Modeling of Interparticle Forces Modified with Mobile Surfactant Chains

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Introduction

Nanoparticles with grafted polymer chains have been a popular object of study for some time, but only recently the research focus has shifted from the particles with fixed binding sites towards the ones with mobile anchors. When two such particles approach each other, the grafted chains can migrate from the near-contact area, redistributing non-uniformly on the particles' surfaces. **Here, we quantitatively explore how the interactions between spherical colloid particles are modified in the presence of mobile surfactants via Monte Carlo simulations. We study how the forces between the core particles depend on the anchor site distribution and chain length and compare our results to the system with fixed anchors.** The research would be useful in predicting the colloid/polymer mixture behaviour (e.g. self-assembly of patchy particles) and designing coatings, rubber and ceramic materials.

Simulation setup

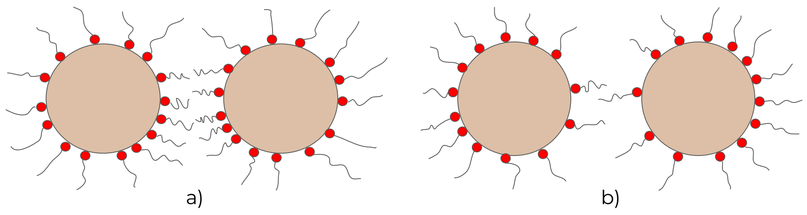

Figure 1: Diagram of the behaviour of polymer chains with (a) fixed and (b) mobile anchors.

- When particles approach each other, chains start to compress, adding to the repulsive interaction (Figure 1a)
- In the mobile chains case, some chains instead may drift away from the near-contact area due to the excluded volume interactions (Figure 1b)

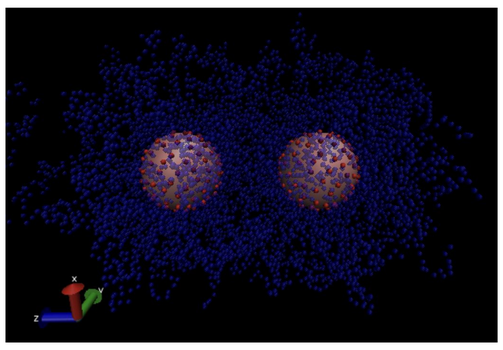

Figure 2: Snapshot of the simulated (fixed) system.

- Canonical ensemble Monte Carlo simulations
- Nanoparticle (NP) radius: 5σ, 10σ; number of beads in a chain: 15, 30, 60; chain density: 0.127, 0.191, 0.255, 0.382 chains/σ^2 (for NP of radius 5σ, it is equal to 40, 60, 80 and 120 grafted chains respectively).

Anchor Density Profile

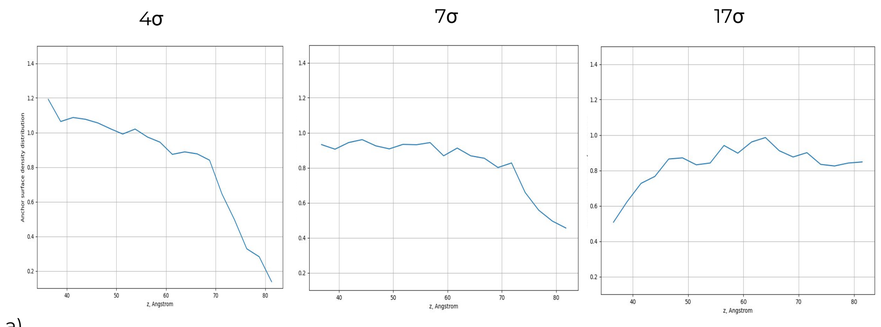

Figure 3: Anchor redistribution for different values of separation between nanoparticles: a) anchor density profile of left particle as a function of coordinate; b) supporting diagram.

Force Profiles

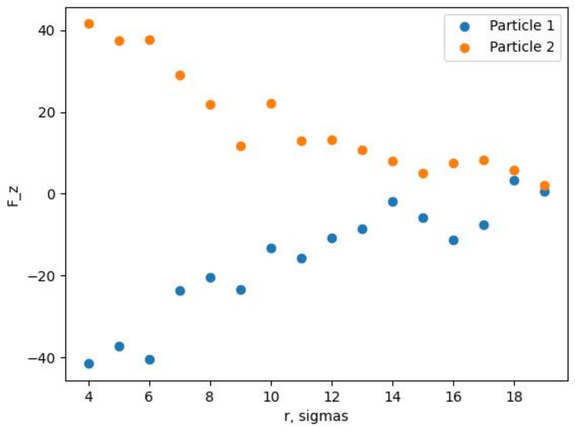

Figure 4: Forces calculated for each particle along the line of approach (mobile chains; polymer length 30 grafted at 0.255 chains/σ^2)

- **Polymer chains are represented as sequences of beads**
- **Lennard Jones potential for nonbonded interactions (bead-bead and bead-NP)**
- **Harmonic potential for bonds**

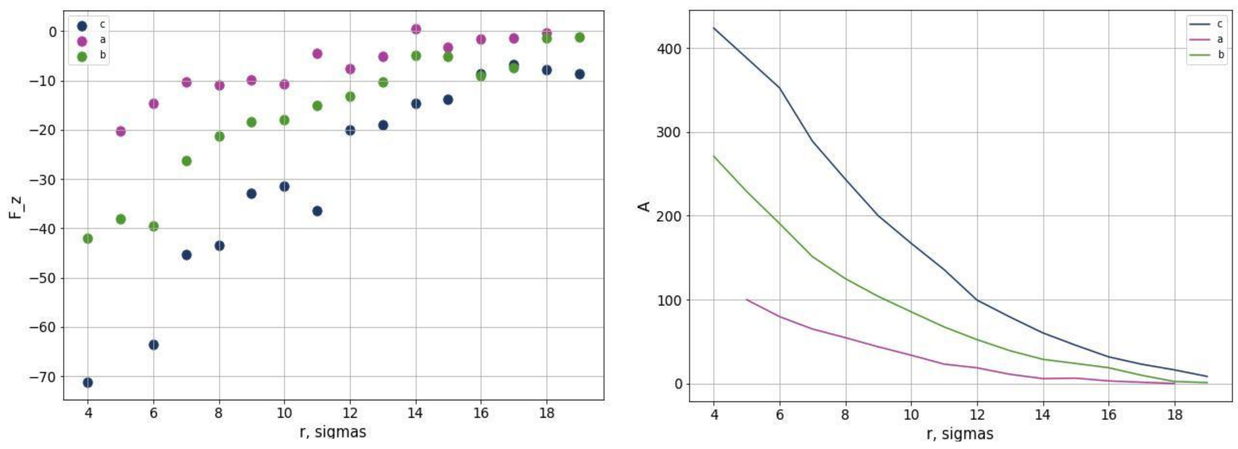

Figure 5: Average forces on a large particle (left) and Helmholtz free energy (right) for a mobile system with chains of length 30 beads and (average) grafting densities (a) 0.191 chains/σ^2, (b) 0.255 chains/σ^2 and (c) 0.382 chains/σ^2.

- **Polynomial dependence on the grafting density**
- **With increase in grafting density mobile chains have "less freedom" and force variance decreases**

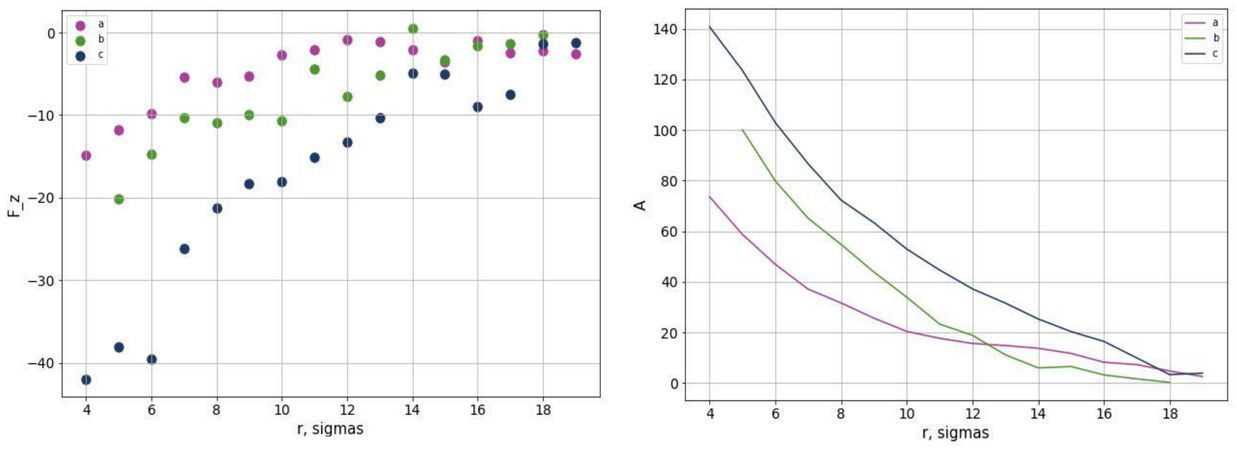

Figure 6: Average force on a large particle (left) and Helmholtz free energy (right) for a mobile system with (average) grafting density 0.191 chains/σ^2 and chain lengths (a) 15 beads, (b) 30 beads and (c) 60 beads.

- **Twofold increase in free energy for a fourfold increase in polymer length**
- **Chain growth increases conformational entropy and therefore force variance**

Figure 7: Average force and free energy for fixed and mobile systems with chains of length 30 (top) and 15 beads (bottom) grafted at density 0.382 chains/σ^2 as a function of separation distance between large particle surfaces.

- **In "fixed" systems chain are distributed uniformly across the particle surfaces**
- **Chain mobility has a significant effect on the free energy of the system at small separation distances due to chain drift from the near-contact area**

Conclusion

- **Due to chain drift from the near-contact area, free energy of systems with mobile anchors is significantly lower compared to the system with fixed anchors for small particle separation distances**
- **Dependence of interparticle interactions on grafting density and chain length is explored for systems with mobile anchors**
- **Research could be applied to nanoparticles with weak coordination bonds to the grafted chains, SAA with long heads and short tails and such**