Lecture 6: Transport coefficients

I. Intro to transport coefficients

* In our last lecture, we encountered three coefficients that appeared in our flux expressions:

$$\underline{q} = -k \underline{\nabla} T \qquad k\text{: thermal conductivity}$$

$$\underline{j}_A = -\rho D_{AB} \underline{\nabla} \omega_A \qquad D_{AB}\text{: binary (mutual) diffusion coefficient}$$

$$\underline{\underline{\tau}} = \mu \left[(\underline{\nabla}\underline{v}) + (\underline{\nabla}\underline{v})^T \right] \qquad \mu\text{: viscosity}$$

* They have physical meanings: rate of transport of energy, mass, and momentum, respectively.

* They depend on the material. They are material properties.

* We will talk about three aspects of transport properties:

- Units and order of magnitude (from experiments)
- Corresponding states (semi-empirical)
- theory and prediction

II. Units and O.O.M. from experiments

A. Viscosity

* Viscosity has units of Pa·S in SI and Poise in the CGS system.

$$1 \text{ Pa} \cdot \text{S} = 1 \frac{\text{kg}}{\text{m} \cdot \text{s}}$$

$$1 \text{ Poise} = \frac{1 g}{cm \cdot s} = 10 \text{ Pa} \cdot s$$

* viscosities are generally between 10^{-5} to 10^{0} Pa·s for most cases of interest.

	Gas	Liquid
typical	10^{-5} Pa·s	10^{-3} Pa·s to 10^{0} Pa·s
example	air = 1.813×10^{-5} Pa·s	water = 1.002×10^{-3} Pa·s glycerol = 0.934×10^{0} Pa·s (20°C, 1 atm for both)

* Note: $\frac{\mu_{liq}}{\mu_{gas}} \approx 10^2$

B. Thermal Conductivity

* thermal conductivity is usually given in $\frac{W}{mK}$ in SI.

$$1 \frac{W}{mK} = 1 \frac{kg\, m}{s^3 K}$$

* Thermal conductivities range from 10^{-2} W/mK to 10^{2} W/mK

	Gas	Liquid (*)	Solid (**)
typical	10^{-2} W/mK	10^{-1} W/mK to 10^{0} W/mK	10^{2} W/mK
example	O_2 = 0.0266 W/mK (300K, 1 atm)	H_2O = 0.689 W/mK (300K, sat press)	Cu = 384 W/mK (291.2 K)

(*) Also solid insulators; non-metal liquids

(**) metals, liquid metals

*Again, note: $\frac{k_{liq}}{k_{gas}} \approx 10^2$, $\frac{k_{solid}}{k_{liq}} \approx 10^2$

C. Mass Diffusivity

* Mass diffusivities are typically given in m^2/s (SI units), but also occasionally in cm^2/s (CGS) or $\mu m^2/s$.

* Mass diffusion coefficients usually range from 10^{-13} m^2/s to 10^{-5} m^2/s.

	Gas	Liquid	Solid
typical	10^{-5} m^2/s	10^{-9} m^2/s	10^{-13} m^2/s
example	$H_2O-N_2 = 2.59 \times 10^{-5}$ $\frac{m^2}{s}$ (gas, 305K, 1atm)	$EtOH-H_2O = 7.43 \times 10^{-10}$ $\frac{m^2}{s}$ (liquid, $x_{EtOH} = 0.68$)	He-Silica = 2.4×10^{-14} m^2/s (trace He in SiO_2)

* Note D_{AB} goes down (opposite of μ, k) from gas → liq → solid

$$\frac{D_{AB,liq}}{D_{AB,gas}} \approx 10^{-4} \qquad \frac{D_{AB,sol}}{D_{AB,liq}} \approx 10^{-4}$$

III. Corresponding States

* In thermodynamics, you learned that gas/liquid critical behavior had important universal features that seem to be shared among all pure substanes.

* therefore, scaling variables by their critical values, led to a collapse of the two phase envelope

(show Fig 2 from Gugenheim, J. chem Phys, 1945.)

* Aside: Why is this so?

- Rigorously only true for spherically symmetric molecules with the same, universal intermolecular potential. (see e.g. Pitzer, J. Chem. Phys. 1939) This isn't strictly true, but is often pretty good.
- It turns out though, that near the critical point, behavior is even more universal, even if the intermolecular potentials are not self-similar. So, corresponding states is still useful!

* Thus, when scaled by the critical value, the gases or liquids are in "corresponding states" relative to their critical point.

* It turns out, one can show (using statistical mechanics) that transport properties can also obey a corresponding states principle (same assumptions as thermodynamic states).

* This means we can use corresponding states (by scaling by critical values of η_c, k_c, $D_{AB,c}$) to organize and (*) correlate our experimental (or simulation) data. It also helps us to observe trends with respect to temperature & pressure dependence.

* Show slides of corresponding states data.

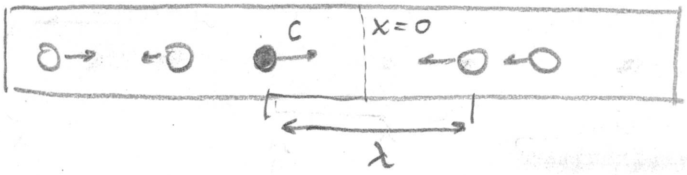
* Unfortunately corresponding states does not explain why the properties have these trends. We need theories for that.

IV. Theory for transport coefficients

* In general, this is hard. One needs statistical mechanics. We will only do a very simple theory for dilute gases. Liquids are much harder.

A. Random walk model (elementary kinetic theory)

* Consider a 1D gas with mean free path λ and mean molecular velocity, c.



← area : λ^2

(just one slice of the gas of thickness, λ)

avg time between collisions : $\tau = \frac{\lambda}{c}$ ← for values, see p. 15 in Deen

* What is the diffusivity of the gas?

* What is the flux?

50% probability to go either left or right.

$$+x\text{-dir}: \quad \frac{\#\text{ atoms}}{\text{time} \cdot \text{area}} = \frac{0.5 \cdot n|_{x=0^+}}{\tau \quad \lambda^2}$$

$$-x\text{-dir}: \quad \frac{\#\text{ atoms}}{\text{time} \cdot \text{area}} = \frac{0.5 \quad n|_{x=0^-}}{\tau \, \lambda^2}$$

$$J_x^{(m)}\Big|_{x=0} = \frac{0.5}{\lambda^2 \tau}\left(n|_{x=0^+} - n|_{x=0^-}\right)$$

- the concentration is the ~~#~~ # of atoms / volume:

$$c|_{x=0^+} = \frac{n|_{x=0^+}}{\lambda^3}, \quad c|_{x=0^-} = \frac{n|_{x=0^-}}{\lambda^3}$$

- therefore:

$$J^{(m)}_x|_{x=0} = \frac{1}{2}\frac{\lambda}{\tau}\left(c|_{x=0^+} - c|_{x=0^-}\right)$$

$$\lim_{\lambda\to0} J^{(m)}_x|_{x=0} = \lim_{\lambda\to0} \frac{1}{2}\frac{\lambda^2}{\tau} \underbrace{\frac{c|_{x=0^+} - c|_{x=0^-}}{\lambda}}_{\text{negative gradient}}$$

$$= -\frac{1}{2}\frac{\lambda^2}{\tau}\frac{dc}{dx}\Big|_{x=0}$$

$$\frac{dc}{dx} = \lim_{\lambda\to0}\frac{\underset{\substack{\uparrow\\ c_1\\ R\to L}}{c|_{x=0^-}} - \underset{\substack{\uparrow\\ c_0\\ L\to R}}{c|_{x=0^+}}}{\lambda}$$

$$\boxed{J^{(m)}_x|_{x=0} = -D\frac{dc}{dx}\Big|_{x=0}}$$

$$\boxed{D = \frac{1}{2}\frac{\lambda^2}{\tau}}$$

* For 3D, 1/2 → 1/6 (3 independent directions)

* Intuition? (from kinetic theory of gases)

$$\lambda = \frac{k_B T}{\sqrt{2}\pi d^2 P} \qquad c = \left(\frac{8 k_B T}{\pi m}\right)^{1/2}$$

k_B: Boltzmann, T: temperature

d: molecular diameter, P: pressure

m: mass per molecule

$D \propto \lambda c$	$D\uparrow$ as $T\uparrow$

This checks out w/ corresponding states data.

* There is a more complex version of this theory called "Chapman - Enskog" theory. It uses Lennard-Jones potentials. It is good for low-density gases.

B. Everything is a diffusivity

* How about viscosities or thermal conductivities? It turns out we can re-write viscosities as "momentum diffusivities" and conductivities as "thermal diffusivities" and use kinetic theory like above.

$$\underline{j}_A = -D_{AB}\,\underline{\nabla}(\rho_A) \quad \text{species mass}$$

$$q = -\frac{k}{\rho \hat{C}_p}\,\nabla(\rho \hat{C}_p T) \quad \text{energy}$$

$$\underline{\underline{\tau}} = \frac{\mu}{\rho}\left[\rho(\underline{\nabla}\underline{v}) + \rho(\underline{\nabla}\underline{v})^T\right] \quad \text{momentum}$$

D_{AB} : mass diffusivity

$\alpha = \dfrac{k}{\rho \hat{C}_p}$ thermal diffusivity

$\nu = \dfrac{\mu}{\rho}$ momentum diffusivity (kinematic viscosity)

* All have same units of m^2/s or cm^2/s

* Note how ρ is in the denominator for α & ν. This is why corresponding states plots change for α & ν versus D_{AB}.

* How predict viscosity?

let $D_{AB} = \nu \Rightarrow \boxed{\mu = \rho D_{AB}}$

* How predict thermal conductivity

let $D_{AB} = \alpha \Rightarrow \boxed{k = \rho \hat{C}_p D_{AB}}$

* Some final notes:

- Ratio's of the various diffusivities are important dimensionless numbers

$$Pr = \frac{\nu}{\alpha} = \frac{\mu \hat{C}_p}{k} \quad \text{Prandtl number} \left(\frac{\text{momentum}}{\text{heat}}\right)$$

$$Sc = \frac{\nu}{D_{AB}} = \frac{\mu}{\rho D_{AB}} \quad \text{Schmidt number} \left(\frac{\text{momentum}}{\text{species mass}}\right)$$

$$Le = \frac{\alpha}{D_{AB}} = \frac{k}{\rho \hat{C}_p D_{AB}} = \frac{Sc}{Pr} \quad \text{Lewis number} \left(\frac{\text{heat}}{\text{species mass}}\right)$$

- Simulations can be used to predict transport coefficients. This is very much an active area of research. Good bridge between empirically observed (experimental) results and theory.