1. Introduction. Convection and Diffusion.
2. The Convective Fluxes.
Thermodynamics tells us that systems move towards their state of stable equilibrium, where temperature, pressure and chemical potentials are constant.

Transport phenomena study how that happens.

Even if we are not at equilibrium (e.g. temperature is not constant), we can still use thermodynamic quantities, like $T$, $P$, $U$, etc…, which are defined within small volumes, that we treat like material points. These volumes are large enough so that thermodynamic can be applied (i.e. there are enough particles so that fluctuations can be neglected) and yet all variations due to macroscopic gradients are negligible.

This is the condition of **Local Equilibrium**.

$$\frac{\lambda \nabla T}{T} \leq \frac{\delta T}{T} = \frac{1}{\sqrt{N}} \ll 1$$

So we can speak of, say, a **temperature distribution**, $T(r,t)$. 
Convection and Diffusion

**Flux** of $F$ (mass, energy, momentum, chemical species):

$$\frac{F}{S \Delta t} = \frac{fV}{S \Delta t} \begin{cases} \text{Convection} \\ \text{Diffusion} \end{cases}$$

**Diffusion:** No net material fluxes

**Convective fluxes**

- $J_{Fc} = f v$
- $J_{Mc} = \rho v$
- $J_{Qc} = \rho v^2$
- $J_{Uc} = \rho v (c_v \Delta T/M_W)$
- $J_{Ac} = c_A v$

Convective transport is reversible.
Diffusive Fluxes - Constitutive Relations

- **Diffusive flux of** $F$, $J_{Fd} = -D_{F} \nabla (\rho f)$; $[D_{A}] = m^{2}/s$.

  - $f=1$; No diffusion (by definition).
  - $f=v$; Newton’s const. rel. $D_{Q} = \frac{v}{\rho} = \frac{\mu}{\rho}$ (kinematic viscosity). → $J_{Qd} = \tau = -\mu \frac{dv}{dy}$.
  - $f=cT$; Fourier’s const. rel, $D_{U} = \kappa/\rho c = \alpha$ (thermal diffusivity). → $J_{Ud} = -k \frac{dT}{dy}$.
  - $f=xA$; Fick’s const. rel. $D_{M} = D$ (molecular diffusivity). → $J_{Ad} = -D \frac{dcA}{dy}$.

\[
\frac{dS}{dt} = -\frac{1}{T} \frac{dE_{mecc}}{dt} \propto -J_{Fd} \cdot \nabla (\rho f).
\]

**Diffusive transport is irreversible**
Kinetic Theory of Diffusion

\[ n = n(y) = \text{number density.} \]

\[ \delta v \sim \sqrt{\frac{3kT}{m}} \ll V = \text{velocity fluctuations} \]

\[ \lambda = \text{mean free path} \]

\[ J_d = \left( \frac{1}{6} m \delta v \right) [n(z - \lambda)] - \left( \frac{1}{6} m \delta v \right) [n(z + \lambda)] \quad n(z \pm \lambda) = n(z) \pm \lambda \frac{dn}{dz} + \cdots \]

\[ J_d = -D \frac{dc}{dz} \quad c = mn \quad D = \frac{1}{3} \lambda \delta v \]

(Maxwell, 1860)
\[ \mathbf{J}_A = -D \nabla c_A \quad D = \text{Diffusivity} \quad [D] = m^2/s \quad \text{(Fick’s constitutive eqn.)} \]

\[ c \leftrightarrow T; \quad \mathbf{J}_U = -\kappa \nabla T = -\alpha \nabla u. \quad u = \rho cT; \quad \alpha = \kappa/\rho \]

\[ \kappa = \text{thermal conductivity}; \alpha = \text{heat diffusivity} \quad [\kappa] = W/(m K) \quad [\alpha] = m^2/s \]

\[ c \leftrightarrow v; \quad \mathbf{J}_Q = \tau = -\mu \nabla v = -v \nabla q. \quad q = \rho v; \quad v = \mu/\rho \quad \text{(Newton constitutive eqn.)} \]

\[ \mu = \text{(dynamic) viscosity}; \quad v = \text{kinematic viscosity} \quad (\text{momentum diffusivity}) \]

\[ [\mu] = Kg/(m s) \quad [v] = m^2/s \quad 1 \text{cP} \ (10^{-2} \text{Poise}) = 10^{-2} \text{g}/(\text{cm s}) = 10^{-3} \text{kg}/(\text{m s}) \]

**Dilute gas:** \[ v = \alpha = D = \lambda v/3 \]

# collisions / time = \[ n \, \delta v \, \sigma_0 = 1/\tau = v / \lambda \Rightarrow \lambda = 1 / (n \, \sigma_0). \quad [\lambda = 1 / (\sqrt{2} \, n \, \sigma_0)]; \quad \sigma_0 = \text{scattering cross section} = \pi d^2 \]

\[ D = \alpha = v = \frac{1}{3} \lambda \delta v = \frac{1}{n \sigma_0} \sqrt{\frac{kT}{6m}} \]

**Note:** \( \mu = mnv \) does not depend on \( n \) (nor on \( P \)).
Brownian Motion

Macromolecules are too large (with typical size $R > 0.1 \, \mu m$) to be affected directly by thermal fluctuations. However, when they are immersed in a fluid, they are affected by collisions with fluid molecules, which are much smaller and therefore thermally fluctuates. The result is the so called Brownian motion.
Diffusion and Random Walk

\[ R = \sum_{i=1}^{N} r_i \quad |r_i| = \ell \quad (= \lambda \sqrt{2}) \]

\[ \langle R^2 \rangle = \langle R \cdot R \rangle = \sum_{i=1}^{N} \langle r_i^2 \rangle + \sum_{i=1}^{N} \sum_{j=1}^{N} \langle r_i \cdot r_j \rangle = N \ell^2 \]

\[ N = (\Delta t)/\tau = (\Delta t) \delta \nu/\lambda \]

\[ \langle R^2 \rangle = 6D(\Delta t) \quad D = \frac{1}{3} \lambda (\delta \nu) \quad \text{(self-diffusivity)} \]

We saw that \( D = \lambda \delta \nu / 3 \) is also the gradient diffusivity: \( J = Vc - D \nabla c \)

Important consequence:

\[ c \propto P \propto \exp(-\phi/kT) \quad \text{(Boltzmann distribution, } \phi = \text{ potential)} \]

\[ J = 0 \rightarrow \nabla c/c = V/D \rightarrow \nabla \phi / kT = -M \nabla \phi / D \]

\[ D = MkT \]

Einstein (1906)
In General: What is Diffusion?

**Self-Diffusion**

\[ R^2 = 6 D^S t \]
\[ D^S \propto \ell v \]

\[ D^s \approx d\langle R^2 \rangle/dt = \text{temporal growth of the mean square displacement of a tracer particle immersed in a uniform medium.} \]

**Gradient Diffusion**

\[ J_M = - D^G \nabla c \]

\[ D^G = J_M / \nabla c = \text{proportionality term between mass flux and concentration gradient.} \]

\[ D^S = D^G = D_m \text{ only for linear systems, that is when } D \text{ does not depend on } c. \]

(Einstein, 1906; more generally, fluctuation-dissipation theorem, 1954)
Effect of Diffusion

At steady state, \( T = T_f, c = c_f, \) and \( v = v_f, \) which are equal to their values at the wall.

The characteristic time necessary to reach steady state is the ratio between the square of the characteristic length, \( L^2, \) and the diffusivity of energy (i.e. \( \alpha \)), momentum (i.e. \( \nu \)) or mass (i.e. \( D \)).

Note: typical values for water: \( \alpha \approx 10^{-3} \text{ cm}^2/\text{s}, \ D \approx 10^{-5} \text{ cm}^2/\text{s}; \ \nu \approx 10^{-2} \text{ cm}^2/\text{s}. \)

Accordingly, diffusion times for mass are much slower than those of thermal or momentum diffusion.
Convection / Diffusion

\[ \frac{\text{convection}}{\text{diffusion}} = \frac{J_{\text{conv}}}{J_{\text{diff}}} = \left\{ \begin{array}{l}
Re = \frac{VL}{\nu} = \text{Reynolds number} \\
Pe_Q = \frac{VL}{\alpha} = \text{Re Pr} = \text{Peclet number (heat)} \\
Pe_M = \frac{VL}{D} = \text{Re Sc} = \text{Peclet number (mass)}
\end{array} \right\} \]

\[ Sc = \frac{\nu}{D} \approx 10^3 - 10^4 = \text{Schmidt number} \]

\[ Pr = \frac{\nu}{\alpha} \approx 1 - 10 = \text{Prandtl number} \]

\textbf{In liquids:} \quad Sc \approx 10^3 - 10^4; \quad Pr = \approx 1 - 10 \quad \rightarrow \quad Pe_M >> Re, Pe_Q.

\textbf{In gases:} \quad Sc \approx Pr \approx 1 \quad \rightarrow \quad Pe_M \approx Re \approx Pe_Q \]