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Submitted on: 05/23/2012
Principal Investigator: Yoda, Minami .
Award ID: 0933360
Organization: Georgia Tech Research Corp
Submitted By:
Yoda, Minami - Principal Investigator
Title:
Equipment Grant for Interfacial Velocimetry and 3D Liquid-Phase Thermometry in Microfluidic Devices

Project Participants

Senior Personnel

Name: Yoda, Minami
Worked for more than 160 Hours: Yes
Contribution to Project:

Post-doc

Name: Kazoe, Yutaka
Worked for more than 160 Hours: Yes
Contribution to Project:
Dr. Kazoe, who was at Georgia Tech from March 2009 through April 2010, was a Japan Society for the Promotion of Science (JSPS)
Postdoctoral Fellow.

Graduate Student

Name: Cevheri, Necmettin
Worked for more than 160 Hours: Yes
Contribution to Project:
Mr. Cevheri joined Dr. Yoda's group in August 2009 as a new Ph.D. student after completing his M.S. at the Middle East Technical University (Ankara, Turkey).

Undergraduate Student

Technician, Programmer

Other Participant

Research Experience for Undergraduates

Organizational Partners

Other Collaborators or Contacts

The equipment from this grant was used for the research supported by NSF project CBET-0828782, a collaboration with Dr. Susan Olesik, currently the Chair of the Department of Chemistry at Ohio State University, and her Ph.D. students Joseph Zewe and Tian Lu.

Activities and Findings

Research and Education Activities: (See PDF version submitted by PI at the end of the report)

Findings: (See PDF version submitted by PI at the end of the report)

Training and Development:

Mr. Cevheri has become familiar with evanescent-wave particle velocimetry techniques. He has also, through his research and coursework, become familiar with colloid and interfacial science, a topic that is not part of the standard mechanical engineering curriculum.

Outreach Activities:

Dr. Yoda organized a summer research program to bring students from Westminster High School and Pace Academy in Atlanta to the School of Mechanical Engineering at Georgia Tech for 6-8 week projects mentored by various faculty and graduate students. To date, nine (five female and four male) high school students have participated in this program.

Journal Publications

Kazoe, Y; Yoda, M, "Experimental Study of the Effect of External Electric Fields on Interfacial Dynamics of Colloidal Particles", LANGMUIR, p. 11481, vol. 27, (2011). Published, 10.1021/la202056

Yoda, M; Kazoe, Y, "Dynamics of suspended colloidal particles near a wall: Implications for interfacial particle velocimetry", PHYSICS OF FLUIDS, p. , vol. 23, (2011). Published, 10.1063/1.366200

Kazoe, Y; Yoda, M, "Measurements of the near-wall hindered diffusion of colloidal particles in the presence of an electric field", APPLIED PHYSICS LETTERS, p. , vol. 99, (2011). Published, 10.1063/1.3643136

M. Yoda and M. Kim, "Studying interfacial transport with evanescent wave-based particle velocimetry and thermometry", Heat Transfer Engineering, p. , vol. , (2012). Accepted,

Books or Other One-time Publications

M. Yoda, "Nano(Evanescent-wave)-Particle Velocimetry", (   ). Book, Accepted
Editor(s): B. Bhushan
Collection: Encyclopedia of Nanotechnology
Bibliography: Springer

M. Yoda, "Studying interfacial transport with evanescent wave-based particle velocimetry and thermometry", (2011). Conference Proceedings, Published
Editor(s): S. G. Kandlikar, S. K. Mitra, Y. Peles
Collection: Proceedings of the ASME 2011 9th International Conference on Nanochannels, Microchannels and Minichannels (ICNMM11)
Bibliography: American Society of Mechanical Engineers

N. Cevheri and M. Yoda, "Evanescent-wave particle velocimetry studies of electrokinetically driven flows: Divalent counterion effects", (2012). Conference paper, Published
Collection: Proceedings of the 2012 3rd Micro/Nanoscale Heat & Mass Transfer International Conference (Atlanta, GA)
Bibliography: Paper number MNHMT2012-75274

Web/Internet Site

Other Specific Products

Contributions

Contributions within Discipline:

In terms of colloid science, these experiments have demonstrated that an electric field applied parallel to the wall creates an additional nonlinear electrokinetic force that repels near-wall (i.e., those less than 300 nm from the wall) particles of radii ranging from 0.2 um to 0.5 um. The measurements verify previous theoretical predictions of a force that scales with the square of the electric field magnitude and the square of the particle radius, albeit with a magnitude one to two orders of magnitude greater than that predicted by the theory (note that the original theory was developed for 'remote wall-sphere interactions').

In terms of fluid mechanics, this result suggests that knowledge of the near-wall particle distribution will be required to accurately measure near-wall velocity fields with particle velocimetry techniques (e.g. micro-PIV and evanescent-wave particle velocimetry). Without this knowledge, using tracers of different diameters in these techniques will give different results for the velocity field for a shear flow where there is an electric field parallel to the wall, such as combined electroosmotic and Poiseuille flow.

Contributions to Other Disciplines:

In terms of microfluidics, understanding and controlling the near-wall, or near-surface, transport of dielectric colloidal particles suspended in a conducting fluid in the presence of an electric field is also of interest in a variety of immunoassays. The transport of such particles is also relevant to the transport of large biomolecules (e.g. proteins, DNA, RNA) because the diffusion and convection of such molecules is often approximated by the transport of colloidal particles with an equivalent hydrodynamic radius.

In immunoassays, polystyrene particles ('beads') functionalized with a 'probe,' typically an antibody or DNA oligonucleotide, are commonly used to preconcentrate 'target' analytes (e.g. a protein). Alternatively, the surface of the wall is functionalized with different probes for different targets. Optimizing the mass transport of beads or a large biomolecule to a 'collection surface' for subsequent processing and analysis is hence a key enabling technology in microfluidic-based immunoassays. A fundamental understanding of how an electric field applied parallel to the wall affects the near-wall dynamics of colloidal particles could result in new technologies to improve the performance of microfluidic immunoassays.

Moreover, given that the nonlinear electrokinetic force scales with the square of the particle size, these observations may lead to new methods for size-based separation that is independent of the charge of the biomolecule or particle, and is inherently compatible with the electrokinetically driven flows common in lab-on-a-chip microfluidic devices.

Contributions to Human Resource Development:

One doctoral student, Mr. Necmettin Cevheri, has been educated in optical diagnostic techniques for fluid mechanics, as well as colloid and surface science. In addition, a postdoctoral researcher, Dr. Yutaka Kazoe, further developed his expertise in evanescent-wave diagnostic techniques and colloid science during his 13-month stay with Dr. Yoda's group.

Contributions to Resources for Research and Education:

Dr. Yoda plans to use the results on electrokinetically driven flows in a four-week module on microfluidics in the undergraduate technical elective in fluid mechanics, ME 4340, which will be taught in Spring semester 2013 at the Georgia Institute of Technology (GT). This course is the only introduction at the undergraduate level to microfluidics in the G. W. Woodruff School of Mechanical Engineering at GT, which is the largest Mechanical Engineering program in the nation with 2000 undergraduate majors as of Fall semester 2011. Dr. Yoda last taught this course in Spring semester 2011 to a student body that was ~30% African-American and ~10% Hispanic.

Contributions Beyond Science and Engineering:

Conference Proceedings

Categories for which nothing is reported:

Organizational Partners

Any Web/Internet Site

Any Product

Contributions: To Any Beyond Science and Engineering

Any Conference

Research Findings

Dynamics of Near-Wall Colloidal Particles in EDF

The major findings of this work, which have already been published,[2,3] are that:

1) Applying an electric field of magnitude E parallel to the wall induces a wall-normal "lift" force that repels negatively charged PS and SiO_2 particles from the negatively charged fused-silica wall. This nonlinear electrokinetic force appears to have a magnitude that scales with E^2 and a^2, for a = 110–463 nm and E = 15–31 V/cm, which is admittedly a quite limited range of parameters. The force also appears to be independent of the particle zeta-potential, at least for the range of ζ_p studied here of −99.9 mV to −57.4 mV. The scaling of this force with E and a is in agreement with previous theoretical predictions of a "dielectrophoretic-like" force due to the nonuniform electric field in the gap between the particle and the wall.[4] However, the estimates of the magnitude of this force give values that are 30–40 times greater than that that predicted by the theory. This discrepancy may be due to the limitations of the theory, which only considered "remote" particle-wall interactions for $a/(h+a) \ll 1$; $a/(h+a) = 0.4 - 0.9$ in these experiments.

2) The applied electric field does not affect the Brownian diffusion of the particles, which is already hindered by the additional hydrodynamic drag due to the presence of the wall. Even under conditions where the electrophoretic force magnitude exceeds that of the Stokes drag on the particles based on their Brownian velocity, the diffusion coefficient for particle motion parallel and normal to the wall at different distances from the wall is in good agreement with the theories of Faxén[5] and Brenner.[6]

This work has also been presented in three keynote talks:

- M. Yoda (2010) "Interfacial velocimetry and microscale thermometry," International Symposium on Micro/Nano Flow Measurement Techniques, Horiba International Conference, Tokyo, Japan
- M. Yoda (2010) "Dynamics of suspended colloidal particles near a wall: Electrokinetic effects and implications for particle velocimetry," 63rd Annual Meeting of the American Physical Society Division of Fluid Dynamics, Long Beach, CA
- M. Yoda (2011) "Studying interfacial transport with evanescent wave-based particle velocimetry," ASME Ninth International Conference on Nanochannels, Microchannels and Minichannels, Edmonton, Canada

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2 Y. Kazoe and M. Yoda (2011) "Experimental study of the effects of external electric fields on interfacial dynamics of colloidal particles" *Langmuir* **27**, 11481

3 Y. Kazoe and M. Yoda (2011) "Measurements of the near-wall hindered diffusion of colloidal particles in the presence of an electric field" *Applied Physics Letters* **99**, 124104

4 E. Yariv (2006) "'Force-free' electrophoresis?" *Physics of Fluids* **18**, 031702

5 H. Faxén (1922) "Der Widerstand gegen die Bewegung einer starren Kugel in einer zähen Flüssigkeit, die zwischen zwei parallelen ebenen Wänden eingeschlossen ist" *Annalen der Physik* **373**, 89

6 H. Brenner (1961) "The slow motion of a sphere through a viscous fluid towards a plane surface" *Chemical Engineering Science* **16**, 242

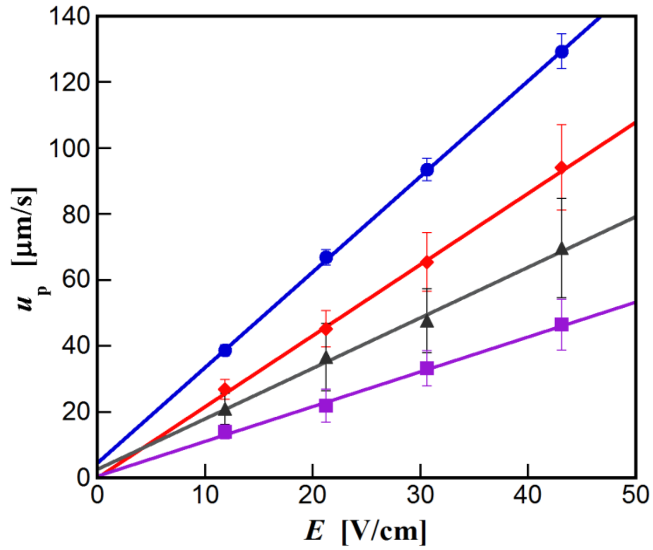

Figure 2 Plot of the particle velocities u_p measured with evanescent-wave particle velocimetry as a function of electric field magnitude E for the base fluid (●), as well as the α = 0.5% (◆), 1% (▲) and 2% (■) Mg^{++} solutions. The error bars denote the standard deviation of these data.

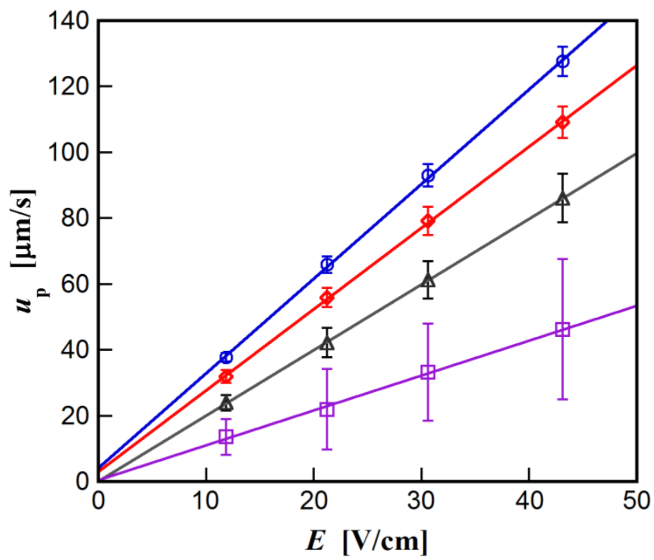

Figure 3 Similar to the previous Figure, but for the base fluid (○), as well as the α = 0.5% (◇), 1% (△) and 2% (□) Ca^{++} solutions.

Figure 2 shows the particle velocity u_P measured by evanescent-wave particle velocimetry as a function of electric field magnitude E for the base fluid (●), as well as the α = 0.5% (◆), 1% (▲) and 2% (■) Mg^{++} solutions. The solid lines are curve-fits to the data obtained by linear regression, and these results are the average of four independent experiments in the same channel. Figure 3 shows similar results for the base fluid (○), as well as the α =0.5% (◇), 1% (△), and 2% (□) Ca^{++} solutions. These results are also the average of four independent experiments performed in the same channel. The particle velocities at a given E decrease as the Mg^{++} or Ca^{++} fraction increases, consistent with adsorption of the divalent cation on the negatively charged fused-silica wall reducing the magnitude of the wall zeta-potential.

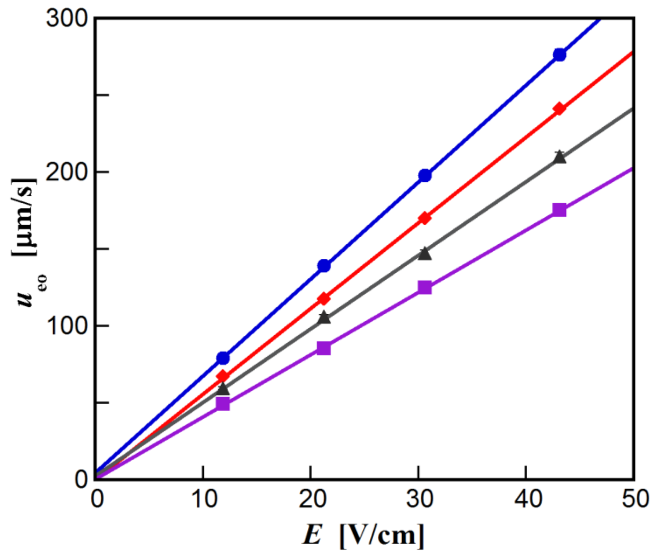

Figure 4 Plot of the electroosmotic flow velocities u_{eo} as a function of electric field magnitude E for the for the base fluid (●), as well as the α = 0.5% (◆), 1% (▲) and 2% (■) Mg^{++} solutions. The error bars are the uncertainty in these data based on the standard deviations in u_p and ζ_p.

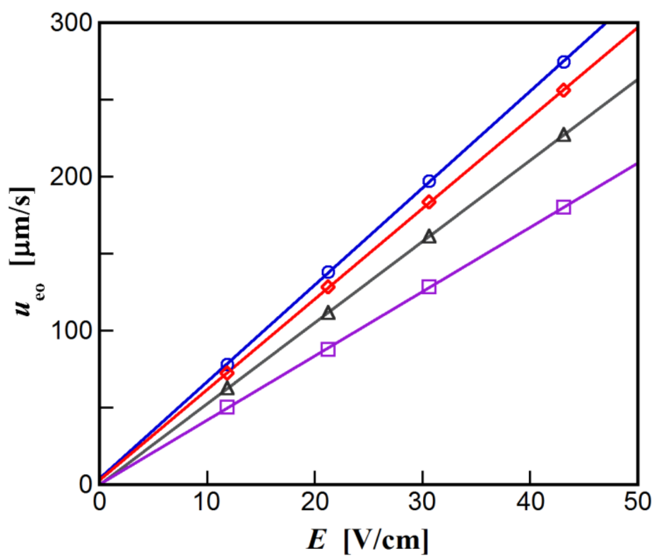

Figure 5 Similar to the previous Figure, but for the base fluid (○), as well as the α = 0.5% (◇), 1% (△) and 2% (□) Ca^{++} solutions.

As expected, u_P is a linear function of E, since, the particle velocity is the superposition of the electroomostic and electrophoretic velocities:

$$u_P = u_{ep} + u_{eo} = \frac{\varepsilon}{\eta}(\zeta_p - \zeta_w)E \qquad (2)$$

where ε and η are the permittivity and dynamic viscosity, respectively, of the fluid. The EOF velocity can then be calculated from these data using the measured values of ζ_p. Figures 4 and 5 show the EOF velocity u_{eo} as a function of electric field magnitude for the base fluid, as well as the Mg^{++} and Ca^{++} solutions, respectively. The solid lines again represent curve-fits to the data obtained by linear regression. Like the particle velocities, the electroosmotic flow velocities at a given E decrease as the Mg^{++} or Ca^{++} fraction increases.

Since the slope of $u_{eo}(E)$ is the electroosmotic mobility,

$$\mu_{eo} = \frac{\varepsilon}{\eta}\zeta_w \qquad (3)$$

the data in Figures 4 and 5 can then be used to determine ζ_w. The wall zeta-potentials obtained from linear regression of these data are ζ_w = −90.7±2.2 mV for the base fluid; −80.6±4.5 mV, −69.1±5.3 mV, and −59.0±2.2 mV for the α = 0.5%, 1% and 2% Mg^{++} solutions, respectively; and −84.9±1.1 mV, −76.3±2.5 mV, and −60.5±5.8 mV for the α = 0.5%, 1% and 2% Ca^{++} solutions, respectively. Based on these results, both Mg^{++} and Ca^{++} have a significant effect on the wall zeta-potential (and hence u_{eo}), reducing it by about one-third for α = 2%.

The results from this work have been presented at two conferences:

- N. Cevheri and M. Yoda (2011) "The effect of multivalent counterions on electrokinetically driven flows," 64th Annual Meeting of the American Physical Society Division of Fluid Dynamics, Baltimore, MD
- N. Cevheri and M. Yoda (2012) "Evanescent-wave particle velocimetry studies of electrokinetically driven flows: Divalent counterion effects," ASME paper MNHMT2012-75274, Proceedings of the 3rd Micro/Nanoscale Heat & Mass Transfer International Conference, Atlanta, GA

Mr. Cevheri is currently studying effect of varying the ionic strength and pH of the "base" monovalent electrolyte solution on EDF, and plans to present his findings at the 16th International Symposium on Applications of Laser Techniques to Fluid Mechanics in Lisbon, Portugal this July.

Although results are not shown here, we were unable to detect any significant differences in the near-wall particle distributions $c(h)$ due to the presence of Mg^{++} or Ca^{++}. The divalent cation concentrations studied here may simply be too low to affect $c(h)$, or the differences in $c(h)$ may be smaller than the uncertainty of these experiments. We are currently working with the group of Prof. Terry Conlisk in the Department of Mechanical and Aerospace Engineering at the Ohio State University to investigate why divalent cations, at least at these concentrations, have no discernible effect on the near-wall particle distribution.

Future Plans for the Confocal Laser Scanner

The used Yokogawa CSU-10 confocal laser scanner will be coupled to the Leica DMIRE2 inverted epifluorescent microscope by Vashaw Scientific (Norcross, GA) in early June 2012. We expect to use this laser scanner to obtain liquid temperature fields with a spatial resolution of a few μm near the free surface of evaporating liquid layers (of depth significantly greater than the Laplace length scale) driven by a horizontal temperature gradient using temperature-sensitive laser-induced fluorescence (LIF), also known as fluorescence thermometry (FT). Dr. Yoda, in collaboration with Prof. Roman Grigoriev of the School of Physics at Georgia Tech, is currently studying the transport of mass, momentum and energy in the liquid and vapor phases of simple fluids such as water and methanol, as well as binary water-alcohol mixtures with support from the Thermal Management Program at the Office of Naval Research.

Understanding the role of thermocapillarity and solutocapillarity due to variations in surface tension because of temperature and mixture fraction (for binary mixtures where the components have different volatilities) is one of the major objectives of this work. Measuring the temperature field near the liquid-vapor interface will help clarify when thermo- and solutocapillarity are significant. Most of this work has focused to date on measuring velocity fields using 2D-2C particle-image velocimetry, but Dr. Yoda's doctoral student Benjamin M. Chan is developing and calibrating a two-color FT[7] method suitable for use in evaporating water layers.

[7] P. Lavieille, F. Lemoine, G. Lavergne, and M. Lebouché (2001) "Evaporating and combusting droplet temperature measurements using two-color laser-induced fluorescence" *Experiments in Fluids* **31**, 45

Research Activities

This equipment grant (supported by ARRA funds) was used for three items:

1) a water-cooled electron multiplying CCD (EMCCD) camera (Hamamatsu C9100-13);
2) to refurbish the plasma tube in a 5 W argon-ion laser (Coherent Innova 90-5) already available in Dr. Yoda's lab ; and
3) a used confocal laser scanner (Yokogawa CSU-10).

Although the confocal laser scanner, purchased from Visitech International (Sunderland, United Kingdom), has been received at Georgia Tech, the CSU-10 has not yet been coupled to the Leica DMIRE2 inverted epifluorescent microscope already available in Dr. Yoda's lab. The research that we expect to perform with the confocal laser scanner is briefly described in the Findings portion of this report.

The final report for this grant will therefore focus on the research activities using the EMCCD and argon-ion laser, which were used to support NSF research project CBET-0828782 and Army Research Office (ARO) grant W911NF-10-1-0290. There is therefore substantial overlap between the reports for this equipment grant (CBET-0933360) and CBET-0828782.

Over the 30-month period of this grant, the first two piece of equipment have been used extensively to study electrokinetically driven flows (EDF), or flows of aqueous electrolyte solutions driven by a voltage gradient through microchannels of depth H. In EDF, an electric field of magnitude E is applied parallel to the wall to drive the charged fluid and mobile counterions in the electric double layer (EDL), a screening layer that neutralizes the (usually negatively) electric charge of the surface of the microchannel wall. The EDL consists of two layers: the inner Stern layer consisting of immobile counterions "attached" by electrostatic forces to the surface of the wall, and the outer diffuse layer containing mobile counterions subject to random thermal fluctuations. The surface charge of the channel wall is characterized by the electric potential at the outer edge of the Stern layer, the wall zeta-potential ζ_w. The thickness of the EDL is characterized by the Debye length scale λ_D, which is typically of $O(0.1-10$ nm) for aqueous electrolyte solutions . The resulting electroosmotic flow (EOF) has a "boundary layer-like" velocity profile in the EDL, and the neutral fluid in the bulk beyond the EDL, which is driven by viscous effects (*vs*. the electric field) has a uniform velocity profile. The speed of this uniform flow u_{eo} is in most cases proportional to ζ_w. EDF is commonly used in microfluidic lab-on-a-chip devices because EOF with its uniform velocity profile has less convective dispersion than parabolic Poiseuille flow.

Two aspects of EDF were studied, namely:

I. the dynamics of suspended near-wall colloidal particles;

II. the effect of trace amounts of divalent counterions, which can significantly reduce electroomostic flow (EOF) velocities by reducing the magnitude of ζ_w by adsorption onto the walls of the microchannel.

Dr. Yoda's group has developed an evanescent wave-based particle velocimetry technique called multilayer nano-particle tracking velocimetry (MnPTV),[1] where the exponential decay in the intensity of the evanescent-wave illumination is used to determine the 3D position of suspended colloidal tracers within 400 nm of the wall as a function of time. In EDF, these suspended particles, have a surface charge characterized by the particle zeta-potential ζ_p, and therefore have an electrophoretic velocity u_{ep} that in most cases is proportional to ζ_p. So the motion of the colloidal tracers in EDF is due to electrophoresis and EOF.

These data were used to determine the fluctuations in particle displacements due to Brownian diffusion parallel and normal to the wall. Note that this close to the wall, Brownian diffusion is anisotropic because the particles are subject to both Stokes drag and an additional hydrodynamic drag force due to the presence of the wall.

These data were also used to obtain near-wall particle velocities, which should be the superposition of u_{eo} and u_{ep}. Although the 3D position of the particle at different times could, in theory, be used to obtain all three velocity components, the wall-normal velocity component is negligible this close to the wall because of the no-flux condition. These data were therefore used instead to determine the two velocity components parallel to the wall and the steady-state distribution of the tracer particles along the wall-normal coordinate z. Unlike our previous MnPTV studies in Poiseiulle flows, the velocity profiles in EDF are uniform in the thin EDL limit where λ_D is much less than the size of the tracer, and so the particle velocities parallel to the wall should be independent of h.

Dynamics of Near-Wall Colloidal Particles in EDF

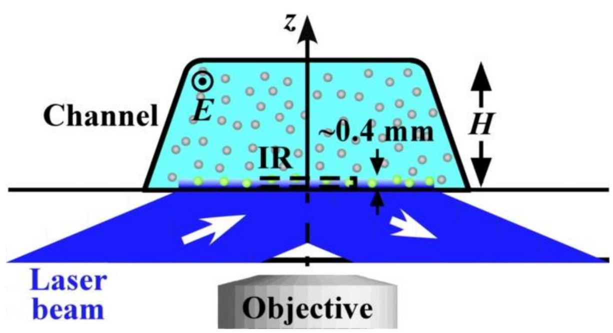

Figure 1. A cross-section of the fused-silica microchannel and the bottom wall of the channel: fluorescent particles next to the bottom wall of the channel are illuminated by evanescent waves. The direction of the flow and the electric field E are normal to the page.

The study of the dynamics of near-wall colloidal particles in electrokinetically driven flow was led by Dr. Yutaka Kazoe, who was at Georgia Tech from March 2009 through April 2010 as a Japan Society for the Promotion of Science (JSPS) postdoctoral researcher (Dr. Kazoe currently an Assistant Professor in the Department of Applied Chemistry at the University of Tokyo, Japan). Steady and fully-developed EDF through fused-silica microchannels with cross-sectional dimensions of 306 μm × 38 μm (H) was created by applying steady electric fields of magnitude E = 15, 22 and 31 V/cm using a

[1] H. F. Li and M. Yoda (2008) "Multilayer nano-particle image velocimetry (MnPIV) in microscale Poiseuille flows" *Measurement Science and Technology* **19**, 075402

dc power supply (Fig. 1). The working fluid was an aqueous 1 mmol/L sodium tetraborate (Na_2B4O_7) solution (pH 9.0, conductivity 314 μS/cm) with a Debye length scale λ_D, which characterizes the thickness of the EDL, of 6.8 nm. At the beginning of each experiment, the flow was driven for about 60 s by a small pressure gradient of O(1 kPa/m) created by the ~5 mm height difference between the free surfaces of the reservoirs upstream and downstream of the channel. This weak Poiseuille flow is referred to here as the $E = 0$ case.

Experiments were performed using five different types of particles:

- Four different carboxylate-modified fluorescent polystyrene (PS) spheres with radii (mean ± standard deviation) $a = 110 \pm 12$ nm; 240 ± 22 nm; 371 ± 34 nm and 461 ± 34 nm and zeta- potentials $\zeta_p = -60.6 \pm 4.3$ mV; -57.4 ± 3.1 mV; -96.2 ± 2.9 mV and -99.9 ± 3.2 mV, respectively; and
- Fluorescent colloidal silica (SiO_2) spheres of $a = 463 \pm 60$ nm and $\zeta_p = -91.7 \pm 2.5$ mV.

In all cases, the properties of the tracers suspended in the working fluid were determined by light scattering using a Malvern Instruments Zetasizer. The particles were suspended in the $Na_2B_4O_7$ solution at nominal volume fractions $\phi = 0.02–0.13\%$, corresponding to a number density $c = O(10^{16}\ \text{m}^{-3})$.

The particles were illuminated by evanescent waves at a wavelength of 488 nm over a ~1100 μm × ~300 μm elliptical region next to the bottom wall of the channel with a root mean square (rms) surface roughness of 3 nm. The fluorescence from the particles was imaged by the EMCCD camera; at least 1000 image pairs over an area of 512 × 144 pixels (130 μm × 33.6 μm) in the center of the elliptical region were acquired over a total time of 40–60 s at an exposure of 0.5 ms with a temporal spacing between the images in the pair $\Delta t = 1.3–2.2$ ms.

The center of each particle tracer in a given image was located using cross-correlation with a Gaussian intensity distribution. Next, the particle edge-wall separation h was estimated from the brightness or intensity of the particle image after correcting the images for EMCCD camera nonlinearities. Under the assumption that the particle image intensities have an exponential decay identical to that of the evanescent-wave illumination:

$$h = z_p \ln\left\{\frac{I_p^0}{I_p}\right\} \tag{1}$$

where $z_p = 158 \pm 4$ nm is the intensity-based penetration depth (*i.e.*, the length scale of the exponential decay) of the evanescent wave, I_p is the area-averaged intensity of each particle image, and I_p^0 is the intensity of the images of particles attached to the wall (*i.e.*, $h = 0$), which was determined in separate calibration experiments. The uncertainty in h was 4.5–12 nm, and only particles at $h \le 300\ \text{nm} \approx 2z_p$ were considered in these studies.

The ensemble of h values over at least $O(10^4)$ particle images was then used to estimate the steady-state near-wall particle distribution in terms of the particle number density profile $c(h)$. After removing images of overlapped and flocculated particles, the particle displacements between the two images in the pair were determined by matching the particles in the first image to their nearest neighbor in the second image.

Divalent Counterion Effects in EDF

As noted previously, the EOF velocity is proportional in most cases to ζ_w. The wall zeta-potential can be changed by nonspecific adsorption of multivalent cations onto the negatively charged fused-silica microchannel wall, however, because ζ_w is, strictly speaking, the electric potential one counterion diameter away from the actual surface of the wall. Moreover, these divalent cations can also adsorb onto the negatively charged surface of the tracer particles, changing ζ_p and hence the electrophoretic velocity of the tracers.

A study of how divalent counterions (here, cations) affect electrokinetically driven flow and the near-wall dynamics of colloidal particles in EDF was led by doctoral student Necmettin Cevheri, who was supported by NSF grant CBET-0828782 and ARO grant W911NF-10-1-0290. Steady and fully-developed EDF through fused-silica channels of depth H = 33 μm was studied at electric field magnitudes E = 11.9, 21.2, 30.6 and 43.1 V/cm. These experiments considered the flow of seven different aqueous electrolyte solutions, all with an ionic strength of 10 mmol/L:

- a "base" monovalent electrolyte solution consisting of 9 mmol/L sodium chloride (NaCl) and 1 mmol/L sodium hydroxide (NaCl) at pH10.5
- three different solutions with small amounts of the divalent cation Mg^{++} consisting of the base solution and enough magnesium chloride ($MgCl_2$) so that the divalent cation fraction $\alpha \equiv [Mg^{++}]/[Na^+]$ = 0.5%, 1% and 2%
- three different three different solutions with small amounts of the divalent cation Ca^{++} consisting of the base solution and enough calcium chloride ($CaCl_2$) so that the divalent cation fraction $\alpha \equiv [Ca^{++}]/[Na^+]$ = 0.5%, 1% and 2%.

The divalent cation fractions studied here were limited to a maximum value of 2% because too many of the tracer particles were immobilized (presumably due to electrostatic forces) on the microchannel wall at higher values of α, making it impossible to obtain images suitable for MnPTV.

Fluorescent carboxylated polystyrene particles of radius a = 105±15 nm (based on the manufacturer's specifications) were suspended in all seven solutions at nominal volume fractions $\phi = 1.6\times10^{-4}$ corresponding to a number density $c = 3.3\times10^{16}$ m^{-3}. The particle zeta- potentials for the suspended particles, determined again by light scattering using a Malvern ZetaSizer, were: ζ_p = –49.1±1.2 mV for the base fluid; ζ_p = –49.1±0.5 mV, –47.1±1.0 mV, and –43.1±0.6 mV for the α = 0.5%, 1% and 2% Mg^{++} solutions, respectively; and ζ_p = –49.1±0.8 mV, –47.1±0.5 mV, and –44.8±0.4 mV for the α = 0.5%, 1% and 2% Ca^{++} solutions, respectively. The results at α = 2%, as well as results (not shown here) at higher divalent cation fractions, suggest that Ca^{++} has slightly less affinity than Mg^{++} for the surface of these carboxylate-terminated PS particles.

The particles were illuminated by evanescent waves with z_p = 142 nm at a wavelength of 488 nm, and a region 136 μm×37 μm; 500 image pairs over a total acquisition time of 150 s were imaged by an EMCCD at an exposure of 0.49 ms with a temporal spacing between the images in the pair Δt = 10 ms. Only the images of particles at $h \leq 400$ nm ≈

$2.7z_\mathrm{p}$ were considered in these studies were processed as described previously to obtain the particle displacements parallel to the wall and the steady-state particle number density profile $c(h)$.