MODELING THE ELECTROKINETICS OF NANOPARTICLES FOR CONTROLLED ASSEMBLY

Michael D. Vahey[1], Robert J. Barsotti[1], Ryan Wartena[1], Yet-Ming Chiang[1], Francesco Stellacci[1] and Joel Voldman[1]

[1]Massachusetts Institute of Technology, USA

ABSTRACT

We present a predictive framework for the controlled assembly of nanoparticles onto the surface of small (15 - 150 nm) electrode gaps using the dielectrophoretic (DEP) force. By combining Brownian dynamics (BD) simulations with continuum descriptions for the spatial distributions of nanoparticles, we arrive at a concise analytic description for the number of particles assembled as a function of the applied voltage, nanoparticle properties, and geometric parameters, such as the size of the electrode gap. Our model is predictive and successfully describes the presence of a voltage threshold, below which no assembly is observed.

Keywords: nanoparticles, dielectrophoresis, Brownian dynamics simulation

1. INTRODUCTION

Nanoparticles assembled on a surface have enormous potential for applications ranging from low-power electronic devices to chemical and biological sensors. One technique for creating these assemblies uses the dielectrophoretic (DEP) force created by nanometer- to millimeter-scale electrodes to direct particles to or within the electrode gap [1]. Current methods of nanoparticle assembly are predominantly based upon empirically determined parameters. Realizing the full potential of these devices, however, requires the ability to quantitatively understand and thus control both the number and location of the assembled particles, a prospect made more difficult by the combined stochastic and deterministic character of particle dynamics at the nanoscale. Here we present a framework for modeling the assembly of particles which can be customized for an arbitrary range of geometries, particles, and operating conditions, taking into account both linear (i.e. electrophoresis) and nonlinear (i.e. dielectrophoresis, induced charge electrophoresis) electrokinetic phenomena.

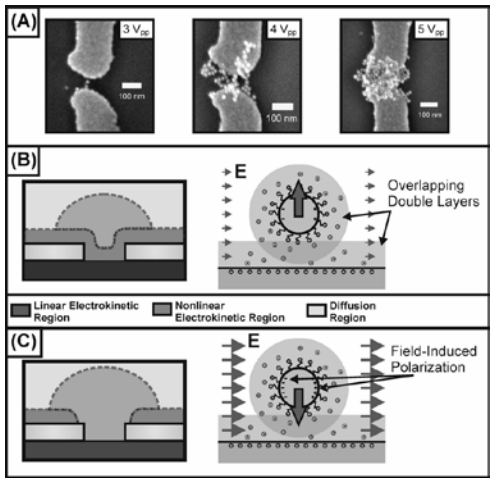

Figure 1. (A) SEM images illustrating the nonlinear relationship between applied voltage and the number of assembled particles. (B) and (C) Assembly as a competition between thermal motion (diffusion) and both linear and non-linear electrokinetic phenomena.

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2. THEORY

Nanoparticles subject to both external forces and thermal fluctuations undergo a biased random walk. The stochastic nature of the resulting dynamics presents researchers with two primary approaches to modeling assembly; Brownian dynamics (BD) simulations and continuum models. BD simulations correctly account for the stochastic nature of particle movement, but are computationally expensive. Alternatively, continuum models offer a computationally convenient framework for treating the average behavior of large ensembles of particles, but are deterministic and thus do not recapitulate the true dynamics of assembly.

Instead, we have combined both approaches, using a few BD simulations to determine the boundary conditions for a fast, intuitive continuum model. The basis for the continuum model is the concept of a Region of Influence (ROI), inside of which deterministic forces dominate (e.g. DEP and electrostatic), and outside of which thermal fluctuations, as manifested by diffusion, dominate (Figure 1). We use BD simulation to determine the size and shape of the ROI, accounting for its evolution as particles are assembled (Figure 2), and then define the surface of this region as an absorbing boundary in the diffusion equation. We then solve this simple partial differential equation numerically using the exact boundary, or obtain an analytic solution by approximating the boundary using spherical harmonics.

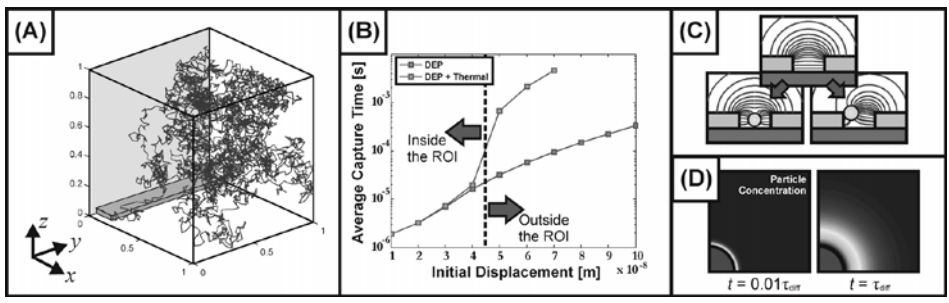

Figure 2. From Brownian dynamics to a continuum model. (A) Brownian dynamics simulations give the trajectory of single nanoparticles subject to both thermal and deterministic forces, revealing a sharp transition (B) in mean capture time for particles initialized outside the ROI. (C) Accounting for distortion of the electric field and ROI by assembled particles allows us to model the self-limiting aspect of assembly. (D) Analytic solution obtained by treating the ROI as a hemisphere.

3. EXPERIMENTAL

To test the predictions of the model, we use electrode gaps fabricated using either electron-beam lithography or localized melting of a 100-nm-wide constriction in a 300-nm-wide wire [2]. This produces electrode gaps ranging from 15 – 150 nm. By placing a droplet of the nanoparticle suspension over the electrode gap and actuating the electrodes, we have access to a large range of experimental parameters, including the amplitude, frequency, and duration of the applied electric field, particle concentration, and solvent properties. Post-assembly SEMs of the electrode gaps allow us to count the number of particles assembled for a given experimental condition.

4. RESULTS AND DISCUSSION

We have used our model to suggest a number of testable predictions for the scaling of nanoparticle assembly with both physical and operating conditions. Experimental observation of assembly as a function of voltage agrees quantitatively with the proposed model (Figure 3). Importantly, this agreement requires the introduction of unexpected nanoscale phenomena; for instance, the presence of a voltage threshold for assembly can be explained by including electrostatic repulsion between the negatively charged substrate and citrate stabilized gold nanoparticles [3]. The range of this model's applicability - both with respect to experimentally accessible degrees of freedom as well as the ease with which it can be extended to other types of particles and electrode geometries - suggest that controlled assembly of a few to hundreds of particles may be possible to within the limits of Poisson statistics.

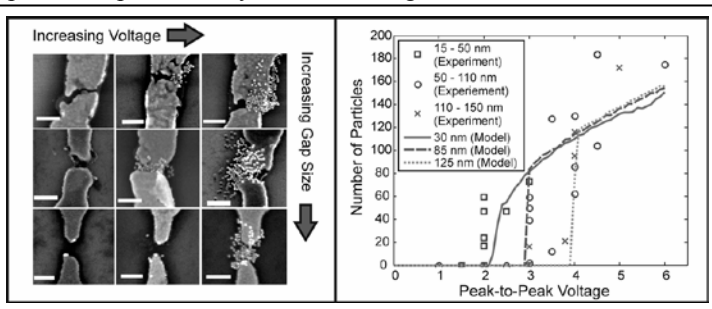

Figure 3. Experimental and modeled assembly of nanoparticles as a function of applied voltage at 1MHz for a durations of 120s. A threshold voltage, below which no particles are assembled, is observed and increases with the size of the electrode gap. Scale bars = 200 nm.

5. CONCLUSIONS

We have developed a predictive description of nanoparticle assembly combining BD simulations and continuum modelling. This model quantitatively predicts particle dynamics, including such emergent behaviour as a threshold voltage for assembly. Future work will focus on extending the applicability of the model and testing its predictions over a broader range of experimental conditions.

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