DIRECTED SELF ASSEMBLY OF COLLOIDAL PARTICLES FOR HIGH ASPECT RATIO BANDS

Varun Lochab¹, Andrew Yee², Yanrong Li³, Minami Yoda², A. Terrence Conlisk¹, and Shaurya Prakash^{1*}

¹Department of Mechanical and Aerospace Engineering, The Ohio State University, Columbus, OH, USA

²The George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA, USA

³Department of Mechanical Engineering, Ibaraki University, Hitachi, Japan

ABSTRACT

Current state-of-art nano- (< 100 nm diameter) and colloidal particle (> 100 nm, < 1 μ m) assembly methods require particle aggregation followed by assembly to fabricate usable structures. A single-step method that aggregates and assembles particles dynamically in a continuous-flow system has the potential to provide new avenues for nanomaterial fabrication. Here, we present observations with initial analyses of the mechanics of directed self-assembly of colloidal particles into stable, high aspect-ratio bands within microchannels in combined steady Poiseuille and electroosmotic flow with opposed applied pressure and potential gradients.

INTRODUCTION

Recent advances in nano-/colloidal particle synthesis enable a broad range of tunable functions using different size and surface charge. With a wide variety of designed and engineered properties possible for both nano- and colloidal particles, these material systems present a major building block for generating new assembled materials with remarkable functionality [1]. At present, the fundamental understanding of particle migration/aggregation required to predict and eventually engineer such materials is lacking, and there are few, if any, practical and systematic approaches for particle aggregation and subsequent assembly into usable structures. In this paper, we present observations of a new type of particle assembly along with initial efforts to analyze the mechanics of the assembly of colloidal particles in stream-wise bands within continuous flow in a microchannel.

In 1961, Segré & Silberberg [2] reported that particles migrate slowly to a thin concentric region at a radial location about 0.6 times the pipe radius in the Poiseuille flow of a dilute suspension of neutrally-buoyant rigid spherical particles in a Newtonian fluid. Later, Jeffrey and Pearson [3] observed that particles denser than the fluid migrated rather rapidly to a location near the pipe walls for downwards Poiseuille flow in a vertical pipe, and towards the centerline for upwards flow (Figure 1a).

Bretherton [4] showed that when inertia was neglected with respect to viscous forces, no force along the lateral (*i.e.*, cross-stream) direction can exist for a body of revolution, for example, a spherical particle in a unidirectional flow. The lateral migration of the particle is therefore due to the inertia of the fluid and the particle. Particularly, the migration of non-neutrally buoyant particles, as observed by Jeffrey and Pearson, was explained by inertial forces called ‘slip-shear’ induced lift forces, which dictate that a particle travelling faster than the undisturbed fluid flow migrates towards the boundaries while a particle lagging the fluid velocity migrates towards the center of the channel [5-7].

Hogg [6] provided another model and described that fluid inertia affects the particle motion either by inertial interaction with the wall or, if the particle is moving in a sufficiently large domain relative to particle size, the inertial effects of the far field, arising

from Oseen-like inertial corrections. In Hogg’s work [6], the ratio of magnitude of the wall effect to the inertial effects of the far field scaled with channel Reynolds number, $Re^{-1/2}$. Where, $Re (= \rho U_c H / \mu)$ is the channel Reynolds number based on the channel height, H as the critical length scale and centerline velocity U_c . For $Re \ll 1$, inertial interactions with the walls dominate the lateral motion of the particle, while for $Re \gg 1$, Oseen-like inertial migration effects dominate, and thus, the fluid may be treated as unbounded. For $Re \sim 1$, however, both types of effects are important. Saffman [8, 9] studied inertial effects in Oseen-like regions, and obtained the slip-shear induced lift force on a particle moving relative to the fluid in an unbounded linear shear flow. Later, Drew [10] and McLaughlin [11] considered the particle migration in the shear flow bounded by a single planar wall. Ho and Leal [12] also studied the inertial lift forces in the Poiseuille flows for $Re \ll 1$, where inertial interactions with the walls dominate.

Given the various scaling parameters (discussed in more details in the results and discussion section), in this work, initial analysis on mechanics of directed self-assembly of colloidal particles is developed using the methods described by Hogg [6].

Figure 1: (a) Particles with a slightly greater density lag the fluid in an upwards Poiseuille flow due to negative buoyancy and migrate towards the pipe axis, while they lead the fluid in a downwards flow and migrate towards the walls. (b) A negatively charged neutrally buoyant particle leads the flow due to electrophoresis in combined Poiseuille and counter EOF; the particle experiences a lift force towards the channel walls. (c) A negatively charged neutrally buoyant particle lags the combined flow due to electrophoresis in combined Poiseuille and electroosmotic “co-flow”; the particle then experiences a lift force towards the center of the channel. Dotted lines show particle motion in response to the lift forces.

Hogg reported that for the flow of non-neutrally buoyant article in vertical channels that the denser non-neutrally buoyant particles

in downward Poiseuille flow will migrate to the wall when they lead the flow, and move towards the center of the channel (Figure 1a) in upwards flow when they lag the flow, in agreement with the observations by Jeffrey and Pearson.

We *hypothesize* here that similar ‘slip-shear’ effects can be induced by the electrophoretic motion of charged colloidal particles in combined Poiseuille and electroosmotic (EO) flow, where particles can either lead or lag the undisturbed fluid velocity based upon the direction of the applied electric field (*cf.* Figure 1b, 1c). An extensive literature search yielded only two recent papers [7, 13] that report observations of electrophoretic-induced migration in combined Poiseuille and EO flow.

In a recent report by the Yoda group, colloidal particles not only aggregate near the wall in combined Poiseuille and opposing EOF, but also form stream-wise bands in the channel under a range of parameters [14]. We also conjecture that this phenomenon could be due to fluid flow instabilities, the exact nature of these flow instabilities remains yet unknown.

METHODS

Model polydimethylsiloxane (PDMS) microchannel (4 cm [L; x] × 34 μm [H; y] × 340 μm [W; z]) were fabricated using well-accepted soft lithography methods. Briefly, we spin-coated (2150 RPM, 60 s) photoresist (SU-8 2025, MicroChem Corp., Newton, MA) on silicon wafer after it was cleaned in Piranha solution (4:1, H₂SO₄:H₂O₂) and blow dried with Nitrogen. Wafer was subjected to a two-step pre-exposure bake at 65° C (5 min) and 90° C (10 min), respectively to evaporate the remaining solvent and to densify the photoresist film. We employed a thin, transparent film, and printed (10,000 dpi) negative photomask for the near-UV (320-450 nm) flood exposure (240 mJ/cm²) of the wafer. Later, two-step post-exposure bake at 65° C (3 min) and 90° C (10 minutes) was executed, and the photoresist was developed for 7 minutes in SU-8 developer and hard-baked at 200° C for 15 minutes to yield a positive mold of the model microchannel.

Figure 2: (a) Schematic of the microchannel (4 cm [L; x] × 34 μm [H; y] × 340 μm [W; z]) (b) Scanning Electron Microscopy (SEM) micrograph of channel cross-section. (c) Experimental setup showing TIRF for imaging near-wall (~500 nm) particles. (d) Stream-wise bands assemble near the glass wall spanning the width of the channel, as shown in the schematic.

Liquid PDMS was degassed and poured on the silanized ((Tridecafluoro-1,1,2,2-Tetrahydrooctyl) – Trichlorosilane) mold and was cured for 4 h at 70° C. PDMS microchannels were then bonded to the fused quartz glass slides (Figure 2) by exposing both to O₂ plasma at 45 W RF power and 280 mTorr pressure for 40

seconds.

The flow experiments used a dilute colloidal solution (particle fraction = 0.17, 0.33 % v/v) of negatively charged neutrally buoyant polystyrene particles (radius $a = 245$ nm, zeta potential ~ -50 mV) in sodium tetraborate solution (1 mM), driven by opposed Poiseuille and EO flow (Figure 2) as reported earlier [14]. Total internal reflection fluorescence (TIRF) microscopy (Figure 2) was used for visualizing polystyrene nanoparticles within the first ~ 1 μm of the channel walls [14].

High aspect ratio bands with cross-section of a few μm and length comparable to the channel length of $O(\text{cm})$ were observed (Figure 2d). In all cases, band formation was preceded by particle aggregation near the channel walls. Two-dimensional flow analysis was done where the effect of side walls ($H/W = 0.1$) was neglected. The top and bottom walls are subjected to no-slip boundary conditions and symmetric wall zeta potential ($\zeta_w \sim -100$ mV) was used for modeling and analysis. For evaluation of particle migration to the walls, we use analytical force expressions for inertial forces reported previously [8, 9, 12].

RESULTS AND DISCUSSION

After the potential difference was applied ($T = 0$ s), the particles migrated to the wall (Figure 3), and subsequently formed high-aspect ratio stream-wise bands in combined Poiseuille and opposing EOF, for certain combinations of pressure and potential gradients as reported previously [14].

Figure 3: Near-wall bands at $\Delta P_{12}/L = 0.56$ bar/m and $\Delta V_{12}/L = -117$ V/cm switched on at $T = 0$ s. Image area: $203 \mu\text{m} \times 203 \mu\text{m}$.

Flow Analysis

Fluid velocity profiles were obtained by solving the coupled Navier-Stokes and Poisson-Boltzmann equations for 2D flow. As with previous reports, we assume fully developed, steady flow with no-slip boundary condition at the physical microchannel walls, whereas reservoir conditions were as shown in Figure 2a. The stream-wise (x) momentum equation is given by:

$$\frac{\partial P}{\partial x} = \mu \frac{d^2 U}{dy^2} - \epsilon E_x \frac{d^2 \phi}{dy^2} \quad (1)$$

The potential distribution, $\phi(y)$, is obtained analytically from the solution of Poisson-Boltzmann equation [16], where, for boundary conditions, wall zeta potential (ζ_w) is assumed to be symmetric for the top and bottom walls; P is pressure, and U is fluid velocity; μ and ϵ are dynamic viscosity and permittivity of water, respectively, at 1 atm and 25° C. Equation 1 is linear, thus, the solution for the flow velocity can be decomposed into two parts.

$$U = U_{\text{Poiseuille}} + U_{\text{EOF}} \quad (2)$$

Figure 4: (a) Fluid velocity profiles across the channel, where direction of flow is in x -direction (cf. Figure 2d). (b) Negative fluid velocity ($U < 0$), i.e., flow reversal, near the wall due to opposing EO flow. (c) Point of zero shear represent the position where the forces due to pressure-gradient ($\Delta P_{12}/L = 0.56$ bar/m) and opposing potential gradient balance; this results in an inflection point ($d^2 U/dy^2 = 0$) in the velocity indicating that flow instabilities might exist.

We observe two specific characteristics of the resultant velocity profile (Figure 4a, 4b) for the conditions in our experiments: 1) an inflection point ($d^2 U/dy^2 = 0$); 2) flow reversal near the walls ($U < 0$).

The inflection point is at ~ 80 nm from the wall for the conditions ($\Delta P_{12}/L = 0.56$ bar/m) used in the experimental data reported here and there is zero shear, where the forces due to applied pressure and adverse potential gradient balance at ~ 30 nm from the wall. The presence of inflection point indicates the possibility of flow instability arising near the wall. Previous reports [15] have suggested that, at the inflection point ($d^2 U/dy^2 = 0$), where the viscous force term ($\mu d^2 U/dy^2$) vanishes to zero and the lateral energy gradient ($d(P + \rho U^2/2)/dy$) exists, any small disturbance to the flow could be amplified by the energy gradient without being dampened by viscous losses, making the flow unstable.

Particle Dynamics

The lateral migration of the particles in unidirectional fluid flow has been previously attributed to fluid and particle inertia [4, 6]. Ho and Leal [12] solved for inertial lift forces, F_I , on neutrally buoyant spheres in 2D unidirectional flows, where the Oseen inertial correction [6] is negligible compared with the interactions with the walls.

$$F_I \propto U_c^2 a^4/H^2 \quad (3)$$

These inertial lift forces yield an equilibrium position away from the wall where net force on the particle is zero, similar to that also observed by Segré & Silberberg [2].

As described in the introduction section, for the experimental conditions reported here and use of dilute colloidal suspensions leading to band-formation, no complete model have been reported. The first step is to confirm whether the particles will travel to the near-wall region as opposed to the channel centerline. Since, we use negatively charged particles that lead the fluid flow by the electrophoretic velocity (relative particle velocity), $\epsilon \zeta_p E_x/\mu$.

For instance, at $\Delta P_{12}/L = 0.56$ bar/m & $\Delta V_{12}/L = -100$ V/cm, the particle velocity, $U_p = 0.0091$ m/s at the channel center, while $U_c = 0.0083$ m/s. Thus, the particles lead the fluid velocity, where the ratio of magnitude of particle relative velocity to the channel center line velocity is 0.10, rounded to the second decimal place. Moreover, $R_c = 0.16$ based on channel center line velocity of combined Poiseuille flow and EOF; the ratio of magnitude of the wall effects and inertial effects from Oseen like inertial regions is $2.50 (R_c^{-1/2})$, thus, both effects are comparable [6].

Figure 5: (a) The particle movement towards the wall in response to slip-shear lift forces. (b) Poiseuille flow, $\Delta P_{12}/L = 0.34$ bar/m, and (c) particle crowding in combined Poiseuille flow and EOF as $\Delta V_{12}/L = -28$ V/cm is applied [5].

Hogg's analysis solved for lateral migration of particles in Poiseuille flow for R_c of order unity, where both wall effects and far field effects were important. For denser non-neutrally buoyant particles in downward Poiseuille flow in vertical channels, he also observed that the particle migration velocity (and, hence the lateral force) reaches a maximum at ~ 0.15 the depth of the channel due to wall effects. For combined Poiseuille and opposing EOF, negatively charged neutrally buoyant particles lead the flow due to electrophoresis and migrate to the wall (Figure 5) as observed experimentally here.

Hogg introduced the effect of buoyancy using the normalized parameter B , ratio of Stokes' settling velocity ($V_b = \frac{2}{9} a^2 \Delta \rho g/\mu$) to the channel center line velocity (U_c). The equation for particle motion with no acceleration is given by equation 4; while for the normalized equation 5, σ , hydrodynamic stress on the particle, is normalized by $\mu U_c/a$ and area is normalized by a^2 , and $\hat{b}$ is the unit vector in direction of body force:

$$\int \sigma \cdot \hat{n} dS = -6\pi\mu a V_b \hat{b} \quad (4)$$

$$\int \sigma^* \cdot \hat{n} dS^* = -6\pi B \hat{b} \quad (5)$$

Using particle Reynolds number $R_p = \rho U_c a^2/\mu H$ and channel Reynolds number as $R_c = \rho U_c H/\mu$, he found that the lift forces in a vertical channel scale as $O(BR_p^{1/2})$ given $1 \gg R_c B^2$ and $1 \gg \alpha^2/B$, where $\alpha = a/H$.

If Hogg's analysis can be extended to the effects of slip-shear due to electrophoretic motion, the parameter B_e would be the ratio of particle electrophoretic velocity (V_e) to the channel center line

velocity. Under the thin EDL assumption (here, $\lambda/a \sim 10^{-2}$) for electrophoretic force on the particle [17], the equation for particle motion is given by:

$$\int \sigma \cdot \hat{n} dS = -6\pi\mu a V_e \hat{b} \quad (6)$$

$$\int \sigma^* \cdot \hat{n} dS^* = -6\pi B_e \hat{b} \quad (7)$$

Here, equation 6 was normalized as equation 5. For $\Delta P_{12}/L = 0.56$ bar/m and $\Delta V_{12}/L = -100$ V/cm, channel Reynolds number is 0.16, while the parameters $R_e B_e^2 = 0.0015$, and $\alpha^2/B_e = 0.0006$ satisfy the regime conditions solved by Hogg: $1 \gg R_e B_e^2$ and $1 \gg \alpha^2/B_e$.

Hogg's analysis in this regime considered the gravitational body force. If the analysis can be used for the electromagnetic body forces, the lateral lift force scales as $O(B_e R_p^{1/2})$, thus, the lift forces induced by electrophoretic motion of the particles scales linearly with B_e (the ratio of particle electrophoretic velocity, $V_e \propto \Delta V_{12}/L$, to the channel center line velocity), whose magnitude increases as potential gradient is increased.

The higher lift forces at higher potential gradient should result in a higher particle fraction at a given x-location. This increase in particle fraction is supported by the observation that the location of banding moves upstream as the applied potential difference was increased (Fig. 6a, 6b), suggesting that banding likely depends on particle fraction as well, and consequently particle aggregation near the wall may be a precursor, if not a prerequisite, to particle assembly into stream-wise bands.

Figure 6: (a) Bands move upstream at higher $|\Delta V_{12}/L|$. At $x \approx 0$ cm, $\Delta P_{12}/L = 0.73$ bar/m, no bands were observed at $\Delta V_{12}/L = -47.3$ V/cm compared to (b) $\Delta V_{12}/L = -94.6$ V/cm. However, bands were observed downstream for $\Delta V_{12}/L = -47.3$ V/cm. Image area: $203 \mu\text{m} \times 203 \mu\text{m}$.

SUMMARY AND CONCLUSION

Previous experimental studies report that particles from a dilute colloidal solution self-assemble into stream-wise bands in a continuous flow system with opposed Poiseuille and EO flow. Here, we show that the fluid velocity has an inflection point near the wall, which likely indicates the presence of flow instabilities. For particle aggregation, our analysis suggest that the particles could migrate towards the walls due to inertial-type lift forces due to an electrophoretic "slip" velocity. When the EO flow opposes the Poiseuille flow, the negatively charged particles leads the fluid flow due to electrophoresis, and a particle leading the fluid flow migrates towards the wall, by using previously reported analysis methods. However, for an accurate description of particle motion, the analysis of Hogg, who considered particle-fluid slip due to buoyancy mismatch, will need to be extended to particle-fluid slip due to electromagnetic forces.

ACKNOWLEDGEMENTS

We acknowledge the support from the US Army Research Office through grant number W911NF-16-0278. We also thank the staff of Nanotech West, The Ohio State University, for helping with device fabrication and characterization.

REFERENCES

- [1] O. Gang, "Nanoparticle assembly: from fundamentals to applications: concluding remarks," *Faraday Discussions*, 186 (2016), pp. 529-537.
- [2] G. Segré and A. Silberberg, "Radial Particle Displacements in Poiseuille Flow of Suspensions," *Nature*, 189 (1961), pp. 209-210.
- [3] R. C. Jeffrey and J. R. A. Pearson, "Particle motion in laminar vertical tube flow," *Journal of Fluid Mechanics*, 22 (1965), p. 721.
- [4] F. P. Bretherton, "The motion of rigid particles in a shear flow at low Reynolds number," *Journal of Fluid Mechanics*, 14 (1962), p. 284.
- [5] J. Zhang, S. Yan, D. Yuan, G. Alici, N. T. Nguyen, M. Ebrahimi Warkiani, *et al.*, "Fundamentals and applications of inertial microfluidics: a review," *Lab on a chip*, 16 (2016), pp. 10-34.
- [6] A. J. Hogg, "The inertial migration of non-neutrally buoyant spherical particles in two-dimensional shear flows," *Journal of Fluid Mechanics*, 272 (1994), p. 285.
- [7] Y. W. Kim and J. Y. Yoo, "Axisymmetric flow focusing of particles in a single microchannel," *Lab on a chip*, 9 (2009), pp. 1043-5.
- [8] P. G. Saffman, "The lift on a small sphere in a slow shear flow," *Journal of Fluid Mechanics*, 22 (1965), p. 385.
- [9] R. Mei, "An approximate expression for the shear lift force on a spherical particle at finite Reynolds number," *International Journal of Multiphase Flow*, 18 (1992), pp. 145-147.
- [10] D. A. Drew, "The lift force on a small sphere in the presence of a wall," *Chemical Engineering Science*, 43 (1988), pp. 769-773.
- [11] J. B. McLaughlin, "The lift on a small sphere in wall-bounded linear shear flows," *Journal of Fluid Mechanics*, 246 (1993), p. 249.
- [12] B. P. Ho and L. G. Leal, "Inertial migration of rigid spheres in two-dimensional unidirectional flows," *Journal of Fluid Mechanics*, 65 (1974), p. 365.
- [13] D. Yuan, C. Pan, J. Zhang, S. Yan, Q. Zhao, G. Alici, *et al.*, "Tunable Particle Focusing in a Straight Channel with Symmetric Semicircle Obstacle Arrays Using Electrophoresis-Modified Inertial Effects," *Micromachines*, 7 (2016), p. 195.
- [14] N. Cevheri and M. Yoda, "Electrokinetically driven reversible banding of colloidal particles near the wall," *Lab on a chip*, 14 (2014), pp. 1391-4.
- [15] Hua-Shu Dou, "Viscous flow instability of inflectional velocity profile", Presented in Fourth International Conference on Fluid Mechanics, (2004).
- [16] P. Dutta and A. Beskok, "Analytical solution of combined electroosmotic/pressure driven flows in two-dimensional straight channels: finite Debye layer effects," *Analytical chemistry*, 73 (2001), pp. 1979-86.
- [17] R. F. Probstein, *Physicochemical hydrodynamics : an introduction*. New York: Wiley, 1994.

CONTACT

*Shaurya Prakash, Email ID: prakash.31@osu.edu