

# **BAE 820 Physical Principles of Environmental Systems**

**Mean free path, Brownian motion and Fick's law**

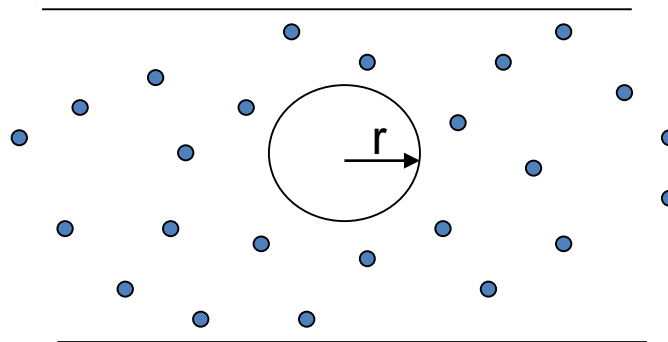
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# Particles too small for Stokes' law

- Stokes' law assumes that the fluid in which the particle is moving in a continuous medium.
- When a particle becomes as small as  $\lambda$ , or smaller than the average distance between molecules, then its interaction with molecules changes.

# Mean free path $\lambda$

- Mean free path ( $\lambda$ ): the average distance traveled by a gas molecule through a medium between collisions with other gas molecules.
- When the radius of the particle  $r$  is approximately equal to  $\lambda$ , slippage occurs.
  - Slippage: A small particle sliding between the gas molecules when  $r \approx \lambda$ .



# The Knudsen number ( $K_n$ )

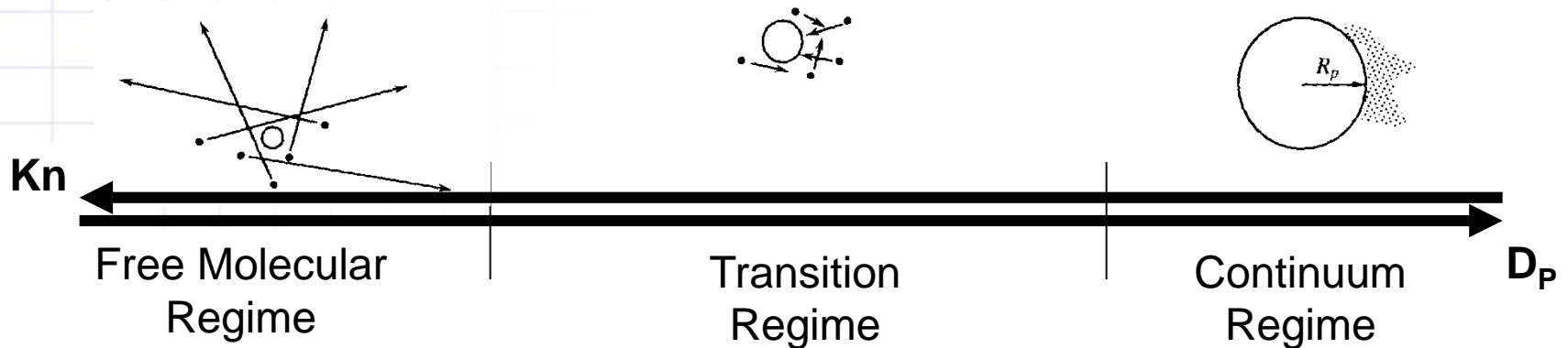
- $K_n$  is a dimensionless number defined as the ratio of the molecular mean free path length to a representative physical length scale, e.g. the radius of a particle.

$$K_n = \lambda/r$$

$K_n \ll 1$ ( $K_n < 0.1$ )	Continuum regime: the fluid appears to the particle as a continuum, and the laws of continuum mechanics apply. No slip condition holds.
$K_n \approx 1$ ( $0.1 < K_n < 10$ )	Transition regime: transport is controlled by both continuum mechanics and kinetic theory. Slip correction is required
$K_n \gg 1$ ( $10 < K_n$ )	Free molecule regime: transport controlled by the kinetic theory of gases

# The Knudsen number ( $K_n$ )

- $K_n$  describes how the fluid "views" the particle, i.e. is the motion governed by the rules of molecules or of macroscopic objects



# The Cunningham correction factor

The effect of the slippage is to lower the drag force, which causes the particle to move faster.

$$F_d = F_{d\text{-Stokes}} / C_c$$
$$v = v_{t\text{-Stokes}} C_c$$

Where  $C_c$  is the Cunningham correction factor, it has the following general form

$$C_c = 1 + K_n [\alpha + \beta \exp(-\gamma / K_n)]$$

When  $\alpha$ ,  $\beta$ , and  $\gamma$  are experimentally determined constant,  
 $\alpha = 1.257$ ,  $\beta = 0.40$ , and  $\gamma = 1.10$

When  $r \approx \lambda$ , a particle will settle 2 times faster as it would when Stoke's law predictions are used.

# The Cunningham correction factor

For large and small particles the following simple forms of the Cunningham correction factor can be used

- When  $r \gg \lambda$  ( $K_n \ll 1$ , continuum regime)

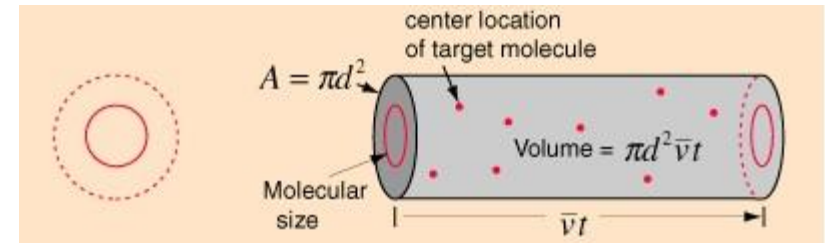
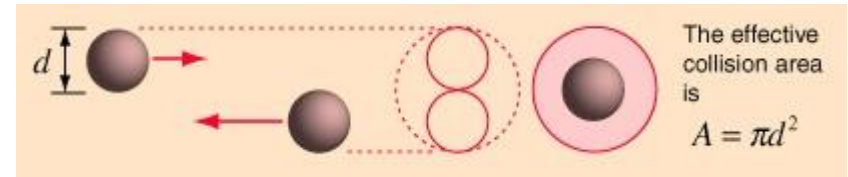
$$C_c \approx 1 + \alpha K_n = 1 + 1.257 K_n$$

- When  $r \ll \lambda$  ( $K_n \gg 1$ , free molecule regime)

$$C_c \approx (\alpha + \beta) K_n = 1.657 K_n$$

# Mean free path of gas molecules

- Let  $N$  = number of molecules per unit volume;
- $\bar{v}t$  = average distance traveled by a molecule per unit of time;
- The volume swept =  $\pi d^2 \bar{v}t$ ;
- The number of projected collisions will be  $\pi d^2 \bar{v}t N$ .
- A statistical average of the number of collisions per unit time would be  $\sqrt{2} \pi d^2 \bar{v}t N$ .





# Mean free path of gas molecules

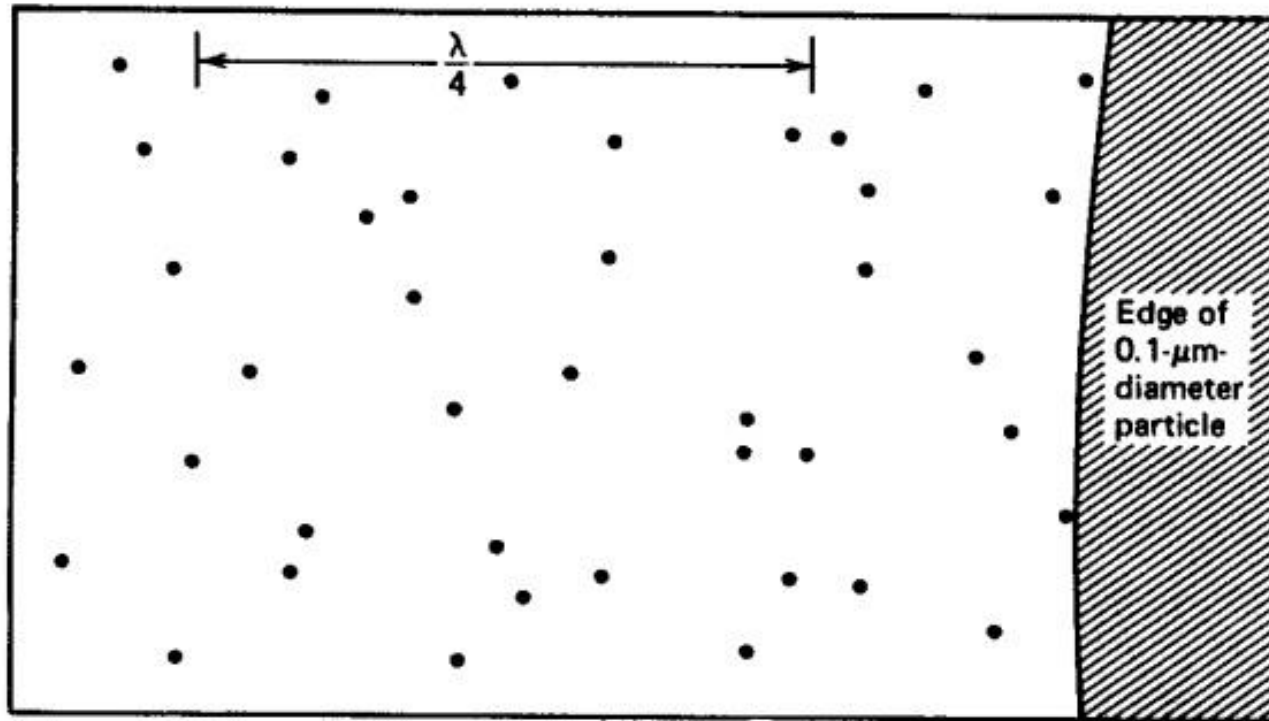
Therefore,

$$\lambda = \frac{vt}{\sqrt{2}\pi d^2 vt N} = \frac{1}{\sqrt{2}\pi d^2 N} = \frac{RT}{\sqrt{2}\pi d^2 P \times 6.02 \times 10^{23}} = \frac{k_B T}{\sqrt{2}\pi d^2 P}$$

Where  $k_B$ , the Boltzmann constant, is the ratio of the molar gas constant  $R$  to Avogadro's number

- The mean free path  $\lambda$  depends on  $T$  and  $P$ .
- Diameters of air molecules (nitrogen or oxygen) are around  $3.7\text{\AA}$ , which will result in  $\lambda = 0.067\ \mu\text{m}$ , for air at one atm and  $298\text{K}$ .
- In practice, the diameter of gas molecules is not well defined. Typically, gas molecules do not behave like hard spheres, but rather attract each other at larger distances and repel each other at shorter distances. Different definitions of the molecular diameter can lead to slightly different values of the mean free path.

# Relative size and spacing of air molecules



**Relative size and spacing of air molecules at standard conditions**

# Mean free path of water molecules

- Since the molecular weight of water is 18, and density is 1 g/cm<sup>3</sup>, the number density of molecules in liquid water is

$$N = 1 \times 6.02 \times 10^{23} / 18 = 3 \times 10^{22} \text{ cm}^{-3} = 3 \times 10^{28} \text{ m}^{-3}$$

- The inter-molecular spacing of water molecules can be estimated as

$$r_0 = \sqrt[3]{\frac{3}{4\pi N}} = 2 \text{ \AA}$$

- The spacing between the hydrogen and oxygen atoms in the molecule is about

$$r = 1 \text{ \AA} = 1 \times 10^{-10} \text{ m}$$

Therefore,

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 N} = \frac{1}{\sqrt{2}\pi(2 \times 10^{-10})^2 \times 3 \times 10^{28}} < 2 \text{ \AA}$$

The mean free path is smaller than the average inter-molecular spacing. Therefore it makes little sense to talk about the mean free path of a water molecule in liquid water itself. The concept makes much more sense when talking about molecules in the gas phase where there is some actual room to move before interactions occur.

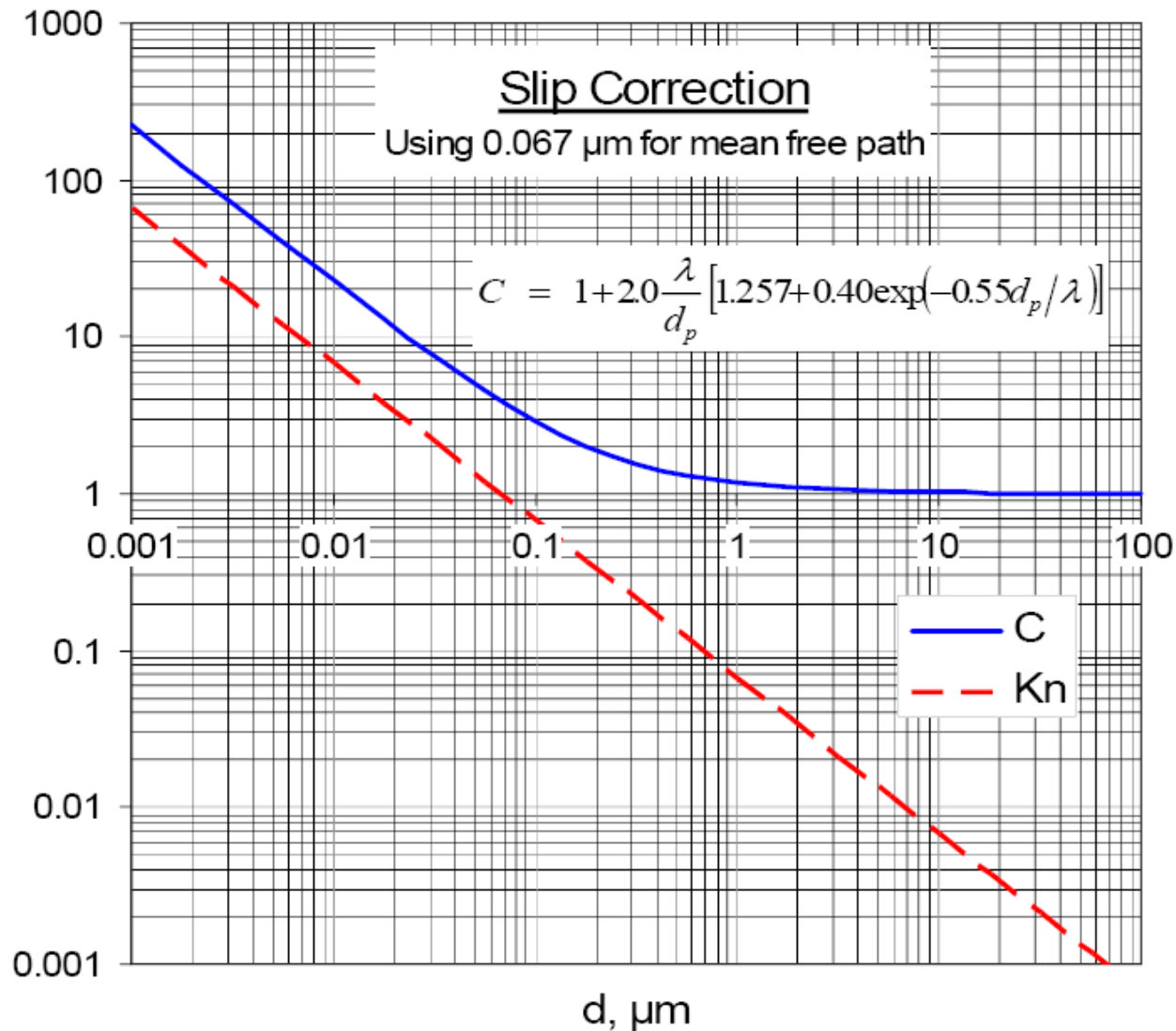
# Magnitude of the Cunningham correction factor

For air at one atm and 298K,  $\lambda = 0.067 \mu\text{m}$

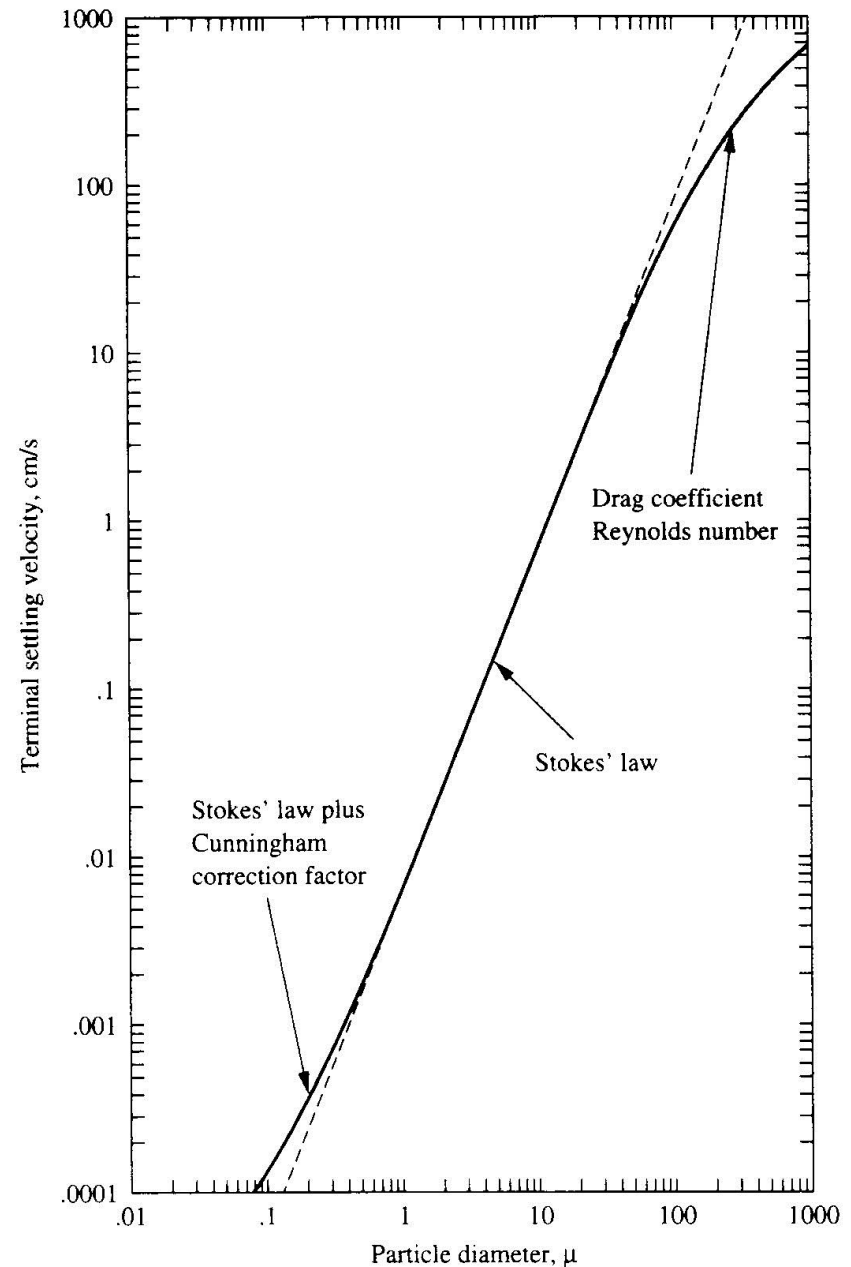
The slip correction factor is generally needed for particles less than  $10 \mu\text{m}$  in diameter

$D_p$ ( $\mu\text{m}$ )	$C_c$
50	1.003
20	1.008
10	1.017
5	1.034
1.0	1.168
0.5	1.339
0.1	2.920
0.01	22.781

For any conditions near STP, it is quite reasonable to use  $\lambda=0.067 \mu\text{m}$  in the above equation for C. The graph below shows the resulting values for Kn and C.



- Stokes' law has been well verified for the range of conditions in which its assumptions hold good.
- However, for both very large and very small particles these assumptions break down.
- The situation is illustrated in the figure to the right.



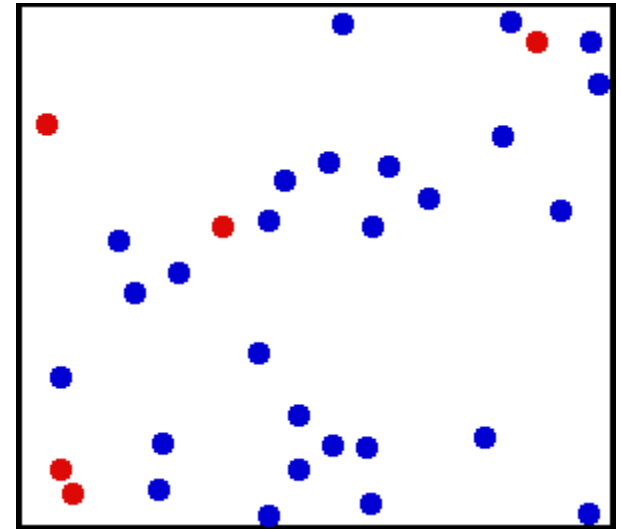
**FIGURE 8.6**  
Terminal settling velocities for spherical particles with specific gravity = 2, in standard air.

- Since most of the industrial particle collectors work on particles with diameters in the range of 1 to 70  $\mu\text{m}$ , most are designed on the basis of Stokes' law in the early stages.
- For the final design calculation, the Cunningham correction factor is often used.



# The Brownian motion

- Brownian motion is the random motion of particles suspended in a fluid resulting from their collision with the molecules in the fluid. The term can also refer to the mathematical model used to describe such random movements
- The Brownian motion is the purely result of the innumerable collisions between all the particles in the system. If the inertia of the particle is small due to its small size, the force of an individual collision is enough to make it move. At different times the particle is hit more on one side than another, leading to the seemingly random nature of the motion.





# The Brownian motion and diffusion

- In a uniform solution or suspension, Brownian motion does not cause any net change in the concentration with time in any part of the solution. But if the concentration is not uniform, then Brownian motion tends to equalize the concentration.
- Fick's law is the result of the random motion of individual particles. The random motion of particles result in the transport of matter from a region of higher concentration to a region of lower concentration.

# Fick's first law

Substances diffuse from regions of high chemical potential to regions of low chemical potential, e.g. from a concentrated solution into a more dilute solution. The driving force for diffusion is the gradient of chemical potential.

Fick's first law

$$J = -D\left(\frac{dC}{dx}\right)$$

- J is the flux (quantity of substance diffusing per unit time through a unit area)
- D is the diffusion coefficient
- C is the concentration
- x is the distance.

The negative sign emphasizes that diffusion occurs in the direction of a drop in concentration.

# Diffusion coefficient

- D have the units of  $\text{cm}^2/\text{s}$
- The interpretation of most types of diffusion experiments is based on Fick's second law, which is obtained from Fick's first law by introducing the idea of conservation of mass.

# Fick's second law

- The equation of continuity

$$\frac{\Delta C}{\Delta t} = \frac{J_x - J_{x+\Delta x}}{\Delta x}$$

$$\frac{\partial C}{\partial t} = - \frac{\partial J}{\partial x}$$

- Substitution of Fick's first law yields

$$\frac{\partial C}{\partial t} = - \frac{\partial(-D\frac{\partial C}{\partial x})}{\partial x} = D\frac{\partial^2 C}{\partial x^2}$$

Which is known as Fick's second law

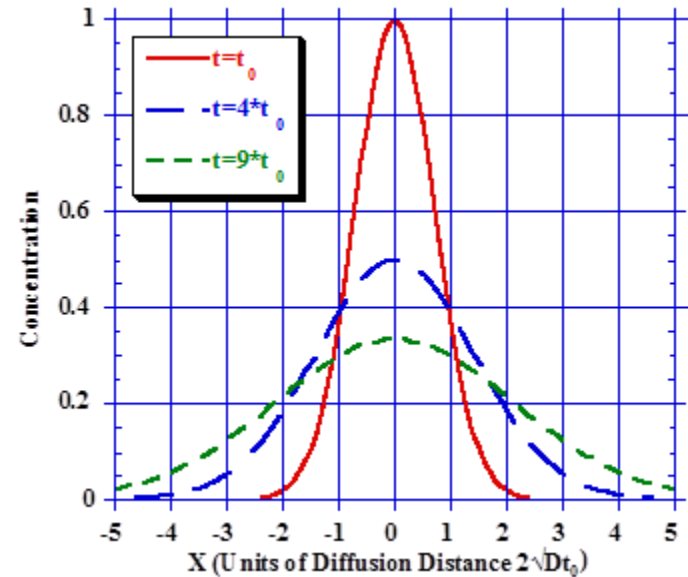
# The Gaussian curve

- When  $\int_{-\infty}^{\infty} C(x, t) dx = Q$

The diffusion equation has the following solution

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

- The left figure shows the characteristic bell-shaped curves of the diffusion of Brownian particles. The distribution begins as all the particles are located at the origin at time  $t=0$ , and for increasing times they become flatter and flatter until the distribution becomes uniform.



# The Gaussian curve

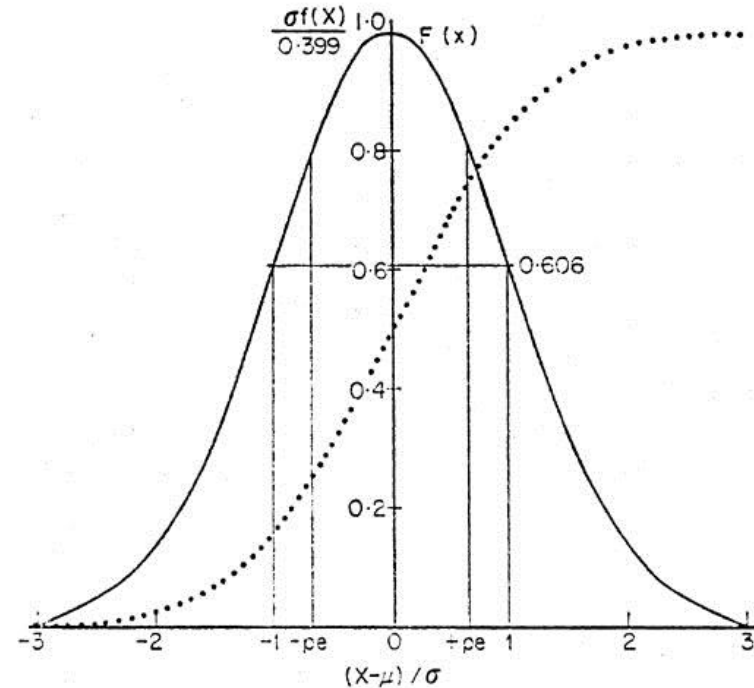
- Compare the derivative curve for diffusion with the probability Gaussian curve.

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp \left[ -\frac{1}{2} \left( \frac{x - \mu}{\sigma} \right)^2 \right].$$

- The diffusion coefficient can be calculated from the shape of the bell-shaped probability curve.

$$D = \frac{\sigma^2}{2t}$$

Where  $\sigma$ , the standard deviation, is the half width of the probability curve at the inflection point. The inflection points are at a height of 0.606 of the maximum ordinate.



# Connecting Fick's law to Brownian motion

- Assuming  $n$  particles are present at the zero level,  $n+\Delta n$  at a distance  $l$  below this level, and  $n-\Delta n$  at a distance  $l$  above. According to Fick's law, the flux of particles crossing the zero level upwards during a time  $t$  is given by

$$J \cdot t = D \frac{\Delta n}{l} \cdot t$$

- From the point view of Brownian motion

$$J \cdot t = l \left[ \frac{1}{2} \frac{n+(n+\Delta n)}{2} - \frac{1}{2} \frac{n+(n-\Delta n)}{2} \right] = l \frac{\Delta n}{2}$$

- Therefore,

$$D \frac{\Delta n}{l} \cdot t = l \frac{\Delta n}{2} \Rightarrow D = \frac{l^2}{2t}$$

# Mean free path and diffusivity of gas

- In gases, the diffusion coefficient is proportional to the average molecular velocity times the mean free path.

$$D \approx \frac{\lambda^2}{2\tau} = \frac{\lambda}{2} \frac{\lambda}{\tau} = \frac{\lambda v_{ave}}{2}$$

- In kinetic theory, a more careful analysis reveals

$$D = \frac{\lambda v_{ave}}{3}$$

Where

- $v_{ave}$  is the average molecular velocity
  - $\lambda$  is mean free path
  - $\tau$  is the average time between collisions.
- 
- Though the velocities of molecules are often very high (hundreds of meters per second), the molecular motion of a species can be very slow due to molecular collisions.



# Problem solving #2

- A typical value for a diffusion coefficient is  $D=1.8 \times 10^{-5} \text{ m}^2/\text{s}$  for perfume in air. Please estimate how far is the distance the perfume will diffuse in one hour (assuming there is no convection).

## Problem solution #2

- $L = \sqrt{2DT} = \sqrt{2 \times 1.8 \times 10^{-5} \times 3600} = 0.36\text{m}$