2-D Crystals of Colloidal Particles on a Planar A/C Electrode

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Let me introduce my co-workers. Jeff Fagan is a 4th-year PhD student working with Paul Sides and me on this project. Jeff is hoping to land a post-doc or teaching job this summer when he finishes.

During the last few years, a number of us have been trying to understand the formation of 2-D colloidal crystals on the surface of electrodes. We think we do now understand the mechanism in dc electric fields. But particles have also been observed to aggregate in a/c fields. In a/c fields the mechanism is more subtle.
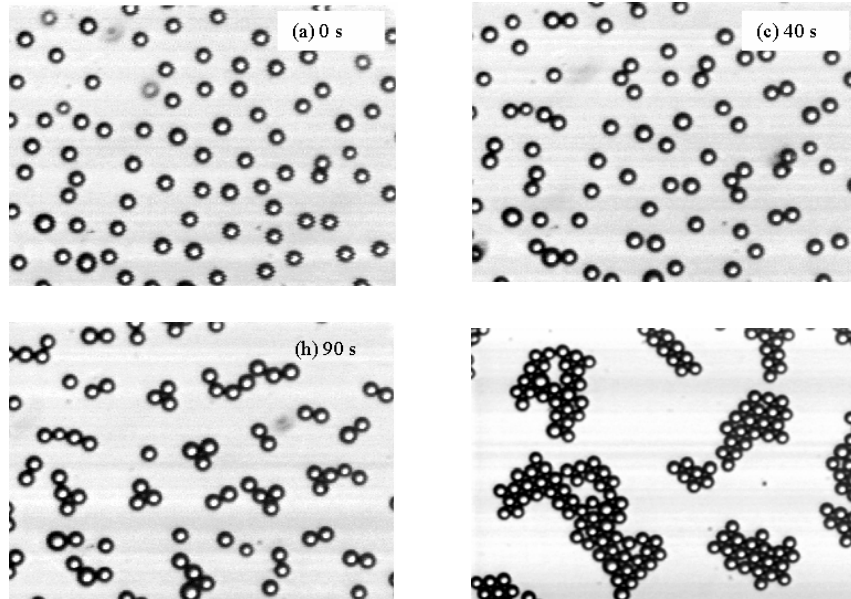
Today I will review some of the previous observations of aggregation on d/c and a/c electrodes. Then I will summarize some of our experiments monitoring the elevation of single particles using TIRM which, we will see, provides a new dimension to the study of this phenomena.

Aggregation on D/C Electrodes

Böhmer, *Langmuir* **12**, 5747 (1996)
Solomentsev *et al.*, *Langmuir*, **16**, 9208 (2000)
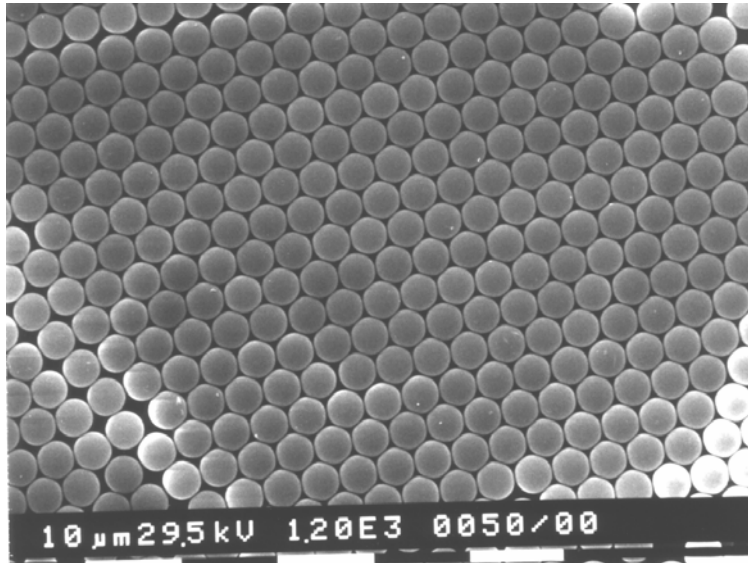(10 μm PS in 1 mM $NaHCO_3$ at 60 V/m)

(a) 0 s

(c) 40 s

(h) 90 s

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Virtually all of the past studies of aggregation have used video microscopy to measure the rate of lateral motion over the surface of the electrode. These images show how the assembly proceeds as a function of time.

You are looking down through a microscope on the surface of a planar electrode. The particles are initially uniformly dispersed before the electric field is applied. Application of a d/c field causes the particles to aggregate forming crystallites that combine to form larger crystals.

Seminar presented at the Dept. of Chemical Engr., University of Alberta, March 10, 2005.

Application:

more efficient production of multilayer nano composites
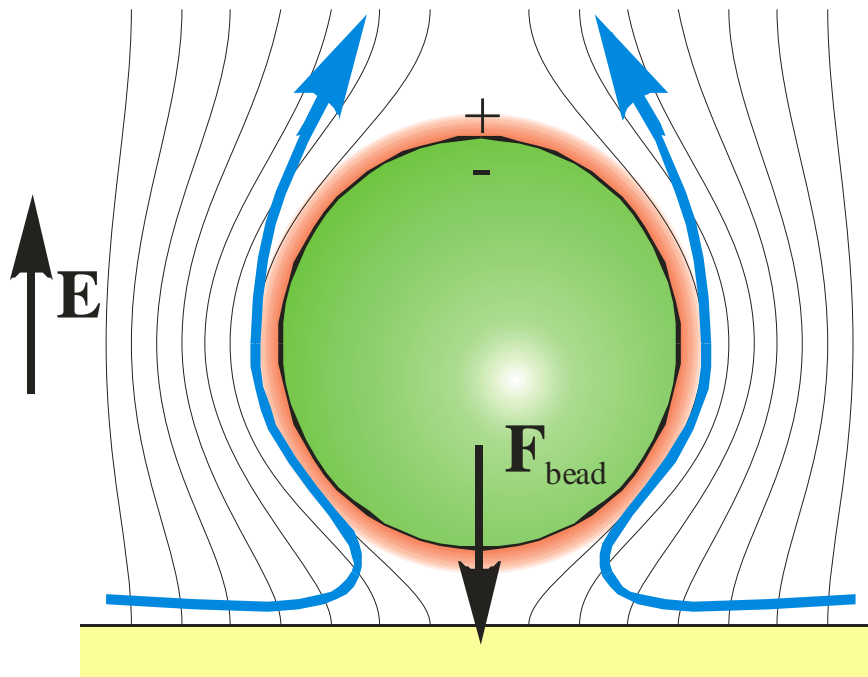

10 μm 29.5 kV 1.20E3 0050/00

Photomicrograph courtesy of Philips Research Labs

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Eventually a very large 2-D colloidal crystal is obtained such as the one shown here. These have applications in CRT displays, for example. After depositing one layer, and fixing it in place, a second layer with different composition can similiarly be deposited. This same process can be thus used repeatedly to manufacture multilayered nanocomposites.

A/C fields are preferred in commercial processes to avoid the accumulation of electrode reaction products and the depletion of reactants, but we still don't understand the mechanism for assembly in a/c fields.

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"Electrokinetic" Model
(**E** acts on counterion cloud of <u>particle</u> to cause flow)

Our dc experiments are well modelled using an electrokinetic mechanism in which an electric field that pulls the particle toward the electrode would push the oppositely charge counterion cloud away from the electrode, resulting in an electroosmotic flow away from the electrode as shown here. That draws fluid toward the particle along the surface of the electrode. Another particle nearby could become entrained in the flow causing lateral aggregation of particles.

Of course, if the direction of the electric field were reversed, we would expect the electroosmotic flow to occur in the opposite direction. Thus we expect that adjacent particles would then move apart rather than together.

Reversing D/C Electric Field Causes Disaggregation
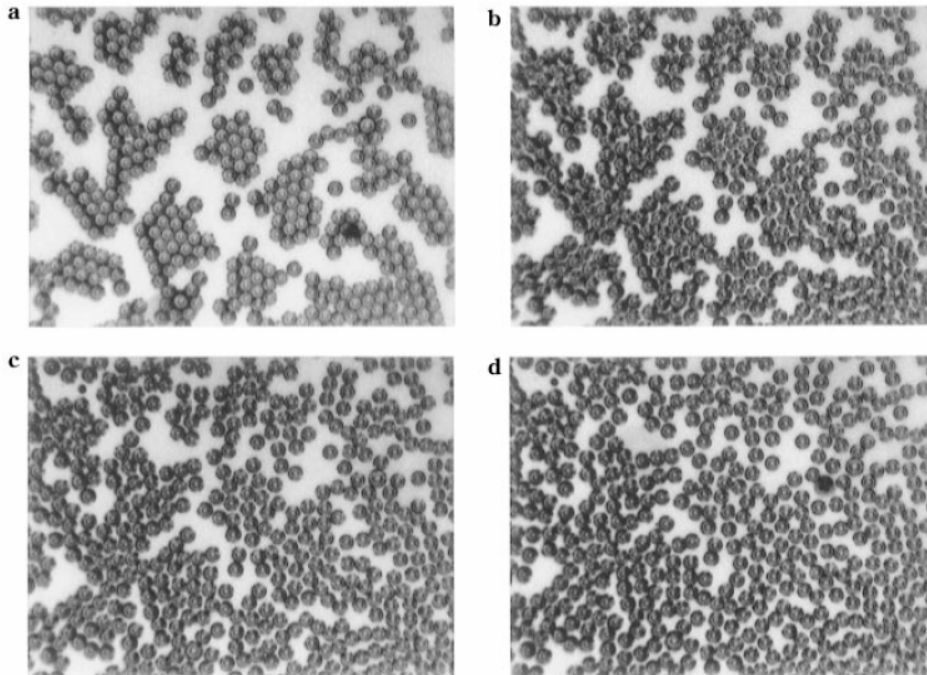
Böhmer, *Langmuir* **12**, 5747 (1996)

Figure 2. Breaking up of clusters upon reversal of the potential (−1 V) for a 10 μm polystyrene latex, after 0 s (a), 20 s (b), 40 s (c) and 60 s (d).

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Indeed, if I reverse the direction of the electric field, we do observe disaggregation of particles instead of aggregation.

On the basis of this electrokinetic mechanism, we would not expect aggregation in a/c experiments. Instead we would expect particles to move together during half of an a/c cycle and move apart during the second half, leading to no net relative motion.

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A/C Fields Can Also Cause Aggregation

Kim *et al., Adv. Colloid Interf. Sci.* **96**, 131 (2002)
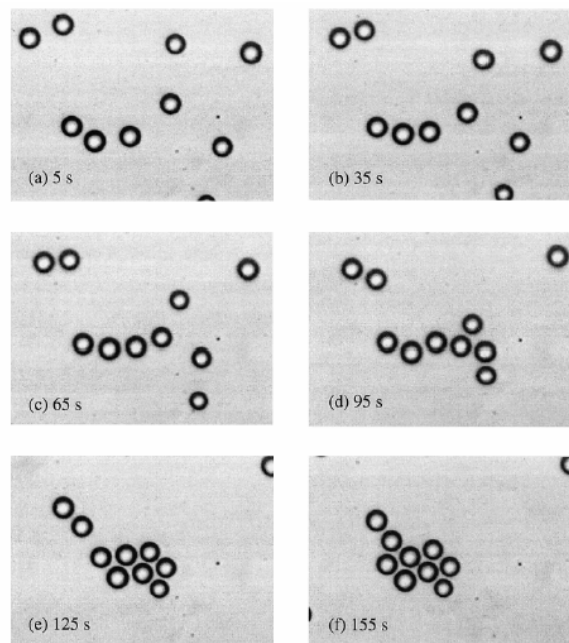(10 µm PS in 0.1 mM NaHCO$_3$ at 3300 V/m, 50 Hz)

Fig. 2. Video images of a cluster of polystyrene latex particles (9.7 µm diameter, $\zeta = -78$ mV) aggregating. Note that the particles fail to come into apparent contact. 50 Hz, $E_{rms} = 33$ V cm^{-1}. Square-wave cycles.

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Nonetheless, aggregation is observed in a/c fields, as shown in this slide. In order to observe aggregation in reasonable times, we need much larger a/c electric fields than in the d/c case. The amplitude of the oscillating electric field is 50 times larger in these experiments than in the previous d/c experiments.

This suggests that the mechanism involves a 2nd order effect relative to the d/c mechanism. Indeed there are several 2nd order effects which were neglected and are possible candidates for a/c aggregation.

Aggregate Rate Depends on a/c Frequency

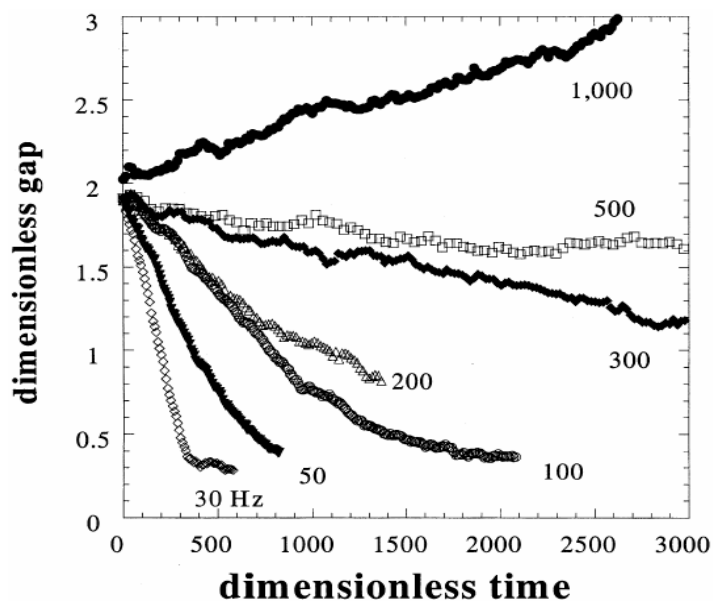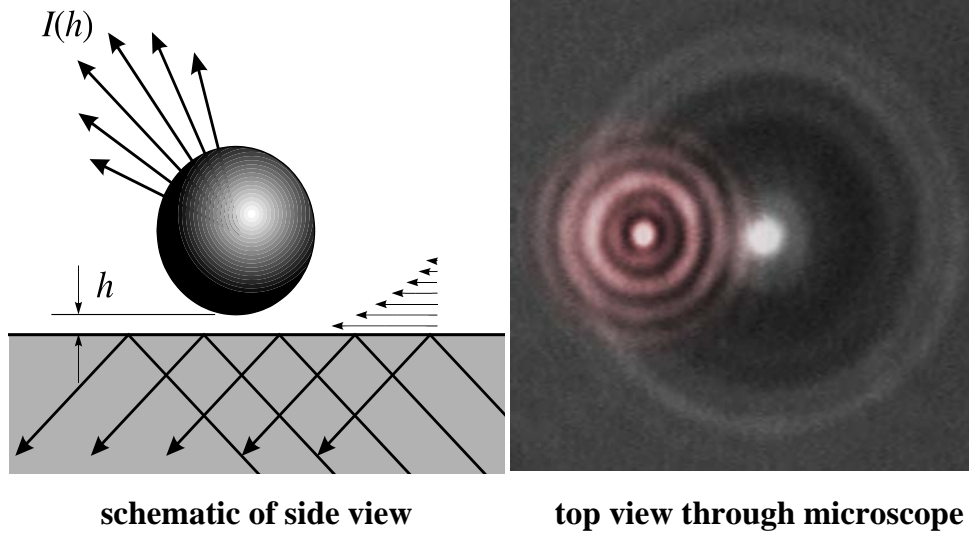Kim *et al., Adv. Colloid Interf. Sci.* **96**, 131 (2002) – 10μm PS, 0.1mM NaHCO$_3$

Fig. 4. Trajectories as a function of frequency. E_{rms} in the range 27–35 V cm^{-1}, square-wave cycles. The 'gap' between particles (center-to-center distance minus $2a$, where a = particle radius) is made dimensionless by a, and the time is made dimensionless by $a\eta/\varepsilon\zeta E_{rms} = 0.02$ s, where η and ε are the viscosity and permittivity of water. The voltage signal was square wave, and each symbol is the average of several experiments with different pairs of particles.

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The rate of aggregation depends on the frequency of the a/c field. Indeed, at the highest frequency, particles moved apart instead of together.

This was the status of understanding when Jeff started his PhD in the fall of 2001. We decided to exploit the capabilities of TIRM to monitor the elevation of a single particle in a/c fields.

Instantaneous Elevation *h*(*t*) Monitored by
Scattering of Evanescent Waves
Prieve & Walz, *Applied Optics* 32, 1629 (1993)

$I(h)$

h

schematic of side view

top view through microscope

$$I(h) = I_0\, e^{-\beta h}$$

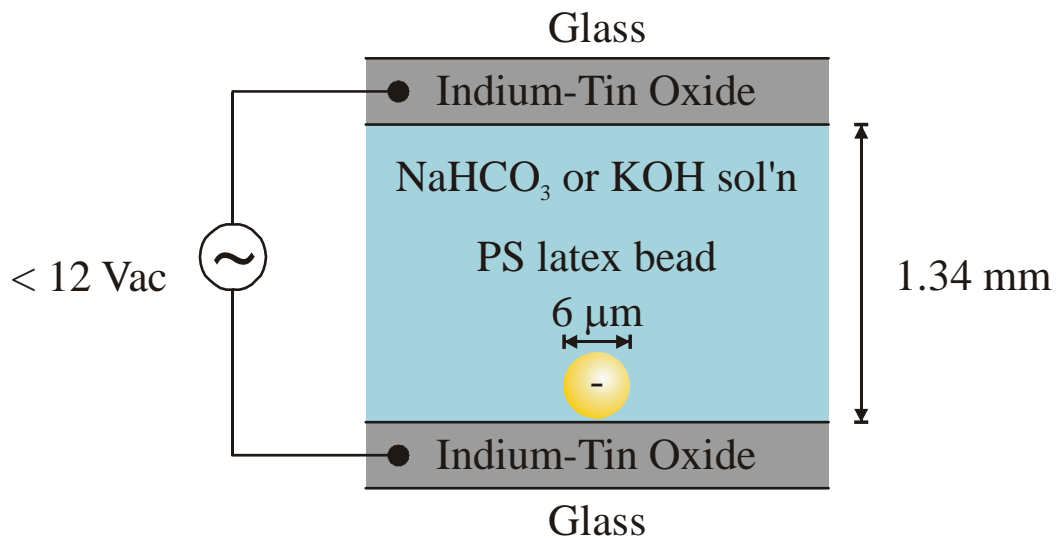where $\beta = \dfrac{4\pi}{\lambda}\sqrt{(n_s \sin\theta)^2 - n_f^2}$

typical $\beta^{-1} = 100$ nm (**Δ*h* = 1 nm produces Δ*I* = 1 %**)

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TIRM is a method to monitor fluctuations in the instantaneous distance separating a Brownian sphere and a transparent plate. We measure the scattering of light by a single sphere when it's illuminated by an evanescent wave, which is produced by reflecting a laser beam off the glass-water interface at a sufficiently glancing angle that total reflection occurs.

An evanescent wave propagates parallel to the interface and its amplitude decays exponentially with the distance from the interface. As a consequense, the scattering intensity also decays exponentially. Because of this exponential sensitivity, a very small change in h produces a measureable change in intensity. We can detect changes in h of the order of 1 nm.
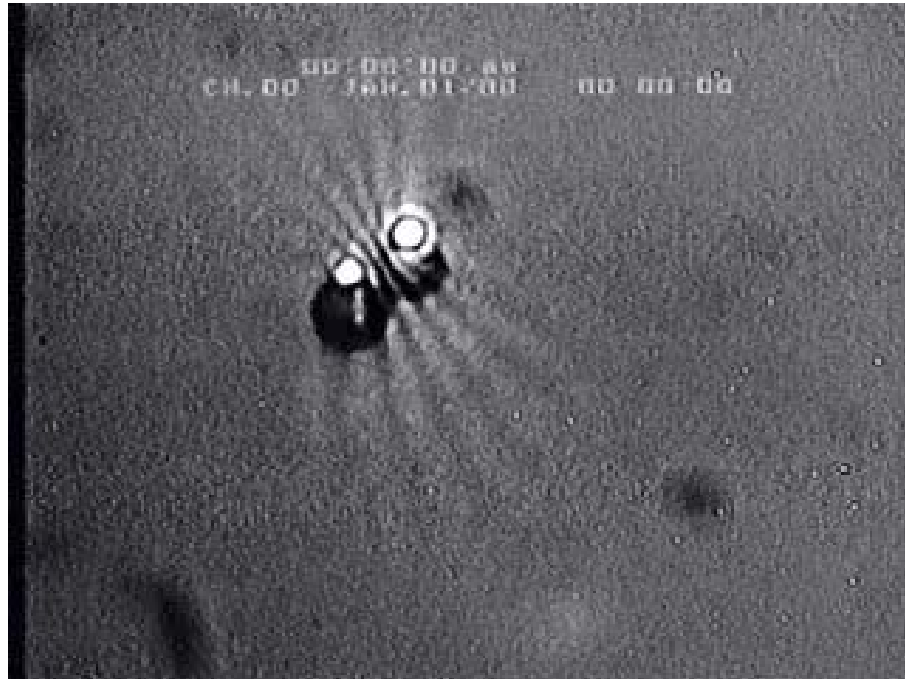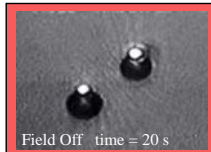
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The Experiment

Glass

Indium-Tin Oxide

NaHCO$_3$ or KOH sol'n

PS latex bead
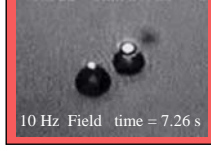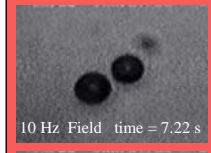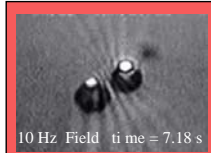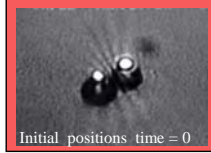
6 μm

< 12 Vac

1.34 mm

-

Indium-Tin Oxide

Glass

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Experiments were done in a cell formed by two microscope slides sandwiching about 1 mm of fluid containing the particle to be studied. The inner surface of the microscope slides is coated with a film of indium-tin oxide, a transparent semi-conductor, which allows us to apply a current between the two parallel electrodes.

We will be looking at the motion of a single latex bead located very near one of the electrodes. The size of the bead is greatly exaggerated in this schematic.

Movie of TIRM Experiment
Two 6 μm PS beads in 0.13 mM KOH over ITO Electrode

Initial positions time = 0

10 Hz Field time = 7.18 s

10 Hz Field time = 7.22 s

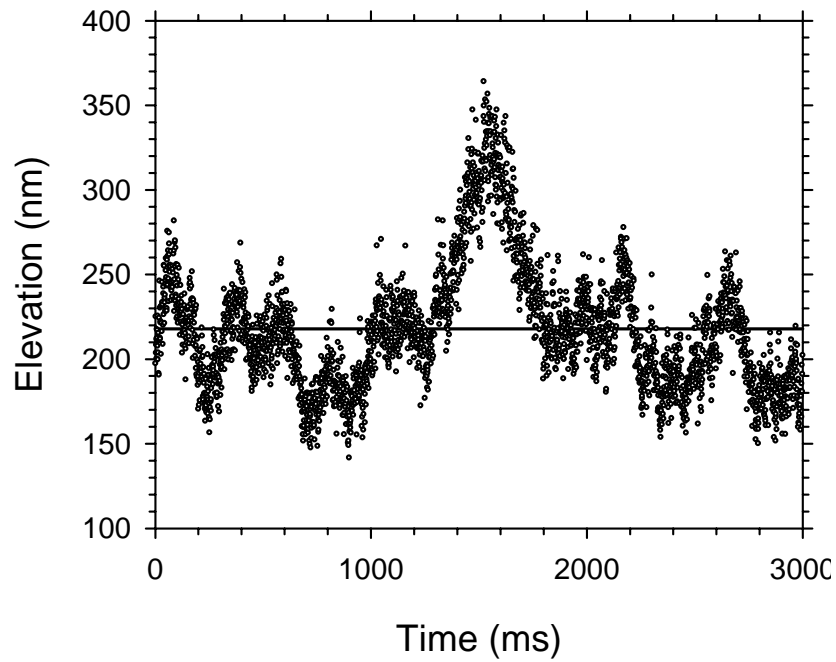10 Hz Field time = 7.26 s

Field Off time = 20 s

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Here you see two 6-micron PS particles levitated above a transparent electrode. The bright spot at the top of each particle is the light scattered from the evanescent wave. Those are interferences fringes running perpendicular to the line connecting the centers of the two spheres.

Once this video clip starts, you will see about 15 seconds of Brownian motion of these particles with no voltage applied to the electrode. Then you will see what happens when a 10 Hz a/c voltage is applied. The bright spots will blink about 10 times per second as the particles rise and fall above the electrode under the action of the electric field. You will also see the particles slowly drift apart. This demonstrates that an a/c electric field applied normal to the electrode also causes adjacent particles to drift laterally. It is the mechanism of this lateral motion which motivates this study.

This video clip was obtained using KOH as the electrolyte. Had we replaced KOH with the same concentration of NaHCO$_3$, we would find that the particles also oscillate up and down at the same frequency as the applied electric field, but the lateral drift of particles would bring them together rather than apart.

All the remaining results I will show are obtained for a single sphere.

Brownian Fluctuations (no Field)
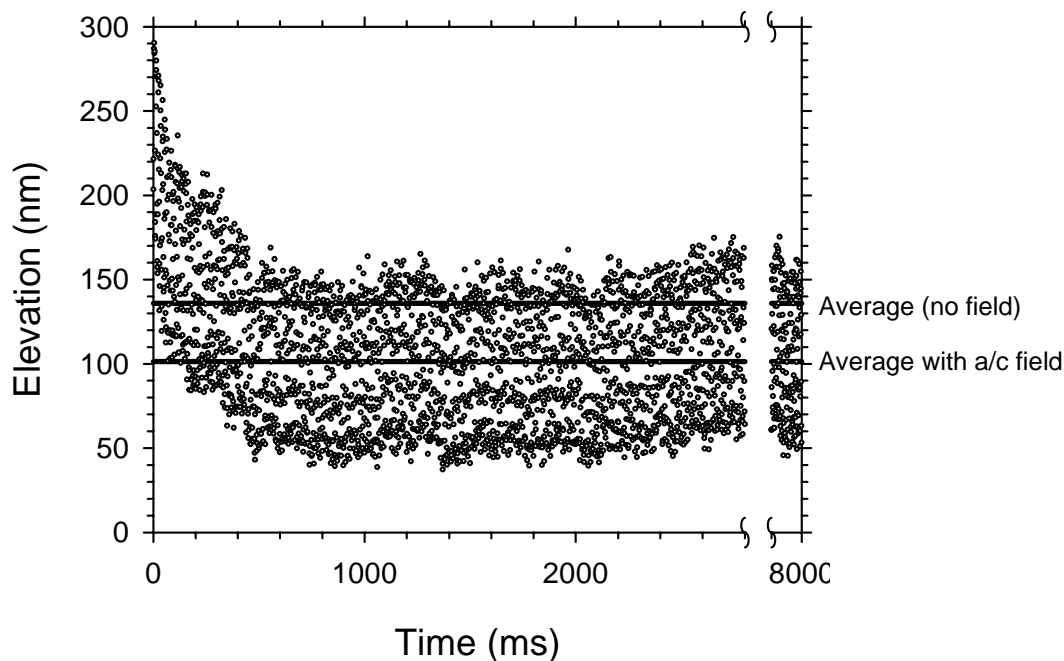### 6 μm PS bead in 0.13 mM KOH over ITO Electrode

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Here are some sample observations of elevation fluctuations caused purely by random Brownian motion normal to the electrode. We can record the elevation at 1 millisecond intervals.

Brownian Fluctuations After A/C Field Starts
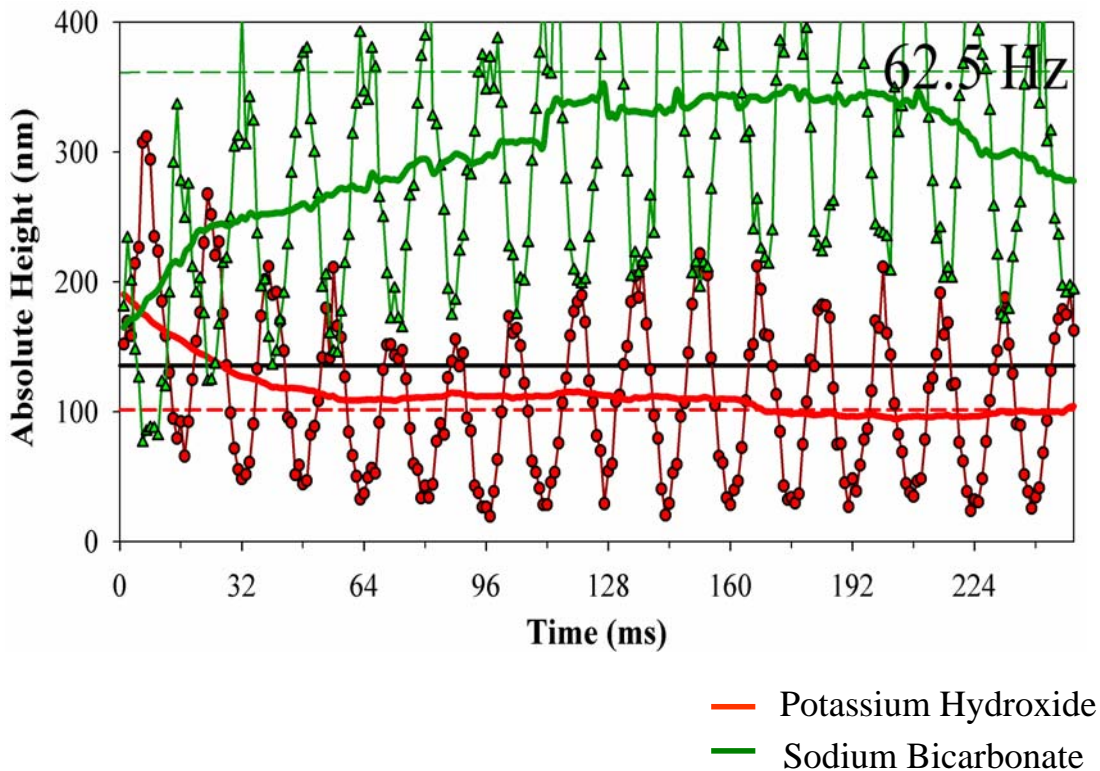## 6 μm PS bead in 0.13 mM KOH over ITO Electrode (3 V, 100 Hz)

Here are results under very similar conditions immediately after the start of applying 3 volts peak-to-peak at 100 Hz. The scale of the axes is the same. Qualitatively, the trajectory looks very different: we now have a very broad band of positions compared to that with Brownian motion alone.

Transient Approach to Stationary Oscillations

Particle Behaves Oppositely in KOH and NaHCO$_3$

62.5 Hz

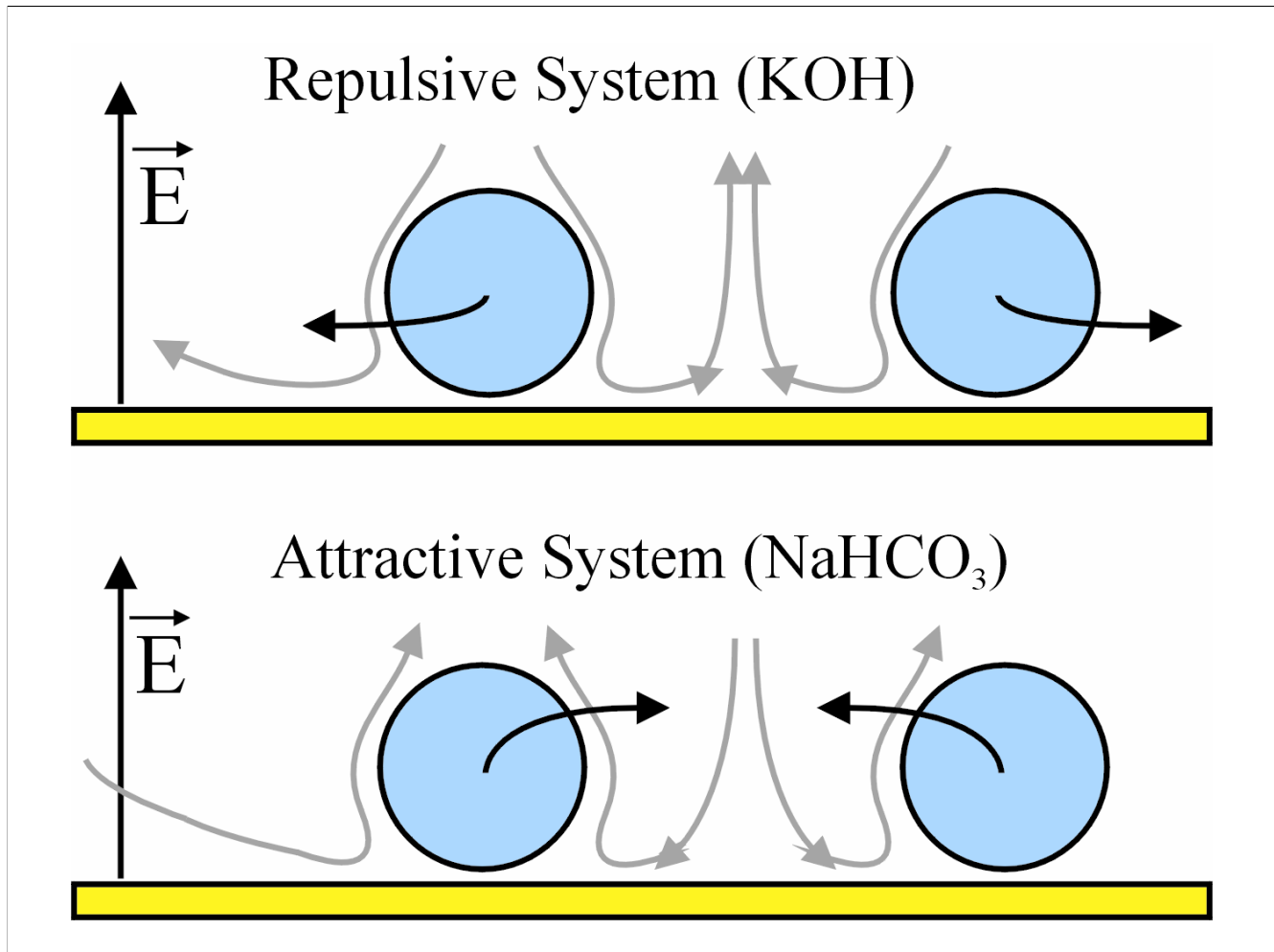— Potassium Hydroxide
— Sodium Bicarbonate

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This is the first 250 ms of the 3000 ms from the previous slide. In this view it is clear that the particle oscillates up and down in elevation at the same 100 Hz frequency in response to the oscillating electric field. This is why the band is so broad.

Before the a/c voltage was applied, this particular particle underwent Brownian fluctuations around a mean elevation of about 140nm. The initial electric field pushed the particle up to almost 300 nm, but after about 1 second of a/c voltage the particle's elevation dropped to about 100 nm, well below the no-field average. The heavy red curve shows the running average decreasing with time in KOH.
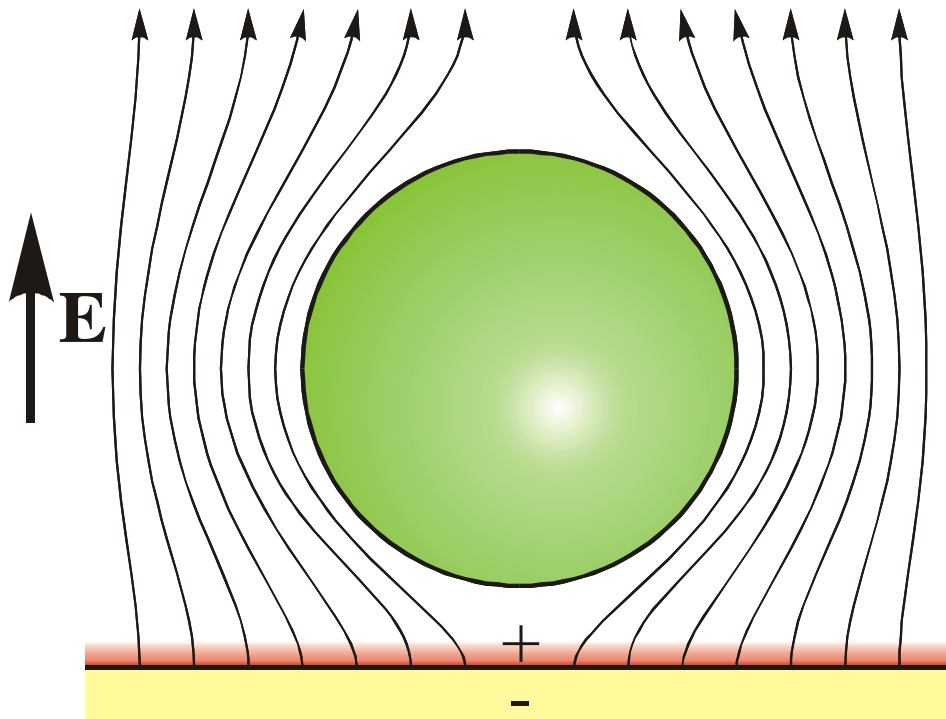
The green data is the analogous result obtained if KOH is replaced by NaHCO$_3$. Changing the electrolyte causes the average elevation to drift upward instead of downward. This dichotomy in elevation changes is also seen in the lateral motion: particles drift apart in KOH (recall the video clip) but drift together in NaHCO$_3$.

With a change in electrolyte from KOH to NaHCO$_3$, the opposite average behavior observed in both the elevation changes and in the lateral motion suggests that the same mechanism is responsible for both components of motion. That mechanism is the electroosmotic flow.

In KOH, the net flow is downward over the particle (pushing it closer to the electrode); those same streamlines then continue outward along the surface of the electrode away from the point of near contact between each particle and the electrode. Entrainment in this outward flow would cause nearby particles to move away from each other. In NaHCO$_3$, the direction of the streamlines is apparently reversed, causing nearby particle to aggregate together and causing each particle to be pushed away from the electrode.

What about counterion cloud on electrode?
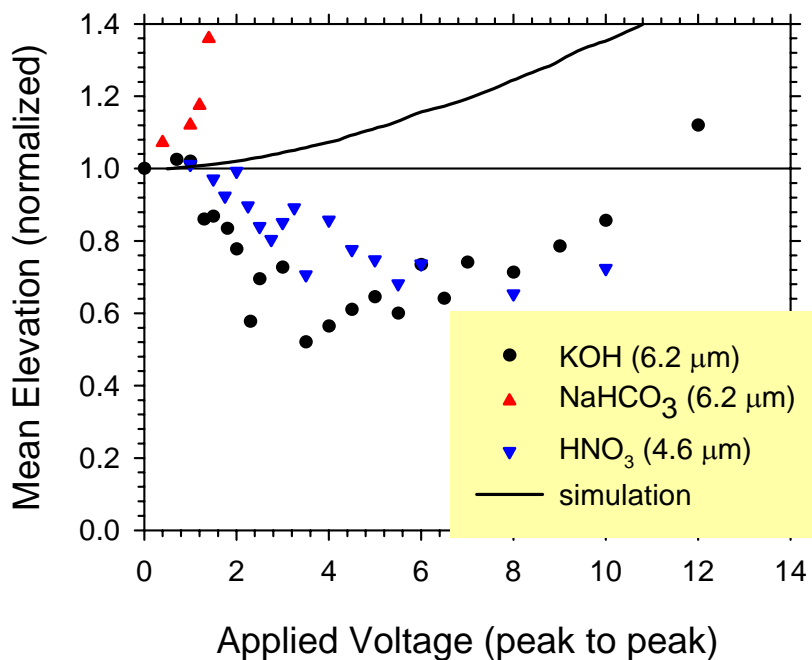## (<u>uniform</u> potential on electrode produces no flow)

So why is the direction of net flow opposite in the two electrolytes? The zeta potential of the particle is not much different in the two electrolytes; in particular its sign does not reverse. So the reason is not likely to be associated with the electroosmosis driven by the particle's double layer.

Instead, we believe the mechanism is associated with electroosmosis driven by the the double-layer on the electrode (indicated in orange color above). If the current density varies over the surface of the electrode (in particular, under each particle), the zeta potential on the electrode will be perturbed differently at each radial position depending on the kinetics of the electrode reactions. In different electrolytes, the electrode re-dox reactions can be expected to differ and so do their kinetics.

Final Avg Elevation Depends on Amplitude & Electrolyte

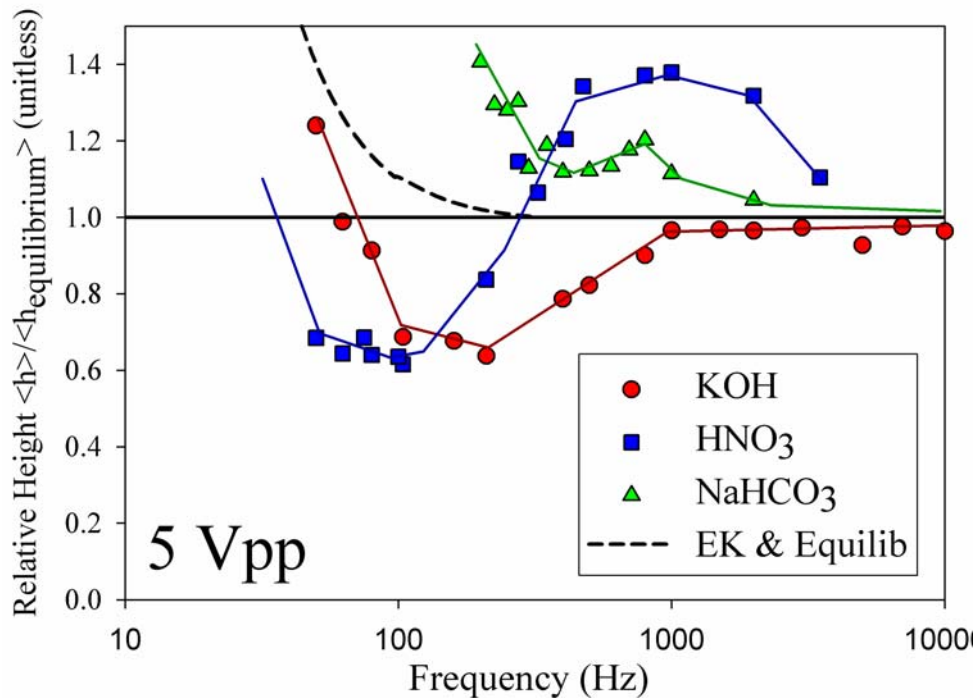### 4.6 or 6.2 μm PS beads in 0.13 mM over ITO Electrode (100 Hz)

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This slide summarizes two more series of similar experiments in which the electrolyte KOH was replaced by sodium bicarbonate or nitric acid. Instead of dropping to a minimum as the amplitude is increased, the mean elevation increases monotonically in bicarbonate. Of course, the zeta potential of the surfaces does depend on the pH, which is quite different in these 3 electrolytes; however all 3 cases correspond to like charge on the two surfaces. Nonetheless we see opposite trends in the electrolytes.

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Final Avg Elevation Also Depends on Frequency
4.6 or 6.2 μm PS beads in 0.13 mM over ITO Electrode (5 Vpp)
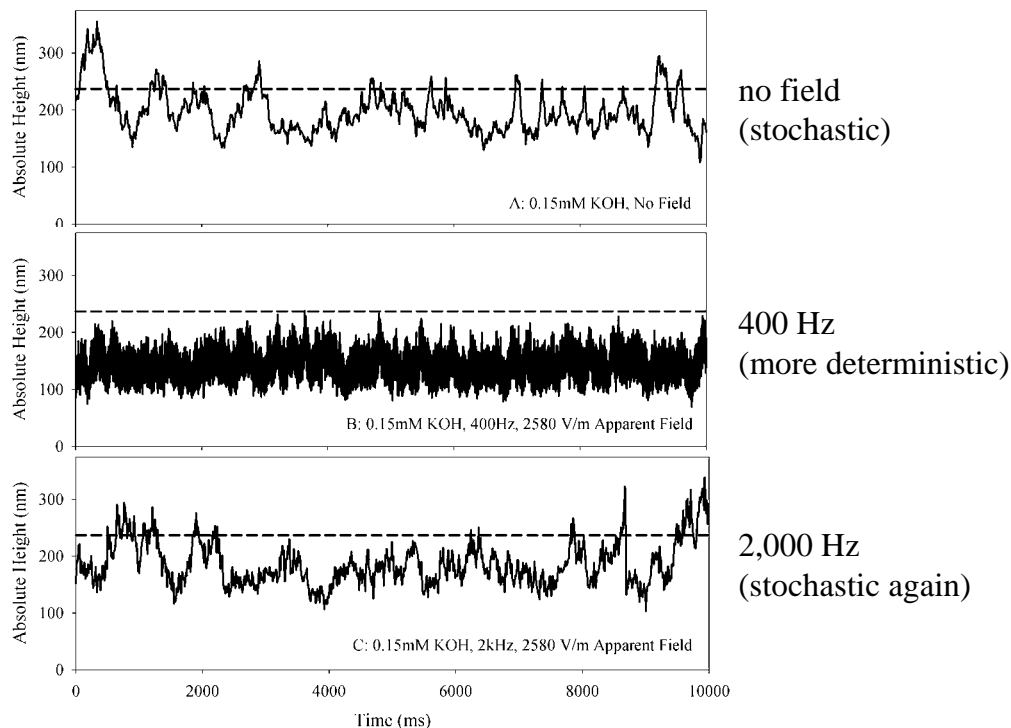

It is particularly interesting to examine the change in <h> as a function of frequency. Here we again observe depression in <h> in KOH and HNO3 at 100 Hz, and elevation in NaHCO3 that we observed on the last slide. However, as the frequency is increased, we see different behaviors in the 3 electrolytes. Most interesting is the reversal in direction of the change in <h> in HNO3 , which occurs at around 300 Hz.

Brownian Motion Dominates at High Frequency

6 µm PS bead in 0.13 mM KOH over ITO Electrode (5 Vpp)

no field
(stochastic)

400 Hz
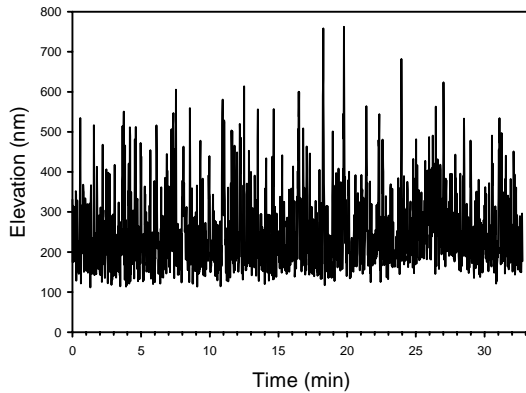(more deterministic)

2,000 Hz
(stochastic again)

At high frequencies, the normal motion of the particle appears to become stochastic again. This slide compares trajectories measured with no field, moderate frequency and high frequency.

At moderate frequencies, the particle is moving up and down in a deterministic fashion, producing a trajectory which looks very different from the other two trajectories on this slide. Of course, this is because the motion of the particle at moderate frequencies is primary the up and down deterministic oscillations.

By contrast, at high frequencies, the motion appears to be primarily stochastic again. If it is indeed stochastic, we ought to be able to apply the same analysis technique to measure interaction forces which we have applied in the absence of any electric field.
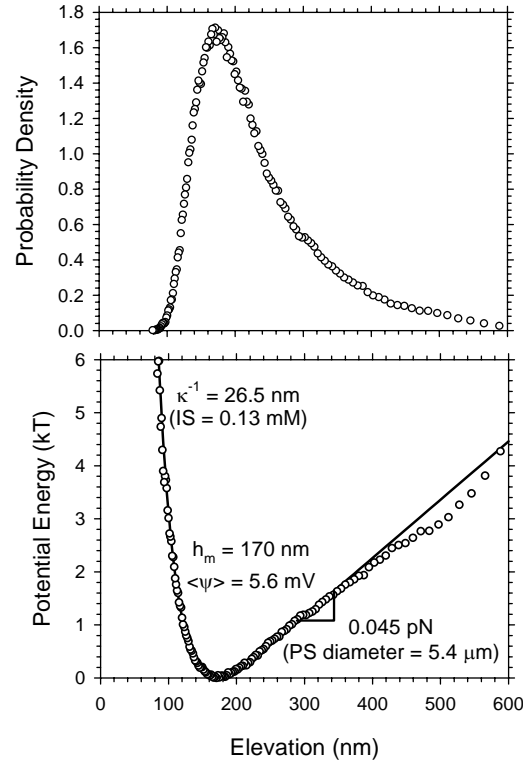
Analysis of Stochastic Fluctuations in Elevation

4.6 µm PS bead in 0.13 mM HNO_3 over ITO Electrode

Boltzmann's Eqn

$$p(h) = Ae^{-\phi(h)/kT}$$

κ^{-1} = 26.5 nm
(IS = 0.13 mM)

h_m = 170 nm
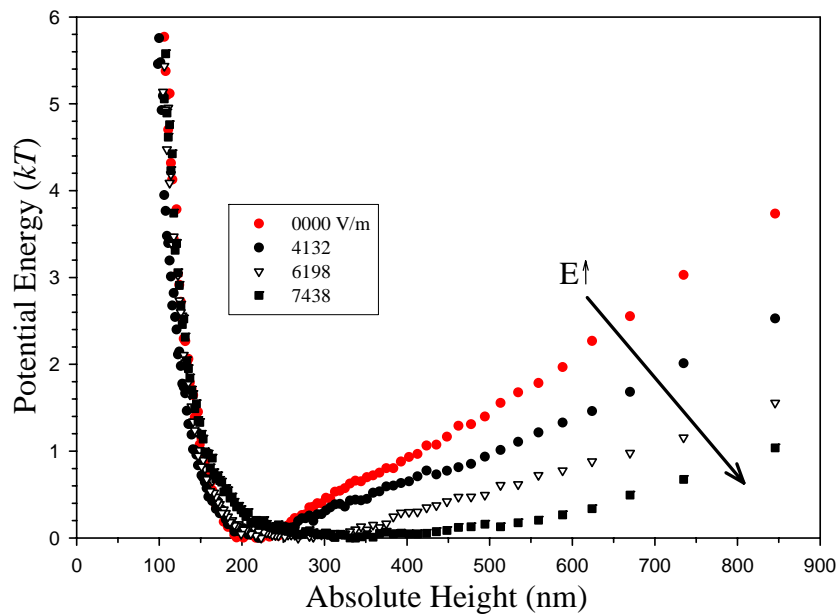$\langle\psi\rangle$ = 5.6 mV

0.045 pN
(PS diameter = 5.4 µm)

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For purely stochastic motion, we deduce the PE profile by applying Boltzmann's equation to the histogram of elevations measured over a long period of time.

In this case, that leads to a linear increase in potential energy with elevation at large elevations. The slope of that line is the net weight of the particle, which is small fraction of a piconewton in these experiments.

We will now apply the same analysis to the fluctuations in elevation observed at 10 kHz.

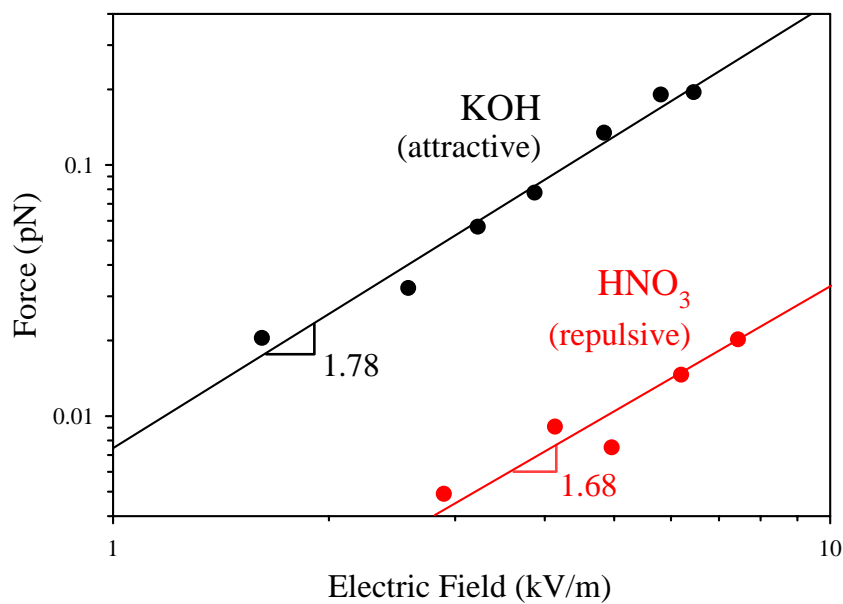# A/C Field Causes Particle to Get Lighter in HNO$_3$

4.6 μm PS bead in 0.13 mM HNO$_3$ over ITO Electrode (10 kHz)

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The slope of the linear portion of the profile is decreased, suggesting that an upward forces is being exerted on the particle by the a/c field. From the amount of decrease in slope, we can infer that upward force.

Force is Nonlinear in E

Here you see the force exerted as a function of the applied field strength. It is repulsion in nitric acid and attractive in KOH. In either case, the dependence on field strength obeys a power law with an exponent slightly less than 2.

Conclusions

- **Added new dimension (z) to video microscopy (x,y) study of self-assembly**
  - ➢ normal motion of single sphere is axisymmetric (2D)
  - ➢ lateral motion of pairs is 3D

- **Normal motion of single particle correlates with lateral aggregation of 2D ensemble (at least at low frequencies)**
  - ➢ KOH: decreased elevation and disaggregation of pairs
  - ➢ NaHCO$_3$: increased elevation and aggregation of pairs

- **Strong dependence on electrolyte**
  - ➢ KOH, NaHCO$_3$ and HNO$_3$ show very different trends with frequency and amplitude of E

- **More than one E^2 force is suggested**
  - ➢ low frequency → current is primarily Faradaic
  - ➢ high frequency → current is primarily capacitive (non-Faradaic)

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