DYNAMICS OF SUSPENDED COLLOIDAL PARTICLES NEAR A WALL

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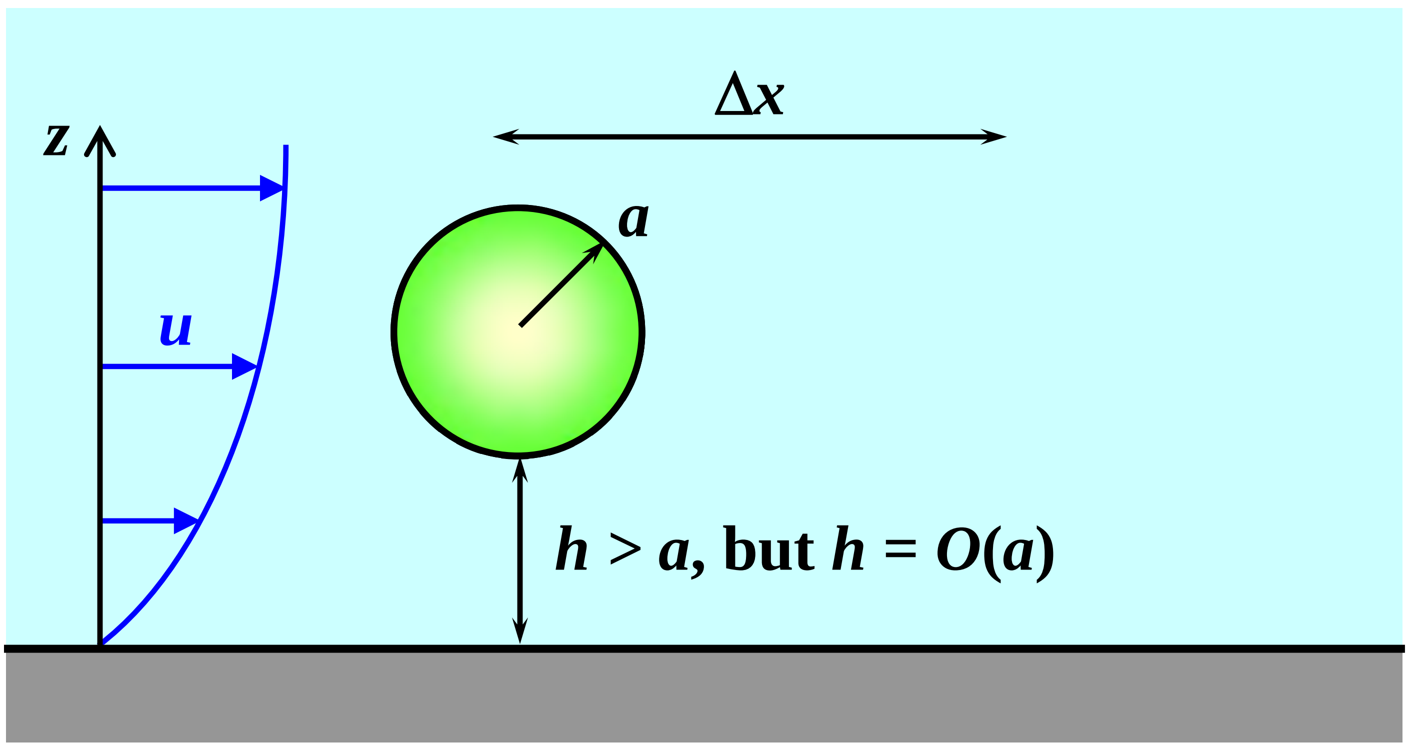
OUTLINE

- **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

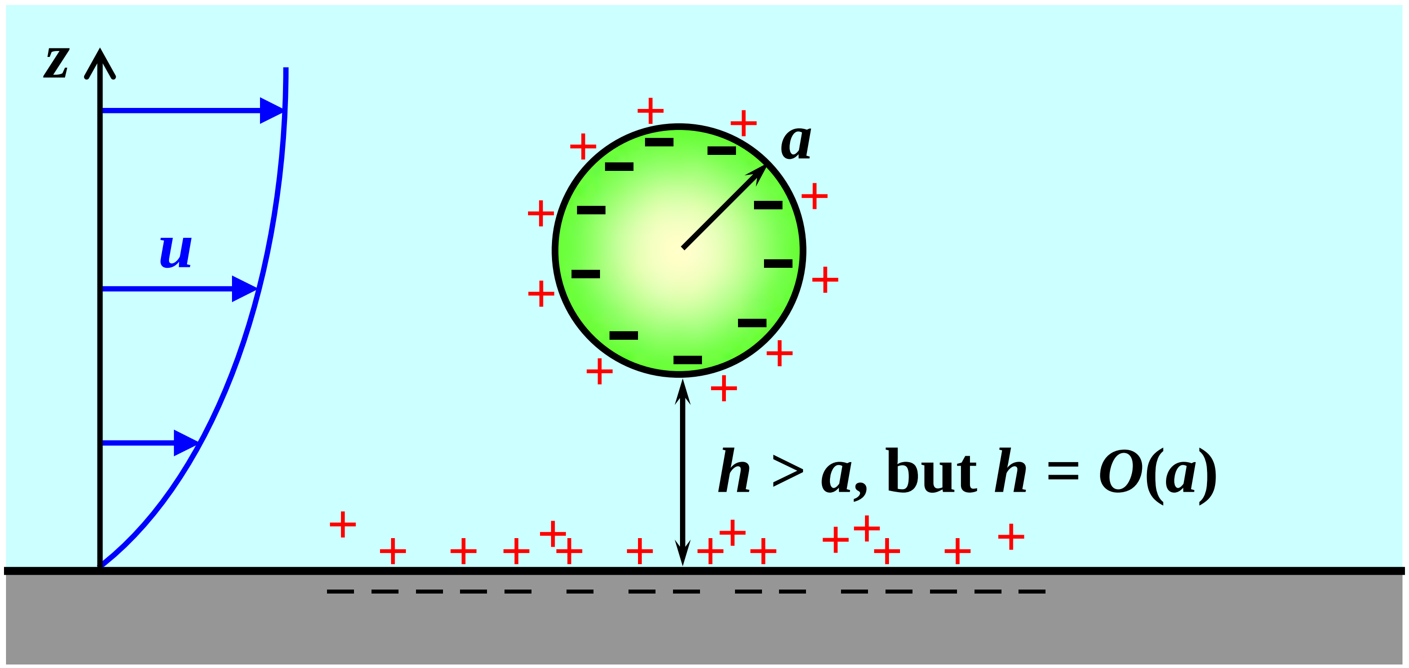
- **What are the dynamics of a particle suspended in a flowing fluid near a solid wall?**
  - How is the particle velocity related to the fluid velocity?

- **A few complications**
  - $a \approx 1$ μm: Brownian effects significant
  - $h = O(1$ μm$)$: surface forces may be significant



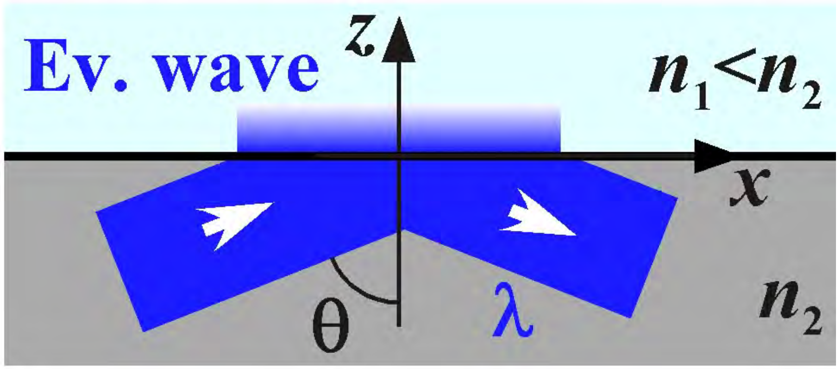
A PARTICLE NEAR A WALL

- **Another complication**
  - Wall, particle surfaces charged
  - Fluid conducting with mobile ions: electric double layers (EDL) on particle, wall surfaces

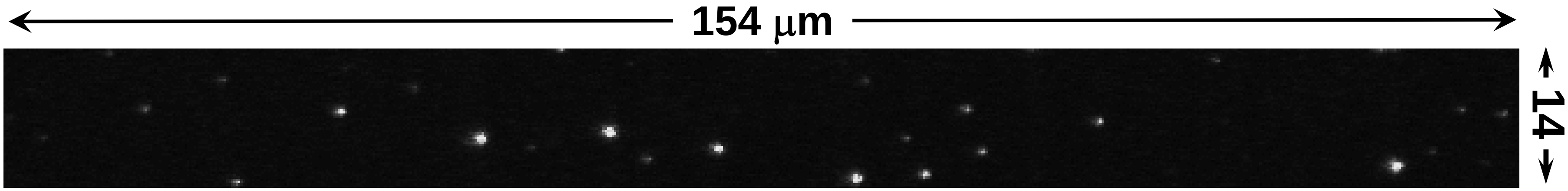


INTERFACIAL TRANSPORT

- **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 ⇒ surface forces significant
- **Characterize transport within $O(1\ \mu m)$ of the wall**
  - Track fluorescent particles (a = 50 nm–500 nm) illuminated by evanescent waves created at solid-fluid (refractive index) interface by total internal reflection of light
  - $I(z) = I_o \exp\{-z/z_p\}$
  - $z_p = f(\lambda, \theta, n_1, n_2) \approx 100$ nm for glass-water interface
  - Image $z \leq 4z_p$ based on imaging system noise floor



EVANESCENT WAVE PTV

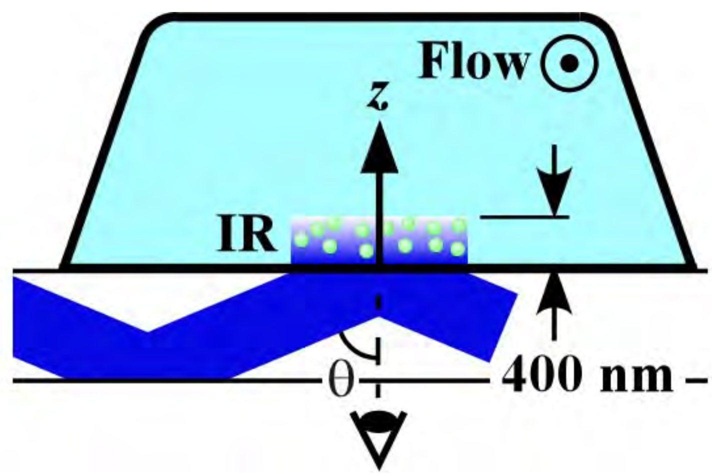


$a \approx$ 50 nm; Δt = 6 ms (exp. 1 ms)

- **Brownian effects: $Pe = O(1\text{–}10^2)$**
  - Particle "mismatch"
  - Asymmetric diffusion ⇒ overestimation of velocities

  Sadr *et al*. 07

Channel

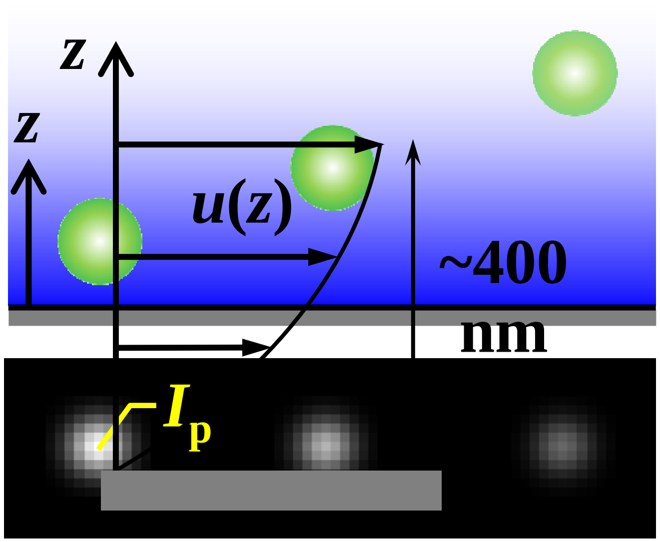


- **Nonuniform particle distribution**
  - EDL interactions, vd Waals effects
  - Measure particle displacements <u>and</u> distributions
- **Nonuniform illumination**
  - Range of particle image sizes and intensities

MULTILAYER PTV

- **Exploit nonuniform illumination to determine particle distributions <u>and</u> velocity profiles for z < 400 nm**
  - Assume particle image intensity $I_p(z)$ has exponential decay with length scale z_p **Li & Yoda 08**
  - Particle edge distance from wall

$$h = z_p \ln\{I_p^0 / I_p\}$$

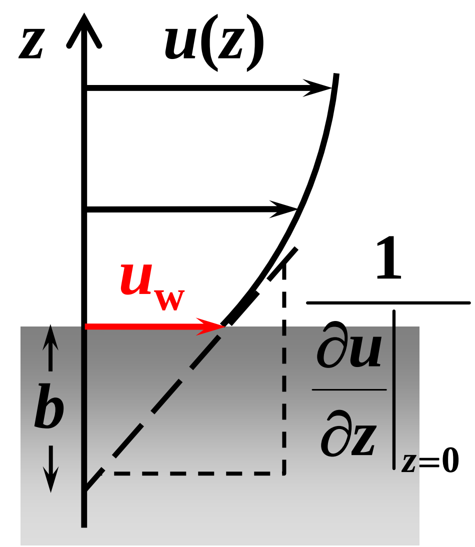


- **Steady-state particle distribution**
  - Variation in particle images (σ of I_p^0 = 9%), average over ensemble of $O(10^5)$ particles
- **Near-wall (particle and fluid) velocity profile**
  - "Bin" particles into different layers based on h, then determine velocities parallel to wall at different z using particle tracking

POISEUILLE FLOWS

SLIP

- **Is the no-slip boundary condition valid for z < 1 μm?**
  - Navier partial-slip BC: $$u_\mathrm{w} = b\left.\frac{\partial u}{\partial z}\right|_{z=0}$$
    b = slip length
- **Studies report b ~ O(10–100 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, …

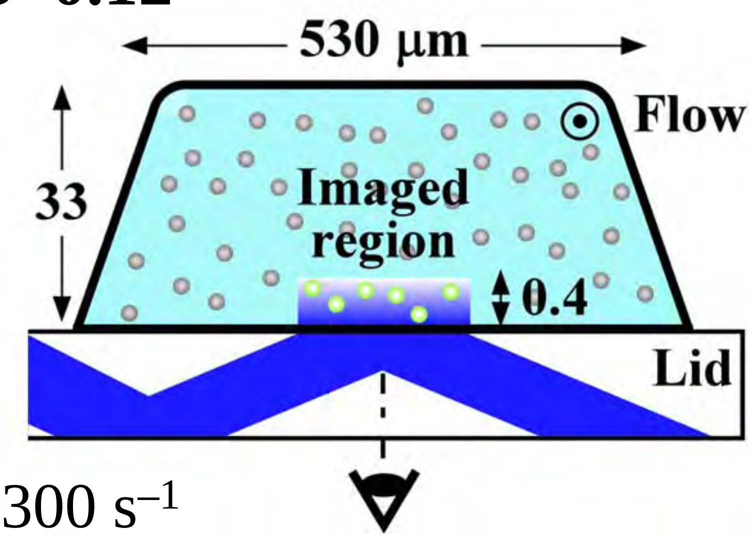


POISEUILLE FLOW EXPTS.

- **Study slip in fully-developed Poiseuille flow through H = 33 μm deep channel: Re_H = 0.03–0.12**
  - Compare with exact solution

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

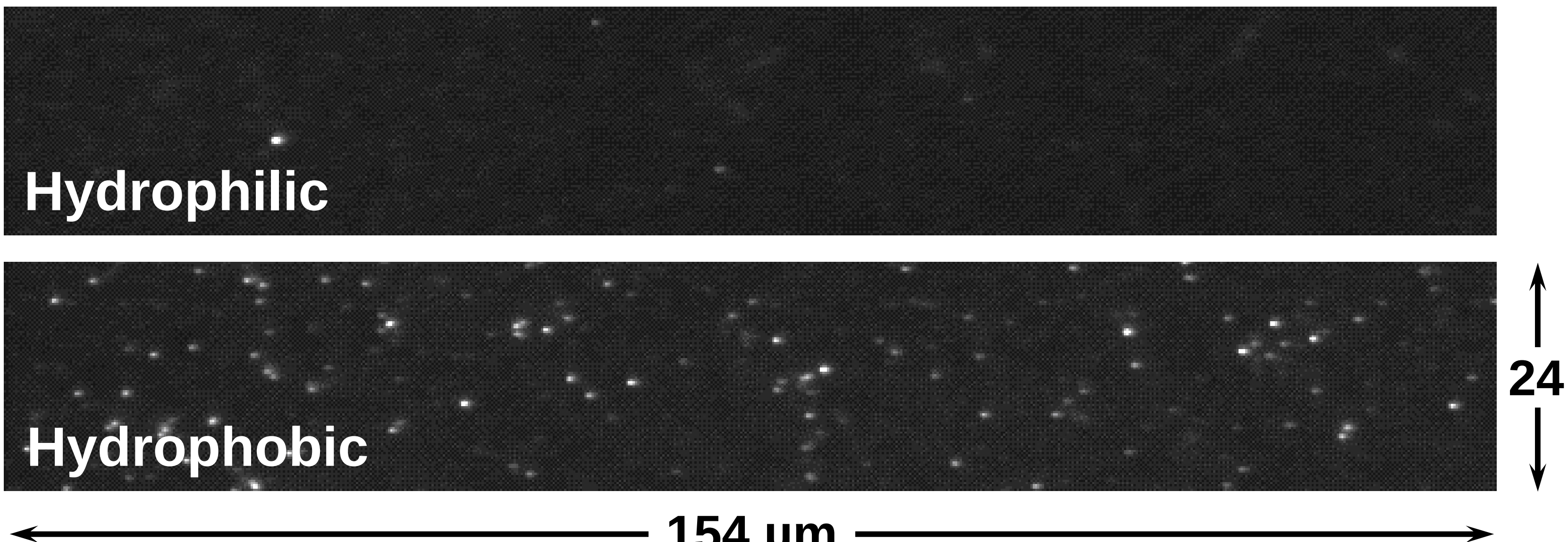
channel AR = 16



  - 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 ~3 nm ⇒ contact angle 28 ± 4°
  - Hydrophobic channels coated with ~2 nm thick monolayer of OTS ⇒ contact angle 100 ± 4°

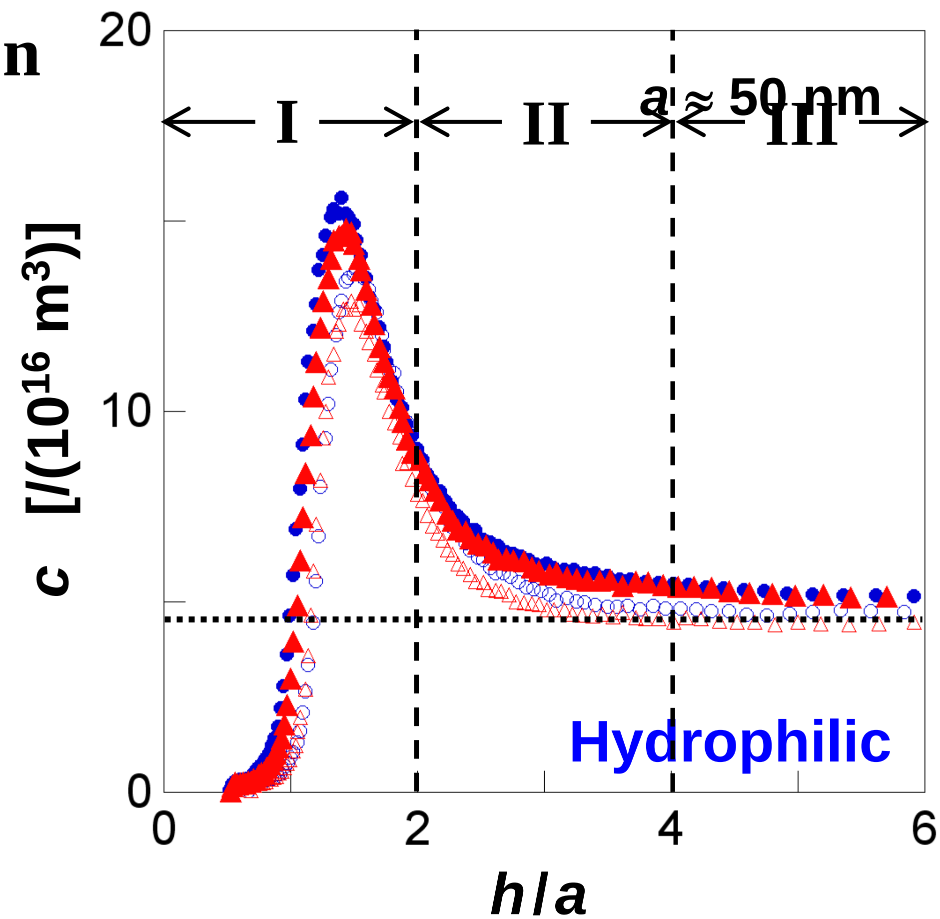
EXPERIMENTAL DETAILS

- **Fluids**
  - Monovalent electrolyte solutions: different salt concentrations (2 and 10 mM), pH (~6.4 and ~7.7)
  - Particles: $a \approx 50$ nm fluorescent polystyrene; $\phi \approx 20$ ppm
  - Fluid with particles degassed for each experiment
- **Averaged "background" images** (over 1200 images)



PARTICLE DISTRIBUTIONS

- **Nonuniform distribution**
  - Few particles at $h/a < 1$
  - Similar results for hydrophobic channel
- **"Bin" particles into 3 (sub)layers (particle center at $z = h + a$)**
  - $1 \le z_{\mathrm{I}} / a \le 3$
  - $3 \le z_{\mathrm{II}} / a \le 5$
  - $5 \le z_{\mathrm{III}} / a \le 7$

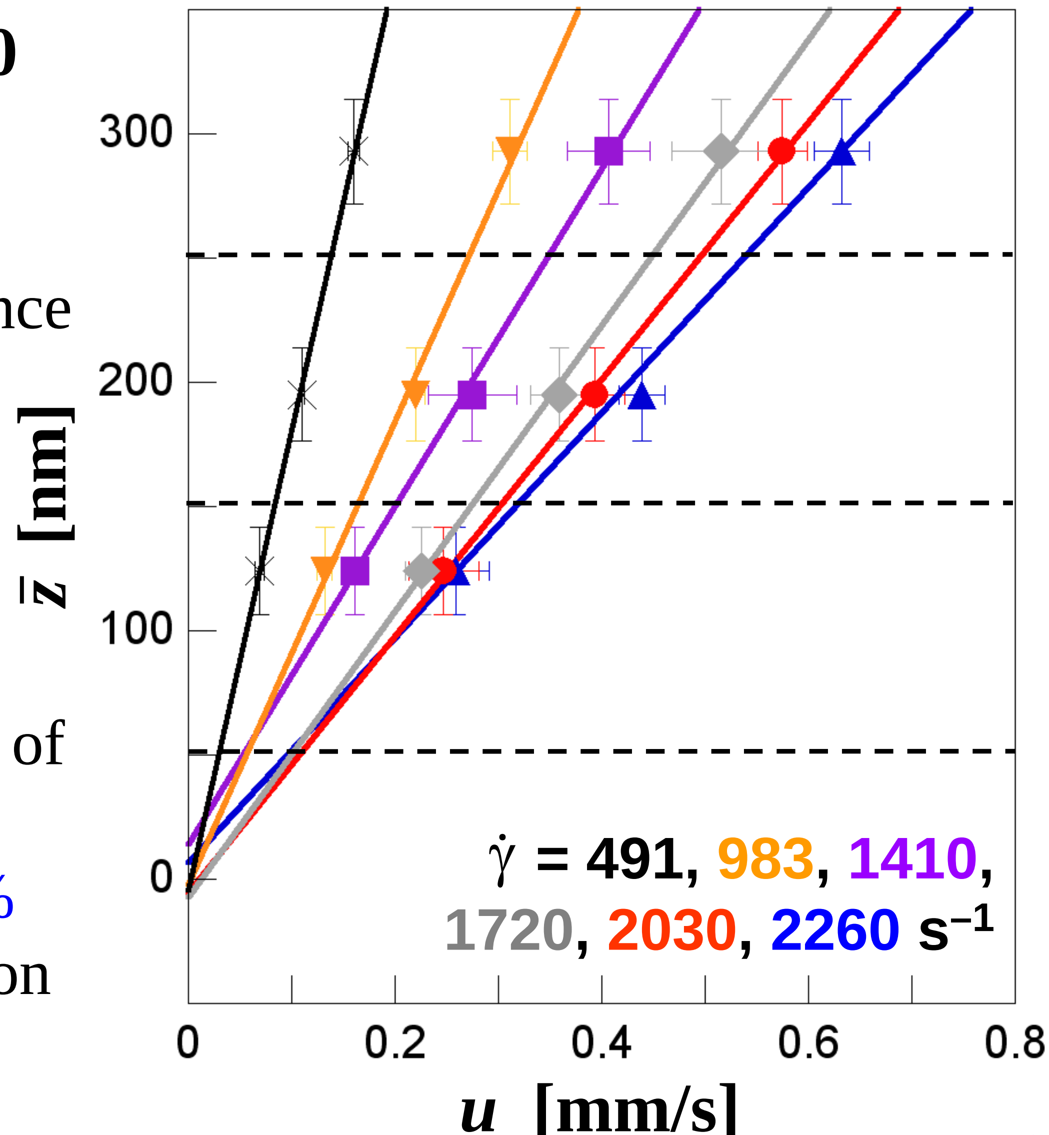


- **Use number density to determine avg. z for each layer**

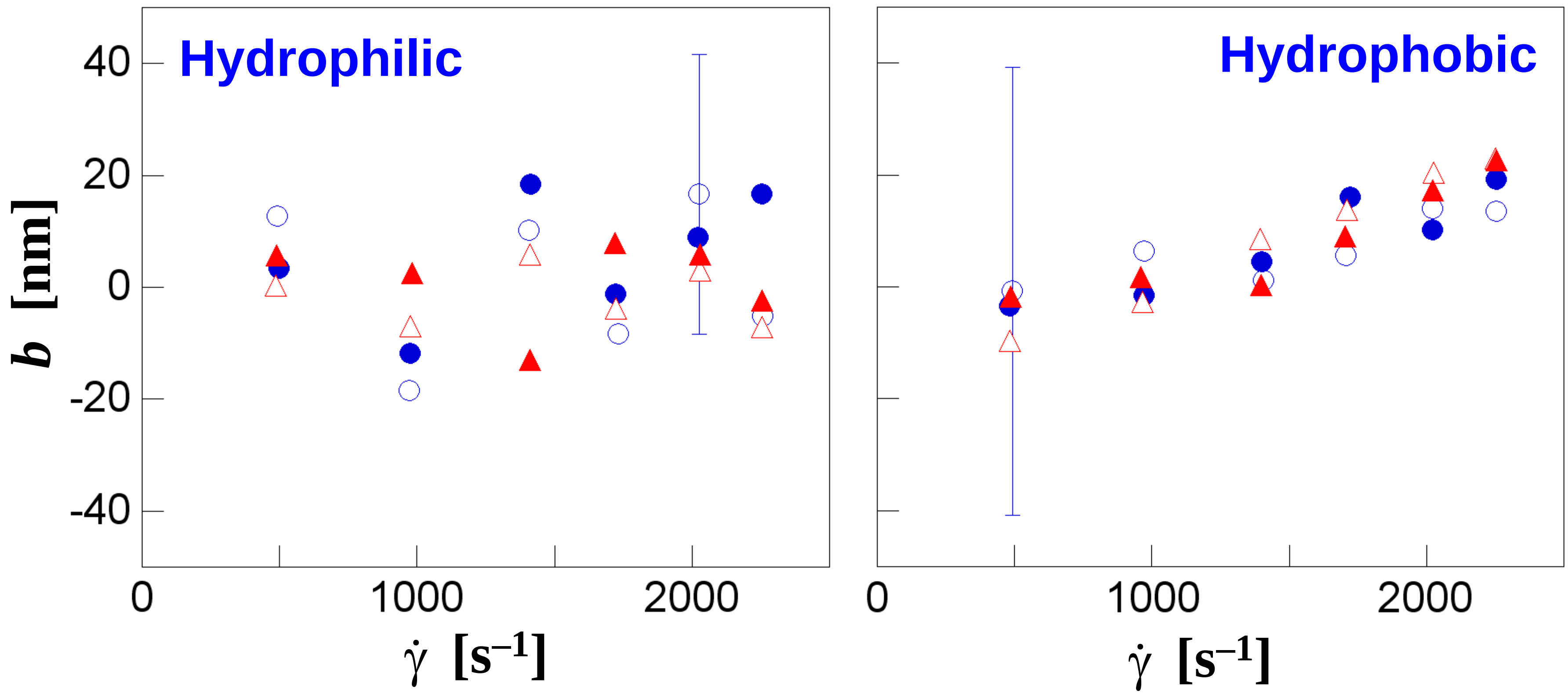
$$\bar{z}_{\mathrm{I}} = \int_{\mathrm{I}} c(z)\, z\, dz \Big/ \int_{\mathrm{I}} c(z)\, dz$$

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* <u>and</u> *z***
  - Shear rates within 4.5% of exact solution for hydrophilic case and 5% for hydrophobic cases (on average)



SLIP LENGTHS



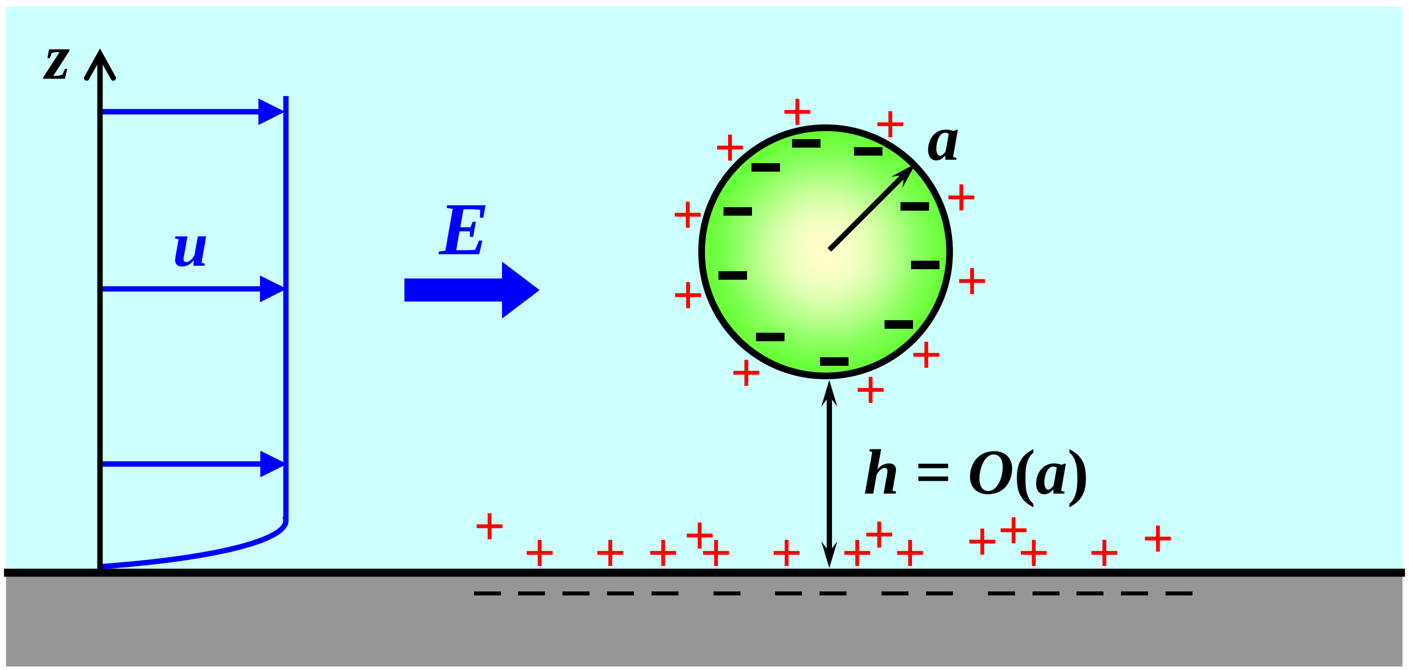
- **In all but one out of 48 cases, *b* < experimental uncertainty**
  - In that case, $b = 23 \pm 22$ nm
  - Hydrophobic: *b* "more organized"; increases with shear rate

Li & Yoda 10

ELECTROKINETICALLY DRIVEN FLOWS

A PARTICLE NEAR A WALL

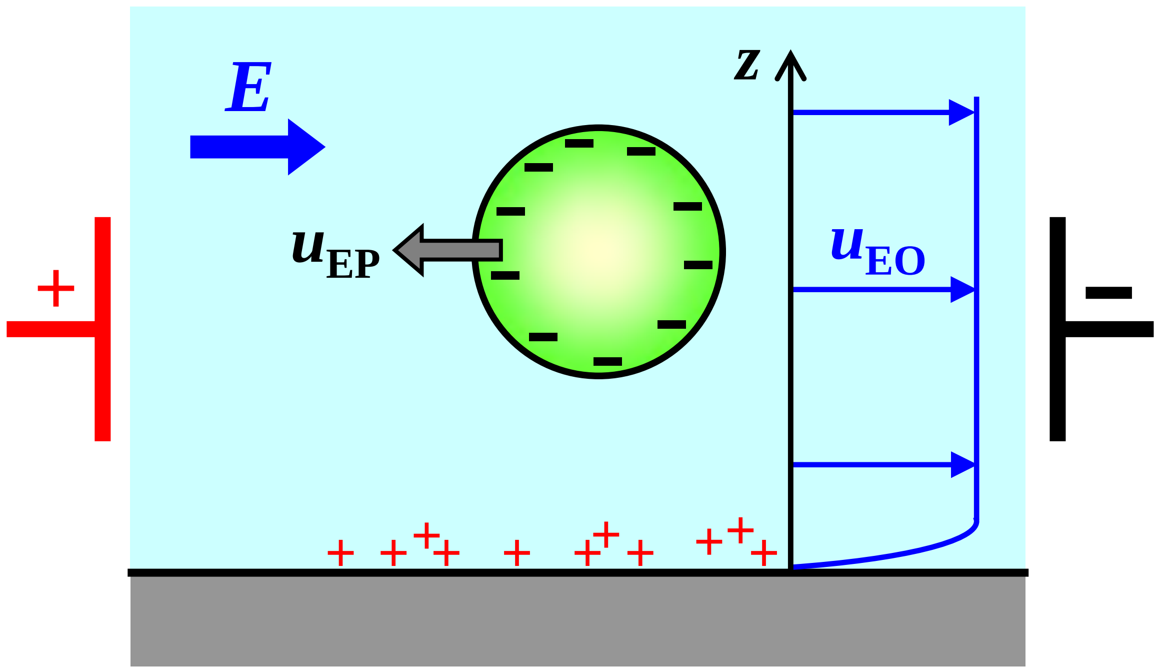
- **In addition to Brownian effects, charged particle and wall, conducting fluid with mobile ions**
  - For electrokinetically driven flows, external electric field parallel to wall



ELECTROKINETIC EFFECTS

- **Electroosmosis: counterions in wall EDL driven by *E***
  - Fluid away from walls driven by motion of fluid in EDL ⇒ uniform flow outside EDL
- **Electrophoresis: charged particle driven by *E***
- **Particle transported by electroosmotic flow, subject to electrophoresis**
  - Measured particle speed

$$u_{\mathrm{P}} = u_{\mathrm{EO}} - u_{\mathrm{EP}}$$



BROWNIAN DIFFUSION

- **Do electrophoretic forces alter near-wall (Brownian) diffusion?**
- **Balance thermal forces with Stokes drag**
  - In unbounded fluid, Stokes-Einstein relation $D_\infty = \dfrac{kT}{6\pi\mu a}$
  - Additional hydrodynamic drag due to wall $\Rightarrow$ anisotropic diffusion parallel, normal to wall
  - For diffusion parallel to wall **Faxén 22**

$$\frac{D_{\parallel}}{D_\infty} = 1 - \frac{9}{16}\left(\frac{a}{z}\right) + \frac{1}{8}\left(\frac{a}{z}\right)^3 - \frac{45}{256}\left(\frac{a}{z}\right)^4 - \frac{1}{16}\left(\frac{a}{z}\right)^5$$

  - For diffusion normal to wall, approximation of infinite series

Brenner 61; Bevan & Prieve 00

$$\frac{D_{\perp}}{D_\infty} = \frac{6(z/a)^2 - 10(z/a) + 4}{6(z/a)^2 - 3(z/a) - 1}$$

EXPERIMENTAL DETAILS

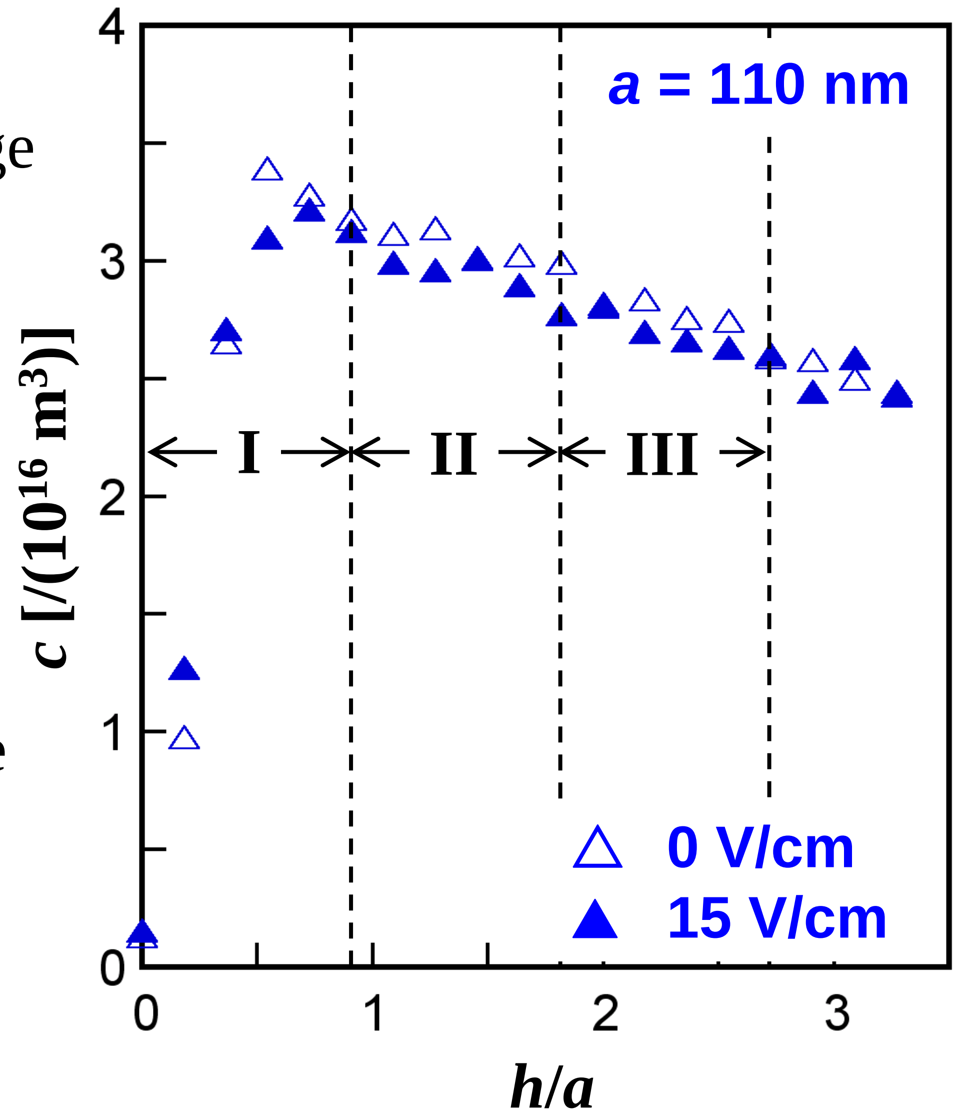
- **Four different fluorescent polystyrene tracers**
  - a = 110±12 nm; particle zeta-potential ζ_P = –60.6±4.3 mV
  - a = 240±22 nm; ζ_P = –57.4±3.1 mV
  - a = 371±34 nm; ζ_P = –96.2±2.9 mV
  - a = 461±34 nm; ζ_P = –99.9±3.2 mV
  - Tracers in monovalent electrolyte solution (1 mM, pH~9) ⇒ Debye length scale λ < 7 nm
- **Electrokinetically driven flows**
  - E = 15 V/cm, 22 V/cm, and 31 V/cm
  - Weak Poiseuille flow (E = 0 V/cm) ⇒ Measured u_P < 7 μm/s
- **Image pairs (exp. 0.5 ms) spaced (within pair) by Δ*t* = 1.3 ms, 1.6 ms, 1.9 ms and 2.2 ms**

PARTICLE DISTRIBUTIONS

- **Number density *c***
  - Normalized particle edge distance

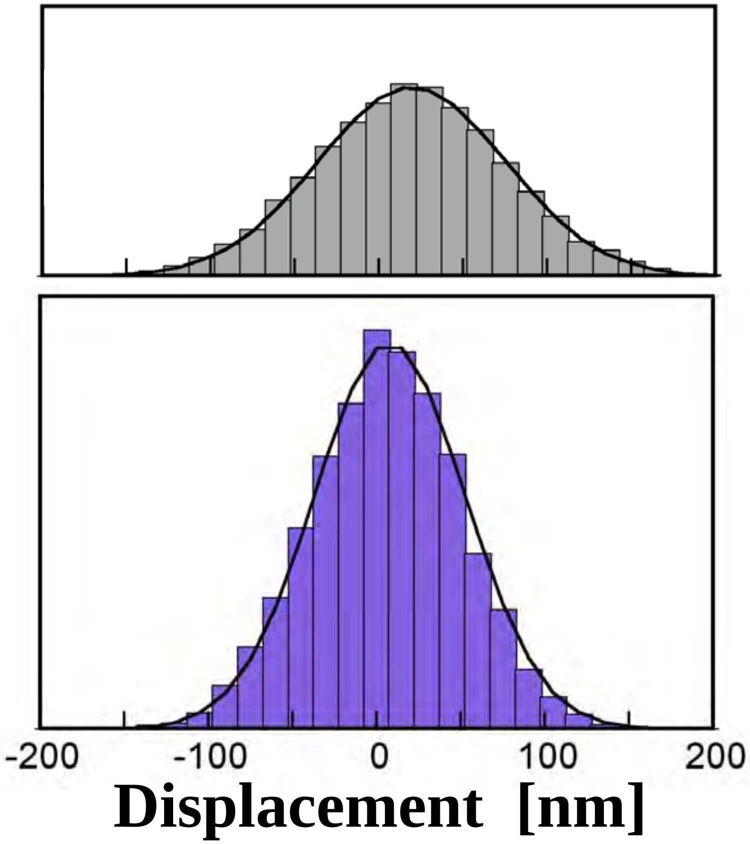
$$\frac{h}{a} = \frac{z_p}{a} \ln\left\{\frac{I_p^0}{I_p}\right\}$$

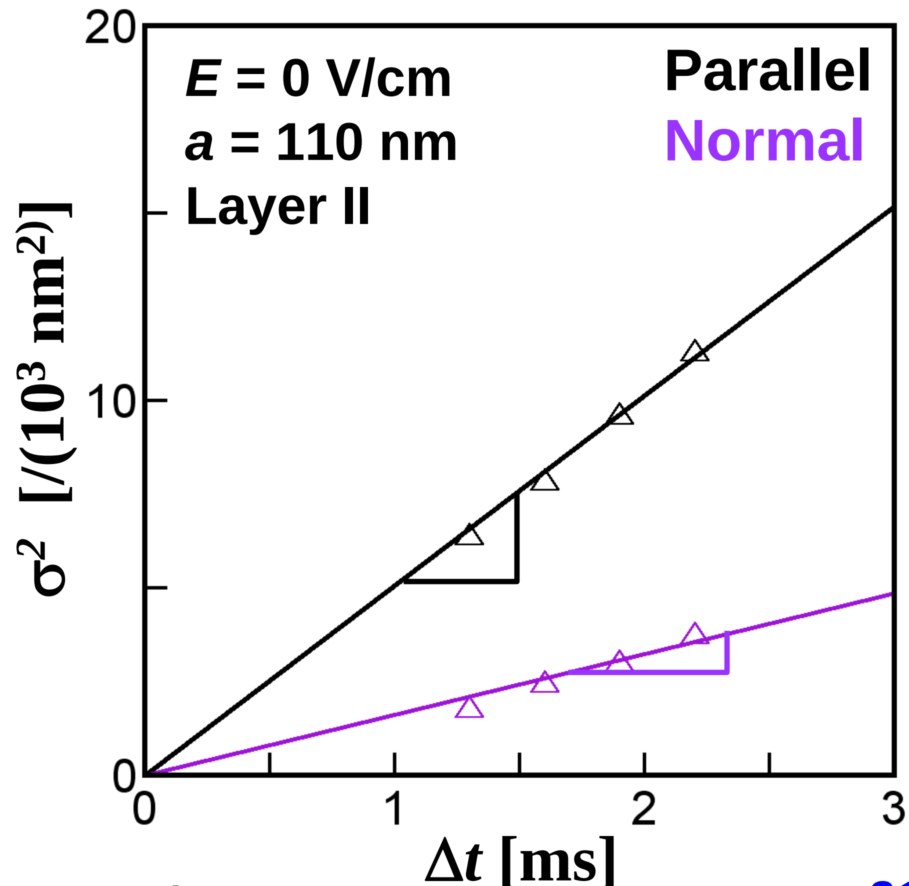
- **Divide $O(10^5)$ particle images into three (100 nm thick) layers**
  - In each layer, determine particle displacements parallel, normal to wall by particle tracking



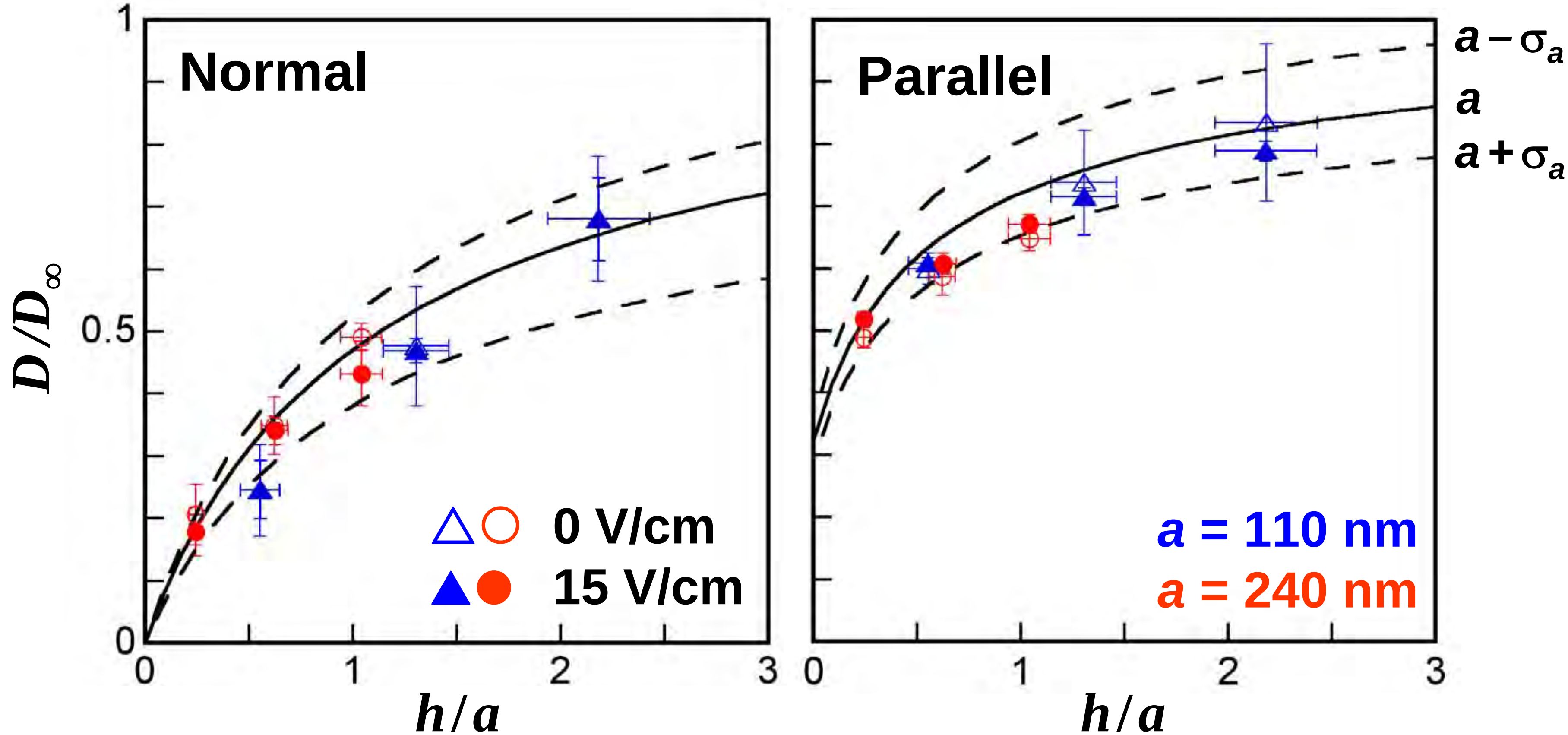
ESTIMATING DIFFUSION

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





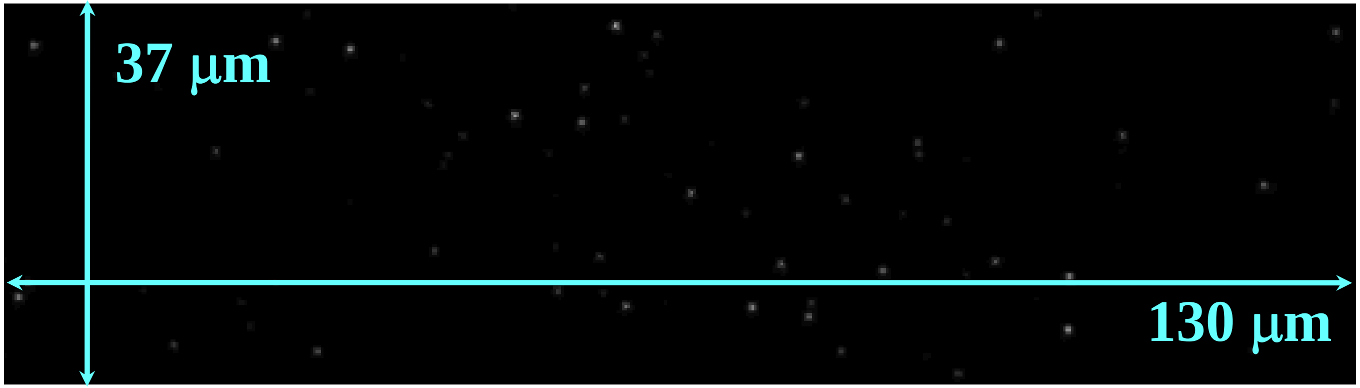
DIFFUSION RESULTS



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

FLOW VISUALIZATION

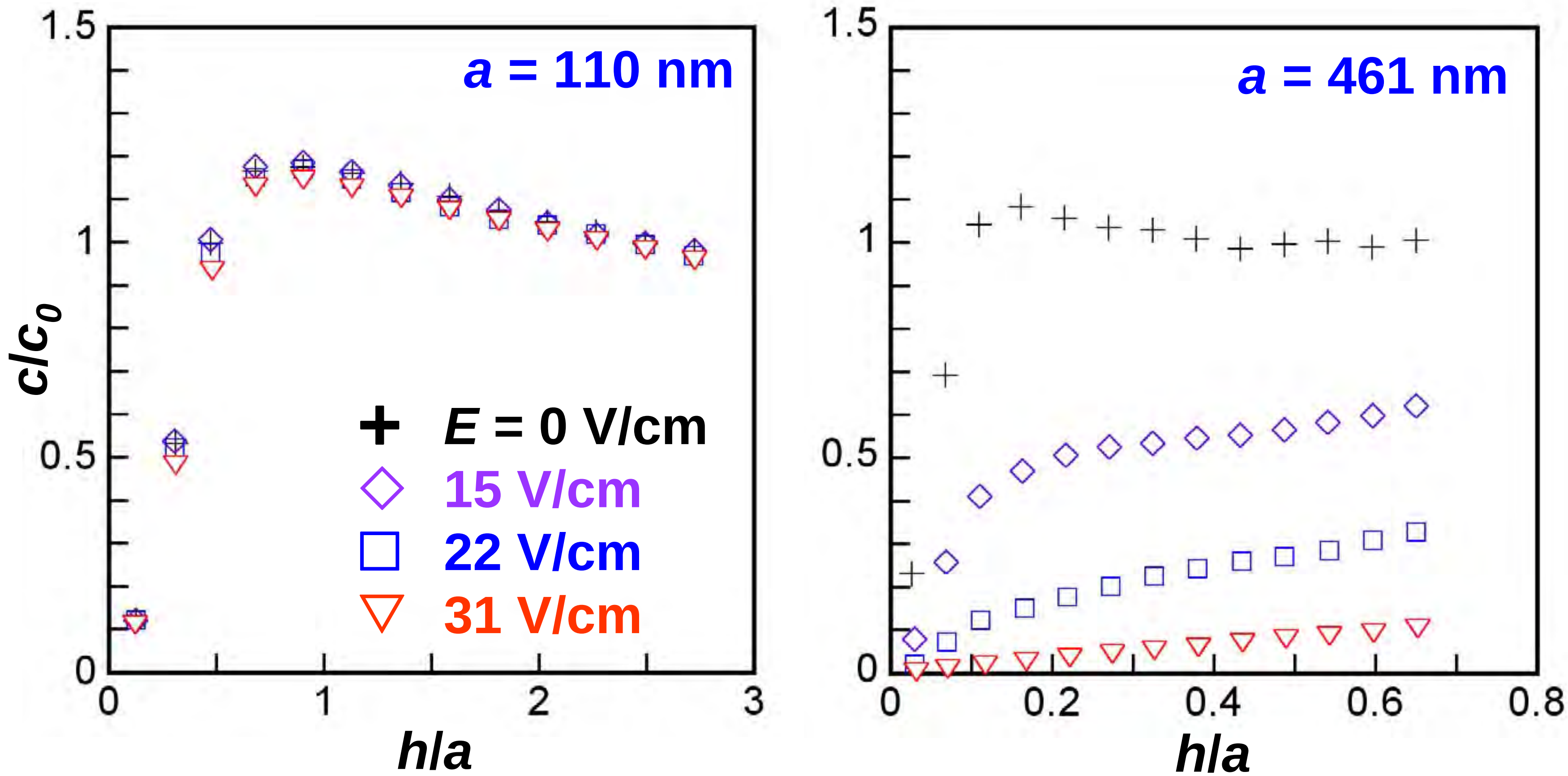
***a* = 110 nm**



***a* = 461 nm**

- **Electrokinetically driven flow: *E* = 0 V/cm, then 31 V/cm**
  - *E* drives larger particles farther away from wall

PARTICLE DISTRIBUTIONS



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

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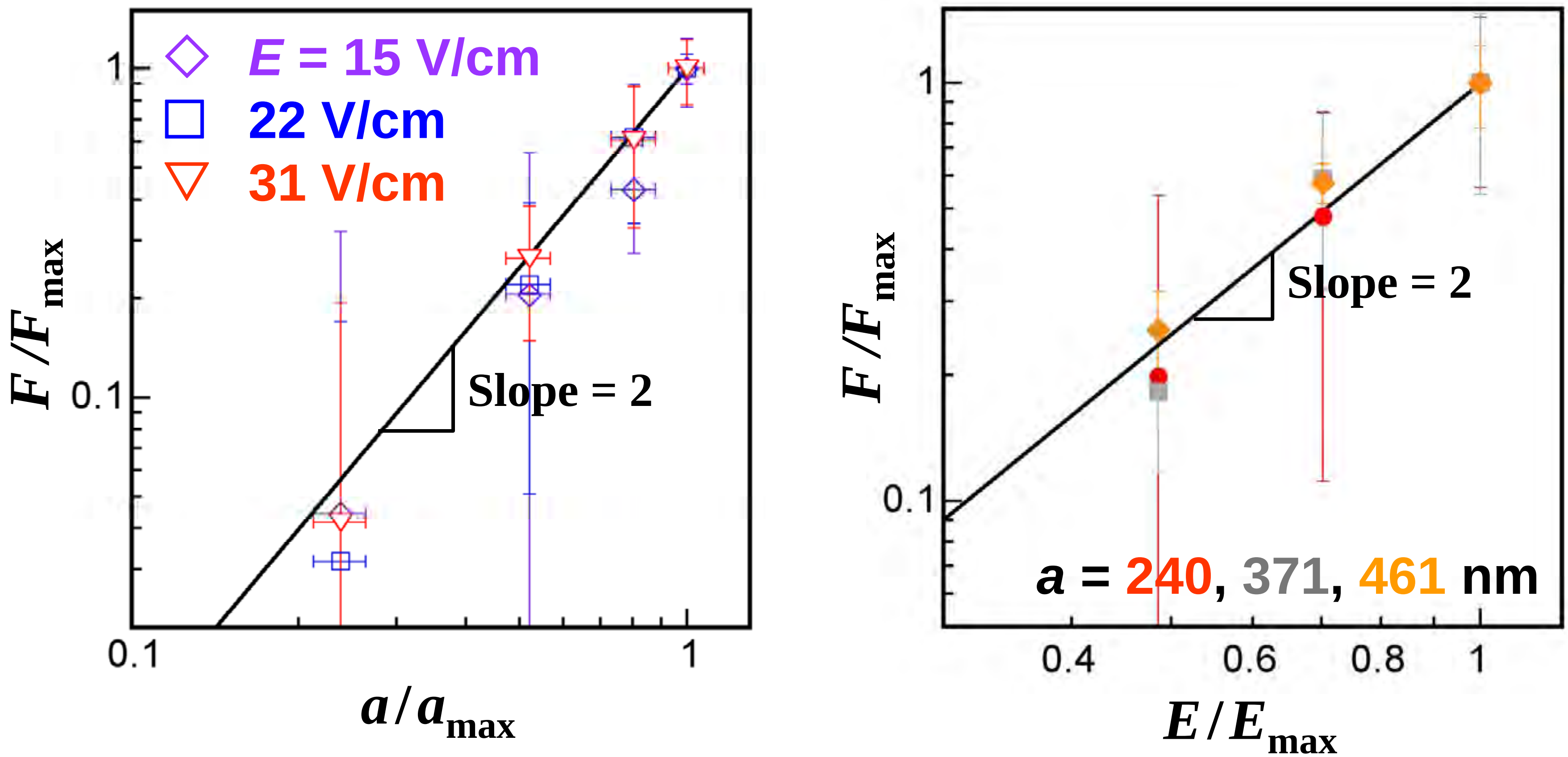
"LIFT" FORCE



- **Estimate lift force assuming Boltzmann distribution**
  - Force on particle $F \propto a^2$, E^2: no discernible effect of ζ_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 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

ACKNOWLEDGEMENTS

- **Haifeng Li: Poiseuille flow**
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