Direct Numerical Simulations of Electrophoretic Deposition of Charged Colloidal Suspensions

Jae Sung Park^a and David Saintillan^b

Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign

1206 W Green Street, Urbana, Illinois 61801, USA

^apark80@illinois.edu, ^bdstn@illinois.edu

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Abstract

Motivated by applications in the field of nanomanufacturing, we perform large-scale numerical simulations of the electrophoretic deposition of suspensions of charged colloids in an electrolyte. A simulation method is developed to model the full deposition process that captures linear electrophoresis, dipolar interactions, van-der-Waals forces, steric interactions, Brownian motion, as well as electric and hydrodynamic interactions with the electrodes. Using a fast algorithm, suspensions of up to 5,000 particles are simulated, and results are reported for the final deposit microstructure as a function of field strength. The simulation results demonstrate that regular crystalline colloidal assemblies are obtained at low field strengths and volume fractions, while more random structures with frequent defects are formed in stronger fields and at higher volume fractions, in agreement with recent deposition experiments.

Introduction

The development of new materials to meet specific properties is of practical importance in modern technological applications as devices become more specialized and miniaturized. To this end, the electrophoretic deposition (EPD) process provides an effective and low-cost method for producing designer materials with a specific microstructure. Although the basic mechanisms of electrophoretic deposition are well known and have been studied extensively [1], a detailed, quantitative model for the dynamics and kinetics of deposition is still lacking, and is needed to optimize the deposition process. Specifically, understanding the full deposition process and the influence of various parameters on the microstructure of the deposits will play a crucial role in the optimization of EPD in experiments.

In the present work, we develop a quantitative, detailed physical model of the electrophoretic deposition process, and apply it to simulate the deposition of large-scale suspensions of colloidal spheres under steady electric fields. The physics of EPD are first discussed as they will ultimately guide operating conditions to manufacture desired materials, and the model and simulation algorithms are described. We then present simulation results using an efficient simulation method [2], with focus on the characterization of the deposit microstructures and their relation to operating conditions. In particular, the influence of electric field strength on the deposit microstructure is analyzed in detail.

Physics of electrophoretic deposition

The electrophoretic deposition process involves complex physics, including linear electrophoresis, dipolar interactions, colloidal forces, interactions with electrodes, and Brownian motion. Here, we propose to study the full EPD process, including the dynamics in suspension and deposition on the electrodes. Electrophoresis denotes the motion of a charged particle in an electrolyte under an external electric field. The mechanism for this motion is well known, and has been studied for decades [3]. When a particle with constant zeta potential ζ is placed in a viscous electrolyte, particle migration arises due to electrophoresis as a result of the interaction of the native Debye layer with

an external electric field \mathbf{E}_0 . In the case of thin-Debye-layer limit, the electrophoretic velocity is simply given by the Helmholtz-Smoluchowski formula $\mathbf{U}^{\text{EP}} = (\epsilon \zeta / \eta) \mathbf{E}_0$, where ϵ is the electric permittivity of the solution, and η is the viscosity of the solution. This simple result is valid for a single non-polarizable particle in an unbounded domain, in a weak applied field, and in the thin Debye layer limit. In addition to this classical linear electrophoresis, additional particle-particle interactions may arise as a result of Maxwell stresses in the electrolyte, which result in dipolar interactions between suspended particles (an effect similar to dielectrophoresis). This effect is known to lead to relative motions and chaining, and can have a significant influence on the suspension microstructure [2]. Having analyzed pair interactions between identical spheres in previous work [4], interactions in a full suspension can be calculated in a pairwise manner. Colloidal particles are also subject to van-der-Waals interactions, which can lead to particle aggregation. Finally, the deposition process onto the electrodes involves electric and hydrodynamic interactions with the electrodes under EP (which result in a slow-down of the deposition near the surface), as well as dipolar, van-der-Waals and steric interactions with the electrodes [5].

Simulation method

The simulation method used in the electrophoretic deposition simulations will be discussed in more detail elsewhere [5]. We make use of the algorithm developed in our previous work [2], which is only outlined here. To model the EPD process, we consider a suspension of N identical spheres of radius a suspended in a viscous electrolyte. The electrophoretic cell is a periodic domain of linear dimension $L_x \times L_y \times L_z$, and the electric field points in the z-direction, where L_z corresponds to the electrode spacing. To calculate particle motions, a Langevin equation is used, which models the displacement of a given particle over a short time step of length Δt as follows:

$$\Delta \mathbf{x}_{\alpha} = \mathbf{U}_{\alpha} \Delta t + \sqrt{\frac{2k_{B}T\Delta t}{6\pi\eta a}} \mathbf{w},\tag{1}$$

where U_{α} is the deterministic velocity of particle α , k_BT is the thermal energy of the solvent, and w is a random vector whose components follow a Gaussian distribution with zero mean and unit variance. The velocity U_{α} includes linear electrophoresis, dielectrophoresis, and van-der-Waals interactions as well as single particle corrections for interactions with the cell electrodes. In particular, the velocity contributions resulting from interactions with other particles in the electrophoretic cell are calculated using an efficient smooth particle-mesh Ewald algorithm previously developed in our work [2,6]. Because of the use of finite time steps to advance particle positions, care must be taken to avoid particle overlaps. Here, we use a contact algorithm to prevent overlaps and to capture excluded volume interactions with cell electrodes. A full account of the simulation methods and the contact algorithm can be found in [2].

Results

Figure 1 shows snapshots of the electrophoretic deposition of 4,000 non-conducting, equal-sized spheres in a cell of dimension $L_x \times L_y \times L_z = 40^2 \times 60$ at $E_0 = 40$ V/cm. Initially, particles are distributed in a tall pseudo-cell of dimension $L_x \times L_y \times 16L_z$ that contains the actual cell, and only 230 spheres are distributed inside the actual cell to set the initial volume fraction of 1% as shown in Fig. 1(a). We only account for the interactions between spheres inside the actual cell, while there are no interactions with spheres outside the actual cell, where they only undergo linear electrophoresis causing them to move down towards the actual cell. When the spheres enter the actual cell, they start to interact with neighboring spheres inside the cell. Starting from an initial random distribution, negatively charged spheres are continually deposited on the surface of the anode owing to the dominant effect of linear electrophoresis, and the deposition process yields a deposit of layered particles as seen in Fig. 1(f). It is found that crystalline structures are observed in the lower layers of the deposit, and the structure is observed to slowly deteriorate with distance from the cell electrode.



Figure 1. Snapshots the particle distribution during the electrophoretic deposition of a suspension of 4,000 particles at (a) t = 0 to (f) t = 4000. The initial volume fraction is set to 1% and the final volume fraction becomes 17.45%.

In Fig. 2, the effect of the electric field strength on deposit structure is considered. At low field strength, a regular particle arrangement is observed, and it is seen to form a nearly perfect crystal in Fig. 2(a). However, as the electric field strength increases, the deposit structure becomes a polycrystal with several defects inside the deposit and more specifically line defects in the lowest layers. These deffects can be understood from the limited time particles have to diffuse in strong fields. These observations are all in agreement with experimental observations [5].

To further investigate the deposit microstructure, we calculate the coordination number (number of nearest neighbors) in the deposits of Fig. 2 within 1.5 < z < 8 (i.e., excluding the lowest layer), as illustrated in Fig. 3. When spheres are deposited to achieve the highest average density, a deposit structure can be hexagonal close-packed (HCP) or face-centered cubic (FCC), with the coordination number of 12 for each particle. As can be noticed by considering the mean and standard deviation of the coordination number distributions in Fig. 3(d)-(f), the deposits formed at low field strength (e.g., 20 V/cm) display a more regular crystal structure than those formed at higher field strengths, which must therefore have a lower packing fraction. In addition, we also calculate the radial pair distribution function g(r) inside the deposit structures; g(r) exhibits peaks at fixed positions, indicating a clear crystal structure. As shown in Fig. 4, the radial distribution function for the low field strength displays sharp peaks at longer distances than for the high-field strength, suggesting



Figure 2. Deposits produced by EPD at different electric field strengths. Increasing field strengths results in less regular particle arrangements, in qualitative agreement with experimental observations (experimental images courtesy of J. Kuntz and A. Pascall, Lawrence Livermore National Laboratory).



Figure 3. (a)-(c) Coordination number of particles in the deposits and its distributions obtained for field strengths (a)-(d) $E_0 = 20$ V/cm, (b)-(e) $E_0 = 40$ V/cm, and (c)-(f) $E_0 = 60$ V/cm. When the deposit structure is crystalline, each sphere has 12 neighbors, corresponding to a coordination number of 12.

a more regular crystal structure. In the inset of Fig. 4(a), we also show the pair distribution function of the FCC structure and compare it with that of the deposit. As expected, the pair distribution function of the FCC structure shows clear sharp peaks (delta functions) at specific distances. It is found that the peak locations of both functions appear to match with reasonable agreement, indicative of an FCC crystal structure, which is consistent with the findings on the coordination number.

Summary

We have used direct numerical simulations to model and investigate the electrophoretic deposition of colloidal suspensions. Using an efficient simulation algorithm, we were able to capture the full process of electrophoretic deposition, which allowed us to analyze deposit microstructure and to assess the effects of operating parameters. We found in our simulations that the deposits obtained by EPD are crystalline in the lower layers, and become less regular with distance from the electrode. The final deposits produced at different field strengths were compared, and a regular particle arrangement was observed to be formed at low field strengths, which is in qualitative



Figure 4. Radial distribution functions at different field strengths. Inset: a closer look at the short distance range, also showing the radial distribution function of a faced-centered cubic crystal in (a).

agreement with experimental results. To better characterize the deposit microstructure, we also calculated the coordination number and radial distribution function inside the deposits, and better particle arrangements and clearer crystal structure were found to be obtained at low field strengths owing the ability of particles to diffuse and rearrange. Comparisons of the pair distribution function in the deposits with that for an FCC crystal showed good agreement, suggesting that the deposits obtained by this method display an FCC structure.

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