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Langevin dynamic simulations of two- and three-dimensional polymer-particle flocculation for the development of behavioural modification techniques

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ABSTRACT

This study employs two- and three-dimensional Langevin dynamic simulations to investigate the fundamentals of polymer-particle flocculation and assess the impact of the Kratky-Porod bending rigidity, polymer concentration, and adsorption potential strength on the resulting structures. The present work explores flocculation in enclosed computational cells under stagnant conditions, utilising a bead-spring finitely-extensible nonlinear elastic (FENE) model to represent macromolecular polymer chains. The model incorporates various interaction potentials between monomers, particles, and walls including the FENE potential, bending rigidity, the Weeks-Chandler-Anderson potential, and a shifted and truncated Lennard-Jones potential to facilitate adsorption dynamics. Variations in bending rigidity are shown to directly influence the formation and growth of flocculents, revealing distinct conformation behaviours. It is shown that more flexible polymers form compact clusters on the surface of particles, while rigid polymers lead to more elongated tails upon adsorption, impacting flocculent size and structure. Polymer concentration also alters cluster formation rates and morphology, transitioning from compact, tightly bound structures at low concentrations to larger flocculents with higher concentrations. Modifying the shifted and truncated Lennard-Jones potential strength demonstrates how stronger adsorption interaction strengths yields larger, dense clusters, contrasting with weaker interaction strengths leading to smaller, more porous formations. Simulations performed in three dimensions are shown to validate the emergent dynamics observed in two dimensions, demonstrating that cluster formation and growth mechanisms are consistent across both, with minor variations due to adsorption surface area relative to the size of the monomers, confirming the applicability of two-dimensional findings to real-world three-dimensional polymer systems. This computational study provides valuable insight into the impact of various physical and chemical parameters on the multifaceted nature of flocculation dynamics, crucial for processes such as settling and the implementation of behavioural modification techniques, to improve flow, mixing and separation behaviour of particle-laden flows, across many industrial and environmental settings.

Introduction

The addition of high molecular weight polymers in low concentrations to a wide range of particle-fluid systems holds promise for

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many processing techniques, such as the separation of fine solids in liquid suspensions. In recent decades, the application of polymeric settling agents has been a focus of many research endeavours [1,2]. This technique has been demonstrated to be effective at improving processes such as filtration and thickening in a variety of industrial applications [3–5]. Of importance to this study are its applications within nuclear decommissioning and waste management, with turbidity reduction, as well as improved settling and sediment consolidation rates [6] being of great value as tools to address challenges faced in those applications. Further, the use of polymeric flocculants to improve processes is not limited to industrial settings. For instance, polymeric colloidal-sized particles (with diameters $<1 \mu m$) are not capable of undergoing settling in river flows without the aid of induced aggregation. In some cases, a natural process occurs in which fibrillar extracellular polymeric substances are released by microorganisms within a river or water ecosystem, which can facilitate flocculation [7,8].

Despite having been demonstrated in laboratory-scale rigs and wastewater flows, a deeper understanding of the dynamics driving flocculation in these systems is still lacking [9,10]. Designing and optimising separation processes driven by gravity requires a comprehensive grasp of both the flocculation and sedimentation dynamics specific to the system. Specifically, understanding the impact of the emergent flocculent (or floc) structures and morphologies (such as their fractal dimension and porosity) on hindered settling regimes is crucial. Determination of the most influential size of flocculated aggregates is key in establishing the interfacial settling rate. For instance, the formation of microflow channels in fractal aggregates has been shown to induce fluid flow within the porous microstructures, which leads to a reduction in drag and boundary layer separation [11,12]. Aggregate densification has also been observed wherein smaller aggregates are able to penetrate larger structures through these microflow channels [13].

Typically, both the beneficial properties of both natural and synthetic polymers are combined to tailor their properties for maximum efficiency, referred to as behavioural modification [4]. Without developed understanding surrounding the effect of polymer properties on subsequent flocculation, the ability to predict the optimal system parameters for desired outcomes is poor, and these techniques are often applied inefficiently. Moreover, using polymers in sensitive applications like nuclear waste processing and water treatment is crucially dependent on improved understanding and proven effectiveness. In such systems, particle sizes are usually in the micro or nano range, with flocculation increasing the particle size distribution for better solid removal. Flocs are formed primarily through bridging, wherein particles are 'bridged' to one another by high molecular weight polymer chains. It is important to note that this form of aggregation differs from that induced by other behavioural modification techniques, such as varying the ionic strength, adjusting the pH or coating particles to improve contact mechanics [14,15]. Polymer adsorption onto the particle surface occurs through various means [16], such as hydrogen bonding, electrostatic/hydrophobic interaction and ion bridging (for anionic polymers). It has been demonstrated that flocculation is sensitive to the full polymer chain length, often referred to as the contour length [4]. An initial constraint on the bridging process is that the polymer must be large enough to extend away from the particle, upon adsorption, at least twice the thickness of the electric double layer, though studies indicate that aggregation can still occur with smaller polymers since the electric double layer will be compressed, potentially allowing for van der Waals interactions to dominate [17].

Synthetic polymer flocculants can also be produced to possess various advantageous electrostatic properties, with most being classified as either positively, negatively or neutrally charged [5]. Non-ionic flocculants (which possess <1 % charged functional groups) such as polyacrylamide possess high molecular weights, which aids with the bridging process. Polyacrylamide is widely used due to its monomer, acrylamide, being water-soluble, reactive, and economically favourable. It has therefore been the focus of many studies in recent years [18–20]. The stiffness of polymers is also an important parameter which influences both adsorption conformities, as well as the morphology of emergent structures after flocculation [21]. Intrinsic to the polymer chain are properties such as the bond angle between monomers as well as the torsional potentials. The full effect of these properties on the conformity of the polymer is often characterized by a 'persistence length' [22], which quantifies the bending stiffness. Ionic strength has been shown to affect the persistence length in experiments, with higher ionic strengths leading to charge screening and more coil-like conformations with lower persistence lengths [23]. The Kratky-Porod model is also often used to describe semi-flexible polymers, which assumes that the cost of bending energetically is related quadratically to the bending angle [24]. From this model, various means to recover the effective persistence length have been proposed [25,26]. Increased bending rigidity restricts the flexibility of polymer chains, making them less adept at conforming around particles and forming bridges effectively. This in turn also impacts the ability of polymers to create strong connections between particles, affecting the strength and stability of resulting flocs [27]. Furthermore, local fluid properties also play an important role. For instance, the resulting flocculant structure has been shown to be susceptible to breaking under fluid shear [28].

Over the years, various polymeric-phase modelling techniques [29] have revealed fascinating behaviours in simple systems like stagnant tanks [30] and shear or turbulent flows [31]. More comprehensive understanding of how polymers interact with particles is also critical in the polymer synthesis industry, impacting the properties of polymer nanocomposites such as viscosity, glass transition temperature, and electrical conductivity [32–34]. Milchev and Binder [35] used Monte Carlo simulations to study the adsorption of a finite-length polymer to a surface, discovering that the polymer's conformities transitioned from a three-dimensional random coil to a nearly two-dimensional elongated coil at temperatures significantly lower than the critical adsorption point. Studies also suggest that the emergent structures in polymer-particle interactions depend crucially on interaction strength, affecting the various proportions of chains and loops. The length of the polymer chain also plays a crucial role in the resulting adsorption dynamics [36]. Arkin and Janke [37] investigated the structural characteristics of a polymer within an attractive sphere, characterising the conformity of the polymer by its radius of gyration and gyration tensor. A diverse system phase diagram was obtained, with behaviour encompassing configurations ranging from desorbed states to partially or entirely adsorbed conformations. Li et al. [38] further studied adsorption dynamics surrounding the conformational properties of an adsorbed polymer on a nanoparticle using off-lattice Monte-Carlo and Metropolis algorithms, describing the resulting configuration in terms of trains, loops and tails [39]. At low polymer-nanoparticle interaction strengths, trains, loops and tails were observed, whereas for high strengths loops were eliminated in favour of trains and tails.

Despite recent progress, many questions remain, especially regarding the dynamics underpinning polymer-particle bridging and flocculation, since most simulation studies only consider the adsorption behaviour onto one particle. Furthermore, the Monte-Carlo and Metropolis algorithms employed are limited in their monomer migration modelling, since they often fail to account for properties such as chain rigidity and other interactions which may occur between monomers such as Weeks-Chandler-Anderson potentials. This study aims to use nonequilibrium Langevin dynamic simulations to fully simulate the dynamics of flocculation and to uncover the effect of various polymer chain properties on polymer-particle interaction and the emergent structures which are formed.

Methodology

Polymer chain modelling

In this study, flocculation is considered under stagnant conditions in order to isolate the effects of solely diffusion and polymerparticle interaction on the flocculation mechanisms to better understand the direct effects of the various polymer and particle properties on the adsorption and resulting structure formation. To achieve this, Langevin dynamics along with a bead-spring polymer model is utilised to model polymers as macromolecular chains of interacting beads (monomers), as employed in various Brownian and Langevin dynamic studies [38,40,41]. An example of a polymeric chain of monomers which forms the basis for the polymeric phase is presented in Fig. 1. Here, subscript *i* refers to bead *i* in a series of connected beads of total size, N_B beads. Each monomer bead possesses a diameter σ , with $\mathbf{r}_i^* = \mathbf{r}_i/\sigma$ the non-dimensional Cartesian position vector of monomer *i*. The dimensional position vector \mathbf{r}_i of each bead in a polymer chain evolves through obeying the following Newtonian equation of motion [29]:

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

Here, m_b is the mass of the bead, t is time, V_i is the total interaction potential calculated at the bead's current position, ξ is the drag coefficient, $u_{F,i}$ is the local fluid velocity at the bead position, which in the present context is assumed to be zero throughout representing stagnant conditions, k_B is the Boltzmann constant, T is temperature and $\eta_i(t)$ is a Brownian noise term satisfying both $\langle \eta_{ia}(t) \rangle = 0$ and $\langle \eta_{ia}(t)\eta_{ib}(t') \rangle = \delta_{a,b}\delta(t-t')$. Since a constant bead diameter is used in the present study, σ , then time can be nondimensionalised using the Brownian bead timescale $\tau_b = \sqrt{m_b \sigma^2/k_B T}$, and space using the bead diameter. If the diffusion coefficient is further introduced as $D = k_B T/\xi$, this allows us to rewrite Eq. (1) as:

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

where variables superscripted with (*) represent terms non-dimensionalised using the above conventions for distance and time scales. The contributions to the overall interaction potential, V_i^* , for each bead are given by:

$$V_i^* = V_{i,F}^* + V_{i,B}^* + V_{i,W}^* + V_{i,P}^* + V_{i,WALL}^*.$$
(3)

The first term $V_{i,F}^*$ represents the bonds between the monomers using the finitely extensible nonlinear elastic (FENE) spring force described using the potential:

$$V_{i,F}^{*}(\delta \mathbf{r}^{*}) = -\frac{K_{F}^{*}R_{0}^{*2}}{2} \ln \left[1 - \left(\frac{\delta \mathbf{r}^{*}}{R_{0}^{*}}\right)^{2}\right],\tag{4}$$



Fig. 1. Schematic of a single modelled monomer chain forming a polymer. Dashed orange lines represent FENE springs connecting monomer beads (solid circles).

where $\delta r^* = |\mathbf{r}_{i+1}^* - \mathbf{r}_i^*|$ is the separation between two adjacent beads in the polymer chain, $K_F^* = K_F/k_BT$ is the non-dimensional FENE energy scale and R_0^* is the maximum FENE bond length. This interaction potential is only included in the calculation of neighbouring beads in the chain of monomers. The next potential, $V_{i,B}^*$, is the Kratky-Porod bending potential used to model the effects of bending rigidity observed in real semi-flexible polymers, wherein acute polymer angles are less favoured energetically due to molecular constraints. The Kratky-Porod potential is given by:

$$V_{i,B}^*(\theta_i) = K_B^*(1 + \cos(\theta_i)), \tag{5}$$

where θ_i is the angle formed by two adjacent separation vectors, i.e. $\theta_i = \cos^{-1}(\hat{n}_{i+1} \cdot \hat{n}_i)$ with $\hat{n}_i = (\mathbf{r}_i^* - \mathbf{r}_{i+1}^*)/|\mathbf{r}_i^* - \mathbf{r}_{i+1}^*|$. $K_B^* = K_B / k_B T$ represents the non-dimensional bending rigidity scale. This can be related to the intrinsic polymer persistence length by $l_p = K_B^* \sigma$ [41]. The next term in Eq. (3), $V_{i,W}^*$, represents steric interactions between monomers and is given by the following repulsive Weeks-Chandler-Anderson potential:

$$V_{i,W}^{*}(\delta \mathbf{r}^{*}) = 1 + 4 \left[\left(\frac{\sigma}{\delta \mathbf{r}^{*}} \right)^{12} - \left(\frac{\sigma}{\delta \mathbf{r}^{*}} \right)^{6} \right], \tag{6}$$

which contributes to the total potential for all pairs of monomers within a maximum distance corresponding to the minimum of the potential, $\delta r^* < \delta r^*_{max} = 2^{1/6}$, beyond which the potential is zero. The penultimate term, $V^*_{i,P}$ represents the adsorption interaction with particles. Particles are represented by rigid-body isotropic spheres of constant diameter, $d_P = 10\sigma$. Polymer beads in close proximity to the particle are able to interact through this potential. The polymer-particle interaction potential is a truncated and shifted Lennard-Jones potential which takes the form [38]:

$$V_{i,P}^{*}(\delta r^{*}) = K_{LJT}^{*} \left[\left(\frac{1}{\delta r^{*} - s^{*}} \right)^{12} - 2 \left(\frac{1}{\delta r^{*} - s^{*}} \right)^{6} \right] + V_{0,P}^{*},$$
(7)

with $s^* = 4.5$ for polymer-particle interactions, and $s^* = 9.0$ for particle-particle interactions. The term $V_{0,p}^*$ represents a shift in the interaction potential given as:

$$V_{0,P}^{*}(\delta r^{*}) = -K_{LJT}^{*} \left[\left(\frac{1}{\delta r_{C}^{*} - s^{*}} \right)^{12} - 2 \left(\frac{1}{\delta r_{C}^{*} - s^{*}} \right)^{6} \right],$$
(8)

with the cutoff distance $\delta r_c^* = 5 + s^*$. Finally, the domain has been chosen to represent an impenetrable tank such that wall boundaries exist at both extents of all three dimensions. To achieve this, a wall potential is included which is only active when the polymer position exceeds the extent of the computational domain, which possesses the form:

$$V_{WALL}^*(\delta^*) = 10\delta^{*2},\tag{9}$$

with δ^* the non-dimensional wall penetration distance.



Fig. 2. Summary of potentials involved when calculating interactions between two particles (grey circles) and a three-bead polymer (white circles). Blue lines represent potentials included in Eqs. (2) and (10).

Particle phase modelling

The particle equation of motion is similar to that of the monomer beads, and is given by:

$$\frac{d^2 \mathbf{r}_{P,i}^*}{dt^{*2}} = -\nabla V_{P,i}^* - \frac{1}{D} \left(\frac{d \mathbf{r}_{P,i}^*}{dt^*} - \mathbf{u}_{F,i}^* \right) + \sqrt{\frac{2}{D}} \eta_i^*(t^*), \tag{10}$$

with $r_{P,i}^*$ representing the position vector of particle *i*, which iterates over all the particles in the simulation up to the total number of particles, N_{PAR} . Here, the parameter *D* represents the diffusion coefficient of the particle phase, which scales via the Stokes drag relation of inversely proportionality to its increase in radius, hence D = 0.5.

In all simulations, the non-dimensional particle diameter is fixed at $D_p^* = 10$. The total potential, $V_{i,p}^*$, accounting for particleparticle, particle-bead and particle-wall interaction takes the form:

$$V_{i,P}^{*} = V_{i,W}^{*} + V_{i,P}^{*} + V_{i,WALL}^{*},$$
(11)

with $V_{i,W}^*$ acting between particles and $V_{i,P}^*$ acting between the particles and beads. The strength of the interaction is identical to the form given in the previous subsection. An illustrative summary of the interactions involved between monomer beads and particles is provided in Fig. 2.

Simulation setup and solution algorithm

The simulation domain in the two-dimensional cases is a 100×100 computational channel cell in (x^*, y^*) , and for the threedimensional cases $100 \times 100 \times 100$ in (x^*, y^*, z^*) . These were chosen to ensure sufficient space for flocs to form while making sure initial injection conditions would lead to prompt interactions to reduce long runtimes. A Monte-Carlo approach was adopted by performing $N_{MC} = 50$ full simulations within each domain in order to obtain an indication of the mean flocculation behaviour over many realisations. It should be noted that while Monte-Carlo methods are used in this study, they serve solely as an ensemble averaging tool for the analysis performed. The underlying particle and polymer dynamics are governed by time-resolved Langevin equations. The Monte-Carlo component refers to the use of multiple independent simulation realisations, each initiated with randomly seeded positions for particles and polymers. To initialise each realisation, $N_{PAR} = 15$ particles are injected randomly throughout the domain. Depending on the number of polymers studied, an initial bead for each polymer is then injected before 'growing' the polymer randomly by choosing a direction on the unit circle, and injecting a subsequent polymer, ensuring no overlap with pre-injected beads or particles. This occurs until a total number of beads per polymer $N_{BPP} = 32$ have been injected. The injection routine then moves onto the next polymer. Examples of an initial injection condition for both the two- and three-dimensional simulations are presented in Fig. 3.

At each simulation step, Eqs. (3) and (10) are solved for each bead and particle using the Verlet-velocity integration method with constant timestep $\delta t^* = 0.002$. Wall conditions are enforced through activation of the wall potential in both Cartesian directions beyond either extent, i.e. 0 and 100. In calculating contributions to the potential terms in Eqs. (3) and (10), the domain is subdivided into a 10 × 10 (×10) coarse grid, with properties in brackets representing those present in the three-dimensional simulations. At the start of each timestep, all monomer beads and particles are assigned a position among the discrete cell co-ordinates within this grid. When calculating potentials, only adjacent (both cardinal and diagonal) cells are considered. The coarseness of this grid was chosen to ensure the potentials beyond adjacent cells would be negligible, justifying their exclusion from the full potential calculations.

Each realisation is simulated for $N_T = 40,000$ timesteps ($t^* = 80$), during which time considerable flocculation occurs in most cases. Simulation results are then averaged across 50 independent realisations for the two-dimensional cases, and 10 independent



Fig. 3. Initial injection state for realisation of polymer-particle flocculation simulation in the two-dimensional cell (left) and the three-dimensional box (right). Smaller white spheres represent monomers, whereas larger grey spheres represent particles.

realisations for the three-dimensional cases, sufficient to produce negligible statistical error in temporal observations of cluster properties such as radius of gyration and fractal dimension.

The simulation parameters used throughout each realisation are presented in Table 1. To ensure numerical stability and convergence, the integration timestep was fixed at $\delta t^* = 0.002$, a value established through dedicated initial sensitivity studies. These tests assessed the sensitivity of the simulations by varying the timestep and monitoring the consistency of key metrics, including total system energy, cluster growth dynamics, and polymer conformation. Additionally, the spatial resolution used for calculating potential gradients was validated by refining the interaction grid and confirming negligible differences in particle trajectories and floc structure. These analyses confirmed that the chosen temporal and spatial discretisations provided stable, accurate results across all parameter sets investigated, without the emergence of numerical divergences.

In this study, the effect of the Kratky-Porod potential strength, the FENE potential strength and the concentration of polymers in the system are studied. Chemical and physical parameters are given in Table 2, which shows the values of the parameters which are varied, along with their default values, indicated in bold. The parameter values used in this study were selected to span a physically meaningful range which captures the key dynamics of polymer-particle flocculation. The non-dimensional FENE spring constants were chosen to represent moderately flexible extensible polymer chains that have been studied before in the context of single particle adsorption [27], enabling further investigation of conformational effects on floc structures during adsorption and bridging. While higher values are commonly used to constrain chains in previous studies, lower values are sufficient in the present context where long-range elasticity is desirable for surface interactions and entanglement dynamics. Similarly, the Lennard-Jones interaction strength was selected to explore weak to strong adsorption regimes in line with the ranges of other studies [38]. Collectively, these parameters allow controlled exploration of flocculation mechanisms while maintaining numerical stability and relevance to practical systems.

Results and discussion

The results presented in this study explore the effects of the Kratky-Porod bending rigidity, polymer concentration, and truncated and shifted Lennard-Jones potential strength on flocculation dynamics. We initially present analysis in two dimensions which provides valuable insights into the dynamics of polymer-particle interactions, allowing for a controlled and more fundamental investigation of the various parameters influencing floc formation. By examining these factors in two dimensions, a clear understanding of how polymer flexibility, concentration, and adsorption strength affect floc structure and dynamics can be established, which can then be extended to more complex three-dimensional systems. The foundational understanding in two dimensions is critical for predicting and interpreting behaviour in three-dimensional simulations, where it is important to ascertain and demonstrate whether the added spatial complexity influences flocculation outcomes. Furthermore, due to computational complexity and availability of resources the threedimensional simulations can only consider 10 Monte Carlo samples, though the quality of the statistics observed are improved due to the increased number of monomer beads and particles present in order to retain the same volume fraction of both phases.

Effect of Kratky-Porod bending rigidity

First we consider the effect of the Kratky-Porod bending rigidity strength on flocculation dynamics throughout the two-dimensional simulations. The strength, K_B^* , is varied between 1.0 and 5.0, corresponding to persistence lengths $l_p = \sigma$ and $l_p = 5\sigma$, respectively. It is expected that with $l_p = \sigma$ or $K_B^* = 1.0$ the stiffness will be negligible since the correlation in polymer chain vectors will be very low, whereas for $l_p = 5\sigma$ or $K_B^* = 5.0$, there will be a correlation across around one-sixth of the polymer chain, imparting strong rigidity to its eventual conformities.

Fig. 4 demonstrates a typical initial condition for a $K_B^* = 3.0$ simulation, along with a final instantaneous snapshot of the simulation at $t^* = 80$. By the end of this realisation, it is evident that significant flocculation has occurred, with particles separated into four discrete 'clusters', connected with intermediate polymers. At this intermediate bending rigidity strength, a variety of behaviour and polymer conformities adsorbed onto the particle surface is displayed. There is evidence of loops, trains and tails, with some polymers curling up and contracting, and others stretching out, increasing the likelihood of adsorption onto further particles. Although the polymer–polymer interactions are modelled using a purely repulsive WCA potential, the apparent aggregation of polymers observed in Fig. 4 arises due to adsorption onto shared particle surfaces. The attractive polymer-particle interactions, governed by the truncated and shifted Lennard-Jones potential (Eq. (7)), promote multiple polymers to bind to the same particle or to particles in close proximity. This results in spatial clustering of polymer chains around particles, which manifests as polymer aggregation in the flocculated structures. Importantly, this behaviour does not originate from direct polymer-polymer attraction, but is instead mediated by the

Table 1				
Simulation pa	rameters f	or	flocculation	study.

Parameter	Value
N_T – Number of timesteps per realisation	40,000
N_S – Sample frequency (timesteps)	500
$N_{MC, 2D}$ – Number of 2D Monte-Carlo realisations	50
$N_{MC, 3D}$ – Number of 3D Monte-Carlo realisations	10
δt^* – Simulation timestep	0.002

Table 2

Chemical and physical parameters for flocculation study. Parameters which are varied display their default values in bold (used when the effect of a different parameter is the subject of analysis).

Parameter	Value
$N_{POL, 2D}$ – Number of polymers in 2D realisation	10, 20, 30
$N_{POL, 3D}$ – Number of polymers in 3D realisation	200
$N_{PAR, 2D}$ – Number of particles in realisation	15
$N_{PAR, 3D}$ – Number of particles in realisation	150
N _{BPP} – Number of beads per polymer	32
R_0^* – Maximum bond length	1.6
D – Diffusion coefficient (monomer, particle)	5.0, 0.5
d_P^* – Particle diameter	10.0
K_{FENE}^* – FENE potential magnitude	5.0, 10.0, 15.0
K_B^* – Kratky-Porod bending rigidity	1.0, 3.0, 5.0
K_{LTT}^* – Lennard-Jones potential magnitude	0.1, 0.5, 1.0



Fig. 4. Initial condition at polymer and particle injection (left) and final flocculated state (right) for $K_B^* = 3.0$ flocculation study.



Fig. 5. Examples of typical polymer conformities for flocculation events. Effect of K_{BEND}^* is demonstrated with $K_{BEND}^* = 1.0$ (left), $K_{BEND}^* = 3.0$ (middle), $K_{BEND}^* = 5.0$ (right).

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adsorption dynamics and the spatial confinement near particles.

Three typical adsorption and polymer-particle conformation states are presented in Fig. 5 for the three values of K_B^* considered. At low bending rigidities, it is energetically favourable for polymers chains to curl up as they move due to Brownian motion. This causes ball-like clusters of polymers to form on the surface of the particles with radii just smaller than that of the particles themselves. In this sense, they act like further 'sticky' intermediate particles in the floc. As the bending rigidity strength is increased, ball-like structures still form, though trains, loops and tails are also viable and evident. These can attach to more than one particle, increasing the strength of the resulting floc, with particles tending to cluster closer together with the potential for one or two trains separating them. Finally, at the highest bending rigidity strength studied, $K_B^* = 5.0$, tails and trains are much more apparent, since any trains will energetically favour wrapping around the polymer, and any tails will stretch out beyond the particle. Though the cluster size will be larger, particles will have larger separation distances since the adsorption point of further particles on the polymer chain need not be close to the initial particle due to the extension of the tail, as evidenced in Fig. 5 (right).

To determine the temporal evolution of floc growth characteristics, various quantities were monitored. Henceforth we define particles to belong to the same cluster if an interconnected chain of particles and/or polymer beads can be traced between the two particles. Particles and polymers are defined as 'connected' if their positions satisfy the following expression:

$$|\mathbf{r}_i - \mathbf{r}_j| < \frac{d_i^*}{2} + \frac{d_j^*}{2} + 0.2,$$
 (12)

with r_i , r_j the position vectors of the two particles or monomer beads, and d_i^* , d_j^* their respective diameters. The additional term is included so that objects which are marginally not touching will still be included in the cluster. Cluster identification was performed using a depth-first search algorithm, whereby particles and polymer beads were assigned to the same cluster if a continuous connection could be traced between them. Two entities (monomer-monomer, monomer-particle, or particle-particle) were considered connected if their separation satisfied the above criterion (Eq. (12)).

Fig. 6 (left) shows the effect of modifying the bending rigidity on the temporal evolution of the maximum cluster size, C_{MAX} (i.e. the number of particle constituents) of all clusters present in one realisation. Over time, the results show immediate divergent behaviour, such that the systems with polymers with low bending rigidity, $K_B^* = 1.0$, tend to possess smaller clusters. This is likely due to the nonexistence of tails present upon full adsorption, since the polymers tend to curl up on themselves more frequently due to their greater flexibility. As the bending rigidity is increased, clusters with larger constituents can occur. Since tails are more likely to exist for the midrange bending rigidity strength, $K_B^* = 3.0$ (Mortimer and Fairweather, 2023), further adsorption from a single polymer is more likely, hence larger flocs are expected to form. The largest flocs were found in the $K_B^* = 5.0$ simulation, where longer tails lead to much larger structures spanning more of the domain. Fig. 6 (right) demonstrates the effect of bending rigidity on the mean cluster size, C_{MEAN} . On average, it is interesting to note that the midrange bending rigidity tends to produce the largest clusters, in number of constituents at least. This is likely because two effects are at play: firstly, the polymers are flexible enough to wrap around the particle, creating a tighter bond with the adsorption region; secondly, the slight rigidity means that tails are likely to occur, and so interaction with further particles is also likely.

The size of a cluster may also be characterised by its radius of gyration, which is calculated using the following expression:

$$R_{G}^{*2} = \frac{1}{C} \sum_{i=1}^{C} \left| \boldsymbol{r}_{P,i}^{*} - \boldsymbol{r}_{mean}^{*} \right|^{2},$$
(13)

with C the total number of particle constituents in a cluster. Fig. 7 (left) illustrates the effect of bending rigidity on the temporal



Fig. 6. Temporal evolution of maximum cluster size (left) and mean cluster size (right) for flocculated clusters of particles. Effect of K_B^* is demonstrated.

evolution of the mean radius of gyration of clusters. In agreement with Fig. 6, the most flexible polymers lead to smaller clusters on average, reaching values of around $R_G^* = 8.0$, which is consistent with a tightly packed three-particle cluster. Increasing the bending rigidity leads to larger clusters beyond $R_G^* = 10.0$, though the adjustment from $K_B^* = 3.0$ to $K_B^* = 5.0$ shows only a small difference, in line with the mean cluster sizes shown in Fig. 6. The combination of these two observations implies that the existence of polymer tails in both systems provides the ability for flocs to form with particles at larger separation distances.

To further determine the characteristics of the formed flocs, the two-dimensional fractal dimension was also determined. In order to do so, the area, A_c , of all particles enclosed in growing concentric circles of radius r_c around the centre of mass of the cluster was measured. Using the relation, $A_C = r_C^{D_F}$, the mean gradient was extracted from the relation $\log(A_C) = D_F \log(r_C)$ in order to calculate the two-dimensional fractal dimension, D_F . Fig. 7 (right) indicates similar behaviour for all bending rigidity strengths studied during the initial period ($t^* < 40$). Once flocculation begins to occur and additional particles begin to join pre-formed flocs, the polymers with $K_B^* = 3$ become slightly more one-dimensional. This is likely due to the formation of flocs with increased radii of gyration, which are more elongated in structure. The existence of tails in these flocs may also lead to more one-dimensionality. Interestingly, the lowest and highest bending rigidity strengths both provide similar eventual fractal dimensions, which are more two-dimensional in nature, despite creating the largest and smallest mean floc sizes. In both cases, clusters of particles are likely to contain more compact regions at the core of the cluster, since the lack of tails present in the $K_B^* = 1.0$ case leads to more dense clusters, and in the $K_B^* = 5.0$ case more particles can join the clusters along unadsorbed sections of the polymer chains.

Standard deviations for the measured observables (cluster sizes, radius of gyration, and fractal dimension) were found to be relatively consistent across the range of bending rigidity values studied. The standard deviations in cluster size and radius of gyration were typically close to 1.0, while the fractal dimension exhibited lower variability, with standard deviations approximately 0.04. This suggests that bending rigidity influences the mean structural properties of flocs, but does not induce substantial variability across simulations under fixed conditions.

The polymer conformation is also important in elucidating the adsorption and subsequent floc formation dynamics. The temporal evolution of mean polymer radius of gyration is presented in Fig. 8 (left), which exhibits very different behaviour depending on the flexibility of the polymer. For high rigidity polymers, $K_B^* = 5.0$, the radius of gyration increases, as the polymers stretch out adopting conformities similar to those shown in Fig. 5 (right). As the polymer becomes more flexible, the mean radius of gyration is reduced, with the lowest rigidity strength, $K_B^* = 1.0$, predicting polymer conformities with radii of gyration of just below $R_{P,G}^* = 3.0$, consistent with the ball-like structures observed in Fig. 5 (left). The temporal evolution of the mean polymer fractal dimension is presented in Fig. 8 (right). Again, the most one-dimensional structures (i.e. extended polymers) are observed for the most rigid polymers, with more flexible polymers increasing their fractal dimension over time, adopting more two-dimensional ball-like conformities.

Effect of polymer concentration

Many studies indicate that polymer concentration plays an important role in resultant flocculation, with low doses insufficient to instigate any meaningful clustering, and high doses causing effects such as steric stabilization wherein polymer coverage on particles is sufficiently high such that attachment sites are limited [19,42]. Here we vary the number of initially injected polymer chains, both decreasing and increasing it from the default setup between $N_{POL} = 10$ and $N_{POL} = 30$.

Fig. 9 demonstrates an example of an initial dispersed state (left) and an eventual flocculated state (right) for the highest polymer concentration considered. Various phenomena are evident in the final flocculated state. The leftmost particle in the right panel is fully adsorbed, meaning no other polymers are able to adsorb onto the surface, indicating steric stabilization. Furthermore, a large, aggregated floc in the top-right is observed, with some particles trapped inside the structure even though they have no monomers in contact with them. We also see that polymers are able to wrap up on one another, sometimes being trapped. This effect is likely more



Fig. 7. Temporal evolution of mean cluster radius of gyration (left) and mean fractal dimension (right) for flocculated clusters of particles. Effect of K_B^* is demonstrated.



Fig. 8. Temporal evolution of mean polymer radius of gyration (left) and fractal dimension (right). Effect of K_B^* is demonstrated.

pronounced in two dimensions due to the reduction in degrees of freedom.

Fig. 10 (left) demonstrates the effect of polymer concentration on the maximum number of particles present in flocculated clusters over time. As expected, the rate at which the largest clusters form is proportional to the number of polymers present in the system, with the rate reducing over time as more larger clusters are formed and fewer particles left in the system are able to further flocculate. The mean cluster size in Fig. 10 (right) follows a similar trend, with clusters containing more particles on average for an increased polymer concentration. Evidence of steric stabilization is not observed here, which may be due to the analysis technique adopted, since polymers in close proximity to other polymers may be counted as part of the same cluster. That said, at the polymer concentrations studied, and using the chosen $K_B^* = 3.0$ value, full adsorption of a polymer chain to the particle surface is rare, with large clusters more akin to those evidenced in Fig. 9 (right), in that smaller clusters may join to larger ones through intermediate polymer chains.

The mean cluster radius of gyration in Fig. 11 (left) follows a similar trend to those present in Fig. 10, such that increased polymer concentrations lead to larger clusters formed in terms of physical size. By the end of the simulation time studied here, the mean radius of gyration is shown to be highly sensitive to the polymer concentration, with doubling the concentration almost doubling the mean radial size of the resulting flocs. Fig. 11 (right) shows the effect of the polymer concentration on the temporal evolution of the mean fractal dimension of the clusters. The most two-dimensional clusters are observed for the lowest polymer concentration, $N_{POL} = 10$, which is likely due to the fact that these clusters tend to be smaller, and so emergent fractal structure is limited, with smaller clusters tending to be more compact. As the polymer concentration is increased, more complex structures can occur, which are less likely to be similar to packed spheres in morphology. Increased polymer concentration can also increase the spacing between particles which can lead to an increased total area of the cluster and more porosity, which reduces the fractal dimension of the floc. It is also of note that



Fig. 9. Initial condition at polymer and particle injection (left) and final flocculated state (right) for $N_{POL} = 30$ flocculation study.



Fig. 10. Temporal evolution of maximum cluster size (left) and mean cluster size (right) for flocculated clusters of particles. Effect of N_{POL} is demonstrated.



Fig. 11. Temporal evolution of mean cluster radius of gyration (left) and mean fractal dimension (right) for flocculated clusters of particles. Effect of K_8^* is demonstrated.

within the simulation time studied (t^{*} < 80), both the mean radius of gyration and the mean fractal dimension show signs of stabilization, indicating clusters reaching their maximum stable sizes. In contrast to bending rigidity, polymer concentration had a noticeable impact on the variability of observables. As the number of polymers increased, the standard deviations in cluster size and



Fig. 12. Temporal evolution of mean polymer radius of gyration (left) and fractal dimension (right). Effect of N_{POL} is demonstrated.

radius of gyration generally decreased, indicating improved consistency in the floc structure at higher polymer densities. This trend likely reflects the greater statistical averaging achieved in systems with more polymers contributing to cluster formation.

The temporal dynamics of the polymer chains are presented in Fig. 12. The mean radius of gyration demonstrates an initial period ($t^* < 20$) wherein the polymers begin to stretch out, an effect which is most evident for the lowest polymer concentration, likely due to more space being available and less frequent interactions with particles. After this period, interactions with and adsorption onto particles leads to a reduction in the radial size of the polymer chains, with the lowest polymer concentration leading to eventual larger chains after flocculation takes place. Interestingly, the most curled up polymers occur at $N_{POL} = 20$. This is likely due to the fact that the polymer concentration is just higher than that of the particle phase, so each polymer is able to interact with at least one particle, curling up around it with additional polymers able to form bridges between clusters. This is further evidenced by the $N_{POL} = 20$ simulation possessing the most one-dimensional mean fractal dimensions in Fig. 12 (right), with polymers wrapping around particles, or stretching out when not in the presence of particles, leading to elongated low fractal dimension conformities. Again, the simulation undergoes a period where polymers are not interacting with particles and are stretching out, reducing their fractal dimensions, before adsorption and flocculation occur, increasing once more.

Effect of truncated and shifted Lennard-Jones potential strength

Finally, the effect of the truncated and shifted Lennard-Jones potential on resulting flocculation dynamics is studied. An example of the effect of doubling the default value of the strength of the interaction to $K_{LT}^* = 1.0$ is demonstrated in Fig. 13.

In this case, the adsorption strength of polymer chains to particles is stronger since the potential well is deeper. From the instantaneous snapshot it is observed that most of the polymers in the system have undergone some kind of adsorption of at least one or two monomer beads, with some instances where the particle surface is almost entirely wrapped around in the upper-right of Fig. 13 (right). There is also much evidence of bridging, particularly in the upper-left of the image where a binary particle floc has joined another cluster as a tail has been attracted to another tertiary-particle floc.

The temporal evolution of maximum cluster size in Fig. 14 (left) presents some interesting findings, in that the largest clusters are found in the midrange $K_{LJT}^* = 0.5$ system, though it is clearly evident that more flocculation occurs as K_{LJT}^* is increased beyond $K_{LJT}^* = 0.1$. An explanation for this is likely that the stronger attraction between monomers and the particle surface leads to the collapsing of tails onto the surface over short timescales, with clusters formed due to stronger adsorption strengths being more compact and less likely to interact with other clusters, raising the mean cluster size. This is in line with the mean cluster size in Fig. 14 (right), which seems to stabilize for $K_{LJT}^* = 0.1$ at around $t^* = 60$. This is likely the point at which multiple smaller clusters have formed, contracted in on each other, with the chance of encountering other clusters reduced. At very low adsorption strengths, $K_{LJT}^* = 0.1$, the clusters formed are almost twice as low in constituent number as for $K_{LJT}^* = 0.5$. This is expected, since the chance a polymer chain will adsorb to the particle will be much reduced, and the thermal energy the chain possesses may be insufficiently small to remain in the potential well surrounding the particle for very long.

Considering the effect on the mean radius of gyration in Fig. 15 (left), similar observations are made. The largest (in radial size) clusters are found in the $K_{LTT}^* = 0.5$ system, where tails are less likely to collapse in upon the particle surface, and so it is energetically favourable for subsequent flocculation events to occur. Another important observation to be made is that initial flocculation actually occurs faster for the $K_{LTT}^* = 1.0$ system, since adsorption is more likely initially, and during this time tails may still be present in the



Fig. 13. Initial condition at polymer and particle injection (left) and final flocculated state (right) for $K_{LT}^* = 1.0$ flocculation study.



Fig. 14. Temporal evolution of maximum cluster size (left) and mean cluster size (right) for flocculated clusters of particles. Effect of K_{LJT}^* is demonstrated.

system. For $K_{LJT}^* = 0.1$, flocculation is slow, again attributable to the weakened adsorption strength leading to reduced clustering. This system also exhibits the most two-dimensional fractal dimension which, for low cluster numbers, may be more attributable to the fractal dimension of single particles ($D_F = 2.0$). Clusters are observed to be more one-dimensional for the two increased K_{LJT}^* values studied, with polymer chains separating particles in the clusters leading to a more porous structure for the $K_{LJT}^* = 1.0$ case and bridging for $K_{LJT}^* = 0.5$ both causing this quantity to fall. The variability of measured observables under different Lennard-Jones interaction strengths was similar in magnitude to that observed in the bending rigidity study. Standard deviations in cluster size and radius of gyration were again around 1.0 by the end of the simulations, while the fractal dimension showed lower variability, around 0.02. These results suggest that while increasing interaction strength strongly influences mean structural outcomes, the ensemble spread of these properties remains relatively narrow.

Investigation into the radius of gyration of the polymer chains in Fig. 16 (left) suggests similar initial behaviour, which is expected since polymers are unlikely to be near particles at injection, and this parameter does not affect the polymer dynamics. When flocculation begins to occur, the radius of gyration reduces faster for the polymers with increased K_{LJT}^* , as they collapse or curl up onto the surface of the particle, whereas for $K_{LJT}^* = 0.1$, interaction reduces this slightly, but at a lower rate and chains are likely to remain mobile around the particle surface for longer. The resultant fractal dimension in Fig. 16 (right) for all three values of K_{LJT}^* studied are very similar, indicating that upon adsorption, polymer chains eventually adopt similar conformities.

Three-dimensional simulations

It is important to determine the extent to which the above effects are confirmed by three-dimensional simulations, which more closely resembling polymeric systems encountered in the real world, as well as to ascertain any further emergent phenomena which arise due to adsorption on a spherical surface rather than a circumferential length. In order to address this, further simulations were



Fig. 15. Temporal evolution of mean cluster radius of gyration (left) and mean fractal dimension (right) for flocculated clusters of particles. Effect of K_{LTT}^* is demonstrated.



Fig. 16. Temporal evolution of mean polymer radius of gyration (left) and fractal dimension (right). Effect of K_{LT}^* is demonstrated.

conducted within a $100 \times 100 \times 100$ cubic cell in (x^* , y^* , z^*). Extrapolating the two-dimensional simulations to three dimensions, the equivalent volume is increased by a factor of 10, since the enclosing volume surrounding the particle spheres would be $d_p^* \times 100 \times 100 = 10 \times 100 \times 100$. Using this, the number of particles and polymers are further increased by a factor of 10, obtaining 150 particles and 200 polymer chains. Beyond these modifications, the same parameters used in the bending rigidity study are chosen. We choose to demonstrate this for only one parameter set due to the high computational cost associated with calculating contributions to interaction potentials between over 5000 constituents, though it is expected that any deviations from the two-dimensional simulations identified would similarly persist across alternate variations of key parameters.

Example snapshots of final particle configurations representing the effect of variations in K_B^* are presented in Fig. 17. In these plots, identical coloured particles indicate that they belong to the same cluster, which may be due to particle contact or polymer bridging. The left plot demonstrates the system with low bending rigidity, $K_B^* = 1$. In this, the clusters are relatively tightly bound, indicating low radii of gyration, whereas as the rigidity is increased, particles within cluster exhibit more and more separation, as bridging between particles due to more rigid tails hanging away from the particles is more energetically favourable. By $K_B^* = 5$, the particles themselves are rarely in contact, with bridging being the primary mechanism for floc formation.

The effect of the bending rigidity on the temporal evolution of the maximum and mean cluster sizes is presented in Fig. 18, indicating a strong dependence on K_R^* , as observed in the two-dimensional simulations. An interesting difference from the latter simulations is that the flocculation rates tend to be similar at the start of the simulation, before $t^* = 20$. The initial interaction with polymers due to the additional translational degree of freedom is shown to be the same regardless of bending rigidity. After this initial period, for the most flexible polymers, the maximum cluster size grows more slowly compared to that of the higher rigidity cases, indicating that flexibility hinders the aggregation process. Again, this is attributable to the flexibility allowing for greater conformational entropy, reducing the likelihood of stable cluster formation. Furthermore, since clusters are more compact in this case, the likelihood of two clusters interacting (which is the primary mechanism for the largest maximum cluster size growth rate) is reduced. As the rigidity increases, the maximum cluster size observed in the simulations also increases, similar in rate to what was observed in the two-dimensional simulations (Fig. 6). The higher rigidity reduces the conformational freedom of the polymers, leading to the promotion of tails and bridging, and increases the overall interaction range of the cluster for further flocculation. The mean cluster size follows a similar trend, though similar growth rates are again observed for $K_B^* = 3$ and $K_B^* = 5$. Comparing the clusters visually in Fig. 17, it seems that the midrange bending rigidity tends to have the propensity to form clusters which are more compact compared with those formed by the most rigid polymers, hence the driving flocculation mechanism is likely the existence of hanging tails, whereas the physical size and interparticle distance means that the $K_B^* = 5$ clusters can undergo flocculation easier due to their larger collision cross section.

The evolution of the mean cluster radius of gyration is presented in Fig. 19 (left), which initially demonstrates the same effects as in Fig. 18, wherein the growth rates are similar, independent of rigidity. Interestingly, after this initial period the growth rate begins to slow for a short time. This is likely due to the particles having interacted with their nearest neighbours, forming intermediate structures and increasing the volume between them and their surrounding clusters, which have also undergone this initial aggregation process. By $t^* = 25$, the radii of gyration of the clusters begins to increase again, with the more rigid polymers permitting the flocs to grow faster, as discussed earlier. For flexible polymers, not only do they contain fewer constituents (Fig. 18), but they are more compact in size, attributable to the conformation of the polymer chains onto the surface of the particles and the infrequency of tails forming. Both the more rigid polymer cases exhibit similar growth rates, in accordance with Fig. 18 (right) which tends to slow down by the end of the time simulated. The evolution of the fractal dimension of the clusters is demonstrated in Fig. 19 (right), which this time uses volume instead of area. Again, the fractal dimension remains similar as the initial flocs begin to grow, during the period in which available surface for adsorption is maximised and hence similar sized flocs and growth rates occur. As flocs begin to form, the clusters become more two-dimensional, with this process occurring more dominantly for the midrange bending rigidity strength ($K_B^* = 3$). This reduction in fractal dimensionality is analogous to the trends observed in Fig. 7 (right). Furthermore, the transformation over time



Fig. 17. Instantaneous three-dimensional cluster formations. Colours are unique and represent particles belonging to same cluster either due to particle-particle contact or connected via polymer bridges. Left: $K_B^* = 1$, middle: $K_B^* = 3$, right: $K_B^* = 5$. Polymers are omitted from the images for improved cluster clarity.



Fig. 18. Temporal evolution of maximum cluster size (left) and mean cluster size (right) for flocculated clusters of particles in three-dimensional simulations. Effect of K_n^* is demonstrated.



Fig. 19. Temporal evolution of mean cluster radius of gyration (left) and fractal dimension (right) in three-dimensional simulations. Effect of K_B^* is demonstrated.

from more three-dimensional clusters to two-dimensional morphologies further strengthens the motivation for use of two-dimensional simulations, since clusters which form tend to possess more two-dimensional features, with particles joined by polymer bridges tending to grow outward from a central point in a plane-like fashion, likely facilitated by the inherent rigidity between bonds in the structure

which makes bending inwards or collapsing in on itself energetically unfavourable, hence the structure is likely to exhibit flatter characteristics as it evolves and grows.

The observed trends in the maximum cluster size in the three-dimensional simulations can be directly compared to analogous behaviour observed in two-dimensional systems, where the role of bending rigidity was similarly influential in dictating cluster formation. In the two-dimensional systems, increasing K_B^* led to larger more disperse clusters. This behaviour is mirrored in the threedimensional results, where higher rigidity leads to a more rapid increase in the maximum and mean number of particles contained within a cluster. The comparison suggests that the principles governing cluster formation in two-dimensional systems extend to three dimensions, albeit with various dimensional-specific nuances that influence the rate and extent of clustering such as the available length (or surface area in three dimensions) relative to the circumference (or surface area of the monomer in three dimensions) differing.

Conclusions

This study used Langevin dynamic simulations to elucidate polymer-particle flocculation processes, as well as the influence of the Kratky-Porod bending rigidity strength, polymer concentration and the Lennard-Jones potential on the resulting structures. The work reveals intricate and distinctive behaviours, depending on the polymer properties and concentration, in the formation and evolution of particle flocs. The analysis of these simulations offers insights into the structural characteristics, size, and shape of the resulting flocs, providing understanding on how variations in polymer properties influence the flocculation process.

Modifying the value of the Kratky-Porod bending rigidity demonstrates a direct correlation between the polymer chain persistence length and the resulting flocculation behaviour. At lower K_{R}^{*} values, where polymer flexibility is high, the formation of compact, balllike clusters on particle surfaces is evident. As the bending rigidity increases, the presence of polymer tails and trains becomes more prominent, facilitating the adhesion of particles and the formation of larger and more elongated flocs. The increase in K_{R}^{*} not only impacts the sizes of the resulting clusters but also influences their internal structure, leading to variations in fractal dimensions and radial gyration. The temporal evolution of cluster sizes and characteristics further illustrates the impact of bending rigidity on the development of flocs. Lower K_B^* values tend to produce smaller and more compact clusters initially, while higher K_B^* values generate larger clusters with increased separation distances between particles due to extended tails. Notably, midrange bending rigidity values $(K_{R}^{*} = 3.0)$ exhibit a balance between flexibility and rigidity, resulting in the formation of clusters with larger constituent sizes and lower fractal dimensions compared to the extremes considered in the study. The polymer's conformation is also shown to play an important role in influencing the dynamics of flocculation, which is shown to be intricately related to the flexibility of the polymer. Variations in bending rigidity directly impact the polymers' motion, influencing their ability to adopt specific conformations upon interaction with particles. At lower bending rigidities ($K_B^* = 1.0$), highly flexible polymers tend to form compact, spherical structures due to frequent curling and coiling motions. These conformations facilitate the formation of small, tight clusters on particle surfaces, limiting the potential for extended interactions between particles and reducing the overall size of the resulting flocs. Contrastingly, at increased bending rigidities ($K_{R}^{*} = 5.0$), the polymer's reduced flexibility restricts excessive curling, promoting the formation of elongated tails and trains. These extended conformations provide more binding sites for particles, enabling the creation of larger, more spread-out flocs with increased separation distances between particles within the clusters.

The influence of polymer concentration was also explored, with the number of polymers ranging from $N_{POL} = 10$ to $N_{POL} = 30$, revealing a significant role in flocculation dynamics. Varying the concentration greatly affects the rate and size of cluster formation, with higher concentrations leading to larger clusters and increased rates of flocculation. The morphological characteristics of the resulting clusters, such as fractal dimensions and radial gyration, are demonstrated to vary with polymer concentration, exhibited as a transition from more compact, spherical structures to more complex and extended configurations as N_{POL} increases.

Finally, the effect of the truncated and shifted Lennard-Jones potential was investigated. Varying the monomer-particle interaction strength led to distinct polymer-particle interactions, significantly impacting cluster formation and characteristics. Higher K_{LJT}^* values lead to stronger adsorption between polymers and particles, resulting in larger clusters with rapid initial flocculation. In contrast, the lowest K_{LJT}^* values produce smaller clusters, indicating weaker polymer-particle interactions and slower flocculation rates. The temporal evolution of mean cluster sizes, radii of gyration, and fractal dimensions further explains these trends, highlighting how increased K_{LJT}^* values prompt more one-dimensional, tightly packed structures, while lower K_{LJT}^* values yield more porous, less compact formations. Interestingly, despite diverse cluster sizes and shapes, all K_{LJT}^* values lead to polymer behaviour which converges on similar fractal dimensions, suggesting a commonality in polymer conformations upon adsorption.

The effects of modification of the bending rigidity were also analysed from three-dimensional simulations. The results strongly validated the emergent dynamics observed in our two-dimensional simulations, affirming the robustness of our model across different spatial dimensions. By replicating the qualitative behaviours and structural trends seen in two dimensions, we demonstrated that the underlying mechanisms driving cluster formation and growth are consistent, regardless of dimensionality, with some caveats associated with differences in available adsorption surface area. Specifically, the progression from more compact aggregates at lower bending rigidity to more loosely bound ones at higher rigidity in three dimensions mirrors the patterns identified in two dimensions. This consistency across dimensions reinforces the accuracy and usefulness of two-dimensional simulations in capturing the essential dynamics of the system, thereby enhancing confidence in the general applicability of our findings to real-world scenarios where three-dimensional interactions are predominant. It is hence concluded that the findings in three dimensions not only reinforce the conclusions drawn from two-dimensional studies but also provide a broader context for understanding how bending rigidity modulates cluster dynamics in polymer systems, regardless of dimensionality.

Although the simulations were performed using non-dimensional units, the results are directly relevant to real-life systems through appropriate scaling of key parameters such as bead size, mass, and temperature, along with particle and fluid properties. By mapping the non-dimensional Brownian timescale, τ_B , to experimental values (for instance, assuming monomer bead diameters on the order of 10 *nm* and ambient thermal conditions), the simulated timescales correspond to nanoseconds, and the flocculation behaviours observed occur on time and length scales consistent with those in colloidal and environmental polymer-particle systems.

This study provides comprehensive insights into the multifaceted nature of flocculation dynamics, and the influence of various important polymer properties, including bending rigidity strength, concentration and the truncated and shifted Lennard-Jones potential. Understanding these relationships is crucial for designing and controlling flocculation processes in various industrial and environmental applications, where the formation and stability of particle aggregates are essential considerations. Future research should further investigate the nuanced interactions between polymer properties and flocculation dynamics by performing more computationally intensive simulations of three-dimensional systems offering enhanced predictive capabilities and practical applications in diverse fields.

While the present study uses Langevin dynamics to model the overdamped motion of polymers and particles, similar systems could also be explored using molecular dynamics (MD) simulations. MD offers greater resolution of inertial effects and atomic-scale interactions, particularly when solvent molecules are explicitly included. However, Langevin dynamics is more computationally efficient for the mesoscale, coarse-grained systems considered here, where thermal noise and friction dominate the dynamics. Both approaches can capture flocculation and aggregation behaviour when parameterised consistently, though Langevin dynamics is often more appropriate for modelling dynamics relevant to bulk-scale systems in viscous media. Finally, the effect of fluid shear has also been demonstrated to play an important role in flocculation (Lockwood et al., 2021), and as such the techniques considered here should be coupled to a fluid dynamic solver in order to determine the role that non-trivial flows have to play.

CRediT authorship contribution statement

L.F. Mortimer: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **M. Fairweather:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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