Chapter 4: Transport in an Infinite Medium

Definitions

- Flow rate, volume *flux* or volume current (*i*)
  - Total volume of material transported per unit time
  - Units: m^3s^{-1}
- Mass *flux*
- Particle *flux*

Definitions

- Particle *fluence*
  - Number of particles transported per unit area across an imaginary surface
  - Units: m^{-2}
- Volume *fluence*
  - Number of particles transported per unit area across an imaginary surface
  - Units: $m^3 m^{-2} = m$

Definitions

- Fluence rate or flux density
  - Amount of "something" transported across an imaginary surface per unit area per unit time
  - Vector pointing in the direction the "something" moves and is denoted by **j**
  - Units: "something" $m^{-2}s^{-1}$
  - Subscript to denote what "something" is

Definitions

TABLE 4.1. Units and names for j and jS in various fields.

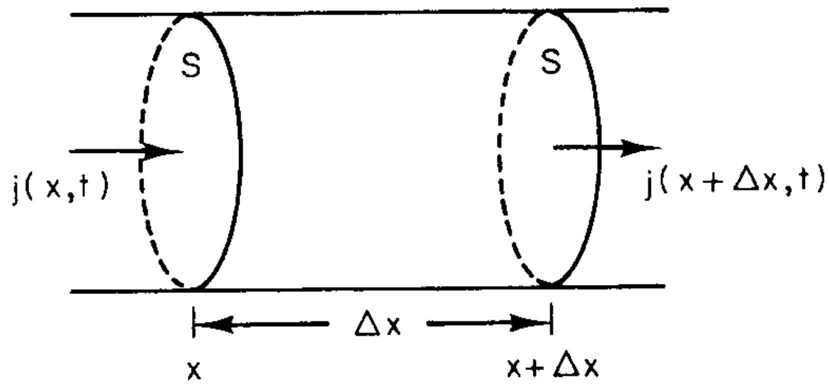
	j		jS	
	Units	Names	Units	Names
Particles	$m^{-2}\ s^{-1}$	Particle fluence rate Particle current density Particle flux density Particle flux	s^{-1}	Particle flux Particle current Particle flux
Electric charge	$C\ m^{-2}\ s^{-1}$ or $A\ m^{-2}$	Current density	$C\ s^{-1}$ or A	Current
Mass	$kg\ m^{-2}\ s^{-1}$	Mass fluence rate Mass flux density Mass flux	$kg\ s^{-1}$	Mass flux Mass flow
Energy	$J\ m^{-2}\ s^{-1}$ or $W\ m^{-2}$	Energy fluence rate Intensity Energy flux	$J\ s^{-1}$ or W	Energy flux Power

Continuity Equation: 1D

- We deal with substances that do not "appear" or "disappear"
  - Conserved
- Conservation of mass leads to the derivation of the continuity equation

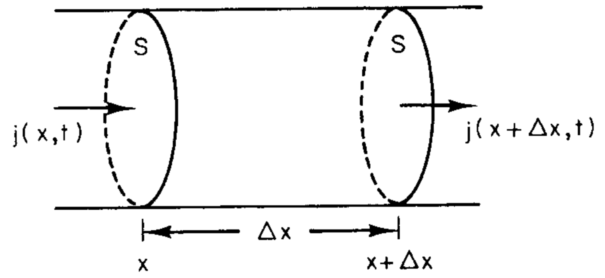
Continuity Equation: 1D

- Consider the case of a number of particles
  - Fluence rate: j particles/unit area/unit time
- Value of j may depend on position in tube and time
  - $j = j(x,t)$
- Let volume of paricles in the volume shown to be $N(x,t)$
  - Change after $\Delta t = \Delta N$



Continuity Equation: 1D

$$\Delta N = \left[j(x,t) - j(x+\Delta x,t) \right] S\Delta t$$



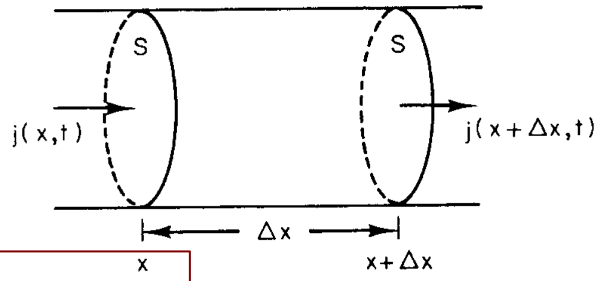
- As Δx→0,

$$j(x,t) - j(x+\Delta x,t) = -\frac{\partial j(x,t)}{\partial x}\Delta x$$

- Similarly, increase in N(x,t) is,

$$\Delta N(x,t) = N(x,t+\Delta t) - N(x,t) = \frac{\partial N}{\partial t}\Delta t$$

Continuity Equation: 1D



- Hence,

$$\frac{\partial}{\partial t} N(x,t) = -(S\Delta x)\frac{\partial}{\partial x} j(x,t)$$

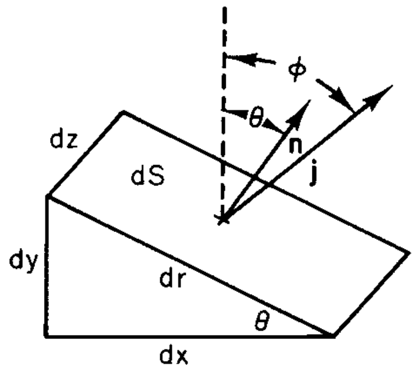
- Then, the continuity equation in 1D is,

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

Continuity Equation: Alternative Forms

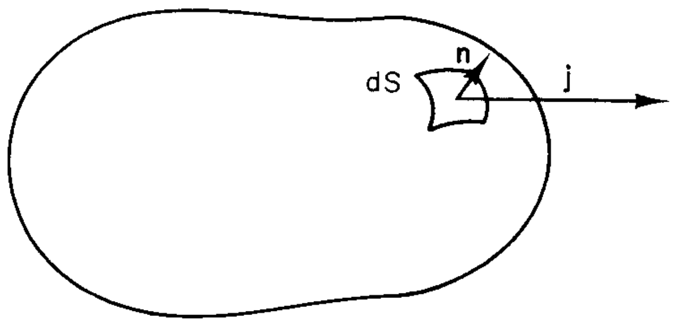
- 3D: Integral form

$$\frac{\partial}{\partial t}\underset{\text{enclosed volume}}{\iiint} C\,dV = -\underset{\text{surface enclosing the volume}}{\iint} j_n\,dS$$



- 3D: Differential form

$$\frac{\partial C}{\partial t} = -\text{div}\ j_m$$



Drift or Solvent Drag

- One simple way the solute particles can move is to drift with constant velocity
  - Uniform electric or gravitational field
  - Carried along by solvent
- Solute fluence rate $\mathbf{j}_s$ is given by,

$$\mathbf{j}_{\mathbf{s}} = C \cdot \mathbf{j}_{\mathbf{v}}$$

Brownian Motion

- Application of thermal equilibrium at temperature T
- Kinetic energy in 1D = $k_B T/2$
- Kinetic energy in 3D = $3k_B T/2$
- Random motion → mean velocity $\overline{v} = 0$
  - can only deal with mean-square velocity $\overline{v^2}$

$$\frac{1}{2} m\overline{v^2} = \frac{3k_B T}{2} \Rightarrow v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}}$$

Brownian Motion

TABLE 4.2. Values of the rms velocity for various particles at body temperature.

Particle	Molecular weight	Mass (kg)	v_{rms} ($m\ s^{-1}$)
H_2	2	3.4×10^{-27}	1940
H_2O	18	3×10^{-26}	652
O_2	32	5.4×10^{-26}	487
Glucose	180	3×10^{-25}	200
Hemoglobin	65 000	1×10^{-22}	11
Bacteriophage	6.2×10^{6}	1×10^{-20}	1.1
Tobacco mosaic virus	40×10^{6}	6.7×10^{-20}	0.4
E. coli		2×10^{-15}	0.0025

Motion in a Gas

- Brownian motion of particles: collisions
- Mean Free Path
  - Average distance between successive collisions
- Collision Time
  - Average time between successive collisions

Motion in a Gas

- Consider $N(x)$ to be number of particles without collision after a distance x
- For short distances dx, probability of collision is proprtional to dx

$$dN = N(x)\left(\frac{1}{\lambda}\right)dx \quad \rightarrow \quad N(x) = N_0 e^{-x/\lambda}$$

Motion in a Gas

- Average distance = mean free path

$$\bar{x} = \frac{1}{N_o}\int_0^\infty x\frac{N(x)}{\lambda}dx = -\lambda\left[e^{-x/\lambda}\left(\frac{x}{\lambda}+1\right)\right]_0^\infty = \lambda$$

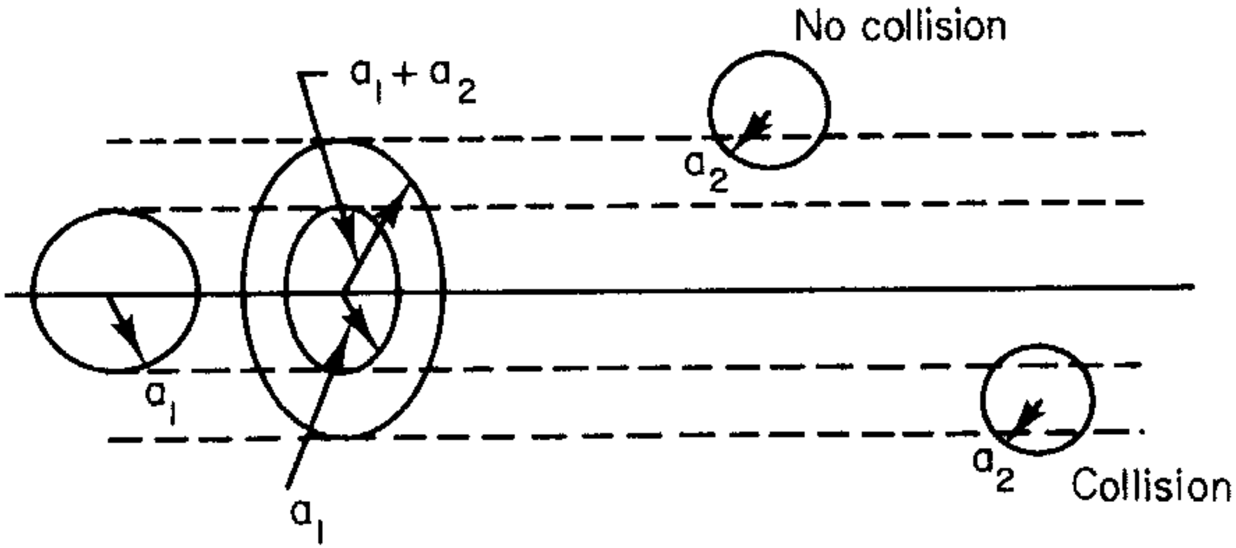
- Similar argument can be made for time

$$N(x) = N_0 e^{-x/t_c}$$

  - Collision time = t_c

Motion in a Gas

- Need to evaluate λ and t_c
- Consider one particle moving with a radius a_1
- Consider stationary particles with radius a_2



- Calculate collision possibilities

Motion in a Gas

- After moving a distance x, volume covered is given by,

$$V(x) = \pi(a_1 + a_2)^2 x$$

- On average, when a particle travels mean free path, there is one collision
  - Average number of particles in V(λ)=1
  - Concentration = 1/V(λ)

$$C = 1/V(\lambda) = 1/\pi(a_1 + a_2)^2 \lambda \Rightarrow \lambda = \frac{1}{\pi(a_1 + a_2)^2 C}$$

Motion in a Gas

- Collision *Cross Section* is $\pi(a_1 + a_2)^2$
  - Important for radiation interaction
- Example: gas at STP, volume of 1 mol = 22.4 L (C= 2.7×10^{25} m^{-3}), a_1=a_2=0.15 nm
  - λ=0.13 μm
  - 1000 times the molecular diameter
  - Assumption of infrequent collisions justified

Motion in a Gas

- Given mean free path λ,

$$t_c = \frac{\lambda}{\overline{v}}$$

- Taking the average speed as v_{rms},

$$t_c \approx \lambda \left(\frac{m}{3k_B T} \right)^{1/2}$$

  - Dependence on $m^{1/2}$ and λ
  - For air and room temperature, $t_c = 2\times10^{-10}$s

Motion in a Liquid

- Direct substitution in Gas equations?
- For water,
  - $\lambda = a = 0.1$ nm $\rightarrow$ assumption broken
  - $t_c \sim 10^{-13}$ s $\rightarrow$ much more frequent
  - Wrong calculations

Problem Assignments

- Information posted on web site
- Problems 1,4,5,6