Nanoparticle Composite Materials: Controlling Nanoparticle Organization and Nanoparticle Effects on Polymer-Composite Dynamics

by

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Abstract

One of the main challenges of the materials science is synthesizing materials with custom designed properties. One approach to address this challenge is creating composite materials. Combining nanoparticles (NP) and polymers is a common way to realize such composites. Due to the interesting properties of NP (eg. quantum confinement and high surface-to-volume ratio), nanoparticles have many desirable features. Polymers are one of the most ubiquitous materials are also highly controllable. In this thesis use molecular dynamics simulations as our primary tool to study polymer-nanoparticle composite materials.

In the first part of our research, we study the dynamics and stability of DNA-functionalized NP superlattices. Our findings can possibly lead to a general design rule for DNA-functionalized NP that consequently can lead to synthesize of NP lattices by design. Ordered structures of NP can show many interesting properties. For example, a cubic diamond (CD) lattice of NP can exhibit a complete optical bandgap. Due to its low volume fraction and the need for highly directional bonds, the CD lattice is one of the most challenging crystallographic symmetries to synthesize. Using DNA-functionalized NP and combined with the DNA origami self-assembly approach, we introduce a method to create NP that will form bonds with tetrahedral symmetry and synthesize the cubic diamond lattice. We show the importance of longer-ranged interactions between NPs for the relative stability of the two polymorphs of the diamond lattice: CD and hexagonal diamond (HD). We also study the different factors affecting the relative stability of CD lattice as a function of NP size and DNA stiffness values. We show that the rotational degrees of freedom dominate the change in free energy of lattices as a function of NP size. Furthermore, we study the equilibrium crystallite shape of the CD lattice. We find that, by changing the stiffness of DNA linkers, it is possible to tune the crystallite shape of CD lattice from a complete octahedron to a cube-truncated octahedron.

In the second part of our research, we study the effects of NP size on the dynamical and structural properties of interfacial polymers. Our findings can possibly leads to synthesize of materials with fundamentally different behavior using different relative size of the NP and the polymer chain. NPs can also be used to improve the properties of polymeric materials (eg. mechanical, electrical and optical); many of these properties can be tuned by NP size. We study
the effects of the NP size and the attractive interaction strength between the NP and polymers on the dynamics and structure of interfacial polymers. The dynamics changes results in changes of the glass transition temperature ($T_g$) of the composite. We find that the relative size of the NP compared to the polymer chain plays an important role in the dynamics and structural behavior of interfacial polymers; the relative size can fundamentally and dramatically change the composite behavior. The glass transition temperature for composite with smaller NP size relative to polymer chain increases linearly by increasing the interaction strength; in contrast, NPs with a size comparable or larger than that of the polymer chains from a layer with very slow dynamics (“bound layer”) around the NP. The bound layer “cloaks” the effects of NP on the rest of polymer, resulting in a saturation of $T_g$ as the interaction strength increases. The NP also changes the structure and alignment of interfacial polymer chains; these changes diminish as the NP size decreases.
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Chapter 1

Introduction

1.1 Nanoparticles

Nanoparticles (NPs) are objects that are 1-100 nm in size at least in one dimension. The occurrence of NPs is not restricted to man-made materials. There are many examples of NPs in nature: DNA, proteins and enzymes are examples of NPs in living cells, and they also can be found in volcanic ashes, ocean sprays [2,3]. Knowingly or unknowingly, humans have been using NPs for thousands of years. The Lycurgus cup (Fig. 1.1) is an example of use of NPs in the 4th century. The mixture of gold and silver NPs results in interesting optical effects: the cup has a green color for reflected light and a red color for the transmitted light. NPs are distinguished from their bulk counterpart, because of interesting and useful properties that occur as the size of material reaches nanometer scale. This difference in properties of NPs can be divided to two categories:

1. Finite size effects: the novel and new properties that comes from small length scales and spatial confinement. When the particle size becomes comparable to the electron wavelength in the material, new properties (quantum mechanical nature of materials at small length scale) arise. One of the most important properties of materials that changes as the particle size decreases is its optical properties. For example, in the case of semiconductor NPs, the band gap increases as the NP size decreases (quantum confinement); in the
case of metallic NPs the optical excitation is in the form of plasmon resonance (collective oscillation of electrons inside the NP) [4, 5].

2. Surface-to-volume ratio: By decreasing the NP size, the fraction of atoms on the surface of the NP increases. In the case of a spherical particles, the fraction of particles on the surface

\[ f = \frac{4\pi r^2}{4\pi r^3/3} = \frac{3}{r} \]  

(1.1)

has an inverse relation with the NP radius. This increase in the ratio can change the melting temperature and reactivity of NPs and also reduces the material necessary for applications, where the interface is important (eg. catalytic applications) [4, 5].

These changes in the NP properties are size and shape dependent, and these size and shape dependency can be used to tailor the properties of NPs. For example, the color of NPs changes as the size of NP changes. Figure 1.2 shows the color of spherical gold NPs as a function of size. The size and shape can also change the interfacial interactions of NPs with its surroundings.

1.1.1 Nanoparticle composite materials

Composite materials are made of a combination of two or more different materials that are held together without any chemical bond. If at least one of the materials used in the composite is in the nanometer scale, the resulting material is termed a NP-composite material. Many of inorganic NPs have desirable mechanical, optical, electrical and thermal properties. Organic NPs (eg. polymers) show desired flexibility (mechanical elasticity) and chemical functionality. To fully take advantage of the different NPs properties, creating NP composite is necessary. The polymer industry is one of the largest industries using NP-composites to improve the properties of materials. Food packaging industries, electronics, automotive and optical devices [6, 7] are some of the applications of NP-composite materials. In this thesis, we focus on polymer-nanocomposite (PNC) materials.

1.1.2 Ordered structure of NPs and self-assembly

Ensembles of NPs, specially ordered structures, due to their collective optical behavior and properties (eg. coupling of excitons and plasmons), offer a pathway to smaller optical devices.
Figure 1.1: The Lycurgus cup. a) The color of the cup is green, when the light is reflected from the surface of the cup. b) The color of the cup is red, when the light is transmitted through it. Credit: British Museum.
Thanks to recent developments in the nanostructure synthesis methods, it is now possible to create a range of ordered structures. Two major approaches to the synthesis of ordered structures are top-down and bottom-up:

1. Top-down approach: In this approach, the nanomaterial is synthesized by altering or reducing the size of a macro object [9].

2. Bottom-up approach: In this approach, individual components and molecules designed such that they are able to assemble to create a more complicated structure [9]. Self-assembly is the organization of different particles (components) to create an ordered or a functional structure.

Self-assembly can be categorized into two different categories, spontaneous and driven. The driven self-assembly is a process that dissipates energy and requires an external source of energy (eg. photoinduced self-assembly of the NPs) [10]. The spontaneous self-assembly is the process that does not require any additional energy. In this thesis, we only discuss spontaneous self-assembly processes; we use self-assembly to refer to spontaneous self-assembly [11, 12]. The driving force of self-assembly can be interactions between particles (components), or it can be due to an external field or combination of both. One way to create a self-assembled system is to design different component such that the desired structure is a local or global free energy minimum. The desired structure is formed by trapping the system in one the free energy minima (not necessarily the global minimum).
We use Gibbs free energy to quantify relative stability of different structures. Thus, it is important to understand individual components in Gibbs free energy and their effects on the structure of the self-assembled materials. The Gibbs free energy \( G = H - TS \) has two parts, enthalpic \( H \) and entropic \( TS \). By design of the particle’s shape and their interactions, the enthalpy and entropy of assembly can be manipulated to result in the desired structure. It is possible to create ordered structure just by manipulating one part of the free energy. Figure 1.3 shows an example of entropy-driven self-assembly of NPs in an ordered structure, the different shapes of NPs, and their corresponding structure. In this case, the excluded volume interaction is the only energetic interaction between particles [1].

One way to have a desired functional and self-assembled structure is creating specific interactions between different components. Specificity of the interactions results in a selective bonding between different components participating in the process. If the interactions are identical for each particle, and the entropic effects do not play a role in the assembly, the result can be a trivial close-packed structure. Thus, the specificity of interactions plays an important role in self-assembly processes. The interactions also should be directional to have control on relative position of particles.

We now provide examples of applications of the ordered structures of NPs. One of the most important applications of self-assembled structures of NPs is their optical properties. Controlling and modifying the light and matter interaction in nano-scale requires fine control of the structure of particles. In the previous section, we mentioned interesting optical properties of NPs. Gathering the NPs in an ordered or disordered ensemble shows new properties that are not seen in the individual NPs (e.g., localized surface plasmon resonance) [13]. These differences in optical properties arise from cooperative behavior of NPs, mainly through coupling of the plasmons and excitons in the materials. Self-assembly offers a simple and less expensive way to create ordered structures of NPs. The ordered structure of the NPs has many interesting and useful optical properties that do not occur in their atomic counterpart (e.g., photonic metamaterials) [14]. One of the most important classes of ensembles of NPs is photonic lattices. Photonic lattices show an optical bandgap, where a range of wavelength cannot propagate through materials. The bandgap opens the possibility to manipulate light in three dimensions. Some of the proposed and demonstrated applications are trapping light in a spatial area for specific frequencies, and create a loss-less waveguide to control the path of light in 3D [15].
Figure 1.3: Entropy driven packing of NPs with different shapes and their corresponding structures. There are four categories, that are indicated by different colors. For example, particles in the Blue and green categories lead to crystalline structures. The subcategories are distinguished by different shades. This figure is reproduced from reference 1.

These structures can also be used in metamaterials, plasmon-enhanced solar light harvesting, photocatalysis, chemical and biological sensors, logic gates, and waveguides below diffraction limit (This is possible due to coupling of photon with a surface plasmon of a NP with smaller size than the photon wavelength), and many more applications [16–23].

1.2 Ordering NPs using DNA

DNA usually known as the carrier of the genetic information is one of the most studied nanomaterials. The Watson-Crick pairing [24] offers a specific, predictable and programmable bonding. DNA satisfies the dimensional size of nanomaterial; the B-DNA double helix has the diameter of $d \approx 2\text{nm}$, the distance between bases is around 0.34 nm, and the helical pitch is around 3.4 nm or 10 base pairs. The persistence length of the dsDNA is about 50 nm, make it a good candidate to create rigid structures on the nm scale, while ssDNA (single stranded DNA) is still flexible
enough to explore the volume around it, leading to rapid kinetics of the hybridization process. The technology for synthesizing the DNA with the desired sequence is widely and commercially available. There are numerous resources available about their properties. Nature has given us many tools (e.g., enzymes) to manipulate their shape and properties. It can be easily modified and functionalized to attach to inorganic molecules. It also shows thermodynamic stability (carries genetic information successfully). In 1982 Seeman proposed the use of DNA to create ordered lattice structure, [25] leading to the field known as structural DNA nanotechnology. The ultimate goal of structural DNA nanotechnology is the rational design of materials and fine control on the position of the different component relative to each other. Two of successful methods of using DNA to create 2D or 3D structures, are DNA origami structures, and DNA-functionalized NP as building blocks. We briefly explain these two methods in the following sections.

1.2.1 DNA-functionalized NP

DNA can easily be functionalized to bond with inorganic NPs to create DNA-functionalized NP (Fig 1.4(a)) [26,27]. There are many different approaches to synthesize DNA-functionalized NP. Here, we mention a few of them. One approach is functionalizing one end of DNA with a thiolated molecule that can bond covalently with the NP. The thiolated molecule is shown as blue cone in Fig.1.4(a). Another approach to synthesize DNA-functionalized NP is functionalizing the DNA with biotin and functionalize NP by a specific protein (e.g., streptavidin). The strong affinity between biotin and streptavidin creates a stable DNA-functionalized NPs. Other methods include electrostatic adsorption of DNA on the surface of NP, or using van der Waals interactions [28]. DNA-functionalized NPs can be thought of as artificial atoms, where the NP act as the nucleus and DNA strands form bonds connecting these artificial atoms. Using two NPs functionalized with a complementary sequence, it is possible to connect two NPs together via the hybridization of complementary ssDNA to create a double helix (Fig. 1.4(b), (c) and (d)). This method, can be used to create ordered structures of NPs. Using DNA as a bond has many advantages relative to their atomic counterpart. In atomic structures, the bonding properties (e.g., bond-length, bond energy) are determined by the electronic structure and size of the atoms, that are fixed for each atom. Consequently, the DNA-functionalized particle properties are easily tunable. The bond-length can be tuned by changing NP size or DNA-linker length, the
bond energy and stiffness can be tuned by choosing the DNA sequence, and the lattice constant, can be modified either by DNA length or particle size. Figure 1.6 shows the three different axes that can be tuned using different designs of NPs. Besides the use of DNA-functionalized NPs in synthesizing ordered structures, they have numerous applications in the medical sciences (e.g., biosensors and drug delivery) [29,30]. For example, the drug molecules can be attached to DNA and when the NP reaches the target DNA, the target DNA create a dsDNA with the DNA attached to NP and it releases the drug [31]. Another application is biosensing, the NPs are functionalized with the complementary part of the target DNA when the target DNA is present it acts as a linker between the NPs, creating NP aggregates that result in a shift in the optical properties of NPs [32]. They can also be modified to bind to cancer cells and be used in imaging of cancer cells [33].

1.2.2 Challenges in DNA-functionalized NP self-assembly

Predicting and designing the outcome of the self-assembled structure just by the rational design of the individual parts is one of the most important goals of the assembly of DNA-functionalized NPs. There are many different crystal symmetries that are synthesized by using DNA-functionalized NPs (e.g., face-centered cubic, body-centered cubic) [37]. Since the particles should be in exact position relative to each other, and there are empty spaces between particles, lattices with low coordination number (6 or less) need highly directional bonds to prevent the aggregation of the particles in a close-packed structure. Specifically, one of these symmetries with very important optical properties (e.g., complete optical band-gap) is the cubic diamond (CD) lattice; but due to isotropic nature of functionalization, creating structures with low coordination numbers seems challenging. Creating NPs with highly directional bonds open a new way to create lattices with more control over their structures; especially, lattices with open structures. The other challenge in the self-assembly of NPs is the polymorphism. For example, particles with tetrahedral bond symmetry can be arranged in a CD or hexagonal diamond (HD) structures. To create the desired structure, control and manipulation of particles to favor one structure over the other are very important. Thus, it is useful to study the effects of NP design on the interactions between particles on polymorphism.
NP with directional bonds using DNA origami cages

It is possible to use multiple strands of DNA to create motifs [41], and then use these motifs to create different structures. Figure 1.5(a) shows examples of motifs and structures created using those motifs. It is also possible to use one long strand of DNA with multiple short strands of DNA as “staples” to bend and form the long strand of DNA into different structures. Figure 1.5(b) shows examples of different shapes made by the DNA origami method. Figure 1.5(a) and (c) show different 3D DNA structures in the form of polyhedrons (tetrahedron, dodecahedron). These nanostructures have sharp vertices that potentially can be used to create directional interactions. We mentioned that one of the challenges in self-assembly of DNA-functionalized NP is creating highly directional bonds. The DNA-origami structures and isotropically functionalized NP can be used to create an effective NP with highly directional bonds. This is achievable by creating DNA-origami cages with highly directional bonds that can host NPs or be used as a template for NP organization. Figure 1.5(c) shows a schematic example of cages synthesized experimentally to create NPs with effective directional bonds. At each vertex of DNA-origami cage, there are ssDNA that can be used as linker DNA to other NPs.
Figure 1.4: The schematic of DNA-functionalized NPs. (a) The schematic of DNA-functionalized NP. (b) Two NPs are connected by DNA bonds. The DNA sequence of the free end of DNA strands that are bonded to the blue and red NP are complementary. Thus they can hybridized and create a dimer of blue and red NP. (c) Nine DNA-functionalized NPs are bonded in BCC structure. (d) The hybridization of the two linker DNA. The complementary sequence of the DNA hybridize to create a double stranded of DNA. Figure a is reproduced from ref 34. Figures b and c are reproduced from ref 35. And figure d is reproduced from ref 36.
Figure 1.5: Examples of DNA origami methods to create different structures. (a) The creation of different motifs, using multiple strands of DNA and the corresponding structures made from motifs. (b) Examples of 2D structures created by DNA origami method. A long ssDNA is folded to a specific shape using smaller DNA strands as staples. (c) Different cages built from multiple ssDNA to create a larger and rigid structure to host the NPs. At each vertex of the cage there are DNA linkers; these linkers can bond with ssDNA on the DNA-functionalized NP. Figure (a) is reproduced from ref 38. Figure (b) is reproduced from ref 39. Figure (c) is reproduced from ref 40.
Using DNA-functionalized NPs, it is possible to synthesize lattice with different symmetries, particle sizes, and lattice constants.

**Figure 1.6:** Different ways to change the lattice structure. Using DNA-functionalized NPs, it is possible to synthesize lattice with different symmetries, particle sizes, and lattice constants.
1.3 Creating better polymeric materials using NPs

Up to this point, we have mainly focused on different ways that polymeric materials (DNA) can enhance and create new properties of NPs (self-assembly of NPs into ordered structure). In this section, we focus on different ways that NPs can be used to improve or enhance the polymeric materials. Many of pure polymeric materials have poor mechanical strength, thermal conductivity, electrical conductivity, or optical properties (e.g. optical resistivity) [42,43]. Some of them also have a large thermal expansion relative to metallic materials that make it challenging to use them in the same structure. To create polymeric materials with desirable properties, composite materials are needed. The polymeric material composites have successfully improved some of the properties of pure polymers [42,43]. Many of these improvements in polymer composites properties are either related to unique properties of NPs themselves, or it arises based on polymer-NP interfacial interactions [44]. Thus, using a composite component that maximizes the interfacial area is desirable. NPs due to their large surface-to-volume ratio and their unique optical, electrical and mechanical properties, are one of the best candidates to synthesize polymeric material composites.

1.3.1 Glass formation

In order to process the polymer-NP composite materials, they need to flow. Thus, one of the important properties of PNC materials is the glass transition temperature $T_g$. Glasses are materials that mechanically (e.g. stiffness, viscosity) behave similar to crystalline solids, but they lack the long range order. The glass transition can happen by rapid cooling of liquids to avoid crystallization, or when no stable crystalline state exists. If a liquid cool down sufficiently fast, the molecules do not have enough time to rearrange themselves to reach to the equilibrium structure and fall out of equilibrium as an amorphous structure. Many polymers, due to their structure, can be cooled without crystallization. This property of polymeric materials makes them a good candidate to study the glass transition problem. The glass transition temperature can be defined from thermodynamic and dynamic points of view. References 45–50, provide a set of sources of reviews of glass transition problem, and theories to explain the glass transition problem. In this thesis, we just focus on the dynamic definition of $T_g$. 
Dynamic definition of $T_g$

In this section we define the dynamic definition of $T_g$. As the liquid’s temperature decreases the dynamics of molecules become slower, and consequently the structural relaxation time (the time that the density-density correlation decays) of molecules increases. Considering relaxation time as an temperature activated process, the relaxation time can be described by Arrhenius behavior [51]

$$\tau = \tau_0 \exp(\Delta G/k_b T)$$

, where $\tau$ is the relaxation time, $\Delta G$ is activation energy (the free energy necessary for the system to change its configuration), $k_b$ is the Boltzmann constant, and $T$ is the temperature. Close to $T_g$ the activation energy increases dramatically, and consequently, structural relaxation time increases significantly. The reason for this increase in the activation energy is not clear, and it is one of the most important unanswered questioned in glass formation studies. The behavior of the relaxation time can be described using an empirical Vogel-Fulcher-Tamman (VFT)

$$\tau = \tau_0 e^{\frac{D T_0}{T - T_0}}$$

(1.2)

equation. Figure 1.7 shows the relaxation time as a function of inverse temperature. Conventionally $T_g$ is defined when the relaxation time reaches 100 seconds. Since the activation energy dramatically increases close to $T_g$ ($\tau(T_g) = 100s$), even for few degrees below it, the relaxation time becomes so large that experimentally is not practical to measure relaxation time.

1.3.2 Polymer structure

Many properties of polymeric materials depend on the shape and properties of individual polymer chains (eg. viscoelasticity) [52]; thus, understanding the properties of a single chain (eg. shape) can be the first step in understanding the behavior of polymeric materials as a whole. One of the simplest models for a polymer chain is a Gaussian chain. While this model is not a chemically specific model, it does provide successful coarse-grained models of the polymers. As the polymer becomes longer, the chemical details of monomers play a less important role in the general dynamical behavior of polymers in large length scales. Thus, the Gaussian chain model can provide insights into the behavior of polymer dynamics. A Gaussian chain is a chain where
the distance between every two monomers along the chain follows a Gaussian distribution

\[ G(r_1, r_2, n) = (2\pi nb^2/3)^{3/2} \exp\left(-\frac{3(r_2 - r_1)^2}{2nb^2}\right). \]  \hspace{1cm} (1.3)

where \( b \) is the segment’s length, \( r_1 \) and \( r_2 \) are the positions of two monomers, and \( n \) is the number of monomers between the two chosen monomers. This model can be used to describe the shape of the polymer chains at each instant of time. Using the Gaussian chain approximation, it can be shown [53] that the shape of a Gaussian chain is an ellipsoid with the semi-axis ratio of \( 1 : \frac{1}{\sqrt{6}} : \frac{1}{2\sqrt{6}} \), where the longest semi-axis is along the end-to-end distance of the chain. Thus, at each instant of time polymer chain is an anisotropic object.
1.3.3 Interfacial polymers effects on the dynamics of PNC materials

Since the interface between NPs and polymer matrix depends on the dispersion of NPs, the dispersion of NPs in the polymer matrix is an important factor contributing the properties PNC. The interaction strength and sign (attractive or repulsive) between polymers and NPs plays an important role in the dispersion of NPs in the polymer matrix. Thus, it is important to understand the dynamical properties of PNC as a function interaction strength between NP and polymers. The addition of NP to the polymer matrix can change its $T_g$. The value and sign of this change in the $T_g$ depends on the strength and sign of the interaction. Because most of the inorganic NPs are hydrophilic, and polymers usually are hydrophobic, the NPs usually tend to phase separate from the polymer matrix. One way to create a well dispersed PNC is creating an attractive interaction between the NPs and polymer matrix. This attractive interaction leads to increase in the glass transition temperature. Many researchers assumed that the increase of interaction strength should increase the glass transition temperature of PNC, but the experimental data often show no change in $T_g$ [54–56]. Experimental results have also shown that the glass transition temperature ($T_g$) of PNC is very close to the pure polymer $T_g$ [54–56]. On the other hand, the MD simulations of PNC show a significant increase in glass transition
temperature as the interaction strength increases [57–64]. The answer to this mystery lies in the interfacial polymer chains. The attractive interaction between the NPs and polymers leads to the slowdown of the polymer dynamics near the interface (“bound layer”). This layer of monomers around the NP decouple the effect of NP on the polymer matrix; this results to the reduction of the expected amount of increase in $T_g$ from MD simulation studies. The bound layer plays an important role in the shift in $T_g$. Although the NP size can change the properties of nanocomposites, there is little understanding about theoretical reasons behind this change in behavior of bound layer as a function of NP size.

1.4 Contributions of this Thesis

Our research focuses on the study of PNC materials. We use molecular simulation as our primary tool, to study the behavior of PNCs. Our research can be divided into two main parts. The first part is the study of DNA self-assembled NPs crystal structures, specifically cubic diamond structure chapter 2. The second part of our studies is focused on NP size effects on the PNC dynamics and glass formation.

1.4.1 Self-assembly of DNA-functionalized NP

In the previous sections, we mentioned that, due to use isotropically functionalized NPs, one of the challenges in the self-assembly of NPs is creating open structures, which requires highly directional bonds. We also mentioned CD lattices have many interesting optical properties. By combining the DNA functionalized NP strategy with the DNA origami approach, the possible lattice structures have been expanded to include the cubic diamond lattice [65].

Using DNA-origami cages, it is possible to create NPs with effective directional bonds (Fig 1.9) with tetrahedral symmetry. In chapter 3, we study CD lattices generated using these DNA-origami cages. We first explain why in experiment CD lattices are more stable than its competitive structure hexagonal diamond (HD). We see that just considering the short range interaction (first neighbor) is not enough, to differentiate the HD and CD. The coulombic interaction between negatively charged DNA-origami cages plays an important role in differentiating the CD and HD free energies and thus their relative stability. Our finding, the notion of im-
Chapter 1 - Introduction

Figure 1.9: The schematic of effective NP with tetrahedral symmetry directional bonds. The red ssDNA linkers at each vertex act as highly directional interactions. The green strands linkers keep the NP (functionalized with complementary sequence of green ssDNA) inside the tetrahedral cage. This figure is reproduced from ref 65.

The importance of second neighbor Coulombic interaction, can be useful to design DNA-origami cages that preferably choose the desired symmetries.

Using DNA-functionalized NP lattices in functional devices requires a robust and stable lattice. Moreover the NP size plays an important role to determining the properties of CD lattices. We use molecular simulations to investigate how NP size and DNA stiffness affect the structure, stability, and crystallite shape of NP superlattices. We see that the entropy is the main component changing the relative stability of diamond lattices as a function of NP size and DNA stiffness. We find that increasing NP size or DNA stiffness increases free energy, and thus decreases the relative stability of lattices. On the other hand, increasing DNA stiffness results
in a more precisely defined lattice structure. Thus, there is a trade off between structure and stability of the lattice. To study the factors affecting the entropy of the lattice, we consider translational and rotational degree of freedoms. We see that the translational and rotational degree of freedom have opposite effects on the stability as the NP size increases. This information can be useful to establish rules for rational design of NPs that leads to desired structures.

In the previous part of the introduction we mentioned that these functionalized NPs can be considered as an artificial atoms. By choosing different DNA linker sequences, the stiffness of these DNA strands can be changed, thus it is possible to tune the bond stiffness of these artificial atoms. We study the effect of DNA stiffness on the crystallite shape of the CD lattice. We use Wulff construction method to predict the equilibrium crystallite shape of the cubic diamond.

### 1.4.2 Effects of size on polymer-NP composites interfacial polymer

In chapter 3, we study the dynamics and glass formation of the polymer-NP composites as a function of NP size. We specially, focus on the effect of NP size on the interfacial polymers dynamics and structure. The modification of interfacial polymer behavior is one of the primary sources of property modifications of polymer-nanoparticle composites. The general expectation is that very small NPs (smaller than polymer chains), plastisize the polymer composite and reduce the desired changes, (eg. $T_g$ and reinforcement) of the composites [66]. Using molecular simulations, we explore the degree to which interfacial polymer structure and dynamics, and thus the material properties, depend on the scale of the NP size. We show that the changes to the interfacial polymer diminish as we decrease the NP size. In particular, the changes in the interfacial relaxation time diminished for smaller NPs. This diminishing of the bound layer leads to a significant increase in $T_g$ of the materials. Thus the smaller NP has stronger effect on the polymeric materials and potentially can be a better candidate to modify the PNC properties.
Chapter 2

Stability of Cubic Diamond Lattices

2.1 Introduction

In the introduction (chapter 1) we discussed applications of NP-based materials, such as optical or electronic materials, biosensing, drug delivery and others [67–70]. Many of these properties can be tuned by change of particle size (e.g., optical properties) and DNA stiffness. In this chapter, we study the stability of lattices synthesized with NPs with tetrahedral interaction symmetry.

One of the challenges to control self-assembly of NPs is controlling the directionality of interactions between NPs. Since the NPs are usually functionalized uniformly, their interactions are correspondingly isotropic. As a result, the lattices realized correspond to close-packed structures where NP have 8 or more nearest neighbors. Creating ordered structures for open lattices (coordination number less than 6) has proved more challenging. In traditional atomic and molecular systems, such low coordination lattices require directional interactions. In particular, one important symmetry that proved elusive for NP assembly strategies is the diamond lattice. To overcome this challenge, we combined the DNA origami method to create a tetrahedral cage that can host a NP inside them (NP with directional bond) Fig 1.9 with spherically DNA-functionalized NP to create DNA-functionalized NPs with directional interactions that are able to self-assemble into cubic diamond (CD) symmetry [65], opening the possibility to realize
Chapter 2 - Stability of Cubic Diamond Lattices

these novel materials. The methods to create NPs with customizable directional interactions, is an area of ongoing research [71, 72]. CD and hexagonal diamond (HD) both have bonds with tetrahedral symmetry; the experimental results show that the CD structure is more favorable, rather than HD or combination of CD and HD. We first find why the CD experimentally occurs. We find that the weaker electrostatic repulsion of the tetrahedral cages in the CD structure in compare to HD leads to a more stable lattice that is observed experimentally. We find that, since these lattices are grown in a salt solution, the effective electrostatic interaction between tetrahedral cages follows the Debye-Huckel theory eq. 2.13. The truncated vertices of these cages have the most contribution to their repulsion. In section 2.4, we will explain why the truncated nature of the tetrahedral cages is important.

Since the CD lattice is experimentally synthesized, we focus on the CD lattice. In order to better control the properties of diamond structured NP lattices, we need an improved understanding of the factors that control lattice stability and crystallite shape. NP size can potentially alter both the lattice stability as well as the optical properties of lattices, both due to changes in the NP optical properties and changes of the lattice spacing. We study the relative stability of CD superlattices as a function of NP size and DNA stiffness using molecular dynamics (MD) simulations. We evaluate the relative stability of lattices based on their free energy. We find that entropic effects dominate the changes of free energy. We break the entropic effects into the contributions from the translational and rotational degrees of freedom. We find that the translational entropy stabilizes the lattice as the NP size increases; in contrast the rotational degrees of freedom have a destabilizing effect as the NP size increases. The contributions to the entropy from the rotational orientation outweigh those of the translational degrees of freedom. We show that we can enhance the lattice stability (lower free energy) by increasing the flexibility of the DNA strands, which in turn increases the contribution from the rotational entropy. On the other hand, increasing the flexibility results in a less well-defined structure. Thus, from a design perspective, there is a balance between enhancing stability and optimizing the desired order. The important role played by entropy in diamond packings has been recognized previously. [73,74]. For example, Ref. 73 showed that the degree of truncation of tetrahedra, similar to the functionalized NP we study, is central to the packing (entropic effects) that determine the stability of the CD lattices.

We also evaluate the equilibrium shape of the cubic diamond crystallites using the Wulff
construction [75]. The Wulff construction predicts crystallite shape based on the surface free energy. Since the experimental method for making NP lattices is a quasi-static process, the equilibrium shape should correspond to the crystallite shape in experiments [76, 77]. In most cases, the simulation results for surface energy can be anticipated from a simple approximation for the number of broken bonds along any crystal face. However, we find that when the DNA are flexible enough to allow reorientation at the surface, alternate bonds form that reduce the surface energy, and the resulting predicted crystallite shape is different from that expected for atomic systems with diamond structure (eg. diamond, Si) [78–80].

2.2 Modeling

2.2.1 Tetrahedral cage model (for MD simulation)

We first describe how we mimic the tetrahedral DNA origami “cages” that were experimentally used to create tetra-functional NP; see Fig. 2.1(a) for a schematic of the experimental system. Experimentally, the edges of the tetrahedral cage are constructed from “bundles” of 10 double-stranded (ds) DNA that are linked together to form relatively rigid “beams” [65]; the cross-section of these bundled beams is roughly rectangular. Since the individual DNA strands play no functional role in the edges other than structural integrity, in our coarse-grained model we simplify by representing each edge of the tetrahedral cage by 7 beads with a diameter comparable to that of the dsDNA bundles (Fig. 2.1(b)); specifically, the diameter of the particles corresponds to average of the side of a bundle cross-section. Each tetrahedral site is described by a Weeks-Chandler-Andersen (WCA) potential

\[
V_{WCA} = \begin{cases} 
V_{LJ}(r) - V_L J 2^{1\over 6}\sigma & r < 2^{1\over 6}\sigma \\
0 & r > 2^{1\over 6}\sigma 
\end{cases} \tag{2.1}
\]

where, \( \sigma = 0.65\text{nm} \),

\[
V_{LJ} = 4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right) \tag{2.2}
\]

is Lennard-Jones (LJ) potential, and \( r = 2^{1\over 6}\sigma \) is the minimum of LJ potential. The diameter of particles along the edge is \( 9.9\sigma = 6.44\text{nm} \); this value is chosen to mimic the thickness of the tetrahedral cage in the experiment. Particles along the edge are linked by a finitely extensible...
nonlinear elastic (FENE) potential

\[ V_{\text{FENE}} = -\frac{kR_0^2}{2} \ln \left[ 1 - \left( \frac{r - \Delta}{R_0} \right)^2 \right] + 4\epsilon \left[ \left( \frac{\sigma}{r - \Delta} \right)^{12} - \left( \frac{\sigma}{r - \Delta} \right)^6 \right] + \epsilon. \] (2.3)

For the standard FENE potential, \( \Delta = 0 \), \( \sigma = 1 \), and \( R_0 \) is the maximum bond length. Here, \( \Delta \) is a shift in the equilibrium bond length and \( R_0 + \Delta \) is the maximum bond length. See table 2.1 for parameters.

To make the edges more rigid, next-nearest neighbor edge particles are also bonded via a FENE potential with a bond length chosen to prefer linearity among triplets. As Fig. 2.1(b) shows, the vertices of the tetrahedral cage are truncated, and consist of three particles, tethered to a fourth bead (blue bonds in Fig 2.1b) that represents the first nucleotide of the DNA linker connected to the tetrahedron. The three vertex beads are linked both to each other (red bonds in Fig 2.1b), and to edge beads of the cage. Finally, to improve the rigidity of the cage structure, we include a bond between the first bead of the DNA at the vertex and the particle at the center of tetrahedron (yellow bonds in Fig. 2.1b). The details of these interactions and their coefficients are provided in Table 2.1.

Table 2.1: The bond potential parameters for the tetrahedral cage and NP force sites. For the NP bonds \( \Delta = d/2 - 0.96 \), where \( d \) is NP diameter and 0.96 is the minimum of FENE potential when \( \Delta = 0 \), which insures that the minimum of bond potential is at \( d/2 \). The distance between vertices of dodecahedron is \( l = d/2.8 \), where \( d \) is the dodecahedron circumscribed sphere’s diameter.

<table>
<thead>
<tr>
<th>Particle type</th>
<th>Bond</th>
<th>( k )</th>
<th>( R_0 )</th>
<th>( \epsilon )</th>
<th>( \Delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahedral cage</td>
<td>Edge beads, first neighbor</td>
<td>240</td>
<td>1.5</td>
<td>8</td>
<td>6.36</td>
</tr>
<tr>
<td></td>
<td>Edge beads, second neighbor</td>
<td>240</td>
<td>1.5</td>
<td>8</td>
<td>13.67</td>
</tr>
<tr>
<td></td>
<td>Vertex to center</td>
<td>240</td>
<td>1.5</td>
<td>8</td>
<td>36.52</td>
</tr>
<tr>
<td></td>
<td>Vertex to edge</td>
<td>30</td>
<td>1.5</td>
<td>1</td>
<td>15.08</td>
</tr>
<tr>
<td></td>
<td>Edge to edge</td>
<td>30</td>
<td>1.5</td>
<td>1</td>
<td>9.15</td>
</tr>
<tr>
<td>Nanoparticle</td>
<td>Center to vertex</td>
<td>30</td>
<td>1.5</td>
<td>1</td>
<td>( d^2 ) - 0.96</td>
</tr>
<tr>
<td></td>
<td>Vertex to vertex</td>
<td>30</td>
<td>1.5</td>
<td>1</td>
<td>( l - 0.96 )</td>
</tr>
</tbody>
</table>

In order to have a tetrahedral edge that mimics the rod like nature of the tetrahedral edges in the experiment, we choose the bond length \( (7.32\sigma = 4.76) \) between edge monomers somewhat smaller than the size of the excluded volume interactions \( (9.9\sigma = 6.44nm) \) of these monoers, so that their exclusion zones overlap. For nearest neighbor edge monomers, there are no non-bonded
interactions to avoid large values of the pair interactions due to this overlap. At each vertex there is a ssDNA attached to the tetrahedron. The DNA model is described in a subsequent section. This DNA has two distinct regions: a spacer region of 7 nucleotides that has no complement, and a “sticky” region of 8 nucleotides that are complementary to the ssDNA attached to NP. The DNA sequence is chosen in such a way that it can only connect with the DNA of NPs, and cannot bond to the DNA of the other tetrahedra. To ensure that DNA strands are roughly normal to the vertex of the tetrahedron, we use an angle bond potential

\[ V_{\text{angle}} = K (1 + \cos(\theta)) \]  

(2.4)

where \( \theta \) is the angle made between the DNA site at the vertex of the tetrahedron with the center of tetrahedron and the next DNA site. The strength of the stiffness, \( K \), varies between 0.5 to 2.0 for different systems similar to the DNA stiffness.

### 2.2.2 Tetrahedral cage model (for ground state energy calculations)

To estimate the difference in the ground state energy of CD and HD lattices, we use a slightly different model for the tetrahedral cages. The difference in the ground state energy between CD and HD, comes from difference in relative orientation of tetrahedral cages. Since the electrostatic interaction between tetrahedral cages follows Debye-Huckel theory, the vertices have the most important contribution to the electrostatic repulsion of the tetrahedral cages. The repulsive interaction is introduced between the centers of monomers on the edges of the tetrahedral cage.

We use 20 beads per edge. Thus, there are monomers at the vertex of each tetrahedral cage that results in more accurate calculations.

Tetrahedra are modeled by a collection of 20 sites along each edge of the tetrahedron (Fig. 2.2). There are FENE and angle bonds between these particles to ensure a rigid structure. The diameter of each particle is \( \sigma \), the mean diameter of the DNA bundles that make up the edges of the experimental tetrahedral linkers. At each vertex of tetrahedron there is a DNA strand with 7 spacer bases, and 8 bases encoded to link to DNA of the NP. At the center of each tetrahedron is a spherical NP of diameter 14.5 nm. The resulting total number of force sites for each tetrahedral unit is 237.
Figure 2.1: Schematics of the tetrahedral cage, the NP, and the lattice (a) Schematic of tetrahedral cage bond structure used in the MD simulation. The red lines show ssDNA linkers, each dsDNA in the tetrahedral edge is represented by gray cylinder. The green lines are ssDNA that connect with NPs functionalized with the complementary sequence, and consequently hold the NP in the middle of the tetrahedral cage. The figure also shows the cross-section of edge (relative position of 10 dsDNA bundle). (b) Schematic of the tetrahedral cage used in experiment. The spheres show the particle positions and the lines show the bonds between particles. Different colors show different bonds explained in the main text. The sphere size are not representative of the actual size of particles. (c) The schematic of NP used in the MD simulation. Small spheres show the position of the vertices, the large sphere shows the central particles and the lines show the bonds between vertices. (d) The screen-shot of the lattice box in the simulation.
2.2.3 Nanoparticle model

To mimic the polyhedral shape of a typical nanoparticle, we model a NP by a collection of 20 force sites located at the vertices of a dodecahedron. Each dodecahedral site is also described by the WCA potential used for tetrahedral sites, but with diameter $\sigma = 1$. In addition, there is a force site at the center of the dodecahedron, for a total of 21 force sites for each NP. Each vertex site is bonded via the FENE potential to the nearest neighbor vertices and to the center of the dodecahedron. The bonds are stiff so that the NP is rigid and maintains its shape during the simulation. Since the sites on the vertices are small relative to the dodecahedron, so we include an excluded volume interaction with the NP center with a range corresponding to the inscribed sphere of the dodecahedron (see table 2.3). There are ssDNA attached to each vertex, for a total of 20 ssDNA attached to each NP. Each DNA strand consists of 15 nucleotides: 7 spacers and 8 linkers. The sequence for the sticky ends of DNA is chosen so that NP can only bond with a tetrahedral cage and cannot bond to other NPs. The values for FENE bonds are given in table 2.1. To ensure that DNA strands are roughly normal to the vertex of the tetrahedron, we use an angle bond potential eq. 2.4, where $\theta$ is the angle made between the DNA site at the vertex of the NP with the center of NP and the next DNA site; these angle interactions are identical to those used for the DNA attached to the tetrahedral cages.

2.2.4 DNA model

For DNA, we use a simple two-site coarse-grained model that was previously developed to describe DNA-functionalized NP assemblies [65, 81, 82]. In this model each DNA nucleotide consists of two force sites: (i) the sugar and phosphate back-bone, that are described by a WCA potential with $\sigma = 1.0$, and (ii) the nucleobase site, that are described by a WCA potential with $\sigma = 0.35$. The backbone sites are bonded to each other, as well as to a nucleobase with a FENE bond to create ssDNA. To mimic the rigidity of the backbone there is an angle potential eq. 2.4 between each three consecutive backbone monomers. The only attractive interactions are between nucleobases (A-T or C-G) of distinct ssDNA strands, which leads to the formation of dsDNA. A LJ potential is used to model the attraction between different bases with a cutoff radius of $r_c = 2.5\sigma$ where $\sigma = 0.35$ is related to WCA potential for the bases and $\epsilon = 1.0$. There details of these potentials are in table 2.2.
To make sure that the base is in a right angle relative to the backbone of DNA, there is a harmonic angle potential,
\[
v_{\text{perp}} = \frac{1}{2} k_{\text{perp}} (\alpha - \frac{\pi}{2})
\]  
(2.5)

We present most results in Lennard-Jones (LJ) reduced units, where the unit of length is given in terms of \( \sigma \) (diameter of the DNA backbone beads), temperature is in units of \( \epsilon/k_B \), and time is in the units of \( \sigma \sqrt{m/\epsilon} \). Following [82] the diameter can be approximately mapped to real units with \( \sigma \approx 0.65 \text{ nm} \).

The pair interactions between different units – sites of the tetrahedral cages, NPs, or DNA – are given by an expanded WCA potential
\[
V_{\text{expand}}^{\text{WCA}}(r_{ij}) = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij} - \Delta_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij} - \Delta_{ij}} \right)^{6} \right]
\]
(2.6)

where \( \Delta_{ij} = (d_i + d_j)/2 - 2^{1/6}\sigma \), where \( d_i \) and \( d_j \) are the diameters of particles \( i \) and \( j \). The additional shift of \( \Delta_{ij} \) by \( 2^{1/6} \) ensures the particle repulsion occurs for any \( r_{ij} < (d_i + d_j)/2 \). Interactions are truncated for \( r_{ij} > \Delta_{ij} + 2^{1/6}\sigma \) to avoid attractions. The values of particles diameters are given in the table 2.3.

**Table 2.3**: The particle diameter for excluded volume interactions given by eq. 2.6. For details about the interactions between DNA sites see ref. 82.

<table>
<thead>
<tr>
<th>Particle type</th>
<th>Diameter (( \sigma ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahedral cage, central particle</td>
<td>40</td>
</tr>
<tr>
<td>Tetrahedral cage, edge particles</td>
<td>9.9</td>
</tr>
<tr>
<td>Tetrahedral cage, central particle</td>
<td>40</td>
</tr>
<tr>
<td>NP, central particle</td>
<td>ranging between 40 to 120</td>
</tr>
<tr>
<td>DNA backbone</td>
<td>1</td>
</tr>
</tbody>
</table>
2.3 Methods

2.3.1 Debye-Hückel theory

DNA is negatively charged, and the repulsion between DNA strands may destabilize the lattice. Thus, DNA-functionalized superlattices are usually grown in a salt solution, since the salt solution screens the negative charge of DNA, reducing the repulsion between DNA strands. Debye-Hückel theory explains how the effective electrostatic potential of a charge behaves in the presence of solution with charge carriers.

The Debye-Hückel approximation can be derived by starting with the Poisson equation

$$\nabla^2 \psi = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{\rho e}{\epsilon_r \epsilon_0} \tag{2.7}$$

where, $\psi$ is electric potential, $\rho$ is charge density and $\epsilon_r \epsilon_0$ is permittivity of the medium. The local density of charges can be calculated using Boltzmann statistics,

$$\rho(r) = n_+(r) + n_-(r) = n_{0+} \exp(-q \beta \psi(r)) + n_{0-} \exp(-q \beta \psi(r)), \tag{2.8}$$

where $n_\pm$ is the concentration of positive or negative charges, $\psi$ is the potential, $q$ is the electrostatic charge, and $\rho$ is the density. Combining eq. 2.8 and eq. 2.7, we can calculate the effective potential of a charge in an ionic solution.

$$\nabla^2 \psi = \frac{4\pi}{\epsilon} \sum_i n_i q_i e^{\beta q_i \psi}. \tag{2.9}$$

Equation 2.9 is called Poisson-Boltzmann equation. At low salt concentrations, the Poisson-Boltzmann equation can be expanded to obtain a linear approximation.

$$\nabla^2 \psi \approx \frac{4\pi}{\epsilon} \sum_i n_i q_i - \beta \sum_i n_i q_i^2 \psi = q_{\text{total}} - K^2 \psi \tag{2.10}$$

where

$$K^2 = \frac{8\pi \beta}{\epsilon I} \tag{2.11}$$

is the screening parameter and

$$I = \frac{1}{2} \sum_i q_i^2 C_i \tag{2.12}$$

is the ionic strength.
The first term in the right side of eq. 2.10 is zero if the solution is neutral. Equation 2.10 is analytically solvable, and the solutions are shown in eq. 2.13. In the low salt concentration limit, the effect of the electric potential of charges decays exponentially. In section 2.4, we use this theory to calculate the effective electrostatic interaction between DNA-origami tetrahedral cages

\[\psi = \frac{qe^{-K(r-a)}}{\epsilon r(1 + Ka)} \approx \frac{qe^{-Kr}}{\epsilon r}. \quad (2.13)\]

### 2.3.2 Dynamical matrix

The dynamical matrix approach is a method to calculate the normal-modes dispersion relation of the lattice, using a simple model for the potential energy between the particles [83, 84]. We start by writing the position of particle as a function of time in three different terms

\[r(t) = r_m + r_{0\mu} + um,\mu(t) = r_{0,\mu} + u_{m,\mu}(t), \quad (2.14)\]

where \(r(t)\) is the position of particle at time \(t\), \(r_m\) is the position of unit-cell, \(r_{0\mu}\) is the ideal position of particle in unit-cell relative to \(r_m\), and \(u_{m,\mu}(t)\) is the deviation of particle from its ideal position in the lattice. We consider a harmonic approximation of the potential.

\[U = U_0 + \frac{1}{2} \sum_{m,\mu,\alpha,n,\nu,\beta} \Phi_{\alpha,\beta}^{\mu,\nu}(m,n)u(\mu,\nu)u(n,\mu) \quad (2.15)\]

where the \(\Phi_{\alpha,\beta}^{\mu,\nu}(m,n) = \frac{\partial^2 U}{\partial u(\mu,\nu)\partial u(n,\nu)}\), \(m\) and \(n\) are sum over the unit-cells, \(\alpha\) and \(\beta\) are sum over spatial dimensions and \(\mu\) and \(\nu\) are sum over basis in the unit cell (in our case NP and tetrahedral cage). Using this harmonic approximation, the equation of motion can be written just in terms of the deviation of particles from their ideal positions.

\[M_{\alpha} \ddot{u}_{\alpha}(m,\mu) = -\sum_{n,\nu,\beta} \Phi_{\alpha,\beta}^{\mu,\nu}(m-n)u_{\beta}(n,\nu). \quad (2.16)\]

Solving eq. 2.16 for many particles in the position space can be challenging, to facilitate the solution of equation of motion we write it in the Fourier space (using plane-wave solution eq. 2.17).

\[u_{\alpha}(m,\mu,t) = \frac{1}{\sqrt{NM}} \frac{1}{2\pi} \int d\omega \sum_{q} u_{\mu,\alpha}(q)e^{i\omega t}R_{m-n} \quad (2.17)\]
Substituting eq. 2.17, into eq. 2.16, results in

\[ \omega^2 u_{\mu,\alpha}(q) = \sum_{\nu,\beta} D_{\alpha,\beta}^{\mu,\nu}(q) u_{\nu,\beta}(q) \]  

(2.18)

where,

\[ D_{\alpha,\beta}^{\mu,\nu}(q) = \frac{1}{\sqrt{M_{\mu} M_{\nu}}} \sum_m \Phi_{\alpha,\beta}^{\mu,\nu}(m) e^{-iq.R_m} \]  

(2.19)

is the dynamical matrix, \( \omega \) is the frequency of vibration and the \( q \) is wave vector. The eigenvalues of the dynamical matrix represent \( \omega^2 \) as a function of \( k_r \) and \( k_\theta \).

The Hamiltonian in the Fourier space can be written as a sum of its normal modes of vibration. To find the Hamiltonian we first write the Fourier transform of position in terms of normal mode of vibration.

\[ u_{\mu,\alpha}(q,t) = \sum_\lambda e^{\lambda \mu,\alpha}(q)Q_{\lambda}(q,t) \]  

(2.20)

Substituting eq. 2.20 to eq. 2.17 provides a relation between the normal coordinates in Fourier space with the position of particles in the real space

\[ u_{\alpha}(m,\mu,t) = \frac{1}{\sqrt{NM}} \sum_{q,\lambda} e^{\lambda \mu,\alpha}(q)Q_{\lambda}(q,t)e^{q.R_m} \]  

(2.21)

Using eq. 2.21, eq. 2.18 and eq. 2.17, the Hamiltonian can be written in terms of vibrational normal modes in Fourier space. The final result is presented in eq. 2.22

\[ H = \frac{1}{2} \sum_{q,\lambda} (|P_{\lambda}(q)|^2 + \omega_{\lambda}^2(q)|Q_{\lambda}(q)|^2) \]  

(2.22)

This is a harmonic Hamiltonian. Thus the partition function can be calculated analytically, assuming that \( \omega(q) \) is known.

### 2.3.3 Simulation methods to calculate the ground state energy of Cubic Diamond and Hexagonal Diamond

The CD lattice consists of two interpenetrating FCC (faced-center cubic) lattices. Similarly, the HD lattice consists of two interpenetrating HCP (hexagonal closed-pack) lattices; thus, the tetrahedral cages (we use the model described in section 2.2.2) in CD (HD) are in a FCC (HCP) lattice structure. In the rest of thesis, the CD and FCC are used to refer to cubic diamond lattice;
HD and HCP are used to refer the lattice with hexagonal diamond symmetry. To evaluate the ground-state energy of FCC or HCP lattices, we create configurations with all NP-tetrahedron DNA links completely intact, and enforce the lattice symmetry of the NP and tetrahedron centers. We use a system of 125 unit cells, each of which contains four NP, for a total of 500 NP and 500 tetrahedra, or 421,000 coarse-grained sites. The resulting simulation box has a minimal dimension of 598 nm (for the smallest dimension of the HCP system, which has a non-cubic unit cell). The connectivity of an example configuration is shown in fig 2.2. In the absence of long-ranged interactions, the energies of FCC and HCP lattices are indistinguishable. Long-ranged interactions arise from screened Coulombic interactions between the negatively charged DNA backbones. Because the tetrahedral edges consist of 10 bundled duplexes, the charge along the edges is substantially larger than for any single DNA strand. Accordingly, we only account for charge interactions between the sites along the tetrahedral edges of our coarse-grained model. We model the screened interaction by a repulsive Yukawa (Debye-Huckel)

\[ V = A \frac{e^{-r/\lambda}}{r/\lambda} \]  

potential between the tetrahedron edge sites of different tetrahedra. The potential is truncated at \( r_c = 137 \text{ nm} \), substantially larger than the largest \( \lambda = 6.5 \text{ nm} \) we consider. Since we calculate only the ratio of the energy of the FCC to that of the HCP lattice, the value for the strength \( A \) of the interaction is irrelevant. The vertices of the tetrahedron represent the first nucleotide of the linking DNA strand, since the vertices are truncated in experiments. Accordingly, the vertices are not included in the energy calculation. Note that including vertices would substantially diminish the difference in energy between FCC and HCP.

Since calculation of the ground-state energy of the lattice does not require information about time evolution of the lattice, it is possible to simulate large lattice.

### 2.4 The ground-state energy difference between CD and HD lattices

We examine configurations of basis particles linked by tetrahedra in either FCC or HCP arrangements. The system size is chosen to minimize the ground state energy of the lattice structures. When only short-ranged interactions are included, there is no energy difference between FCC
Figure 2.2: Visualization of the molecular model used to evaluate the relative energies of lattice types in the molecular simulation studies. (a) A dodecahedral gold nanoparticle with DNA strands linked at each of the 20 vertices. Red sites of the DNA are spacer bases that do not bond with other DNA. The blue and white sites are the linking regions of the DNA, which can connect to DNA of tetrahedra. (b) The tetrahedral linking unit. There are 20 sites along each edge to represent the bundled DNA duplexes used in experiments. From each vertex emanates a single DNA strand with 7 spacers and 8 linkers. (c) Example of the diamond lattice to show the relative structure of NP and tetrahedra.
Chapter 2 - Stability of Cubic Diamond Lattices

and HCP arrangements, as we expect. However, we recognize that there will be a longer-ranged repulsive interaction between DNA backbones, which is amplified along the edges of the tetrahedra where many are linked together. Accordingly, we model this repulsion between tetrahedral edges by including a screened Coulombic interaction (Debye-Huckel theory), with a screening length $\lambda$. In the FCC (or CD) configuration, the faces of tetrahedra are aligned Fig 2.3 (a), while in the HCP (or HD) only alternating planes align Fig 2.3(b). As a consequence, the longer-ranged repulsion between edges gives rise to an energy gap between structures that favors the FCC structure 2.3(c). The size of this gap is related to the screening length of the potential, as shown in Fig. 2.3(c). The truncation of tetrahedral cages, plays an important role in the ratio of energies. Since, the interaction between tetrahedral cages decays exponentially, the closest parts of neighbor tetrahedra (vertices) are important. For complete tetrahedra, positions of vertices, are identical for CD and HD symmetries; thus, the most important contribution to the repulsion for complete tetrahedra is very close for HD and CD (assuming, $\lambda$ is shorter than the distance between the second neighbors in the lattice). In the case of complete tetrahedra, the difference between CD and HD is related to the parts of tetrahedron that are away from vertices. Since the truncated tetrahedra, do not have sharp vertices (unlike a complete tetrahedron), the difference between CD and HD is more pronounced; this difference is dependent on the degree of truncation. The truncation of complete tetrahedra, provides a mechanism to control the change in the relative energy of CD and HD. Thus, the medium-ranged repulsion of the truncated tetrahedral linkers provides a thermodynamic driving force to favor FCC (or CD) over otherwise very similar structures.
Figure 2.3: The ratio of repulsive interaction energy for CD and HD lattices. (a) Snapshot of the simulation for FCC (or cubic diamond) configuration. (b) Snapshot of the simulation for HCP (or hexagonal diamond) configuration. (c) Ratio of electrostatic energy for FCC (or CD) and HCP (or HD) organizations, based on screened Coulombic interactions between the negatively charged DNA bundles that comprise the tetrahedral cages. The lower energy of FCC organizations is favored.
2.4.1 Simulations and lattice preparation to calculate the Gibbs free energy

We simulate the coarse-grained model via molecular dynamics (MD) calculations, carried out using the LAMMPS simulation suite [85]. To examine the stability of CD lattices, we first create defect free, fully bonded lattices. The lattice consists of 64 tetrahedral cages (we use the model described in section 2.2.1) and 64 NPs, yielding a regular triclinic box (non-orthogonal with equal size lengths) of 64 primitive unit cells. Since the cubic diamond lattice can be considered as two identical inter-penetrating FCC lattices (with a shift of $b/4$ in each direction, where $b$ is the FCC lattice constant), each particle type (tetrahedron or NP) is organized in an FCC lattice.

To create a CD lattice with DNA fully linked among NP and tetrahedra, we follow a two-step procedure. First, we simulate a single unit cell to form the links between the DNA strands connecting a NP and tetrahedron. We position the centers of the NP and tetrahedron at the ideal lattice positions for the CD structure (points $(0,0,0)$ and $(b/4, b/4, b/4)$ and link the center of the NP or tetrahedron to the lattice position via a strong harmonic potential. Since the NP is modeled as a dodecahedron (and each dodecahedron implicitly includes 5 co-centered tetrahedra), it is possible to create DNA links between one of these implicit tetrahedra of the dodecahedron and tetrahedral cage with no stress. The lattice constant $b$ is chosen to geometrically allow for a connection between the NP and tetrahedron to form only along the nearest linking strand, preventing the formation of defects in this unit cell; this linked strand will not be stress free, but we will release this constraint later. We then perform a MD simulation of the primitive unit cell in a triclinic box with periodic boundary conditions in an NVT ensemble at temperature 0.09 (below the DNA melting temperature $T_{M}$). In the second step we replicate the fully bonded primitive cell generated in step 1 (with unwrapped periodic boundary conditions) to create a 4 by 4 by 4 lattice. We then remove the harmonic constraint on the central particles so they can freely move and simulate the lattice in an NPT ensemble at zero pressure and $T = 0.09$ to ensure there is no external stress on the DNA linkers. We use zero pressure since the osmotic pressure in experiments is very small. To study systems with different NP sizes, we change only the size of the isotropically functionalized NP, not the tetrahedral cage size, since this is more readily varied experimentally. We perform simulations for particle sizes ranging from $d = 40\sigma$ to $120\sigma$, mapping to 26-78 nm in diameter.
2.4.2 Surface energy calculation

To find the crystallite shape of the CD lattice, we use the Wulff construction method. This method requires the values of surface energy for different crystalline plane symmetries. To evaluate the surface energy of crystal facets with different symmetries, we must create lattices that are non-periodic in the direction normal to the facet under consideration. We use the same procedure employed for the periodic lattices just described to create fully bonded lattices with an exposed face. The system consists of a slab of diamond lattice that is periodic in the plane parallel to two lattice vectors, and non-periodic normal to the free surface ($z$ direction). We again use $P = 0$ after the initial defect-free lattice is formed. We consider three different symmetries of the exposed face: (100), (110), or (111). Depending on the symmetry of the lattice plane, we used either a cubic (100) or triclinic box (110 and 111). For triclinic boxes, the angle between $c$ (the unit-cell vector in the $z$ direction) and the other 2 unit-cell vectors is $90^\circ$; $a$ and $b$ (unit-cell vectors) lie in the $xy$ plane. The size and angle between $a$ and $b$ are determined by the symmetry of plane. For the smallest system considered, the surface consists of 16 NPs, and the slab consists of 8 layers transverse to the surface (4 layers each of NP and tetrahedra). Each system consists of at least 128 NPs and tetrahedra in total. To ensure that our results are not affected by the finite size of the slab, we performed simulations with 6, 8, or 10 layers of NP for the 111 facet. The surface energy for different thicknesses was constant within the limits of uncertainty of the calculation, so we do not anticipate any finite size effects in our reported results.
Chapter 2 - Stability of Cubic Diamond Lattices

2.5 Lattice stability

2.5.1 Lattice structure

Before we calculate the stability from the relative free energy, we provide a reference for the effects of changing NP size and DNA stiffness on the crystal structure. To do so, we evaluate the structure factor

\[ S(q) = \frac{1}{N} \left\langle \sum_{j \neq k} e^{-i q \cdot (r_j - r_k)} \right\rangle \] (2.24)

where \( r_j \) is the position of the center of a NP or tetrahedral cage, and \( q \) is the wave vector.

Figure 2.4 shows \( S(q) \) for diamond lattices for representative particle sizes and DNA backbone stiffness values; the stiffness (or persistence length) is directly linked to salt concentration. For all systems, the simulated \( S(q) \) reproduces the theoretically expected locations for at least the first 6 peaks of \( S(q) \), confirming the mechanical stability of the cubic diamond lattice. The higher order peaks become "smeared" due to lattice vibrations. Figure 2.4(a) shows that, increasing the DNA stiffness (equivalent to lower salt concentration) results more sharply defined peaks, which are discernable up to larger \( q \) values. For example, for stiffer DNA \( (k = 2.0) \), we can distinguish two peaks near \( q/q_0 = 4.2 \), which for more flexible DNA \( (k = 0.5) \) combine to a single broad peak. Thus, as might be anticipated, increasing DNA stiffness results in a more precisely defined structure of the lattice. Fig. 2.4(b) shows that the lattice structure is only weakly affected by the NP size. The challenge is to understand the balance between optimizing the precise structure of the lattice and its relative stability.

2.5.2 Lattice vibrational spectrum

Since we are dealing with lattice systems, their free energy will be determined from the lattice vibrational spectrum. In principle, we could directly evaluate the dispersion relation \( \omega(q) \), but the size of the system (up to 48896 force sites) and complexity of the potentials make the necessary matrix diagonalization computationally infeasible. Thus, we need to consider a simplified representation of the system. We expect that the vibrational spectrum is primarily encoded in the vibrational properties of the centers of mass of the NP and tetrahedra. Thus, we can coarse-grain the vibrational motion of the complete system from our MD simulations to the vibrations of the centers of mass of the NPs and tetrahedral cages; the mass of these sites...
Figure 2.4: The structure factor $S(q)$ for the cubic diamond lattice. (a) The structure factor for different DNA stiffness values. We label peaks by their corresponding Miller indices, known for the cubic diamond lattice. For stiffer DNA, the specific peaks of $S(q)$ can be discerned for larger values of $q/q_0$ than for flexible DNA. In this sense, the stiffer DNA results in a better structured lattice. (b) The structure factor for different NP sizes. The effect of changing NP size on the structure is less pronounced than changing the DNA stiffness. For clarity of the figure, data are shifted vertically.
corresponds to the total mass of NPs and tetrahedral cages (including DNA strands) from the MD simulation. To obtain the dispersion relation, we use the dynamical matrix approach [83, 84]. The dynamical matrix

\[ D^{-1}_{\mu\nu}(q) = \frac{1}{k_B T} \langle u_\mu(q) u_\nu(q) \rangle \]  

is defined by the correlation function of the Fourier transforms of the NP and tetrahedral coordinates \( u_\mu(q) \) and \( u_\nu(q) \) [86].

The dynamical matrix can be related to the normal mode dispersion relation by assuming a simplified harmonic model for the interactions among the lattice sites [83, 84]. Specifically, one assumes a simple potential between lattice sites

\[ V = \frac{1}{2} k_r \sum_n \delta r_{ij}^2 + \frac{1}{2} r_0 k_\theta \sum_n \delta \theta_{ijk}^2, \]  

where we sum \( n \) over all of unit-cells, \( \delta r_{ij} \) is the distance between particles \( i \) and \( j \) relative to the ideal separation \( r_0 \), and \( \delta \theta_{ijk} \) is the angle (relative to its ideal value) between particles \( i \) and two nearest neighbors \( j \) and \( k \). The radial bond constant \( k_r \) mimics the elasticity of the DNA bond between NPs and tetrahedral cages, and \( k_\theta \) is related to the rotational degrees of freedom of sites around their centers. The constants \( k_r \) and \( k_\theta \) will be determined from the dynamical matrix.

We directly calculate these frequencies \( \omega \) using the dynamical matrix from the eigenvalue problem of eq. 2.18. Since we have coarse grained our simulation lattice to a \( 4 \times 4 \) lattice of NP and tetrahedra, we are limited to just 4 different wave vectors \( q \) for each of six branches, the number of which is determined by having two particles in each unit-cell. The symbols in Fig. 2.5 shows the calculated \( \omega \) for the three lowest branches along the the most common symmetry directions, (100) and (111); there are only two sets of points, since the two lowest branches are degenerate (see appendix). We focus on the lowest branches because they have the most significant contribution to the free energy. Since the dynamical matrix is related to the potential of eq. 2.26, its eigenvalues are functions of \( k_r \) and \( k_\theta \), and we can use our results to estimate these parameters, and thus estimate the free energy. The appendix provides an analytical expressions for the functional dependence of \( \omega \) on \( k_r \) and \( k_\theta \), along with further details of the theory. Based on data for the two directions, (100) and (111), accounting for degeneracy, and that the origin is a common point among the symmetry directions, we have a total of 13 unique points to determine \( k_r \) and \( k_\theta \). The solid lines in Fig 2.5) show the resulting
Figure 2.5: The dispersion relation obtained from simulation and fit with theory for the (100) and (111) directions. The points are the values calculated from MD simulation based on the eigenvalues of the dynamical matrix (Eq. 2.18). The solid line is the fit with the formula in the appendix. This data is for the system with DNA stiffness of $k = 1.0$ and NP size $d = 40\sigma$. $\bar{q} = qa/2\pi$ is the reduced wave vector and $a$ is the lattice constant.

fit for the dispersion relation, which matches well with the available data. We will use these fit values in the next section when we evaluate the free energy.

2.5.3 Lattice Free Energy

We now proceed to evaluate the relative thermodynamic stability as a function of particle size and DNA stiffness. To do so, we need to evaluate the change in Gibbs free energy $\Delta G = \Delta E - T\Delta S + P\Delta V$, as a function of particle size or DNA stiffness. The smallest particle size (diameter $40\sigma$) and smallest stiffness ($k = 0.5$) is chosen as the reference state, and the free energy for all other sizes is evaluated relative to that system. Since we use $P = 0$, the $P\Delta V$ term is not needed, and the Gibbs free energy reduces to Helmholtz free energy. Using equation 2.22, the Helmholtz free energy

$$F = -k_B T \ln \left( \sum_\lambda \int e^{-\beta H(q,\lambda)} \, dq \right)$$

(2.27)
**Figure 2.6:** Difference in free energy of the lattice for different DNA stiffness values as a function of NP size; the reference system is the system with smallest NP size and $k = 0.5$. Increasing NP size increases the free energy, which means a relative decrease in stability. Similarly, increasing stiffness increases free energy (reduces stability).

We have already numerically and analytically evaluated the dispersion along the (100) and (111) directions, and we can use the resulting fit values of $k_r$ and $k_\theta$ to numerically calculate the free energy when we integrate over all directions; the result is shown in Fig. 2.6.

Our lattice free energy data (Fig. 2.6) show that the relative free energy increases with increasing NP size and with increasing DNA strand stiffness. In other words, the larger NP or stiffer strands have a decreased relative thermodynamic stability. Recall that increasing stiffness results in a more precisely defined diamond structure (Fig. 2.4); thus, a balance must be struck between optimizing the structure through DNA stiffness and the relative thermodynamic stability.

From a design perspective, it is helpful to know how different aspects of the lattice vibrations affect the free energy. For example, how much of the stability originates from energetic versus entropic effects? The free energy is separable into energetic and entropic contributions to $\Delta F = \Delta E - T\Delta S$. The energy can be extracted directly from simulation the data, and independent of NP size and stiffness. This is due to the fact that there are almost no non-bonded interactions
with NP, unless NP are so large that they overlap. Additionally, DNA bonding does not vary with NP size, so the DNA do not significantly contribute to $\Delta E$. Consequently, entropy is the controlling factor in the free energy.

We wish to parse the entropy into the contributions from the rotational and vibrational degrees of freedom. In our dynamical matrix approach, the free energy (entropy) is a complicated function of $k_r$ and $k_\theta$, and is defined only numerically when we integrate over all lattice directions. This makes it difficult to study the effects of rotational and vibrational degrees of freedom separately. Therefore, we use an even simpler potential that captures the essential features of the free energy from the more complex dynamical matrix calculation. Specifically, we ignore correlations of the vibrations, and consider each NP and tetrahedron as an independent oscillator. In this independent harmonic approximation,

$$V = \sum_{i=1}^{N_{\text{NP}}} \left( \frac{1}{2} k_{\text{trans}} \Delta r_i^2 + \frac{1}{2} k_{\text{rot}} \Delta \theta_i^2 \right) + \sum_{i=1}^{N_{\text{tet}}} \left( \frac{1}{2} k_{\text{trans,tet}} \Delta r_i^2 + \frac{1}{2} k_{\text{rot,tet}} \Delta \theta_i^2 \right),$$  

(2.28)

where $\Delta r_i^2$ is the mean-square translational vibration of the centers of NP or tetrahedra, and $\Delta \theta^2$ is the mean-square angular vibration. In this harmonic representation, the force constants $k_{\text{trans}}$ and $k_{\text{rot}}$ can be determined from the typical size of the lattice vibrations. $k_{\text{trans}}$ and $k_{\text{rot}}$ are related to, but distinct from $k_r$ and $k_\theta$. Fig. 2.7 shows the average time dependence of $\langle r^2(t) \rangle$ and $\langle \theta^2(t) \rangle$ for both the tetrahedra and the NP for many NP sizes at $k = 1.0$; $\theta(t)$ is the angle between the vector defined from the center of a NP or tetrahedron to a chosen vertex at times $t_0$ and $t_0 + t$ (where $t_0$ is an arbitrary initial time).

The vibrational amplitudes saturate at characteristic values $\langle u^2 \rangle$ for translations and $\langle \phi^2 \rangle$ for rotations for $t \gtrsim 10^4$. In other words, lattice particles vibrate around fixed positions, with no diffusion of the NPs or tetrahedra. Note that, Fig. 2.7(a) and (b) shows that $\langle u^2 \rangle$ is essentially the same for NP and tetrahedra, while Fig. 2.7(c) and (d) shows that $\langle \phi^2 \rangle$ differs for NP and tetrahedra. To show these trends more clearly, Fig. 2.8 shows $\langle u^2 \rangle$ and $\langle \phi^2 \rangle$ for all NP sizes and DNA stiffness values. For the translational component $\langle u^2 \rangle$, we average the contribution from the NP and tetrahedra, since the values for each are essentially identical. In contrast, the rotational displacement $\langle \phi^2 \rangle$ is significantly different for NP and tetrahedra. Specifically, $\langle \phi^2 \rangle$ of NP decreases with increasing NP diameter, while $\langle \phi^2 \rangle$ increases for tetrahedral cages as the NP diameter increases. The opposite behavior of the angular displacement can be understood geometrically. Specifically, we can relate $\langle \phi^2 \rangle$ to an arc length $s$ via $\langle \phi^2 \rangle \approx (2s/d)^2$ where $d$ is
Figure 2.7: The time dependence of the translational and rotational vibration of the tetrahedral cages and NPs. The translational mean-squared displacement $\langle r^2(t) \rangle$ for (a) NP and (b) tetrahedra are very similar; the saturation value $\langle u^2 \rangle$ of the MSD increases for both NP and tetrahedra with increasing NP size. The rotational mean-squared displacement $\langle \theta^2(t) \rangle$ for (c) NP and (d) tetrahedra differ significantly. Specifically, the saturation value $\langle \phi^2 \rangle$ for NP decreases as the NP size increases, while $\langle \phi^2(t) \rangle$ for tetrahedral cages increases as the NP size increases. Note that dependence on NP size of the rotational MSD of NPs is different than the other three MSDs. All data are for the system with stiffness $k = 1.0$. The black, red, green, blue and brown lines correspond to $d = 40, 60, 80, 100, 120\sigma$, respectively.
the diameter of the NP or tetrahedron. Since the NP and tetrahedra are connected, the arc length \( s \) must be the same for either particle type. Thus, as NP diameter increases, \( \langle \phi^2 \rangle \) will decrease for NP, even as it grows for tetrahedra.

Based on the independent oscillator approach, the relative entropy as a function of NP size or DNA stiffness can be separated into translational and rotational degrees of freedom. In this approximation, \( k_{\text{trans}} = 3k_B T/\langle u^2 \rangle \), and the translational contribution to the entropy is

\[
\Delta S_{\text{trans}} = \frac{3}{2} k_B \left[ \ln \left( \frac{\langle u^2 \rangle}{\langle u^2 \rangle_{\text{ref}}} \right)_{\text{NP}} + \ln \left( \frac{\langle u^2 \rangle}{\langle u^2 \rangle_{\text{ref}}} \right)_{\text{tetra}} \right].
\]

The reference \( \langle u^2 \rangle_{\text{ref}} \) corresponds to the system with a NP diameter 40\( \sigma \). In principle, eq. (2.29) should also contain a \( T \langle u^2 \rangle d \langle u^2 \rangle / dT \) term, but this term can be eliminated based on the \( T \) dependence of \( \langle u^2 \rangle \); specifically, simulations show that the \( \langle u^2 \rangle \) depends linearly on temperature (as would be expected for nearly harmonic vibrations), provided we do not closely approach the melting temperature. Linear \( T \) dependence of \( \langle u^2 \rangle \) implies that \( T \langle u^2 \rangle d \langle u^2 \rangle / dT = 1 \), and independent of particle size. Similar to the translational component, \( k_{\text{rot}} = 3k_B T/\langle \phi^2 \rangle \), and the relative entropy from the rotational degrees of freedom is given by

\[
\Delta S_{\text{rot}} = \frac{3}{2} k_B \left[ \ln \left( \frac{\langle \phi^2 \rangle}{\langle \phi^2 \rangle_{\text{ref}}} \right)_{\text{NP}} + \ln \left( \frac{\langle \phi^2 \rangle}{\langle \phi^2 \rangle_{\text{ref}}} \right)_{\text{tetra}} \right].
\]

Based on the values obtained for \( \langle u^2 \rangle \) and \( \langle \phi^2 \rangle \), we show the resulting contributions to the free energy from the translational and rotational degrees of freedom for NP and tetrahedra (Fig. 2.9). The contribution to the entropy from translational degrees of freedom is the same for tetrahedra and NP, so we do not show them separately; Fig. 2.9(a) shows that \(-T\Delta S_{\text{trans}}\) decreases with increasing NP size. Fig. 2.9(b) shows that the rotational contribution \(-T\Delta S_{\text{rot}}\) has to opposite dependence on NP size – increasing free energy with increasing size; we can further dissect the rotational contribution from NP and tetrahedra. For tetrahedra, \(-T\Delta S_{\text{rot}}\) shows the same qualitative behavior as \(-T\Delta S_{\text{trans}}\). In contrast, \(-T\Delta S_{\text{rot}}\) for NP decreases with increasing NP size. The reason for opposite behavior of the rotational entropy of NP and tetrahedra is precisely the reason for the difference in \( \langle \phi^2 \rangle \), discussed previously. Given the overall increase in the free energy with NP size, it is apparent that the dominant contribution to the free energy comes from rotations of the NP. Thus, this is a natural term to target if one wishes to affect the relative stability of diamond NP lattices.

The qualitative effects of DNA stiffness (determined experimentally from salt concentration) are the same for all components: increasing stiffness decreases the entropy, and thus increases
free energy. Moreover, the quantitative variation of the free energy with stiffness is simpler than is apparent in Fig. 2.9(a) and (b). To illustrate this fact, we replot the contributions to the entropy for each stiffness value relative to the entropy of the smallest NP with the same stiffness. Fig. 2.9(c) shows that, when shifted this way, the size dependence of the entropy is the same for all stiffness values. Thus, the effect of the stiffness, at least over the range we have studied, is to introduce a simple shift of the entropy.
Figure 2.8: (a) The characteristic translational MSD $\langle u^2 \rangle$ of the NPs and tetrahedral cages as a function of NP size for different DNA stiffness. (b) The characteristic rotational MSD $\langle \phi^2 \rangle$ of NPs as a function of NP size for different DNA stiffness. This decrease in $\langle \phi^2 \rangle$ is the main factor decreasing the stability the CD lattice. (c) The rotational MSD $\langle \phi^2 \rangle$ of tetrahedral cages as a function of NP size for different DNA stiffness values. The translational and rotational MSD decreases as the stiffness increases. The black, red, green and blue lines correspond to $k = 0.5, 1.0, 1.5, 2.0$ respectively.
Figure 2.9: Free energy of the rotational and the translational degrees of freedom. (a) The change in the translational free energy $-T\Delta S_{\text{trans}}$ as a function of NP diameter for many stiffness values. The free energy is reported relative to the reference system ($d = 40\sigma$ and stiffness $k = 0.5$). (b) The change in the total rotational free energy $-T\Delta S_{\text{rot}}$. (c) The translational free energy and rotational free energy of NPs and tetrahedral cages as a function of NP size. Different stiffness values are plotted relative to the smallest NP with the same stiffness, to eliminate shifts of free energy due to changes of stiffness. The systems with different stiffness have the same behavior as a function of NP size, suggesting that the DNA stiffness just shifts the free energy by a constant.
2.6 Crystallite shape from the Wulff construction

To find the equilibrium shape of the crystallite, one should find the shape that minimizes the surface free energy of the crystallite for a given volume. The Wulff construction is a method to determine the equilibrium shape of a lattice symmetry based on the ratio between the surface energy $\gamma$ and the distance $\ell$ between crystallite center and the facet plane. Specifically, the ratio

$$\lambda = \frac{\gamma_{hlk}}{\ell_{hlk}}$$

(2.31)

does the surface energy $\gamma_{hlk}$ of facet normal to the $hкл$ direction to the distance $\ell_{hlk}$ of that facet from the crystallite center should be constant for all facets with different symmetries. For each possible facet, one considers a plane, where the normal to the plane is in ($hкл$) direction, and the distance from the center to the facet is $\ell$. The subset of these planes that enclose the smallest volume around the center determine the shape of the crystallite.

We focus on surface energies of the (100), (110) and (111) surfaces. Since NP only interact with their nearest neighbors (short-ranged interaction), it is expected that the lower index planes are most important [87]. The snapshot of the simulated systems is shown in Fig 2.10. For a given facet symmetry, the surface energy will be determined by the number of broken links, which may depend of which of the possible parallel planes is exposed. This is because, in the ideal CD lattice, all of tetrahedral cages have the same orientation, but the opposite orientation from the NP, and all of the implicit tetrahedra of the NPs (dodecahedron) share the same orientation. The net result is that there are two possible scenarios, depending on the symmetry of the exposed face: (i) the number of broken bonds on the surface will be 2, and thus surface energy does not depend on the position on the plane; or (ii) the number of broken bonds can be either 1 or 3 depending on which parallel plane is exposed. We choose the plane that leads to one broken bond, since this has lower energy. Because the tetrahedral cages and internal tetrahedra in NPs are in opposite directions, in order to have one broken bond on both sides of the slab, one surface will consist of tetrahedral cages, and the other will consist of NPs.

As described in the methods section, we can evaluate the surface energy of these interfaces from a simple “broken bond” model, assuming no distortion of the crystal structure, as well as directly from MD simulation, where interfaces may distort. In the broken bond approximation, we simply count the number of broken bonds per unit area for the chosen crystallographic plane.
and estimate the surface energy for each facet using the hybridization energy of DNA. The resulting surface energy for this approximation is shown in the Fig 2.11, which predicts that the (111) face should have the lowest surface energy. In this case, Wulff construction predicts the equilibrium crystallite is an octahedron, the same shape as atomic systems with diamond structure (e.g. diamond, Si, or SiO₂) [78].

To test the validity of the predictions from the broken bond approximation, we evaluate the surface energy via MD simulations for slabs with facets of the same symmetries (100), (110), and (111) for NP diameter 40 and for variable values of the DNA stiffness. We define the surface energy

\[ \gamma_{hkl} = \frac{E_{hkl} - E_{\text{bulk}}}{2A_{hkl}}, \]

where the \( E_i \) is the total energy of the simulated slab, \( E_{\text{bulk}} \) is the energy of bulk lattice, and \( A_i \) is the area of exposed surface, and we express surface energies relative to the (111) plane.
so that we can easily compare to the broken bond approximation. We find that the ratio \( \gamma_{110}/\gamma_{111} \) from the MD simulation (1.22) is nearly the same as predicted by the broken bond approximation (1.23), independent of the DNA stiffness. For the (100) plane, the broken bond model predicts the relative surface energy \( \gamma_{100}/\gamma_{111} = 1.73 \), and as a result the (100) plane would have little impact on the crystallite shape. However, the MD simulations show that \( \gamma_{100}/\gamma_{111} \) is sensitive to DNA stiffness (Fig. 2.11), and can deviate significantly from the broken bond model prediction. For small stiffness, \( \gamma_{100}/\gamma_{111} \) is substantially smaller than expected from the broken bond approximation, and approaches the broken bond prediction for large stiffness. We can understand the reduction of \( \gamma_{100}/\gamma_{111} \) by the fact that flexible strands make it possible for

**Figure 2.11:** The surface energy of (100) plane as a function of DNA stiffness \( k \) and their corresponding crystallite shapes. The cyan, purple and yellow plane correspond to (111), (100) and (110) respectively. The (100) plane surface energy increases as the DNA stiffness increases; as a result the contribution of (100) plane in determining the crystal shape decreases. At the stiffness \( k = 2.0 \), the crystallite shape is an octahedron. The contribution of (110) plane (the yellow planes) is not significant.
some surface particles to reorient and form bonds with particles on the interior. Specifically, to create the (100) facet, we must break two of four bonds for each surface particle that were intact in the bulk system; for tetrahedra at the surface, they have enough flexibility at small $k$ to rotate towards NP in the interior layer, and create bonds with some dangling free strands of the NP. This is only possible since the interior NP have many more strands than are needed to create four bonds. Thus, when the NP are on the surface and tetrahedra are interior, there will be no free DNA strands on the interior layer tetrahedra, since all tetrahedral cages inside the slab are already bonded. Thus, for the (100) direction, we create interfaces with tetrahedral cages on both sides of the slab, since this bonding through surface reorientation leads to a lower surface energy. See Fig. 2.10(c) for an illustration of this phenomenon.

The variation in the surface energy $\gamma_{100}/\gamma_{111}$ with DNA stiffness implies variability in the crystallite shape, using the Wulff method. Given that $\gamma_{110}/\gamma_{111} = 1.22$ independent of stiffness, the Wulff construction predicts that the crystallite shape will vary from a simple cube (for $\gamma_{100}/\gamma_{111} \lesssim 0.57$) to a simple octahedron (for $\gamma_{100}/\gamma_{111} \gtrsim 1.73$). Fig. 2.11 illustrates the expected crystallite shapes for the four stiffness values examined. At the smallest $k = 0.5$, the shape is cube (100) (purple) truncated at the corners by an octahedron (111) (cyan). As $k$ increases, the truncation by the octahedron increases, such for $k \geq 1.0$ the shape is dominated by the octahedron, truncated by the cube. For the largest stiffness, the shape is essentially octahedral, though a careful inspection shows that the (110) plane (yellow) does slightly truncate the edges. This is also the shape predicted by the broken bond model. The importance of the (111) and (100) planes in the crystallite shape of DNA-functionalized NP lattices with diamond structure has been observed previously experimentally [88].

Exploiting the possibility of surface reorientation offers a path to control the crystallite shape. One approach to affect the reorientation of particles and consequently crystallite shape, is to change the DNA stiffness as done here. Another possible approach is to use the DNA origami method to alter the geometry of the cages, and thereby change the bonding ability of cages and NPs. The difference in the number of possible DNA linking locations between the tetrahedra (four) and NP (20), coupled with sufficient flexibility of the DNA, results in a more stable system (lower surface energy) when tetrahedral cages are on the surface than when NPs are on the surface. Such increase stability should make the crystallite more resistant to heterogeneous melting at the interface.
2.7 Conclusions

We have studied the effects of NP size and DNA stiffness on the stability of the CD lattices. We found that the increase of stiffness and NP size (in the range of this study) increase the free energy and consequently decrease the relative thermodynamic stability of these lattices. On the other hand the increase the stiffness improves the structure of these lattices. So there is a potential trade off between having a well structured lattice or more stable lattice. The less stiff DNA leads to a more stable system, and this effect has seen previously in the patchy particles systems [89]. By separating the free energy into parts, we demonstrated that the rotational degrees of freedom of NPs are the dominant factor reducing lattice stability as the NP size increases, while the other degrees of freedom (rotation of tetrahedra and translational degrees of freedom of both types of particles) stabilize it. We also studied the crystallite shape of the CD lattice. we found that the softer DNA linkers, decrease the surface energy and consequently alters the equilibrium crystallite shape. Specifically, the predicted shape of crystallite for CD lattices without surface reorientation is an octahedron, which shifts toward cubic when surface reorientation is possible.
Diminishing effects of NP size on bound layer

3.1 Introduction

Nanoparticles in polymeric materials can change the dynamics of polymer chains. This change in dynamics can depend on the strength and sign of interaction, and NP size. In this chapter we study the effects of NP size and interaction strength in the PNC materials dynamics. For many applications of polymer composites, property modifications are improved by having NP well dispersed within the composite [90–92]. To ensure dispersion at equilibrium, it is usually the case that highly favorable polymer-NP interactions are needed. However, strongly attractive interactions can lead to the creation of a “bound” layer near the NP interface with relaxation that is orders of magnitude slower than that of the surrounding polymer matrix [93–96]. It is expected that this slowed relaxation should be manifest in an increase in the overall glass transition temperature \( T_g \) of PNCs. However, many experiments report little or no change of \( T_g \), even with very strongly interacting NP. Recent work suggests that the bound layer can “insulate” the NP, so that the interfacial interactions of the bound layer with the surrounding polymer matrix are highly compatible, leading to little change in the polymer matrix behavior [97]. In this limit of bound polymers, \( T_g \) becomes nearly independent of polymer-NP interaction strength. While
it is known that decreasing NP size will increase the relative fraction of interfacial polymers, it is not well known how changes to the NP size affect the properties of these interfacial polymers. Thus, to have a better control over the property modification of PNCs, it is important to consider a systematic study of the effect of NP size on the behavior of interfacial polymer dynamics and structure.

In the following sections, we study the effects on NP size on the interfacial dynamics of polymer composites, and how this relates to changes in the overall glass transition temperature. To do so, we begin by examining the dependence of relaxation on the distance from the nanoparticle interface for various NP sizes. We then consider how the overall relaxation, which averages over this relaxation gradient, changes with NP size. We find that the effects of NP on interfacial relaxation and bound polymer diminish as NP become smaller. In addition, we study the structural effects of NP size on the bound layer. We show how both the polymer shape (quantified by the gyration tensor) and the alignment with the NP are altered approaching the surface of the NP. We see that both the shape and alignment change near the interface, but that the effects become weaker as the NP size decreases. Our data suggest that when NP diameter becomes smaller than the chain radius of gyration, their impact on structure is greatly diminished. Moreover, these changes appear entropically driven, since there is almost no effect of the polymer-NP interaction strength on changes of chain structure. Overall, for small NP, the “cloaking” by bound polymer is less effective. The less effective bound layer makes the glass transition temperature of the composite more sensitive to NP interactions, consistent with experimental results [98].

3.2 Modeling

3.2.1 Polymer model

The polymer composite is modeled as an ideal, uniform dispersion of NP within a polymer matrix, following the simulation parameters and protocol we have used in earlier work. Polymer chains are modeled via a Keremer-Grest bead-spring model [99], where each chain consists 20 monomers, and monomers have a diameter $\sigma$. Non-bonded monomers interact via a Lennard-Jones (LJ) potential that is truncated and shifted beyond a cutoff distance $r_c = 2.5\sigma$, which
includes attraction among monomers.

\[ V_{\text{LJshift}}(r) = V_{\text{LJ}}(r) - V_{\text{LJ}}(r_c) - (r - r_c) \frac{dV_{\text{LJ}}(r)}{dr} \bigg|_{r=r_c} \]  

(3.1)

where \( V_{\text{LJ}} \) is Lenard-Jones potential (eq. 2.2). Bonded monomers are linked by a finitely-extensible nonlinear elastic (FENE) potential eq. 2.3, with \( k = 30\epsilon \) and \( R_0 = 1.5\sigma \).

### 3.2.2 NP model

Many NPs have a faceted shape rather than ideally spherical shape (e.g. gold NP). To capture the faceted feature of NPs we choose to use icosahedron shape. Each NP consists of a collection of beads (identical to the monomers of polymer chains) that are linked to form an icosahedral NP with specified size. We study three different NP sizes that consist of 356 beads, 104, or 12 beads, which corresponds to an icosahedron of edge length \( a = 6.6\sigma \) (6 monomers per edge), \( 4.4\sigma \) (4 monomers per edge) or \( 2.1\sigma \) (two monomers per edge) respectively. This size can be converted to an approximate diameter by \( d = \frac{\sqrt{3}}{6}(3 + \sqrt{5})a \), which corresponds to the diameter of an inscribed sphere that touches the faces of the icosahedron; the resulting diameters are \( d = 10.0 \), \( 6.6 \), and \( 3.3 \), respectively. Each site of NP is tethered to its position by a FENE spring that allows for a small surface roughness of the NP facet and let the NP thermalize; for the tether we use a stiffer spring (\( k = 45 \)), and larger mass for NP particles (\( m_p = 2m \)), where \( m_p \) is the mass of the NP sites, and \( m \) is the mass of polymer monomers, the smaller bond-length parameter (\( R_{0p} = 1.0 \)) is used in compare to the polymer chains. For interactions between the nanoparticle force sites, we use the same form of LJ interaction as used for non-bonded monomers. The NP site are close enough (\( 2\frac{\sigma}{6} \)) to prevent polymer chain monomers from penetrating the NP surface (in the range of interaction strength and temperatures that are used). To model the interaction between the NP and polymers, we use an attractive LJ interaction, also truncated beyond \( 2.5\sigma \). We use a variable polymer-nanoparticle interaction strength \( \varepsilon \). The interfacial dynamics depend strongly on this parameter.
3.3 Methods

3.3.1 Intermediate Scattering Function

Calculation of the $T_g$ from the dynamical definition needs the relaxation time values. We use the intermediate scattering function

$$F(q,t) = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} \exp(iq.(r_j(t) - r_i(0)))$$

(3.2)

to calculate the relaxation time. The intermediate scattering function calculates the Fourier transformation of the density-density correlation function as a function of time and wave vector $q$. In other words, the scattering function is a measure of similarities of configuration of a system of particles as a function of time and wave vector $q$. Since we are interested in segmental (monomers) relaxation time, we choose $q = 7.0, q_0 \approx 7$, the location of the primary peak in the monomer structure factor where the coherent intermediate scattering function usually decays most slowly (the scale related to the segmental spacing). $F(q,t) = 1$ for identical configurations; It decays as the configuration of monomers deviates from their initial configuration. The scattering function can be separated into two parts, the self-part

$$F(q,t) = \frac{1}{N} \sum_{i=1}^{N} \exp(iq.(r_i(t) - r_i(0))),$$

(3.3)

and distinct-part

$$F(q,t) = \frac{1}{N} \sum_{i=1}^{N} \sum_{j \neq i} \exp(iq.(r_j(t) - r_i(0))).$$

(3.4)

Figure 3.1 shows an example of the self-part of intermediate scattering function.

The relaxation time can be defined based on the decay of intermediate scattering function. We use a stretched exponential function to describe different relaxation processes in intermediate scattering function. In this thesis we are interested in the scattering function of different parts of polymer-NP composite separately; thus, we just focus on self part of intermediate scattering function.

3.3.2 Gyration (shape) tensor and orientation function

To study and quantify the structural effects of NP on polymer chains, defining the quantities that describe the shape of polymer chain is needed. We use the gyration tensor and orientation
Figure 3.1: Intermediate scattering function fitted to eq. 3.7 (for the system with $\varepsilon = 2.0$, and $T = 0.46$). The circles are representing the simulation data, the red line is representing the fitted function, and the black, blue and green lines show the three terms on the right side of eq. 3.7 respectively. The black line is related to vibrational relaxation, the blue line is related to the polymer matrix relaxation time and the green line is related to the bound layer relaxation time. The decay of the green line (bound layer relaxation time) occurs orders of magnitude slower than the decay of the blue line; this shows that the relaxation time of the bound layer is decoupled from the polymer matrix.

The gyration tensor is defined as

$$S_{\alpha \beta} = \frac{1}{N} \sum_{i=1}^{N} (r^\alpha_i - r^\alpha_{cm})(r^\beta_i - r^\beta_{cm}),$$

where $N$ is the number of monomers per chain and $i$ is the monomer index, $\alpha$ and $\beta$ indicate axis directions, and $r_{cm}$ is the center of mass of the chain. The gyration tensor describes the second moment of the position of particles distribution. There are many shape descriptors can be calculated from the gyration tensors. The radius of gyration, asphericity and anisotropicity of a particles distribution can be calculated from gyration tensor. Most of these shape descriptor are functions of the eigenvalues $\lambda_1^2 < \lambda_2^2 < \lambda_3^2$ of gyration tensor. For example radius of gyration is defined by $R_g^2 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$, and asphericity is defined by $b = \lambda_3^2 - \frac{1}{2}(\lambda_1^2 + \lambda_2^2)$. As it was mentioned in the introduction chapter 1, the polymers in melts have an ellipsoid-like shape. The
physical meaning of the square root of the eigenvalues $\lambda_1, \lambda_2$ and $\lambda_3$ are the semiaxis of the ellipsoid and the eigenvectors are in the semiaxis directions. These quantities usually used in polymer physics to describe the shape of the polymer in the solution and melt. The ratio of eigenvalues can be another quantity to indicate the degree of anisotropy of the polymer.

To study the relative orientation of a polymer relative to a surface, the second Legendre polynomial $P_2(\cos \theta) = \frac{1}{2}(3\cos^2 \theta - 1)$ can be useful, where the $\theta$ is the angle between the polymer semiaxis and the normal vector to the surface. This function is $-\frac{1}{2}$ when the semiaxis is parallel to the surface, and 1 when the semiaxis is perpendicular to the surface.

### 3.3.3 MD simulations

Each simulation consists of a single NP surrounded by 400 polymers, and periodic boundary conditions yield a correspondence to an ideal dispersion. This simplification allows us to easily probe the distance dependence of the relaxation from the NP surface, which is critical to explain the changes in the dynamics and glass transition of the overall composite. Simulations are performed in an NVT ensemble along an isobaric path ($P = 0.1$) at temperatures ranging from 0.40 to 0.80, in units relative to the polymer-polymer interactions; the interaction strength between NP and polymers ranges from $0.1 \leq \varepsilon \leq 3.0$, where $\varepsilon$ is defined relative to the polymer-polymer interactions. Since the NP size varies while the number of chains and chain length are fixed, the concentration, or filling fraction varies, and has values of $\phi = 0.042$ ($d = 10.0$), 0.0128 ($d = 6.6$), and 0.0015 ($d = 3.3$). The small filling fraction for the smallest NP avoids the possibility of polymers that bridge between the NPs, which could give rise of other effects that would complicate our interpretation. All results are reported in reduced units of the monomer diameter and interaction strength $\varepsilon_0$. These reduced units can be approximately converted to real units, where $\sigma = 1$ nm, $\varepsilon_0 = 1$ kJ/mol (equivalent to $T_g \approx 100^\circ$C) and the time is in picoseconds for a simple polymer such as polystyrene.
3.4 Effects of NP size on dynamics of bound polymers

Our primary focus is to address how the NP size affects relaxation and glass formation, as well as the possibility of a bound layer near the NP surface. To probe the dynamics of the polymer composite, we focus on the self-intermediate scattering function.

3.4.1 Distance dependence of relaxation time

We quantify the spatial gradient of relaxation as a function of distance from the NP by calculating Eq. ?? conditioned on the radial distance $r$ of a monomer from the NP at the time origin. Since monomers typically move only a fraction of a diameter over the relaxation time of $F_{\text{self}}(q,t)$, it does not matter whether we condition the position based on its starting value, or the position after a relaxation time. Figure 3.2 shows the variation of the $F_{\text{self}}(q,t)$ for different layers (each of thickness $0.5\sigma$) at a reference polymer-NP interaction strength $\varepsilon = 0.25$ and $2.0$ at $T = 0.46$ for NP size $6.6\sigma$. As shown in previous work [97], the relaxation near the surface is qualitatively different for weak versus strong polymer-NP interactions; namely, relaxation is enhanced near the weakly interacting substrate, and slowed (by several order of magnitude) at the strongly interacting substrate. In either case, the layers further away from the NP interface approach the relaxation behavior of a pure polymer melt at the same thermodynamic conditions.

To quantify the relaxation for various NP sizes and distances relative to the NP surface, we examine the characteristic relaxation time of $F_s(q_0, t, r)$ as a function of distance $r$ from the NP. We extract the relaxation time from $F_s(q_0, t, r)$ using a two-step relaxation

$$F_{\text{self}}(q, t, r) = (1 - A(r))e^{-t/\tau_s} + A(r)e^{-t/\tau_\alpha(r)}\beta(r),$$

(3.6)

where the first term is a vibrational relaxation, and the second term represents the primary, or $\alpha$-relaxation. The vibrational relaxation time is essentially independent of $T$, NP size, and $\varepsilon$, and we fix $\tau_s = 0.29$; the $t^{3/2}$ dependence arises from a Gaussian approximation to $F_s(q, t)$ with displacements that are intermediate between ballistic and Brownian motion (fractional Brownian motion) [100]. The $\alpha$-relaxation time $\tau_\alpha(r)$ as a function of distance $r - d$ from the NP surface is shown in Fig. 3.3 for two different interaction strength $\varepsilon = 2.0$ (strong interaction) and $\varepsilon = 0.25$ (weak interaction) and all NP sizes studied. As expected, for the $\varepsilon = 2.0$,
the relaxation time increases near the NP interface, while the opposite behavior occurs for weak polymer-NP interaction strength. The important observation is that, the change in the relaxation time relative to the pure polymer (whether it is increased or decreased) is smaller for smaller NP size. This effect can be quite substantial. For example, for the largest NP ($d = 10.0\sigma$) with $\epsilon = 2.0$, the relaxation time near the interface in roughly three orders of magnitude larger than the smallest NP ($d = 3.3\sigma$), and the separation of these scales only grows with decreasing temperature. The effect of NP size on relaxation is less pronounced for weak polymer-NP interaction strength.

In order to emphasize the effect of NP size on polymer relaxation, we focus on the first layer where the dependence of the relaxation time as a function of interaction strength is largest. Fig. 3.4 shows the relaxation time of the first layer as a function of interaction strength for different NP sizes. The sensitivity of $\tau_{\text{surface}}$ to the interaction strength increases as the NP size increases, further demonstrating that the effect of NP on the first layer increases for larger NP sizes.
Figure 3.3: The relaxation time of polymer as a function of distance from NP surface. The relaxation time of polymer layers for different NP sizes (circle for $d = 3.3$, square for $d = 6.6$ and triangle for $d = 10.0$) and the interaction strength $\epsilon = 0.25$ and $\epsilon = 2.0$. 
Figure 3.4: The relaxation time of the closest layer of monomer to the NP surface as a function of interaction strength for different NP sizes. The range of variation in the relaxation time as a function of interaction strength is more pronounced as the NP size increases.
3.4.2 Bound polymer relaxation and glass transition

The distance profile for the relaxation provides a detailed picture for the spatial variation of the dynamics, but such detail is not readily accessible to most experiments. However, when the relaxation time of the interfacial layer becomes significantly larger than that of the polymer matrix, earlier work has shown that the overall relaxation function does indicate a distinct relaxation process of the interfacial layer, commonly referred to as the “bound polymer”. The dependence of the gradient of relaxation on NP size suggests that the effects of bound polymer should be diminished for smaller NP, which we now consider. The intermediate scattering function $F(q_0, t)$ for the system as a whole for different NP sizes is shown in Fig. 3.5 for a reference $T$ and $\varepsilon$. The bound polymer contribution to $F(q_0, t)$ is apparent from the additional relaxation process at large $t$, most readily seen on a double-logarithmic scale. Such bound polymer is only apparent when the polymer-NP interaction strength exceeds that of the polymer-polymer interactions ($\varepsilon \gtrsim 1$). The data show that the amplitude of the bound layer contribution to $F(q_0, t)$ decreases for smaller NP. However, we should be careful to point out that this effect is primarily due to the change in NP concentration, not the NP size. We will address concentration effects later in the manuscript. For systems with a distinct bound relaxation, $F(q_0, t)$ can be described by including an additional relaxation process, specifically, [97,101,102]

$$F_{self}(q,t) = (1 - A)e^{-(t/\tau_s)^{3/2}} + (A - A_b)e^{-(t/\tau_\alpha)^{\beta}} + A_b e^{-(t/\tau_b)^{\beta_b}}, \quad (3.7)$$

Using this functional form, we extract the fit parameters, and we show the resulting bound layer relaxation time $\tau_b$ in Fig. 3.6. As expected from the relaxation near the NP surface (Fig. 3.4), $\tau_b$ decreases as the NP size decreases. In other words, smaller NP are less effective at creating a potentially non-equilibrium surface layer.

To highlight the effects of changes in the bound relaxation time that would be most experimentally overt, we evaluate the dynamical glass transition temperature $T_g$. Typically, the relaxation time is defined by the time at which $F(q_0, t)$ reaches a reference value. Accordingly, we define the overall polymer-NP relaxation time $\tau$ from $F(q, \tau)/A = e^{-1}$, i.e. the time when $F(q, t)$ has decayed by a factor of $1/e$ from its plateau value. Note that this value of $\tau$ is distinct from either $\tau_\alpha$ or $\tau_b$ obtained from the three-scale fit (Eq. 3.7). Thus, $\tau$ represents a weighted combination of the polymer matrix relaxation $\tau_\alpha$ and $\tau_b$. We define $T_g$ here by the temperature at which the relaxation time reaches a reference time 1000 in LJ units. We plot the values of $T_g$
Figure 3.5: The intermediate scattering function for different NP sizes the black, red and blue colors are related to system with $10.0\sigma$, $6.6\sigma$ and $3.3\sigma$ respectively. The lines are fitted curve with eq. 3.7. The presented data are for systems with interaction strength of $\epsilon = 2.0$ and temperature $T = 0.46$.

obtained from both the overall relaxation time $\tau$ and the matrix relaxation time $\tau_\alpha$ as a function of interaction strength for different NP size in Fig. 3.7. As the NP size decreases and the bound layer has a less substantial role, and the difference between the glass transition of the polymer matrix and that of the overall polymer-NP composite diminishes. For the smallest NP size (and smallest NP concentration) that we study, there is no discernable effect of the bound polymer on the glass transition, and $T_g$ is nearly the same as the pure polymer for all interaction strengths. We discuss effects of concentration in the following section.

3.4.3 Concentration effects

A potentially confounding effect in our results is that the amount of polymer is fixed for all NP sizes studied, and thus the NP concentration decreases as we decrease the NP size, which diminishes the relative amount of bound polymer. To separate the influence of this concentration change from that due to the changes in the NP size, we study the intermediate scattering function restricted to a shell around the NP of variable size, allowing us to mimic the effect of a variable
Figure 3.6: The bound layer relaxation time as a function of temperature for different NP sizes. The decrease in the bound relaxation time as the NP size decreases shows the decoupling of relaxation time between bound layer and polymer matrix is diminishing as the NP size decreases.

NP concentration. We use this method to examine a range of effective concentrations without adding the complication that would arise from chains that might bridge between NP at high NP concentration or small NP size, and we wish to separate such effects. The results for the relaxation of bound layer as a function of temperature for different effective NP concentrations $\phi$ is shown in Fig. 3.8 a. The data are all from the system with NP diameter $d = 6.6\sigma$. The bound layer relaxation time is entirely insensitive to the change in the filling fraction. In other words, the relaxation time of the bound polymer should not depend on concentration, provided the bound layers are not so close that they might interact with each other.

To better illustrate how concentration affects the relaxation and bound polymer properties, we calculate the bound polymer fraction $A_b$ as a function of NP concentration, Fig. 3.8 shows the effect of concentration on the bound polymer only alters the relative fraction $A_b$ of bound polymer, reflected by the increasing value of $A_b$ with concentration. This natural to expect, since as higher concentration, there will be, relatively speaking, less matrix polymer.

To compare the effect of NP size on $T_g$ without any change in NP concentration, we calculate
the dynamical glass transition temperature for different particle sizes \( d = 10.0\sigma \) and \( d = 6.6\sigma \) at the same filling fraction \( \phi = 0.0426 \).

Figure 3.9 shows \( T_g \) for the overall composite and polymer matrix for particle sizes \( d = 10.0\sigma \) and \( d = 6.6\sigma \) as a function of interaction strength. (Note that, for the smallest NP size, truncating the region over which we evaluate relaxation to achieve the same effective concentration results in too few monomers to obtain a reliable dynamical glass transition temperature.) The data show that \( T_g \) increases more rapidly with concentration for the smaller NP size than larger NP size. One interpretation is that the smaller NP size has a larger surface to volume ratio for the same NP concentration, and thus can have a larger impact on \( T_g \), even though the bound relaxation time \( \tau_b \) is smaller for smaller NP. An enhanced effect on \( T_g \) for smaller NP size has been observed experimentally [98]. For the concentration we show here (\( \phi \approx 5 \% \)), the scale of \( T_g \) changes is comparable to that seen experimentally.

Instead of calculating relaxation time and \( T_g \) for a shell around NP, corresponding to different concentrations, we performed simulations at fixed NP concentration \( \phi = 0.042 \) for all NP sizes. In this way, we can study the effects rising from overlap of “bound layers” of NPs; an example of these effects is bridging. Bridging happens when a polymer chain is part of two different NPs.
Figure 3.8: The bound layer relaxation time as a function of temperature for different filling fractions and bound polymer fraction $A_b$ as a function of NP concentration $a$ bound layer relaxation time. The inset is the value of $A_b$ for different NP density. The data is calculated at $\epsilon = 2.0$ for different densities $(0.012, 0.025, 0.030, 0.042, 0.060, 0.075, 0.090, 0.1)$.

bound layer. $\phi = 0.042$ is the concentration already used for the largest NP size ($d = 10.0$); for smaller NP sizes, we achieve the same concentration by reducing the number of polymer chains in the simulation box. For the smallest NP size, the surface-to-volume ratio of the NP is quite large; as a consequence, the separation between NP at this concentration is so small that the interfacial zones of NP overlap. The absence of a bulk-like matrix prevents the distinction between bound and bulk relaxation at this concentration for the smallest NP size. Quantitatively, this is manifest by the absence of a distinct bound relaxation of the type that was observed in Fig. 3.5. This complication does not arise for NP size $d = 6.6\sigma$. For that case, we extract the bound relaxation time, which we compare to the same NP size at lower concentration in Fig 3.6. The bound relaxation time for the two concentrations are nearly indistinguishable; this result is consistent
with the result in Fig. 3.6. Thus, provided the concentration is not so large that interfacial zones of NP overlap, the bound layer relaxation is concentration independent. At concentrations where interfacial zone overlap, there is no distinction into bulk or bound categories. This also means that the “cloaking” effect of the bound layer should be eliminated at high concentration; as a result, the effect of smaller NP on $T_g$ at the same concentration should become stronger, even though the effect on the interfacial relaxation time is weaker. The overlap of interfacial zones explains the linear increase in $T_g$ for the smallest NP, that is fundamentally different than the larger NP sizes where there is no overlap between interfacial polymers. The polymer matrix and overall $T_g$ are shown in Fig. 3.10.
Figure 3.10: The glass transition temperature for systems with different NP sizes and same concentration. (a) The glass transition temperature for the polymer matrix for different NP sizes with identical NP concentration. NP size $d = 3.3$ is not included, since matrix and interfacial relaxation are not distinct. The smaller NP has a larger effect on matrix $T_g$. (b) The glass transition temperature for the overall composite for all NP sizes with identical NP concentration. Again, the smaller NP has a larger effect; the behavior of the smallest NP ($d = 3.3$) is qualitatively different due to the overlap of the interfacial zones between NP.
3.5 Effects of NP size on structure of bound polymers

In this section, we aim to clarify the consequences of the NP on the orientation and chain dimensions of polymers approaching the NP interface. In particular, we shall show that changes to in the chain dimensions and orientation are entropically dominated. In other words, the changes we find are essentially independent of the strength of NP interaction. As a first step, we show the monomer density profile as a function of distance from the NP surface in Fig. 3.11 at a reference interfacial interaction strength $\varepsilon = 2.0$. The monomers form relatively well-defined layers near the NP surface, as known from previous work [97]. The amplitude of these density peaks increases modestly with increasing $\varepsilon$. Notably, the density of monomers nearest the NP surface is larger for small NP. A naive free volume argument would suggest that the relaxation should then be slowest near the smallest NP; however, as we have already demonstrated, this is the opposite of the actual behavior of the interfacial relaxation time, which decreases for smaller NP. This basic observation demonstrates the limitations of simple free volume ideas to predict the interfacial relaxation.

Numerous earlier works have examined how interfaces can alter chain dimensions [103–110]. Here, we focus on what role NP size plays, and to what degree the NP interactions are important. To quantify the shape of polymers, we use the gyration (shape) tensor (see 3.3.2). We evaluate the eigenvalues ($\lambda_1^2 < \lambda_3^2 < \lambda_2^2$) which define the overall chain radius of gyration $R_g^2 = \sum_i \lambda_i^2$. The differences in $\lambda_i^2$ are informative on the shape anisotropy of the chain. Figure 3.12 shows the $R_g^2$, along with the largest and smallest eigenvalues of gyration matrix as a function of distance from the NP center for all NP sizes studied for a representative strong and weak interfacial interaction $\varepsilon$. Approaching the NP interface, the value of the overall $R_g^2$ increases, indicated a modest expansion of chains near the NP surface. The increase of $\lambda_3^2$ and decrease of $\lambda_1^2$ indicates that the polymers closer to the NP are stretched along the longest principal axis, and compressed along the shortest principal axis. The net effect of the stretching and compression leads to a more anisotropic object. The amplitude of changes diminishes with decreasing NP size. All of these changes are independent of the polymer-NP interaction strength, and thus changes in the polymers structure near the NP interface is entropic origin, arising from the packing constraints at the NP surface.

It is natural to expect that the packing constraints at the NP surface that cause changes in polymer shape also give rise to changes in the orientation of polymers relative to the NP.
Figure 3.11: The monomer density profile as a function of distance from the NP surface for the three NP sizes considered here. Distance from the surface is defined by the distance from the center, minus the diameter of the inscribed sphere of the NP. The inset is the monomer density profile as a function of distance from the center of NP.

surface. To quantify the orientation of polymers, we evaluate the orientational order parameter defined by the angle $\theta_i$ between the chain center of mass position vector $\mathbf{r}_{cm}$ relative to the NP center and the semi-axis eigenvector $\mathbf{e}_i$ of the gyration tensor, associated with eigenvalue $\lambda_i$. Mathematically, the orientation is defined from the second Legendre polynomial

$$\langle P_2(\cos \theta_i) \rangle = \frac{1}{2} \langle (3 \cos^2 \theta_i - 1) \rangle$$

(3.8)

By construction, $\langle P_2(\cos \theta_i) \rangle$ ranges from $-0.5$ (orthogonal vectors) to 1 (parallel vectors), and $\langle P_2(\cos \theta_i) \rangle = 0.0$ when the vectors are uncorrelated (random relative orientation). Figure 3.13 shows the orientation of the eigenvectors $\mathbf{e}_1$ and $\mathbf{e}_3$, corresponding to the smallest ($\lambda_1$) and largest ($\lambda_3$) chain dimensions. Approaching the polymer matrix (large distance from the NP), $\langle P_2(\cos \theta_i) \rangle \approx 0$ for all orientations, demonstrating that chains in the matrix are randomly
oriented. The polymers close to the NP tend to align their long axis $\mathbf{e}_3$, with the surface of the NP, demonstrated by the decrease in $\langle P_2(\cos \theta_3) \rangle$, since alignment with the surface implies a perpendicular orientation relative to $\mathbf{r}_{cm}$. In addition, $\langle P_2(\cos \theta_1) \rangle$ increases near the NP surface, indicating that the smallest polymer axis weakly aligns with the center of mass direction (perpendicular to the surface of NP). Like the changes in chain size, the orientation effects are not dependent on the strength of polymer-NP interactions, and thus are similarly entropic in origin. Also similar to the chain size, the amplitude of the orientation changes diminishes for smaller NP. In the case of largest NP ($d = 10.0\sigma$) the edge length of the icosahedron is roughly equal to the end-to-end distance of polymers, so that polymer interface is locally flat. For smaller NPs, the facets do not promote alignment as strongly. This is probably not surprising, since in the limit where the NP size is comparable to the monomer size, there should be little to no effect on chain dimensions or orientation. These effects of size of the icosahedral NP on chain dimensions and orientation are similar to those previously reported for polymers near an ideal spherical NP [103,109,110].

When the NP size is similar to that of the chain size, the alignment of chains results in a localization of the entire chain near the NP interface. As illustrated in Fig. 3.14, the chains nearest the largest NP have nearly all their monomers localized at the surface. In contrast, Fig. 3.14 also shows the smallest NP, where surface chains have many monomers that extend beyond the NP interface.
Figure 3.12: NP effects on chain dimensions and orientation. (a) The radius of gyration $R_g^2$ increases for chains nearest the NP surface. Different NP sizes are distinguished by the smallest distance relative to the NP center for a given dataset. For each NP size, we show a weak polymer-NP interaction strength ($\varepsilon = 0.25$, triangles) and a strong interaction ($\varepsilon = 2.0$, circles); the similarity of these different strengths shows that the origin of changes is entropically dominated. (b) The largest eigenvalue of the gyration tensor $\lambda_3$ increases near the interface, while (c) the smallest eigenvalue of gyration matrix $\lambda_1$ decreases. Since $R_g^2 = \sum \lambda_i^2$, the increase in the overall radius of gyration can be attributed to increases in the longest axis of the chain.
Figure 3.13: Chains alignment with the NP interface. We evaluate the orientational parameter (Eq. 3.8) for the eigenvectors $e_1$ and $e_3$ of the gyration tensor, corresponding to the smallest and largest semi-axis, respectively. The data show that the longest axis aligns parallel to the interface (normal to the radial direction), and the shortest axis aligns normal to the interface. In other words, the inherently asymmetric chains align their longest axis with the NP surface. We show data for two different interaction strength ($\epsilon = 2.0$ circles, and $\epsilon = 0.25$ triangles) to show that the effect is nearly independent of polymer-NP interactions.
Chapter 3 - Diminishing effects of NP size on bound layer

Figure 3.14: The snapshots of MD simulation of systems with different NP sizes. For clarity, the polymer chains in contact with NP is shown. (a) The system with particle size $d = 3.3\sigma$. Most of polymer chains expands far away from the surface of the NP. (b) The system with NP size $d = 6.6\sigma$. Most of polymer chains are aligned with the surface and just a few of them expands far away from NP. (c) The system with NP size $d = 6.6\sigma$. Most of polymer chains are aligned with the surface and just a few of them expands far away from NP. This indicates that when the particle size is in the order of polymer chain size, they have enough space to align with the NP surface. For the NP size smaller than polymer chain, the polymer chain do not have enough room to align with NP surface.
3.6 Conclusions

We explored the effect of NP size on the structure and dynamics of interfacial polymers. We found that smaller NP have a smaller effect on the relaxation time of the interfacial layer. As a consequence, when substrate attraction is strong and bound polymer emerges, the separation of relaxation time between this bound layer and polymer matrix is less pronounced; this leads to a less effective decoupling of the NP from the polymer matrix. This may also be related to how NP size affects the structure of polymers near the interface. Polymers tend to align themselves along the surface for the largest NP size that we studied, resulting in chains that are localized at the surface. This alignment diminishes for smaller NP size, and surface chains tend to extend further into the polymer matrix, increasing the effective range of interactions between NP and polymer matrix. This shows that the relative size of polymer and NP plays an important role in the glass transition temperature and dynamics of polymer-NP composite materials.
Conclusions

In this thesis, we focused on the study of nanoparticle composite materials. We used molecular simulations as our primary tool to explore the behavior of these materials. We find that the size of NPs can have a dramatic change in the behavior of PNCs.

We first studied the self-assembly of DNA-functionalized NPs with tetrahedral bond symmetry (tetrahedral cages) and spherically DNA functionalized NPs. Among two very similar structures (cubic diamond and hexagonal diamond) possible with tetrahedral bond symmetries, just cubic diamond was preferred experimentally. We saw that the electrostatic interactions between second-neighbor interactions play an important role in determining stability of the lattice. The cubic diamond is more favorable than hexagonal diamond in large part due to the repulsion of tetrahedral cages is weaker for cubic diamond. This shows that modifying the second neighbor interaction can distinguish between two polymorphous structures.

We also studied the relative stability of the cubic diamond lattices as a function of NP size and DNA stiffness by calculating the Gibbs free energy. We saw that the entropy dominates the difference in the free energy of the lattice. We also studied the effects of rotational and translational degrees of freedom on Gibbs free energy and consequently on the stability of cubic diamond lattices. We found that increasing NP size increases the translational vibration of both tetrahedral cages and NPs. For the rotational degrees of freedom, the effect of increasing NP size has different effects on NPs and tetrahedral cages. The rotational vibrational amplitude
increases for the tetrahedral cages and decreases for NPs. We also show that the increase in
the vibrational amplitude (translational or rotational) decreases the Gibbs free energy. Thus,
the translational degrees of freedom and tetrahedral rotational degrees of freedom increases the
stability of lattice, and the NP’s rotational degree of freedom decreases the stability of cubic
diamond lattices as NP size increases. These finding can help to rationally design lattices with
control on their stability.

In the last part of our study of the cubic diamond lattice, we predicted the equilibrium
shape of crystallite. To do so, we used Wulff construction method that predicts the shape of the
crystallite based on the surface free energy of different plane symmetries. We found that the
specific functionalization method of NPs (tetrahedral cages) and DNA stiffness, can tune the
crystallization path of the lattice, to create different crystallite shapes. This is in contrast with
atomic systems, where the control of crystallite shape can be challenging.

In this work we have studied a perfect lattice without any defects. All of NPs have the same
size; and all of tetrahedral cages DNA set up to bond with one of the internal tetrahedrals in
the dodecahedron (NP). It can be useful to take to account the possible presence of defects and
study their effects on lattice behavior. In the case of CD lattice (important optical properties),
it is also useful to study effects of lattice dynamics (rotational and translational vibration) on
the optical properties of the CD lattices. Specifically, it could be interesting to see the effects
of lattice vibrations on the optical band gap. Here we just studied the crystallite shape cubic
diamond lattice with tetrahedral cage functionalize NPs; it is important to find a set of general
rules for functionalization of NPs (cages with different symmetries) to control the crystallization
pathways of these particles. Finally, we did not change the hybridization energy of DNA (used
the same DNA sequence for all systems), the change in the energy of lattices, in this case, for
different NP sizes was zero. Thus, the change in the free energy $\Delta G = \Delta E - T\Delta S + (P = 0)\Delta V$
is just a function of the change in the entropy $\Delta G = -T\Delta S$. The next step would be the study
of the effect of sequence choice on the lattice stability. Since the choice of sequence alters both
entropic and enthalpic parts of free energy difference $\Delta G = \Delta E - T\Delta S + (P = 0)\Delta V$, there
can be interesting effect as the temperature changes. We have calculated the dispersion relation
and dynamical matrix foe the CD lattice; these information can be used to extract many of
the mechanical and themodynamical properties of the lattices (eg. elastic constants and heat
capacity).
In the second part of this thesis, we studied the effect of NP size on the dynamics and $T_g$ of polymer materials with small amounts of embedded NP. We quantified the bound layer around the NPs by calculating their dynamics and structures, and we saw that the bound layer diminishes as the NP size decreases. The diminishing of the bound layer can possibly have a dramatic effect on the $T_g$ of the materials. The relaxation time of the bound layer around NP approaches the polymer matrix relaxation as the particle size decreases; this indicates that the decoupling of relaxation time between the polymer matrix and bound layer becomes weaker as the NP size decreases. We also see that at high concentration, where the majority of polymers are part of interfacial polymers, the $T_g$ has a much higher value, and increases linearly as a function of interaction strength. This behavior of $T_g$ is fundamentally different than lower concentrations, where there is a distinction between interfacial polymers and polymer matrix relaxation time. The $T_g$ increases linearly with the increase of interaction strength.

Furthermore, we study the structure of interfacial polymer chains. We see that the orientation of the interfacial polymer depends on the relative size of polymers and NPs. For the NP sizes close to the polymer size, the structure, and alignment of the polymer changes. The interfacial polymers tend to align themselves to the surface of NPs. The aspect ratio of polymers also increases. These alignments and change in the aspect ratio diminish as the relative size of NP to polymer chain decreases.

In this work, we used NPs with icosahedron symmetries. This work can be expanded to systems with NPs with different symmetries that can be dramatically different than icosahedron (e.g. cubic and rods) on dynamics and structure of the interfacial polymer chains. Specifically, it is interesting to see the effect of sharp edges and vertices in objects like tetrahedron and cube; or in general, an analytical study of the effect of surface curvature on the behavior of the bound polymer. As it was mentioned in the introduction part, one of the most important problem in PNC materials is the dispersion of NPs. Since DNA on the DNA functionalized NP can be modified with many chemical molecules, they can be an important candidate to solve poor dispersion of NPs in the polymer matrix.

At the end, we hope our findings help to create new design strategies for rational design of materials with desired properties.
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