Final Report
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Electrohydrodynamic Flows in Electrochemical Systems

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ABSTRACT

Recent studies have established a new class of assembly processes with colloidal suspensions.[1] Particles are driven together to form large crystalline structures in both dc and ac fields. The current work centers on this new class of flows in ac fields.[2] In the research carried out under the current award, it was established that: (i) Small colloidal particles 'crystallize' near an electrode due to electrohydrodynamic flows induced by an sinusoidally varying applied potential. (ii) These flows originate due to disturbances in the electrode polarization layer arising from the presence of the particles. Inasmuch as the charge and the field strength both scale on the applied field, the flows are proportional to the square of the applied voltage. (iii) Suspensions of two different sorts of particles can be crystallized and will form well-ordered binary crystals. (iv) At high frequencies the EHD flows die out. Thus, with a homogeneous system the particles become widely spaced due to dipolar repulsion. With a binary suspension, however, the particles may become attractive due to dipolar attraction arising from differences in electrokinetic dipoles. Consequently binary crystals form at both high and low frequencies.

SUMMARY AND CONCLUSIONS

The process by which an externally applied electric field causes colloidal particles in a suspension to move toward and then deposit on an electrode is termed *electrophoretic deposition* (EPD). Employed commercially since at least the 1930s[3], EPD is typically thought of as being analogous to the formation of high-density deposits by sedimentation. According to Hamaker and Verwey[4] there is an analogy between sedimentation and EPD: "...we conclude that the parallelism between the formation of an adherent layer by sedimentation and by electrophoresis is not merely accidental but that these two are identical." This view is maintained in early[5] as well as more recent[6] reviews. However, numerous experimental observations show that the analogy between EPD and sedimentation is incomplete[7]. Particle motion transverse to the applied field is observed

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[1] M. Trau, D. A. Saville & I. A. Aksay "Field-Induced Layering Of Colloidal Crystals" *Science* **272** 706-709 (1996).

[2] When the proposal was approved for funding, budget constraints dictated that the work be more narrowly focused. Accordingly, electrohydrodynamic processes were studied in ac fields where electrochemical reactions were absent.

[3] Harsanyi, E., U.S. Patent No. 1897902 (1933).

[4] Hamaker, H. C. & Verwey, E. J. W. 'The role of the forces between the particles in electrodeposition and other phenomena' *Transactions of the Faraday Society* **36**, 180-185 (1940).

[5] Pickard, W. 'Remarks on the Theory of Electrophoretic Deposition' *Journal of the Electrochemical Society* **115**, 105C-108C (1968).

[6] Sarkar, P. & Nicholson, P. S. "Electrophoretic deposition (EPD): Mechanisms, kinetics, and application to ceramics" *Journal of the American Ceramic Society* **79**, 1987-2002 (1996). Van der Biest, O. O. & Vandeperre, L. J. "Electrophoretic deposition of materials" *Annual Review of Materials Science* **29**, 327-352 (1999).

[7] Giersig, M. & Mulvaney, P. "Formation of Ordered 2-Dimensional Gold Colloid Lattices by Electrophoretic Deposition" *Journal of Physical Chemistry* **97**, 6334-6336 (1993) and "Preparation of Ordered Colloid Monolayers by Electrophoretic Deposition" *Langmuir* **9**, 3408-3413 (1993). Trau, M., Saville, D. A. & Aksay, I. A. "Field-induced layering of colloidal crystals" *Science* **272**, 706-709 (1996) and Assembly Of Colloidal Crystals At Electrode Interfaces. *Langmuir* **13** 6375-6381 (1997)

under a variety of conditions - including both steady and oscillatory applied fields - with particles composed of metallic, polymeric, inorganic, and even biological materials, ranging in size from 3 nm to 50 μm. Particles migrate over relatively long distances (5–10 particle radii) to form planar aggregates even though the electrostatic interactions between identical particles (both Coulombic and dipolar) are repulsive.

In the first stage of the work done under the current award, the hypothesis that EHD flow is responsible for the aggregation of colloidal particles in electric fields was investigated. The primary focus was on spherical particles in fields oscillating at frequencies of several hundred Hz or higher. First, scaling expressions were derived to describe the EHD flow engendered by field inhomogeneities in the polarization layer; the inhomogenities arise from the presence of particles. The free charge density was modeled for a perfectly polarizable electrode with an alternating potential, neglecting the presence of particles. Then the point dipole approximation is used to describe perturbations in the field near the electrode due to the particles, taking account of mobile charge in the particle double layer. This produces lateral body forces in the polarization layer. Combining these ingredients yields a simple scaling expression for the EHD velocity that brings particles together. According to the analysis, the aggregation rate scales with the square of the field strength and inversely with frequency. Similar scaling arguments indicate that EHD flow also occurs in steady fields, but with magnitude comparable to electroosmotic flow.

To test the predictions of the scaling model, experimental techniques were developed to track the movements of a multitude of particles using video microscopy and image analysis. Then the 'disappearance' of singlets (non-aggregated particles) was measured as a function of time over a wide range of field strengths and frequencies. The data were interpreted in terms of a second-order aggregation rate constant to establish the effects of the main electric field parameters (applied potential and frequency). Finally, comparison of the EHD model with experimental results showed that the scaling theory provides an accurate picture.[8]

The next stage involved developing a model of electrohydrodynamic processes around a single particle near and electrode. First it was shown that the field strength at the edge of the polarization layer approaches a constant value in oscillatory fields at appropriate frequencies. The effect of a nearby particle was then explored numerically using a finite element scheme. Although the particle distorts the electric field strength along the electrode, the field strength becomes increasingly uniform in the limit as the Debye length decreases. An analytical solution for the electric potential around a particle in a uniform field near an electrode was derived that accounts for surface conduction on the particle surface (which determines the particle dipole coefficient). Then the axisymmetric stream function was derived for flow around the particle. Under typical conditions the EHD flow is directed radially inward toward the particle and decays as r^{-2} far from the particle. This solution provides a representation of the EHD flow around a particle.

Finally, the EHD flow around a particle was studied experimentally. Submicron fluorescent tracer particles were tracked around an isolated particle over a wide range of

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[8] W.D. Ristenpart, I.A. Aksay & D. A. Saville "Assembly of Colloidal Crystals by Electrohydrodynamic Flow: Kinetic Experiments and Scale Analysis" *Physical Review E* **69** 021405 (2004)

applied potentials and frequencies. Quantitative measurements of the tracer velocities are in excellent agreement with the analytical theory, where the particle surface conductivity is used as a fitting parameter.[9]

In a related activity, an undergraduate student carried out experiments to develop an 'electrohydrodynamic pen' to form patterned arrays on an electrode. A prototype device employing an electrified microcapillary was assembled and used to 'draw' colloidal lines with 10-micron resolution. A patent application was filed with the US Patent Office.

At an early stage of the work, a patent application was filed and a patent granted on "Electrohydrodynamically Patterned Colloidal Crystals."[10]

[9] Papers describing the theoretical and experimental verification are under preparation.
[10] United States Patent #6,533,903 B2 March 18, 2003

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1. Electrically Guided Assembly of Planar Superlattices in Binary Colloidal Suspensions.
Physical Review Letters **90** 128303 (2003)
(with W. D. Ristenpart & I. A. Aksay)

2. Assembly of Colloidal Crystals by Electrohydrodynamic Flow: Kinetic Experiments and Scale Analysis *Physical Review E* **69** 021405 (2004)
(with W.D. Ristenpart & I.A. Aksay)

PATENTS

1. Electrohydrodynamically Patterned Colloidal Crystals
United States Patent #6,533,903 B2 March 18, 2003
(with R. Hayward, H. Poon, Y, Xiao & I. A. Aksay)

2. C.G. Rusin, W.D. Ristenpart, D.A. Saville, I.A. Aksay, "A Colloidal "Pen" for Producing Colloidal Crystals," U.S. Provisional Patent Application Serial No. 60/316,813 (08/2001); Docket No. 02-1843-1.

3. C.G. Rusin, W.D. Ristenpart, D.A. Saville, I.A. Aksay, "A Colloidal "Pen" for Producing Colloidal Crystals," Invention Disclosure. Docket No. 02-1843-1 (2001).

PRESENTATIONS

1. Studies in Electrohydrodynamics
Microgravity Transport Processes in Fluid, Thermal, Materials, and Biological Sciences II, September 30 - October 5, 2001, Banff, Alberta, Canada

2. Light-Induced Colloidal Motion and Aggregation Near an Electrode Surface
AICHE Annual Meeting, November 4-9, 2001 Reno, NV
(with W. D. Ristenpart & I. A. Aksay)

3. Particle Organization in Electrically-Modulated Colloidal Systems
APS Division of Fluid Dynamics Annual Meeting, November 18-20, 2001 San Diego, CA
(with W. D. Ristenpart, M. Slowik & I. A. Aksay)

4. Electrically-Tunable Assembly of Binary Colloidal Arrays
76th Colloid & Surface Science Symposium, Ann Arbor Michigan, June 2002
(with W. D. Ristenpart and I. A. Aksay)

5. Light-Induced Motion and Aggregation of Colloids Near an Electrode Surface: Kinetic Experiments. 76th Colloid & Surface Science Symposium, Ann Arbor Michigan, June 2002 (with W. D. Ristenpart and I. A. Aksay)

6. Electrically Guided Assembly of Colloidal Particles
   6th NASA Microgravity Conference – Cleveland, August 2002
   (with W. D. Ristenpart and I. A. Aksay)

7. Electrically Guided Assembly Of Colloidal Particles - Plenary Lecture
   Electrokinetics 2002 - Cracow Poland, August 2002

8. Electrically-Tunable Assembly Of Binary Colloidal Structures
   AICHE Annual Meeting - Indianapolis, IN, November 2002
   (with W. D. Ristenpart, & I. A. Aksay)

9. Assembly of Binary Colloidal Arrays in Electric fields
   APS Division of Fluid Dynamics Annual Meeting, Dallas, TX, November 2002
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10. Electrically Guided Self-Assembly Of Binary Colloidal Crystals.
    Materials Research Society, Boston MA December 2002
    (with W. D. Ristenpart, & I. A. Aksay)

11. Electrically Guided Assembly of Planar Superlattices in Binary Colloidal Suspensions.
    77th ACS Colloid & Surface Science Symposium - Atlanta, GA, June 2003
    (with W. D. Ristenpart, & I. A. Aksay)

12. Assembly of Colloidal Particles by Electrohydrodynamic Flow.
    AICHE Annual Meeting – San Francisco, CA, November 2003
    (with W. D. Ristenpart, & I. A. Aksay)

13. Electrically Guided Assembly of Planar Superlattices in Binary Colloidal Suspensions
    AICHE Annual Meeting – San Francisco, CA, November 2003
    (with W. D. Ristenpart, & I. A. Aksay)

14. Micropatterned Colloidal Assemblies by E-field Guiding
    Third World Congress - Nanocomposite 2003, San Francisco, CA, November 2003
    (with I. A. Aksay)

15. Micropatterned Colloidal Assemblies by E-field Guiding
    Materials Research Society Annual Meeting - Boston MA, December 2003
    (with I. A. Aksay)

16. Assembly of Colloidal Particles by Electrohydrodynamic Flow

International Conference on Electrokinetics (ELKIN 2004)
Pittsburgh, PA June 2004
(With W. D. Ristenpart and I. A. Aksay)

17. Electrokinetics & Electrohydrodynamics (Invited Sectional Lecture)
International Conference on Theoretical and Applied Mechanics
(ICTAM 2004) Warsaw, Poland August 2004.

18. Assembly of Colloidal Particles by Electrohydrodynamic Flow
(Plenary Lecture) Field-Assisted Nanocolloid Self-Assembly Workshop
University of Twente, Enschede, The Netherlands,
November 2004 (With I. A. Aksay)

19. Electrohydrodynamic Flow Around Colloidal Particles Near an Electrode
AICHE Annual Meeting – Austin, TX November 2004
(With W. D. Ristenpart and I. A. Aksay)

BS THESIS

C. G. Rusin "Patterning Colloidal Crystals with UV Light"
Princeton University (2001)

PhD THESIS

W. D. Ristenpart "Electric Field Induced Assembly of Colloidal Particles" Princeton University (2005)

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