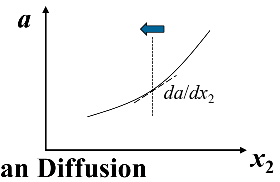
Transport Properties

- Consider the **diffusional transport** properties of a gas (or any matter)
- Diffusion usually modeled as proportional to gradient of some macroscopic property (***a***)



Fourier's Law

"heat" flux $q_2 = -k \dfrac{dT}{dx_2}$

thermal conductivity

Newtonian Fluid

shear stress $\tau_{12} = \mu \dfrac{du_1}{dx_2}$

(dynamic) viscosity

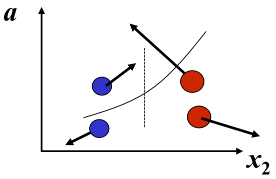
Fickian Diffusion

diffusive mass flux $j_{A,2} = -D_{AB} \dfrac{d\rho_A}{dx_2}$

mass diffusivity (or diffusion coefficient)

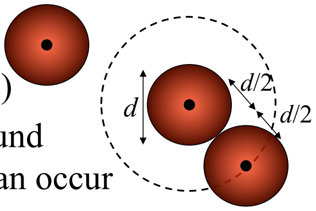
- Each of these is a flux of some property: energy, momentum, mass
  - due to a nonequilibrium condition (gradient)

Diffusion and Molecular Motion



- **What is the source/cause of diffusion**?
  - a molecule "carries" its properties as it moves
  - *diffusion is transport of a property by the random motion of molecules*
    - recall – already illustrated that pressure results from one-way momentum flux (transport) due to random molecular motion
- When collision occurs, molecular property transport by that molecule's journey ends (momentum & energy transferred)
- So **rate** of diffusion ought to be related to
  - how far molecule moves before a "collision" = **mean free path**
  - and how often collisions occur = **collision frequency**
- Basic understanding of these concepts can be developed using simple "hard-sphere" model

Simple Collision Estimation Model



- Consider hard sphere gas molecules of diameter *d* (all alike)
- Can describe a simple region around each molecule where collisions can occur
  - **sphere-of-influence with radius *d*** (=*d*/2+*d*/2)
    - collision occurs whenever distance between molecular centers closes to this value
- Now that we have defined "when" a collision occurs, can ask how often collisions occur

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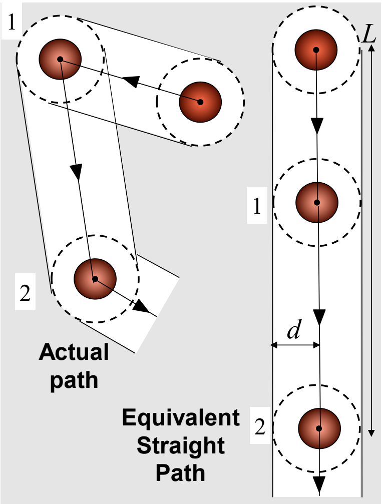
Collision Frequency



- Consider path swept out by our molecule
- Number of collisions depends on number of other molecules in its path

$$= V_{cylinder} \times n$$

number density

$$= A_{cyl} \times L \times n$$

assume molecule moves with avg. molec. speed

$$= \pi d^2 \times \overline{C} \Delta t \times n$$

- Then **collision frequency** (#/time), $\theta = n(\pi d^2)\overline{C}$

$$\theta = n\sigma\overline{C}$$

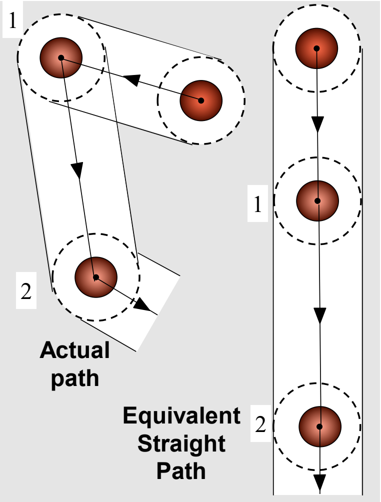
collision cross-section

not same as LJ parameter

Mean Free Path

- How far (on average) will our molecule travel between collisions?
  - given by *time between collisions* × *avg. molec. speed*
- Called the **mean free path**

$$\lambda = \frac{1}{\theta}\overline{C} = \frac{\overline{C}}{n\sigma\overline{C}} = \frac{1}{n\sigma}$$



Warning

- Careful - for this simplistic approach to find θ we assumed all other molecules in path of our molecule were:
  - identical (same size) to our molecule (possible)
  - and were not moving (not true)
- Will see later that $\theta = n\sigma\overline{g}$ ← **mean relative speed between molecules**
  - and for identical molecules, $\overline{g} = \sqrt{2}\ \overline{C}$
- So for our previous case

$$\lambda = 1/\sqrt{2}n\sigma$$

STP Values for Air

- What is typical value for mean free path in air at STP? $\lambda = 1/\sqrt{2}n\sigma$
  - N_2, O_2 have d ~ few Å, e.g., ~3×10^{-8} *cm*
    - so $\sigma \sim \pi d^2 \sim 3\times10^{-15}\ cm^2$
  - at STP, $n \sim 2.7\times10^{19}\ cm^{-3}$
  - so $\lambda \sim cm/(1.4\times3\times2.7\times10^4) \sim 9\times10^{-6}\ cm \sim$ **90 *nm***
  - Comparing

$\lambda >> \Delta > d$

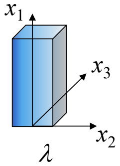
λ	$\Delta=n^{-1/3}$	d
90 nm	3 nm	0.3 nm

- What is typical value for collision frequency at STP? $\theta = \bar{C}/\lambda$
  - assuming mean speed similar to speed of sound,
    $\theta \sim 330/9\times10^{-8} \sim \mathbf{4\times10^9\ s^{-1}}$ (~0.1-0.5*ns between collisions*)

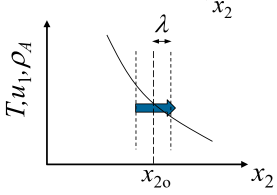
Pressure/Temperature Scaling

- Interesting to examine how λ and θ scale with temperature and pressure
- **Mean free path**
  - $\lambda \propto 1/n \propto T/p$
  - *mean free path increases at lower density (low p, high T)*
- **Collision frequency**
  - $\theta \propto n\,\bar{C} \propto (p/T)\,T^{1/2} \propto p/T^{1/2}$
  - *collisions occur more often at high p and low T*
    - *but for fixed density, more often at high T*

Heuristic Diffusion Model



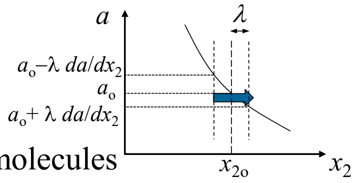
- Now that we have simple model for molecular motion, we can apply it to diffusion
  - **find physical expressions for k, μ, D**
- Consider 1-d gradient in ρ_A, u_1 or T at plane located @ x_{2o}



- Molecules crossing x_{2o} carry their mass, momentum, energy
  - those moving rightward (in gradient direction) carry “more” than leftward moving
    - so net flux of property will be rightward
- Molecule carries properties from its last collision position
  - so look at molecules that are ±λ away from x_{2o}

Heuristic Diffusion Model: Fluxes

- We want to know net flux of property across x_{2o} due to gradient



- Start with **1-way number flux**
  - number_molec/area/time
  - should depend on how many molecules present (or number density n) and how fast they are moving (e.g., mean speed $\bar{C}$)
  - turns out $=n\bar{C}/4$ (see V&K Ex. II5.1a)

mass of molec.

mass specific property

- Then 1-way flux of property = $n\bar{C}/4 \times m \times a(x_2)$
  - using 1st term in Taylor expansion $a(x_{2o}\pm\lambda)=a_o\pm\lambda\, da/dx_2$
- **Net flux** $\cong n\bar{C}/4 \times m \times [(\cancel{a_o}-\lambda\, da/dx_2)-(\cancel{a_o}+\lambda\, da/dx_2)]$

Heuristic Diffusion Model: Net Flux

- So net property flux $\cong -\frac{1}{2} nm\bar{C}\,\lambda\; da/dx_2 = -\frac{1}{2}\rho\bar{C}\,\lambda\; da/dx_2$
- Compare this expression to basic versions for j, τ and q

Property	da	Net Flux	Diff. Expression	Diffusivities
Mass	dY_A	$-\rho\bar{C}_A\lambda/2\;\; dY_A/dx$	$-\rho D_{AA}\, dY_A/dx$	$D_{AA} \approx \bar{C}_A\lambda/2$
Momentum	du	$-\rho\bar{C}\lambda/2\;\; du/dx$	$^*\; -\mu\, du/dx$	$\mu/\rho \approx \bar{C}\,\lambda/2$
Energy	$de \sim c_v dT$	$-\rho\bar{C}\lambda/2\; c_v\, dT/dx$	$-k\, dT/dx$	$k/\rho c_v \approx \bar{C}\,\lambda/2$

- **Takeaways**
  - all diffusivities scale as $\bar{C}\lambda = \theta\,\lambda^2 \propto \bar{C}/n\sigma$ (and units l^2/t)
    - diffusion depends on how far molecules go between collisions and how fast they move (or how often they collide)
    - larger λ, faster $\bar{C}$ (less time between collisions) ⇒ higher diffusivities
  - ratios of diffusivities O(1) for gases

** minus since exerted force = mom. loss*

Comments on These Results: μ, *D*

$$D \approx \mu/\rho \approx k/\rho c_v \approx \bar{C}\;\lambda/2$$

- Implicitly assumed "weak gradients" (~ equilibrium)
  - gradient at x_{2o} and $x_{2o}\pm\lambda$ nearly the same
- Estimates for μ reasonably close for gases (especially monatomic)
- Suggests Schmidt number $(Sc) \equiv \mu/\rho D \cong 1$
  - close for monatomic gases (~5/6)
- Reasonable (p,T) scaling for μ
  - $\mu \propto n\, T^{1/2}\,(1/n) \Rightarrow \mu \neq \mu(p)$ and $\mu \propto T^{0.5}$

correct for ideal gases   *closer to $T^{0.7}$ for noble gases, air*

Comments on These Results: *k*

$D \approx \mu/\rho \approx k/\rho c_v \approx \bar{C}\,\lambda/2$

Eucken correction
can be derived from
more accurate analysis
(Chapman-Enskog)

- Under-predicts thermal conductivity k
  - e.g., ~2.5×low for monatomic gas ($k/\rho c_v \approx 2.5\,\bar{C}\,\lambda/2 = 2.5\mu/\rho$)
  - mostly because we ignored correlation between molecular speed and energy
    - higher energy molecules move faster (across plane)
  - specifics of previous collision before crossing plane are also important
- With Eucken correction, suggests Prandlt number

$$Pr \equiv \mu/\rho\alpha = \mu c_p/k = 2/5\,\gamma$$

thermal diffusivity,
$\alpha = k/\rho c_p$

Gas (low T)	γ	Pr
Monatomic	5/3	2/3
Diatomic	7/5	14/25≅0.56

good agreement with data

not close, actual value ~0.75

Comments on These Results: *k*

$\mu/\rho \approx k/(2.5\rho c_v) \approx \bar{C}\,\lambda/2$

- Why disagreement for diatomic gases (and polyatomics)?
  - because Eucken correction should only apply to part of molecular energy correlated to molecular speed

$$e = e_{tr} + e_{int}$$

- So consider $k = k_{tr} + k_{int} = 2.5\mu\, c_{v,tr} + \mu\, c_{v,int}$
- Then $Pr = \dfrac{\gamma c_v \mu}{k} = \dfrac{\gamma c_v \mu}{2.5\mu\, c_{v,tr} + \mu\, c_{v,int}} = \dfrac{\gamma}{1.5\,(c_{v,tr}/c_v) + 1}$

$$= \frac{\gamma}{1.5\,(\frac{3}{2}(c_p - c_v)/c_v) + 1} = \frac{\gamma}{\frac{9}{4}(\gamma - 1) + 1} = \frac{4\gamma}{9\gamma - 5}$$

- Now return to low T diatomic gas with γ=1.4

$\Rightarrow Pr = 0.74$ *very close to experimental value 0.75*