Assembly of Metal Nanoparticles into Nanogaps

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The directed assembly of nanoparticles and nanoscale materials onto specific locations of a surface is one of the major challenges in nanotechnology. Here we present a simple and scalable method and model for the assembly of nanoparticles in between electrical leads. Gold nanoparticles, 20 nm in diameter, were assembled inside electrical gaps ranging from 15 to 150 nm with the use of positive ac dielectrophoresis. In this method, an alternating current is used to create a gradient of electrical field that attracts particles in between the two leads used to create the potential. Assembly is achieved when dielectrophoretic forces exceed thermal and electrostatic forces; the use of anchoring molecules, present in the gap, improves the final assembly stability. We demonstrate with both experiment and theory that nanoparticle assembly inside the gap is controlled by the applied voltage and the gap size. Experimental evidence and modeling suggest that a gap-size-dependent threshold voltage must be overcome before particle assembly is realized. Assembly results as a function of frequency and time are also presented. Assembly of fewer than 10 isolated particles in a gap is demonstrated. Preliminary electrical characterization reveals that stable conductance of the assembled particles can be achieved.

1. Introduction

Dielectrophoresis (DEP) is the force felt by a polarizable object when it is placed in a nonuniform electric field. In vacuum, when a polarizable object is placed into an electric field, polarization charge is induced at the surface of the object; if the applied electric field is nonuniform, it interacts with this polarization charge to attract the object towards the point of strongest field. This also happens in solution, when an object with a larger polarizability than the solvent molecules interacts with a nonuniform field (positive DEP). When objects of lower polarizability interact with a field, the polarization charge aligns such that the object is pushed away from the region of highest field (negative DEP). DEP has been demonstrated to manipulate micrometer-sized objects such as cells for over three decades.

One of the major challenges for nanotechnology is the manufacturing of devices with easily scalable approaches. While there are many obstacles to be overcome in nanom
Directed Assembly of Nanoparticles

2. Results

2.1. Gap Formation

Gaps used in this work were formed either by direct patterning with electron-beam lithography (EBL) or by a localized melting technique. Gaps formed by direct patterning had widths of 30 to 150 nm (controlled via the electron dose level during EBL) and the wires were 300 nm wide with almost hemispherical ends. Gaps were also formed using a localized melting technique introduced by Richter et al.[35] Gold wires that overlap in a ≈100-nm-wide by 30-nm-long region (Figure 1) were subjected to a voltage sweep over time. As the voltage increases, greater current densities pass through the junction of the two wires, causing large increases in temperature. Once the melting point of gold is reached, a sharp decrease in current level is observed, indicating gap formation. The gap resistance after the break usually exceeds 3 × 10¹² Ω when measured at 300 mV. Scanning electron microscopy (SEM) imaging revealed gaps with widths ranging from 10–70 nm. A similar strategy was employed using an alternating voltage at 1 MHz, gradually increasing the ac voltage until wire failure occurred. It is the authors’ opinion that localized melting for fabricating nano-gaps is simple, requiring no complicated lithographic techniques, and due to its reliance on only electrical current could be technologically valuable.

Gold particles[36] stabilized by a proprietary coating that has an overall negative surface charge (probably similar to citrate molecules), were chosen for this study partly because of their unique optical and electronic properties, but mainly because of their solubility in water, monodispersity, and commercial availability.

Prior to DEP assembly of nanoparticles, the substrates were immersed in a toluene solution of hexanethiol and nonanethiol. Both molecules bind (through their thiol group) to the metallic leads. The dithiol molecules chemically bind mostly orthogonally to the surface with only one thiol group.[37] The second thiol group stays on the surface on the self-assembled monolayer (SAM) ready to bind to the nanoparticles once they are brought into the gap by the DEP force.[17–19,23,34] The SAM, therefore, serves as a molecular glue, binding the nanoparticles to the wires. Control experiments where the dithiol molecules were not used resulted in inconsistent nanoparticle assembly.

The experimental set-up used for dielectrophoretic assembly is shown in Scheme 1 with details provided in the Experimental Section. Briefly, a 0.1–0.25 mL drop of aqueous nanoparticle solution was placed over the sample, covering all devices on the chip. An alternating voltage of a given magnitude and frequency was applied for a set amount of time. An oscilloscope was used to monitor the changes in conductivity of the nanoparticle bridge when testing for the conditions of fused versus isolated particle assembly (see below). After these conditions had been established, experiments were performed without the oscilloscope; the second electrode was connected directly to ground.

2.2. Assembly Versus Voltage and Concentration—Fused Versus Isolated Particle Assembly

The assembly of nanoparticles into nanogaps has been shown for isolated individual particles[9,15–17,23,34] and for fused metallic particles[20,21] using similar conditions. Using our experimental set-up it was possible to achieve both types of assembly (Figure 2) and to detect the creation of a fused metallic wire bridging the gap in real time. When a...
The key controlling factors differentiating the two types of assembly are found to be the applied peak-to-peak voltage and the nanoparticle concentration in solution. At a nanoparticle concentration of $7 \times 10^{13}$ particles mL$^{-1}$, 15 out of the 17 (15/17) assembled at voltages of 3 V$_{pp}$ and higher were found to be filled with fused particles. When $V_{pp}$ was below 3 V, fused wire assembly was not observed (0/6) and isolated particles could be seen in subsequent SEM images. At a more dilute nanoparticle concentration ($7 \times 10^{10}$ particles mL$^{-1}$), the voltage required for fusing increases. Voltages larger than 4.5 V$_{pp}$ were needed to observe fused particles in the gap ($\approx 69\%$, 9/13) while at voltages equal to or lower than 4 V$_{pp}$ almost all gaps (28/29) showed isolated particle assembly. As our goal was to study the assembly of isolated particles, we performed experiments with these latter conditions (with nanoparticle concentrations of $7 \times 10^{10}$ particles mL$^{-1}$ and lower voltages).

2.2.1. Assembly Versus Voltage and Gap Width

To investigate assembly as a function of voltage and gap width, assemblies were carried out for 120 s at a given alternating $V_{pp}$ and a frequency of 1 MHz. After the assembly of isolated particles, the samples were imaged by SEM and the number of particles captured in each gap was counted. A 400-nm-diameter circle centered on the middle of the gap was drawn and only nanoparticles within this circle were considered as captured. SEM images were also used to measure the gap width. Gap widths were measured at their narrowest points.

Figure 3 demonstrates the effect of voltage and gap width on nanoparticle assembly. A threshold voltage must be reached before any nanoparticle assembly is realized, as seen in previous work. As the gap width is increased, the threshold voltage required for nanoparticle assembly in-
creases. At an average gap width of 30 nm (widths ranging from 15 to 50 nm) and voltages below 2 V_{pp}, no assembly was observed. For slightly larger gaps (85 nm average; widths from 50–110 nm) assembly was not observed until 3 V_{pp}, and for the largest gaps tested (125 nm average, widths from 110–150 nm), assembly was not observed until approximately 4 V_{pp} on eight out of nine gaps tested. The use of larger gaps was also observed to increase the voltage necessary for fusing. Isolated nanoparticle assembly was achieved on gaps >70 nm at 4.5 V_{pp} and on gaps >105 nm at voltages of 5 and 6 V_{pp}. The number of assembled particles captured in the gap increased with increasing voltage for all gap widths when voltages larger than the threshold voltage were applied.

2.2.2. Assembly Versus Time

To achieve the assembly of a very few (<10) isolated particles in the gap, it was necessary to limit the assembly time. Operating at a frequency of 1 MHz and at voltages near the threshold for a given gap size resulted in the capture of a few nanoparticles. For small electrode gaps, ≈15–40 nm, 2 V_{pp} assemblies were performed for 5, 10, 30, 60, and 120 s, while on larger electrode gaps, ≈55–90 nm, 3 V_{pp} assemblies were performed for similar durations. As illustrated in Figure 4, the shortest assembly times resulted in the assembly of fewer than 10 particles in the gap. Increased assembly time resulted in more nanoparticles in the gap for all gap widths at voltages above the threshold value.

2.2.3. Assembly Versus Frequency

To study the effect of frequency on nanoparticle assembly, peak-to-peak voltages near the threshold (2.5–4 V_{pp}) were applied. Assemblies were carried out for 120 s at frequencies of 10 kHz, 100 kHz, and 1 MHz. Figure 5 shows a strong dependence of nanoparticle assembly on frequency. At lower frequencies more nanoparticle assembly is seen and fusing occurs more readily. As frequency is increased, fewer nanoparticles assemble and the particles remain isolated.

2.3. Post-Assembly Electrical Characterization of Nanoparticle Bridges

The assembly of nanoparticles in a gap was characterized in the dry state at room temperature with dc I–V measurements between 0 and 300 mV prior to SEM imaging (Figure 6). Isolated particles generally showed a high resistance (2.5 MΩ to 60 GΩ). Using higher applied voltages led to more nanoparticle assembly and lower-resistance devices. These devices were measured in the dry state 16 h after assembly. The current levels of the devices were stable up to 20 electrical sweeps.

2.4. Modeling

2.4.1. Nanoparticle Transport

In order to predict how experimental variables would affect the assembly of nanoparticles into nanogaps, we have modeled the forces that govern the DEP assembly of particles. Specifically we have modeled the dielectrophoretic force, the particles' thermal motion, and the electrostatic repulsion between the substrate and the particles. The problem was solved by determining the regions of space over which each force becomes dominant.

The small size of the nanoparticles and the associated significance of thermal fluctuations precludes the use of deterministic models for particle assembly. Instead, we adopt a continuum model formulated in terms of the number density of nanoparticles, c(r,t), where r is the dis-
The quantity \( c(r=r_0,t) \) multiplied by the incremental volume \( dV \) may be thought of as giving the expected number of nanoparticles in a volume \( dV \), centered around \( r=r_0 \), at time \( t \). Because the nanoparticle solution is dilute and the length scales we are interested in are small, the relevant volume element \( dV \) will generally contain exceptionally few nanoparticles; at the concentrations adopted, a cube measuring a few micrometers per side would be necessary to encompass a single particle with reasonably high probability. The consequence of modeling a discrete system using smooth functions of space and time is that the model will not capture the statistical fluctuations inherent in the assembly process. Since we are primarily interested in how the number of assembled particles depends on different operating parameters, a relatively simple way to reintroduce statistical fluctuations into our model is to treat assembly as a series of events following a Poisson distribution. Accordingly, after we have determined the number of particles collected at time \( n(t) \), we can approximate the standard deviation as \( [n(t)]^{1/2} \). Inherent in any process with a distribution of this form is that the variability in the number of particles assembled becomes larger (in a fractional sense) when one is interested in smaller numbers of particles, since \( n^{-1/2} \) diverges as \( n \to 0 \). As a result, we must emphasize that the model predicts assembly only in a statistical sense, and is expected to be more accurate in predicting larger numbers of assembled particles.

**Figure 3.** a) SEM images of assembly as a function of voltage and gap width after assembly for 120 s at 1 MHz and a nanoparticle concentration of \( 7 \times 10^{10} \) particles ml\(^{-1}\). Top row: Small gaps at \( V_{pp} = 1.5 \) V (left), 2 V (center), and 3 V (right). Middle row: Medium gaps at \( V_{pp} = 2 \) V (left), 3 V (center), and 4 V (right). Bottom row: Large gaps at \( V_{pp} = 2 \) V (left), 3 V (center), and 4 V (right). Scale bars = 200 nm. b) Plot of experimental data and theoretical model for nanoparticle assembly using DEP as a function of voltage and gap width. Data is plotted as a function of voltage for three different gap-width ranges: 15–50 nm, average = 30 nm; 50–110 nm, average = 85 nm; 110–150 nm, average = 125 nm. The theoretically predicted number of particles is shown at the average gap widths.
Within this continuum framework, we describe nanoparticle transport in terms of the conservation equation:

$$\frac{\partial c}{\partial t} + \nabla \cdot J = 0$$

(1)

where the nanoparticle flux is represented by $J$ and is given by:

$$J = -D \nabla c + \frac{c F_{\text{total}}}{6 \pi R \mu}$$

(2)

Here, $D$ denotes the nanoparticle diffusivity, $F_{\text{total}}$ denotes the net (deterministic) force acting on a nanoparticle, and $c$ is the concentration of nanoparticles. We have taken the mobility as the coefficient of drag on a sphere from Stokes’ law, where $\mu$ denotes viscosity and $R$ denotes the radius of the nanoparticle.

To specify the equation governing $c(r,t)$, we define the total force as the sum of the contributions of an electrophoretic (EP), dielectrophoretic (DEP), and drag term:

$$F_{\text{total}} = F_{\text{EP}} + F_{\text{DEP}} + F_{\text{Drag}}$$

(3)

To complete the problem formulation, we constrain the nanoparticle flux normal to any phase boundary, $S$, (e.g., the substrate, electrodes, or droplet) to vanish:

$$n \cdot J_n = 0 \rightarrow (n \cdot c F_{\text{total}})|_{S} = 6 \pi R \mu D (n \cdot \nabla c)$$

(4)

Given a description of the total force, it is possible to solve for the number density of suspended nanoparticles. Rather than proceeding to solve this partial differential equation directly, however, we pursue a simpler framework for describing nanoparticle assembly. Specifically, we rely upon the disparate magnitudes and length scales over which each contribution of the total force acts to reduce the problem to a much simpler form.

### 2.4.2. Forces and Scaling

Dielectrophoresis refers to the force on a polarizable object in the presence of nonuniform electric fields. In the special case where the electric field across a particle deviates only slightly from its value at the center of that particle, a dipole approximation of the DEP force is appropriate. For a spherical particle of radius $R$, in media of permittivity $\varepsilon_m$ acted upon by applied field $E_0$, the dipole component of the DEP force is given by:

$$F_{\text{DEP}}^{(1)} = 2 \pi R^2 \varepsilon_0 \text{Re} \left\{ \frac{CM(\omega)}{\varepsilon_0 + 2 \varepsilon_m} E_0^2(r, \omega) \right\}$$

(5)

Here, $CM(\omega)$ denotes the Clausius–Mossotti factor, in this case given by:

$$CM(\omega) = \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + 2 \varepsilon_m}$$

(6)

where $\varepsilon_p$ and $\varepsilon_m$ are the complex permittivities of the particle and media, respectively. For a particle with permittivity $\varepsilon$ and conductivity $\sigma$, the complex permittivity at frequency $\omega$ is of the form $\varepsilon = \varepsilon_0 + 2 \sigma j \omega$. For the special case of a perfectly conducting particle ($\sigma_0 \rightarrow \infty$), the $CM$ factor reduces to unity, the value used in our model. In addition to the dipole contribution to the DEP force (Eq. (5)), we take into consideration the effects of higher-order polarization moments and forces.\(^{[39]}\) These higher-order corrections to the DEP force are of particular importance when the field is changing rapidly as is the case close to the electrode gap.

Our objective is to calculate the DEP force associated with idealized gap geometries. Even in the case of rectangular electrodes, determining the spatial dependence of the DEP force produced requires numerical analysis. Some preliminary insight can be obtained, however, by considering the asymptotic scaling of the electric field at a few different distances: those larger than the gap width but smaller than the electrode width, and those much greater than the electrode width. At length scales larger than the gap width (15–150 nm) but smaller than the electrode width ($\approx 300$ nm), the electrodes can be approximated by a long, narrow slit, for which the field scales as $r^{-1}$ and the DEP force as $r^{-2}$. At distances larger than the electrode width, the electrodes
produce a dipole field, scaling as $r^{-3}$, with an associated DEP force scaling as $r^{-7}$. Since we are primarily interested in distances on the order of hundreds of nanometers, we expect the DEP force to decay slightly faster than $r^{-3}$. This prediction is supported by our numerical models, which suggest a scaling of $\approx r^{-4}$ up to distances of a few hundred nanometers.

In contrast to DEP, the electrophoretic (EP) force is proportional to the electric field, and is given by:

$$F_{\text{EP}} = \mu_{\text{EP}} C_D E$$

(7)

where $\mu_{\text{EP}}$ denotes the electrophoretic mobility, and $C_D$ denotes the drag coefficient. Choosing $C_D$ according to Stokes’ Law gives the correct expression for the electrophoretic velocity in Equation (2). Because the EP force depends upon the polarity of the field, when the gap is driven with ac fields of sufficiently high frequency, the average contribution of this force is negligible compared to that of DEP. However, when the length scales of interest are of the order of 10 nm, our calculations show oscillation of the particles by the EP force may be present at frequencies as high as 1 MHz. This particle oscillation could have a range of effects, including inducing fluid flow in the surrounding medium, which could alter the assembly process.

In addition to the oscillatory EP force associated with the applied field, the negatively charged nanoparticles will be electrostatically repulsed by the negatively charged substrate when they are within a few Debye lengths. Assuming a very low to zero salt concentration in the aqueous dilute nanoparticle solution, we used values from literature at our measured pH value of 8 for the zeta potentials of the nanoparticles ($\approx -40$ mV), silicon dioxide substrate ($\approx -105$ mV), and gold electrodes coated primarily with a methyl terminated SAM ($\approx -80$ mV). Measurements of the electrical conductivity of the nanoparticle suspension suggest a Debye length of $\approx 10$ nm. Accordingly, we expect electrostatic repulsion to play a significant role for particles within a few tens of nanometers of the substrate. This is in contrast to DEP, which is generally significant for distances of a few hundreds of nanometers. Although this force will generally be more localized than DEP, it will nonetheless hinder or block nanoparticle assembly in cases where the applied voltage is not sufficiently high for it to be overcome.

In addition to EP and DEP, the nanoparticles may also be acted upon by convection of the surrounding fluid. This convection could arise from numerous sources, including thermally induced flows (from localized changes in the fluid’s density and/or electrical properties), Marangoni flows, or induced-charge electro-osmosis (ICEO). Because we expect thermal gradients in our system to be small, we suspect that ICEO is the most significant source of induced convection. Briefly, as the polarity of the electrodes changes under the applied voltage, counterions from the surrounding fluid form a double layer at the electrode surface, resulting in a net space charge density. The applied electric field then acts on this charge, pushing fluid away from the gap along the axis of the electrodes. The fluid expelled from the gap is balanced by a net inward flow from above and to the sides, which could potentially entrain nanoparticles, carrying them closer to the gap for assembly. The significance of ICEO depends on the extent of the electrode screening, and would thus be expected to be greatest at lower frequencies, provided the screening is not complete.

Figure 5. SEM images of assembly as a function of frequency. Assembly increases drastically with decreasing frequency. Assembly conditions were 120 s, 3.5 Vpp, $\approx 100$-nm gap size, $7 \times 10^{10}$ particles mL$^{-1}$, 1 MHz (top), 100 kHz (center), 10 kHz (bottom). Scale bars (top and center) = 200 nm. Scale bar (bottom) = 500 nm.
We must also note that, although we expect electrode screening to be greatly diminished at frequencies of 1 MHz or greater, the fact that the Debye screening length is comparable to the size of the gap presents the possibility that ICEO persists even to rather high frequencies, greatly increasing the complexity of the problem. To proceed, we model the fluid as static and restrict our analysis to frequencies (1 MHz) where ICEO is not expected to be dominant.

2.4.3. Determining the Region of Influence

The primary forces acting on a nanoparticle are thus the electrostatic repulsion associated with the fixed surface charge on the substrate and electrodes, the DEP force, and thermal motion, which is manifested by the diffusive term in Equation (2). Additionally, these forces exhibit very different spatial dependencies. While the electrostatic force is typically confined to within $\approx 10$ nm of the substrate, the DEP force extends $\approx 100$ nm from the electrode gap, and thermal motion is independent of location relative to the gap. It follows that at sufficiently high voltages, there will exist a region surrounding the gap in which DEP overwhelms both thermal motion and the repulsion of the substrate. Any particle entering this region will experience no barrier to its assembly in the gap. We refer to this as the region of influence (ROI).

An illustration of the regions where different forces dominate assembly is given in Figure 7. At lower voltages, we find that DEP still overwhelms thermal motion within a particular region, but is no longer sufficient to overcome the electrostatic repulsion. For this case, nanoparticles may be held in a stable equilibrium above the electrodes without contacting any surface; accordingly, no particles are assembled.

To determine the size and shape of the ROI, we use the numerical results from the force calculations to determine the trajectory of particles initialized at various locations with respect to the origin, taken as the center of the electrode gap. To conservatively approximate the effects of thermal motion, the net force is calculated by the sum of the electrostatic repulsion, DEP, and an outward radial force.

Figure 6. SEM images and corresponding $I$–$V$ characteristics of devices assembled using DEP. Stable current levels are seen through 20 electrical sweeps. Scale bars = 200 nm.

Figure 7. Schematic image showing regions where different forces dominate during DEP assembly of nanoparticles into nanogaps at voltages lower (left) and higher (right) than the threshold voltage.

Electrostatic Region  DEP Region (ROI)  Diffusion Region
with a magnitude given by the approximate rms value of thermal motion on the nanoparticles. If a particle contacts the electrode or substrate surface, its initial position is added to the locus of points defining the ROI. Note that in cases where the electrostatic repulsion prevents the particles from contacting the surface, the ROI will not exist; this is despite the fact that DEP may overwhelm thermal motion over a large region.

2.4.4. Simplifying the Equations for Nanoparticle Assembly

Once a description of the ROI is obtained, we may use the concept to simplify the problem defined by Equations (1–4). We do this by recognizing that we have constructed the ROI such that particle transport inside this region is determined predominantly from the migration term in Equation (2), whereas outside of it, transport is primarily diffusive. Because the dynamics inside the ROI are essentially deterministic, particles that enter this region by diffusion are quickly and irreversibly assembled in the gap, or otherwise held in equilibrium against the electrostatic repulsion. In either case, the probability of finding a freely suspended particle in the ROI can be approximated to zero; for a finite particle flux, as defined in Equation (2), large forces constrain the free-particle density to be small. Assembly is thus limited primarily by the rate at which particles diffuse into the ROI, independent of the details of their transport once inside this region.

This presents a very useful simplification: once the size of the ROI has been determined, we need only solve a diffusion equation in the external region, subject to the boundary condition that the density of free particles in the ROI is uniformly zero. Furthermore, although the ROI has a fairly complex shape, we may, to leading order, approximate it as a hemisphere. This approximation can be thought of as taking the first term in a series expansion of the actual shape of the surface, and simplifies the analysis considerably, by constraining the nanoparticle probability density to have spherical symmetry. We estimate the upper bound for the error associated with this approximation by calculating the standard deviation of the points on the actual ROI from the mean: typically about 30%. By modeling the ROI as hemispherical with radius \( a \), we obtain:

\[
\frac{\partial c}{\partial t} = \frac{D}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c}{\partial r} \right) \tag{8}
\]

\[
c(r = a, t) = 0; \quad c(r \to \infty, t) = c_0
\]

Here, \( c_0 \) denotes the original, bulk concentration of nanoparticles in the droplet, in units of particles per m\(^3\). In forcing \( c \) to approach \( c_0 \) at large \( r \), we are assuming that the depletion of particles does not penetrate a distance comparable to the size of the droplet for all times of interest. This problem permits an analytic solution:

\[
c(r, t) = c_0 \left[ 1 - \frac{a}{r} \text{erfc} \left( \frac{r - a}{2 \sqrt{D t}} \right) \right] \tag{9}
\]

To calculate the expected number of particles in the gap, we recognize that the time rate of change of the assembled particles is equal to the net flux of particles into the ROI. Since we have modeled the problem as purely diffusive outside of the ROI, the migration term in Equation (2) vanishes from the calculation, and the surface integral of the inward flux over the ROI becomes:

\[
\frac{\partial n}{\partial t} = - \int_{\Gamma_{\text{ROI}}} (n \cdot \mathbf{J}) dS = c_0 \int_{\Gamma_{\text{ROI}}} D(n \cdot \nabla c) dS = 2\pi a D \left[ r \frac{\partial c}{\partial r} \right] \bigg|_{r=a} \tag{10}
\]

Evaluating and integrating with respect to time, we obtain:

\[
n(t) = 2\pi a D t \left[ 1 + \frac{2a}{\sqrt{\pi Dt}} + \frac{a^2}{3Dt} \right] \tag{11}
\]

As an initial condition, we have used that, at \( t=0^+ \) (immediately after the electrodes have been turned on), all of the particles initially inside the ROI are instantaneously assembled, so that \( n(t=0^+) \) is given by the bulk concentration of nanoparticles \( c_0 \) times the volume of the ROI. This initial condition is represented by the third term, proportional to \( a^2 \), and has a value of \( \approx 10^{-3} \) particles for typical conditions in our experiments. Accordingly, it may be ignored for all practical purposes. Additionally, at sufficiently long times (i.e., \( t \approx a^2/D \)), the second term, proportional to \( a^3 \), may also be neglected to an excellent approximation. The expression for \( n(t) \) then reduces to a linear relationship with time, and depends on voltage and electrode geometry through the size of the ROI, \( a \).

At this point, we note that since this derivation has neglected the effects of assembled particles on the electric field and DEP force, it approximates the assembly dynamics only when sufficiently few particles have accumulated in the electrode gap to not significantly effect the electric fields, so that the parameter \( a \) remains constant. In reality, particles that assemble in the gap will be polarized by the applied electric field. For highly conductive particles, the field induced by this polarization will tend to oppose the applied field, resulting in a decrease in the DEP force and thus the size of the region of influence. We may introduce a first correction to Equation (11) by including the approximate dependence of \( a \) on the number of assembled particles, \( n \). With this modified description of \( a \), we find the first-order correction for \( n(t) \) to be given by:

\[
n(t) = \frac{2\pi a_0 D t}{1 - 2\pi a_0 D t (\Delta a/\Delta n)} \tag{12}
\]

This has the advantage of remaining finite as \( t \to \infty \). The new parameter, \( \Delta a/\Delta n \), is determined numerically, and typically has a value of approximately \( -6 \times 10^{-10} \) m. Complete details of the methods used to model nanoparticle assembly and calculate the first-order correction are given in the supporting information.
3. Discussion

3.1 Assembly as a Function of Voltage and Concentration—Fused Versus Isolated Particles

The observation of fusing as a function of voltage and nanoparticle concentration suggests that nanoparticle melting is due to Joule heating. Once a critical number of nanoparticles is reached, high currents are able to pass through the assembly. The high current passing through these particles causes localized melting and the formation of conductive metallic bridges. At lower \( V_{pp} \) the current is not large enough to cause melting. At lower nanoparticle concentrations, a larger DEP force (higher peak-to-peak voltages) is needed to assemble the number of nanoparticles necessary for the current density required for melting.

3.1.2. Assembly as a Function of Voltage and Gap Width

Figure 3 shows experimental data points for the number of particles assembled as a function of \( V_{pp} \) and gap width along with the predictions of the model at the average gap width of each experimental range (30 nm, 85 nm, and 125 nm). Given the many differences between the set-up assumed in the model (idealized gap geometries as compared with the irregular gap shapes used in the experiment, no interparticle interactions, induced flows, or electrochemical reactions) and that used in experiments, good agreement is achieved mostly in predicting the threshold voltages required for assembly.

The appearance of a voltage threshold for particle assembly in both the experimental and theoretical work shows the significance of electrostatic repulsion between the particles and the electrode/substrate surfaces. In the absence of any electrostatic force, nanoparticle assembly would occur down to very low voltages, since the DEP force only needs to overcome the random thermal motion of the particles. Also, in the absence of electrostatic forces our model predicts that the number of particles assembled should be independent of gap size at this length scale (see discussion below). The dependence of this voltage threshold on the size of the gap supports the idea that the DEP force must reach a critical value to overcome the electrostatic repulsion between charged particles and surfaces.

For voltages exceeding the threshold, the number of particles assembled appears to be largely independent of the gap size. In terms of the model we propose, this represents the relatively weak dependence of the size of the ROI on the size of the gap; while smaller gaps produce a stronger, more confined DEP force for a given voltage, larger gaps produce a weaker DEP force which acts over a larger area. Simulations show that this independence of gap size, after the threshold voltage is reached, is approximately true for gaps up to 150 nm, and is corroborated by experimental observation.

The model slightly over-predicts the observed threshold for the smallest gap sizes. Gap sizes were measured at their narrowest width. In many cases, this smallest gap size is not the average gap size. The model assumes a uniform gap at the smallest size. This would overestimate the electrostatic repulsion felt by the particles from the electrode surface as compared with the experimental reality, causing the shift seen in the threshold. This effect would be expected to be greatest for the narrowest gaps, as small changes in gap width result in large changes in the electrostatic repulsive force.

The model also seems to slightly under predict the number of assembled particles at 4.5 \( V_{pp} \) and above. At higher voltages, irreversible water dissociation may become a factor, leading to the generation of protons, which weakens the electrostatic repulsion term.\(^{[45]}\)

3.1.3. Assembly as a Function of Time

Previous work has used a resistor in series with the gap to make DEP assembly self-limiting.\(^{[15,17,18,24]}\) In these works, the assembled particles were significantly larger than the gaps onto which they were assembled, allowing for a single particle to bridge the gap. This creates a low-resistance bridge. Preliminary experiments using a 1 k\(\Omega\) to 1 M\(\Omega\) resistor in series with our gaps have shown no self-limiting behavior. This is likely due to the ratio of gap size to nanoparticle radius in our system. Our gaps are larger or the same size as the diameter of our particle, making it difficult for a single particle to bridge the gap. The nanoparticle bridges we formed have higher resistances (2.5 M\(\Omega\) to 60 G\(\Omega\)) than the resistors we placed in series with the gap. Future experiments will use smaller gap sizes to enable single-particle assembly.

To achieve assembly of a small number of particles we decided to operate near the threshold voltage. As seen in Figure 3, there is a rather steep increase in the number of particles assembled when operating for 120 s, hence it was necessary to limit the assembly time to achieve the assembly of <10 nanoparticles.

3.1.4. Assembly as a Function of Frequency

At low frequencies, assembly was found to drastically increase. A counterion cloud surrounds the particles, which at low frequencies can respond to changes in the electrical field.\(^{[12,14]}\) This counterion cloud increases the effective radius of the particle, thereby increasing the DEP force, which scales as \( r^2 \).

Another potential factor contributing to the frequency dependence is the existence of ICEO flows. At low frequencies, where greater amounts of charge accumulate in the double layer around the electrodes, ICEO flows would be expected to play a larger role. These flows potentially change the system dynamics and increase nanoparticle assembly.

4. Conclusions

We have modeled and demonstrated the effect of voltage and gap size on the assembly of 20-nm-diameter gold nanoparticles into nanogaps. The model accurately describes
of the presence of repulsive electrostatic interactions between nanoparticles and surfaces. The model introduces a spatial region of influence (ROI) where the DEP force overcomes Brownian motion. The ROI is independent of gap size when considering only DEP forces and Brownian motion; the gap-size dependence of particle assembly is due to the electrostatic interactions. Assembly was observed to increase with increased assembly time and to increase with decreasing assembly frequency. The fabrication of smaller gaps will allow for the assembly of single particles. Future improvements to the theoretical study will include consideration of induced flows, interparticle repulsions and electrochemical reactions. Future experimental studies on controlled assembly will analyze parameters such as temperature, electrode geometry, and particle functionalization.

5. Experimental Section

Si wafers with 700 nm of thermally grown SiO2 were used as the underlying substrate for the devices. Gold wires were patterned by EBL. PMMA (2%) in Anisole was spin coated onto the SiO2 substrates at a speed of 1000 rotations per minute for 90 s. The resist was then baked at 135 °C for 90 min. EBL was performed on a IBM VS-26 with a LaB6 source at 50 KV, at doses ranging from 400–1100 μC cm⁻². Development was then carried out in a 2:1 solution of Isopropyl Alcohol (IPA): Methyl Isobutyl Ketone (MIBK) for 80 s, followed by immersion in an IPA bath. An adhesion layer of 4–7 nm of Cr or Ti followed by 15–25 nm of Au was deposited using electron-beam evaporation at a rate of ≈0.1 nm s⁻¹. Lift-off was performed by immersing the substrate in N-methylpyrrolidone at 120 °C for 30 min followed by low power sonication for 30–60 s. Optical lithography was used to define the large optical pads and to align them to the patterned gold wires. An adhesion layer of 10 nm of Cr followed by 500 nm of Au was deposited to form the pads using electron-beam evaporation followed by lift-off, as described above. The devices were imaged by SEM on a Raith 150 EBL tool. The gold electrodes were immersed into a 95:5 10mMol toluene solution of Hexane Thiol:Nonanedithiol overnight, followed by washing in toluene for 2 h.

Gold wires with overlapping leads were used to form narrow gaps via a localized melting technique, described by Richter et al. [35] Using a microprobe station (Cascade Microtech Model 11000) the voltage was swept across the wire from 0 to 2 V in increments of 2.5 mV until a drastic decrease in current level was seen, which is indicative of gap formation. The resistance of wires after the break was then measured using an Agilent 4155C semiconductor parameter analyzer.

Gold particles, 20 nm in diameter, were purchased from British Bio Cell International and used at the as-purchased concentration (7 × 10¹³ particles mL⁻¹) or diluted with deionized water to a concentration of 7 × 10¹⁰ particles mL⁻¹.

Scheme 1 shows the experimental set-up used for dielectrophoresis of nanoparticles. A function generator (Agilent 33250A) was connected to one side of the device through the microprobe station. The second side of the device was connected to ground. Nanoparticles were introduced to the system in one of two methods. The sample was placed on the probe station and a 0.1–0.25 mL drop of aqueous nanoparticle solution was placed on the sample, completely covering all devices (this method was used for 90% of the results presented here). Alternatively, the sample was placed in a small polyethylene tray (2 cm by 2 cm with a 5-mm lip) which was then filled with 2.5 mL of aqueous nanoparticle solution. This method was found to give comparable results to the drop method. After assembly onto several devices on the same substrate, the drop was absorbed with a Kim-Wipe, or the sample was removed from the tray and blown dry with compressed air. Resistance of the nanoparticle bridge was measured at 300 mV. SEM imaging of the nanoparticle assemblies was then performed.

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