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Supporting Information

Assembly of Metal Nanoparticles into Nanogaps

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Supporting Information

The following is a description of the procedure for modeling nanoparticle assembly, with emphasis on the statement of the problem, the assumptions used, and their expected limitations.

Statement of the electrical problem

To determine the electric fields produced by the both the applied potential and the fixed surface charge, the system we must solve is given by:

$$\nabla \cdot [e \nabla j] = -F \sum_{i}^{N} z_i c_i \qquad (1)$$

$$\frac{\partial c_i}{\partial t} + \mathbf{v} \cdot \nabla c_i = -\nabla \cdot \mathbf{N}_i \qquad (2)$$

$$\mathbf{N}_i = -D_i \left[\nabla c_i + \frac{z_i F}{RT} c_i \nabla j \right] \qquad (3)$$

Equation (1) represents Gauss's Law, while (2) and (3) specify the conservation equation for the ith species in the electrolyte. Here, c_i, $\mathbf{N}_i$, D_i and z_i represent the concentration, flux, diffusivity and valence respectively, f is the electric potential, F is the Faraday constant, R is the universal

gas constant, T is the temperature, e is the permittivity and $\mathbf{v}$ is the fluid velocity. In general, this system constitutes a complicated non-linear problem. In order to proceed, we make several assumptions which make the problem tractable. The solution that we obtain will be self-consistent, but it will not be universally valid. To begin, we assume that the electric potential can be written as the sum of a DC component and an AC (sinusoidal) component: $f = f^{DC} + f^{AC}$. The DC component is associated with the fixed surface charge of the electrodes and substrate, while the AC term follows from the applied potential. Additionally, we assume that each c_i can be similarly decomposed into a DC and AC term. Ignoring convection, the equations then become:

$$\nabla \cdot \left[e \nabla \left(\boldsymbol{j}^{\,DC} + \boldsymbol{j}^{\,AC} \right) \right] = -F \sum_i^N z_i \left(c_i^{DC} + c_i^{AC} \right) \tag{4}$$

$$\frac{\partial c_i^{AC}}{\partial t} = D_i \nabla^2 \left(c_i^{DC} + c_i^{AC} \right) + \frac{z_i F}{RT} D_i \nabla \cdot \left[\left(c_i^{DC} + c_i^{AC} \right) \nabla \left(\boldsymbol{j}^{\,DC} + \boldsymbol{j}^{\,AC} \right) \right] \tag{5}$$

We may now divide equations (4) and (5) into time-dependent and time-independent equations. For (5), we have:

$$0 = D_i \nabla^2 c_i^{DC} + \frac{z_i F}{RT} D_i \nabla \cdot \left[c_i^{DC} \nabla \boldsymbol{j}^{\,DC} + \left\langle c_i^{AC} \nabla \boldsymbol{j}^{\,AC} \right\rangle \right] \tag{6}$$

$$\frac{\partial c_i^{AC}}{\partial t} = D_i \nabla^2 c_i^{AC} + \frac{z_i F}{RT} D_i \nabla \cdot \left[c_i^{AC} \nabla \boldsymbol{j}^{\,DC} + c_i^{DC} \nabla \boldsymbol{j}^{\,AC} + c_i^{AC} \nabla \boldsymbol{j}^{\,AC} - \left\langle c_i^{AC} \nabla \boldsymbol{j}^{\,AC} \right\rangle \right] \tag{7}$$

Splitting the equations in this way presents no simplification unless we assume that the applied AC potential is at a *sufficiently low voltage and sufficiently high frequency* that the AC concentration, c_i^{AC}, tends towards zero. Physically, this corresponds to a field changing so rapidly that ions in the fluid are unable to respond, driving the AC component of the

concentration towards zero. When this occurs, equations (6) and (7) decouple, and the DC concentration and potential can be determined by solving the Poisson-Boltzmann equation:

$$\nabla^2 j^{DC} = -\frac{F}{e} \sum_i^N z_i c_{i,0} e^{-\frac{z_i F}{RT} j^{DC}} \qquad (8)$$

In equation (7), we also drop all terms involving c_i^{AC}, except for the time derivative, which will not necessarily be small at very high frequencies. This gives us:

$$\frac{\partial c_i^{AC}}{\partial t} \approx \frac{z_i F}{RT} D_i \nabla \cdot \left[c_i^{DC} \nabla j^{AC} \right] \qquad (9)$$

Since the DC concentration is known from equation (8), equation (9) is now linear, allowing us to treat the AC potential and concentrations as being sinusoidal in time, such that $?/?t\ ?\ j?$. Substituting this result into equation (4) and considering only the AC terms, we have:

$$\nabla \cdot \left[\left(e + \frac{s}{jw} \right) \nabla j^{AC} \right] = 0 \qquad (10)$$

where the electrical conductivity, s, is defined by:

$$s \equiv \frac{F^2}{RT} \sum_i^N z_i^2 D_i c_i^{DC} \qquad (11)$$

Using (8) to solve for the DC potential, ion concentrations, and conductivity, we are then able to solve equation (10) for the applied AC potential. We note that the AC potential is not governed simply by Laplace's equation, since the conductivity in the vicinity of the electrodes is made non-uniform by the (DC) ion distribution.

As we have stated, the validity of our approach to this problem requires that the applied potential have sufficiently low amplitude and sufficiently high frequency. Others [1] have shown that

the primary time scale governing diffuse-charge dynamics is given by $\lambda_D L/D$, where λ_D denotes the Debye length, L denotes the geometric length scale, and D denotes the characteristic species diffusivity. Using typical values for these parameters suggests that our treatment of the model should be reasonably accurate at frequencies over 100 kHz.
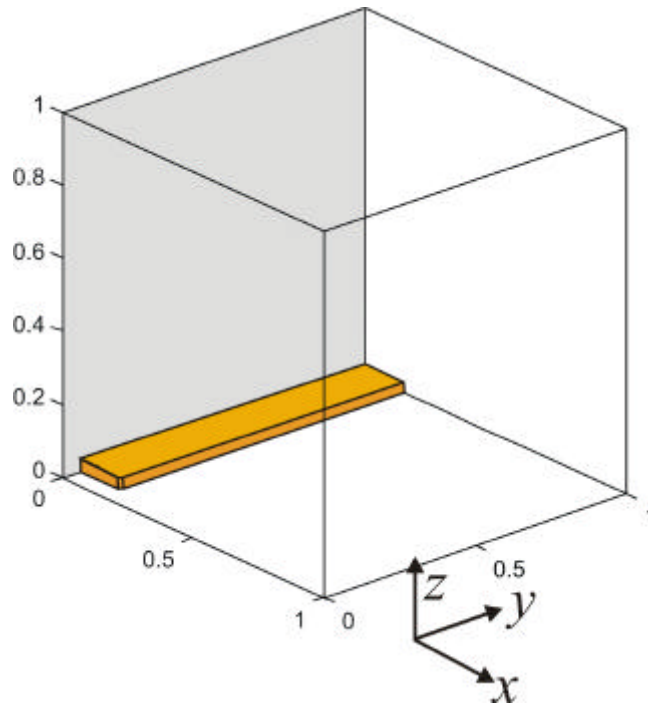
Finite Element Models

To solve for both the AC and DC potentials, we use the geometry depicted in figure S.1. Here, we have exploited the symmetry of the structure in the planes both parallel (normal given by the x axis) and perpendicular (normal given by the y axis) to the electrode axis. To solve for the electric fields associated with the fixed surface charge, we convert the assumed zeta potentials to an equivalent charge per unit area for the gold and the silicon dioxide surfaces. The bounding

walls are set as electrical insulation / symmetry, while the top surface is assumed to be sufficiently far away from the surface to serve as the bulk potential. Because we do not know the precise ionic constitution of the solvent, we use the measured electrical conductivity of the water-nanoparticle solution to approximate the full Poisson-Boltzmann equation (the volume fraction of nanoparticle to solvent is such that we expect the particles themselves to contribute negligibly to the bulk electrical conductivity). This gives us:

$$\nabla^2 \boldsymbol{j}^{DC} = -\frac{F}{\boldsymbol{e}} \sum_i^N z_i c_{i,0} e^{-\frac{z_i F}{RT} \boldsymbol{j}^{DC}} \ ; \ -\frac{F c_0}{\boldsymbol{e}} \sinh\left[\frac{F \boldsymbol{j}^{DC}}{RT}\right] \qquad (12)$$

For the effective bulk concentration, we use:

$$c_0 = \frac{RT \boldsymbol{s}_0}{2 F^2 D} \qquad (13)$$

Here, $\boldsymbol{s}_0$ (= 3.83*10^{-3} S/m) denotes the measured (bulk) electrical conductivity, and D (= 0.66*10^{-9} m^2/s) denotes the effective species diffusivity, taken to be that of citrate in water.

Once we have solved equation (12) for the potential and ion distributions associated with the fixed surface charge, we proceed to calculate the fields resulting from the applied potential, using equation (10). Since we assume that these high frequency fields have negligible effect on the ion distribution, the significance of the non-uniform ion distribution enters only through their local modification of the media conductivity.

Calculating EP and DEP Forces

Once we have solved for both AC and DC potentials throughout the fluid, we are able to determine the associated forces acting on a nanoparticle. Although both AC and DC terms in the total electric field will exert an electrophoretic and dielectrophoretic force on the particle, we simplify the calculations by preserving only the electrophoretic contribution of the DC field and the dielectrophoretic contribution of the AC field. Comparing the ratio of the EP and DEP forces associated with the DC field, we obtain:

$$\frac{F_{EP}}{F_{DEP}} \sim C \left(\frac{z_{NP}}{z_{substrate}} \right) \left(\frac{l_D}{R} \right)^2 e^{\frac{z}{l_D}} \tag{14}$$

Where C is a dimensionless constant ~ 3, $?$ denotes the zeta potentials of the nanoparticle (NP) and substrate, $?_D$ is the Debye length, R is the effective particle radius, and z is the distance from the substrate. For $?_D \sim R$, we see that even one Debye length from the substrate, the EP force associated with the DC potential is nearly one order of magnitude stronger than the DEP force. To simplify the force associated with the AC potential, we assume that the EP force will displace the particle a negligible distance over one period of the field, so that the time averaged contribution is essentially zero. These assumptions lead us to treat the EP and DEP forces as being defined separately by the DC and AC electric field solutions. Calculations of the DEP force are performed using a subset of the streamforce program described in [2].

Radius of Influence

Given the EP and DEP forces associated with a particular electrode geometry, we determine the size of the region of influence (ROI). To do this, we define thermal motion as being directed radially outwards with a magnitude of:

$$|F_r| = \frac{kT}{2R} \qquad\qquad (15)$$

We then assign random starting positions to particles throughout the simulation domain and calculate their trajectories subject to EP, DEP and thermal motion. If a particle comes in contact with the electrode or substrate inside the gap, it is counted as assembled. Repeating this process 10,000 times for each geometry and comparing the number of initialization points inside and outside the ROI gives us an estimate for the volume of the ROI, from which we extract an equivalent radius for further calculations.

Behavior of particles in and around the ROI

To predict the behavior of particles in the vicinity of the gap and more precisely define the concept of the ROI, we perform Monte Carlo simulations on a restricted domain close to the electrodes, yet extending beyond the ROI by about 1 µm. In this domain, we compare capture times for particles acted upon by DEP alone with those acted upon by both DEP and randomly generated thermal motion. Values for the x-, y-, and z-components of thermal motion are generated using Matlab's 'randn' command, and scaled to have an RMS value equal to equation (15). We perform a numerical integration in time to determine the trajectories of the particles,

and the simulation terminates when the particles are immobilized on the substrate (z = 0) in or near the electrode gap. For each point in which thermal motion is included, the times represent an average of capture times over 100 Monte Carlo simulations. Particles are initialized at varying heights above the substrate (x-axis). We find that when the initial displacement first exceeds the size of the ROI, there is a rapid divergence between DEP and DEP + thermal capture times (figure S.2). This supports our model of particle transport as consisting of two regimes (diffusion dominant and DEP dominant) defined by the surface of the ROI.
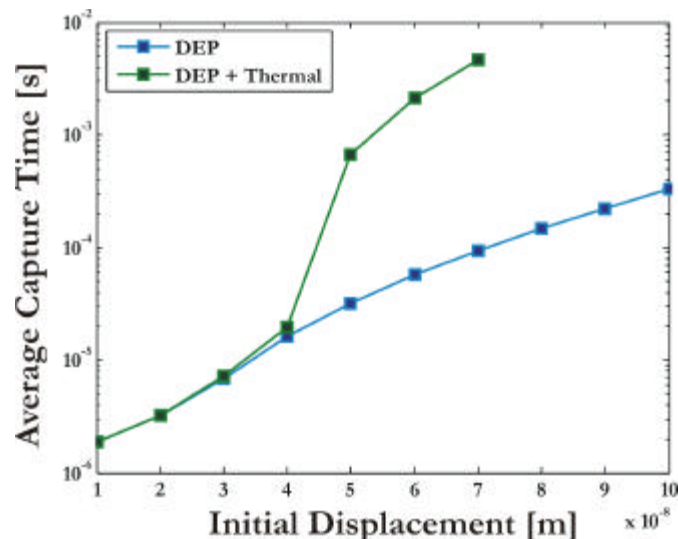
First Correction for Non-linear Effects

The final component to our model is to introduce an approximate correction to nanoparticle assembly accounting for the interactions between particles in suspension and those previously assembled. Since the particles are substantially more conductive than the surrounding solvent,

assembled particles tend to focus the electric field into a more confined region. When a large number of particles have been assembled, it is expected that the field will no longer penetrate far into the fluid, but will instead be confined inside the more conductive path which the assembled particles provide. In this way, assembly is a self-limiting process.

To approximately account for the effects of previously captured particles on further particle assembly, we calculate the dipole field induced around a perfectly conducting particle assembled in the gap. Adding this field to the applied field, we recalculate the DEP force and the ROI. Because the captured particles are conducting, the induced field will tend to oppose the applied field, resulting in a decrease in the size of the ROI. We use this incremental decrease in a (ROI radius) with n (number of assembled particles) to obtain the linear term in a Taylor expansion for $a(n)$:

$$a(n) \approx a(0) + \left.\frac{\Delta a}{\Delta n}\right|_{n=0} n + O(n^2) \qquad (16)$$

In equation (16), we have introduced a new parameter, $\partial a/\partial n$, which must be determined numerically. Calculating the change in the ROI (∂a) associated with a single assembled particle ($\partial n = 1$) completes the formulation of this model. Because ∂a will, in general, depend upon where in the gap the particle assembles, we determine ∂a for a range of particle positions, and use the average in the final model.

Of course, since $n = n(t)$, this modification implies that $a = a(t)$. This means that the solution given by equation (9) in the main article no longer strictly satisfies the transient diffusion equation, since a is now a function of time. Still, if we restrict our interest to cases where a

changes sufficiently slowly with time, this serves as a reasonable approximation. Requiring that the region of influence vary much less rapidly than the diffusion over the same length scale, a, leads to:

$$\frac{a^2}{D} << a\left[\frac{da}{dt}\right]^{-1} \qquad (17)$$

which we combine with equation (11) in the main article to obtain:

$$2\boldsymbol{p}\, c_0 a^2 \frac{\Delta a}{\Delta n} << 1 \qquad (18)$$

For all cases considered in this paper, this condition is very easily satisfied, with the left hand side typically on the order of 10^{-7}.

References

[1] M. Z. Bazant, K. Thornton, & A. Ajdari, Phys. Rev. E, **70**, 021506 (2004).

[2] A. Rosenthal, B. M. Taff, & J. Voldman, Lab on a Chip 6 (2006)