



Controlling the Surface Properties of Polymer Coated Colloids via Targeted Nanoparticles

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Abstract

This poster outlines a novel method for controlling the surface properties of polymer coated colloids by utilizing targeted nanoparticles which attract to the monomers of certain polymers types. In our cases, two different polymer chains were attached to a single colloid at random, evenly distributed positions. The attraction of nanoparticles to one type of polymer caused the compression of those polymer chains, and subsequently the surface properties of the colloid became that of the other, non-compressed, polymer chains. We utilized Coarse Grained Molecular Dynamics (CGMD) simulations to demonstrate these properties of the colloid-polymer systems. This mechanism provides a proof of concept for a principle which could later be utilized in drug delivery systems and molecular self-assembly applications.

Background

Polymers have previously been used on the surface of colloids to exhibit different colloids based on the polymers actively represented on the surface¹⁻³. However, these polymers were compressed using mechanisms such as light⁴, temperature⁵, pH⁶, and ultra-sonic waves^{7,8}. Previously, we demonstrated that the exposure of nanoparticles to a colloid covered in polymer chains can collapse the chains if the nanoparticles are attractive to the polymer chains^{9,10}. Using this notion, and the previous studies of polymer-covered colloids, we decided to see if the nanoparticles could be used as an alternative compression mechanism.

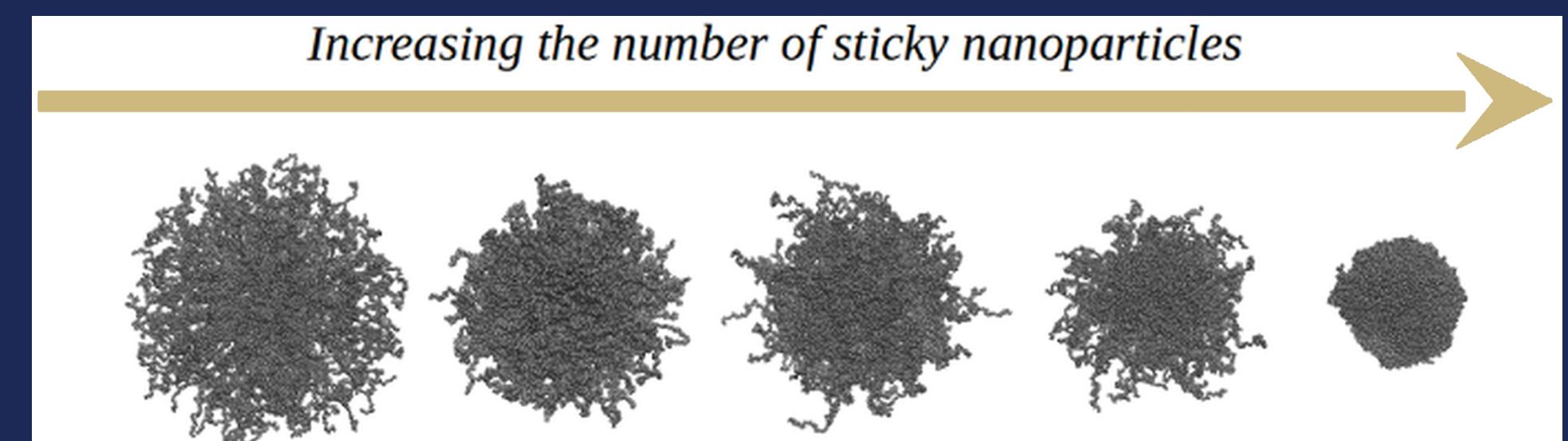


Figure 1: As the concentration of attractive (sticky) nanoparticles increases, the compression of the polymer chains on the colloid also increases. This colloid only has one type of polymer chain grafted to the surface in order to demonstrate the compression of the chains.

Theory

Using two different types of nanoparticles, it should be possible to collapse specific types of polymer chains based on which type of nanoparticle was exposed to the colloid-polymer system. All of this would be due to the interactions between one monomer in the polymer chain, the nanoparticle, and then another monomer in the polymer chain. This would cause the chain to kink in the local area around the nanoparticle and the two interacting monomers, and consequently "compress" a slight bit. With the introduction of many nanoparticles, this slight compression would add together until the whole chain decreases in overall size significantly. In order to confirm this as a proof of concept, LAMMPS¹¹ was used to conduct CGMD simulations of the system.

Simulation

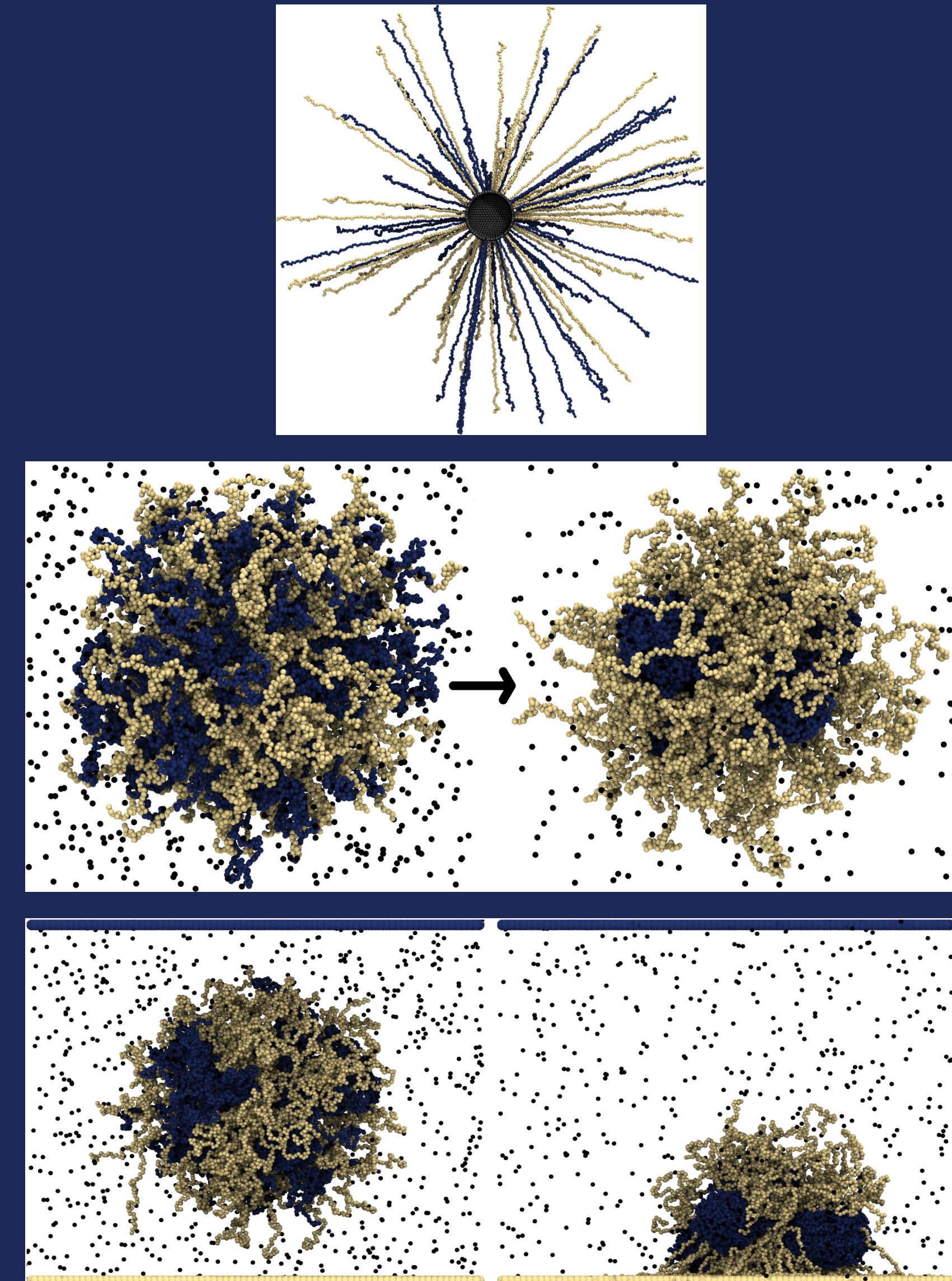


Figure 2 (top): A cross sectional view of a purple colloid with the polymers anchored to the surface. For the purpose of this demonstration, the colloid was cut in half and any polymers which would have extended past this half have also been omitted

Figure 3 (middle): The two types of polymer chains are colored in both blue and gold. The black nanoparticles are attracted to the blue polymer chains only. The arrow indicates the change over the simulation time, where the blue chains collapsed due to the interactions with the black nanoparticles. For this (and all other) simulations, the units were calculated using Lenard Jones units, with $\sigma = 1$ monomer/nanoparticle diameter and all masses = 1. The only attractive interactions are between nanoparticles and the blue monomers, which are defined using a Lenard Jones potential with $\epsilon = 1.0$. All other interactions are repulsive Van der Waals interactions with all diameters = 1σ .

Figure 4 (bottom): With the blue polymer chains compressed, the gold polymer chains dominate the surface properties, and the colloid exhibits their properties as though the blue chains were mostly not present on the surface. This leads to the colloid being attracted to the gold wall (all like-colored monomers attract in this case), and stick to it. If the gold polymer chains were compressed, the colloid would instead attach and stick to the blue wall.

Binding (cont.)

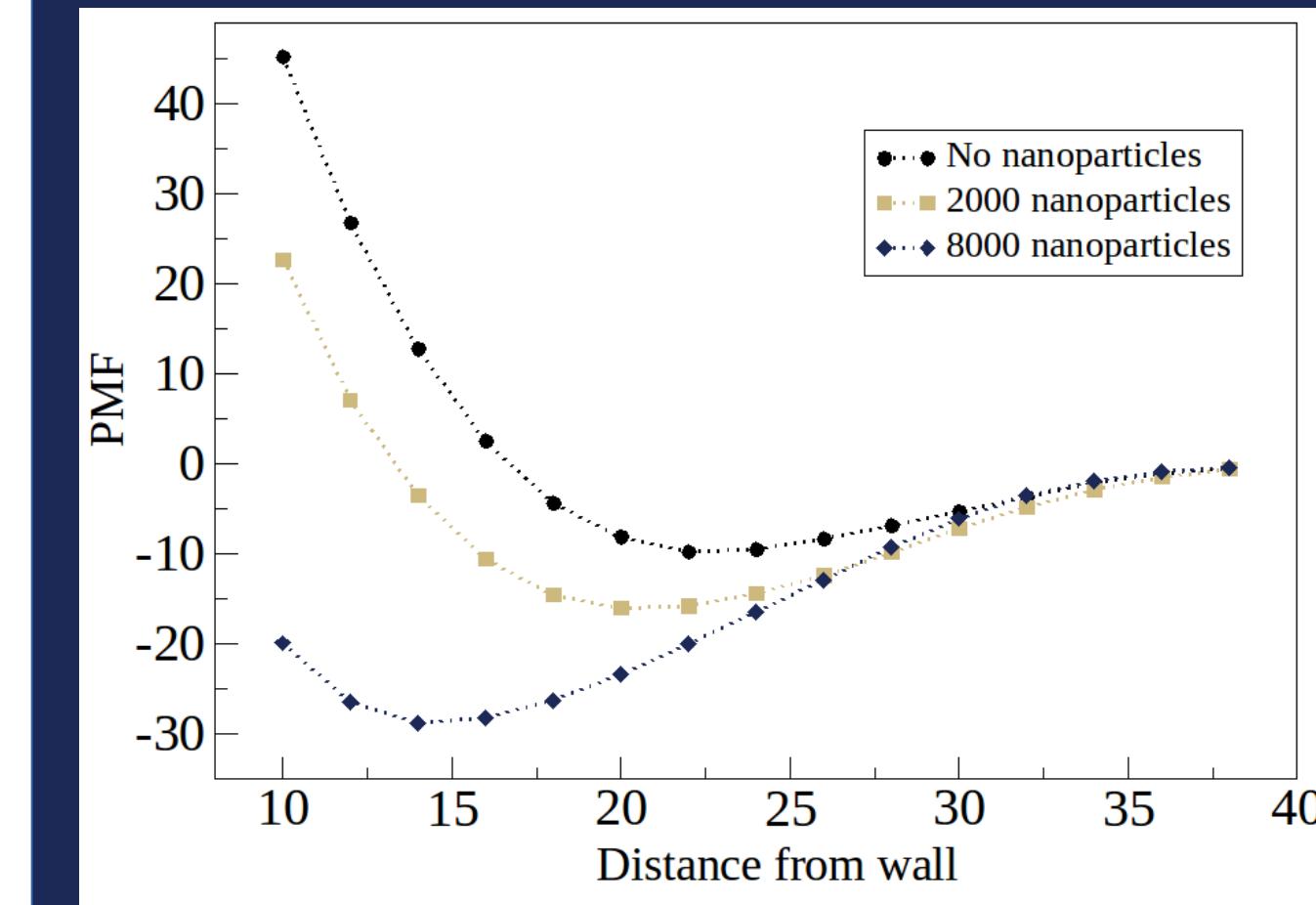


Figure 6: A graph of the potential of mean force (PMF) was found for different colloids at distances from the wall by fixing the colloid at the point and observing the displacement of a linear spring fixed to the colloid at that point. In these systems all of the polymer are statically bound to the colloid.

Greater compression of the non-attractive polymer chains cause the colloid to stick closer and stronger to the wall in the statically bound polymer systems. The energy well is very defined at the high concentrations of the nanoparticles, where the colloid would sit very closely to the wall (Figure 6, blue data set). The same effect was found when keeping nanoparticle counts constant, and increasing the potential of the LJ interaction between the polymers and wall.

Future Work

Since this is a proof of concept work, viable polymers and nanoparticles still need to be identified. The time dynamics of the dynamic bonds would also be interesting and useful to observe.

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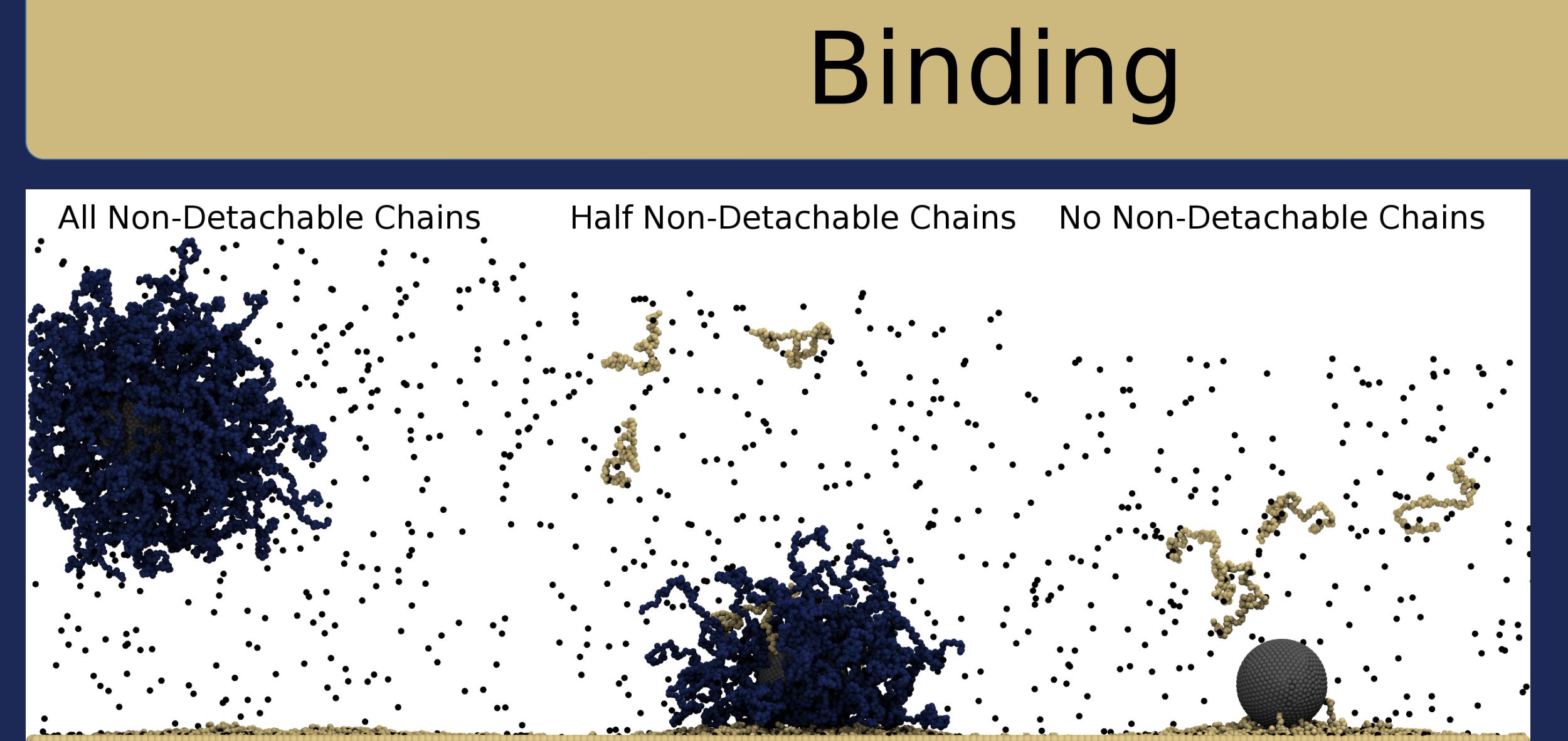


Figure 5: With the full number of non-detachable chains, the colloid is able to push itself away from the wall in this time frame, however as the number of non-detachable chains lowers, the colloid no longer detaches from the wall, and instead it still binds. The nanoparticles (black) in this system are attracted to the non-detachable chains (blue).

In these systems the polymer is not bound to the colloid by a static, permanent bond. Instead one type of polymer (gold) is bound to the colloid using the same type of LJ potential which was used to simulate the attractiveness of a nanoparticle to a polymer, allowing the gold polymers to detach from the colloid. The other type of polymer in the system (blue) was bound using the original static bonds. Since the gold polymers were attracted to the gold wall while the blue polymers were not, the colloid would detach from the wall over time if a large amount of blue polymers were present. If the blue polymers had too low of a density on the sphere surface, the colloid would stay attached to the wall (Figure 5). The reason for this mechanism seems to be as follows: first, the colloid is attracted to the wall like normal, in part because of the (in this case slight) compression of the blue polymers. As the colloid approaches the wall, the blue chains become compressed below their brush height as the gold chains pull the colloid closer to the wall. The force of the blue chains being below their brush begins to push back on the colloid, until the push back force is enough to break the bonds of most of the gold polymers with the colloid, in which case the colloid detaches from the wall. In the cases where less blue chains are present, the density is lower, meaning there is a lower brush height, meaning the push back force is too low to cause the bonds with the gold polymers to break (this is a similar effect to what is shown in Figure 6).

- [1] Mahmudi M, Simchi A, Imani M, Hafeli UO. Superparamagnetic Iron Oxide Nanoparticles with Rigid Cross-linked Polyethylene Glycol Fumarate Coating for Application in Imaging and Drug Delivery Superparamagnetic Iron Oxide Nanoparticles with Rigid Cross-linked Polyethylene Glycol Fumarate Coating fo. *J Phys Chem C*. 2009;113:8124-8131. doi:10.1021/jp900798r.
- [2] Cheng S, Carroll B, Bocharova V, Carrillo JM, Sumpter BG, Sokolov AP. Focus: Structure and dynamics of the interfacial layer in polymer nanocomposites with attractive interactions. *J Chem Phys*. 2017;146(20):203201. doi:10.1063/1.4978504.
- [3] Banga RJ, Krovi SA, Narayan SP, et al. Drug-Loaded Polymeric Spherical Nucleic Acids: Enhancing Colloidal Stability and Cellular Uptake of Polymeric Nanoparticles through DNA Surface-Functionalization. *Biomacromolecules*. 2017;18(2):483-489. doi:10.1021/acs.biomac.6b001563.
- [4] Discekici EH, Pester CW, Treat NJ, et al. Simple Benchtop Approach to Polymer Brush Nanostructures Using Visible-Light-Mediated Metal-Free Atom Transfer Radical Polymerization. *ACS Macro Lett*. 2016;5(2):258-262. doi:10.1021/acsmacrolett.6b00004.
- [5] Yameen B, Ali M, Neumann R, Ensinger W, Knoll W, Azzaroni O. Ionic Transport Through Single Solid-State Nanopores Controlled with Thermally Nanoactuated Macromolecular Gates. *Small*. 2009;5(11):1287-1291.
- [6] Iwata H, Hirata I, Ikeda Y. Atomic force microscopic analysis of a porous membrane with pH-sensitive molecular valves. *Macromolecules*. 1998;31(11):3671-3678.
- [7] Liu M, Chen X, Yang Z, Xu Z, Hong L, Ngai T. Tunable Pickering Emulsions with Environmentally Responsive Hairy Silica Nanoparticles. *ACS Appl Mater Interfaces*. 2016;8(47):32250-32258. doi:10.1021/acsami.6b11931.
- [8] Won S, Richards S-J, Walker M, Gibson MI. Externally controllable glycan presentation on nanoparticle surfaces to modulate lipid recognition. *Nanoscale Horiz*. 2017;2(2):106-109. doi:10.1039/C6NH00202A.
- [9] M.G. Opferman, R.D. Coalson, D. Jasnow, A. Zilman. Morphological control of grafted polymer films via attraction to small nanoparticle inclusions. *Phys. Rev. E*. 86, 031806:1-7 (2012).
- [10] M.G. Opferman, R.D. Coalson, D. Jasnow, A. Zilman. The Morphology of Polymer Brushes Infiltrated by Attractive Nanoinclusions of Various Sizes. *Langmuir*. 2009;25:8584-8591 (2013).
- [11] S.Plimpton, Fast Parallel Algorithms for Short-Range Molecular Dynamics. *J Comp Phys*. 117, 1-19 (1995).