In 1827, Botanist Robert Brown first observed the continuous wiggling motion of pollen grains in water.

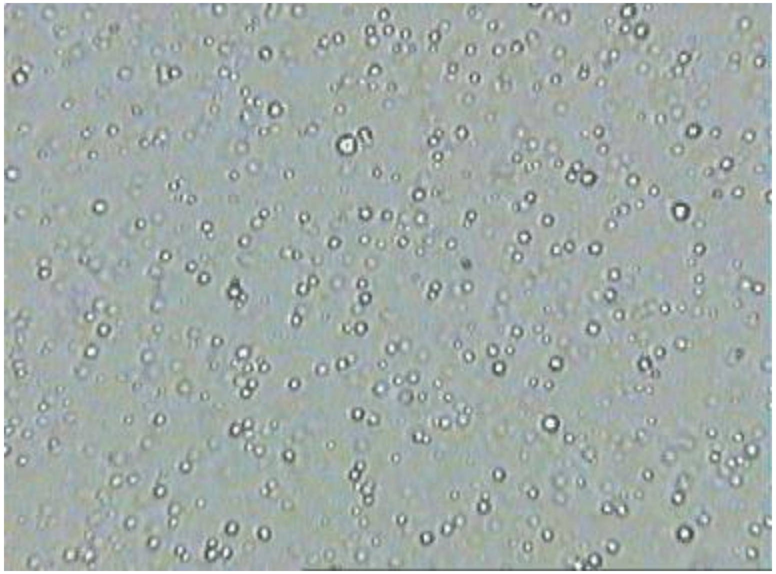
- Diffusion of Particles

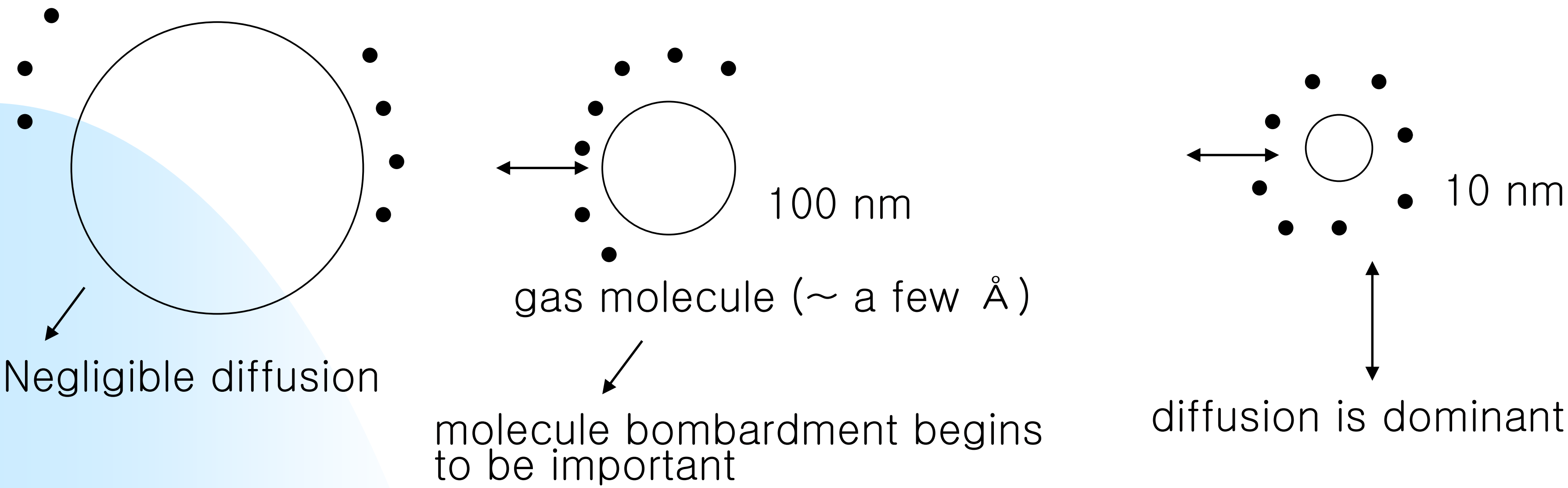
  – Particles suspended in a fluid undergo irregular random motion due to bombardment of surrounding fluid molecules. This is called "Brownian motion of particles" instead of "Brownian motion of fluid molecules"

  – Note that the diffusion of aerosol particles is the result of bombardment of surrounding gas molecules. This means that the particle diffusion is important for only small particles. Let us suppose we have a baseball with 7 – 8 cm diameter in air.

Einstein and Brownian motion

- *Annalen der Physik*, vol. 17, pp 549-560 (1905)
- 'On the Movement of Small Particles Suspended in a Stationary Liquid Demanded by the Molecular-kinetic Theory of Heat'





Particle diffusional flux

$$J_x = -D\frac{\partial n}{\partial x}$$

J: flux #/cm^2· sec

D: diffusion coefficient [cm^2/ sec]

D= function (d_p, T, properties of particle and surrounding fluid)

Diffusion Equation for mono disperse particles

$$\frac{\partial n}{\partial t} = -\nabla \cdot \vec{J} = D\nabla^2 n$$

For polydisperse aerosols

$$n \rightarrow n_p(d_p, \vec{r}, t)dd_p$$

$$\frac{\partial n_p}{\partial t} = D\nabla^2 n_p \longrightarrow$$ A simple form of particle dynamics equation

Let us consider the equation of motion of a single particle caused by the bombardment of surrounding fluid molecules.

$$m_p \frac{d\vec{v}}{dt} = -\frac{3\pi\mu d_p}{C_c}\vec{v} + m_p\vec{a}(t)$$

Random force due to thermal motion bombardment of fluid molecules

$$\frac{d\vec{v}}{dt} = -\frac{f}{m_p}\vec{v} + \vec{a}(t)$$

$$\frac{f}{m_p} = \frac{1}{\tau} = \frac{3\pi\mu d_p}{m_p C_c} \sim \frac{1}{d_p^2}$$

It is more appropriate to consider "a kind of average motion of entire particles" than considering a single particles.
This is called "ensemble average" (average entire particles at fixed time)

For example, if you consider the position of particle (due to diffusion at

$t = t$, $\vec{r} = \vec{r}(t)$)

Its ensemble average $< \vec{r}(t) > = 0$,

But $< \vec{r}(t) \cdot \vec{r}(t) > \neq 0$ $\longrightarrow$ Represent mean square displacement or the mean square intensity of the Brownian motion.

$$\vec{r}\cdot\frac{d\vec{v}}{dt}=-\frac{f}{m_p}\vec{r}\cdot\vec{v}+\vec{r}\cdot\vec{a}(t)$$

: Langevin Equation (Paul Langevin, 1908)
French Physicist

Take
Ensemble average of this equation

$$<\vec{r}\cdot\frac{d\vec{v}}{dt}>=-\frac{f}{m_p}<\vec{r}\cdot\vec{v}>$$

$$<\vec{r}\cdot\vec{a}(t)>=0$$

due to random $\vec{a}(t)$

||

$$\frac{d}{dt}<\vec{r}\cdot\vec{v}>-<\vec{v}\cdot\vec{v}>$$

$$\therefore\frac{d}{dt}<\vec{r}\cdot\vec{v}>=-\frac{f}{m_p}<\vec{r}\cdot\vec{v}>+<\vec{v}\cdot\vec{v}>$$

$\frac{1}{2}m_p<v^2>$: average kinetic energy due to Brownian motion

Because temperature is the only way describing Brownian motion of molecules, the brief transfer of kinetic energy to the Brownian particle must be accompanied by a local cooling of the fluid. Thus, even at thermodynamic equilibrium, small but persistent random fluctuation of temperature exist. ：Einstein

$$\frac{1}{2}m_p < v^2 >= \frac{3}{2}kT$$ (the principle of equipartition of energy)

$$\therefore \frac{d}{dt} < \vec{r} \cdot \vec{v} >= -\frac{f}{m_p} < \vec{r} \cdot \vec{v} > + \frac{3kT}{m_p}$$

$$< \vec{r} \cdot \vec{v} >= \frac{3kT}{m_p}\frac{m_p}{f} + (\exp(-\frac{f}{m_p}t)$$

For $$t >> \tau = \frac{m_p}{f} \sim d_p^2$$

$$<\vec{r}\cdot\vec{v}>=<\vec{r}\cdot\frac{d\vec{r}}{dt}>=\frac{1}{2}\frac{d}{dt}<\vec{r}\cdot\vec{r}>=\frac{3kT}{f}$$

$$<\vec{r}\cdot\vec{r}>=\frac{6kT}{f}t$$

$$<r^2>=<x^2>+<y^2>+<z^2>$$

isotropic $<x^2>=<y^2>=<z^2>$

$$\therefore <x^2>=\frac{1}{3}<\vec{r}\cdot\vec{r}>=\frac{2kTt}{f}$$

Now consider one dimensional diffusion of particles

$$\frac{\partial n}{\partial t}=D\frac{\partial^2 n}{\partial x^2}$$

$$t = 0 \qquad n = N_0 \delta(x)$$

$$x = \pm\infty$$

Dirac delta function vs

Kronecker delta function

$$n(x,t) = \frac{N_0}{2\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right)$$

$$N_0 = \int_{-\infty}^{\infty} n(x,t)\,dx$$

$$<\vec{x}\cdot\vec{x}> = <x^2> = \frac{1}{N_0}\int_{-\infty}^{\infty} x^2 n(x,t)\,dx$$

$$= 2Dt = \frac{2kT}{f}t$$

$$\therefore D = \frac{kT}{f} = \frac{kTC_c}{3\pi\mu d_p}$$

: Equation for particle diffusion
(Stokes-Einstein Equation)

Diffusion coefficient is a function of d_p, T, μ, C_c

Perrin (1910), P.33 Friedlander
carried out experiment in which they measured the position of particles (about 400 nm) at regular intervals in a liquid under an optical microscope

$$N_{av} = \frac{2tRT}{3\pi\mu d_p \overline{x^2}}$$

he found $N_{av} \sim 7.0\times10^{23}$

(exact value $\sim 6.023\times10^{23}$)

if $d_p >> \lambda$ (continuum regime)

$$D \sim \frac{1}{d_p}$$

TABLE 2.1
Aerosol Transport Properties: Spherical Particles in Air at 20°C, 1 atm

d_p (μm)	C	D (cm^2/sec)	Schmidt Number, ν/D	c_s (cm/sec) ($\rho_p = 1$g/cm^3)
0.001	216.	5.14×10^{-2}	2.92	
0.002	108.	1.29×10^{-2}	1.16×10^{1}	
0.005	43.6	2.07×10^{-3}	7.25×10^{1}	
0.01	22.2	5.24×10^{-4}	2.87×10^{2}	
0.02	11.4	1.34×10^{-4}	1.12×10^{3}	
0.05	4.95	2.35×10^{-5}	6.39×10^{3}	
0.1	2.85	6.75×10^{-6}	2.22×10^{4}	8.62×10^{-5}
0.2	1.865	2.22×10^{-6}	6.76×10^{4}	2.26×10^{-4}
0.5	1.326	6.32×10^{-7}	2.32×10^{5}	1.00×10^{-3}
1.0	1.164	2.77×10^{-7}	5.42×10^{5}	3.52×10^{-3}
2.0	1.082			1.31×10^{-2}
5.0	1.032			7.80×10^{-2}
10.0	1.016			3.07×10^{-1}
20.0	1.008			1.22
50.0	1.003			7.58
100.0	1.0016			30.3

if $d_p << \lambda$ (free molecular regime)

$$D \sim \frac{1}{d_p^2}$$

$$< x^2 >= 2Dt \qquad D = \frac{< x^2 >}{2t}$$

$$\sqrt{< x^2 >} = \sqrt{2D}$$ during 1 sec

1 ㎛ particle

$$\sqrt{2 \times 2.77 \times 10^{-7}}$$

$$7.44 \times 10^{-4} cm$$

7 ㎛

Settling distance (1 sec)

$$3.52 \times 10^{-3} cm$$

35 ㎛

0.1 ㎛ $\sqrt{2\times 6.75\times 10^{-6}}$

$3.67\times 10^{-3}cm$

37 ㎛

$8.62\times 10^{-5}cm$

0.862 ㎛

One of the outstanding challenges of nanotechnology is to develop a means to trap and manipulate individual nanoscale objects in solution.

As the object becomes smaller, the Brownian motion of particles makes it difficult to trap the particle.

Cohen et al.(2005) developed the anti-Brownian electrophoretic trap(ABEL trap) that works by monitoring the Brownian motion of the particle (via fluorescence microscopy), and then applying a time dependent feedback voltage to the solution so that the electrophoretic drift exactly cancels the Brownian motion.

Cohen et al.(2005), Method for trapping and manipulating nanoscale objects in solution, APL 86, 093109

Cohen et al. (2006) published another paper " Suppressing Brownian motion of individual biomolecules in solution" in PNAS (Proceedings of National Academy of Sciences).

" This year marks the 101st anniversary of Einstein's explanation of Brownian motion. He showed that the jittering of small particles in water is the cumulative effect of countless collisions with thermally agitated water molecules. Brownian motion is a major transport process at the cellular and subcellular levels and thus is essential for life. Brownian motion also makes the task of studying subcelluar structures in solution difficult; freely diffusing nano-objects do not hold still long enough for extended observation. They succeeded the trapping of TMV(tobacco mosaic virus) 300 nm long and 15 nm in diameter.

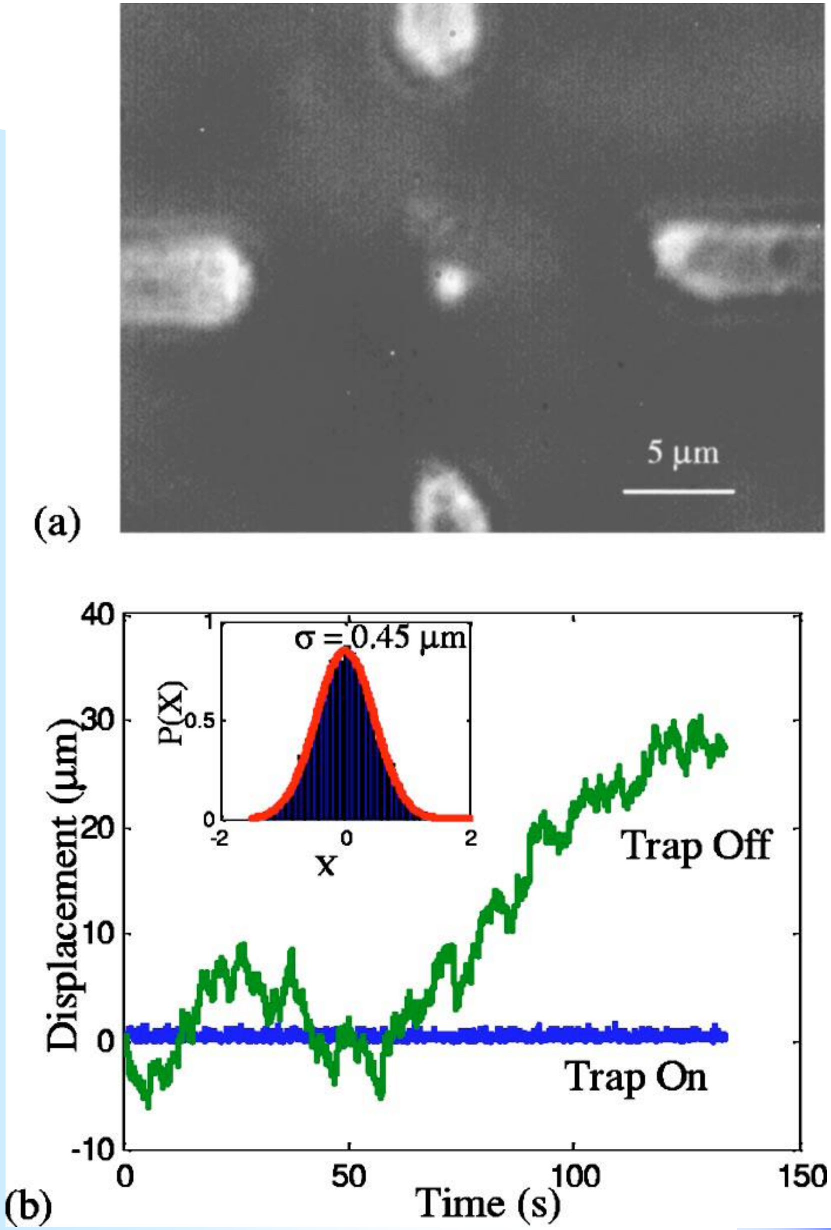


FIG. 2. (Color online) Trapping of a 200 nm particle. (a) Average of 30 video frames showing a single trapped particle. The trapping electrodes are visible protruding from the edges of the image.

(b) Comparison of trajectories of a 200 nm diameter particle with the trap on and with the trap off.

Inset: histogram of displacements from equilibrium.

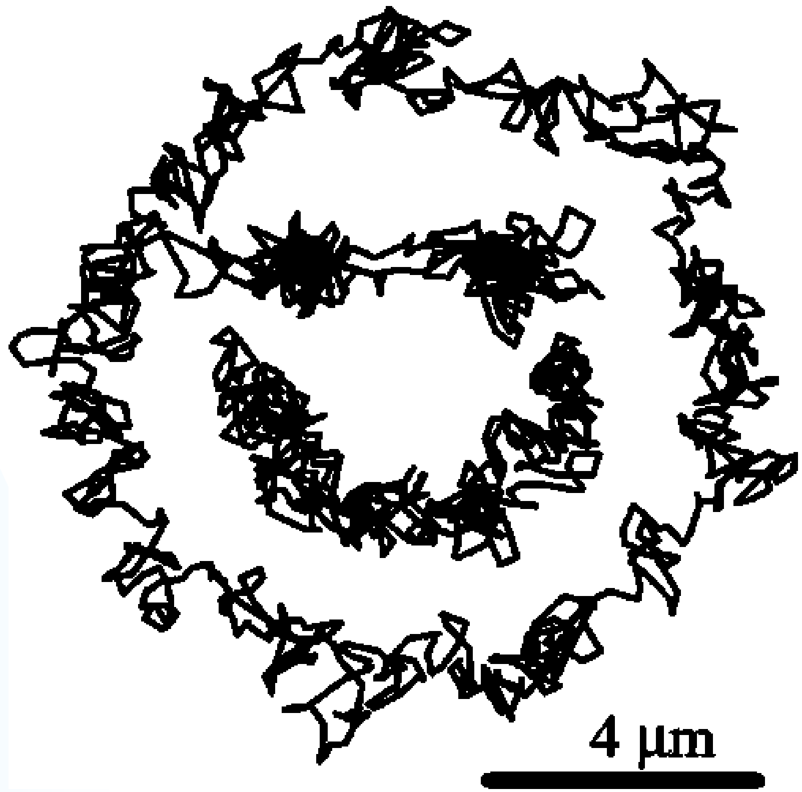


FIG. 3. Trajectory of a 200 nm particle over the course of 1 min, as it was manipulated to draw out a smile face. The trajectory was specified by a file containing 1800 target positions, updated at 30 Hz. (Two of the 1800 data points — those joining the eyes and mouth—are not plotted.)