**Motion of a Single Colloidal Particle
Levitated above an Electrode in an A/C Field**

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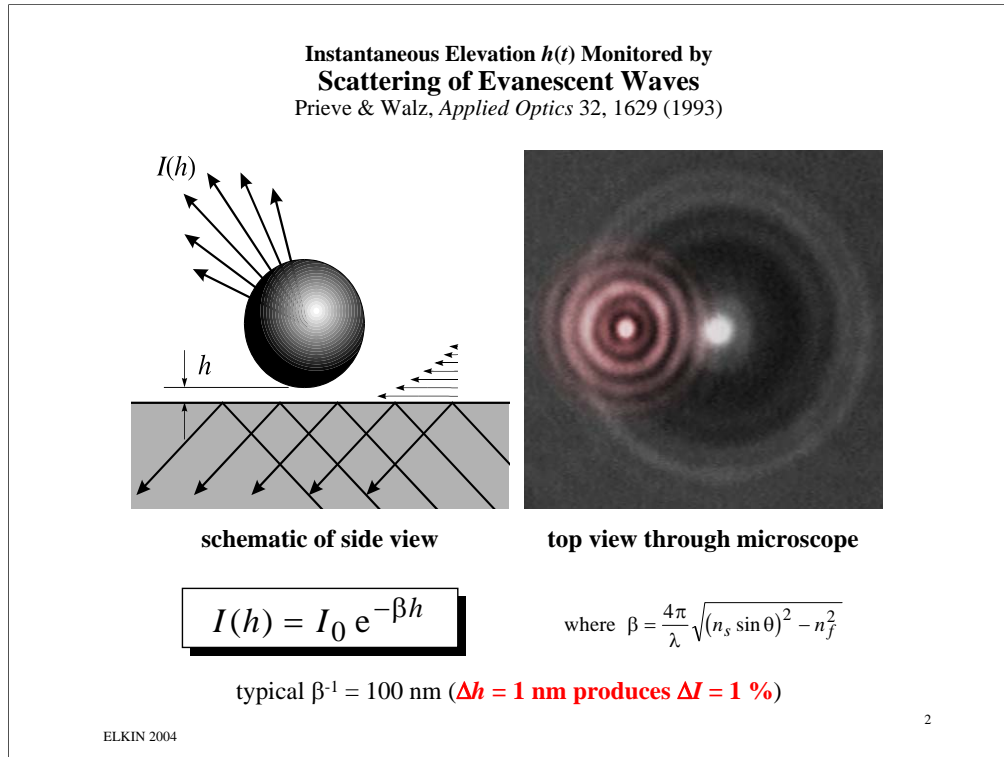
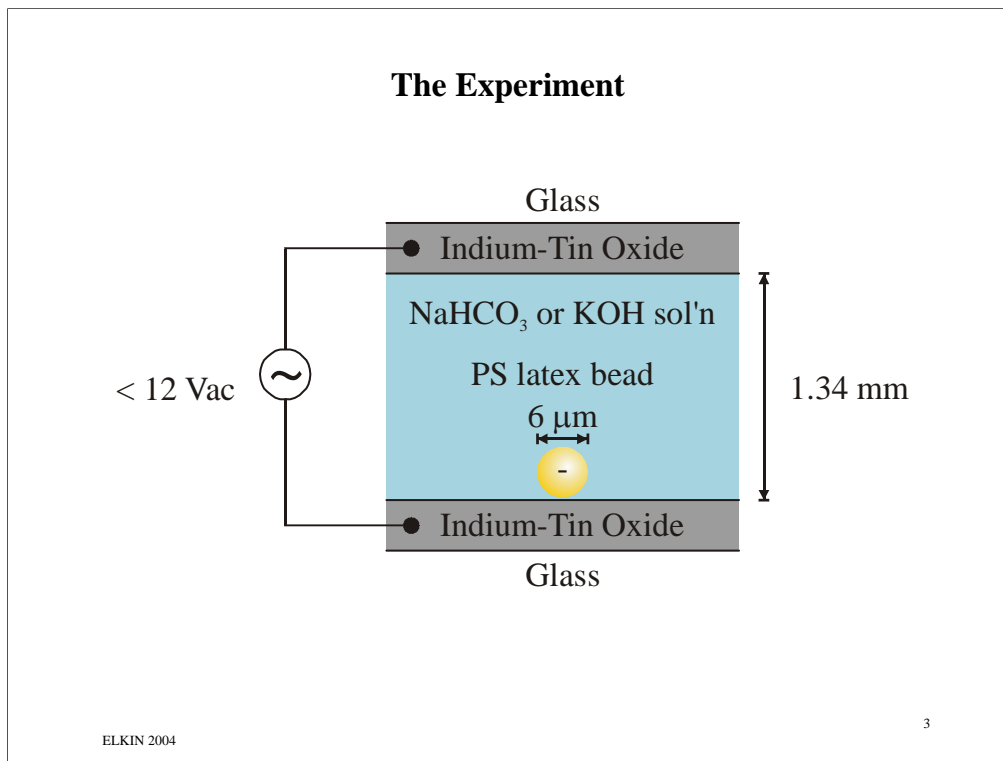ELKIN 2004   1

During the last tens years, a number of groups around the world have been trying to understand the self-assembly of 2D colloidal crystals on the surface of electrodes. Thanks to John Anderson's group, I think we do now understand the mechanism in dc electric fields: electroomotic flow around the particle. But particles have been observed by many groups to aggregate in a/c fields. In a/c fields the mechanism is more subtle.

Today I am going to show you experiments on the normal motion of single particles near a/c electrodes. I think normal motion is relevant to self-assembly because the same electroosmotic flows cause both normal and lateral motion of particles on the electrode surface.

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 β^{-1} = 100 nm (**Δh = 1 nm produces ΔI = 1 %**)

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To monitor the normal motion of the particles we use TIRM which looks at the scattering of a single microscopic particle when it is illuminated by an evanescent wave. Owing to the exponential decay in intensity of evanescent wave itself as we move away from the interface, the scattering also decays exponentially with elevation. 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.

20-minute talk presented in the session on "Electrokinetic Self-Assembly" at the International Electrokinetics Conference, Pittsburgh, PA, June 14, 2004.

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The Experiment

Glass

● Indium-Tin Oxide

NaHCO$_3$ or KOH sol'n

PS latex bead

6 μm

1.34 mm

< 12 Vac

● Indium-Tin Oxide

Glass

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Like those of many other groups, we employ a flow cell constructed of two parallel-plate electrodes sandwiching about 1 mm of fluid containing the particle to be studied. We look down through the upper electrode and observe the response of the particle located near the bottom electrode.

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

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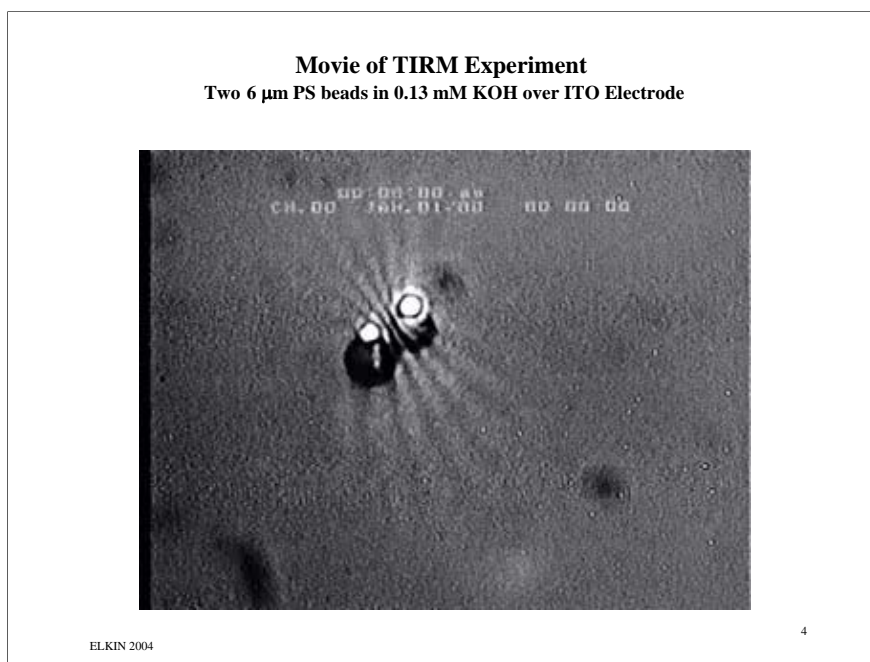
Here you see two 6-micron PS particles levitated above a transparent electrode. The bright spot at the top of each particle is the light scattered from the evanescent wave. Those are interferences fringes running perpendicular to the line connecting the centers of the two spheres.

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.

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

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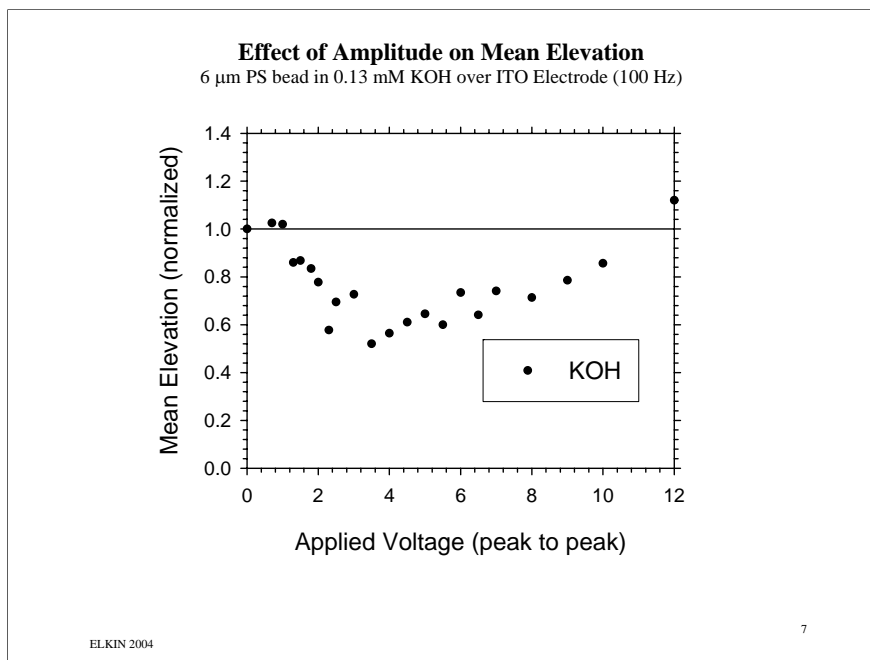**6 μm PS bead in 0.13 mM KOH over ITO Electrode**

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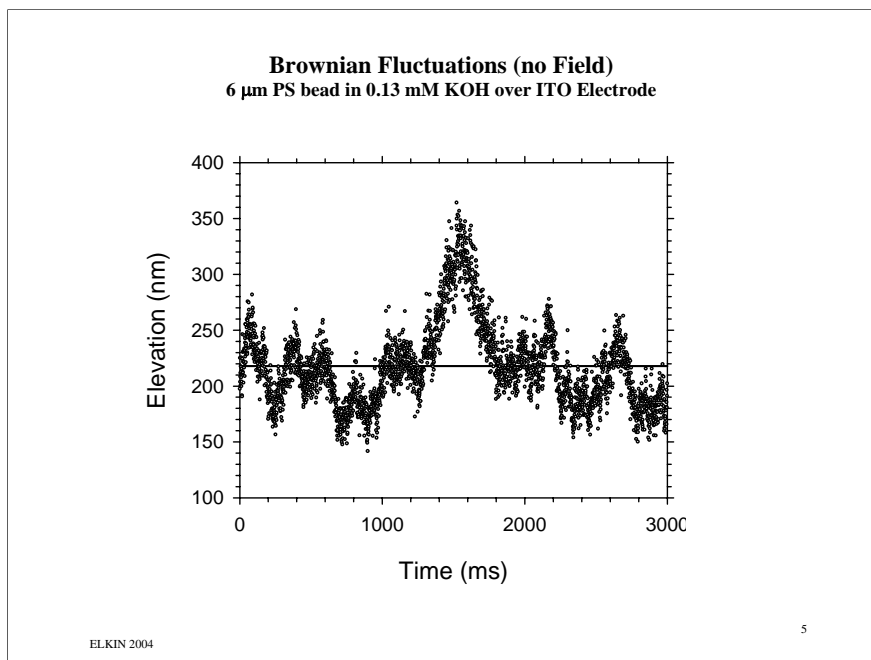
Here are some sample observations of elevation fluctuations caused purely by random Brownian motion normal to the electrode. We can record the elevation at 1 millisecond intervals.

Brownian Fluctuations After A/C Field Starts
6 μm PS bead in 0.13 mM KOH over ITO Electrode (3 V, 100 Hz)
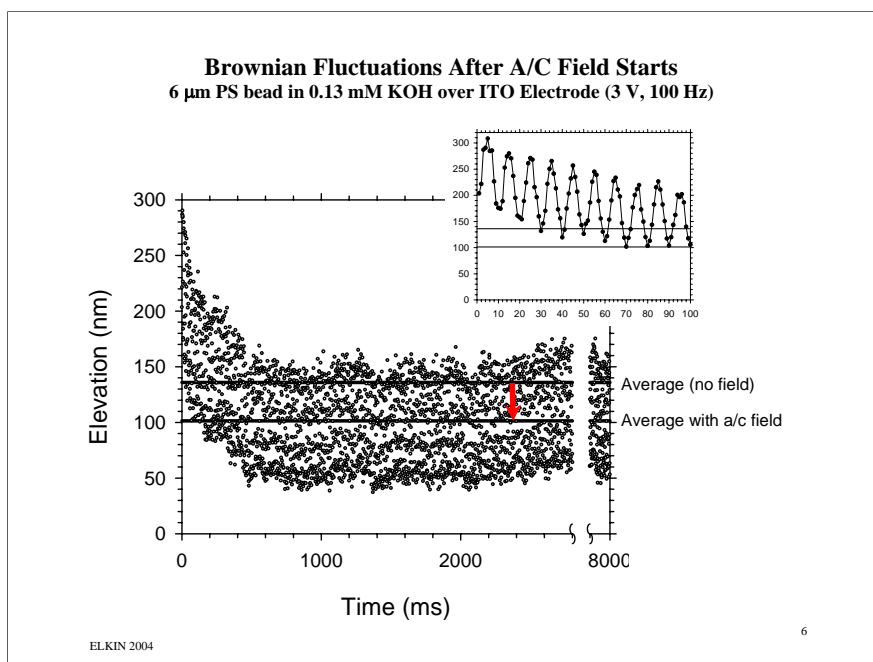
Here are results under very similar conditions immediately after the start of applying 3 volts peak-to-peak at 100 Hz. The insert shows that the particle oscillates up and down in elevation at the same 100 Hz frequency in response to the oscillating electric field.
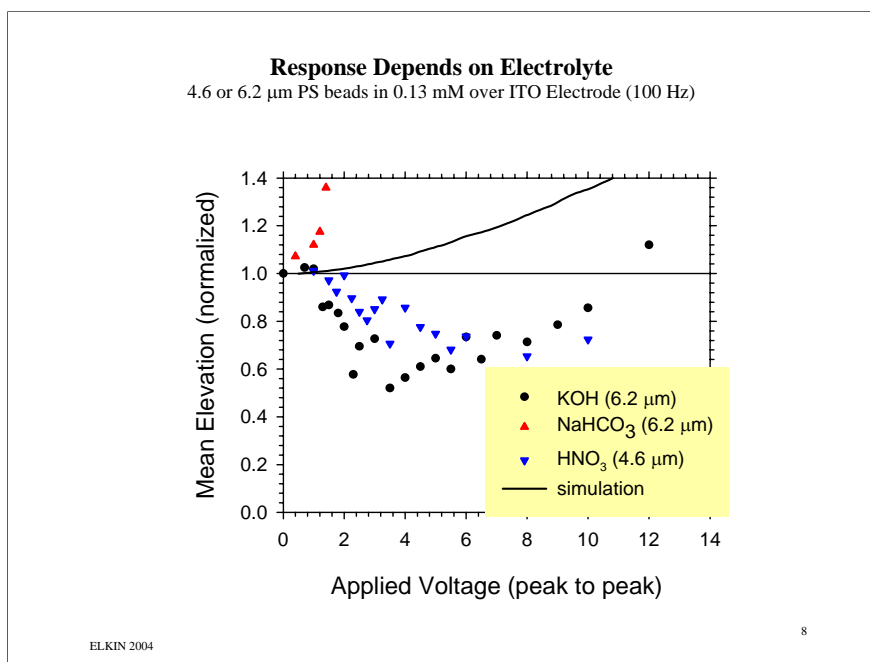
During the first second the particles drifts downward to reach a new stationary position closer to the electrode.

Effect of Amplitude on Mean Elevation
6 μm PS bead in 0.13 mM KOH over ITO Electrode (100 Hz)

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This slide summarizes a number of experiments like this in which the amplitude of the voltage was systematically varied. These elevations have been normalized by the no-field average. Notice that the mean elevation goes through a minimum with the amplitude of the a/c voltage.

Response Depends on Electrolyte
4.6 or 6.2 μm PS beads in 0.13 mM over ITO Electrode (100 Hz)
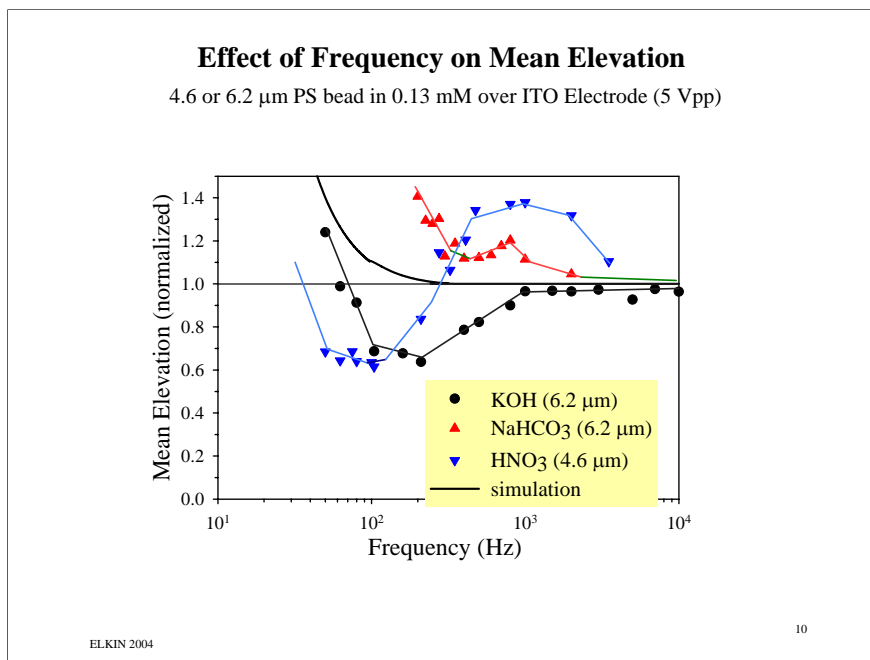
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This slide summarizes two more series of similar experiments in which the electrolyte KOH was replaced by sodium bicarbonate or nitric acid. Instead of dropping to a minimum as the amplitude is increased, the mean elevation increases monotonically 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.
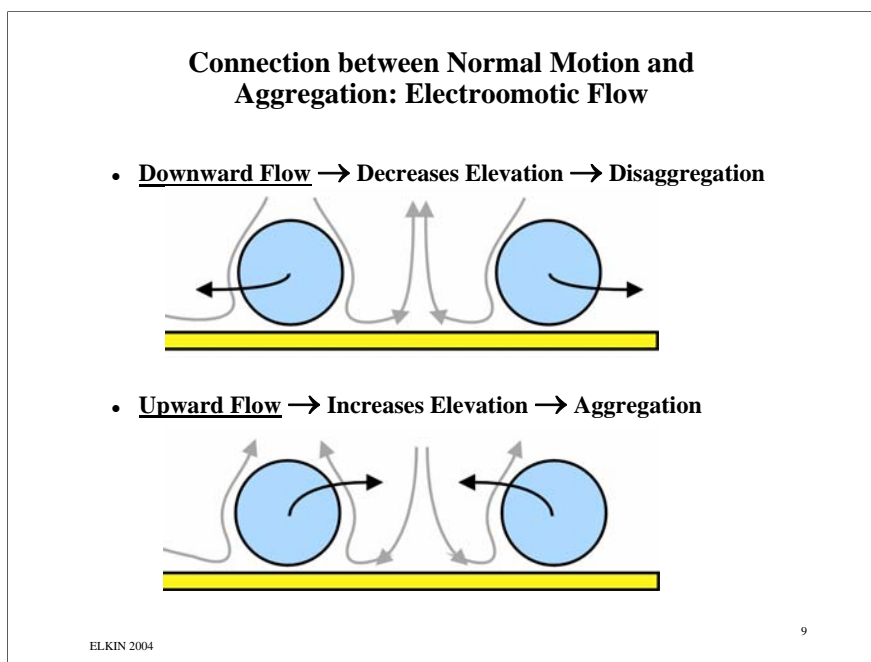
We saw a pair of particles move apart in KOH; similar studies with bicarbonate show pairs moving together. This opposite behavior is also seen in the normal motion of single particles. There is a simple explanation for the strong correlation between normal motion of a single particle and the lateral motion of pairs: the same electroomotic flow causes both.
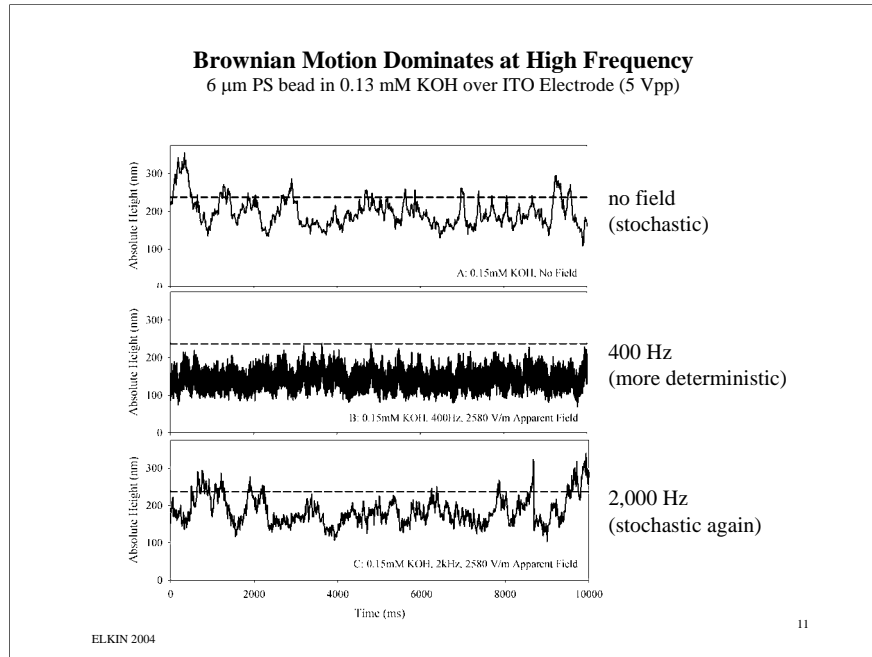
The advantages of studying single particle behavior is 1) we can follow the motion in far greater detail and 2) the motion of a sphere normal to a plate is axisymmetric, meaning that mathematical models are 2D. In contrast, the lateral motion of pairs of particles is inherently a 3D problem.

Effect of Frequency on Mean Elevation

4.6 or 6.2 μm PS bead in 0.13 mM over ITO Electrode (5 Vpp)

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There are even more striking differences in behavior with electrolyte choice when frequency is varied rather than amplitude. In KOH the particle is drawn closer to the electrode at virtually all frequencies and in bicarbonate the particle is pushed away at all frequencies.

In nitric acid, a reversal is observed at a moderate frequency. Unfortunately, we do not yet have the corresponding aggregation behavior.

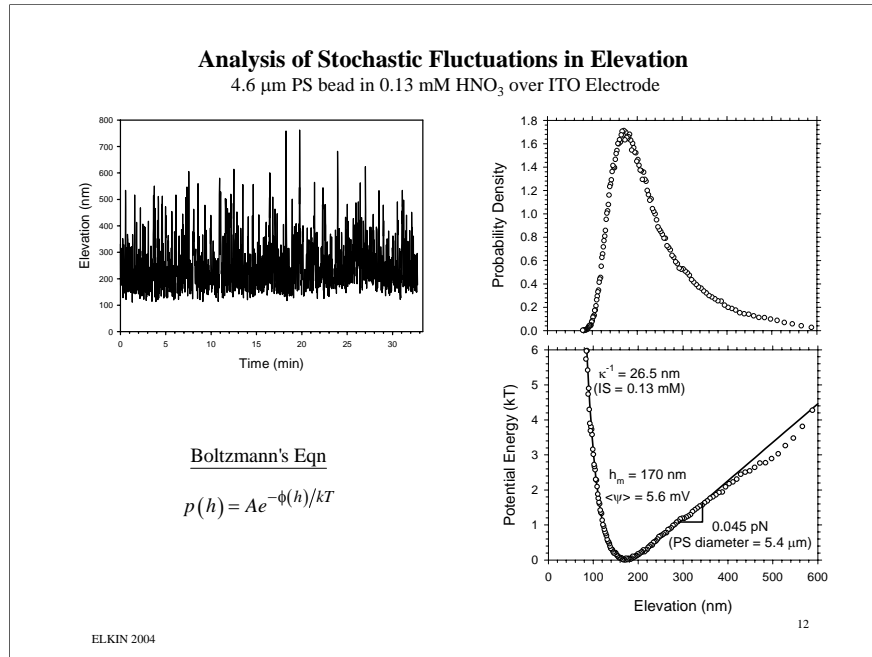Notice that at very high frequencies, all of the electrolytes show the particle tending to the no-field elevation.

20-minute talk presented in the session on "Electrokinetic Self-Assembly" at the International Electrokinetics Conference, Pittsburgh, PA, June 14, 2004.

Brownian Motion Dominates at High Frequency
6 μm PS bead in 0.13 mM KOH over ITO Electrode (5 Vpp)

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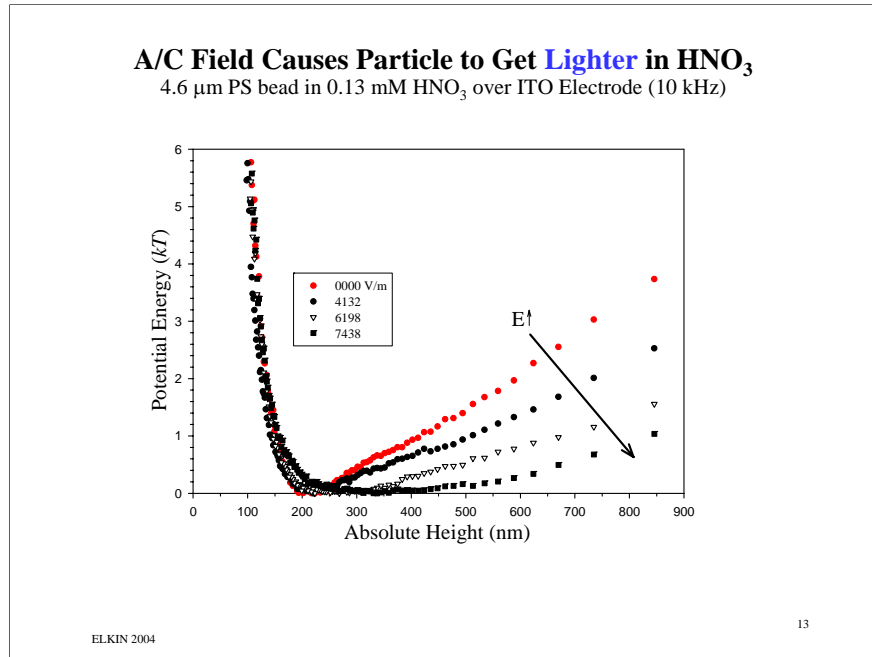
By contrast, at high frequencies, the motion appears to be primarily stochastic again. If it is indeed stochastic, we ought to be able to apply the same analysis technique to measure interaction forces which we have applied in the absence of any electric field.

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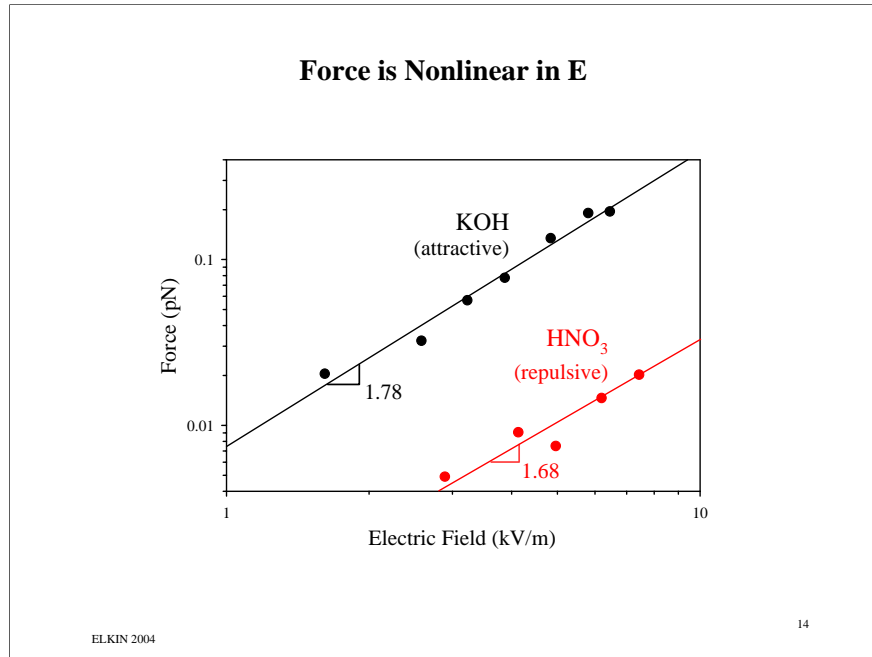
Here you see the force exerted as a function of the applied field strength. It is repulsion in nitric acid and attractive in KOH. In either case, the dependence on field strength obeys a power law with an exponent slightly less than 2.

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Slide 15

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 $\rightarrow$ current is primarily Faradaic
  - ➢ high frequency $\rightarrow$ current is primarily capacitive (non-Faradaic)

for the rest of the story ...

see poster #38 by Jeff Fagan, 6:00pm today

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