Slide 1

Effect of Wall Hinderence on Brownian Motion and Mobility:

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

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In my talk today, I will first summarize briefly Einstein’s 1905 paper on Brownian motion and discuss its signifance for science. Then I will describe my own recent work on Brownian motion which is hindered by the presence of a nearby wall.

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 convenient fictions” — Ernst Mach

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

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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 3

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.

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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.

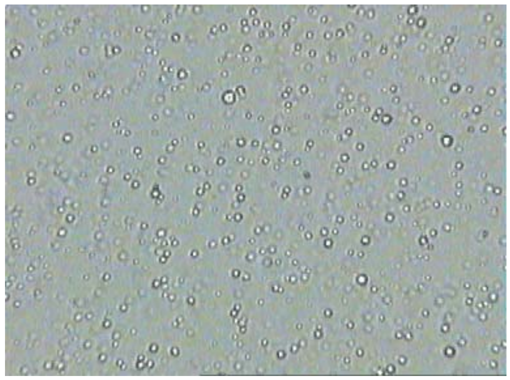
He predicted that microscopic particles dispersed in water would undergo random motion as a result of collisions with water molecules. Moreover, he showed how careful observations of this motion could allow estimating the mass of the water molecules.

Slide 4

Video of Brownian Motion

fat droplets (0.5 – 3 μm) in milk
(http://www.microscopy-uk.net/dww/home/bmhq1.avi)

Click to start movie



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So what is Brownian motion? Here is a video clip I downloaded from the web which shows what we now call Brownian motion of fat particles in milk. If you look carefully, you see that larger particles jiggle more slowly than smaller particles.

Chronology of Events

- ***1827 – Robert Brown's observations***
- ***1850 – Stokes Law for mobility***
- ***1855 – Fick's laws of diffusion***
- ***1860’s – Maxwell and Boltzmann develop kinetic theory of gases***

Brown

Fick

Maxwell

Boltzmann

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Although Einstein was unaware of it, such random motion of tiny particles had been reported in the scientific literature much earlier. The name “Brownian motion” is used to describe this phenomena, which is named after Robert Brown, a British botantist who was the first to claim in 1827 – almost 80 years before Einstein’s paper -- that even dead particles like these fat droplets could exhibit this motion. Before this, most observers of such motion attributed motion to life.

In Einstein’s theory which I will summarize in a minute, he cites the main results of Sir Gabriel Stokes and Adolph Fick. In particular, we know now that Fick’s laws of diffusion represent a continuum model for Brownian motion. But you don’t need to believe in molecules to accept Fick’s laws.

In the 1860’s Maxwell and Boltzmann developed the kinetic theory of gases, which is a comprehensive and molecular description of gases. For example, the theory allowed one to calculate the mean-free path between collisions of gas molecules as well as the frequency of collision.

a “mole” of material

- significance – a mole of any gas occupies 22.4 liters of volume at 1 atm, 0^{o}C
- a mole of oxygen gas weighs 32 grams whereas a mole of hydrogen gas weights only 2 grams
- in 1811, Avogadro suggested that a mole represented a fixed number of atoms or molecules

Avogadro’s Number (a.k.a. Loschmidt’s Number)

- definition – the number of atoms in 12 grams of carbon
- value – 6.0221415×10^{23} (from NIST’s website)
- named after Amadeo Avogadro (1776-1856) who in 1811 suggested such a number existed
- Joseph Loschmidt (1821-1895) estimated the value in 1870 using kinetic theory and density of condensed gases (obtained 4×10^{23})

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To understand what Einstein’s theory actually predicted, we must understand a quantity called a “mole”.

The experiments of Robert Boyle (1662) and Jacques-Alexandre-César Charles (1787) with gases established that different masses of different gases occupied the same volume. The quantity of gas which occupies 22.4 liters of volume is now known as a “mole”.

In 1811 Amedeo Avogadro suggested that a mole of any gas represents the same number of molecules. That number is today called “Avogadro’s number”.

Joseph Loschmidt first estimated this number using the kinetic theory of gases and the density of condensed liquids. His 1870 estimate is about 70% of what we currently know Avogadro’s number to be.

Slide 7

Chronology of Events

- ***1827 – Robert Brown's observations***
- ***1850 – Stokes Law for mobility***
- ***1855 – Fick's laws of diffusion***
- ***1860’s – Maxwell and Boltzmann develop kinetic theory of gases***
- ***1870 – Loschmidt estimates Avogadro’s number***
- ***1877 – Delsaux first suggests thermal agitation as origin of B.M.***
- ***1905 – Einstein's paper on B.M.***
- ***1920 – Perrin's experiments and Avogadro’s number***

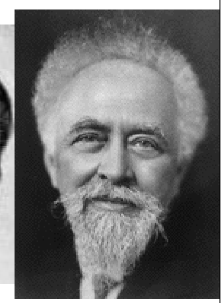

Brown


Fick


Maxwell


Boltzmann


Avogadro


Perrin

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So in 1870 Loschmidt estimates Avogadro’s number. The first published suggestion that Brownian motion is caused by thermal agitation was in 1877, followed by Einstein’s theory in 1905. But it was left to Perrin to actually perform the experiments suggested by Einstein in 1920.

Slide 8

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

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

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

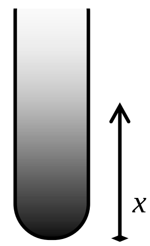
N = Avogadro's number

R = universal gas constant

T = absolute temperature

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

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



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

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Imagine that the microscopic particles whose Brownian motion is going to be measured are heavier than the water they are dispersed in. Then they will tend to settle toward the bottom of the container. But because of Brownian motion or diffusion they do not simply rest on the bottom, but eventually distribute themselves so that the concentration of particles is higher near the bottom (as suggested by the gray-scale in this sketch). This is called “sedimentation equilibrium.

Einstein’s method of determining Avogadro’s number is based on two independent analyses of the concentration profile. First, from mass transfer theory we have the migration of particles downward in the gravitational field and diffusion upward caused by the higher concentration near the bottom. At steady state, the two rates must be equal and opposite so there is no net flux of particles in either direction.

Integrating this differential equation, you obtain a concentration profile for the particles which decays exponentially as you move up from the bottom.

The second analysis is thermodynamic: the particles will distribute themselves at equilibrium so that their free energy per mole is the same at all elevations. There are two contributions to free energy: the gravitational potential energy and their chemical potential which is proportional to the logarithm of concentration. This yields another differential equation which also integrates to yield an exponential concentration profile.

Clearly the two exponentials must be equal if both analyses are correct. Equating the two exponents yields an equation which can be solved for N: Avogadro’s number. This equation involves the universal gas constant R and temperature T whose values were well known in the late 1800’s. So if we can measure the mobility and diffusion coefficient of the same particles, then we can calculate avogadro’s number.

The mobility itself can be caculated from Stokes’ law provided you can measure the diameter of the particles. This leaves just the diffusion coefficient of the particles which Einstein suggested could be measured by observing Browian motion.

Part II – Statistical Analysis of B.M.

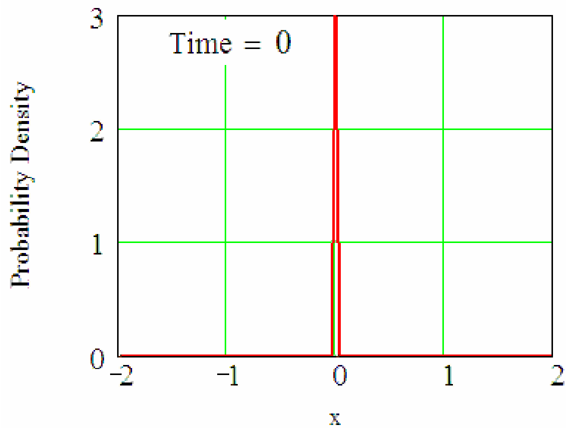
Click here to play animation

Fick's 2nd law: $\frac{\partial p}{\partial t} = D\frac{\partial^2 p}{\partial x^2}$

Initial Condition: $p(x,0) = \delta(x)$

B.C.'s: $p(\pm\infty,t) = 0$

$$p(x,t) = \frac{1}{\sqrt{4\pi Dt}}\exp\left(-\frac{x^2}{4Dt}\right)$$



$$1 = \int_{-\infty}^{\infty} p(x,t)\,dx \quad \text{for all } t$$

$$\bar{x}(t) = \int_{-\infty}^{\infty} x\,p(x,t)\,dx = 0$$

$$\overline{x^2}(t) = \int_{-\infty}^{\infty} x^2\,p(x,t)\,dx = 2Dt$$

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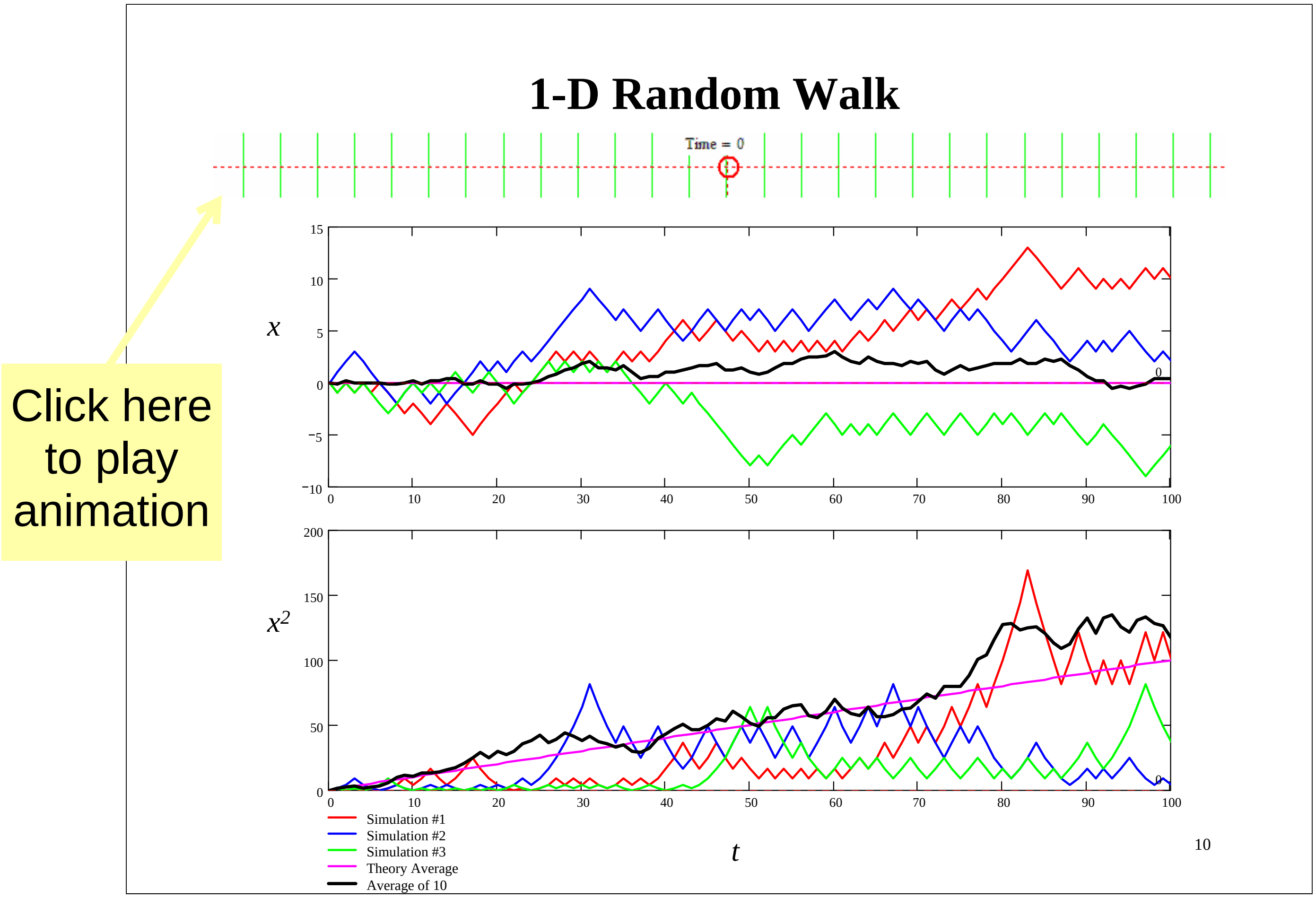
Because BM is random, it is impossible to predict how any single particle will move. But it is possible to predict the average behavior of a large number of particles. The probability of finding a particle at any location satisfies Fick's second law of diffusion from a point source. We further specify that we know for certain that the particle is located at x=0 at time t=0. The solution of this partial differential equation was well known in the late 1800's.

The probability slowly diffuses away from x=0 with time as suggested by this animation. Note that the probability is symmetric on either side of x=0.

If we integrate over all x's, we obtain unity: in other words, the particle must exist somewhere. If we weight x by the corresponding probability, we obtain an average x of zero. This just means that the particle is equally likely to diffuse in the positive direction as in the negative direction. So any positive x's are cancelled by negative x's.

But if we square x before weighting it by the corresponding probability, we obtain a non-zero mean square value. Indeed, this theory predicts that the mean-squared x must grow linearly with time and the rate of growth depends on the diffusion coefficient. This is how Einstein suggested that we can measure the diffusion coefficient of microscopic particles.

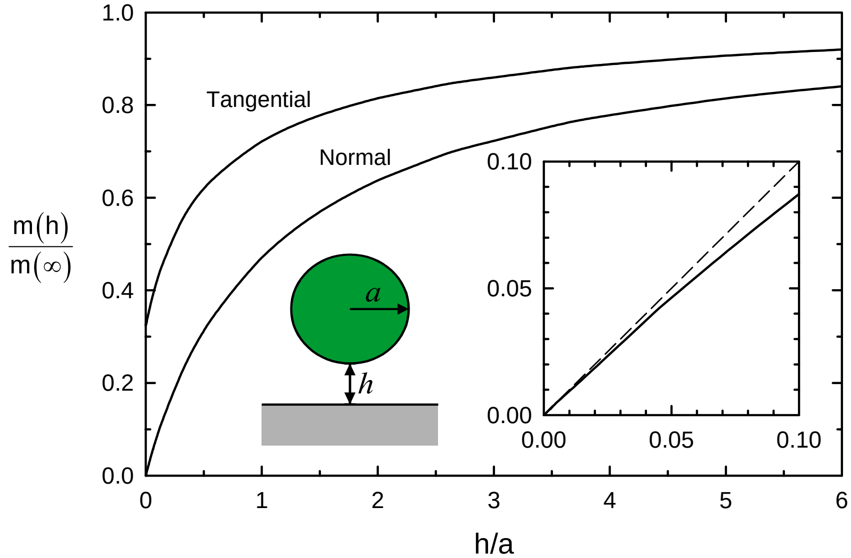


This slide summarizes some Brownian dynamics simulations for 1-D. At each time step, the particle (red circle in top graph) must move either left or right exactly one spatial increment, depending on the flip of a coin. The results for the net displacement from the origin (x) or x^2 is shown in the lower two graphs. Averaging over as few as 10 such simulations yields results in reasonable agreement with the expectations from the previous slide.

By making such observations (in 2-D), Jean Baptist Perrin was able to deduce the diffusion coefficient for single colloidal particles.

Mobility Reduced by Wall

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



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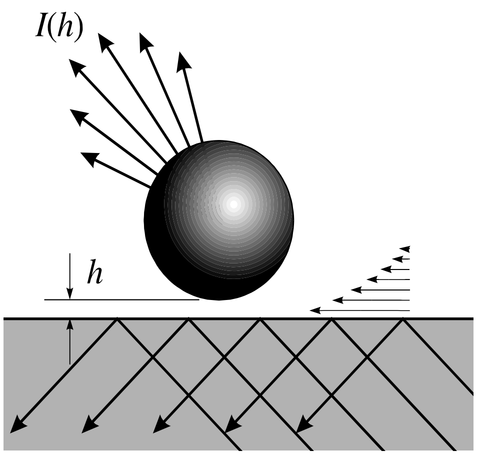
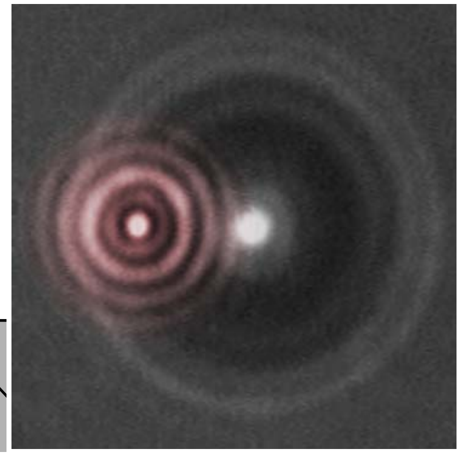
My own work on this problem deals with the hinderence effect of nearby walls on the diffusion coefficient and mobility of particles. The effect on hydrodynamic mobility was calculated by Howard Brenner by solving Stokes' equation in this sphere-plate geometry.

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**

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

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

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

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

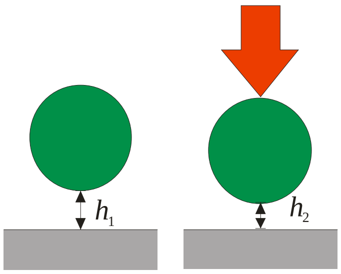
TIRM is a method to monitor fluctuations in the instantaneous distance separating a Brownian sphere and a transparent plate. We measure the scattering of light by a single sphere when it's illuminated by an evanescent wave, which is produced by reflecting a laser beam off the glass-water interface at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

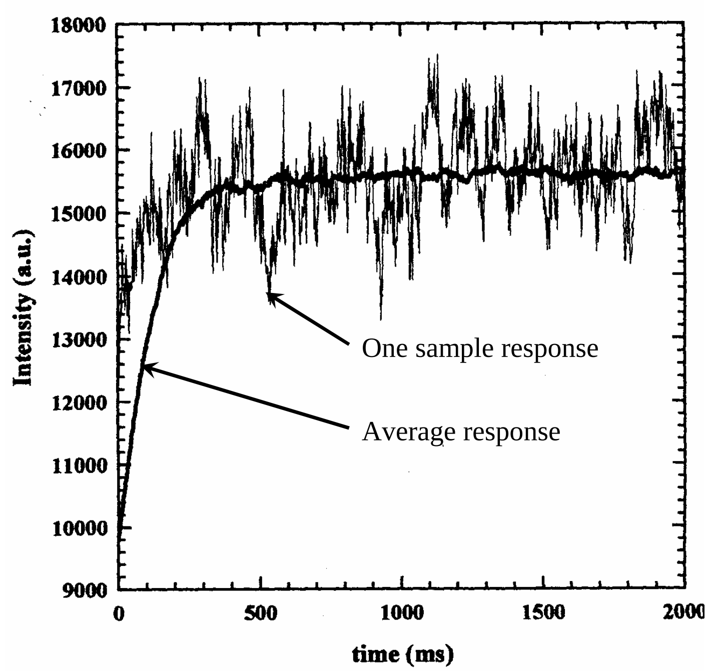
An evanescent wave propagates parallel to the interface and its amplitude decays exponentially with the distance from the interface. As a consequense, the scattering intensity also decays exponentially. Because of this exponential sensitivity, a very small change in h produces a measureable change in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

Response to a Step Downward Force

7 µm PS latex sphere in 1 mM NaCl

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



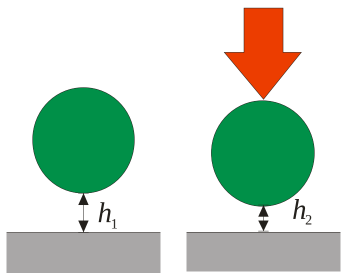


The mobility is determined by observing how the elevation changes in response to a force being applied. In this experiment, the force is exerted by a laser beam focussed on the top of the sphere.

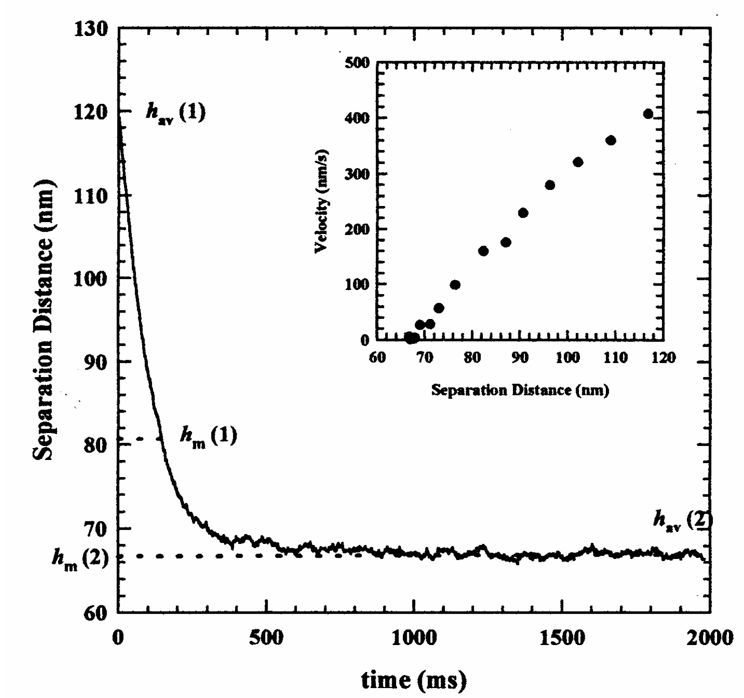
This plot shows the changes in scattering intensity which result when a step-change in the force on a 7-micron particle is exerted by blocking the beam of a laser which is focussed on the particle. Although the step-change in force is a factor of three times the net weight of the particle, the effect on intensity in a single experiment is changes due to Brownian motion. If we repeat this experiment several hundred times and average the intensity as a function of time, we get the dark smooth curve shown.

Average Response to Step Downward Force

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



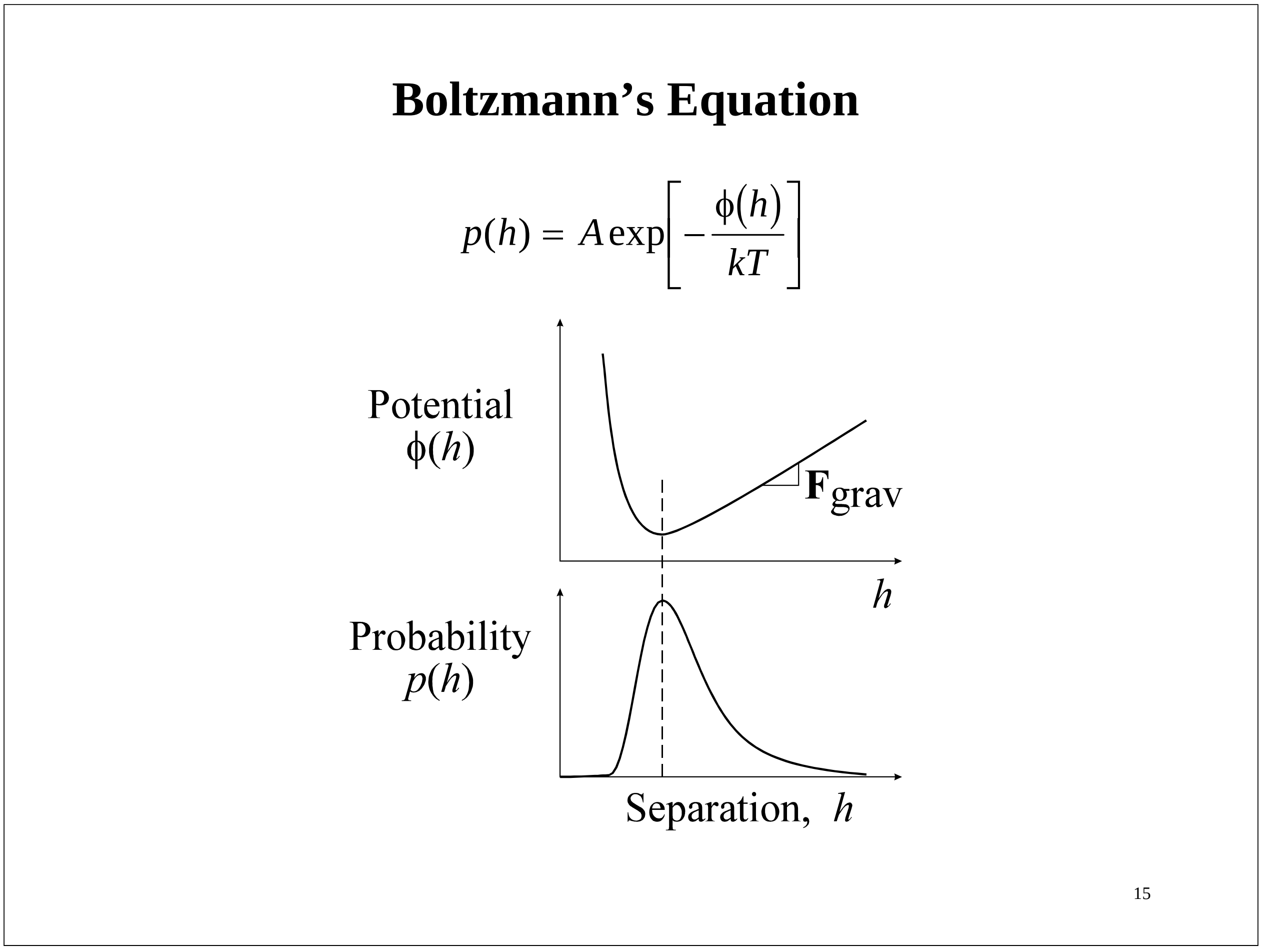
$$\text{mobility} = \frac{\text{velocity}}{\text{force}}$$



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.

Slide 15



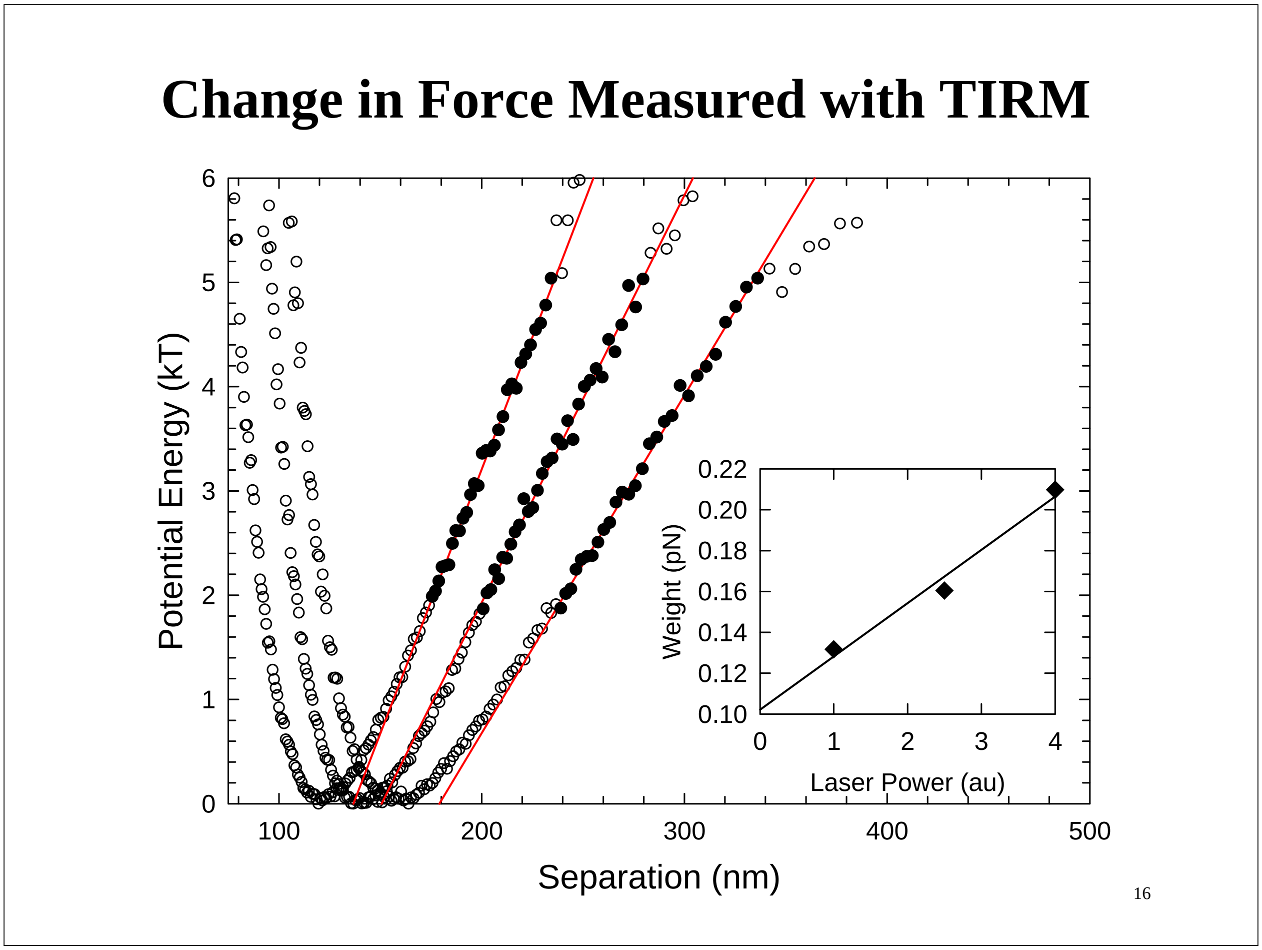
To determine how much force we are exerting on the sphere with the laser beam, we observe the equilibrium distribution of elevations assumed by Brownian motion – both with and without the laser beam.

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.

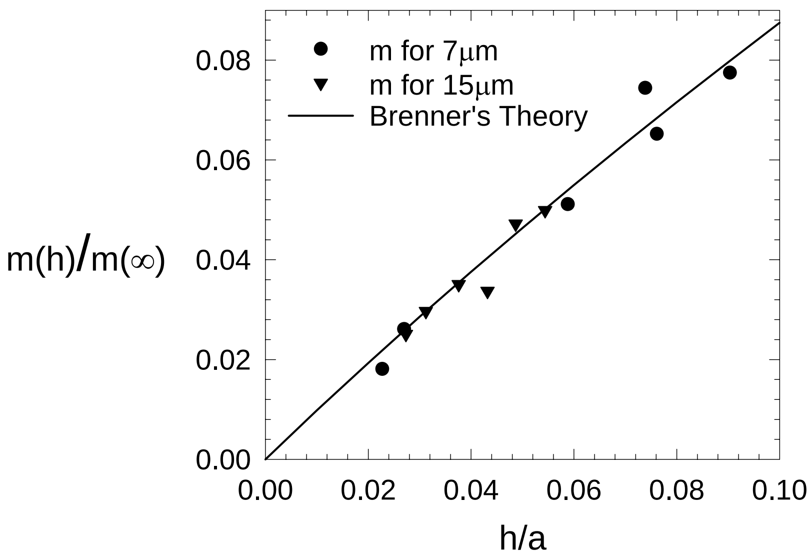


The downward force exerted by the laser beam increases the apparent weight of the sphere, which can be measured by fitting a straight line (shown in red) to the linear portion of the profile at large separations. The slope of this red line gives the apparent net weight.

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.

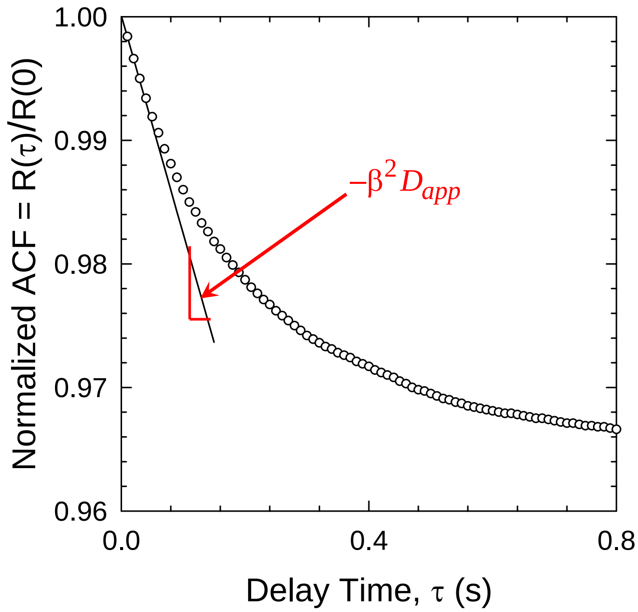
Analysis of Dynamics: the Autocorrelation Function

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

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

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

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



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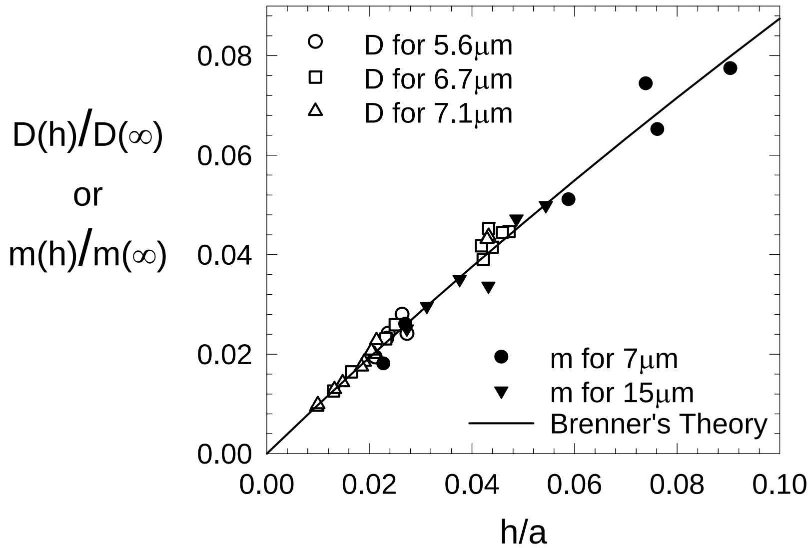
To obtain the diffusion coefficient, we analyze the dynamics of Brownian motion by calculating the autocorrelation function for scattering intensity. The correlation between two intensity measurements taken a time τ apart is expected to decay monotonically with τ. The initial slope is proportional to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

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



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

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

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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**

Umezawa public lecture presented at Dept. of Physics,
University of Alberta, Edmonton, Alberta, March 9, 2005.