FORCES AND INTERACTIONS BETWEEN NANOPARTICLES FOR
CONTROLLED STRUCTURES

by

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ABSTRACT OF THE DISSERTATION

Forces and Interactions Between Nanoparticles for Controlled Structures

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In recent years, structured nanomaterials have started to demonstrate their full potential in breakthrough technologies. However, in order to fulfill the expectations held for the field, it is necessary to carefully design these structures depending upon the targeted application. This tailoring process suggests that a feedback between theory and experiment could potentially allow us to obtain a structure as near optimum as possible. This thesis seeks to describe the theory and experiment needed to understand and control the interactions among nanoparticles to build a functional device for the efficient conversion of sunlight into energy. This thesis will discuss a simulation built from the existing theories explaining nanoparticle interactions and will present how its outcomes can be employed to describe real systems. The forces and dynamics of the nanoparticle system control the way their structure is formed. Thus, in order to understand and predict
the formation of organized nanostructures, simulation of forces and dynamics and their corroboration with experimental results are necessary. These simulations will be extended to more complex systems, and the results will be used to provide a basis for the design of a specific nanoparticle structure, namely a linked linear chain.

The envisioned application of the results achieved with the approach described is the design of a nanoparticle-based organic photovoltaic cell where linear chains of nanoparticles are tethered to the back of the device and then surrounded by a conducting polymer matrix to generate percolation pathways and improve light collection and scattering, and thus efficiency, of the device. To tether the chains in the cell, a foundation is needed to provide structure and control spacing. This foundation is designed and constructed by depositing gold nanoparticles on a substrate patterned using block-copolymer lithography to form a hexagonal array upon which the linear chains will be grown.
Acknowledgement and Dedication

I dedicate this thesis to my parents, George and Ann Mark, who have given me so much love and assistance through the years. I also dedicate it to my fiancé Kathryn Dorst, who has been by my side, helped me through all the rough parts of achieving this, and done so incredibly much for me.
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1. Introduction

1.1 History of Nanoparticles

Colloidal gold has been used since ancient Roman times. It was originally employed to stain glass but it was also adopted by Hindu medicine to prepare potions. In the middle ages the properties of “aurum potabile” were investigated. This was a colloidal form of gold, favored by alchemists and early chemists for its numerous properties. In 1665 gold purple, namely a solution of colloidal gold and stannic acid, was described by Andreas Cassius. This again was used for coloring glass, but its colloidal nature could not be recognized.

It has been said that the birth of nanoscience happened in 1847, when Michael Faraday discovered that the optical properties of gold colloids were different from those of bulk gold. This colloidal gold had been used for centuries as a method of staining glass but it was Faraday’s work that elucidated its unique optical properties. Faraday surmised that the coloration and behavior of the colloidal solution were due to the small size of the gold particles. The first colloidal gold in dilute solution was prepared by Richard Zsigmondy in 1898 [1]. This was to lead to most of the synthetic techniques for colloidal gold nanoparticles (NPs).

1.2 Modern Uses of Nanoparticles

In the modern era, the uses of colloidal gold have multiplied greatly. Among different applications of these particles, one of the primary is as tagging agents [2]. They have been employed to tag antibodies, antigens and other biological molecules to allow their detection by Transmission Electron Microscopy (TEM) [3]: By tagging the
biomolecules with NPs of different sizes, one is able to discriminate among the different entities. The NPs have also been applied as carriers for molecular cargos. NPs can be functionalized with fluorescent dye molecules and specific targets as a means for imaging and quantification [4]. NPs have also been experimentally used as medicinal treatments [5]. NPs can be capped with cell penetrating moieties and small-molecule drugs by covalently binding them to linking units such as peptides or DNA chains that get enzymatically cleaved within the target cell and allow for the release of the drug in the cytoplasm [6].

1.3 Desired Uses of Nanoparticles

One of the goals of nanotechnology is to make NPs more widely applied in drug delivery, imaging, and energy generation. Therapeutic drugs can be carried in a “cage” of linked NPs, in an assembly that is then digested by the body or the cell with subsequent release of the active agent [7]. Another possible application is the use of tagged NP dimers to follow macromolecules in the body via surface enhanced Raman spectroscopy, for example to better understand metabolic processes. These Raman active dimers could also be loaded with antibodies targeting surface proteins of specific cancer cells, to improve early detection and targeted therapy [8].

Other desired uses for colloidal gold NPs include the application as charge collectors and active sites for solar photovoltaic systems [9]. One proposed system uses the surface of the gold NPs as the binding site for the photosensitive molecules [10]. This system utilizes the large surface area provided by low-density assemblies of the colloidal particles to increase interaction rate and conductivity. By tuning the size of the particles it
is possible to induce the emission of scattered light that is then absorbed by the photoactive molecule positioned in close proximity to the scattering centers. Another system places the photoactive molecules in the region of maximum field enhancement induced by the presence of gold NPs [11]. This field enhancement is used in conjunction with molecules capable of active charge separation, necessary to reduce the locale drainage of charges. Closely spaced NPs, owing to their high conductivity, are capable of forming a conductive path to the electrode. The major difference between these approaches is the separation between the particles. In the first one, the particles are touching, to provide as much surface area and conductivity as possible. The second approach utilizes a separation of about one nanometer to maximize the field enhancement and minimize the loss of conductivity.

Organic photovoltaics (OPVs) can take great advantage of the benefits offered by plasmonic nanoparticles. Not only is the surface area enhanced, but the light is scattered more efficiently into the device, allowing it to capture more of the incoming radiation. In addition, if the material responsible for exciton generation is placed near the surface of the nanoparticles, the local field enhancement can be utilized, potentially giving an advantage over devices that do not utilize this effect. The addition of nanoparticles does not hamper the ease of processing that OPVs provide and together with their benefits, a combined plasmonic nanoparticle/organic photovoltaic device is a strong platform for large scale, high efficiency, and low cost photovoltaics.

The design of an effective photovoltaic device incorporating nanoparticles would have a number of particles linked closely together but well separated from other clusters of particles in order to take advantage of both effects. These clusters would have to
preserve the behavior of individual nanoparticles, and expose as many of them as possible to the surrounding media and the incoming light. This approach would lead to a device structure that has now started to appear in many photovoltaic structures: Pillars of active material electrically and mechanically tethered to a conductive substrate [12]. The approach including vertical pillars combines the ideal properties typical of local field enhancement with the ability to target the placement of the active material within the enhanced fields and to form conductive pathways within the material, allowing to exploit the interaction of the incoming photons with the active polymer layer.

1.4 Need for Designed Structures

Both biology- and energy-related applications require a designed structure. The structures can vary significantly, from cages or dimers that have been proposed for use in the medical field, to crystalline, glassy or fractal structures needed to maximize photon-molecule interactions and charge conduction needed in the energy field [13]. Whereas top-down approaches have been employed to some extent [14], the wide use of bottom-up techniques is still lacking. Bottom-up approaches for the synthesis of these structures require either the fine-tuning of the NP-NP interactions to produce the desired structure, the careful control of the kinetics to stop the growth at the desired stage, or the use of directed links between NPs [15,16]. Linking moieties can be of various forms, including complementary nucleic acid strands or dithiolated ligands [17,18]. It has been shown that it is possible to create simple three-dimensional structures using nucleic acid strands [19]. To form these structures in high yield the NPs need to assemble directly into a final crystalline structure without the need of post-synthetic processing, such as annealing or thermal agitation, due to their limited ability to remain functional if heated or cooled
significantly [20]. Although possible, the assembly of NPs in arrays using oligonucleotides is relatively complex, and most likely not scalable. On the other hand, the use of smaller molecules such as dithiolated linkers, despite easier to handle from a synthetic point of view, cannot take advantage of the intrinsic self recognition typical of DNA and thus does not have any intrinsic structural predictability.

1.5 Ways to Obtain the Desired Structure

As a consequence of the inability of thermal treatments to optimize the NP structures post-synthesis, the geometry of the assembly needs to be “right the first time”. There are several ways to achieve this goal: Accurate prediction of the resulting structure [21] and single construction pathway [22] represent two key approaches. It is also possible to isolate the desired structures by purification methods [23]. Purification protocols are often possible but many times they destroy the structure of interest. If the synthesis is done in solution, salts or pH changes can be used to selectively precipitate out unwanted aggregates while preserving the desired ones [24]. This procedure reduces the total yield but can provide a straightforward method to obtain the desired product in high purity. Single construction pathways are useful for producing simple shapes but as the complexity of the shape increases the complexity of pathway design similarly increases [25]. In some instances, computer simulations are required to predict the synthetic pathways. Computational time is generally less expensive than the overall laboratory costs and many possibilities can be tried in silico without the use of reagents.
1.6 Need for Simulation to Elucidate Structure

As computational time is less expensive compared to other methods, it seems preferable to develop methods *in silico* first then confirm them in the laboratory. This experimental methodology is already used in the pharmaceutical industry for designing drugs. The situation in the pharmaceutical industry parallels the one in nanoscale self-assembly. NPs are not as expensive as the precursors used in the pharmaceutical industry however more and more experiments are being carried out involving expensive substrates or custom biomolecules (e.g. recombinant DNA), which increase the overall cost. In other fields such as energy collection and catalysis, the surface molecules and substrates used can be very expensive as well. For the case of NPs used in combination to biological systems and those used for energy, the time involved in experimental setup and execution can be significant. By running a range of likely candidates *in silico* it is possible to reduce the need for a host of experimental trials to discover the best method for the creation of the desired structure.

Another major benefit of *in silico* experimentation is the ability to discover structures that would not be discovered through direct experiments. These structures usually show unusual behaviors that arise from carefully balanced interactions that would not occur commonly or that are too short-lived to be isolated in the laboratory. In systems that have charged surface groups, it is possible to have an attractive interaction within a certain range of distances. This means that there is a stable distance at which the forces between particles are zero. This point is a stable minimum of the system at which particles can aggregate. By changing the ion concentration and dielectric constant of the solvent, the minima can be moved to bring the particles within a distance such that a bridging
molecule can link them. The ion concentration or dielectric constant can then be changed so that there are no minima, with a wholly repulsive force. This would force unlinked particles to separate, halting aggregation and structure formation within a relatively short time frame. This ability to repeatedly initiate and quench aggregation through the concentration of ions or change in pH could be used to build NP aggregates of very well defined sizes in much the same way that polymerization is done to synthesize polymer chains of varying lengths and polydispersity.

Other applications deal with systems of particles of dissimilar sizes. These systems have a very complex behavior that depends on the type and strength of interactions between the smaller particles and between the smaller particles and the larger ones. These forces determine the coverage and inter-particle linking of the large particles by the smaller counterparts and influence the activity of the resulting system.

1.7 Statement of the Problem

There is very little understanding of the whole picture of nanoparticle assembly. A lot of work has been done on elucidating convenient approximate equations for individual forces and much experimental work has been accomplished with little to no concrete knowledge of the forces involved beyond intuition. In simple terms, much of the assembly work reported in the literature has so far been carried out with a trial and error approach.

These challenges come into play when designing a photovoltaic device that takes advantage of the unique properties that gold nanoparticles possess. Thus, the problems this work seeks to address are three-fold:
1) How do the forces at play determine the final structure of assembled nanoparticles?

2) How can we control these forces to build a tailored structure for a particular application?

3) How can we incorporate the nanoparticle structure into the larger framework of a photovoltaic device?

The first problem requires to take into account the whole body of work relative to the description of the forces and to codify it with the goal of modeling the time evolution of a system of particles. The second problem brings the focus back to experimentation, and seeks to understand the predictions made from the model and to turn them into procedures for building a structure which is envisioned as useful as part of a nanoparticle-based organic photovoltaic cell. The third problem addresses the issue of incorporating these structures into an organic photovoltaic cell, and how the construction of that cell might be accomplished.

1.8 Objectives

The objectives of this thesis are three-fold:

i) To design accurate and fast Molecular Dynamics (MD)-like simulations to predict the dimerization of nanoparticles as a first step towards more complex structures.

ii) To extend these simulations to charged nanoparticles and thereby to explore the formation of linear chains of nanospheres which can be used as light harvesting centers in an organic photovoltaic.
iii) To use the knowledge gained to design a prototype for a gold nanoparticle based organic photovoltaic device and to experimentally complete the first steps in realizing that device.

1.9 Method

To tackle these objectives, a combination of experimental and theoretical work must be carried out. A preliminary computational model, encompassing some but not all of the forces, must be developed first. This model will seek to provide all the interactions, both between two nanoparticles and between the nanoparticles and their environment, which are required for simulating the formation of nanoparticle dimers and larger assemblies. A series of simulations will be run, and the results from the simulation will be restructured into a useful form that is comparable to experiments. The outcome of this study will be the description of the shape and the size of each assembled nanostructure, and the comparison of the results to microscopy experiments. The model will then be expanded to a wider range of cases by including a numerically approximate force that takes into account the interaction between charged particles in solution. This model will be used to make predictions about the formation of linear chains of nanoparticles. The forces at play during nanochain formation predicted using the model will be used to guide the experimental work to produce them. These chains of nanoparticles are envisioned as one building block of a device, but a foundation has to be laid before these chains become useful. Hence, a nanoparticle-patterned substrate will be created upon which the nanoparticle chains will be vertically grown using each nanoparticle on the substrate as a seed. The resulting system of vertical nanochains will be embedded with a conducting polymer thus generating a prototype organic photovoltaic device.
The thesis has been built by incorporating manuscripts that have been published or have been submitted for publication. Each of the following chapters will focus on solving one of the aforementioned tasks by reporting the relevant manuscript in its entirety. Each manuscript contains: an introduction to the task, which details previous work as well as the shortcomings that need to be addressed; the methodology used to solve it, including any experimental or theoretical framework or set up; the results of the work, with the data and a discussion of the outcome with reference to the task being investigated; and a conclusion, giving an overview of the results and looking forwards from there.
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Understanding nanoparticle assembly: A simulation approach to SERS-active dimers

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Abstract:

We report herein on a model built to analyze and optimize nanoparticle (NP) dimer formation. The rationale for this work stems from our interest in building effective NP dimer-based tagging systems for surface enhanced Raman scattering (SERS)-based detection of cancerous cells. This model takes into account the behavior of the NPs in solution and the molecules on their surface, to provide a coherent and physically constrained system. The kinetics of formation of dimers and larger assemblies are investigated on suspensions of varying concentrations through a coarse-grained \textit{ad hoc} computer simulation based on a Molecular Dynamics-like approach. Several different effects are considered, including the behavior and interaction of surface molecules, the interactions between the latter and the NPs, and between NPs. The surface molecules are treated as rigid structures that can occupy specific binding sites. A Brownian model is used to both integrate the particle trajectory and provide random thermal forces. These systems show a NP concentration-dependent behavior with respect to the formation of
dimers versus larger assemblies over the timescale of the simulation. The simulations also indicate that these systems form low-density aggregates as opposed to the close packed formations reported previously. A dependence on the properties and the concentration of the linkers is also demonstrated.

1. Introduction

The bottom-up synthesis of gold nanoparticles (NPs) has been the focus of intense research in the past few decades and has led to the discovery of several fundamental synthetic methods that are widely used today [1-4]. A new paradigm shift has however been set in place in the last few years, when it has been recognized that is no longer only important to synthesize the NPs, but it is even more fundamental to impart them a pre-programmable function. Important applications include for example plasmonic sensing, photonic devices, and, more recently, cell tagging systems and drug delivery tools [5-8]. The advantage of using gold NPs for these applications stems from their ease of synthesis [1], stability [9], and non-cytotoxicity [10], and from the possibility to easily tune their surface properties via simple place exchange reactions [11], where capping agents adsorbed or bound to the NP can be replaced by ligands present in solution. In addition, gold NPs with diameters between 10 and 50 nm are ideal for plasmonic applications that take advantage of their intense plasmon band centered at 520 nm [12].

Despite the presence of numerous approaches, the most common method for the synthesis of gold NPs within this size range exploits the reduction of gold by citrate, resulting in systems with tunable size and a surface monolayer of citrate ions. The citrate layer is typically removed by thiol-functionalized molecules via ligand exchange, a reaction that has been fairly well understood, and is primarily due to the higher affinity of
thiols for gold as compared to the loosely bound citrate moieties [13]. In addition, by utilizing a molecule with multiple thiol groups, two or more NPs can be linked together, forming NP assemblies. The number of NPs that constitute each assembly depends on several factors [14], among which the most important are the concentration of the NPs and of the dithiolated linker. The ability of linking plasmonic NPs in assemblies with predictable size and shape and pre-programmable function paves the way for a completely new set of devices and applications, and is especially important for effects that take advantage of near-field enhancement [15-17].

1.1 Bottom-up Synthesis of Dimers

The simplest form of NP assembly is the dimer. Although some methods exist that are utilized to produce this structure, the use of dithiolated linkers to bring the NPs together and lock them in place is most likely the ideal one because it doesn’t rely on the presence of salts (e.g. NaCl) to bring the NPs in close proximity. In addition, the use of rigid dithiolated linkers allows the NPs to be held at a distance short enough to induce near field enhancement effects within the intermetallic junction [18]. This field enhancement has been reported to reach 11 orders of magnitude for closely spaced NPs (i.e. 1-2 nm) [19]. Any molecule placed between the particles experiences this enhanced field, and near field techniques such as surface enhanced Raman spectroscopy (SERS) can take advantage of this phenomenon [20].

Raman spectroscopy provides the characteristic fingerprinting of a molecule, similarly to what observed for NMR spectroscopy, and complements infrared
spectroscopy for molecular characterization [21]. Raman is a useful detection technique due to its wide applicability, owing to its stability within a broad range of experimental conditions, and its insensitivity to atmospheric oxygen and moisture. Despite these advantages, Raman spectroscopy is limited in its detection capability by its typically low cross sections that bring the detection limits to a mere 1 mM [22], and hamper its use for detection and tracking of biomolecules typically found in biological fluids at concentrations well below this limit [23]. This drawback can be overcome in the presence of noble metal NPs, where the field enhancements brought about by the metallic surface can be exploited for SERS-based detection approaches [24]. Typically, SERS based methods have been relying on indirect biodetection, where NP dimers functionalized with specific targeting moieties have been used for tagging, and the SERS signal of specific Raman active dyes bound to the NPs have been used to indirectly identify the presence of the analyte, similarly to what can be achieved with fluorescent dyes such as FITC [25]. We have previously demonstrated the usefulness of NP dimers as tagging systems for heterogeneous protein detection [26], and their applicability as cell tagging systems can be readily envisioned, hence our motivation in understanding how to efficiently build these tagging tools.

Short dithiolated molecules with rigid structures and an inherently large Raman cross section, such as a dithiolated phenyl- or biphenyl- moieties, represent the ideal reporting system that can be exploited to build SERS-based tags. Following this approach, the NPs can be held at a surface separation ideal to maximize the field enhancement between the particles (typically 1-2 nm). Coalescence is usually reduced or entirely avoided by passivating the surface of the NPs with polyethylene glycol (PEG), known to quench
aggregation. Compared to larger nanostructures, dimers provide the largest per-particle field enhancements [27]. These reasons alone could easily justify our interest in understanding the phenomenon of dimer formation, although the more broadly addressable phenomenon of NP assembly and polymerization could be also considered.

The bottom up synthesis of dimers in a controllable way is a task not easily achievable, and studies addressing the phenomenon have started to appear in the recent years [28-30]. Generally the most common approach to dimerization involves the control of NP aggregation through salt [31], or takes advantage of the competition between good and poor solvents [32], especially for anisotropic systems such as gold nanorods. In some instances however, spherical NPs have been dimerized via use of rigid dithiolated linker molecules, which hold the surfaces of the NPs at a well-defined, relatively constant separation. The linker, and thus the separation, can be tuned to provide maximum field enhancement and thus highest SERS signal intensities. The simplest mechanism of dimer formation in solution is to saturate the surface with the linker molecule, removing all the surface charge and allowing diffusion and van der Waals forces to drive the system to assembly.

The method described above is relatively rapid and has been historically exploited for NP assembly, but it is often too fast for reliable formation of dimers without the appearance of larger aggregates. In the absence of quenching, the final reaction product will be a mixture of dimers, trimers, tetramers, and larger aggregates, and the isolation of the dimer would thus require tedious purification and enrichment procedures. The formation of these large assemblies of NPs has been previously studied using computer simulations; however the analysis was limited to large aggregates with long-range
structure and fractal geometry [33]. To avoid the formation of such systems, proper control must be exerted on NP concentration, linker concentration and reaction time. The quenching ligand can be a thiolated charged molecule that prevents the NPs from approaching due to electrostatic repulsion [34], or a large thiolated brush molecule (such as PEG), that provides a physical barrier to dimerization by forcing the surfaces to be at a distance longer than the length of the linker [35], and relying on Brownian motion to move the particles apart. In both cases, very few surface molecules are required to turn the net force from attractive to repulsive.

The goal of the dimerization reaction is thus to maximize the number of dimers and to minimize the number of larger structures. Due to the small variation in hydrodynamic radius and hence mobility, the purification of dimers from solutions containing a mix of monomers, dimers, trimers, and larger aggregates is a challenging task [36]. Therefore, by maximizing the number of dimers in the crude reaction mixtures, a simpler and faster approach for the development of highly effective tags could be achieved.

There are three major control variables used to reach this goal: the concentration of the NPs, the concentration of the linker, and the time allowed for the dimerization to occur. A crude simplification of the method would entail the saturation of the NP surface with linkers, reducing the system to two free variables, NP concentration and reaction time. Experimental systems are charge stabilized, and the removal of a significant amount of the surface charge is required to make the system unstable. Even then, the aggregation is limited by nanoparticle diffusion, which at nanomolar concentrations of large, heavy gold nanoparticles is a slow process. These two delays combine to suggest the likelihood that surface saturation is nearly complete before significant dimerization happens. From
the methodology of [37], a calculation for the monolayer time can be derived for spherical particles. Following this framework, a time of $2.5 \times 10^{-4}$ seconds is found for monolayer formation of linker/brush. A further reduction in complexity can be achieved by fixing the reaction time at a constant value and allowing the NP concentration to vary. This is simple to achieve in a numerical simulation, while in a laboratory setting, varying the reaction time while holding the concentration constant would be easier to implement. The issue is to implement a model that can give reliable numerical results that can be easily used on the bench-top. To this end, we developed a numerical simulation that follows the dynamic behavior of the NPs in solution as the dimerization process occurs.

1.2 Modeling the Bottom-up Synthesis of Dimers

The evolution of the system was principally studied varying the concentration of NPs [37], as the concentration of linkers was held fixed relatively to the number of particles. The rate-determining step of the process was the frequency of NP encounters, and thus it was related to the initial concentration of NPs in solution and their diffusivity. Our simulations used a model that encompasses minimal assumptions and includes only physically controllable parameters. In other words, our approach was targeted toward the generation of a set of output parameters that can be easily monitored during an experiment (e.g. the populations of the various assemblies).

Despite the fact that the evolution of the system was based on the variation of the NP concentration, our simulations not only needed to incorporate the behavior of the NPs in solution but also that of the molecules on their surface. To this end, a mixed coarse-grained Molecular Dynamics (MD) simulation approach was utilized. This approach
combines many of the strengths of Molecular Dynamics and applies them to the modeled system using NPs as the basic units instead of atoms. Only at this level the dynamical behavior is then studied. In addition, the model also incorporates Monte Carlo behavior at the surface molecule level. This approach was chosen to provide a realistic description of the surface of the NP. In NP-NP interactions the surface molecules play a fundamental role; hence a model that accurately depicts the behavior at the surface is one step ahead towards a thorough understanding of the entire system.

1.2.1 Forces

The simulation looks at the interactions between NPs with respect to van der Waals forces [38], as well as forces that arise from the molecules on the surface. These surface molecules provide two forces critical to dimer formation: a short-range repulsive force that prevents NPs from coalescing [39], and a bonding force between the NPs via a dithiolated small molecular linker, which is modeled following Hooke’s law. The behavior of these molecules on the NP’s surface is considered to be dynamic, with molecules adsorbing and desorbing as time progresses. This is implemented as a system where the surface is equilibrated with the solution before the simulation is run, and then the molecules are free to adsorb or desorb as the simulation conditions change. The molecules are added to the surface in a way where the probability of a surface site becoming occupied is proportional to the local concentration of molecules, with desorption being determined by the energy required to remove the molecule from the surface. The simulations were run on model solutions of gold NPs, for an amount of time covering 0.625 ms, with the initial concentration varying from 1 to 256 times that of a standard initial concentration of $4.8000 \times 10^{-10}$ NP/nm$^3$. The long simulation time as
compared to strict MD approaches provides an ample time series for kinetic and kinematic analysis of NP assembly. The NP concentration was chosen to coincide with that commonly used in our bench-top experiments. The NPs being investigated are spherical and have radii normally distributed with a mean of 20 nm and a standard deviation of 1 nm. This size was chosen as it matches closely with the particle sizes obtained using the Turkevich method for citrate-capped gold NPs. This range of concentrations was used to investigate the rate of formation of dimers as a function of the initial concentration of the NPs.

1.2.2 Nanoparticle Concentration

It was desired to find a concentration at which the formation of dimers was enhanced and the generation of byproducts (i.e. trimers, tetramers, and larger aggregates) was suppressed. The local and long-range structures of NP aggregates were extracted from the simulations, along with the relative population of the system in terms of monomers, dimers, trimers, and larger aggregates, and the kinetics of the formation of such aggregates. The results obtained from the simulation were then utilized to design experiments that produce populations of assemblies with the desired size, that enable one-pot syntheses, and that minimize the amount of post-synthetic separation and purification. This information, combined with extension of the simulation to large systems, will allow for more reliable creation of nanostructures and a better understanding and control of the critical pathways and mechanisms.
2. Methods

2.1 Theoretical Basis: Forces

The simulations use a MD–like basis to model the dynamics, applying many of the principles of molecular dynamics, but using NPs as the smallest units, instead of atoms. Three primary interactions were considered: van der Waals (vdW) forces, surface brush interpenetration and compression forces, and linker’s elastic forces.

Van der Waals forces are calculated from an integration of the per-atom interaction over the volume of each NP [38]. This calculation results in Equation 1, the potential between two NPs of radii \(a_1\) and \(a_2\) as a function of the distance \(r\).

\[
U_{vdw} = \frac{A}{3} \left[ \frac{a_1 a_2}{r^2 - (a_1 + a_2)} + \frac{a_1 a_2}{r^2 - (a_1 - a_2)} + \frac{1}{2} \ln \frac{r^2 - (a_1 + a_2)}{r^2 - (a_1 - a_2)} \right] \tag{Equation 1}
\]

Surface brush forces arise from the interaction between molecules attached to the NPs. These interactions are considered within the framework of the extended-Bagchi (EB) theory, reported in the work of Lozsán et al. [39]. Herein, the interaction force from the surface molecule is calculated under two circumstances, as depicted in Figure 1: interpenetration and compression. In the interpenetration regime, represented in Figure 1a, the potential is calculated from the relative overlap of the surface brushes, taking into consideration the volume of both the brush and the solvent, and the solvent-brush and brush-brush interactions. In this regime the molecules interdigitate, increasing the concentration of brushes in the region of overlap. If the brushes are in a good solvent, solvent molecules congregate in the volume of overlap, forcing the NPs apart. If the
brushes are in a poor solvent, the effect is reversed. At some point in the approach of the particles, there is no more volume that can be occupied by the brushes thus they must compress in order to occupy less volume, as seen in Figure 1b. This behavior results in a repulsive force as the brushes lose conformational space and is similar to what observed in elastomers, which utilize the same mechanism to store energy.

![Figure 1. Cartoon representation of brush interpenetration (a) and compression (b)](image)

The critical parameters for this theory are the size of the NPs and the exact form of the radial brush density function. Simplified models typically use a constant radial density [40]. A constant radial density is generally not a good representation for molecules extending outwards from a spherical surface due to the radial vectors diverging from one another, the density of which falls off as $1/r^2$. In addition, when coupled with the Derjaguin approximation [41], a constant radial density model can lead to large errors in the calculated interaction potential [42]. The Derjaguin approximation models the surface of a sphere as a series of concentric rings. This simplification, coupled with a constant brush density, leads to an incorrect calculation of the energy of overlap. The energy calculated is too large and has the wrong functional shape when compared to the experiment. The use of the EB theory solves the problems of the Derjaguin
approximation by calculating the overlap directly via integration. The EB theory thus requires an accurate brush density function to encapsulate the behavior of the NPs as the distance decreases and the brushes interact. Figure 2 shows some commonly used brush density functions, along with the function used in this work: $1/r^2$. The behavior of well solvated alkanes on a spherical surface is well mimicked by a $1/r^2$ density decrease [43-45], where the brush density drops off as the distance from the surface increases.

![Graphs of the radial distribution functions](image)

Figure 2. Graphs of the radial distribution functions for (a) constant, (b) linear, (c) pseudo-homopolymer, (d) pseudotail and (e) $1/r^2$ functions.

Linker forces are those arising from a linker molecule on the surface of the NP. This linker covalently bridges the NPs, giving rise to a tightly bound system. The linkers behave like surface brushes until they come into contact with another NP. When the distance between the surfaces of the two NPs becomes shorter than the length of the linker, the NPs become bound within a short period of time. The linker is chosen to be slightly shorter than the brush, such that the particles have “soft” surfaces that can compress as the particles close to within linking distance. The molecules simulated are
chosen such that under compression the brushes will maintain a surface distance less than the length of the linker, allowing linkage to occur. This is needed to prevent NP-NP coalescence, which would disrupt the simulation and result in unphysical particle motions. The link is treated as a Hookean spring for force calculation purposes, with the spring constant values derived from the bond energies reported by Lim [46]. The linker is mutable and will detach from a NP if the force on the linker overcomes the binding energy. The linker used in the simulations is biphenyl-4,4’-dithiol (DBDT). It is a dithiolated linker comprised of two phenyl groups, as shown in Figure 3 and was chosen because of its length and rigid structure that can keep the NPs at a fixed distance, thus enabling the formation of hot-spots, useful for applications taking advantage of surface enhancement effects.

![Figure 3. Biphenyl-4,4’-dithiol (DBDT), the model linker used in the present work.](image)

2.1.1 Conversion of Potentials into Forces

With the exception of the linker force, all the interactions are calculated as potentials. Thus they must first be converted into forces to be used in a dynamical calculation, and this can be accomplished by calculating the potential at three points centered on the point of interest and separated by a small amount: \( R-\varepsilon \), \( R \), and \( R+\varepsilon \), where \( \varepsilon \) is a small value compared to \( R \), chosen as \( 10^{-6} \times R \). Two slopes are found and the average is taken to calculate the force at a distance \( R \) using \textbf{Equation 2}:
The forces calculated from each of the interactions are summed and used to determine the trajectories of the NPs. The integration method used for the dynamics of the system was first elaborated by Allen [47], and is described in **Equation 3**, where \( \mathbf{r}(t), \mathbf{v}(t) \) and \( \mathbf{a}(t) \) are the kinematic parameters at time \( t \), with time step \( h \). \( \mathbf{B}_r \) is the Brownian kicks to positions and \( \mathbf{B}_v \) is the Brownian kicks to velocity. \( \beta \) is the viscous drag coefficient and \( \gamma \) is equal to \( \beta \times h \), \( c_i \) are the coefficients in the kinematic equations describing the relative intensity of each term in calculating the new kinematic parameters, \( k_B \) is the Boltzmann constant, \( m \) is \( \beta \times h \), the mass of the nanoparticle, and \( T \) the thermodynamic temperature. \( \rho, \sigma_r, \) and \( \sigma_V \) represent instead the defining parameters for the bivariate Gaussian distribution describing the distribution and covariance for the Brownian kicks in position and velocity.

This method incorporates an implicit solution whose contributions to the system are viscosity and Brownian forces. Other solution-mediated forces, such as those arising from charge-charge interactions, are not included as the particle is considered to have a charge-free surface. The Brownian forces are included through impulses to the position and velocity of the particle at each time step, which are drawn from a bivariate Gaussian distribution with parameters shown in **Equation 4**. The equations of motion include these random kicks as well as constants that derive from the viscosity of the solvent, shown in

\[
F = \frac{-S_1 + S_2}{2}; \\
S_1 = \frac{U(R) - U(R - \epsilon)}{\epsilon}; \\
S_2 = \frac{U(R + \epsilon) - U(R)}{\epsilon} \quad \text{Equation 2}
\]
Equation 5. The equations of motion used are derived from those described by Beeman [48].

\[ r(t_{n+1}) = r(t_n) + c_a h v(t_n) + c_b h^2 a(t_n) + c_c h^2 a(t_{n-1}) + B_r \]

\[ v(t_{n+1}) = c_d v(t_n) + c_e h a(t_{n+1}) + c_f h a(t_n) + c_g h a(t_{n-1}) + B_v \]

\[
\begin{bmatrix}
\sigma_r^2 &=& -\frac{k_b T (-2 h \beta + e^{-2 h \beta} - 4 e^{h \beta} + 3)}{m \beta^2} \\
\sigma_v^2 &=& -\frac{k_b T (-1 + e^{-2 h \beta})}{m} \\
\rho \sigma_r \sigma_v &=& \frac{e^{-2 h \beta} k_b T (-1 + e^{h \beta})}{m \beta}
\end{bmatrix}
\]

\[
\begin{bmatrix}
c_a &=& c_1 \\
c_b &=& c_2 + c_3 \\
c_c &=& -c_3 \\
c_d &=& c_0 \\
c_e &=& c_2 - \frac{c_0 c_3}{c_1} \\
c_f &=& c_1 - c_2 + 2 \frac{c_0 c_3}{c_1} \\
c_g &=& -\frac{c_0 c_3}{c_1} \\
c_0 &=& e^{-\gamma} \\
c_1 &=& \frac{1-c_0}{\gamma} \\
c_2 &=& \frac{1-c_1}{\gamma} \\
c_3 &=& \frac{1-c_2}{\gamma}
\end{bmatrix}
\]

2.2 Boundary Conditions

The simulation is initialized with 5000 particles randomly located in a box to achieve the total desired concentration. The solution is also given an initial concentration of brushes and linkers. The surfaces of the NPs have sites where the molecules can bind. The NP surfaces are equilibrated with the molecules in solution and the simulation is then run forward in time.

Several boundary conditions were considered, including cubic, truncated octahedral, spherical, and open. The cubic was rejected as it does not observe full rotational
symmetry and is a large departure from a spherical droplet, whose behavior the simulation wants to capture [49]. The truncated octahedral boundary condition was rejected as it is complex to implement and does not observe full rotational symmetry, despite being closer in shape to a spherical drop than the cubic condition is [49]. A spherical boundary condition was rejected primarily due to the difficulty in the conversion from \( \mathbb{R}^3 \) to the surface of a sphere in \( \mathbb{R}^4 \) and back and the difficulties in data processing and interpretation that such conversions would likely introduce [50,51]. The boundary condition that was selected was the open condition, for its simplicity and ease of use. We therefore used an open system where the initial size of the simulation space was set by the desired concentration, the particle number being held constant at 5000. The open system was chosen to minimize effects that come with a boundary condition. Also, the choice of not using periodic boundary conditions is due to the fact that the ratio between the diffusion length of the NPs and the size of the simulation space over the duration of the simulation was negligible.

2.3 Kinetics of \( n \)-mer Formation

As the simulation runs, the output data are saved at even intervals. This was chosen over irregular saving (i.e. only before and after a dimerization event) because the aggregation reaction is continuous and even time series data made the results easier to interpret, follow, and display. It also has the benefit that all reactions across the 2.5 orders of magnitude of concentration have the same amount of data. Thus for the low concentrations, which produce only a few dimers, and the high concentrations, where the assembly is rather a constant process, the amount of data does not depend on the system being investigated. The saved time slices are then run through a processing algorithm that
calculates the center-to-center distances between particles. The surface-to-surface distance is then evaluated by subtracting the *radii* of the particles from the center-to-center distance. This information is used to build the time evolution of the histograms of the surface separation of the particles. The n-*mer* counts are instead obtained in a different way. As the system evolves, the program keeps track of which particles are linked. This is in turn converted into a series of linked lists and the lists are parsed for length and checked for loops or double counts of particles. The data are then used to form the count numbers of each of the n-*mers*. Each of these data sets is averaged over 10 time slices to give 100 unique data points in each figure.

The data relative to n-*mer* counts are then processed to convert them into concentrations and to correct them for the expansion of the system as the simulation runs. This processing involves calculating the instantaneous size of the simulation volume and the concentration. The kinetics is extracted from these data using a Markov Chain Monte Carlo (MCMC) approach [52]. This method begins with the creation of a transition probability matrix defined by the reactions and kinetics being considered. The assembly reactions are considered to be second order, depending linearly on the concentration of each of the n-*mers* that go into the reaction. The transition probability matrix is derived from the kinetic parameters and the concentration of each reaction. This matrix is then multiplied by the n-*mer* concentration vector that is extracted at each time slice in the calculation. This gives the n-*mer* concentration at the next time slice, which is then used to calculate the transition probability matrix and the cycle repeats. The process is seeded with the initial concentration of the simulation and the n-*mer* population from the simulation then the MCMC calculations are compared. This comparison is then used in a
non-linear least-squares fitting for the kinetic parameters of the reaction, with the concentration being known. The fitting is performed over all samples simultaneously, resulting in a value that best fits all available data. For this dataset, where the maximum aggregate size is the largest seen in simulation, 10 NPs, this results in 25 kinetic parameters shown in Equation 6, where for each $k_{ij}$ the index $i$ represents the size of the existing NP structure (i.e. $i=1$ for monomer, $i=2$ for dimer, and so on) and the index $j$ represents the size of the incoming one. Only one coefficient is used for both I+J and J+I, as a Galilean transformation can be used to switch between the two cases. This fitting allows for results of reactions occurring on timescales of milliseconds to be extended to reactions which typically take minutes.

$$\frac{\partial c_{i+j}}{\partial t} = K_{i,j} c_i c_j$$

Equation 6

$$K_{i,j} = \begin{bmatrix}
k_{11} & 0 & 0 & 0 & 0 \\
k_{12} & k_{22} & 0 & 0 & 0 \\
k_{13} & k_{23} & k_{33} & 0 & 0 \\
k_{14} & k_{24} & k_{34} & k_{44} & 0 \\
k_{15} & k_{25} & k_{35} & k_{45} & k_{55} \\
k_{16} & k_{26} & k_{36} & k_{46} & 0 \\
k_{17} & k_{27} & k_{37} & 0 & 0 \\
k_{18} & k_{28} & 0 & 0 & 0 \\
k_{19} & 0 & 0 & 0 & 0
\end{bmatrix}$$

3. Results and discussion

3.1 Effect of Initial NP Concentration

Dynamical simulations of NPs in solution were run to study linking and assembly. For these simulations, a time step of 2.5 ns was used. This time step was derived from the
dynamical equations used for the model, specifically from the reduced viscous drag time, which provides a unique time-scale internal to the system. The desire is to have $h^* \beta$ be small compared to unity, see Eq. 4. The simulation was run over nine different NP concentrations covering the range between $4.8000 \times 10^{-10}$ NP/nm$^3$ and $1.2288 \times 10^{-7}$ NP/nm$^3$, as shown in Table 1. The concentration of the linker (DBDT) was kept at a constant ratio 10,000 times higher than the concentration of the NPs, and the concentration of the capping agent (herein also called brush) at 50,000 times higher. These concentrations were chosen to ensure the complete coverage of the NP’s surface, though in the simulations most of the particles maintained approximately 1-2% of their surface sites free. Nearly complete coverage is critical in order to avoid encounters not resulting in binding events, and it is thus fundamental to simplify interpretation and processing of the data. The simulations were run for 250,000 time steps, or an equivalent wall clock time of 0.625 ms. This time constraint was necessary for two reasons. First, it provides an ample time series for kinetic and kinematic analysis. Secondly, a simulation ending abruptly can be viewed as a physically realistic assumption about population behavior; on the bench-top, the reaction is in fact often rapidly and effectively quenched with a thiolated PEG to stop the aggregation. 5000 particles were simulated, as this number provided a large enough simulation space where the diffusion lengths are short compared to the size of the space. The simulation did not use periodic boundary conditions, as the ratio of the diffusion length of the NPs to the size of the simulation space over the duration of the simulation was negligible.
Three representative initial conditions among the nine explored will be discussed in this work: $4.8000 \times 10^{-10}$ NP/nm$^3$, $7.6800 \times 10^{-9}$ NP/nm$^3$ and $1.2288 \times 10^{-7}$ NP/nm$^3$. These represent the lowest, median and highest in the concentration series.

In Figure 4, the time evolution of the interparticle separation and the population of the NP aggregates as reported. The lowest concentration, $4.8000 \times 10^{-10}$ NP/nm$^3$, in figure 4 (a,b) shows the dimerization occurring in discrete steps, while the population of dimers is too low to be of any use over this short timescale. As seen in both 4a and 4b, the dimerization occurs in discrete, stable steps with no reverse process occurring, indicating that it is indeed linked dimers that are being formed.

At the median concentration, $7.6800 \times 10^{-9}$ NP/nm$^3$, (c, d) 250 dimers are made with only a small population of trimers. This dimer population however represents only 10% of the total NP count, or about 5% of the total aggregate count. This population, although representing an improvement over the results at lower concentrations, is still too low for use in further applications. Despite forming trimers, no long-range order is seen in figure

<table>
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<th>Simulation (n)</th>
<th>[NP] (NP/nm$^3$)</th>
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<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>9</td>
<td>$1.2288 \times 10^{-07}$</td>
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</table>

**Table 1.** Concentrations of NPs used in the simulations.
4c, that represents the interparticle separation. This indicates that any dimers that do form have time to reconfigure within the timescale of the simulation.

The highest concentration, \(1.2288 \times 10^{-7} \text{ NP/nm}^3\), forms a significant amount of dimers, however large numbers of trimers, tetramers and larger assemblies are formed as well. Of the 5000 particles simulated, 24% of the particles are in dimers, with 21% in trimers and 14% in tetramers. In terms of aggregate population, only 58% of all aggregates are monomers, with 21% of all aggregates being dimers, 12% in trimers and 6% in tetramers. In addition, the population of dimers is decreasing, meaning this will never be an optimal solution. The solution shown in 4 (e, f) has a population of trimers and larger aggregates too large to be used without extensive purification. A second-order structure peak is seen in figure 4e, illustrating that long-range structure is seen in the aggregates. This is seen in parallel with aggregates larger than tetramers, the largest size where all particles are nearest neighbors. The peak height is too large to be completely explained through this mechanism, indicating that some aggregates have an extended structure, likely due to the fast rate of formation.

Figure 4 shows that the situation being simulated is untenable for the preferential production of NP dimers. None of the three simulated systems have sufficient dimer populations with a low population of large aggregates. To be sure this result applies in the general case, the search must be expanded by finding the general kinetics defining the system and expand the calculation of NP aggregate populations to other NP concentrations and longer times. These kinetic equations will define a simple system, one where the only major interaction forces are van der Waals and linker forces. This will
allow the discovery of an optimum NP concentration and time within this system, potentially allowing high purity NP dimers to be made.

**Figure 4.** Time evolution of the interparticle separation (a, c, e) and time evolution of the number of dimers (b, d, f) averaged over 2500 steps in a system with an initial NP concentration equal to $4.8000 \times 10^{-10}$ NP/nm$^3$ (a,b), $7.6800 \times 10^{-9}$ NP/nm$^3$ (c,d), $1.2288 \times 10^{-7}$ NP/nm$^3$ (e,f).
The results presented so far represent 0.625 ms of wall clock time. This time span between onset and quenching of the assembly is likely not achievable in a physical system, and kinetic parameters useful for the design of experiments on a timescale of minutes were desired. Therefore, the population data from the simulations were used as the observed data for a non-linear least squares fitting. The functions that were fit to the observed data were the kinetic equations for the system. Figure 5 shows the result for fitting of the dimerization kinetics using a forward Markov Chain Monte Carlo (MCMC) kinetic modeling [46]. The three datasets being compared correspond to those found in Figure 4.
Figure 5. Comparison of as-simulated and fitted MCMC kinetics for NP concentrations of $4.8000 \times 10^{-10}$ NP/nm$^3$ (a), $7.6800 \times 10^{-9}$ NP/nm$^3$ (b), and $1.2288 \times 10^{-7}$ NP/nm$^3$ (c).

As can be seen, the fit at high concentrations in Figure 5c matches the curve closely, even for larger n-mer sizes. At lower concentrations, the region of good fitting is restricted to the first quarter of the full time series, before the system has time to expand significantly. The lack of a good fit at lower concentrations and the consistent way the observed data lay below the calculated data suggests that the local concentration of NPs is not well represented by the global concentration of NPs. For the intermediate
concentration, this deviation of local NP concentration from global NP concentration occurs after about one quarter of the simulation time, while at lower concentrations it could be happening earlier, with the turn-off occurring earlier as concentration decreases. This analysis takes into account globally averaged NP and nanostructure concentrations and therefore it misses local effects that could be responsible for the deviation of calculated from observed data. The assumption is instead appropriate at higher NP concentrations, where local variations in concentration are not significant with respect to the global concentration. At lower concentrations instead it partially breaks down, with most simulations showing an initial high increment in dimer formation that however falls off over time faster than the kinetics would predict. This behavior is likely due to the distribution of particle separations: Particles that start closer to each other will dimerize more rapidly, whereas the other ones will have to diffuse a significant distance to find each other particle.

3.2 Kinetics

Table 2 shows the rate constants for the NP-NP assembly reactions, as fitted from the population data from the simulations. The reaction rate for 1+N reactions, the first column, are quite similar and large, indicating that this is a major reaction pathway in the assembly of NPs. Surprisingly, the 2+N reactions in the second column have rates almost as high as the 1+N reactions, demonstrating that assembly of large NP structures will occur through both single and double addition. Values for the 3+N reactions vary significantly, with 3+4, 3+6 and 3+7 occurring at a high rate, while 3+3 and 3+5 are occurring at a much slower rate. The reaction rates for 1+N reactions increase as the size of the second aggregate increases until reaching N=5, where they start decreasing. This
initial increase is unsurprising, occurring due to a larger number of NP-NP interactions as the cluster size grows. The decrease is instead surprising and could be caused by geometrical constraints imposed by the fractal structure of the larger aggregates that is not seen in smaller aggregates. For larger clusters, (2,3,4)+N, the maximum is pushed to larger clusters as well, the peak rate at (2,3,4)+6. Overall the rate decreases as the smaller cluster size increases, again as expected.

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<td>1.48×10^{10}</td>
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</table>

**Table 2.** Fitted second order rate constants corresponding to parameters in **Equation 6**, in units of L mol^{−1} s^{−1}.

Based on these values, and given t as the reaction time and c the initial NP concentration, the optimum values for the product t×c (invariant for relative dimer
populations, units of \textit{molar*second}) to achieve maximized dimer-to-trimer formation are: $0.5383 \times 10^{-10}$, $0.2904 \times 10^{-10}$, and $0.0994 \times 10^{-10}$ for maximum trimer populations of 10\%, 5\% and 1\% of the total aggregate population. These lead to relative dimer populations of: 24.52\%, 19.17\%, and 9.37\% for each of those conditions.

### 3.3 Effect of Linker Concentration

The control of the formation of trimers for maximized formation of dimers is the challenge that has been addressed by this simulation and kinetics modeling. A control parameter not directly investigated is the concentration of linkers. This parameter can be addressed, building on the results above, to understand how it controls the behavior of the system. The synthesis of dimers of spheres commonly starts with the replacement of citrate with the linker molecule prior to dimerization. At a concentration of linkers lower than the saturation level, it can be assumed that some particles will have lost enough charge to effectively be able to bind to any other NP. This consideration divides the particles into two classes: class one, with fraction $n$, composed of particles that can link with any other NP, and class two, with fraction $(1-n)$, indicating those particles that cannot link with particles within the same class. The fraction $n$ is system dependent and could be determined experimentally or through theory. This fraction will not be determined in this work, but implications of this fraction will be explored.

This particle fractioning leads to changes in the relative kinetic rates of dimer and trimer formation. The relative rate of dimer formation is based on the probability of the initial particle under consideration and the probability that a second particle can link to it. Considering a particle from class two, the only particle it can link to is a particle from
class one. Conversely, a particle from class one can link to any particle, class one or class two. This gives the following equation for the relative rate of dimer formation as a function of the relative population of class one particles:

\[(1 - n) \times n + n \]  \hspace{1cm} \textbf{Equation 7}

For trimers the situation can be addressed similarly. The dimer on which the trimer can be built upon can either be a pair of class one particles, or a class one linked to a class two particle. A dimer formed from two class one particles can link to either a class one or a class two particle. A dimer made from a class one particle and a class two particle has two different linking sites: one capable of linking to any particle (the class one site) and one capable of linking only to class one particles (the class two site). Thus the relative rate of trimer formation is:

\[((1 - n) \times n) \times \left(\frac{2}{2} n + \frac{1}{2} (1 - n)\right) + n^2 \]  \hspace{1cm} \textbf{Equation 8}

The ratio of these rates, \(r_{\text{dimer}}/r_{\text{trimer}}\) is equal to unity at \(n=1\). Thus in the presence of particles that can bind to any particle (i.e. those in class one) we would have an equal rate of formation for dimers and trimers. In other words, if it is observed that \(r_{\text{dimer}} = r_{\text{trimer}}\) then the contribution of the linker concentration is negligible and the system is reduced to the system explored in simulation. However, as \(n\) approaches 0, the ratio approaches 4. At \(n=0\) the individual rates are zero, thus a ratio equal to 4 cannot be achieved in bench-top experiments. However at a \(r_{\text{dimer}}/r_{\text{trimer}}\) ratio of 3, the \(n\) value is 0.131, that results in a
r_{dimer} of ~25% the bulk rate, and a r_{trimer} equal to about 8% of the bulk rate. As these are relative rate values, they linearly modify the k values shown in Table 2. At the condition of n=0.131, the optimum t\times c values are: 0.3551 \times 10^{-9}, 0.2016 \times 10^{-9}, and 0.0702 \times 10^{-9} for maximum trimer populations of 10%, 5% and 1% of the total aggregate population. These lead to relative dimer populations of: 41.83%, 32.28%, and 15.92% for each of those conditions. The optimum dimer population at n=0.131 is approximately 50% better than the optimum conditions found at the simulation state of n=1, a value that is however reached in a time 15 times longer. At the limiting condition of very low n, the dimer to trimer formation ratio is maximized. The condition herein arbitrarily chosen was n=1/8000, with the optimum t\times c values for dimer formation at this condition are: 0.4416 \times 10^{-6}, 0.2522 \times 10^{-6}, and 0.0823 \times 10^{-6} for the three trimer populations of 10%, 5% and 1% of the total aggregate population. The relative dimer populations of: 47.86%, 37.90%, and 18.53% for this condition are larger but not substantially larger than at n=0.131, with the penalty of taking 1000 times as long, or 15,000 times as long as the n=1 condition.

As compared to the base system of n=1, decreasing n does result in a larger population of dimers. The increase in dimer population, relative to the base system, at a given trimer population seems to asymptotically approach a factor of two. As n decreases, the time required to reach the optimum dimer population increases roughly as 2/n. To give rough time intervals, consider a solution with an initial concentration of 5 \times 10^{-10} M NP, where it is desired to maximize the dimer population. This gives times, for a 5% dimer population, of 0.06, 0.4 and 500 seconds for n=1, 0.131 and 1/8000. As most synthetic techniques for dimer formation take on the order of 500 seconds, it can be observed that these systems operate at a very low n value already. The experimental or
theoretical determination of this population fraction can be achieved by measuring the resulting populations from a dimerization experiment; or calculating which particles, over a distribution of NP’s with varying properties, will be able to link.

4. Conclusion

Assemblies of NPs capable of performing a predetermined function represent the next challenge that needs to be addressed. However, in order to achieve this level of sophisticated control, it is imperative to first understand how the process of NP assembly works and what parameters guide it. In addition, in order to be able to predict how complex structures assemble, it is first of all necessary to unravel all the fundamental aspects related to the assembly of the smallest building block: the dimer. NP dimers are a fundamental tool in applications related to surface enhanced effects, especially in the areas of tagging and tracking. The synthesis of pure suspensions of dimers is therefore a challenge that needs to be addressed, particularly in light of its importance as a starting point for more complex architectures. The construction of a strong, predictive model and of a simulation framework capable of evaluating and reproducing it allows for great flexibility in designing experiments, as ideal conditions can be discovered before the first experiment is run. The model and simulation described in this work were built to take a physically realistic NP system and to investigate its time evolution. The simulation was build to strictly match the physical constraints imposed by the experiments on the bench top. The NP concentration, the linker concentration, and the reaction time were used as variables upon which to build the simulations. Repulsive forces between the NPs and between the linkers on their surface were considered at the basis of the simulation, along with an elastic contribution from those linkers binding two NPs, and Brownian forces
responsible for random kicks to the system. The model demonstrates that the initial concentration of NPs, assuming complete surface coverage, is the condition that most highly influences the assembly process. In addition, the model shows how the assemblies larger than dimers that are being formed have extended rather than close packed structures. Kinetic studies have shown that the NP assembly process take place almost equally via single and double addition. Conversely, the rates for the formation of larger assemblies are limited by the NP concentration in the system and by geometric constraints. The surface coverage of the NPs and the nature of the linkers on the surface have important implications in the optimization of the assembly: The rate of dimer formation can be optimized only by taking into account the ability of the linkers to also modify the charge of the NPs. In conclusion, our model has demonstrated excellent predictive ability, and will enable us to guide the synthesis of functional assemblies more complex than the dimers.

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References

Salt-induced Template-less 1D Assembly of Gold Nanoparticles

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Abstract:

We report on a method for building chains of gold nanospheres without the use of templates or other external constraint mechanisms but mediated by the controlled addition of salt. The possibility of utilizing bottom-up approaches to finely tune the 1D alignment of gold nanoparticles in the absence of a shape-constraining template has only been sparsely addressed and no definitive understanding of the phenomenon has been reported. Our contribution investigates chain formation and stability as a function of the ionic strength of the suspension and the surface properties of the nanospheres. The stability of this system shows a strong dependence on salt concentration and surface charge. Stable systems (with shelf lives on the order of months) are characterized to understand formation and geometry of the structure. Explicit modeling of the forces involved in chain formation is presented as well, and supports the experimental results. Based on the results achieved, the proposed approach could provide a new avenue for
building linear chains of nanoparticles from the bottom up, thus enabling to generate finely tuned structures with enhanced stability and inter-particle spacing not achievable with top-down approaches. It is anticipated that structures of this type could find application in a wide range of research areas, from SERS-based sensing, to plasmonics, to organic photovoltaics.

1. Introduction

Top-down and bottom-up methods have been proposed to form linear chains of gold nanoparticles (NPs), with the former being the most common and most widely agreed upon [1-4]. Top-down methods give good control of size and position but require specialized systems that are currently not useful for continuous manufacturing. Bottom-up methods on the other hand allow for synthesis in the absence of templates and for the placement of the nanoparticles within 1-2 nm from each other, a result not achievable from the top down.

Linear chains of nanospheres retain the useful properties of isolated NPs, such as the high scattering efficiency and active surface, while allowing the formation of conductive paths through the linking moieties, [5-7] or the coupling of the electromagnetic fields at the NP junctions, thus giving rise to near field effects (e.g. the surface enhanced Raman scattering effect), or enabling plasmonic coupling for metamaterials of new generation [8-28]. The advantage of these systems resides in the possibility of incorporating in one material those fundamental characteristics that have so far only been envisioned as belonging to separate components.

Nanochains have been made before through a wide variety of methods involving templates, over-layers, and linkers [29-32]. These methods suffer however one major
flaw: If the structure is not stable without the template, over-layer, or linker, would it be possible to generate from it a functional nanomaterial capable to interact with its surrounding environment?

The herein proposed method for nanochain formation is template-less and like other template-less methods takes advantage of the different interactions between NPs. These internanoparticle interactions are commonly short ranged, especially in aqueous media. The functional shape of each interaction determines how it acts on the system, and by understanding and combining several forces with different characteristic functions, the force field can be finely tuned to directly give rise to the desired structures [33].

The two major forces at play for linear NP assembly are van der Waals (vdW) forces, which are short ranged and rapidly rise in strength as $r^{-6}$, and Poisson-Boltzmann (PB) forces, which decay exponentially as a function of distance and are dependent on the surface charge of the particles as well as the ionic strength of the solvent [34]. The PB forces are repulsive and longer ranged than the vdW forces, which are attractive. The barrier is overcome through Brownian motion. In this work, the forces and energy barriers are explicitly calculated as a function of salt concentration, pH, NP size, NP surface ligands and position to understand the behavior of the system during chain formation.

Our method relies on the slow and controlled formation of chains, achieved when the energy minimum for the system is reached and is based on the single addition of NPs at the end of the chain. By tuning the solvent conditions, both the strength and the range of the PB interaction can be modified. This is investigated both in the model and experimentally, with the salt concentration being the primary parameter to be tuned.
2. Basic Principles

Chain formation is heavily favored over any other assembly paradigm due to the way the PB forces act. If a NP is approaching another NP under chain formation conditions, the repulsion is not sufficient to prevent Brownian motions from bringing the particles close enough to allow vDW forces to become dominant and pull the particles together. The interaction distance of the PB forces is determined by the solvent and the ionic strength of the solution. As the ionic strength increases, the effective charge of each nanoparticle decreases and the effective interaction distance decreases as well. The solvent also affects the distance of interaction through the dielectric constant. The interaction is determined by the formation of a charge double-layer on the particle, with the first layer being the bound charge and the second layer being formed from ions in solution. The effective interaction distance is controlled by the thickness of this outer layer, called the Debye length. When the particles are separated by more than 3 Debye lengths, the effective particle charge is less than 5% of its maximum value. The Debye length in aqueous solution is usually on the order of a few nanometers at millimolar levels of ionic strength [35]. If the ionic strength is high enough, the effective surface charge of the particle can reverse, creating a region on the force vs. ionic strength graph where the repulsive force between particles increases with the ionic strength. This region is generally small but can be observed in systems with a high surface potential, such as NPs [36].

The key of our method is to bring the system to controlled instability using the addition of salt to increase the ionic strength of the solution. Once the system is tuned to a
position where the probability for dimer formation is non-negligible over a time period of minutes, the formation of nanochains will begin starting from the smallest sub-unit: the dimer. After a dimer is formed, the position where a new NP can approach and assemble to the growing chain moves towards the end of the chain. If one NP approaches the dimer from the side, it will experience the charge of both NPs, hence the probability of Brownian motion to overcome this repulsion and generate a triangularly shaped trimer is very small. If it approaches from the end however, the incoming NP only sees one NP of the existing dimer, the other one being hidden by the double layer around it, as seen in the cartoon in Figure 1.

Figure 1. Cartoon representation of the process of nanochain assembly. The red area represents the region where an incoming nanoparticle is most likely to attach to the growing chain.

This mechanism of approach reduces the system to the formation of a dimer, which is modified slightly to take into account the repulsion from the more distant particle(s). This process continues until either the total effective charge of the chain is too strong for a particle to approach at any position or the chain becomes long enough that a new particle does not see the other end of the chain, causing the chain to lengthen ad-infinitum. The overall effect is the formation of chains that are straightened by their self-
interaction, or large clusters are formed as the chains curl on themselves, much as DNA or proteins fold.

3. Nanoparticle Interaction Model

To understand how chain formation can occur, it was important to accurately model the interactions between the nanoparticles. To this end, an extension of the work reported in the literature was utilized [33]. To calculate these forces, a multistep approach was taken. Firstly, the model places the NPs in a solution of surface ligands in water, with the concentration of the ligands matching that used experimentally. The ligands are allowed to adsorb to the particle surfaces and bind there, forming a ligand shell. The particles are then arranged as desired, with two or three particles making up a central cluster at the origin and a single particle placed at the position of interest in space around the central cluster. It is at this point that the forces are calculated, which include the standard set calculated by the model as well as an extension which takes into account the electrostatic interaction. The extensions involve calculating the electrostatic force between nanoparticles, taking into account their surface ligands, the ligand behavior as a function of pH and local electric field, and the screening effect found in aqueous electrolytes. This takes the form of a bivariate spline collocation in bipolar coordinates which represents the local electric field and appropriate boundary conditions, with the tension in the field plane separating the particles being used to calculate the interaction force [34]. The field tension is summed using adaptive Gauss-Kronrod quadrature. This force is added to the ones already calculated by the model, which include the van der Waals forces, the ligand interaction forces, and the “linker” forces. In this work, the forces were calculated for a
single particle approaching a dimer, and for a single particle approaching a linear trimer. From the force information a center-of-mass force and a torque were extracted, and from these a model was built describing how the assembly proceeds as the chain length grows.

4. Experimental Methods

Gold nanospheres were synthesized following the method of Turkevich, Stevenson, and Hillier [37]. Briefly, a solution containing 93 ml of deionized water (18.2 MΩ) and 2 ml of a 0.025 M solution of chloroauric acid trihydrate (Acros Organics) was brought to a boil on a hot plate under vigorous stirring. Subsequently, 5 ml of a 0.01g/ml solution of anhydrous trisodium citrate (Acros Organics) in deionized water (18.2 MΩ) were added. This solution was boiled again for 5 minutes, during which the color changed from light yellow through clear to black and finally dark ruby red. The solution of NPs was then removed from heat and allowed to cool to room temperature. Transmission electron microscopy (TEM) particle sizing gave an average diameter of (19.5±2) nm taken from a sample larger than 100 particles.

5 ml of the as-made nanosphere suspension were diluted to 25 ml with deionized water (18.2 MΩ) in a 50 ml centrifuge tube. To this solution 2.5 μl of a 1.25 x 10^{-2} M solution of biphenyl-4,4'-dithiol (DBDT, Sigma-Aldrich) in THF were added, followed by shaking for 10 minutes upright on a plate shaker. Then, 5 μl of a 1.25 x 10^{-2} M solution of 3-mercaptopropionic acid (Sigma-Aldrich, HPLC grade) in deionized water (18.2 MΩ) were added. The suspension was then shaken for 10 minutes upright on a plate shaker.
After aging the suspension for two weeks, time-lapse UV-Vis spectra were collected using an HR-4000 Spectrophotometer from Ocean Optics that allowed absorption spectra to be captured at video rates (~60Hz), giving the ability to see the assembly process with high temporal resolution. To a quartz cuvette, an appropriate amount (0-20 μl) of a 1 M sodium chloride solution was added to give the correct salt concentration (0-40 mM) when diluted to a total volume of 0.5 ml with the nanosphere solution. The reverse addition was not used due to poor mixing that resulted in inhomogeneous assembly. Figure 2 shows a cartoon of this methodology.

Figure 2. Methodology of sample preparation for in-situ UV-Vis measurement of NP assembly in a cuvette.

Before each acquisition a dark field and a bright field spectrum were collected to remove the effects of the detector and the solvent. Each spectrum consisted of ten 15 ms
exposures averaged together to give a total time for each spectrum of 150 ms. 12,000 spectra were collected, for a total acquisition time of 30 minutes. The spectral data were filtered to remove noise with a 51-point, 1st zero sinc function before being further processed. The spectra were fitted using 5 gaussian peaks corresponding to major peaks in the spectra and a scattering background modeled as a power-law function plus a constant offset. The peak names are assigned in analogy to similar features seen in spectra for nanorods to extend the analogy that chains of nanospheres can have similar optical properties to nanorods. The time evolution of the main peaks was subsequently analyzed to optically study the formation and growth of the linear chains.

Figure 3. Diagram of the UV-Vis data fitting process. The data and the calculated fit, along with the major components of the fit are shown. The data and the calculated fit overlap and are thus not distinguishable in the graph. Components of the fit not treated here are described in the supplemental information.

For scanning electron microscopy (SEM) analysis of the structures, an appropriate amount of a 1 M sodium chloride solution was added to give the correct salt concentration when diluted to a total volume of 0.5 ml with the nanosphere suspension in
a 1.5 ml microcentrifuge tube (Eppendorf). After the allotted time, an 5 μL alloquot of the solution was placed on a cleaned silicon wafer and then put into a vacuum dessicator. The drying time was less than one second for all samples. Imaging was carried out on a Carl-Zeiss Sigma FESEM at 10kV, 2.8 mm WD using the in-lens detector.

5. Results and discussion

5.1 Modeling NP-cluster interactions

Figure 4 shows the center-of-mass force for a single particle around a dimer. As can be expected, these graphs show that there exists a central core of repulsive interaction, with an outer shell which has a net attractive interaction. This duality is caused by the fact that the repulsive electrostatic interaction decays more quickly than the attractive van der Waals interaction as the interparticle separation increases. As the salt concentration increases, the size of the repulsive core decreases as expected, due to the increased screening of the surface charge of the nanoparticles.
Figure 4. Calculated center of mass force acting on a single 10 nm radius NP due to a dimer of the same NPs located at the origin. Regions in the core are repulsive, and in the shell are attractive. Scale of the forces is shown in the colorbar, units are Newtons of force.

This change can also be seen in Figure 5, which shows the tangential force for the same system. The tangential force is the amount by which the incoming NP is pulled to the end of the growing chain and conversely the chain to be pulled to point at the incoming NP. A large tangential force means a strong propensity for the growing chain to be straight and aligned. Interestingly, there is a large net force which works to pull the
incoming single particle around to the end of the dimer, caused by the van der Waals force between the particles. The repulsive electrostatic force works against this but at high salt concentrations, above 10 mM NaCl, its effect is small compared to the large region of space within which the forces are trying to align the particle and the dimer. This could be one reason why at lower salt concentrations, assembly is more random, while at higher salt concentrations it occurs in a more linear fashion.

Figure 5. Tangential force calculated acting on a single 10nm radius NP due to a dimer of the same NPs located at the origin. In the red/green region the force aligns the particles; in the blue region the force acts to dis-align the particles. Scale of the forces is shown in the colorbar, units are Newtons of force.
Trimers present a very similar picture to dimers, with important exceptions. Figure 6 shows the center-of-mass force between a single 10 nm radius NP and a trimer formed from the same NPs. The behavior is similar to what described in Figure 2, but the forces are in general less intense due to the increased size of the core, and the fact that the forces decay very rapidly. This decrease in force indicates that at each stage of the growth, the addition of another particle is less vigorous than the previous stage, thus leading to a self-limiting growth.
Figure 6. Calculated center of mass force acting on a single 10 nm radius NP induced by the presence of a trimer of the same NPs located at the origin. Regions in the core are repulsive, and in the shell are attractive. Scale of the forces is shown in the colorbar, units are Newtons of force.

In Figure 7, the tangential force on a single 10 nm radius NP from a trimer of the same NPs at the origin is plotted. These forces are larger than in the dimer case, meaning that the ratio of the center-of-mass force to the tangential force decreases at each stage. The incoming NP has a smaller force pulling it to the center and a larger force pulling it
to the end of the growing chain, reinforcing linear chain formation as the chain increases in length.

**Figure 7.** Calculated tangential force acting on a single 10 nm radius NP due to a trimer of the same NPs located at the origin. In the red/green region the force aligns the particles; in the blue region the force acts to dis-align the particles. Scale of the forces is shown in the colorbar, units are Newtons of force.

**5.2 UV-Vis Analysis of assembly**

A fitting of the time-dependent behavior of UV-Vis data was carried out to extract information about the state of assembly as a function of time at different salt concentrations. Some of the characteristic parameters from the fit are shown in **Figure 8**.
The scattering exponent, shown in Figure 8a, corresponds to the optical cross section of the scattering centers in the solution, with a lower exponent indicating larger cross sections. Larger cross sections are interpreted to be assignable to larger NP clusters, but the shape factor plays a role as well, with tighter clusters (three particles arranged in a triangle vs a straight line) having a larger effective cross section. As evidenced in Figure 8a, high salt contents induce a rapid decrease of the scattering exponent with time, thus indicating that the NPs are readily aggregating in these conditions. As the structure grows, the individual particle resonances are suppressed due to plasmon coupling between the very close NPs, causing a decrease in the transverse peak amplitude. Figure 8b shows the decrease in the amplitude of the transverse peak, which can be interpreted as the increase in the number of linked NPs undergoing plasmon coupling. In low salt content instances, the amplitude of the transverse peak remains relatively constant, indicating low coupling efficiency in these systems. Well-coupled neighbors also give rise to longitudinal peaks, whose behavior is seen in Figure 8c and 8d. These peaks can be interpreted as evidence for the formation of linear chains of varying lengths, based on drawing a parallel between the spectra of the chains and the spectra of gold nanorods, which shows this behavior. Figure 8c shows the ratio of the transverse to the longitudinal peak on a log scale, and gives the relative ratio of monomers to longer linear forms, which will be dominated by linear tetramers, with the peak amplitude of the latter corrected for their cross section. The behavior of the dark blue curves, those for low salt concentration, at long times can be taken as baseline for the system, with values above the baseline reflecting linear nanostructure formation due to the salt-induced assembly. Figure 8d shows the behavior of the longitudinal peak width at increasing time and salt
concentration. The graph is the result of two contributions: kinetic and form factor. An increase in width corresponds to a kinetically controlled increase in assembly size, with overall narrower widths indicative of a reduced variation from linearity of the nanostructure generated.

**Figure 8.** Fit parameters for the time evolution of the UV-Vis spectra of suspensions of nanospheres induced to aggregate by the addition of salt. a) Scattering exponent, b) ratio of transverse peak amplitude to maximum for the transverse peak, c) ratio of longitudinal to transverse peak amplitude, d) longitudinal peak width. A decreasing scattering exponent indicates larger assemblies, while a decrease in the transverse peak amplitude and an increase of the transverse to longitudinal peak ratio indicate an efficient NP coupling. Smaller increases in the longitudinal peak widths can be interpreted as indicative of the formation of linear assemblies rather than large aggregates.
Taking into account all the above consideration, two distinct regions of salt concentration, one at intermediate concentration (between 7 and 12 mM) and one at high concentration (above 22 mM), caused assembly (see Figure 8a) accompanied by an increase in the longitudinal peak width (Figure 8d), indicating the formation of superstructures of NPs. The assembly behavior is however strikingly different in these two regions, with a large growth in the longitudinal peak (Figure 8c) only seen for the higher salt concentration regime. In solutions where the scattering exponent falls dramatically the formation of these chains observed by the large longitudinal peak is seen as being transitory to forming larger aggregates, indicating that chain formation in these solutions is dynamically unstable. The unstable region with lower salt concentration never forms a high number of linear aggregates, with the assembly mechanism favoring cluster formation. As the salt concentration increases, the transverse peak amplitude (Figure 8b) decreases overall, with a small increase between the two regions of instability.

The combination of slow decay of the scattering exponent and the large increase in the amplitude of the nanorod-like longitudinal peak in the UV-Vis fitting suggests that the best salt concentrations to grow linear chains are those in the region of relative stability between the two zones of aggregation (i.e. for salt concentration higher than 12 mM and lower than 22 mM). At lower salt concentration, assembly proceeds via a dimerization-like process. At higher salt concentrations, where the Debye length is smaller and the fields very local to the particles are higher, the surface charge controls the system to form linear aggregates. As the salt concentration continues to increase, the chains will fold on
themselves, forming larger aggregates, often with a terminus where chain addition is still occurring.

The assembly process described can also be viewed in terms of the elementary forces acting on the system. At very low salt concentrations, the electrostatic force is too strong to allow particles to get close enough for Brownian motion to assemble them. At low salt concentrations, the electrostatic force is weakened due to the reduction in the Debye length to the point where Brownian motions can get the particles close enough that van der Waals forces can assemble them. The electrostatic force is strong enough to prevent the incoming particle from assembling in a chain like fashion, giving these aggregates a more compact shape. At intermediate salt concentrations, the electrostatic force is weakened sufficiently that the incoming NP can bind to the end of the chain without being pushed to one side or another by the electrostatic repulsion. Under these conditions, the optimum location for particle addition to the chain is at the tips, as it benefits from the relatively long ranged van der Waals force from the entire length of the chain while avoiding the electrostatic repulsion from all but the one nanoparticle at the tip. At very high salt concentrations, the Debye length shortens to the point that the van der Waals force causes chain addition *ad infinitum*, as well as being reduced to a strength below which Brownian motion can cause addition of the incoming NP along the side of the chain, as the charge on the rest of the chain is completely screened. The as the now branching chain grows, it coils because of entropic forces that occur only when chains become very long, where the stiffness of the chain is lower than the attractive forces between two parts of the chain which have random-walked.
5.3 SEM Analysis of Assembly

**Figure 9** shows SEM micrographs of samples taken 10 minutes after adding the NP solution to a salt solution. As seen in the UV-Vis data, the 4 mM sample (a) shows no assembly at all, aside from the dimers initially fed into the system. If no dimers were in the initial solution, i.e. no DBDT was added during the ligand exchange of the NPs, no assembly would be seen at salt concentrations up to 40 mM. The 20 mM sample (b), being on the edge of the unstable high-salt region shows some assembly into chains. The population of dimers and trimers is much larger here than it is for the 4 mM sample, indicating that chain formation is occurring. At 40 mM (c), the sample is aggregated but the aggregates are not dense structures, indicating that the formation of the clumps is not a simple addition process but involves precursors that are linear chains or small clusters of particles.
Figure 9. SEM micrographs of TEM grids coated with salt-assembled NPs: a) 4 mM, b) 20 mM, c) 40 mM salt at 10 minutes from mixing. The NP solution was aged for two weeks before collecting the SEM data. It can be observed that the level of assembly and the size of the structures increase with the increase in salt content. The black circles in the background are due to the presence of the TEM grid onto which the samples were deposited.

In Figure 10, the same samples were observed 30 minutes after the assembly had occurred. Again, the 4 mM sample (a) shows no significant assembly. The sample with 40 mM salt (b) shows even larger aggregates than seen before, but like before the aggregates are not dense and instead seem to be made of many fibers intertwined or
coiled in on themselves, with single NP-wide tails protruding from the bundle. This geometry would be caused by the aggregation and coiling of long chains of NPs, which have reached sufficient length so as to reduce their entropy by coiling up, much as polymers and proteins do.

**Figure 10.** SEM micrographs of TEM grids coated with salt-assembled NPs: a) 4 mM, b) 40 mM salt at 30 minutes from mixing. The NP solution was aged for two weeks.

The two cases presented in **Figure 10** are contrary to what is seen in **Figure 11**. In **Figure 11**, the NP are treated the same, but the salt concentration used for assembly is 20 mM. Unlike the other concentrations, a significant fraction of the population is in the form of chains. In some images, one can visualize a chain growing, as the chain and an incoming NP are aligned. The longest contiguous chain seen was 5 NP long, but this was much rarer than the chains of length 4 or 3. This structure is captured by the rapid sample fixing on the silicon wafers.
Figure 11. SEM micrographs of TEM grids coated with salt-assembled NPs @ 20 mM NaCl, 30 minutes from mixing. The NP solution was aged for two weeks.

5.4 Stability of Linear Nanochains

To investigate the stability of the formed structures against disassembly, the salt-induced assembly was carried out at 8 mM salt, within the first zone of unstable assembly found above. This region was chosen because it allowed a 2:1 dilution to bring the sample back to stability. This dilution would not decrease the solution absorbance enough to significantly increase noise in the data, thus allowing for a robust comparison of the spectra before and after dilution. The solution was allowed to assemble for 30 minutes,
after which it was diluted 2:1 with deionized water to bring it into the very low salt stability region. If the structures were not linked, this would result in their disassembly back into individual nanoparticles. The spectra were collected for another 30 minutes to investigate the stability of the resulting solution to further assembly or disassembly.

**Figure 12.** Fit parameters from the UV-Vis spectra of salt induced aggregation and stabilization of nanospheres. Following dilution and an initial decrease in intensity, both the transverse and longitudinal peaks do not change as time progresses, indicative of the fact that dilution effectively arrested the assembly. a) Transverse peak amplitude fit, b) longitudinal peak position fit.

As seen in **Figure 12**, the dilution effectively arrested the assembly process, as indicated by the second half of the graphs being constant and indicative of the absence of variation in both the transverse peak amplitude and the longitudinal peak position. The decrease in amplitude values to ½ of that before the dilution gives good indication that the solution is well mixed, as the change in the amplitudes corresponds to the decrease in concentration by ½. The longitudinal peak does decay slightly, but so does the transverse
peak, and this can be attributed to experimental effects as opposed to a real disassembly of the structures formed to this point, as these decays do not show corresponding shifts in the value of the other fit parameters (see Supporting Information). The ability of the generated nanostructures to remain unaltered following dilution is of extreme importance in terms of processability considerations, and confirms the validity of the proposed method for the creation of nanostructures with actual applicability.

6. Conclusion

The template-less formation of linear chains of NPs is critically driven by the balance of forces between particles. Understanding and utilizing these forces will open up many avenues previously unexplored for controlling and commanding the assembly of NPs, which can have a myriad of uses from plasmonics to photovoltaic devices. Salt-induced assembly offers a simple and inexpensive control mechanism for forming linear chains of NPs with the intrinsic advantage of enabling the rapid arrest of the assembly process by dilution. This methodology is amenable to large-scale production, requiring no great expense and operating on a timescale of minutes. The system can be extended to two controllable parameters: the amount of salt and the amount of surface charge removed. These parameters allow better control over the formation of the chains and enable the inclusion on the surface of the necessary number of moieties that can impart a predetermined function to the structure.
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Supporting Information

**Figure S1.** Non-peak fit components.

**Figure S2.** Transverse peak fit components.
Figure S3. Longitudinal peak fit components.

Figure S4. High-wavelength peak fit components.
Figure S5. Intermediate shoulder peak fit components.

Figure S6. Longitudinal shoulder peak fit components.
References

Large Ordered Arrays of Gold Nanoparticles by Block Copolymer Templating

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Abstract:

This work investigates surface patterning of ordered arrays of metallic nanoparticles via block-copolymer lithographic templating. The nanoparticles used in this investigation are on the order of 20 nm, which is roughly the same as the domain size of available block-copolymer templates. This leads to a one-particle-per-domain structure, allowing these arrays to have large areas covered by isolated nanoparticles. Gold allows for extensive and careful particle surface modification, giving the particles useful and tunable properties. The patterning will be done with a removable template, as opposed to embedding the particles in the polymer. This allows the surface of the particles to be utilized or left bare, as future requirements dictate. These arrays could be used to build ordered vertical silicon nanowires, useful for high aspect ratio photovoltaic devices, or utilized directly for their potentially unique optical properties, including SERS, plasmonics, and diffraction.
1. Introduction

Plasmonic nanoparticles (NPs) are a useful interactive tool for any system that operates in the optical regime. They scatter incoming light effectively and perpendicularly, possess strong collective excitations of the conduction electrons called localized surface plasmons, and have surfaces that can be easily functionalized [1]. Taken together, these properties make plasmonic NPs ideal for forming structures that strongly interact with and usefully modulate the incoming light. The surface of the NPs can be modified with a range of different methods to give them the ability to selectively adhere or bind to macroscopic surfaces or other NPs in a predetermined way. This capability allows the design of devices that interact with light in a predictable way or to set up experiments that unravel the fundamental light-matter interactions at the nanoscale.

Due to the plasmons that are elicited upon exposure to light, large oscillating electromagnetic fields are generated near the surface of the NPs [2]. These fields can couple to the surrounding medium or to other particles [3-5], greatly enhancing any property of the medium that depends on the intensity of the local electromagnetic field [6]. Phenomena such as second harmonic generation (SHG), exciton generation and dissociation, and Raman scattering, all depending on the electric field strength, can potentially be enhanced significantly in devices that include metallic NPs [7]. NP size, inter-NP spacing, and NP position all need to be tuned to optimize the performance [8]. Two-dimensional arrays are conceptually easy to construct and analyze, allowing rapid device fabrication and testing. The particle-particle and particle-substrate distances and interactions can be modified as well, leading to an active substrate that can be used for further development. However, the design of the device has to take into account the
properties of the NPs, and adding NPs or other plasmonic structures to existing device morphologies rarely results in the promised enhancements [9].

Second harmonic generation is a phenomenon that utilizes the non-linear optical properties of a material to combine two lower energy photons into a single higher energy photon. The intensity of this effect depends on the electric field to the fourth power. As NPs create local electric fields with intensities several orders of magnitude higher than the incident energy, a transmissive or reflective film incorporating an array of metallic NPs can result in a much higher light output [10-13]. In this thin-film based approach, the amount of SHG material needed and the required device volume are reduced while giving the same energy output, potentially greatly expanding the usability of SHG devices [14].

If the substrate that the NPs sit on is also a plasmonic material, a coupled resonator can be created which will act as an excellent Surface Enhanced Raman Scattering (SERS) substrate, with detection sensitivity claimed to extend to the single molecule level [15]. The Raman effect utilizes an incoming laser beam which is Stokes-shifted after interacting with the material. The strength of the effect, like SHG, is determined by the electric field to the fourth power for resonances near the plasmon frequency. Plasmonic NPs have been used to produce signal enhancements up to 14 orders of magnitude, with 9 orders being relatively common [6, 16, 17].

In addition to the above uses which only take advantage of the local surface plasmon of the NPs and the large electric field they generate, the application of NP arrays to organic photovoltaic (OPV) devices can utilize all of the beneficial properties of the metallic NPs. The NPs scatter strongly into the plane perpendicular to the incoming
radiation, meaning that any incident light that is not absorbed and hits a NP is bounced into the plane of the device, rather than out of it [18]. This directionality effect improves the use of the available photons, as a photon that moves in the plane has a much larger chance of being absorbed than one that transverses the material. The OPV devices can, of course, utilize the very large local fields created around the NPs for exciton generation and separation, which will be very efficient close to the surface of the NP [19]. After the exciton is generated, if the NP array is electrically connected to the back electrode of the device, the NPs can act as an effectively roughened electrode, collecting charge from a much larger volume of material than would be possible with conventional planar electrodes [20]. Due to the presence of these electrically connected NPs in the OPV medium, the excitons would have a shorter distance to diffuse, resulting in increased collection occurring before recombination can take place [21, 22]. In addition NP arrays can also act as a seeds from which to grow silicon nanowires, thus enabling the creation of columnar silicon arrays and building on the extensive knowledge of silicon processing and device manufacturing [23-25].

There are a range of methods that can be used to generate such arrays of NPs. These methods break down into two broad categories: top-down and bottom-up. Top-down patterning involves defining the position of the NPs on a substrate on which the array will assemble, through lithography or other means. Bottom-up patterning “programs” the pattern into the interactions of the subunits of the system, in this case NPs, such that the desired structure will naturally self-assemble.

Utilizing the top-down approach via conventional lithography gives good large scale control but typically poor nanoscale control [16]. It is possible to pattern a large wafer
with equally spaced holes, but controlling the inter-hole spacing to nanometer precision across the whole wafer is problematic due to the resolution limits on the lithographic system [26]. The particles settle or are drawn by capillary forces into the etched areas of the surface, forming a defined array [27, 28]. The spots on the surface can also be electrostatically defined [29] or chemically pattern the substrate with pads of material that the NP can attach to, while leaving the rest of the surface untouched [26, 30-34]. These all suffer from the same problem, in that unless there is some outside interaction determining the NP spacing, they can land anywhere on the interaction zone and bind, disturbing the local spacing of the array. Spatial control to the nanometer regime is critical to many of the properties that are desired for these NP arrays, and thus conventional lithography is challenged with maintaining the requisite position while still patterning a large area.

Conventional lithography also scales poorly. The size of conventional spherical metallic NPs is less than 50 nanometers, which is at or below the capabilities of photon lithography. To achieve such small features at very well defined spacing means that electron beam lithography would be required, greatly increasing processing time and cost. Electron beam lithography also scales in size very poorly and thus while potentially useful for laboratory scale investigations, is not useful for larger scale deployment or manufacturing of these arrays, which is their envisioned application.[35] To avoid this, block copolymers can be used directly to determine spacing [36]. By using capillary forces in etched block copolymer patterns, it is possible to put two nanoparticles down in parallel [37].

Bottom-up formation of NP arrays on the other hand utilizes the interactions between the NPs and between the NP and the substrate to define the inter-NP spacing. Firstly the
interaction with the substrate needs to be defined to ensure the NP bind to the substrate. The NPs also need to be kept separate from their neighbors, while still allowing for the possibility of further processing to functionalize the array. This control is typically modulated by the ligands present on the surface of the NP. The surface brushes on the particles can have their interaction tuned to cause array formation [38-40]. The particles can be allowed to assemble in very close spacing by utilizing this brush interaction [40-43], but this leads to poor global structure, takes up 80% of the surface with nanoparticles and strongly quenches the main surface plasmon. Longer ligands will prevent the particles from approaching too closely and also space them farther off of the substrate. Ligands which wet the substrate will result in the particles resting closer to the substrate than in the non-wetting case. This could be utilized to tune the NP-substrate distance. Bottom-up methods also extend to other self-assembling systems, such as block copolymers, in which the pattern is generated by the phase separation within a polymer deposited on the substrate. The particles can be embedded or grown in a block copolymer matrix [44, 45], but these particles are then immobilized unless released from the polymer [46].

2. Proposed Methodology

Herein, a method for building micron-scale arrays of gold NPs using a block copolymer templating approach is described. Block copolymer templated NP array formation has several unique advantages, such as the ability to access the raw substrate and to tightly couple the arranged NPs to the substrate. This is useful in substrates designed for SERS and for OPVs, as well as potentially useful for those designed for SHG. In addition, this method requires no bulky ligands to keep the NPs at a
predetermined separation, thus leaving the surface of the NPs free for modification with functional moieties. Taking advantage of the variety of chemistries that can potentially be placed on surface of the NP, the range of devices that NPs can be applied to is greatly enhanced. There is no required post-processing of the substrate after NPs deposition that could damage the NPs or affect their spacing, height, surface chemistry, or electronic and optical properties, preserving whatever built-in NP properties existed before formation of the array. The result of this approach is an array of NPs permanently linked to a substrate but with surfaces free for modification. Post-deposition surface modification allows for instance functionalization with Raman active molecules, OPV polymers, or SHG materials. This possibility gives these arrays great flexibility, as one array can be post-depositionally modified to many potential uses.

**Scheme 1:** Cartoon description of the steps required to deposit the NP array on the substrate using the described block copolymer templating approach.
3. Methods

1 mg/100 µl solutions were made from a polystyrene/poly(methyl methacrylate) block copolymer (PS-b-PMMA) (20.2/50.5 Mn x 10³, Mw/Mn=1.07, PolymerSource) and either toluene or chloroform (Sigma-Aldrich). <100> silicon wafers were sputter-coated with gold to a thickness of 25 nm with an EMS150T ES (Electron Microscopy Sciences), followed by room-temperature annealing for one day. The gold-coated wafers were spun at 6000 RPM on a WS-400-6NPP-LITE (Laurel Technologies) and washed with the solvent that would be used to cast the polymer by depositing 10 µl of the pure solvent on the wafer after 10 seconds of spinning, followed by a drying time of 50 s. The gold-coated wafers were then spin-coated with the polymer solution at 6000 RPM, depositing a 10µl drop of polymer on the surface after the initial 10 s of spinning and allowing a further 50 s for the solvent to evaporate and the surface to dry. The polymer-coated wafers were annealed in a furnace at 165°C for 40 hours under nitrogen. Following annealing, the wafers were UV-etched for 5 minutes under an RC-250B UV light source (Xenon Corp). The wafers were then rinsed with glacial acetic acid and left to dry for one hour. After the wafers were dry, 100 µl of a solution of 10 mg/ml of 16-mercaptohexanoic acid (16-MHA, Sigma-Aldrich) in methanol was placed on each sample and after 30 s the excess was removed and the samples left to fully dry for one hour. The samples were then washed with toluene to remove any leftover 16-MHA.

Spherical gold NPs were synthesized following the procedure of Turkevich, Stevenson, and Hillier [47]. Briefly, a solution containing 93 ml of deionized water (18.2 MΩ) and 2 ml of a 0.025 M solution of chloroauric acid trihydrate (Acros Organics) was brought to a boil on a hot plate under vigorous stirring. Subsequently, 5 ml of a 0.01 g/ml
solution of anhydrous trisodium citrate (Acros Organics) in deionized water (18.2 MΩ) were added. This solution was boiled again for 5 minutes, during which the color changed from light yellow through clear to black and finally dark ruby red. The solution of NPs was then removed from heat and allowed to cool to room temperature. Transmission electron microscopy (TEM) particle sizing gave an average diameter of (19.5±2) nm taken from a sample larger than 100 particles.

5 ml of the as-made nanosphere suspension were diluted to 25 ml with deionized water (18.2 MΩ) in a 50 ml centrifuge tube. To this solution 2.5 μl of a 1.25 x 10⁻² M solution of biphenyl-4,4'-dithiol (DBDT, Sigma-Aldrich) in THF were added, followed by shaking for 10 minutes upright on a plate shaker. Then, 5 μl of a 1.25 x 10⁻² M solution of 3-mercaptpropionic acid (3-MPA, Sigma-Aldrich, HPLC grade) in deionized water (18.2 MΩ) were added. The suspension was then shaken for 10 minutes upright on a plate shaker. This solution was stored for a month before use.

100 μl of the solution of gold NPs was deposited on the wafer and left to dry completely. Excess particles were rinsed off with deionized water. The surfaces were imaged using a Zeiss Field Emission Scanning Electron Microscope at 500 V with the secondary electron and in-lens detectors.

4. Results

Figure 1 shows the SEM images of the resulting NP arrays formed on the gold-coated substrate after all processing steps. The particles are well spaced, with interparticle distances being approximately 40 nm, consistent with the size of the block copolymer. Some clusters of particles are observed as well, especially in Figure 1b. This is likely a
result of the polystyrene islands clustering on the surface before or during the passivation step, such that those areas did not get a significant coating of the 16-MHA, allowing particles to land and adhere there. The gaps around those clusters are the locations where the PS islands used to be, preventing NP binding. The particles are bound to the substrate through the biphenyl-4,4′-dithiol (DBDT) moiety on their surface, which will keep the particles ca. 1 nm off the surface of the gold substrate. As the surfaces were rinsed vigorously before being imaged and the particles are water soluble, it is likely that the particles are not merely adsorbed to the surface but truly bound to the gold substrate through the DBDT linker. The wide area image, Figure 1d, gives an idea of the surface area that can be covered with this technique. Larger area images were not taken, as the individual particles are no longer resolvable at those low magnifications. Despite minor clustering and void areas, the arrays achieved are large scale and extend over a large area of the surface, with 90% of the covered area possessing well-spaced individual nanoparticles.
Figure 1. Gold coated substrate after 10 ul block copolymer deposition in chloroform, annealing at 165°C for 40 hours, UV etch, wash, passivation, PS phase removal and NP deposition. The different panels represent different magnifications of the same array.

Figure 2a shows the Fourier transform of an SEM image of the etched substrate, and Figure 2b a Fourier transform of an SEM image of the substrate after processing, passivation, and NP deposition. As can be seen in the images, the location of the peak in the transforms is in roughly the same location, and corresponds to an inter-feature spacing of about 40 nm. This is the same spacing seen in the SEM images of the NP arrays, shown above, and the etched block copolymer (shown in supplemental information, Figure S5a). This indicates that this peak corresponds to the spacing between PS dots left after etching, and the spacing between the NPs deposited after full substrate processing, suggesting that the pattern of the PS dots is maintained to the final
structure of the NPs on the surface. The larger width of the peak in the Fourier-transformed image with NPs is due to the higher contrast that NPs provide, along with their more uniform intensity than the PS dots.

![Fourier transform images](image)

**Figure 2.** Fast Fourier transform of SEM images of an etched substrate (a) and one with NP deposited on it (b).

**Conclusions**

By utilizing a block-copolymer templating method, that enable thorough control over the size of the domains formed and the specific NP-NP and NP-substrate interactions, it was possible to build large arrays of NPs on a hydrophilic substrate while maintaining the ability of the NPs to be modified following array formation. This ability to form a pattern in polystyrene on a gold substrate, then “image” that pattern with the deposited nanoparticles opens a large field to investigation for the high resolution placement of nanoparticles on a surface. This is critical as many of the effects on the nanoscale depend on separations on the order of a few nanometers, with sensitivities that extend down to the Ångstrom scale. By depositing free nanoparticles, the surface is highly modifiable and tunable, to allow for its use with a range of possible sensors and devices, as well as to probe effects of nanoparticle spacing on materials which interact with light.
Supporting Information

To deposit a thin film, the block copolymer was dissolved in one of two different solvents: toluene and chloroform. Both were done at the same concentrations. As seen in Figures S1 and S2, toluene gives rise to a more even coating and to very good domain formation after annealing. The case was similar for chloroform. A third solvent, tetrahydrofuran, was tried but it either dried too fast or had too low a viscosity, as the films formed from it were uneven.

**Figure S1.** Gold coated substrate after 10ul polymer deposition in toluene.

**Figure S2.** Gold coated substrate after 10ul polymer deposition in toluene and annealing at 165°C for 40 hours.
The Fourier transforms of Figures S1 and S2 are shown in Figure S3 and S4. The initial film shows no discernible structure, with the exception of a possible peak around 0.035 nm\(^{-1}\). However, after annealing, a strong peak at around 0.026 nm\(^{-1}\) appears, corresponding to a domain size of ca. 38 nm, which fits well with the theoretical domain size for the polymer chosen.

**Figure S3.** Fourier transform of SEM images taken of a gold coated substrate after 10 ul polymer deposition in toluene.

**Figure S4.** Fourier transform of SEM images taken of a gold coated substrate after 10 ul polymer deposition in toluene and annealing at 165°C for 40 hours.

Comparing Figures S5 and S6, we can see that toluene, in Figure S5, seems to give a better result than chloroform, figure S6, when looking at the etched samples, as the
domains appear more evenly spread and better spaced. This is corroborated by the Fourier transforms, which show a clear peak for toluene samples, Figure S7, and a rather broad and indistinct peak for the chloroform samples, Figure S8. The Fourier transforms seen in Figure S7 and S8 retain the peak seen in Figure S4, but slightly broadened and thus indicative of a smaller feature size. This meshes well with the proposed mechanism, where individual islands of polystyrene remain on the bare gold surface. The chloroform samples seem to show more holes in the array, but seem to be more regularly packed than the toluene samples, which are more evenly spread but less regularly arranged.

**Figure S5.** Gold coated substrate after 10 ul polymer deposition in toluene, annealing at 165°C for 40 hours and UV etching.
**Figure S6.** Gold coated substrate after 10 ul polymer deposition in chloroform, annealing at 165°C for 40 hours, and UV etching.

**Figure S7.** Fourier transform of SEM images taken of a gold coated substrate after 10 ul polymer deposition in toluene, annealing at 165°C for 40 hours, and UV etching.
Figure S8. Fourier transform of SEM images taken of a gold coated substrate after 10 ul polymer deposition in chloroform, annealing at 165°C for 40 hours, and UV etching.

Figure S9 shows the Fourier transform of the images shown in Figure 1, not including the one shown in Figure 2. All three correspond well with the peaks seen in Figure S8, showing that the structure has been preserved, but transformed from polystyrene islands to bound nanoparticles.
Figure S9. Fourier transform of SEM images taken of a gold coated substrate after 10 ul polymer deposition in chloroform, annealing at 165°C for 40 hours, UV etch, wash, passivation, PS phase removal, and NP deposition.
References

Conclusion

It now seems within reach to create a highly efficient, effective, low cost organic photovoltaic cell based on gold nanospheres. These cells take advantage of both the scattering and the local plasmonic effects provided by metallic nanoparticles, which serve to enhance the ability of the OPV material to absorb the light and efficiently generate excitons. The possibility of combining these two technologies, OPV and metallic nanoparticles, required the design of a radically new style of photovoltaic cell, which can utilize the strengths of all of its constituent materials. The ability to pattern a substrate with a regular array of these particles lays the foundation for the device construction. The knowledge of the methods required to grow chains of these same nanospheres in solution provides the second step for this device. Further, the model and simulations possible with the programs created for this work allow predictions and pre-emptive tuning of the device construction to optimize performance.

The model that was built for this task is capable of simulating systems large enough from which statistical information can be extracted. In the simulations run the results of the experiment match very closely the predictions of the model, validating the dynamics captured within the model. It was possible to extract kinetic information from the simulation and fit that to a second order kinetics model of assembly using a Markov-chain method to extract kinetic parameters for the formation of each cluster of particles. These parameters could then be modified based on assumptions relative to the behavior of particles to predict systems more realistic and thus more complex than that described in the model. The constraints those predictions put on dimer formation have, so far, not
been disproven. Experimental work indeed always approaches, but never exceeds these limits.

Expanding the simulations to include the electrostatic, or double-layer forces, was not a trivial task. There is no satisfactory formulation capable of describing, even approximately, the forces of interaction derived experimentally: The surface charge of the particles is too high and the size of the particles is too small to fall into one of the accepted formulations. Solving this problem required to explicitly calculate the field surrounding a nanoparticle for every interaction modeled, and to repeat the iteration to refine the model taking into account how the surface charges behave in a continuously evolving field. By doing this, the force fields for a single nanoparticle approaching a dimer and a linear trimer were calculated, giving insight into the challenges of linear nanochain formation. The results suggest that the tangential force, which is responsible for aligning the chain, reaches a maximum just as the radial force, which keeps the particles separated, reaches a critical value. This critical value separates the stable and unstable chain formation regions. The way this value is tuned experimentally is through changing the salt concentrations. This sweet-spot in salt concentration allows assembly to occur, but at the same time aligns the incoming nanoparticle to the end of the growing chain, promoting this useful mechanism.

To obtain the most out of these chains in an organic photovoltaic device they need to be tethered to the substrate, and electrically connected to it. In addition, they need to be spaced apart, to take maximum advantage of their light gathering ability. To provide these features, a substrate of well spaced, individual nanoparticles is needed to seed the upward growth of the linear nanochains. This task was accomplished through block-
copolym
er templating, followed by etching, washing, functionalizing, washing and then
depositing NP down on the prepared substrate. These particles have a spacing
commensurate with the spacing expected for the block copolymer template, and electron
imaging suggests that they match the template exactly.

Enhancement of organic photovoltaics through the use of nanoparticles now has a
new avenue of research. No longer are the particles constrained to lie on a surface as a
single layer, or be dispersed into the bulk of the media. The nanoparticle can now be a
fundamental, intrinsic aspect of the device, part of both the structure and function. This
opens new possibilities for the design of organic photovoltaic devices, taking advantage
of the wide range of size, shape, and functionality of metallic nanoparticles.

These results have laid the groundwork for much more investigation into the
incorporation of designed nanoparticle structures into organic photovoltaic devices.
Further work that is envisioned in this field is the optical modeling required to optimize
the spacing of the linear chains, the creation of the envisioned structure using the
methods explored above, and the coupling of an organic photosensitive material to the
surface of the nanochains. Ultimately, the goal is to make the efficiency higher while
reducing both materials and production costs and allowing the devices to be
manufactured on a massive scale, potentially providing inexpensive power for the coming
century.
Appendix

Description of the Simulation

The simulation was written in MATLAB, taking advantage of the embedded subset to allow compilation to an executable or linked library for faster execution. External data processing and visualization was also done in MATLAB, but not restricted to the embedded subset. The simulation code is organized thusly:

**External Calling function (qqueue or ugh)**

This function prepares the parameters for the simulation and calls the simulation routine, **MoEDL**. “qqueue” allows the user to queue several different runs in a GUI and view their progress dynamically, while “ugh” was used for calling **MoEDL** with a preset range of parameters for force calculations for the linear nanochains (Chapter 3). “qqueue” is designed to be a general, extensible graphical interface to the main simulation code.

**MoEDL(N,NPr,NPc,C,NPb,E,T,Vsolvent,delta,iterations,equi,incr,pH,salt,dtms)**

This function is empty currently, except for a further call to the true simulation code, **CP**. It sets up error conditions and handling for the following functions, and could be used to set the interaction distance, though this is set dynamically within **CP** and thus its assertion here is deprecated. This function takes in a number of parameters set by the user:

- **N** – scalar. Number of particles in the simulation.
- **NPr(N)** – 2xN double. Radius of particles in nm, Interaction radius (calculated later or input)
- **NPc(Nb)** – scalar. Concentration of nanoparticles in particles per cubic nm
C(Nb) – 2xNb double. Concentration of surface groups per cubic nm, Molar Volume of surface groups in m^3/mol

NPb(Nb) – 5xNb double. Lengths of each surface group in nm, chi parameter and first three pKa's

E(Nb) – 1xNb double. Binding energy of each group in J/mol, positive for binding

T – scalar. Thermodynamic temperature in Kelvin.

Vsolvent – scalar. Solvent molar volume

delta – scalar. Time interval multiplier (h=delta*tReduced)

iterations – scalar. number of iterations of the simulation

equi – scalar. Maximum number of surface equilibration steps at the beginning of the simulation

incr – scalar. Number of steps between save states and display

pH – scalar. pH

salt - 2xN double. Matrix of concentration/charge pairs - ions from pH must be included

dtms - 1xN double. Vector of percents of various cluster sizes. Must sum to 100

Fractions are x.xE1 IF the population can be written as xE2

OR fractions are xE1 IF pop is x.xE2; x is an integer

CP(N,NPr,NPc,C,NPb,E,T,Vsolvent,delta,iterations,equi,incr,pH,salt,dtms)

CP is the core code of the simulation, and calls all functions responsible for populating the surface of the particles (dynamicSites), calculating the distances between interacting particles (force), and the forces between those particles (findforce). In the
latest iteration, it then calls **NLDLVO2b**, which calculates the nonlinear electrostation interaction between the nanoparticles.

The initial code in this section sets up many of the values used during the simulation and precomputes others for which calculation at each time step is prohibitively expensive. It also allows the simulation to have initial populations that are not merely monomers and to correctly position and populate the space with the desired population of structures. These structures derive from assemblages found in the work done for the limits on dimerization (Chapter 2). It can be used to seed the solution with dimers which might be needed in the future; however it is not currently implemented.

**CP** then calls **startCheck**, which detects if any of the randomly placed NP in the solution space overlap, and moves them if that is true.

**CP** then calls **dynamicSites** in a loop, populating the surface of the particles with ligands. It does this until it hits ‘equi’, set when calling **MoEDL**, or the coverage of each particle is at least 99%. This significantly speeds up the initialization of the simulations. From here, information that requires the population of ligands is calculated, like the mean surface charge density and capacitance calculated in **part1**, needed for calculating the surface charge interactions, and volumetric ligand density, \( \frac{n_i V_{li}}{N_A V_{shell}} \), where \( n \) is the number of ligands on the particle of type \( i \), \( V_{li} \) is the ligand molar volume in cubic meters per mole (from ‘C’), \( N_A \) is Avogadro’s constant and \( V_{shell} \) is the volume of a spherical shell starting at the particle surface with a thickness the same as the length of the brush (length is from ‘C’), which is used in calculating the ligand-ligand forces. The parameters used for the work in chapter 2 are: \( n \approx 12000 \) brushes and 12000 linker per particle, \( V_{li} = 0.000238 \, \text{m}^3/\text{mol} \) for the brush, zero for all others, \( V_{shell} \approx 10000 \, \text{nm}^3 \). The parameters
used for the work in chapter 3 are: $n \approx 5000$ brushes and 2500 linker per particle, $V_{l,i} = 0.0870 \times 10^{-3}$ m$^3$/mol for the brush and $0.1797 \times 10^{-3}$ m$^3$/mol for the linker, $V_{shell} \approx 950$ nm$^3$ for the brush and 1775 nm$^3$ for the linker.

Next, the output values are initialized and the simulation begins. At each timestep, a set of normally distributed random numbers are chosen which will be used for the Brownian motion dynamics later. The simulation time step size, $h$, is calculated from ‘$\Delta$’ × ‘tReduced’, where $tReduced = 2 \frac{m}{kT} a$. The random numbers for Brownian motion are calculated using a time constant, $\beta$, which equals $\frac{6\pi \eta a}{m}$, where $a$ is the particle radius (from ‘NPr’), $\eta$ is the viscosity of the fluid, defined as that of water at 0.001 Pascal-seconds, and $m$ is the particle mass, calculated from the particle size (‘NPr’) and the density of gold, at 19300 kg/m$^3$. The parameters used for the work in chapter 2 are: $h = 2.5$ nanoseconds, $\delta = 0.001$, $tReduced = 2.5$ microseconds, $m \approx 6.5 \times 10^{-19}$ kg, $a \approx 20$ nm, $\beta = 5.8 \times 10^8$ s$^{-1}$. The parameters used for the work in chapter 3 are: $h = 2.5$ nanoseconds, $\delta = 0.001$, $tReduced = 2.5$ microseconds, $m \approx 8 \times 10^{-20}$ kg, $a \approx 10$ nm, $\beta = 2.4 \times 10^9$ s$^{-1}$. The numbers are taken from a bivariate Gaussian distribution with the following parameters:

$$
\begin{align*}
\sigma_r^2 &= \frac{m}{\beta^2} \left[ -2 h \beta + e^{-2 h \beta} - 4 e^{-h \beta} + 3 \right] k_b T \\
\sigma_\psi^2 &= -\frac{m}{\beta^2} \left[ -1 + e^{-2 h \beta} \right] k_b T \\
\rho \sigma_r \sigma_\psi &= \frac{e^{-2 h \beta} (-1 + e^{-h \beta})^2}{m \beta} k_b T
\end{align*}
$$

This serves to control the temperature of the simulation, shown in Figure 1.
Figure 1. Particle temperature as a function of the time during a simulation. The temperature is mostly confined to a region ±5 K from the set point of 300K, with some excursions to ±10 K. The system was sampled every 250 time steps, resulting in 1000 samples per simulation.

If running in interactive mode, a line is printed to the screen which shows the estimated time until simulation completion, based on the current run time and the number of steps left. At this point the positions are updated, using the forces calculated in the last two time steps, along with the current particle velocities, using the equations below:

\[
\begin{align*}
    r(t_{n+1}) &= r(t_n) + c_a h v(t_n) + c_b h^2 a(t_n) + c_c h^2 a(t_{n-1}) + Br \\
    v(t_{n+1}) &= c_d v(t_n) + c_e h a(t_{n+1}) + c_f h a(t_n) + c_g h a(t_{n-1}) + Bv
\end{align*}
\]

\[
\begin{pmatrix}
    c_a = c_1 \\
    c_b = c_2 + c_3 \\
    c_c = -c_3 \\
    c_d = c_0 \\
    c_e = c_2 - \frac{c_0 c_3}{c_1} \\
    c_f = c_1 - c_2 + \frac{2c_0 c_3}{c_1} \\
    c_g = -\frac{c_0 c_3}{c_1}
\end{pmatrix}
\begin{pmatrix}
    c_0 = e^{-\gamma} \\
    c_1 = \frac{1 - c_0}{\gamma} \\
    c_2 = \frac{1 - c_1}{\gamma} \\
    c_3 = \frac{1}{2} - c_2
\end{pmatrix}
\]
where the parameter $\gamma = h^*f$, and $Br$ and $Bv$ are the Brownian kicks to position and velocity described above. $\gamma = 1.45$ for the work in chapter 2, and 5.9 for the work in chapter 3.

*force* is then called, which calculates the distances between particles and returns all particle pairs whose center-to-center distance is less than the interaction distances. The initial interaction distances used are defined for each simulation run in the next section, Simulation Conditions. This gets fed into *findforce* which calculates all the forces between the particle pairs. These pair-wise forces are then compared to previous calculations to determine if the interaction distance is set too long. Long interaction distances slow the simulation greatly, so this has great potential use in accelerating the simulation and allowing it to tune itself. The pair-wise forces are then summed to provide one net force per particle. This force is then used to update the velocities, using the newly calculated force and the two previously calculated forces. If an error is detected, it is dealt with here, with the simulation dumping the current state and an error code. Then the whole loop begins again.

After hitting the required number of iterations successfully, the current time and date are used to make a unique filename, and all input parameters are saved, along with the positions, velocities and forces on each particle at the time points determined by ‘incr’.

**NPp=startCheck(NPp,NPr,NPc,delta)**

This function computes the distances between nanoparticles and if the center-to-center distance is less than the sum of the radii plus a constant (in this case 0.1nm), it
moves one of the particles to a new random location. This is done at the simulation set-up, to ensure no particles overlap. This continues until no pairs fail the test.

\[\text{[sites C]} = \text{dynamicSites}(\text{sites}, E, T, C, NPb, bNPl, cube, NPr)\]

This function is responsible for population the surface of each nanoparticle in the simulation with ligands from the implicit solution surrounding the nanoparticles. For each particle, it finds the number of unoccupied “sites” on the surface and attempts to populate them with the ligands in solution. It does this by computing the number of molecules within a half-hemisphere of one molecule radius from the surface and calculating a random number and comparing them. If the random number is less than the probability of finding a molecule, that site is considered occupied. For occupied sites, it checks to see if the ligand breaks free. Each ligand has a characteristic binding energy set when calling \text{MoEDL}. It then updates the number of ligands left in solution. In the case that it is run during the simulation, it needs the bNPl in case the unbinding ligand is a linked molecule, and will update ‘sites’ and the bound list to deal with the fact that the linker has unbound.

\[[\text{resultphiiso}, K, S] = \text{part1}(\text{NPr}, \epsilon, T, \text{pHlist}, NsL, Is, NPb)\]

This function calculates three parameters for each particle: phiiso, S and K, which correspond to the surface potential, charge and capacitance of that particle. First phiiso is calculated by equating the external surface charge, \(\frac{\varepsilon\phi_{iso}(1+\kappa a)}{a}\) with the surface charge, \(eN_s\left(-\frac{10^{-pK_a}}{10^{-pH}e^{-\frac{\phi_{iso}}{kT}}+10^{-pK_a}}\right)\) and solving for \(\phi_{iso}\), where \(a\) is the particle radius (from \(\text{NPr}\)), \(\kappa\) is the inverse Debye length (calculated from \(\text{Is}\) by \(\kappa = \frac{2N_Ae^2I}{\varepsilon_0\varepsilon_rkT}\), \(e\) is the charge of an electron, \(N_s\) is the number of molecules per square meter (from \(\text{NsL}\), \(\approx3 \times 10^9\)), \(\varepsilon\) is the dielectric permittivity of the solvent (from \(\text{epsilon}\), 80 for water), \(\phi_{iso}\) is the surface
potential in isolation, $pH$ (from $\text{pHlist}$, range 0-14) and $pKa$ (from the last three rows of $\text{NPb}$, $pK_{a1} = 4.65$ for the work in chapter 3) are solution and materials properties, $k$ is Boltzmann’s constant and $T$ is the thermodynamic temperature. $N_s$ is calculated from the total number of charged surface brushes on the nanoparticle divided by its surface area. $K$, the surface capacitance is calculated from the derivative of the second equation, evaluated at the calculated $\phi_{iso}$. $S$ is the surface charge calculated from plugging in the calculated $\phi_{iso}$ into the formula for surface charge and subtracting $K \times \phi_{iso}$. These parameters are used in the linearized Poissiion-Boltzmann model of the electrostatic interaction, but this model is not used for the calculation of the linear nanochains as it was not found to be accurate enough over the range of parameters used.

$\text{[intFCount intCount NPr]} = \text{force(NPp,NPr,cube)}$

This function calculates the inter-NP distance by using a volume subdivision method. The simulation volume is broken into cubes, and each NP is assigned a number representing the cube of space it is in. The size of the cube is dependent on the largest value of the interaction distance of all the particles. The distances are only calculated for particles in the same cube as the current particle of interest, or in neighboring cubes. If this distance is less than the interaction distance set for the particles, it is saved as an interacting pair. To deal with edge cases, the list of neighbors is computed modulo the total number of cubes in the relevant dimension, to get the correct neighbor cube. This feature was not implemented for the work presented in Chapter 2, as all long range forces are attractive and thus boundaries were deemed unneeded, and was unused for the work in Chapter 3, as the particles are held fixed as the forces are calculated.
This function calculates the forces between each interacting particle pair. The forces considered are: van der Waals, ligand compression/interpenetration, linker forces and a linearized form of the solution to the Poission-Boltzmann equation. The Van Der Waals force is based on: Hamaker, H.; The London--van der Waals Attraction Between Spherical Particles. Physica. 1937, 4, 1058-1072. The potential given is:

\[ U_{vdw} = \frac{A}{3} \left[ \frac{a_1 a_2}{r^2 - (a_1 + a_2)} + \frac{a_1 a_2}{r^2 - (a_1 - a_2)} + \frac{1}{2} \ln \left( \frac{r^2}{r^2 - (a_1 - a_2)} \right) \right] \]

Where, \( A \) is the Hamaker constant for gold, set at \( 75.5 \times k \times T \), \( a_i \) are the particle radii (from ‘NPr’, ≈20 nm for chapter 2, 10 nm for chapter 3), and \( r \) is the center-to-center distance (the third row of ‘intFCount’). For brush interpenetration where the brushes don’t touch the surface of the other particle, the potential is:

\[ \Delta G = \frac{1}{V_1} R_n T (V_{k53}(-1 + \phi 2k)(\phi 2k \chi + \log(1 - \phi 2k)) + (V_{k53} + V_{l53}) \]

\[ - 2V_{k53}\phi 2k - 2V_{l53}\phi 2l)(\frac{V_{k53}\phi 2k + V_{l53}\phi 2l)}{V_{k53} + V_{l53} - V_{k53}\phi 2k - V_{l53}\phi 2l} \]

\[ + \log\left(2 + \frac{V_{k53} + V_{l53}}{V_{k53}(-1 + \phi 2k) + V_{l53}(-1 + \phi 2l)}\right) + V_{l53}(-1 \]

\[ + \phi 2l)(\phi 2l \chi + \log(1 - \phi 2l)) \]

For brush interpenetration where the brushes do touch the surface of the other particle, the potential is:
\[ \Delta G = \frac{1}{V_1} RnT(V_{k5n}(-1 + \phi 2k)(\phi 2k\chi + \log (1 - \phi 2k)) + V_{l5n}(-1 + \phi 2l)(\phi 2l\chi + \log (1 - \phi 2l)) + (V_{k5n} + V_{l5n} + V_{f54}(-1 + \phi 2k) - 2V_{k54}\phi 2k + V_{e54}(-1 + \phi 2l)) \\
\] 
\[ \] 
[\begin{align*}
\frac{-2V_{l54}\phi 2l)\chi}{V_{k54} + V_{l54} + V_{f54}(-1 + \phi 2k) - V_{k54}\phi 2k + V_{e54}(-1 + \phi 2l) - V_{l54}\phi 2l} & + \frac{(V_{k54} + V_{l54} + V_{f54}(-1 + \phi 2k) - 2V_{k54}\phi 2k + V_{e54}(-1 + \phi 2l) - 2V_{l54}\phi 2l)}{V_{k54} + V_{l54} + V_{f54}(-1 + \phi 2k) - V_{k54}\phi 2k + V_{e54}(-1 + \phi 2l) - V_{l54}\phi 2l}} \\
\end{align*}\] 

And finally for brush compression, the potential is:

\[ \Delta G = \frac{1}{V_1} RnT(V_{k55}(-1 + \phi 2k)(\phi 2k\chi + \log (1 - \phi 2k)) + (V_{k55} + V_{d55}(-1 + \phi 2k) - V_{d55}\phi 2k - (V_{d55} - V_{d55})(-1 }
\[ + \phi 2l))\chi}{V_{k55} + V_{d55} + V_{d55}(-1 + \phi 2k) + V_{d55}(-1 + \phi 2l)} + \log \left[ \frac{V_{k55} + V_{d55}(-1 + \phi 2k) - V_{k55}\phi 2k - (V_{d55} - V_{d55})(-1 + \phi 2l)}{V_{k55} + V_{d55} + V_{d55}(-1 + \phi 2k) + V_{d55}(-1 + \phi 2l)} \right] \\
[\] 

In these equations, \( V1 \) is the solvent molar volume (.000106 m\(^3\)/mol for chapter 2, 1.8\times10^{-5} m\(^3\)/mol for chapter 3), \( Rn \) is the gas constant (8.134 J mol\(^{-1}\) K\(^{-1}\)), \( T \) is the thermodynamic temperature, \( \phi 2 \) (from ‘phi2’) is the mean surface density of the brushes for particles k and l, \( \chi \) is the Flory-Huggins interaction parameter (from the second row of ‘NPb’, 0.54 for all brushes for both chapters). \( V_{k5n} \) represent the overlap volumes for different states: \( n=3 \) is mixing, \( \delta<\delta<2 \delta \), \( n=4 \) is mixing \( h<\delta \), \( n=5 \) is compression. For mixing, the ‘f’ in \( V_{f54} \) indicates the final state, while \( V_{k53} \) has no change in volume and hence no
need to recompute the volume of overlap. For compression, the lowercase ‘d’ preceding the ‘k5n’ indicates initial state, and the uppercase ‘D’, the final state for the compression calculations. $V_l, V_e, V_{dl}, V_{Dl}$ are the volumes of overlap for the second particle, respectively. The linker force is computed as: $F = -kx$; where $k = 5.75 \times 10^{-9}$, and $x$ is the linker extension, which is the surface-to-surface distance between the particles minus the unstretched linker length (from ‘C’, 1.75 nm for the brushes in chapter 2 and 0.7 nm for the brushes in chapter 3, 1.25 nm for the linker in both). This is only computed for bound particles, those found in ‘bNPI’.

The results from the linearized Poission-Boltzmann are never actually used, while every other force in this section is always used. This makes up the core interactions between the nanoparticles. ‘intCount’ is the number of interactions, returned from force and ‘intFCount’ is the parameters of each interaction: first particle, second particle, center to center distance, $x$ distance, $y$ distance and $z$ distance. The last three are unused in findforce. ‘$V_1’$, the solvent molar volume and ‘phi2’, the brush volumetric density, are parameters used for the brush interpenetration/compression calculations, while all the parameters between ‘phi2’ and ‘intCount’ are precomputed parameters used by the linearized Poission-Boltzmann electrostatic interaction, which is not used. These are useful for systems up to perhaps 100 particles, beyond that memory requirements demand that they be calculated each time. This requirement is deprecated, as the linear equations do not result in an accurate enough model of the electrostatic interaction for useful predictive simulations. This function also calls bound, which updates the bound nanoparticle list, and interpolation3, which returns an approximation of the spherical Bessel function.
[bNPl sites]=bound(sites,p1,p2,bNPl)

This function takes the ID of two nanoparticles, ‘p1’ and ‘p2’, and checks to see if there are free linkers on the surface of one and a free site on the surface of the other. If there is, they are considered linked, and the bound nanoparticle list (‘bNPl’) is updated to include the new pair. In the schema of the simulations, a site with molecule 4 is an unbound linker, and with molecule 5 is a bound linker (updated in the particles columns of ‘sites’).

[Fprime]=interpolation3(R,F,Rprime)

This is a general interpolation function, tuned to run as fast as possible when using the Xk and Yk interpolation points passed to it by findforce. It uses two logical tests, the first for the x-value being smaller than the desired one, the second which exclusive-or’s two shifted versions of the result from the first test to find the crossing point. This allows it to work on an entire matrix in parallel, greatly speeding up execution compared to a simple binary search.

intForce=NLDLVO2b(NPr,NPb,Ns,phiiso,T,pH,kappa,intCount,intFCount,salt)

This function uses spline collocation to exactly solve the electric field using the Poission-Boltzmann equation, \( \nabla^2 \psi = \sinh \psi \), over a 2D plane which cuts the nanoparticles. ‘phiiso’ is used as an initial value which the splines take all over the surface of the NPs. The solution domain is:

\[
\eta_2 \leq \eta \leq \eta_1; \quad 0 \leq \theta \leq \pi
\]

Where \( \eta \) is defined by:

\[
\frac{b}{\sinh \eta_1} = \kappa a_1
\]

\[
\frac{b}{\sinh \eta_2} = \kappa a_2
\]
\[ \frac{b}{\tanh \eta_1} - \frac{b}{\tanh \eta_2} = \kappa a_1 + \kappa a_2 + \kappa h \]

Where \( b \) is a scaling constant, \( \eta_i \) are the coordinates of the particle surfaces in bispherical coordinates, \( \theta \) is a free geometrical coordinate that runs from the surface of one sphere to the other, \( h \) is the surface separation (calculated by subtracting the particle radii (‘NPr’) from the center-to-center distance (third row of ‘intFCount’)), \( a_i \) are the particle radii (from ‘NPr’, \( \approx20 \text{ nm} \) for chapter 2, \( 10 \text{ nm} \) for chapter 3), \( \kappa \) is the inverse of the Debye length, (from ‘kappa’). \( \kappa \) is calculated by:

\[ \kappa = \sqrt{\frac{2 N_A e^2 I}{\varepsilon_0 \varepsilon_r kT}} \]

Where \( N_A \) is Avogadro’s constant, \( e \) is the elementary charge, \( I \) is the ionic strength of the solution, \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon_r \) dielectric constant of the solvent (set as that of water, 80), \( k \) is Boltzmann’s constant and \( T \) is the thermodynamic temperature.

The ionic strength is calculated by:

\[ I = \frac{1}{2} \sum_{i=1}^{n} c_i z_i^2 \]

Where \( c_i \) (from the first row of ‘salt’, zero in chapter 2, ranging from 1 to 40 millimolar in chapter 3) is the molar concentration in moles per cubic meter and \( z_i \) (from the second row of ‘salt’, again zero in chapter 2, \( \pm1 \) in chapter 3) is the charge number of that ion.

This function starts using 16 gridpoints in each dimension, and if that is insufficient to have the Gaussian quadrature converge, the number of points is doubled until it does converge, or hits 256 points in each dimension. No situations encountered so far require more points than this. The change in field values in each iteration is compared to a tolerance value, and if it is less everywhere, the iteration stops. This tolerance value was found by running on a 200x200 grid with a tolerance value of \( 10^{-12} \), and comparing the
results from a series of smaller grids at lower tolerances to find what was needed to be within 1%. A value of $10^{-4}$ was found to be sufficient. Next the collocation points and matrix is set-up, using the sizes of the particles and the center-to-center distance to define the coordinate system. The system is then minimized using propagators derived from the constituent equations. The boundary conditions are dealt with as well, by matching the derivatives of the splines to the corresponding boundary conditions. From this, the force is calculated by Gauss-Kronrod quadrature, a numerical integration method included within MATLAB, which uses 7th order and 15th order Gaussian quadrature to calculate the integral of a function. The force between the particles is calculated by computing the following integral on $\eta=0$:

$$F = 2\pi \int_0^\pi \left\{ \frac{b^2(\cosh \psi - 1)}{(\cosh \eta - \cos \theta)^2} + \frac{1}{2} \left( \frac{\partial \psi}{\partial \theta} - \left( \frac{\partial \psi}{\partial \eta} \right)^2 \right) \right\} \times \left[ 1 - \cosh \eta \cos \theta \right]$$

Where $b$, $\eta$, $\theta$ are geometric parameters, and $\psi$ is the electric field. The grids start at size $16 \times 16$, and the resolution doubles if the force does not converge when integrated using adaptive Gauss-Kronrod quadrature.

**Simulation Conditions**

The molar volume of the brush and the solvent is computed from the density and molecular weight. The brush lengths are computed from ChemBioDraw3D, with the endpoints being the tips of the molecules plus the Van der Walls radius of the atoms at the tips. The binding energies of the brushes to the gold surface are from: Formation and Structure of Self-Assembled Monolayers, Abraham Ulman, Chem. Rev. 1996, 96, 1533-
which estimates it at 40kCal/mol or ~165kJ/mol. pH and salt are set to be as they are under experimental conditions.

For the simulations presented in Chapter 2, the following parameters are used:

\[ N = 5000 \]

\[ NPr(N) = 20 \pm 1 \text{ nm}, \text{ normally distributed. Interaction distance is } 4x \text{ the radius.} \]

\[ NPC(Nb) = \text{Varied, from } 4.8 \times 10^{-10} \text{ to } 1.2288 \times 10^{-8} \text{ NP/nm}^3. \]

\[ C(Nb) = \text{Held at } 50,000x \text{ the NP concentration for the first and fourth brushes (corresponding to the surface brushes and the linkers, respectively). Molar volumes are } 0.000238 \text{ m}^3/\text{mol for the brush, zero for all others.} \]

\[ NPb(Nb) = \text{Lengths were } 1.75 \text{ nm for the brushes, and } 1.25 \text{ nm for the linkers, with the Flory chi parameter set to } 0.54 \text{ for both.} \]

\[ E(Nb) = \text{Binding energy was } 163\text{kJ/mol for the brush and } 164\text{kJ/mol for the linker.} \]

\[ T = 300K \]

\[ V_{\text{solvent}} = 0.00106 \text{ m}^3/\text{mol.} \]

\[ \delta = 0.001 \]

\[ \text{iterations} = 250000 \]

\[ \text{equi} = 500 \]

\[ \text{incr} = 250 \]

\[ \text{pH} = \text{not set, not used.} \]

\[ \text{salt - not set, not used.} \]

\[ \text{dtms - not set, not used.} \]
Each set of simulation conditions (with NP concentration being the only variable) was run 4 times, for a total of 36 simulation runs, of 5000 particles each.

For the forces presented in Chapter 3, the following parameters are used:

N – 3 or 4 (dimer+1 or trimer+1)

NPr(N) – 10 nm. Interaction distance set to 1000 nm.

NPc(Nb) – $5 \times 10^{-10}$, to give a large enough box for long range forces to be calculated.

C(Nb) – Held at 5000x and 2500x the NP concentration for the first and fourth brushes (corresponding to the surface brushes and the linkers, respectively).

Molar volumes are $0.0870 \times 10^{-3}$ m$^3$/mol for the brush and $0.1797 \times 10^{-3}$ m$^3$/mol for the linker.

NPb(Nb) – Lengths were 0.7 nm for the brushes, and 1.25 nm for the linkers, with the Flory chi parameter set to 0.54 for both. The pKa of the brush was 4.87.

E(Nb) – Binding energy was 163kJ/mol for the brush and 164kJ/mol for the linker.

T – 300K

Vsolvent – $1.8 \times 10^{-5}$ m$^3$/mol.

delta – 0.0005

iterations – 1

equi – 500

incr – 300
pH – varied from 0 to 14. Based on measurements of reaction solutions, pH 5-6 was the region of interest.

salt – Cs, the concentration of salt, was varied from 1 to 40 mM.

dtms – 100 (100% monomers)

This set of simulations was run one at a time, for a range of particle separations and angles from the core, for each set of conditions. Each simulation contained only 3 or 4 particles, but the 3rd or 4th one was placed at all the locations desired for force calculation, but could not interact with each other. In essence there were two or three core particles, and 43680 “virtual” particles (480 in distance and 91 in rotation), each one of which could only interact with the particles at the core. The conditions that varied were the salt concentration, from 1-40mM and the pH, from 0-14, in increments of 0.5. Both the linear and non-linear forces were calculated, and compared for accuracy. The linear forces were not good enough to continue using, so the nonlinear forces were used for the calculation of the force plots shown in chapter 3.

To compare the simulation and experiment, both were run over the same set of parameters, with the inputs to the simulation set so as to recreate the physical conditions in the experiment as closely as possible. The simulations were run first over a coarse set of conditions, to narrow down the interesting region for experimentation. Then the experiments were run, along with a higher resolution set of simulations, over the determined experimental conditions.

The images taken from the experimental results are observed using this method: First, the sample is mounted on an SEM stud, and dried overnight in a dessicator. The samples are placed in the SEM, and imaged by selecting a region of the sample at ~1000x
magnification. This region is selected to be away from the edges of the sample plane and the drying ring of the droplet, both of which are far from equilibrium. The zoom is then increased to the desired level, for the chains it was 500,000x, and then the image is shifted slightly so as to center any feature of interest. The shift is no more than \( \frac{1}{4} \) of the frame. The image is taken, the magnification is reduced, and a new region is selected.

### Equations of the forces used

1. **Van Der Waals**

   \[
   U_{vdw} = \frac{A}{3} \left[ \frac{a_1 a_2}{r^2 - (a_1 + a_2)} + \frac{a_1 a_2}{r^2 - (a_1 - a_2)} \right] + \frac{1}{2} \ln \frac{r^2 - (a_1 + a_2)}{r^2 - (a_1 - a_2)}
   \]

   Where, \( A \) is the Hamaker constant for gold, set at \( 75.5 \times k \times T \), \( a_i \) are the particle radii, and \( r \) is the center-to-center distance.

2. **Brush Interpenetration/Compression**
   The particles are denoted \( k \) and \( l \), while \( i \) and \( f \) are used for the initial and final states, respectively. \( mnx \) is the moles of molecules, either \( n=1 \) for solvent or \( n=2 \) for brush, \( \phi nx \) is the volume fraction of the same, where \( x \) is comprised of \( j = k \) or \( l \) for the particle and \( i \) or \( f \) for the initial and final state. \( Vn \) is the molar volume of either \( n=1 \) for the solvent or \( n=2 \) for the polymer. \( Vj \) is the volume of overlap of the interaction. \( Vk5n \) represent the overlap volumes for different states: 3 is mixing, \( 3 \leq h < 2 \), 4 is mixing \( h \leq \delta \), 5 is compression. For mixing, the ‘f’ in \( Vf54 \) indicates the final state, while \( Vk53 \) has no change in volume and hence no need to recomputed the volume of overlap. For compression, the lowercase ‘d’ indicates initial state, and the uppercase ‘D’, the final
state for the compression calculations. \( V_l, V_e, V_{dl}, V_{Dl} \) are the volumes of overlap for the second particle, respectively. \( \chi \) is the Flory-Huggins interaction parameter, \( N \) is Avogadro’s constant, \( k \) is Boltzmann’s constant and \( T \) is the thermodynamic temperature.


\[
\Delta G = \Delta g_{fkl} - (\Delta g_{ik} + \Delta g_{il})
\]

\[
\Delta g_f = N k T (m_{1f} \log(\phi_{1f}) + m_{2f} \log(\phi_{2f}) + \chi m_{1f} \phi_{2f})
\]

\[
\Delta g_i = N k T (m_{1i} \log(\phi_{1i}) + m_{2i} \log(\phi_{2i}) + \chi m_{1i} \phi_{2i})
\]

\[
V_k = \overline{V_{\text{integrated}}} (V_k53, V_k54, V_f54, V_{dk55}, V_{Dk55})
\]

\[
\{V_l, V_e, V_{dl}, V_{Dl}\} = \{\{V_k53, V_k54\}, V_f54, V_{dk55}, V_{Dk55}\}/\{a\rightarrow b, b\rightarrow a\}
\]

\[
\phi_{1f} = m_{1f}/(m_{1f} + n m_{2f});
\]

\[
\phi_{2f} = (n m_{2f})/(m_{1f} + n m_{2f});
\]

\[n = V_{\text{polymer molecule}}/V_{\text{solvent molecule}};\]

Define the expressions for \( m \)

**Expression for \( m \) in the zone \( \delta < h < 2\delta \) for the mixing mechanism, \( \delta \) is the brush length**

\[
m_{2ji} = \sqrt{V_j/2}
\]

\[
m_{1ji} = (V_j - m_{2ji} \sqrt{2})/\sqrt{1}
\]

\[m_{2jf} = m_{2ki} + m_{2li}\]

\[m_{1jf} = m_{1ki} + m_{1li} - n m_{2jf}\]

**Expression for \( m \) in the zone \( h < \delta \) for the mixing mechanism**

\[
m_{2ji} = \sqrt{V_j/2}
\]

\[
m_{1ji} = (V_j - m_{2ji} \sqrt{2})/\sqrt{1}
\]
m2jf = m2ki + m2li

m1jf = m1ki + m1li - n * m2jf - m1

\[ \frac{1}{m1j} = VDj \left( 1 - \frac{m2j}{V1} \right) \]

\[ n = \frac{V2}{V1} \]

**Expression for m in the zone 0 < h < 2δ for the denting mechanism**

m2ji = \( \frac{Vd}{V2} \)

m1ji = \( \frac{Vd - m2ji}{V1} \)

m2jf = m2ki + m2li

m1jf = m1ki + m1li - m1k - m1l

\[ m1j = VDj \left( 1 - \frac{m2j}{V1} \right) \]

n = \( \frac{V2}{V1} \); 

**Now calculate the m values for each section**

**So, let’s write down all the initial states**

**First for the zone δ < h < 2δ, mixing mechanism**

m2ki1 = FullSimplify[(φ2k Vk53)/V2];

m2li1 = FullSimplify[(φ2l Vl53)/V2];

m1ki1 = FullSimplify[(Vk53 - m2ki1 V2)/V1];

m1li1 = FullSimplify[(Vl53 - m2li1 V2)/V1];

**Now for the zone h < δ**

m2ki2 = FullSimplify[(φ2k Vk54)/V2];

m2li2 = FullSimplify[(φ2l Vl54)/V2];

m1ki2 = FullSimplify[(Vk54 - m2ki2 V2)/V1];
m1li2 = FullSimplify[(Vl54 - m2li2 V2)/V1];

**Now for the zone 0<h<2δ, denting mechanism**

m2ki3 = FullSimplify[(φ2k Vdk55)/V2];

m2li3 = FullSimplify[(φ2l Vdl55)/V2];

m1ki3 = FullSimplify[(Vdk55 - m2ki3 V2)/V1];

m1li3 = FullSimplify[(Vdl55 - m2li3 V2)/V1];

Now, let's write down all the final states

**First for the zone δ<h<2δ, mixing mechanism**

m2f1 = FullSimplify[m2ki1 + m2li1];

m1f1 = FullSimplify[m1ki1 + m1li1 - n m2f1];

**Now for the zone h<δ**

m2f2 = FullSimplify[m2ki2 + m2li2];

m2 = (φ2k Vf54 + φ2l Ve54)/V2;

m1 = (Vf54 + Ve54 - m2 V2)/V1;

m1f2 = FullSimplify[m1ki2 + m1li2 - n m2f2 - m1];

**Now for the zone 0<h<2δ, denting mechanism**

m2f3 = FullSimplify[m2ki3 + m2li3];

m1k = VDk55((1 - φ2k)/V1);

m1l = VDl55((1 - φ2l)/V1);

m1f3 = FullSimplify[m1ki3 + m1li3 - m1k - m1l];

Now calculate the φ values for each section

So, let's write down all the initial states

**First for the zone δ<h<2δ, mixing mechanism**
\( \phi_{1ki1} = \text{FullSimplify}\left(\frac{m_{1ki1}}{(m_{1ki1} + n \, m_{2ki1})}\right) \);
\( \phi_{2ki1} = \text{FullSimplify}\left(\frac{n \, m_{2ki1}}{(m_{1ki1} + n \, m_{2ki1})}\right) \);
\( \phi_{1li1} = \text{FullSimplify}\left(\frac{m_{1li1}}{(m_{1li1} + n \, m_{2li1})}\right) \);
\( \phi_{2li1} = \text{FullSimplify}\left(\frac{n \, m_{2li1}}{(m_{1li1} + n \, m_{2li1})}\right) \);

Now for the zone \( h < \delta \)
\( \phi_{1ki2} = \text{FullSimplify}\left(\frac{m_{1ki2}}{(m_{1ki2} + n \, m_{2ki2})}\right) \);
\( \phi_{2ki2} = \text{FullSimplify}\left(\frac{n \, m_{2ki2}}{(m_{1ki2} + n \, m_{2ki2})}\right) \);
\( \phi_{1li2} = \text{FullSimplify}\left(\frac{m_{1li2}}{(m_{1li2} + n \, m_{2li2})}\right) \);
\( \phi_{2li2} = \text{FullSimplify}\left(\frac{n \, m_{2li2}}{(m_{1li2} + n \, m_{2li2})}\right) \);

Now for the zone \( 0 < h < 2\delta, \) denting mechanism
\( \phi_{1ki3} = \text{FullSimplify}\left(\frac{m_{1ki3}}{(m_{1ki3} + n \, m_{2ki3})}\right) \);
\( \phi_{2ki3} = \text{FullSimplify}\left(\frac{n \, m_{2ki3}}{(m_{1ki3} + n \, m_{2ki3})}\right) \);
\( \phi_{1li3} = \text{FullSimplify}\left(\frac{m_{1li3}}{(m_{1li3} + n \, m_{2li3})}\right) \);
\( \phi_{2li3} = \text{FullSimplify}\left(\frac{n \, m_{2li3}}{(m_{1li3} + n \, m_{2li3})}\right) \);

Now, let's write down all the final states

First for the zone \( \delta < h < 2\delta, \) mixing mechanism
\( \phi_{1f1} = \text{FullSimplify}\left(\frac{m_{1f1}}{(m_{1f1} + n \, m_{2f1})}\right) \);
\( \phi_{2f1} = \text{FullSimplify}\left(\frac{n \, m_{2f1}}{(m_{1f1} + n \, m_{2f1})}\right) \);

Now for the zone \( h < \delta \)
\( \phi_{1f2} = \text{FullSimplify}\left(\frac{m_{1f2}}{(m_{1f2} + n \, m_{2f2})}\right) \);
\( \phi_{2f2} = \text{FullSimplify}\left(\frac{n \, m_{2f2}}{(m_{1f2} + n \, m_{2f2})}\right) \);

Now for the zone \( 0 < h < 2\delta, \) denting mechanism
\( \phi_{1f3} = \text{FullSimplify}\left(\frac{m_{1f3}}{(m_{1f3} + n \, m_{2f3})}\right) \);
\( \phi_2 f_3 = \text{FullSimplify}[(n m_2 f_3)/(m_1 f_3 + n m_2 f_3)]; \)

Now calculate G for each case

\[ \Delta G = RT(m_1 \ln(\phi_1) + \chi m_1 \phi_2) \]

So, let's write down all the initial states

**First for the zone \( \delta < h < 2\delta \), mixing mechanism**

\( g_{ki1} = \text{FullSimplify}[R_n T(m_1 k_{i1} \log(\phi_1 k_{i1}) + \chi m_1 k_{i1} \phi_2 k_{i1})]; \)

\( g_{li1} = \text{FullSimplify}[R_n T(m_1 l_{i1} \log(\phi_1 l_{i1}) + \chi m_1 l_{i1} \phi_2 l_{i1})]; \)

**Now for the zone \( h < \delta \)**

\( g_{ki2} = \text{FullSimplify}[R_n T(m_1 k_{i2} \log(\phi_1 k_{i2}) + \chi m_1 k_{i2} \phi_2 k_{i2})]; \)

\( g_{li2} = \text{FullSimplify}[R_n T(m_1 l_{i2} \log(\phi_1 l_{i2}) + \chi m_1 l_{i2} \phi_2 l_{i2})]; \)

**Now for the zone \( 0 < h < 2\delta \), denting mechanism**

\( g_{ki3} = \text{FullSimplify}[R_n T(m_1 k_{i3} \log(\phi_1 k_{i3}) + \chi m_1 k_{i3} \phi_2 k_{i3})]; \)

\( g_{li3} = \text{FullSimplify}[R_n T(m_1 l_{i3} \log(\phi_1 l_{i3}) + \chi m_1 l_{i3} \phi_2 l_{i3})]; \)

Now, let's write down all the final states

**First for the zone \( \delta < h < 2\delta \), mixing mechanism**

\( g_{f1} = \text{FullSimplify}[R_n T(m_1 f_1 \log(\phi_1 f_1) + \chi m_1 f_1 \phi_2 f_1)]; \)

**Now for the zone \( h < \delta \)**

\( g_{f2} = \text{FullSimplify}[R_n T(m_1 f_2 \log(\phi_1 f_2) + \chi m_1 f_2 \phi_2 f_2)]; \)

**Now for the zone \( 0 < h < 2\delta \), denting mechanism**

\( g_{f3} = \text{FullSimplify}[R_n T(m_1 f_3 \log(\phi_1 f_3) + \chi m_1 f_3 \phi_2 f_3)]; \)

Output all the \( \Delta G \)'s

\[(g_1 = \text{FullSimplify}[(g_{f1} - g_{ki1} - g_{li1})])/\text{InputForm}\]
\((Rn*T*(Vk53*(-1 + \phi 2k) * (2k * \chi + \log[1 - \phi 2k]) + (Vk53 + Vl53 - 2*Vk53*\phi 2k - 2*Vl53*\phi 2l)/((Vk53*\phi 2k + Vl53*\phi 2l)*\chi)/((Vk53 - Vl53 - Vl53*\phi 2l) + \log[2 + (Vk53 + Vl53)/((Vk53*(-1 + \phi 2k) + Vl53*(-1 + \phi 2l))]) + Vl53*(-1 + \phi 2l)*(\phi 2l*\chi + \log[1 - \phi 2l])))/V1\)

\((g2=\text{FullSimplify}}[(gf2 - gki2 - gli2)]))//\text{InputForm}\)

\((Rn*T*(Vk54*(-1 + \phi 2k) * (2k * \chi + \log[1 - \phi 2k]) + Vl54*(2k * \chi + \log[1 - \phi 2k]) + (Vk54 + Vl54 + Vf54*(-1 + \phi 2k) - 2*Vk54*\phi 2k + Ve54*(-1 + \phi 2l) - 2*Vl54*\phi 2l)*(((Vk54*\phi 2k + Vl54*\phi 2l)*\chi)/(Vk54 + Vl54 + Vf54*(-1 + \phi 2k) - 2*Vk54*\phi 2k + Ve54*(-1 + \phi 2l) - Vl54*\phi 2l))/V1\)

\((g3=\text{FullSimplify}}[(gf3 - gki3 - gli3)]))//\text{InputForm}\)

\((Rn*T*(Vdk55*(-1 + \phi 2k) * (2k * \chi + \log[1 - \phi 2k]) + (Vdk55 + VDk55*(-1 + \phi 2k) - Vdk55*\phi 2k - (Vdl55 - VDI55)*(-1 + \phi 2l))*(((Vdk55*\phi 2k + Vdl55*\phi 2l)*\chi)/(Vdk55 + VDk55 + Vdl55*(-1 + \phi 2k) + VDI55*(-1 + \phi 2l)) + \log[(Vdk55 + VDk55*(-1 + \phi 2k) - Vdk55*\phi 2k - (Vdl55 - VDI55)*(-1 + \phi 2l))]/(Vdk55 + VDk55 + Vdl55*(-1 + \phi 2k) + VDI55*(-1 + \phi 2l)) + Vdl55*(-1 + \phi 2l)*(\phi 2l*\chi + \log[1 - \phi 2l])))/V1\)

Set up the integrals for the overlap region and some initial conditions

\(Vk53=\text{FullSimplify}}[\int_{0}^{2\pi} \int_{0}^{2\pi} \frac{1}{\sqrt{\sin^2 \theta_1 + \sin^2 \theta_2 - 2 \sin \theta_1 \sin \theta_2 \cos (\theta_1 - \theta_2)}} d\theta_1 d\theta_2 //\{pk->(Rk^2 - Rl^2 + H^2)/(2H), Rk->a+\delta, Rl->b+\delta, H->a+b+h, h->R-a-b\}]\);
\[ V_{k4} = \text{FullSimplify}\left[ \left( \frac{a^2 - R_l^2 + H^2}{2H} \right) \right] \]

\[ V_{f4} = \text{FullSimplify}\left[ \left( \frac{a^2 - R_l^2 + H^2}{2H} \right) \right] \]

\[ V_{d4} = \text{FullSimplify}\left[ \left( \frac{a^2 - R_l^2 + H^2}{2H} \right) \right] \]

\[ V_{d5} = \text{FullSimplify}\left[ \left( \frac{a^2 - R_l^2 + H^2}{2H} \right) \right] \]

\[ V_{l53} = V_{k53} ./ \{a \rightarrow b, b \rightarrow a\}; \]

\[ V_{d5} = V_{k54} ./ \{a \rightarrow b, b \rightarrow a\}; \]

\[ V_{e54} = V_{f54} ./ \{a \rightarrow b, b \rightarrow a\}; \]

\[ V_{d55} = V_{k55} ./ \{a \rightarrow b, b \rightarrow a\}; \]

\[ V_{d55} = V_{k55} ./ \{a \rightarrow b, b \rightarrow a\}; \]

\[ V_1 = \text{solventMolarMass/solventDensity}; \]

\[ V_2 = \text{polymerMolarMass/polymerDensity}; \]

\[ c_k = (3a^2)/(N(3a^2 \delta + 3a \delta^2 + \delta^3)); \]

\[ c_l = c_k ./ \{a \rightarrow b, b \rightarrow a\}; \]

To solve, plug the relevant V values above into the equations for G, then differentiate with respect to distance.

3. Linker
F = - k x; where \( k = 5.75 \times 10^{-9} \), and \( x \) is the linker extension, that is the surface-to-surface distance between the particles minus the unstretched linker length, which is given in the previous section.

4. Electrostatic

\[ \nabla^2 \psi = \sinh \psi \]

Bispherical coordinates, Newton-Raphson iteration, and collocation with bicubic Hermite basis functions are used to solve it.

Domain is:

\[ \eta_2 \leq \eta \leq \eta_1; \ 0 \leq \theta \leq \pi \]

Where \( \eta \) is defined by:

\[
\frac{b}{\sinh \eta_1} = \kappa a_1 \\
\frac{b}{\sinh \eta_2} = \kappa a_2 \\
\frac{b}{\tanh \eta_1} - \frac{b}{\tanh \eta_2} = \kappa a_1 + \kappa a_2 + \kappa h
\]

Where \( b \) is a scaling constant, \( \eta_i \) are the coordinates of the particle surfaces in bi-
spherical coordinates, \( h \) is the surface separation, \( a_i \) are the particle radii, \( \kappa \) is the inverse of the Debye length. \( \kappa \) is calculated by:

\[
\kappa = \frac{2 N_A e^2 I}{\sqrt{\varepsilon_0 \varepsilon_r kT}}
\]

Where \( N_A \) is Avogadro’s constant, \( e \) is the elementary charge, \( I \) is the ionic strength of the solution, \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon_r \) dielectric constant of the solvent, \( k \) is Boltzmann’s constant and \( T \) is the thermodynamic temperature. The ionic strength is calculated by:
\[ I = \frac{1}{2} \sum_{i=1}^{n} c_i z_i^2 \]

Where \( c_i \) is the molar concentration in moles per cubic meter and \( z_i \) is the charge number of that ion.

The force between the particles is calculated by computing the following integral:

\[
F = 2\pi \int_{0}^{\pi} \left\{ \frac{b^2 (\cosh \psi - 1)}{(\cosh \eta - \cos \theta)^2} + \frac{1}{2} \left( \left( \frac{\partial \psi}{\partial \theta} \right)^2 - \left( \frac{\partial \psi}{\partial \eta} \right)^2 \right) \right\} \times \left[ 1 - \cosh \eta \cos \theta \right] \\
+ \frac{\partial \psi}{\partial \theta} \frac{\sin \theta}{\cosh \eta - \cos \theta} \partial \theta
\]

The grids start at size 16x16, and the resolution doubles if the force does not converge when integrated using adaptive Gauss-Kronrod quadrature.