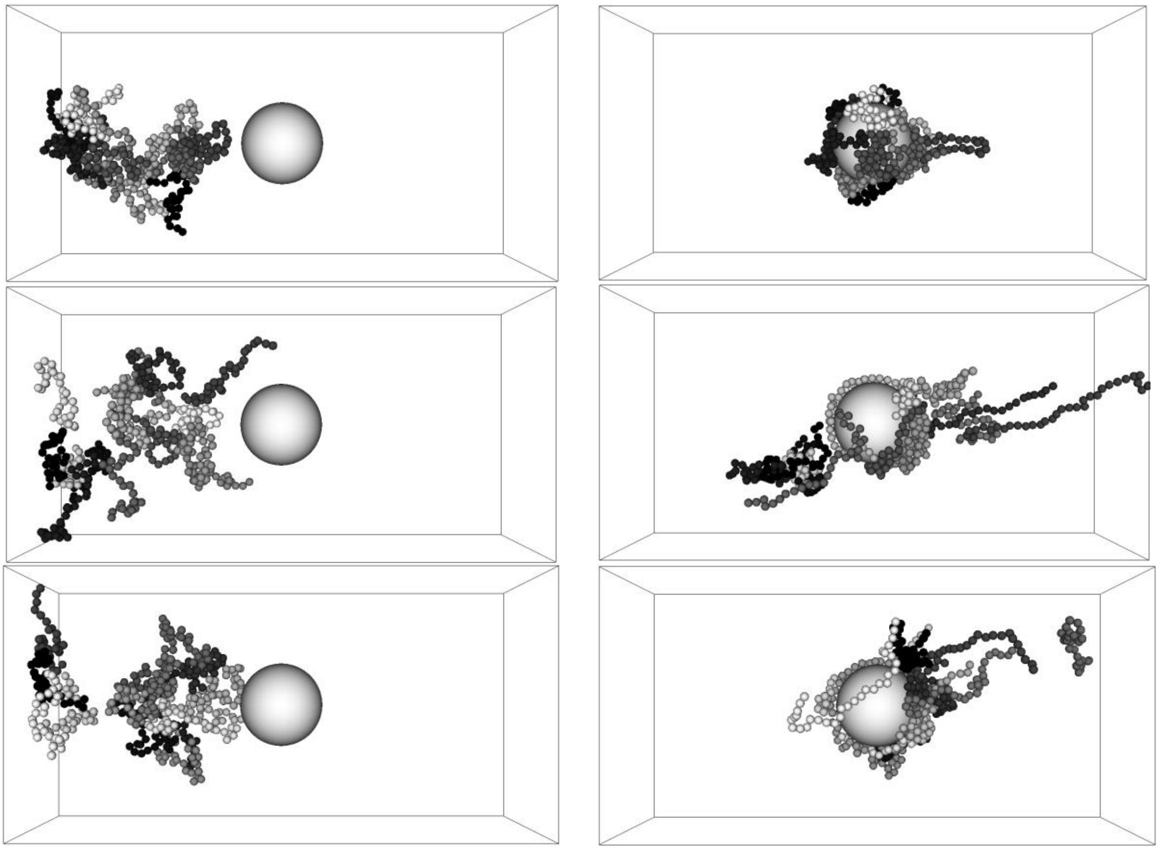

Figure 2: Instantaneous snapshots of polymer-particle interaction at $t^{*} = 1$ (left) and $t^{*} = 10$ (right). Upper: $K_B^{*} = 1$; middle: $K_B^{*} = 3$; lower: $K_B^{*} = 5$.

Results sampled from 100 Monte-Carlo events for each bending rigidity potential strength considered are presented in Fig. 3, which considers the adsorption dynamics of each polymer in the system separately. The left plot illustrates the probability density functions of the number of adsorbed beads from each polymer. The distribution is bimodal in each case, with the left peak representing polymers which did not remain bound to the particle after adsorption. For the two highest bending rigidity strengths, $K_B^{*} = 3.0$ and $5.0$, polymers are less likely to either miss the particle or be removed from the surface. Since these polymers tend to have increased radii of gyration due to their tendency to straighten out more than the curled up $K_B^* = 1.0$ polymers, collision with the particle is more likely. We observe the greatest monomer adsorption for $K_B^* = 3.0$, with lower bending rigidities likely spreading out across the particle surface reducing vacancies for other polymer chains, and higher bending rigidities more likely to hang away from the particle as observed in single-polymer adsorption studies (Mortimer and Fairweather, 2023).

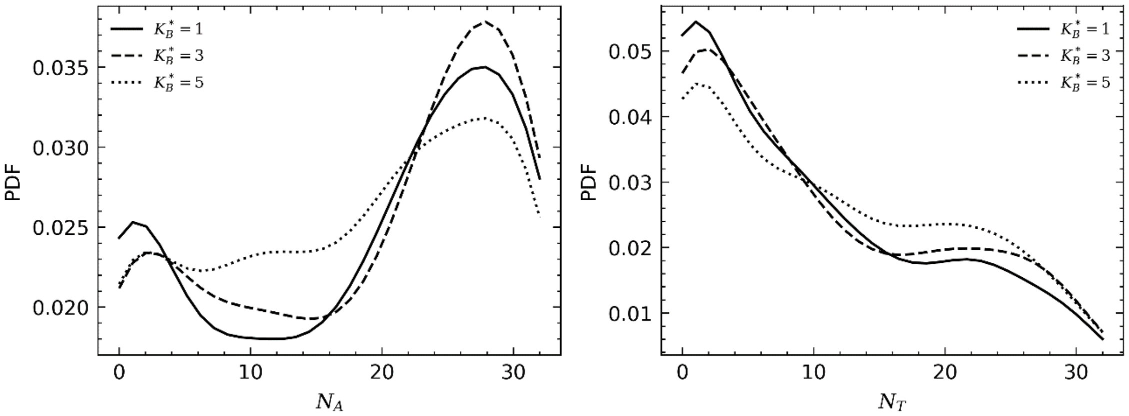

Figure 3: Effect of FENE potential strength on the probability density functions of the number of adsorbed beads from a single polymer, $N_A$ (left) and number of tail beads, $N_T$ (right).

## 4. Conclusions

Simulations of multi-polymer particle adsorption events have been performed using Langevin dynamics. The Kratky-Porod bending rigidity potential has proven to significantly impact the conformation of polymer chains during the process of adsorption. At lower rigidity values, polymers readily adhere to the particle surface, spreading out and achieving high surface coverage. However, as rigidity increases, the inability to flatten results in the formation of cluster-like conformations with elongated tails, often aligned in the streamwise direction leaving further surface for more interactions to occur.

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