

Guest Lecture: Prof. Marcos Intaglietta

Brownian Motion and Diffusion

References

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Crank, J. *The mathematics of diffusion*. Oxford University Press, Oxford, 1980 (2nd. ed.).

Purcell, E.M. “[Life at Low Reynolds Number](#),” Lyman Laboratory, Harvard University, June 1976. Also *American Journal of Physics*, vol. 45, pp. 3-11, 1977.

http://en.wikipedia.org/wiki/Brownian_motion

http://en.wikipedia.org/wiki/Diffusion_equation

Diffusion

Diffusion occurs when a system is not in equilibrium and random molecular motion causes the system to become uniform in its properties, such as the distribution of material, thermal energy and charge. We tend to assume that diffusion is associated with cooling or heating, and the mixing of fluids, however diffusion is seldom the dominant mechanism. Bulk motion of the fluid is the cause of most of the mixing effects that we experience in liquids and gases. While diffusion is important in the detail of these processes, convection is what we most often experience. Were it not for convective motions in the air it would take one year to smell our feet after taking off our shoes due to molecular diffusion. It is the stirring of milk in the coffee that mixes it; molecular diffusion would take so long that the drink would long spoil and evaporate before it was mixed.

The most common example of diffusion in our everyday experience, is the diffusion of heat in a solid. However, at the microscopic level, cells are fundamentally dependant on the process of diffusion to absorb and reject materials from and into the environment, particularly in the immediate proximity of their membranes where convection become very small as a consequence of the no slip condition imposed by solid boundaries to the motion of their surrounding fluid.

A common form of diffusion is viscosity, which determines how momentum diffuses in fluid flow. The diffusion of momentum generally a small effect compared to the effects due to fluid inertia. In breathing and swimming we are not particularly aware of the consequent drag effect due to viscosity. However cellular organism live in a world where viscous diffusion is the dominant effect (see “Life at Low Reynolds Number”, Purcell 1976). Viscosity is a fundamental hydrodynamic property of fluids that determines the existence of boundary layers, which are the critical element for avoiding metal to metal contact all rotating mechanism and thus maintaining the integrity of their surfaces.

Diffusion processes are irreversible and do not run backwards. Diffusion processes are intimately related to entropy, irreversibility, and probability.

Brownian motion

The motion of a particle suspended in a viscous fluid results from fluctuating forces which are the consequence of collisions with molecules of the fluid. As an example a sphere of 1 μm in diameter in air is subjected to 10^{16} collisions per second. The details of Brownian movement cannot be predicted exactly, however, we may assume that the events (collisions, displacements, etc.) are random. Therefore even though we cannot know the details of the phenomenon, we can determine the average behavior.

Theory for one dimensional displacement

Let us analyze the displacements of a particle of mass m along the x axis as a consequence of the action of a random force X acting in the x direction. Both the magnitude and sign of X are random. The velocity of the particle dx/dt and the acceleration d^2x/dt^2 are opposed by a frictional force F , where each of these terms is defined by:

$$\frac{dx}{dt} = \dot{x} ; \quad \frac{d^2x}{dt^2} = \ddot{x} ; \quad F = f \dot{x}$$

The frictional force F opposes the action of the force X , where the frictional coefficient f is given by:

$$f = 6\pi\eta R \quad 1$$

where η is the viscosity of the medium in which the particle moves and R is the radius of the particle (Stokes law). According to Newton's second law we obtain the equation of motion:

$$X - f \dot{x} = m\ddot{x} \quad 2$$

We assume that at $t = 0$ the particle is at the origin $x = 0$, and we wish to determine what will be the average distance $\langle x \rangle$ that the particle has moved from its starting point as time progresses. A convenient variable that allows tracking the distance from the origin independently of the direction of the motion along the x axis is to measure x^2 , and if we let $y = x^2$, the derivatives of this function are:

$$\frac{dy}{dt} = 2x\dot{x} ; \quad \frac{d^2y}{dt^2} = 2\dot{x}^2 + 2x\ddot{x} \quad 3$$

The averages of these functions are:

$$\langle \frac{dy}{dt} \rangle = \langle 2x\dot{x} \rangle ; \quad \langle \frac{d^2y}{dt^2} \rangle = \langle 2\dot{x}^2 + 2x\ddot{x} \rangle \quad 4$$

If we multiply equation 2 by x and take the time average we obtain:

$$\langle xX \rangle - f \langle x\dot{x} \rangle = m \langle x\ddot{x} \rangle \quad 5$$

Comparing equations (5) and (3) we note that we can introduce the variable y into the equation of motion by simple substitution and obtain:

$$\langle xX \rangle - \frac{1}{2}f \langle \frac{dy}{dt} \rangle = m(\frac{1}{2} \langle \frac{d^2y}{dt^2} \rangle - \langle \dot{x}^2 \rangle) \quad 6$$

The kinetic theory of gases indicates that each molecule has an average kinetic energy $\langle KE \rangle$ given by:

$$\langle KE \rangle = \frac{1}{2} m \langle \dot{x}^2 \rangle = \frac{3}{2} kT$$

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where k is Boltzmann's constant whose value is 1.38×10^{-16} ergs/degree and T is the absolute temperature. We make the assumption that the particles in our system have the same kinetic energy as that of a gas, and furthermore since the particle under consideration moves only in one direction it must have one third of the total average kinetic energy. The average velocity squared is then obtained from (7) to be:

$$\langle \dot{x}^2 \rangle = \frac{kT}{m} \quad 8$$

Equation (6) can now be integrated by making the substitution given in (8) and noting that the term $\langle xX \rangle = 0$ since X varies at random. By making the substitution:

$$z = \frac{d}{dt} \langle y \rangle \quad 9$$

we obtain the first order equation:

$$m \frac{dz}{dt} + fz = 2kT \quad 10$$

whose solution is:

$$z = \frac{2kT}{f} + K_1 e^{-\frac{t}{(\frac{m}{f})}} \quad 11$$

where K_1 is a constant of integration. For microscopic particles the term m/f is very small and the exponential term vanishes. It is also shown that this term, which has the units of time, is a measure of the time required by a particle to reach its final velocity when acted upon by the force X . Utilizing the definitions of z and x we obtain:

$$z = \frac{d}{dt} \langle x^2 \rangle = \frac{2kT}{f} \quad 12$$

and integrating we obtain:

$$\langle x^2 \rangle = \frac{2kT}{f} t + K_2 \quad 13$$

where K_2 is a constant equal to zero since $x = 0$ at $t = 0$. This result can be extended to motion of a particle in three dimensions, since equation (13) holds for each of the 3 Cartesian coordinates, therefore the distance $r^2 = x^2 + y^2 + z^2$ from the origin will be three times that given in (13) and the actual distance is given by:

$$r_{rms} = \sqrt{\frac{6kT}{f} t}$$

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This result shows that the average of x squared, i.e., the distance of the particle from its initial position increases with time, although in any given moment the displacement may be either forward or backward with equal frequency. This result was derived Einstein in 1906.

Diffusion

In a suspension all the particles undergo Brownian motion and therefore particles will tend to flow from regions of high concentration to ones with low concentration. This flow is termed diffusion and it causes the concentration of a suspension to be uniform.

The law governing diffusion is obtained experimentally by measuring the flow of particles caused by different concentration differences. The simplest case is that when the concentration c varies only along the x direction and it is independent of time t . Defining J to be the number of particles that passes an area $A = 1$ perpendicular to the concentration gradient, the first law of diffusion, termed Fick's First Law of diffusion, is found to be

$$J = -DA \frac{\partial c}{\partial x} \quad 15$$

where D is a proportionality constant termed the coefficient of diffusion. The phenomenon can also be described by an equation not involving J . To obtain this equation consider a region where there is a concentration gradient along the x axis, and which is bound by planes at x_1 and x_2 in such a fashion that the flow through these planes are J_1 and J_2 respectively. If the J_1 and J_2 are not equal, then the number of particles N in the region will change with time according to:

$$J_1 - J_2 = \frac{dN}{dt} \quad 16$$

If $\langle c \rangle$ is the average concentration of the particles in the region then:

$$N = (x_2 - x_1) \langle c \rangle \quad 17$$

Differentiating (17) with respect to time and using equations (15) and (16) we obtain:

$$J_1 - J_2 = (x_2 - x_1) \frac{d \langle c \rangle}{dt} \quad 18$$

Transposing $(x_2 - x_1) = \Delta x$ and taking the limit $\Delta x \rightarrow 0$ we obtain:

$$\lim_{\Delta x \rightarrow 0} \frac{(J_2 - J_1)}{\Delta x} = -\frac{dc}{dt} \quad 19$$

where the left hand side of (19) is MJ/Mx and the right hand side is Mc/Mt . Introducing the definition of J from Fick's first law we obtain:

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

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which is called Fick's second law of diffusion.

Solutions of the diffusion equation

One dimensional steady state diffusion

Steady state implies that all factors are time independent, therefore $Mc/Mt = 0$ and (17) becomes:

$$\frac{\partial^2 c}{\partial x^2} = 0$$

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whose solution is:

$$c = A_1 x + A_2$$

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where A_1 and A_2 are constants. Given (22) and the first law of diffusion, we have that:

$$J = -D \frac{\partial c}{\partial x} = -DA_1$$

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which shows that J is a constant. A_1 and A_2 are evaluated from specific values of J , D and the boundary conditions.

Time dependent diffusion

A solution of equation (20) is:

$$c(x, t) = A \operatorname{erf} \frac{x}{\sqrt{4Dt}} = At^{-\frac{1}{2}} e^{-\frac{x^2}{4Dt}}$$

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If we plot this function for different times as a function of x we obtain the time course of events for the situation where at time zero the concentration is uniform along the whole x axis, and equal to zero. After this the concentration at x becomes zero for all times, and the concentration at $x = 0$ decreases monotonically with time. The obtained distribution of c as a function of time is equivalent to that observed if we place at time zero a particle source at $x = 0$.

A problem to be solved later is that of a uniform distribution of material from $x = 0$ to positive infinity, which is suddenly being consumed at $x = 0$. To determine the location x_h at which the concentration has decreased by half relative to the original value at $x = 0$ requires solving for the value of the exponent in the following equation:

$$c(x_h, t) = \frac{1}{2} = \operatorname{erf} \frac{x}{\sqrt{4Dt}} \quad 25$$

From the table of the error function $\operatorname{erf} 0.48 = 0.50$, therefore:

$$0.48 = \frac{x_h}{\sqrt{4Dt}} \quad \therefore \quad x_h = 0.96\sqrt{Dt} \quad 26$$

The diffusion coefficient

The result (26) should be compared with the *rms* distance achieved by a particle subjected to Brownian motion along the *x*-axis which from (14) is given by:

$$x_{rms} = \sqrt{\frac{2kT}{f} t} \quad 27$$

which indicates that diffusion and Brownian motion are different aspects of the same phenomenon, and that the diffusion coefficient, which is an experimentally found quantity is related to:

$$D = B \frac{kT}{f} \quad 28$$

where *B* is numerical factor related to the fact that diffusion deals with the flux of a very large number of particles, while Brownian motion refers to only one particle. This factor is shown to be equal to one, and therefore using (1) the diffusion coefficient for a spherical particle in a liquid is:

$$D = \frac{kT}{6\pi\mu R} = \frac{RT}{N} \frac{1}{6\pi\mu R} \quad 29$$

Where *R* is the gas constant and *N* is Avogadro's number.

indicating that the diffusion coefficient is the ratio of kinetic vs. viscous effects. Furthermore, for the same particle the *rms* displacement from its origin is given by (27), namely:

$$x_{rms} = \sqrt{2Dt} \quad 30$$

Note that:

$$D = \frac{x_{rms}^2}{2t} : \frac{1}{2} \frac{x_{rms}}{t} x_{rms} = \frac{1}{2} c\lambda$$

where *c* is the average velocity and λ is the mean free path.

Diffusion coefficient and Reynolds number

The Reynolds number Re results from grouping physical and geometric parameters into a single parameter when the variables and coefficient related by the Navier-Stokes equation are normalized. The Reynolds number is typically defined for situations where a fluid is in motion relative to a surface. Normalization is carried out by identifying a nominal density and viscosity, a velocity and a characteristic length or dimension (i.e., radius or diameter for spheres or circles, length and width for aircraft or ships, and the internal diameter for flow in a pipe or a sphere moving in a fluid).

A simple example is flow in a pipe, for which Re is:

$$Re = \frac{\rho VL}{\mu} = L \frac{\rho V^2}{\mu V} : L \frac{\text{kinetic energy}}{\text{viscous dissipation}}$$

where V is the mean fluid velocity (cm/s), L is the diameter of the pipe (cm), μ is the dynamic viscosity, of the fluid (dyne sec/cm², poise) and ρ is the density of the fluid (g/cm³).

It is apparent that D and Re are similar entities in that they involve the ratio of inertial and viscous effects, with the important difference that the diffusion coefficient is inversely proportional to the nominal dimension of the system, while Re is directly proportional to this parameter.

References

Einstein, A. "Investigations on the theory of Brownian motion". Dover Publications Inc., 1956.
Crank, J. "The mathematics of diffusion". Oxford University Press, Oxford, 1980 (2nd. ed.).

x	Erf x	x	Erf x
0.00	0.000	1.10	0.880
0.10	0.112	1.20	0.910
0.20	0.223	1.30	0.943
0.30	0.328	1.40	0.952
0.40	0.428	1.50	0.966
0.50	0.520	1.60	0.976
0.60	0.604	1.70	0.984
0.70	0.678	1.80	0.989
0.80	0.742	1.90	0.993
0.90	0.797	2.00	0.995
1.00	0.843	5.00	0.999