DYNAMICS OF SUSPENDED COLLOIDAL PARTICLES NEAR A WALL

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OUTLINE

- The problem and its motivation
- The (evanescent-wave PTV) technique
  - Near-wall particle distributions and displacements
- Poiseuille flows
- Electrokinetically driven flows
- Summary
**A PARTICLE NEAR A WALL**

- What are the dynamics of a particle suspended in a flowing fluid near a solid wall?
  - How is the particle velocity related to the fluid velocity?

- A few complications:
  - When $a < h < 1 \mu m$: Brownian effects significant
  - When $h \approx O(1 \mu m)$: surface forces may be significant

$h > a$, but $h = O(a)$
Another complication

- Wall, particle surfaces charged
- Fluid conducting with mobile ions: electric double layers (EDL) on particle, wall surfaces
Microfluidics: flows with length scales of $O(1-10^2 \mu m)$

- Faster diffusion: $\tau_D \propto (\delta_D)^2$
- Large surface areas, small volumes $\Rightarrow$ surface forces significant

Characterize transport within $O(1 \mu m)$ of the wall

- Track fluorescent particles ($a = 50 \text{ nm} - 500 \text{ nm}$) illuminated by evanescent waves created at solid-fluid (refractive index) interface by total internal reflection of light
- $I(z) = I_0 \exp \{-z/z_p\}$
- $z_p = f(\lambda, \theta, n_1, n_2) \approx 100 \text{ nm}$ for glass-water interface
- Image $z \leq 4z_p$ based on imaging system noise floor
Brownian effects: \( Pe = O(1-10^2) \)
- Particle “mismatch”
- Asymmetric diffusion \( \Rightarrow \) overestimation of velocities
  *Sadr et al. 07*

Nonuniform particle distribution
- EDL interactions, vd Waals effects
- Measure particle displacements and distributions

Nonuniform illumination
- Range of particle image sizes and intensities
MULTILAYER PTV

- Exploit nonuniform illumination to determine particle distributions and velocity profiles for \( z < 400 \) nm
  - Assume particle image intensity \( I_p(z) \) has exponential decay with length scale \( z_p \)
  - Particle edge distance from wall \( h = z_p \ln\left\{\frac{I_p^0}{I_p}\right\} \)

- Steady-state particle distribution
  - Variation in particle images (\( \sigma \) of \( I_p^0 \) = 9\%), average over ensemble of \( O(10^5) \) particles

- Near-wall (particle and fluid) velocity profile
  - “Bin” particles into different layers based on \( h \), then determine velocities parallel to wall at different \( z \) using particle tracking
POISEUILLE FLOWS
**SLIP**

- **Is the no-slip boundary condition valid for \( z < 1 \, \mu m \)?**
  - Navier partial-slip BC:
    \[
    u_w = b \frac{\partial u}{\partial z} \bigg|_{z=0}
    \]
    \( b = \) slip length
  - Studies report \( b \sim O(10–100 \, \text{nm}) \)
  - for Newtonian liquids flowing over (mainly) nonwetting surfaces
    - Local methods: slip lengths extrapolated from near-wall velocity data
    - Wide variation in measured slip lengths
    - Nonzero \( b \) attributed to surface wettability, (usually higher) shear rates, dissociated or gaseous layer (“nanobubbles”), change in fluid properties, …
Study slip in fully-developed Poiseuille flow through $H = 33 \, \mu m$ deep channel: $Re_H = 0.03–0.12$

- Compare with exact solution

$$u(z) = \frac{H^2}{2\mu} \frac{\Delta p}{L} \left[ \frac{z}{H} \left( 1 - \frac{z}{H} \right) \right]$$

channel $AR = 16$

- Linear velocity profile for $z < 400 \, nm$: shear rate $\dot{\gamma} \approx 500–2300 \, s^{-1}$

- Hydrophobic, hydrophilic channels etched on same wafer

- Hydrophilic channels: untreated fused-silica walls with rms surface roughness $\sim 3 \, nm \Rightarrow$ contact angle $28 \pm 4^\circ$

- Hydrophobic channels coated with $\sim 2 \, nm$ thick monolayer of OTS $\Rightarrow$ contact angle $100 \pm 4^\circ$
**EXPERIMENTAL DETAILS**

- **Fluids**
  - Monovalent electrolyte solutions: different salt concentrations (2 and 10 mM), pH (~6.4 and ~7.7)
  - Particles: \( a \approx 50 \text{ nm} \) fluorescent polystyrene; \( \phi \approx 20 \text{ ppm} \)
  - Fluid with particles degassed for each experiment

- **Averaged “background” images** (over 1200 images)

![Images showing hydrophilic and hydrophobic surfaces with labeled dimensions: 154 µm and 24 µm]
- **Nonuniform distribution**
  - Few particles at $h/a < 1$
  - Similar results for hydrophobic channel
- **“Bin” particles into 3 (sub)layers (particle center at $z = h + a$)**
  - $1 \leq z_I / a \leq 3$
  - $3 \leq z_{II} / a \leq 5$
  - $5 \leq z_{III} / a \leq 7$
- **Use number density to determine avg. $z$ for each layer**
  \[ \bar{z}_I = \frac{\int_I c(z) z \, dz}{\int_I c(z) \, dz} \]
VELOCITY RESULTS

- Hydrophilic channel (10 mM, pH7.7)
  - Average over 5 expts.
  - Error bars 95% confidence intervals

- Linear curve-fits to data account for uncertainties in $u$ and $z$
  - Shear rates within 4.5% of exact solution for hydrophilic case and 5% for hydrophobic cases (on average)

\[
\begin{array}{|c|c|}
\hline
\gamma & u \text{ [mm/s]} \\
\hline
491 & 983, 1410, 1720, 2030, 2260 \text{ s}^{-1} \\
\hline
\end{array}
\]
In all but one out of 48 cases, \( b \) < experimental uncertainty

- In that case, \( b = 23 \pm 22 \) nm
- Hydrophobic: \( b \) “more organized”; increases with shear rate

\[ \text{Li & Yoda 10} \]
ELECTROKINETICALLY DRIVEN FLOWS
In addition to Brownian effects, charged particle and wall, conducting fluid with mobile ions

- For electrokinetically driven flows, external electric field parallel to wall
ELECTROKINETIC EFFECTS

- Electroosmosis: counterions in wall EDL driven by $E$
  - Fluid away from walls driven by motion of fluid in EDL $\Rightarrow$ uniform flow outside EDL
- Electrophoresis: charged particle driven by $E$
- Particle transported by electroosmotic flow, subject to electrophoresis
  - Measured particle speed
    $u_P = u_{EO} - u_{EP}$

$$E$$

$u_{EO}$

$u_{EP}$
**BROWNIAN DIFFUSION**

- Do electrophoretic forces alter near-wall (Brownian) diffusion?
- **Balance thermal forces with Stokes drag**
  - In unbounded fluid, Stokes-Einstein relation \( D_\infty = \frac{kT}{6\pi \mu a} \)
  - Additional hydrodynamic drag due to wall \( \Rightarrow \) anisotropic diffusion parallel, normal to wall
  - For diffusion parallel to wall
  \[
  \frac{D_{\|}}{D_\infty} = 1 - \frac{9}{16} \left( \frac{a}{z} \right) + \frac{1}{8} \left( \frac{a}{z} \right)^3 - \frac{45}{256} \left( \frac{a}{z} \right)^4 - \frac{1}{16} \left( \frac{a}{z} \right)^5
  \]
  - For diffusion normal to wall, approximation of infinite series
  \[
  \frac{D_{\perp}}{D_\infty} = \frac{6(z/a)^2 - 10(z/a) + 4}{6(z/a)^2 - 3(z/a) - 1}
  \]
EXPERIMENTAL DETAILS

- **Four different fluorescent polystyrene tracers**
  - \( a = 110\pm12 \text{ nm}; \ \zeta_P = -60.6\pm4.3 \text{ mV} \)
  - \( a = 240\pm22 \text{ nm}; \ \zeta_P = -57.4\pm3.1 \text{ mV} \)
  - \( a = 371\pm34 \text{ nm}; \ \zeta_P = -96.2\pm2.9 \text{ mV} \)
  - \( a = 461\pm34 \text{ nm}; \ \zeta_P = -99.9\pm3.2 \text{ mV} \)
  - Tracers in monovalent electrolyte solution (1 mM, pH~9) $\Rightarrow$ Debye length scale $\lambda < 7$ nm

- **Electrokinetically driven flows**
  - \( E = 15 \text{ V/cm, 22 V/cm, and 31 V/cm} \)
  - Weak Poiseuille flow ($E = 0 \text{ V/cm}$) $\Rightarrow$ Measured $u_P < 7 \mu\text{m/s}$

- **Image pairs** (exp. 0.5 ms) spaced (within pair) by $\Delta t = 1.3 \text{ ms, 1.6 ms, 1.9 ms and 2.2 ms}$
PARTICLE DISTRIBUTIONS

- **Number density** $c$
  - Normalized particle edge distance
    \[ h = z_p \ln \left( \frac{I_p^0}{I_p} \right) \]
  - Divide $O(10^5)$ particle images into three (100 nm thick) layers
    - In each layer, determine particle displacements parallel, normal to wall by particle tracking

![Graph showing particle density distribution](image)

- **Graph**
  - $a = 110$ nm
  - $c \left[ \left(10^{16} \text{ m}^{-3}\right) \right]$ vs. $h/a$
  - Points for $0$ V/cm and $15$ V/cm
ESTIMATING DIFFUSION

- PDF of displacements parallel, normal to wall
  - Curve-fit Gaussian: extract $\sigma^2$ for each layer
  - Plot $\sigma^2$ vs. $\Delta t \Rightarrow$ slope $= 4D_{||}(\Delta t)$, $2D_{\perp}(\Delta t)$

\[ E = 0 \text{ V/cm} \]
\[ a = 110 \text{ nm} \]
\[ \text{Layer II} \]
DIFFUSION RESULTS

- Data at $E = 0$ V/cm, 15 V/cm agree and agree with theory
  - $h$-positions of $D_\parallel$, $D_\perp$ determined from particle distributions $c(h)$
- No discernible effect of external electric field on diffusion

$$\frac{D}{D_\infty}$$

Normal

Parallel

$\Delta$ ○ 0 V/cm
$\Delta$ ● 15 V/cm

$a = 110$ nm
$a = 240$ nm

APS/DFD (11/10)
Electrokinetically driven flow: $E = 0 \text{ V/cm, then 31 V/cm}$
- $E$ drives larger particles farther away from wall

$a = 110 \text{ nm}$

$a = 461 \text{ nm}$
PARTICLE DISTRIBUTIONS

- "Electrokinetic lift"
  - Dielectrophoretic-like force due to nonuniform electric field in particle-wall gap

Yariv 06

APS/DFD (11/10)
Estimate lift force assuming Boltzmann distribution

- Force on particle $F \propto a^2, E^2$: no discernible effect of $\zeta_p$
- $F = O(10^{-14} \text{ N})$ for $E = O(10 \text{ V/cm})$
SUMMARY

- Evanescent wave-based particle tracking
  - Measure particle displacements and steady-state particle distributions within $O(100 \text{ nm})$ of wall

- Poiseuille flow
  - Slip lengths of Newtonian liquids over hydrophilic and hydrophobic surfaces zero within experimental uncertainties after accounting for nonuniform tracer distributions

- Electrokinetically driven flow ($E$ parallel to wall)
  - Moderate electric fields appear to have no effect on diffusion
  - Using H-S to predict electrophoretic velocity, even within $O(a)$ of wall gives good estimate of electroosmotic flow
  - Dielectrophoretic-like force $\Rightarrow$ particles farther from wall: force scales as $a^2, E^2$
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