

HH0046 Fick's Law For Diffusion

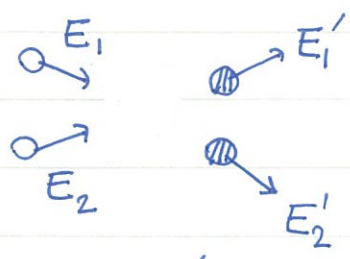
Diffusion in equilibrium - Due to frequent collisions, a molecule's trajectory is rather random,



$$\Delta x(t) \equiv \sqrt{\langle x^2(t) \rangle - \langle x(t) \rangle^2} = \sqrt{\langle x^2(t) \rangle} \propto t^{\frac{1}{2}}$$

The slow spreading of $\Delta x \sim \sqrt{t}$ is called diffusion.

Note that the microscopic collisions not only cause diffusive dynamics but also explain the Boltzmann distribution in equilibrium.



In equilibrium, the transition rate vanishes according to detail balance

$$P(E_1)P(E_2) = P(E_1')P(E_2')$$

$\gamma = \gamma'$ by time-reversal symmetry.

$E_1 + E_2 = E_1' + E_2'$
energy conservation.

It means $P(E)P(E_0 - E) = \text{const.}$

OR $\log P(E) + \log P(E_0 - E) = \text{const.}$

Differentiate with respect to E,

$$\left. \frac{d \log P}{dE} \right|_E - \left. \frac{d \log P}{dE} \right|_{E_0 - E} = 0$$

Since E and $E_0 - E$ are arbitrary,

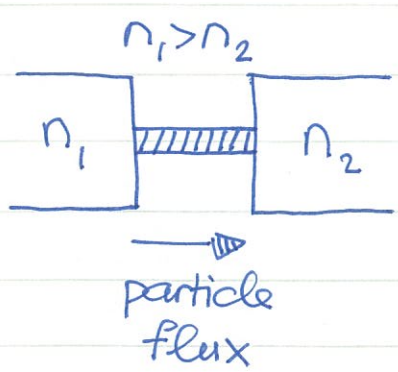
$$\frac{d \log P}{dE} = C$$

equilibrium condition.

Thus, $\log P = CE + D,$

$$P(E) = e^C \cdot e^{DE}$$

← Boltzmann distribution.



Now consider diffusion in non-equilibrium yet steady state. From empirical observations,

$$(\text{particle flux}) \propto (n_1 - n_2)$$

density diff not too large.

Let us be more precise and introduce the flux density of some quantity A:

$$\vec{J}_A = \text{flux density of A} \Rightarrow |\vec{J}_A| =$$

$\overset{\text{MAX}}{\ddot{u}}$
net quantity of A transported across unit area in unit time

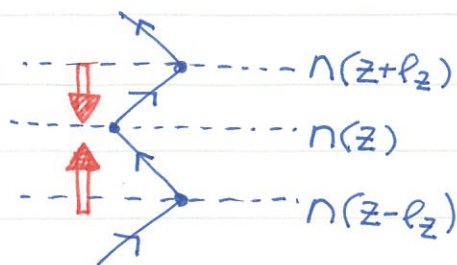
What about the direction? \hat{J}_A is the direction of the unit area when the net transported quantity reaches maximum!

For isothermal diffusion, we find that

$$\vec{J}_n = -D \vec{\nabla} n$$

Fick's law: D is the diffusion constant.

Let's try to find a microscopic explanation of Fick's law.



Assume molecules reach local thermal equilibrium after collisions \rightarrow local density $n = n(z)$ may be different.

$$J_n^z = \frac{1}{2} n(z-l_z) \cdot \bar{c}_z$$

\leftarrow upward flux

$$- \frac{1}{2} n(z+l_z) \cdot \bar{c}_z$$

\leftarrow downward flux.

If the mean free path

l is short,

$$J_n^z \approx \frac{1}{2} \bar{c}_z \frac{dn}{dz} \cdot 2l_z = - \bar{c}_z l_z \frac{dn}{dz}$$

average over the hemisphere,

$$\langle \bar{c}_z l_z \rangle_{\text{hemi}} = \bar{c} l \cdot \frac{1}{2\pi} \int_0^{2\pi} d\phi \int_0^{\frac{\pi}{2}} \sin\theta d\theta \cdot \cos^2\theta = \frac{1}{3} \bar{c} l$$

where $\bar{c}_z = \bar{c} \cos\theta$, $l_z = l \cos\theta$. Finally, we obtain the important relation between \vec{J}_n and n

$$J_n^z = - \frac{1}{3} \bar{c} l \frac{dn}{dz}$$

i.e.

$$\vec{J}_n = -D \vec{\nabla} n$$

$$D = \frac{1}{3} \bar{c} l$$

① Thermal conductivity: We can apply the same idea to heat conduction due to diffusive dynamics. Let us generalize the above derivation for some quantity A .

$$\text{Equilibrium} \rightarrow \vec{J}_A = \rho_A \langle \vec{v} \rangle = 0$$

$$\text{Steady State} \rightarrow \vec{J}_A = -D \vec{\nabla} \rho_A \neq 0$$

No drift flow
is considered
in these cases $\ddot{\circ}$

Suppose the energy density is P_u and its flux density is \vec{J}_u

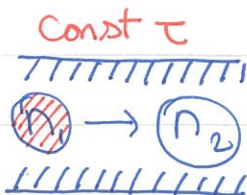
$\vec{J}_u = -D \vec{\nabla} P_u$, note that $\partial_i P_u = \left(\frac{dP_u}{d\tau}\right) \partial_i \tau$ by chain rule,

$\vec{J}_u = -K \vec{\nabla} \tau$ with $K = D \cdot \frac{dP_u}{d\tau} = D \cdot c_v$ ← heat capacity per unit volume.

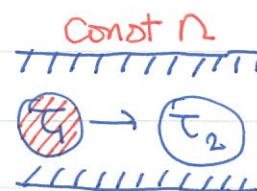
Thus, the constant K is related to microscopic collisions as well,

$K = \frac{1}{3} c_v \bar{c} \ell$

Particle Flux driven by density gradient is similar to energy Flux driven by temperature gradient.



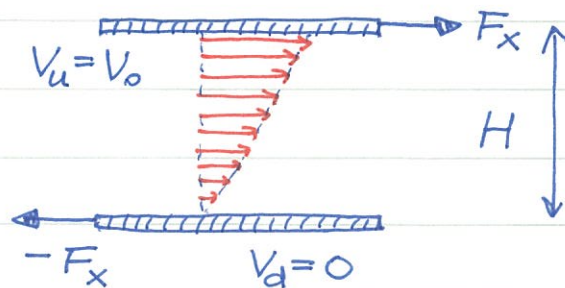
$P_i \propto n_i$



$P_i \propto \tau_i$

⊙ **Viscosity**: We now want to view viscosity as consequence of momentum transverse flow.

$V_x(z) = V_0 \cdot \frac{z}{H} \propto z$ ← $\frac{dv_x}{dz} \neq 0$



The shear stress is $f_x = F_x/A$
From empirical observations,

$f_x = -\eta \frac{dv_x}{dz}$ where η is the viscosity coefficient.

Can this be explained by microscopic collisions as well? Yes!



flux of P_x from the fluid.

Since the slab is moving at const velocity,

$F_x = \text{flux of } P_x \text{ from fluid}$

OR

$f_x = \text{flux density of } P_x \text{ from fluid}$

Q: What happens to the other slab?

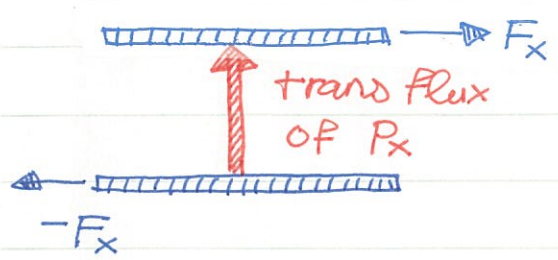
The density of momentum P_x is $P_x = n \cdot M u_x$. Thus, the corresponding flux density is $J_{P_x}^z = -D \frac{dP_x}{dz} = -D n M \frac{du_x}{dz}$

$nM = \rho$ is the mass density, the flux density equals the stress $f_x = J_{P_x}^z$. $f_x = -\eta \frac{du_x}{dz}$ with $\eta = D\rho = \frac{1}{3} \rho \bar{c} l$

It may seem that the viscosity coefficient η depends on the density. Well, it is not!

$\eta = \frac{1}{3} \rho \bar{c} l = \frac{1}{3} \cdot \cancel{n} M \bar{c} \cdot \frac{1}{\cancel{n} \pi d^2} = \frac{M \bar{c}}{3 \pi d^2}$ indep of density n !!

Now we have a refreshing view on viscosity: The steady state without time dependence is reached



$F_x = J_{P_x}^z \cdot A$ on both slabs.

In addition, there is a relation between K and η .

$\begin{cases} K = \frac{1}{3} c_v \bar{c} l \\ \eta = \frac{1}{3} \rho \bar{c} l \end{cases} \rightarrow \frac{K\rho}{\eta c_v} = 1$

$N_2: 1.91$	$H_2: 1.91$
$O_2: 1.90$	$He: 2.40$

The value of $K\rho/\eta c_v$ is not unity for realistic gases, but close (given our derivation is so rough).



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