Slide 1

Effect of Wall Hinderence on Brownian Motion and Mobility:

Is the Ratio Still *kT* as Predicted by Einstein?

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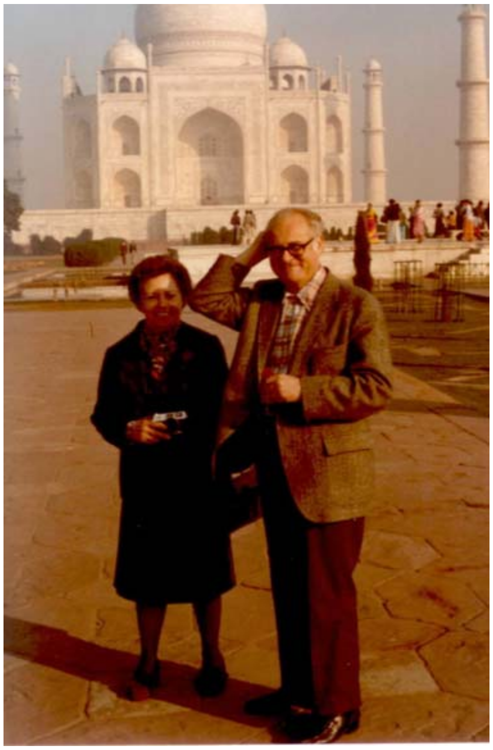
25- minute invited talk presented at session honoring Eli Ruckenstein, AIChE Annual Meeting, Cincinnati, OH, October 31, 2005.

Slide 2

early 1980’s

I was one of Eli’s first PhD students after arriving at the UofD in the fall of 1970. Unfortunately, I was unable to find any photos from that time period, but I did locate a few from the early 1980’s – a few years after I finished my degree and starting teaching at Carnegie Mellon.

Slide 3



All of photos I’ll show today are from a group trip to India ... as you can guess from the backdrop of this picture of Eli and Velina

Slide 4

You might recognize a few of these faces. In back row with the beard is Rakesh Jain who was a close personal friend from my Delaware days. At this time, Rakesh was also a colleague of mine at CM. Between him and Eli is Art Westerberg who was department head then. In the front row on the left is Stan Sandler, who I believe was department head at Delaware then and next to Stan is Jimmy Wei who was Rakesh's PhD advisor at Delaware.

We went to India for Rakesh's wedding. Rakesh managed to get a grant from NSF to pay part of our travel expenses. Of course, we also had to agree to do some technical work like represent the US at a meeting on chemical engineering in developing countries. Anyway, for me at least, this was a very exciting opportunity.

Slide 5

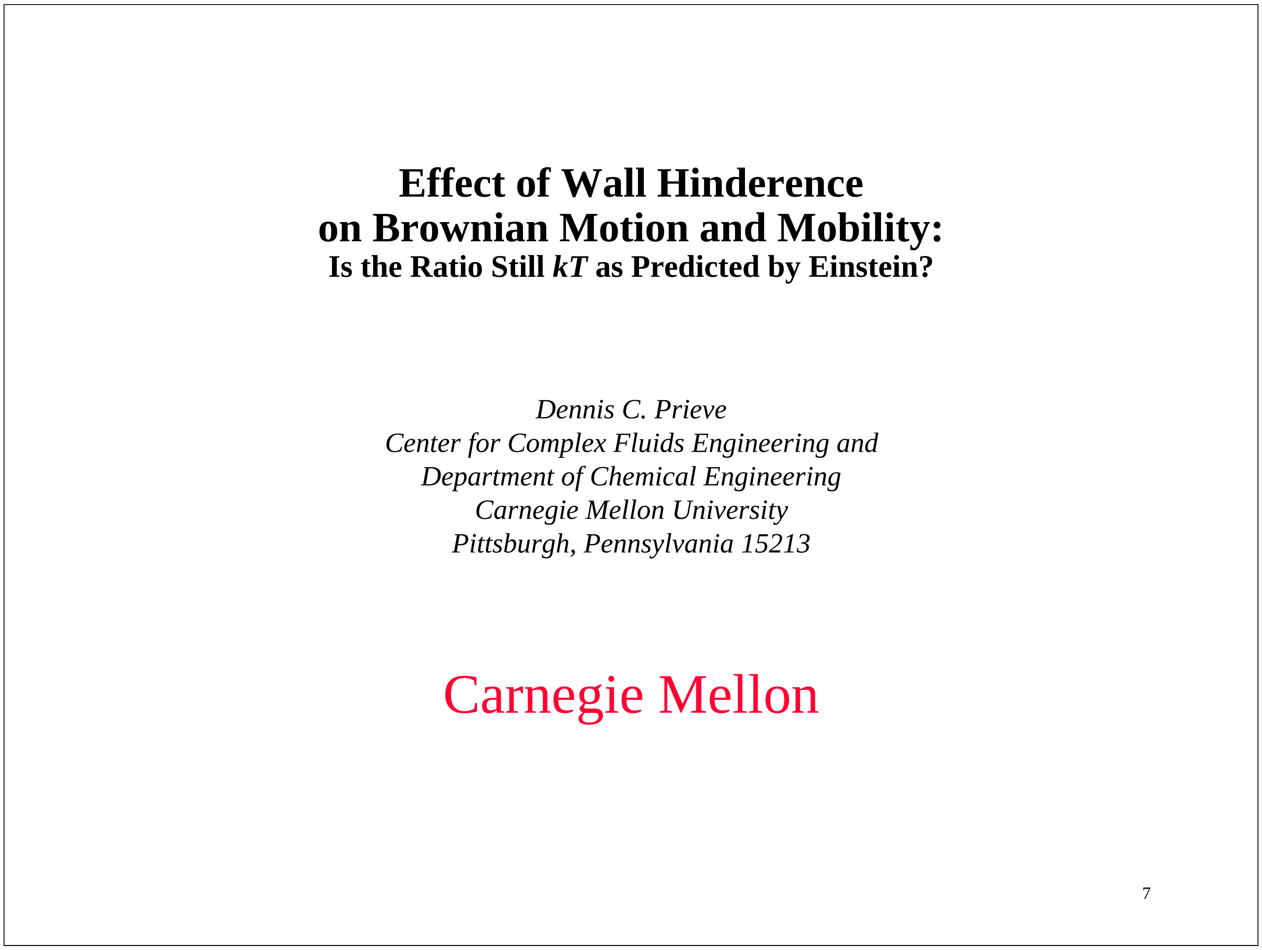
Eli and Velina represented the parents of the bride, who happened to be from Pittsburgh, although not their daughter.

Slide 6

Those of us who know Eli well, know he takes research very seriously. But he could also be playful as suggested by this last photo showing him imitating a doorman at one of the hotels where we stayed.

For me who needed lots of advice, Eli was the perfect PhD advisor. He would stop by my office 5 or 6 times per day to discuss the paper he had just read. Not all of my grad student colleagues found this attention desireable: some felt that their thesis topic was changing 5 or 6 times per day. But he and I bonded early on and I trusted that he would do nothing to harm me and everything to help me. And I was right in doing so.

Slide 7



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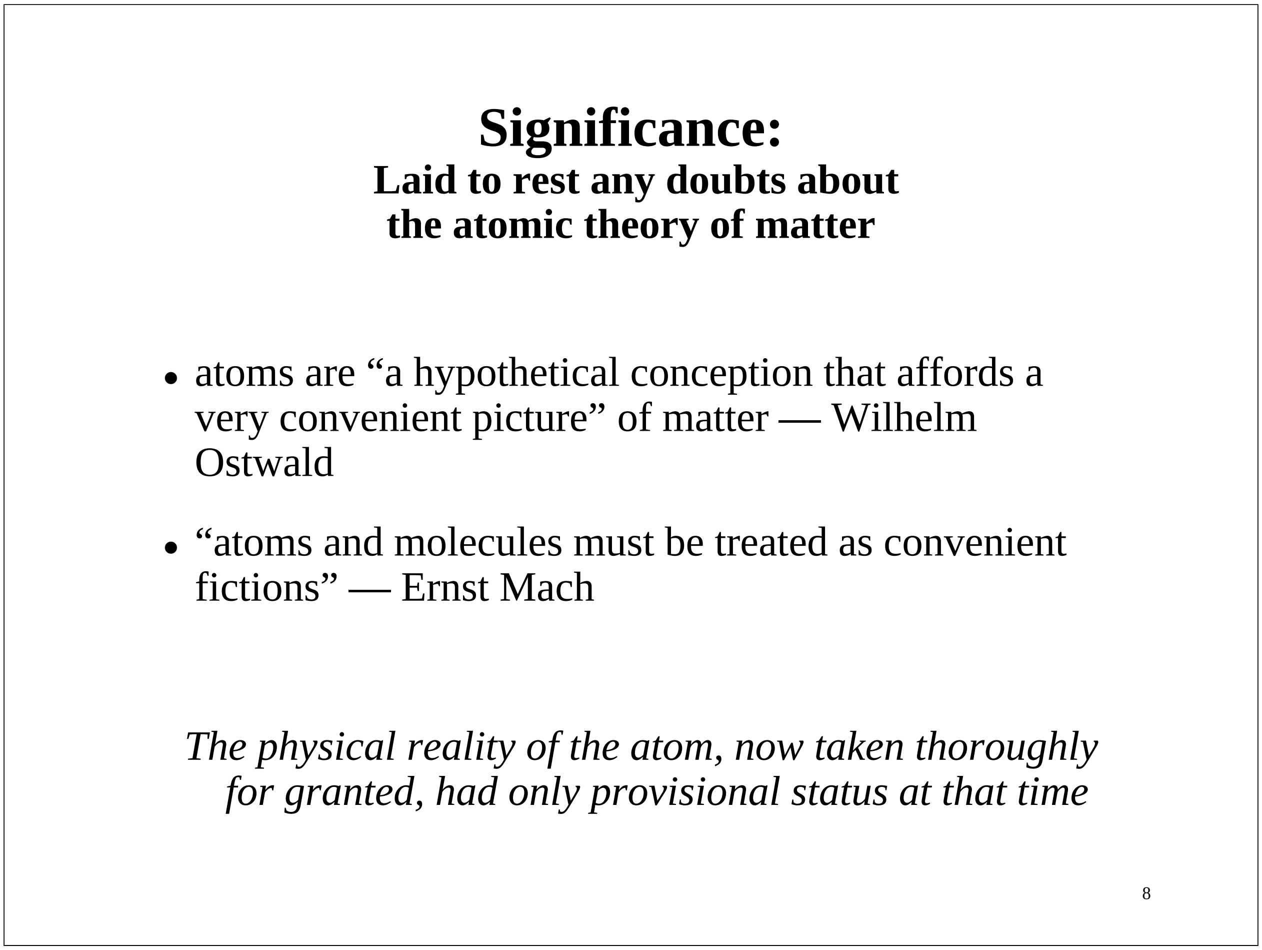
Earlier this year, I was invited to give one of a series of talks at the Physics Dept of University of Alberta on the 1905 papers written by Albert Einstein. In particular, I was asked to talk about Brownian motion.

In the remainder of my talk today, I will try to give a brief look at this paper and our own recent work.

Slide 8



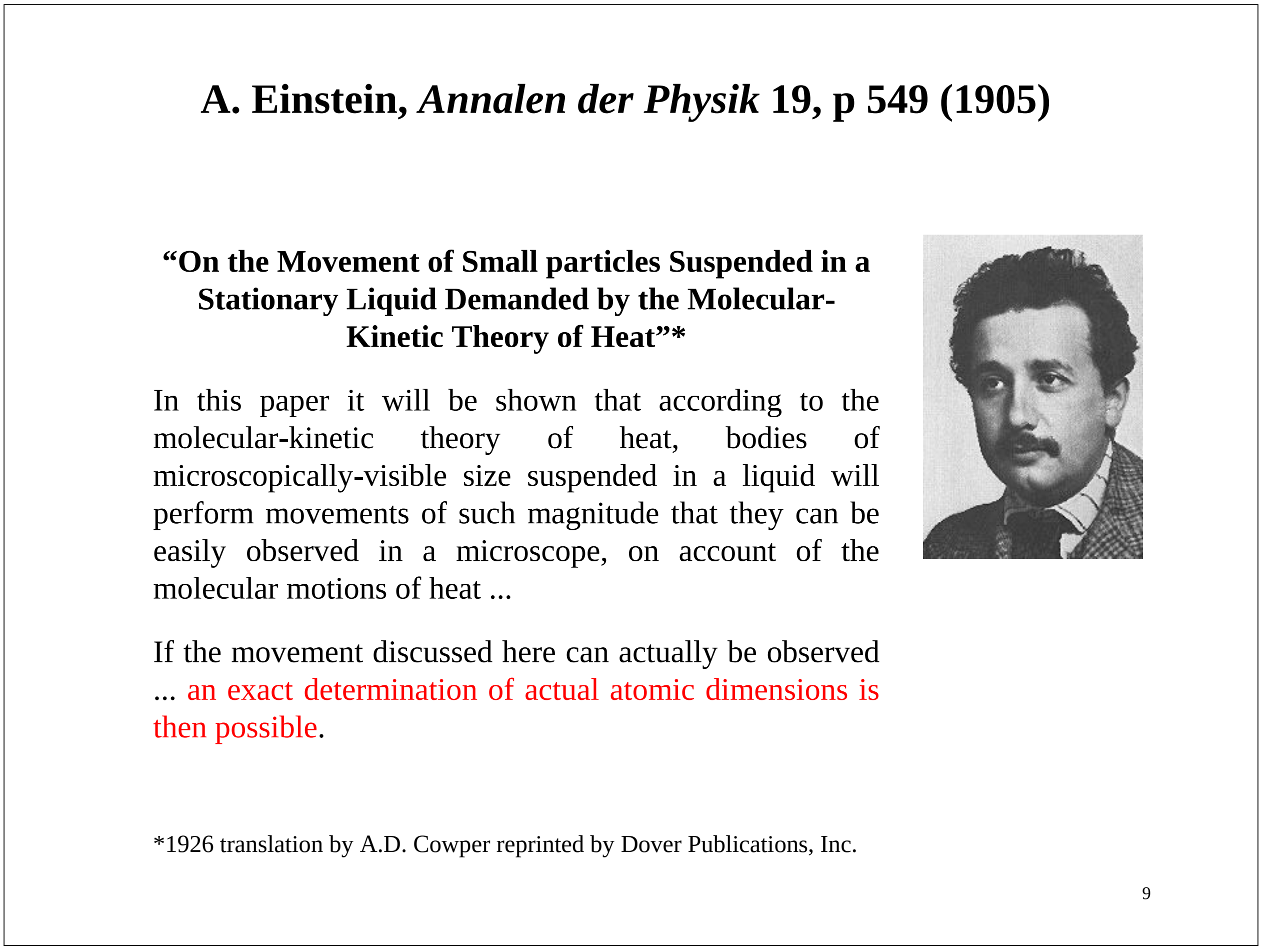
Significance:
Laid to rest any doubts about the atomic theory of matter

- atoms are “a hypothetical conception that affords a very convenient picture” of matter — Wilhelm Ostwald
- “atoms and molecules must be treated as convenient fictions” — Ernst Mach

The physical reality of the atom, now taken thoroughly for granted, had only provisional status at that time

At the turn of the 20th century, the atomic nature of matter was fairly widely accepted among scientists, but not universally. Several senior scientists of the day considered atoms and molecules to be a “convenient fiction.”

Slide 9



A. Einstein, *Annalen der Physik* 19, p 549 (1905)

“On the Movement of Small particles Suspended in a Stationary Liquid Demanded by the Molecular-Kinetic Theory of Heat”*

In this paper it will be shown that according to the molecular-kinetic theory of heat, bodies of microscopically-visible size suspended in a liquid will perform movements of such magnitude that they can be easily observed in a microscope, on account of the molecular motions of heat ...

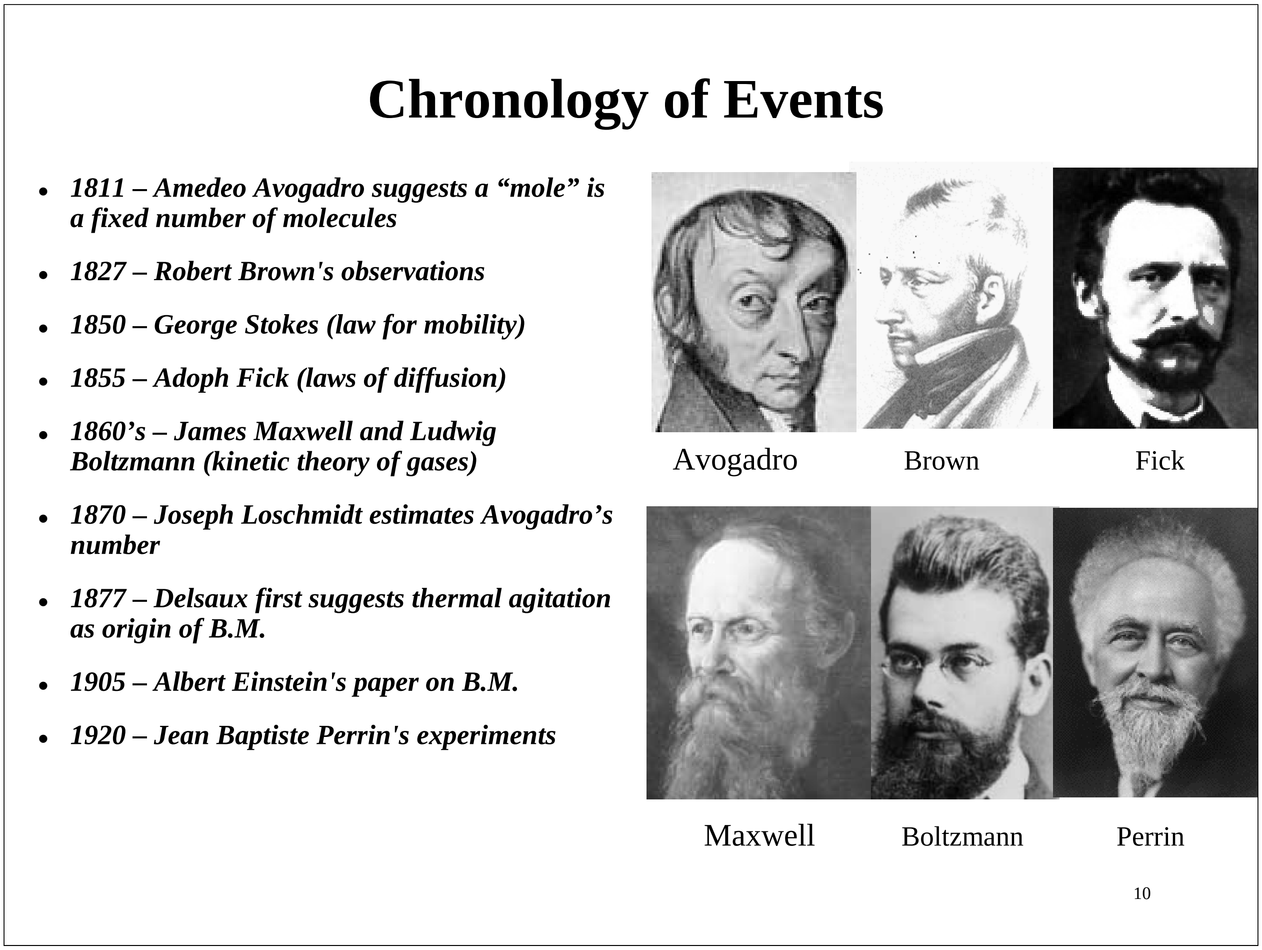
If the movement discussed here can actually be observed ... an exact determination of actual atomic dimensions is then possible.

*1926 translation by A.D. Cowper reprinted by Dover Publications, Inc.

Einstein’s 1905 paper on Brownian motion presented a theory to test this concept. In essence, Einstein suggested a method for measuring the size of single atoms and molecules. If you can measure their size, they must be real.

He predicted that microscopic particles dispersed in water would undergo random motion as a result of collisions with water molecules. Moreover, he showed how careful observations of this motion could allow estimating the mass of the water molecules.

Slide 10



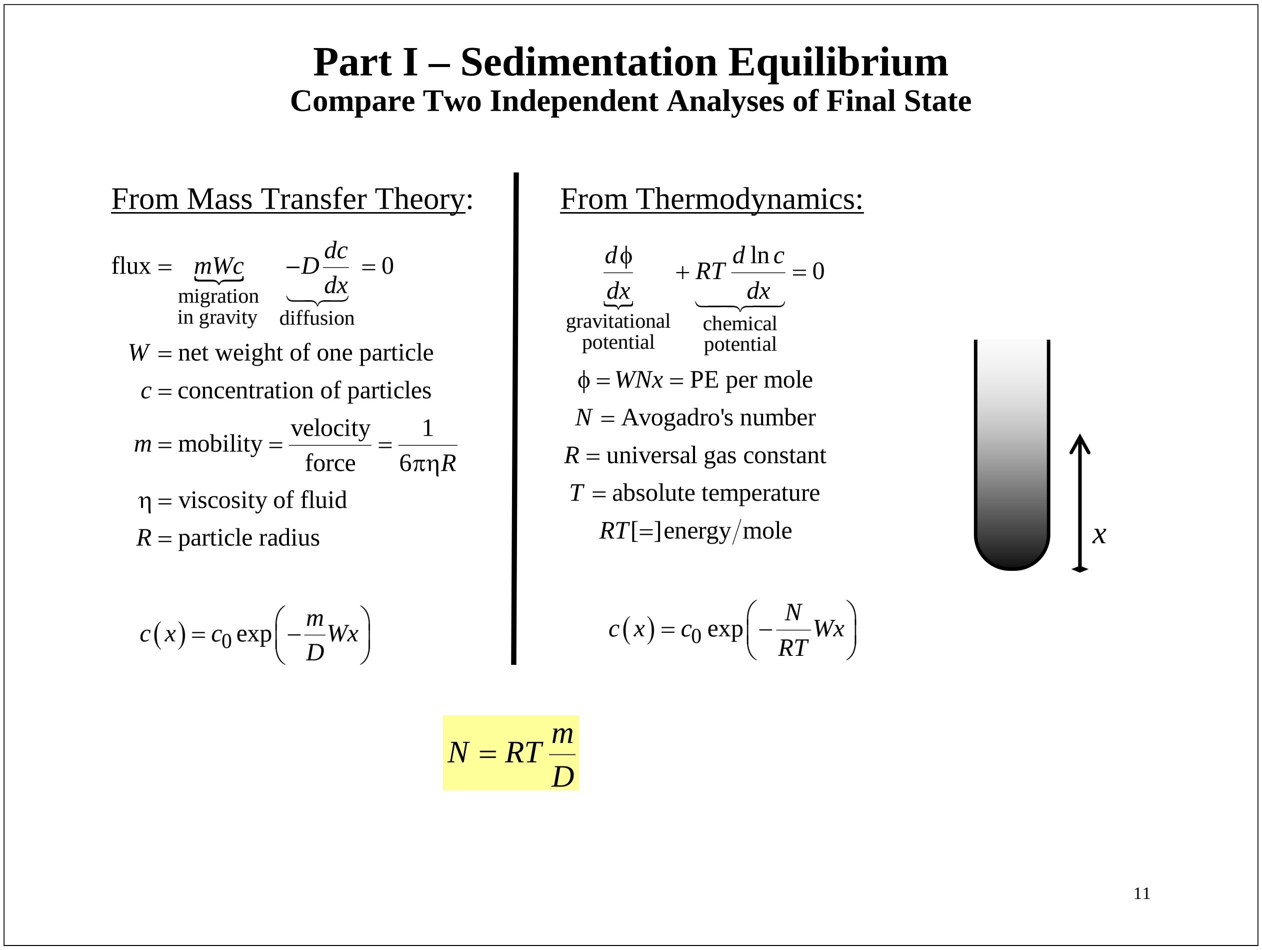
Chronology of Events

- ***1811 – Amedeo Avogadro suggests a “mole” is a fixed number of molecules***
- ***1827 – Robert Brown's observations***
- ***1850 – George Stokes (law for mobility)***
- ***1855 – Adoph Fick (laws of diffusion)***
- ***1860’s – James Maxwell and Ludwig Boltzmann (kinetic theory of gases)***
- ***1870 – Joseph Loschmidt estimates Avogadro’s number***
- ***1877 – Delsaux first suggests thermal agitation as origin of B.M.***
- ***1905 – Albert Einstein's paper on B.M.***
- ***1920 – Jean Baptiste Perrin's experiments***

Avogadro Brown Fick

Maxwell Boltzmann Perrin

Eli instills in his students the importance of history and knowing the literature in any subject. The history in this subject is quite rich but, in the interest of time, I will only list some of the landmarks in this journey.



Part I – Sedimentation Equilibrium

Compare Two Independent Analyses of Final State

From Mass Transfer Theory:

$$\text{flux} = \underbrace{mWc}_{\substack{\text{migration}\\ \text{in gravity}}} \underbrace{-D\frac{dc}{dx}}_{\text{diffusion}} = 0$$

W = net weight of one particle

c = concentration of particles

$m = \text{mobility} = \dfrac{\text{velocity}}{\text{force}} = \dfrac{1}{6\pi\eta R}$

η = viscosity of fluid

R = particle radius

$$c(x) = c_0 \exp\left(-\frac{m}{D}Wx\right)$$

From Thermodynamics:

$$\underbrace{\frac{d\phi}{dx}}_{\substack{\text{gravitational}\\ \text{potential}}} + \underbrace{RT\frac{d\ln c}{dx}}_{\substack{\text{chemical}\\ \text{potential}}} = 0$$

$\phi = WNx$ = PE per mole

N = Avogadro's number

R = universal gas constant

T = absolute temperature

$RT[=]\text{energy}/\text{mole}$

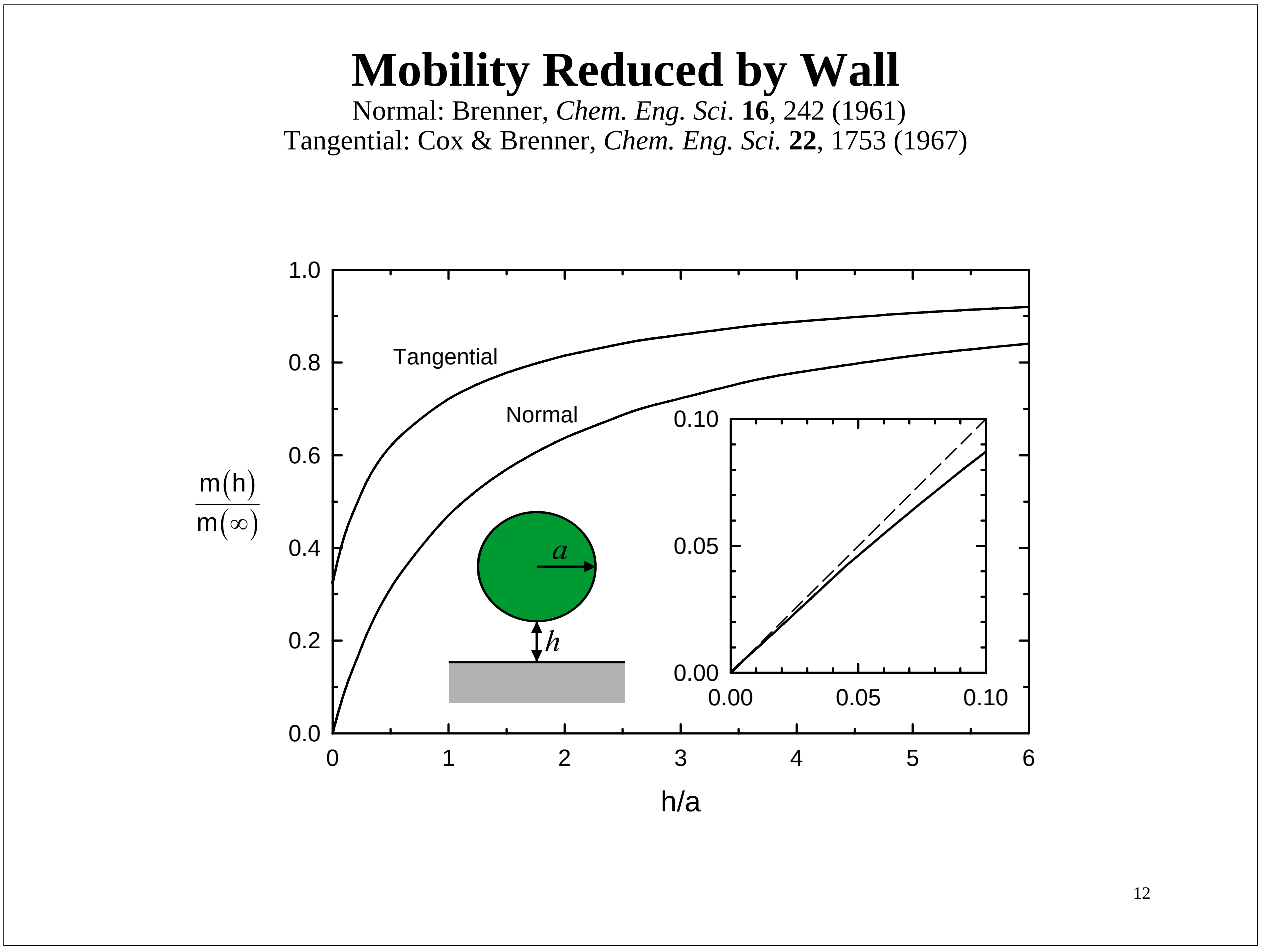
$$c(x) = c_0 \exp\left(-\frac{N}{RT}Wx\right)$$

$$N = RT\frac{m}{D}$$

Einstein suggested that Avogadro's number could be deduced by comparing two analyses of sedimention equilibrium: the thermodynamic approach or equilibrium theory and the mass transfer approach or dynamics theory. Both predict an exponential decay for the steady-state concentration particle profile for dense Brownian particles in a gravitational field.

By equating the coefficients of x in the two expressions, you can deduce Avogadro's number N from this simple ratio of the hydrodynamic mobility to the diffusion coefficient. For microscopic particles, these two quantities can be independently measured. The experiments were performed by Perrin some 15 years later.

Slide 12

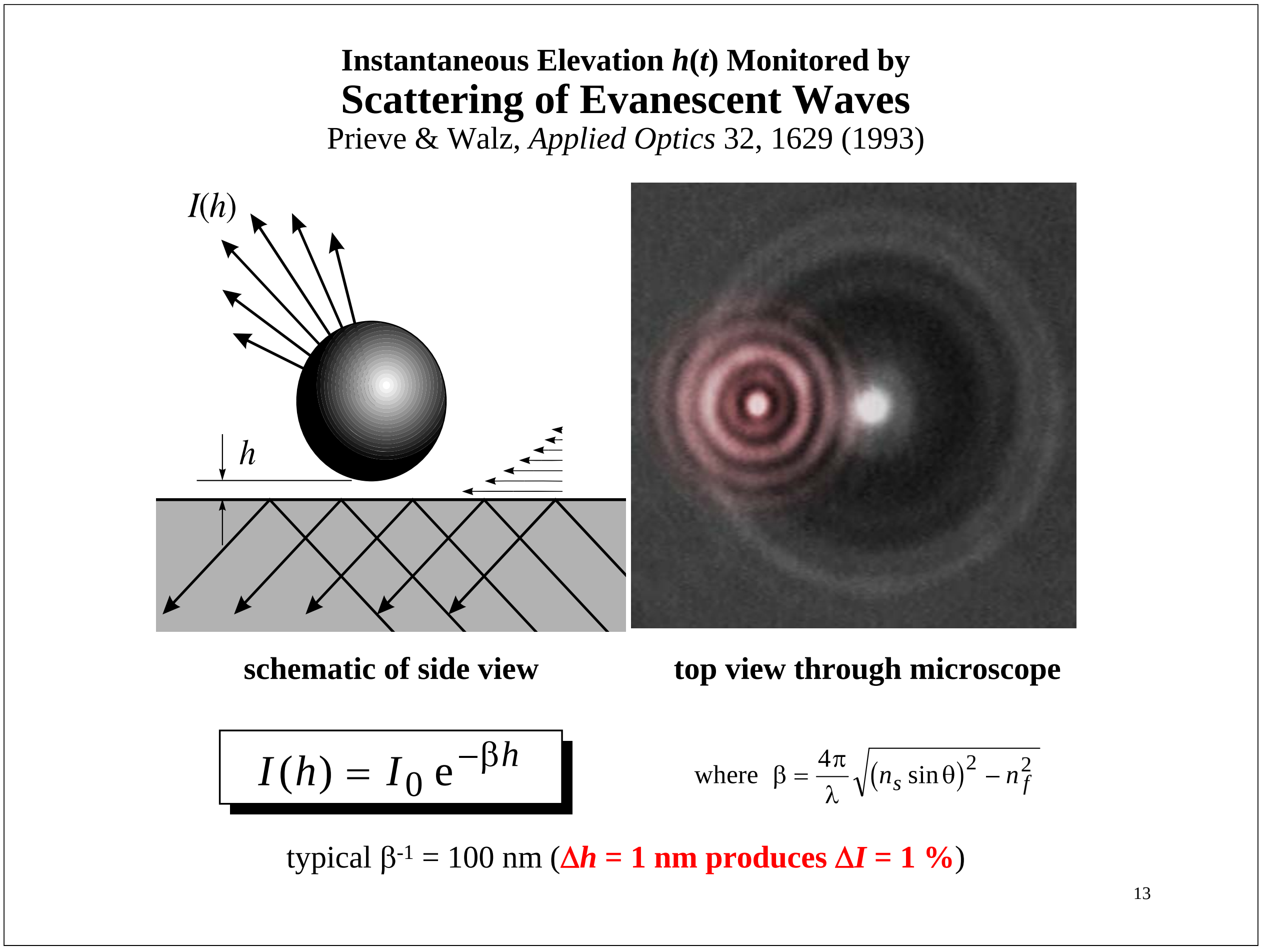


Mobility Reduced by Wall

Normal: Brenner, *Chem. Eng. Sci*. **16**, 242 (1961)
Tangential: Cox & Brenner, *Chem. Eng. Sci.* **22**, 1753 (1967)

My own work on this problem deals with the hinderence effect of nearby walls on the diffusion coefficient and mobility of particles. The effect on hydrodynamic mobility was calculated by Howard Brenner by solving Stokes' equation in this sphere-plate geometry.

Slide 13



Instantaneous Elevation *h*(*t*) Monitored by

Scattering of Evanescent Waves

Prieve & Walz, *Applied Optics* 32, 1629 (1993)

schematic of side view

top view through microscope

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

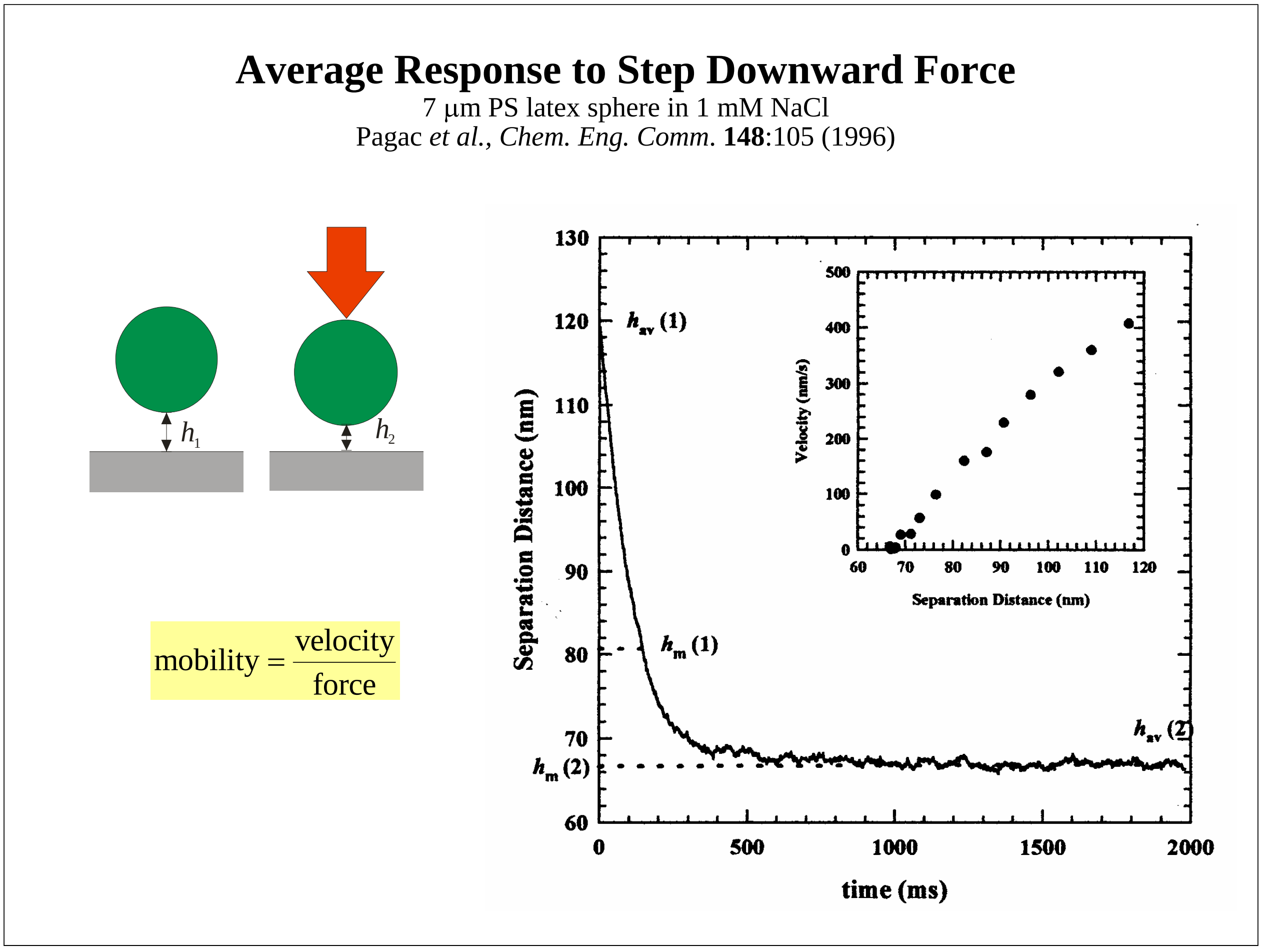
where $\beta = \frac{4\pi}{\lambda}\sqrt{(n_s \sin\theta)^2 - n_f^2}$

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

We are able to measure both the mobility and diffusion coefficient of single Brownian sphere very near a wall using Total Internal Reflection Microscopy.

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.



Average Response to Step Downward Force

7 µm PS latex sphere in 1 mM NaCl

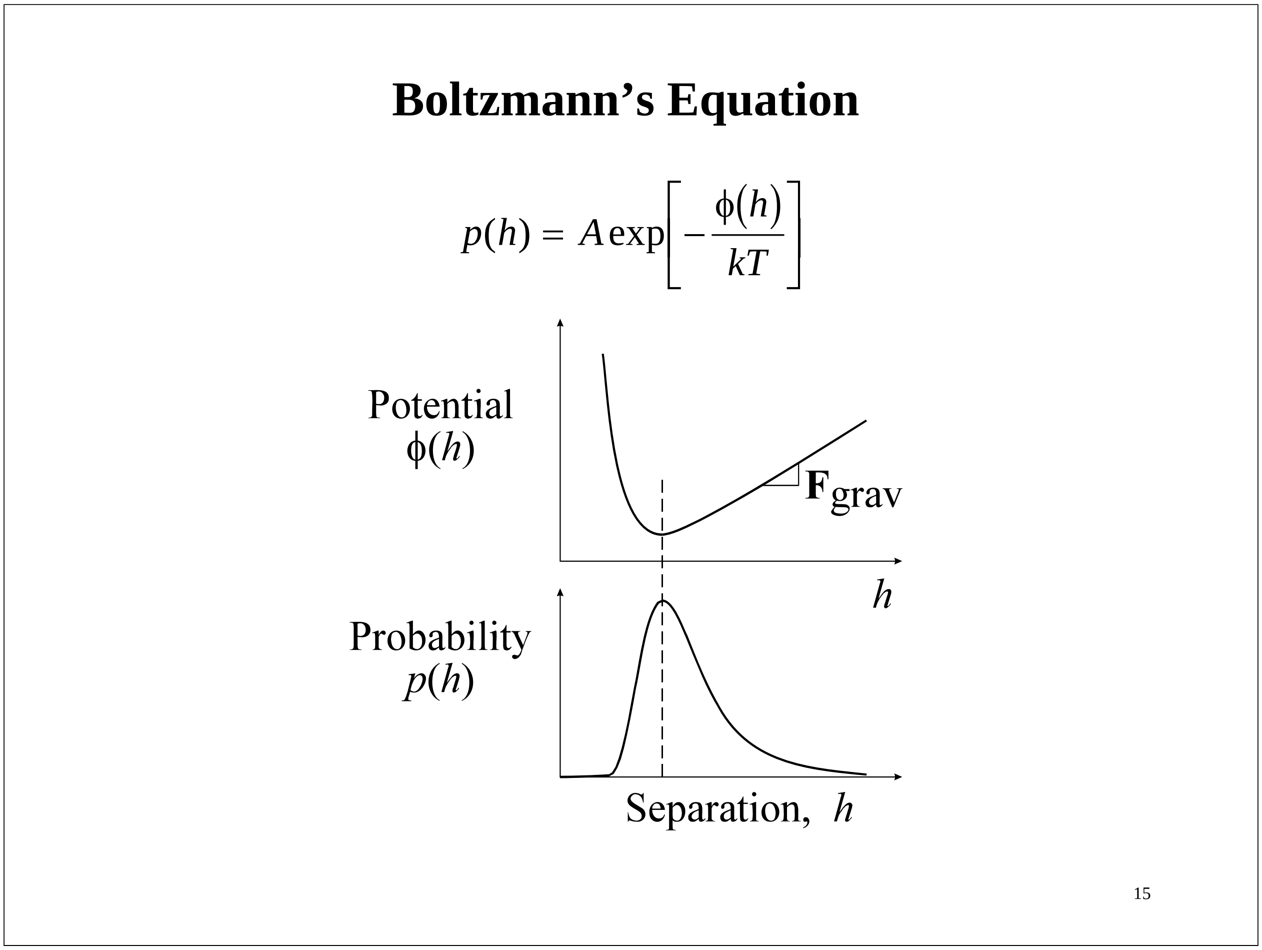
Pagac *et al.*, *Chem. Eng. Comm.* **148**:105 (1996)

$$\text{mobility} = \frac{\text{velocity}}{\text{force}}$$

The mobility is determined by observing how the elevation changes in response to a force being applied. In this experiment, the force is exerted by a laser beam focussed on the top of the sphere.

Using the known exponential relationship between scattering intensity and elevation, we can convert the average intensity-versus-time into this plot of average separation distance-versus-time. The elevation changes from the most probable one for the forces present before the step change to the most probably one for the forces present after the step change.

Differentiating this gives the velocity-versus-separation shown in the insert. If I have time I'll come back to the form which this insert takes. But for now, I'll just note that initial velocity at the larger separation by the step-change in the force that caused it, I get the hydrodynamic mobility of the particle.



Boltzmann's Equation

$$p(h) = A\exp\left[-\frac{\phi(h)}{kT}\right]$$

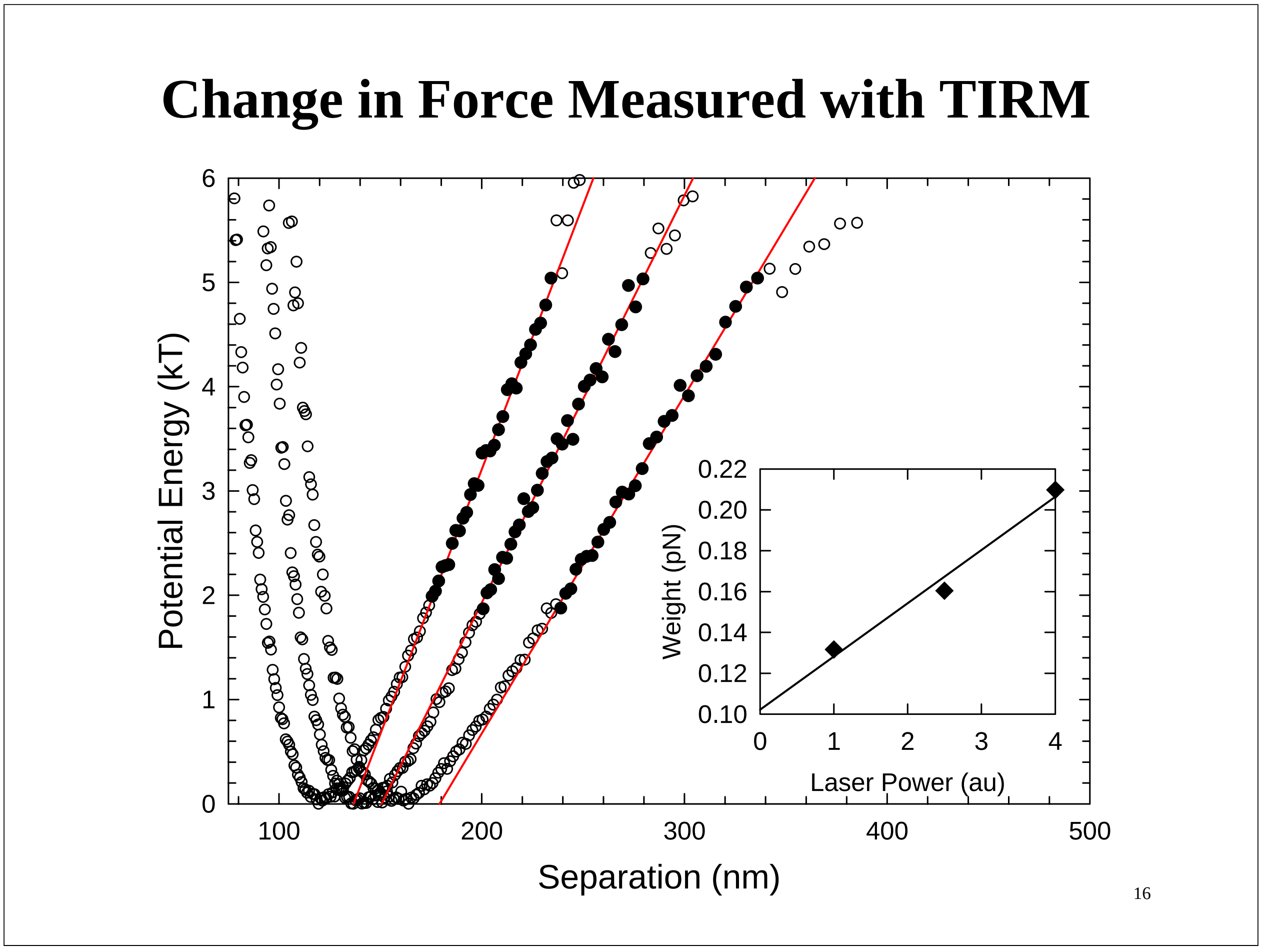
To determine how much force we are exerting on the sphere with the laser beam, we observe the equilibrium distribution of elevations assumed by Brownian motion – both with and without the laser beam.

If only gravity and double-layer repulsion act, the potential energy profile should look something like I've shown here. When the particle is far from the plate -- outside the range of double-layer repulsion -- the slope of the curve corresponds to gravity. At smaller separations between the sphere and the plate, repulsion dominates.

The Boltzmann distribution means that, the lower the particle's potential energy at a given location, the more likely it is to find the particle at that location. Thus the most probable location corresponds to the bottom of the potential energy well, where gravity and double-layer repulsion are equal.

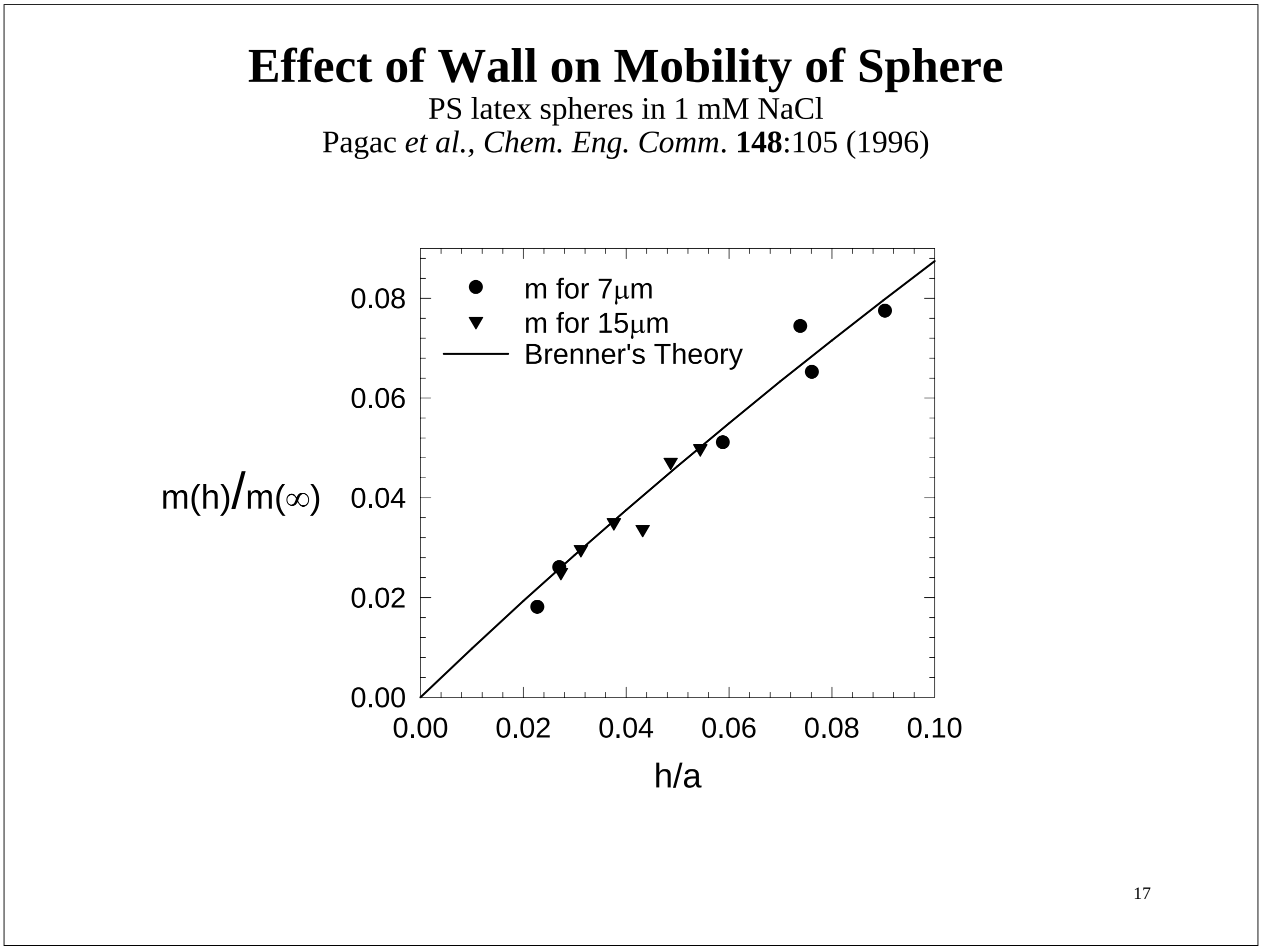
Thus if we can measure this probability density by repeatedly observing the elevation of the particle above the plate, we can deduce the potential energy profile using Boltzmann's equation. This is the basis of our technique.

The difficulty is that this "h" is a very small distance. In the results which I'll show in a minute, h is a few tenths of a micron, which is a few thousand Angstroms. Since this is smaller than the wavelength of visible light, it cannot be directly observed through an optical microscope. Since the sphere itself is not much larger than the wavelength, I also cannot use interferometry.



Change in Force Measured with TIRM

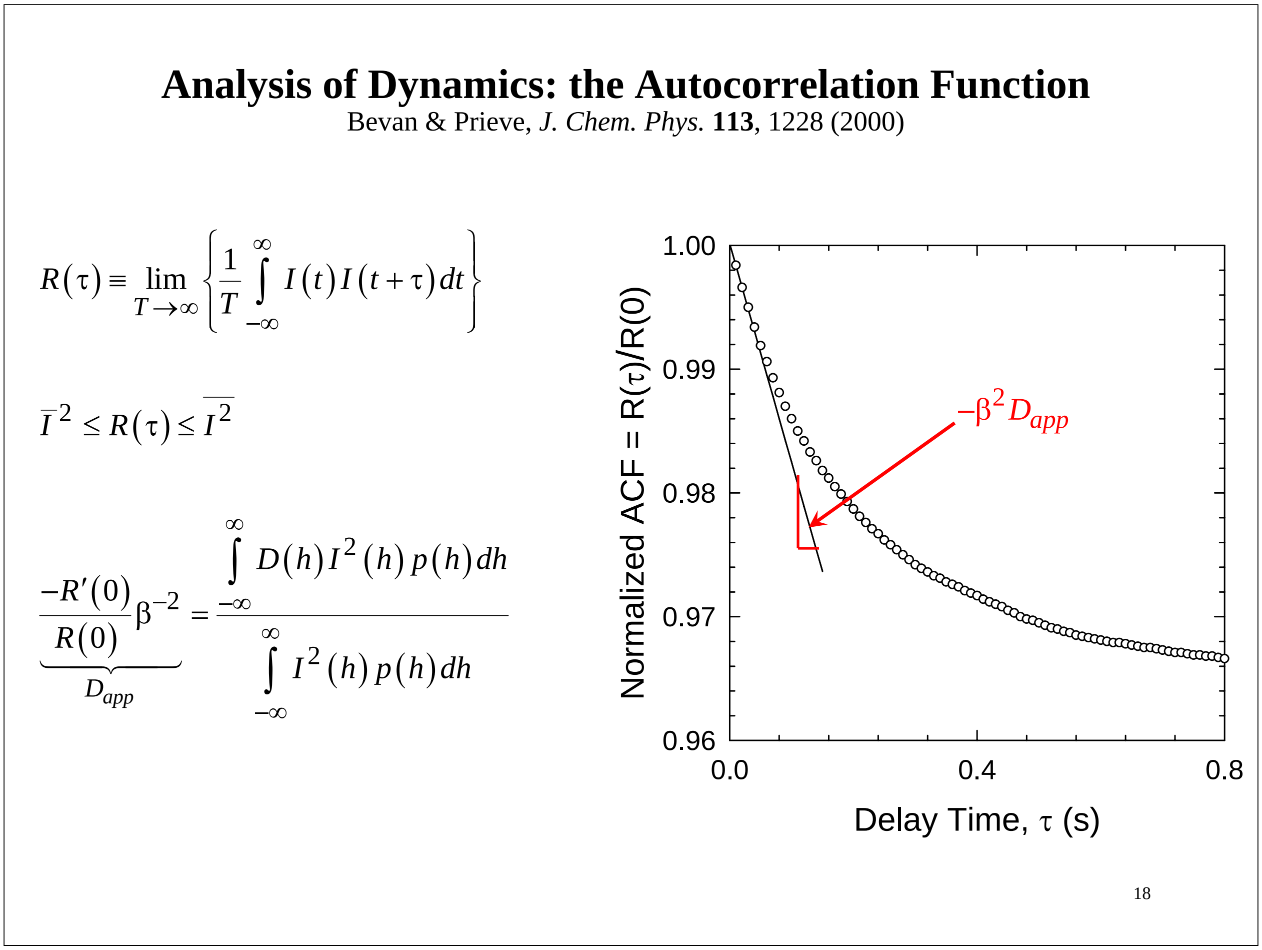
The downward force exerted by the laser beam increases the apparent weight of the sphere, which can be measured by fitting a straight line (shown in red) to the linear portion of the profile at large separations. The slope of this red line gives the apparent net weight.



Effect of Wall on Mobility of Sphere

PS latex spheres in 1 mM NaCl
Pagac *et al., Chem. Eng. Comm*. **148**:105 (1996)

Here are the results for the mobility. The y-axis is the ratio of the mobility measured near the wall to the mobility expected far from the wall (latter is calculated from Stokes' law). Note that the mobilites are severely hindered by the presence of the nearby wall.



Analysis of Dynamics: the Autocorrelation Function

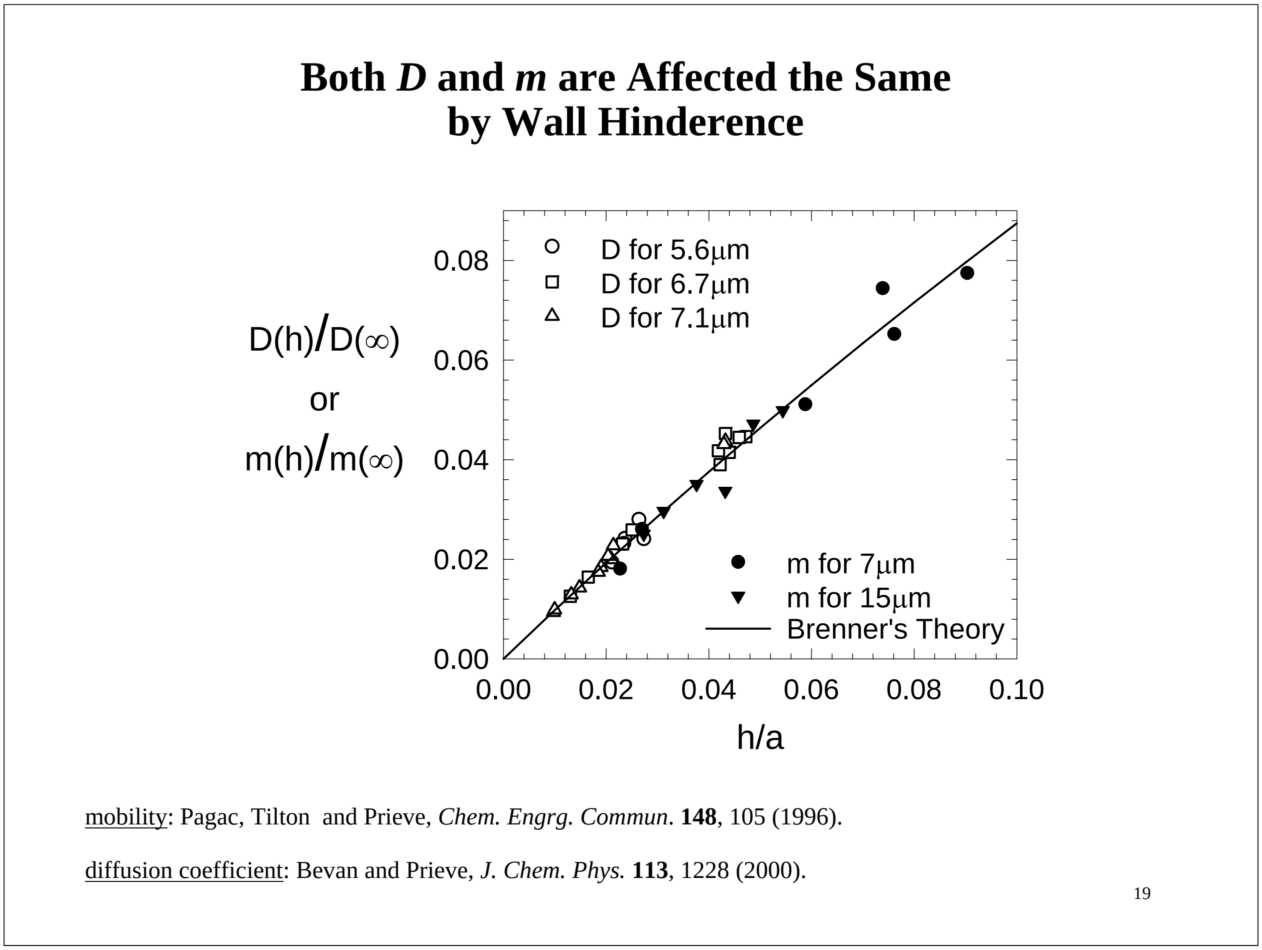
Bevan & Prieve, *J. Chem. Phys.* **113**, 1228 (2000)

$$R(\tau) \equiv \lim_{T\to\infty}\left\{\frac{1}{T}\int_{-\infty}^{\infty} I(t)\, I(t+\tau)\, dt\right\}$$

$$\bar{I}^2 \le R(\tau) \le \overline{I^2}$$

$$\underbrace{\frac{-R'(0)}{R(0)}\beta^{-2}}_{D_{app}} = \frac{\int_{-\infty}^{\infty} D(h)\, I^2(h)\, p(h)\, dh}{\int_{-\infty}^{\infty} I^2(h)\, p(h)\, dh}$$

To obtain the diffusion coefficient, we analyze the dynamics of Brownian motion by calculating the autocorrelation function for scattering intensity. The correlation between two intensity measurements taken a time τ apart is expected to decay monotonically with τ. The initial slope is proportional to the diffusion coefficient.



Both *D* and *m* are Affected the Same by Wall Hinderence

mobility: Pagac, Tilton and Prieve, *Chem. Engrg. Commun.* **148**, 105 (1996).

diffusion coefficient: Bevan and Prieve, *J. Chem. Phys.* **113**, 1228 (2000).

This slide summarizes are measurements of hindered diffusion coefficients on the same slide used to summarize our measurements of hindered mobility. Clearly the fraction by each is reduced as a result of wall hinderence is the same. Thus Einstein's predicted proportionality between mobility and diffusion coefficient (i.e. D = mkT) continues to hold even in the presence of severe wall hinderence.

Conclusions

- **Einstein showed that Avogadro’s number could be determined by measuring *D* and *m* for the same species:**

$$N = RT\,\frac{m}{D}$$

- **Success of Einstein’s theory served as strong confirmation of atomic theory of matter**
- **We showed that this also holds in presence of severe hinderance from nearby wall**