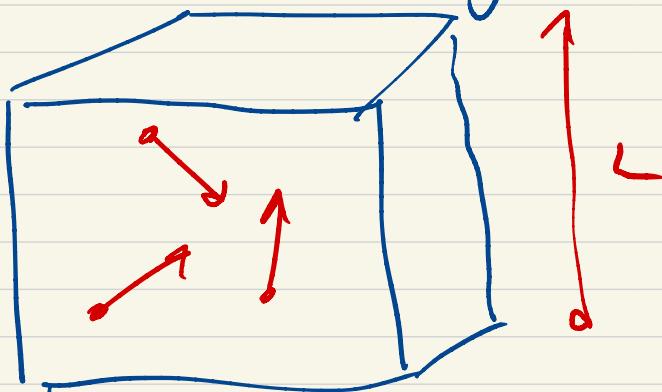


Molecular Thermodynamics

Now that we have our stat. thermo models, we can use them + quantum insights to predict thermo properties of collections of molecules.

Start w/ a box full of translating molecules — a gas.



N particles

T temperature

$$L^3 = V \text{ volume}$$

For simplicity, assume monoatomic, eg Kr

From QM, the energy of a single molecule given by translational PLAB model

$$E = \frac{(n_x^2 + n_y^2 + n_z^2) \pi^2 \hbar^2}{2mL^2}$$

$$n_x, n_y, n_z = 1, 2, \dots$$

Let's assume energies of all atoms are additive.

$$E = E_1 + E_2 + \dots$$

Further, these atoms are indistinguishable — moving about & can't tell apart.

Need partition function

$$Q(n, V, T) = g^{(V, T)} / n!$$

$$g^{(V, T)} = \sum_{n_x} \sum_{n_y} \sum_{n_z} e^{-E(n_x, n_y, n_z) \beta}$$

$$Z_1 = \left(\sum_{n_x} e^{-E_0 n_x^2 \beta} \right)^3$$

factors into
3 identical
parts —
separable

$$\epsilon_0 = \frac{\pi^2 \hbar^2}{2mL^2} \quad \text{sets energy scale}$$

$$Ex \quad Kr, \quad L = 1 \text{ dm} \quad \epsilon_0 = 5.9 \times 10^{-22} \text{ eV}$$

↑ tiny!

$$\Theta = \frac{\epsilon_0}{k_B} = 6 \times 10^{-18} \text{ K}$$

Always interested in $T \gg \Theta$

$$g_{10}(T) = \sum_{n\infty} e^{-n^2(\Theta/T)}$$

Because $\Theta/T \ll 1$, many terms contribute, and we can approx sum as an integral.

$$\approx \int_0^\infty e^{-x^2(\Theta/T)} dx$$

$$= \frac{1}{2} \left(\frac{\pi T}{\Theta} \right)^{1/2} = \underbrace{\left(\frac{2\pi m k_B T}{h^2} \right)^{1/2}}_{L^{-1}} \cdot L$$

"thermal wavelength"

$$\lambda = \left(\frac{h^2}{2\pi m k_B T} \right)^{1/2}, \quad g_{10} = L/\lambda$$

$$Kr, L = 1 \text{ dm} \quad T = 298 \text{ K}$$

$$l = 1.104 \times 10^{-11} \text{ m}$$

$$\mathcal{E}_{1D} = \frac{1 \text{ dm}}{n} \sim 9.0 \times 10^9$$

translational states in 1D,
for 1 particle

$$\mathcal{E}_{3D} = \mathcal{E}_{1D}^3 = \left(\frac{L}{n}\right)^3 = V/n^3.$$

$$\rightarrow (9 \times 10^9)^3 = 7 \times 10^{29}$$

accessible translational states in 3D

$$Q_{Kr}(n, V, T) = \mathcal{E}_{3D}^n / n!$$

$$= \frac{1}{n!} \left(\frac{V}{n^3}\right)^n$$

$$\ln Q = n \ln(V/n^3) - \ln n!$$

$$= n(\ln V - 3 \ln n - \ln n + 1)$$

(Stirling's approximation)

Internal energy

$$U = - \left(\frac{\partial \ln Q}{\partial \beta} \right)_{N,V} = - N \left(\frac{\partial \ln \underline{Z}}{\partial \beta} \right)$$

$$\ln \underline{Z} = \ln V - 3 \ln N$$

$$= \ln V - \frac{3}{2} \left(\ln \beta + \ln \frac{\hbar^2}{2 \pi m} \right)$$

$$\frac{\partial \ln \underline{Z}}{\partial \beta} = - \frac{3}{2} \cdot \frac{1}{\beta}$$

$$U = \frac{3}{2} N \cdot \frac{1}{\beta} = \frac{3}{2} N k_B T$$

$$= \frac{3}{2} n R T$$

$$\text{MOLAR } \bar{U} = \frac{U}{N} = \frac{3}{2} R T$$

Identical to result from gas kinetic theory !!

$$C_V = \left(\frac{\partial \bar{U}}{\partial T} \right)_{N,V} = \frac{3}{2} R \quad \begin{matrix} \text{right on} \\ \text{for } k_r !! \end{matrix}$$

$$P = \frac{N}{V} \left(\frac{\partial \ln Z}{\partial V} \right)_{N, \beta}$$

$$= \frac{N}{V} \cdot \frac{1}{V} \quad \Rightarrow$$

$$PV = N k_B T$$

$$= n R T$$

Cool! QM + PIAB + Boltzmann
 \rightarrow Ideal gas law!!

$$A = -\frac{N}{V} \left[\ln \left(\frac{V}{h} \right) + 1 \right]$$

$$\bar{A} = RT \left[\ln \left(\frac{N V^3}{h} \right) - 1 \right]$$

$$= RT \left[\ln \left(\frac{P}{k_B T} V^3 \right) - 1 \right]$$

Note \bar{A} depends on

$$\frac{N}{V} = \frac{P}{k_B T}$$

Conventional to define standard

state

$$C^\circ = \left(\frac{N}{V} \right)^\circ \quad \text{-or-} \quad P^\circ = k_B T C^\circ$$

molecules
volume

HAS TO BE DEFINED !!

e.g. $\bar{A}^\circ(T) = RT \left[\ln \left(\frac{P^\circ \cdot V^\circ}{k_B T} \right) - 1 \right]$

$$\begin{aligned}\bar{A}(T, P) &= RT \left[\ln \left(P \cdot \frac{V^\circ}{k_B T} \right) - 1 \right] \\ &= A^\circ(T) + RT \ln \left(\frac{P}{P^\circ} \right)\end{aligned}$$

Should look familiar . . .

$$\begin{aligned}A(T, P) &\propto RT \ln P / P^\circ \\ &\text{- or - } RT \ln C / C^\circ\end{aligned}$$

P°

S (entropy) biggy

$$S(N, V, T) = k_B (U_B + \ln Q)$$

$$\begin{aligned}\bar{S} &= \frac{S}{N} = k_B \left(\frac{3}{2} + \ln \left(\frac{V}{N^3} \right) - \ln N + 1 \right) \\ &= k_B \ln \left[e^{5/2} / N^3 (N_A) \right] \\ &= k_B \ln \left[e^{5/2} / N^3 (P/k_B T) \right]\end{aligned}$$

Sackur-Tetrode eq

\bar{S} depends on density N/V

or pressure P

Again, conventional to define
at standard state.

$$\bar{S}^\circ = k_B \ln \left[e^{5/2} / N^3 \cdot C^\circ \right] \quad \text{- or - } (P^\circ / k_B T)$$

ex Kr, 298 K, 1 bar

(4 mol/m³)

$$\Lambda = 1.104 \times 10^{-11} \text{ m}$$

$$c^\circ = \frac{P^\circ}{k_B T} = \frac{1 \text{ bar}}{k_B T} = 2.4 \times 10^{25} \frac{\text{mol}}{\text{m}^3}$$

$$\rightarrow \bar{s}^\circ = 164.085 \text{ J/mol} \cdot \text{K} \quad \checkmark$$

$$\lim_{\substack{T \rightarrow 0 \\ \Lambda \rightarrow \infty}} \bar{s}^\circ = -\infty \quad !! \quad \begin{matrix} \text{Violates 3rd} \\ \text{Law!!} \end{matrix}$$

Why? Our integral approximation fails when $T < \theta_{trans}$.

Suppose our gas is not monoatomic.
 In addition to translational DOFs,
 also has rotational, vibrational.
 that will contribute to thermo properties.

For simplicity, take a diatomic
rotational DOF

rigid rotor model $\text{C} \equiv \text{O}$

$$E_l = \frac{\hbar^2}{2I} l(l+1) \quad g(l) = 2l+1$$

$$= \epsilon_{\text{rot}} l(l+1)$$

$$\epsilon_{\text{rot}} = \frac{\hbar^2}{2I} \rightarrow \Omega_{\text{rot}} = \epsilon_{\text{rot}}/k_B$$

$$I = \mu R_e^2$$

$$q_{\text{rot}}(T) = \sum_{l=0}^{\infty} (2l+1) \left\{ e^{-\epsilon_{\text{rot}}/k_B T} \right\}^{l(l+1)}$$

$$= \sum_{l=0}^{\infty} (2l+1) (e^{-\Theta_{\text{rot}}/\tau})^{l(l+1)}$$

Cannot be summed in closed form. Integral approximation?

ex CO 300 K

$$B = 1.93 \text{ cm}^{-1} \rightarrow E_{\text{rot}} = hcB = 3.8 \times 10^{-23} \text{ J}$$

$$\rightarrow \underline{\Theta_{\text{rot}} = 2.78 \text{ K}}$$

$$e^{-\Theta_{\text{rot}}/\tau} \sim 0.991 @ 300 \text{ K}$$

\rightsquigarrow lots of terms contribute to sum

$l=0$	1
$l=1$	2.94
$l=2$	4.73
⋮	

$$l=20 \quad 0.84$$

$$l=30 \quad 0.011$$

\rightsquigarrow integral approximation ok

$$Q_{\text{rot}}(T) \approx \int_0^{\infty} (2x+1) \left(e^{-\Theta/T}\right)^{x(x+1)} dx$$

$$= T/\Theta_{\text{rot}} \quad \text{wow!}$$

$$Q_{\text{rot}}^{\text{CD}}(300K) \approx 108 \quad \text{states}$$

$$\bar{U}_{\text{rot}} = - \left(\frac{\partial \ln Q_{\text{rot}}}{\partial \beta} \right) = \underline{k_B T}$$

$$\bar{C}_{v,\text{rot}} = \left(\frac{\partial \bar{U}}{\partial T} \right)_v = k_B \quad (\text{or } K)$$

$$\bar{A}_{\text{rot}} = -k_B T \left(\ln T/\Theta_{\text{rot}} \right)$$

$$\bar{S}_{\text{rot}} = \frac{\bar{U} - \bar{A}}{T} = \dots$$

More general formulas available in extended outline for rotations.

Note little quirk of QM, for
symmetric diatomics

$$g = \frac{1}{\sigma} \frac{I}{\partial \text{rot}} \quad \sigma = \begin{cases} \text{sym} \\ \neq \end{cases}$$

< 2

Vibrational DOF

O-mo)

harmonic oscillator model

$$\epsilon_v = (v + \frac{1}{2}) \hbar \nu \quad \epsilon_{\text{vib}} = \hbar \nu$$

$$v = 0, 1, 2, \dots$$

$$\Theta_{\text{vib}} = \frac{\hbar \nu}{k_B}$$

Conventional to shift Θ of energy to start at $\frac{1}{2} \hbar \nu$ (subtract out $\frac{1}{2} \hbar \nu$)

$$\Rightarrow \epsilon_v = v \epsilon_{\text{vib}}$$

$$\begin{aligned} q_{\text{vib}} &= \sum_{v=0}^{\infty} e^{-\epsilon_{\text{vib}} \cdot v / k_B T} \\ &= \sum_{v=0}^{\infty} \left(e^{-\Theta_{\text{vib}} / T} \right)^v \end{aligned}$$

Geometric Series!! $\sum x^n = \frac{1}{1-x}$
 $x < 1$

$$g_{vib}(T) = \frac{1}{1 - e^{-\Theta_{vib}/T}}$$

$$\bar{U}_{vib}(T) = - \left(\frac{\partial \ln g}{\partial \beta} \right)_v + \frac{1}{2} h\nu$$

$$= k_B \frac{\Theta_{vib}}{e^{\Theta_{vib}/T} - 1} + \frac{1}{2} h\nu$$

$$C_v(T) = \text{messy}$$

$$\bar{A}_{vib}(T) = +k_B T \ln \left(1 - e^{-\Theta_{vib}/T} \right) + \frac{1}{2} h\nu$$

$$\text{ex CO } \tilde{\gamma} = 2157 \text{ cm}^{-1} \rightarrow \Theta_{vib} = 3100 \text{ K}$$

$$g_{vib}^{co}(300) = \frac{1}{1 - e^{-\frac{1}{300}}} = \underline{1.11}$$

$$I_2 \quad \tilde{\gamma} = 215 \text{ cm}^{-1} \quad \Theta_{vib} = 310 \text{ K}$$

$$g_{vib}^{I_2}(300) \approx 1.5$$

For most vib modes $\Theta_{vib} \gtrsim T$

$$\rightarrow g_{vib} \sim 1$$

$$\Theta_{vib} \gg T \rightarrow \bar{U}_{vib} = 0 + \frac{1}{2} h\nu$$

$$\rightarrow \bar{A}_{vib} = 0 + \frac{1}{2} h\nu$$

$$\rightarrow \bar{S}_{vib} = 0$$

Compare characteristic T table

Whole molecule

Eg C_2H_6 3 trans DOF

3 rot DOF

$$3N-6 = 18 \text{ vib DOF}$$

all from structure & vib
spectra

$$q^{C_2H_6} = q^{\text{trans}} \cdot q^{\text{rot}}^{(1)} \cdot q^{\text{rot}}^{(2)} \cdot q^{\text{rot}}^{(3)} \\ \cdot \prod q^{\text{vib}}^{(i)}$$

$$Q = \left(\frac{q^{C_2H_6}}{n!} \right)$$

$$\Rightarrow \bar{u} = \bar{u}^{\text{trans}} + \bar{u}^{\text{rot}} + \dots \\ + \bar{u}_{(i)}^{\text{vib}} + \dots$$

Ditto \bar{s}, \bar{A}, \dots

Look @ results in extended
outline.

Non-ideality

Two big assumptions here:

1 molecules don't interact
(PLAB works for all)

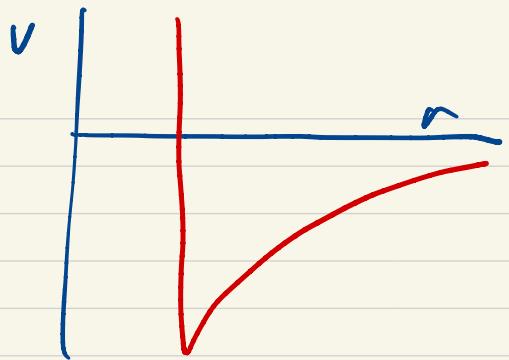
2 internal DOFs are all separable and treated by simple models.

Both assumptions can be relaxed.

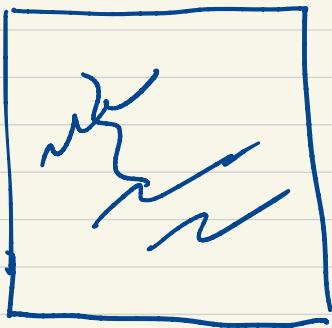
Like many-electron problem, problem generally goes from being solvable by hand to solving using approx simulations.

"molecules" don't interact → ideal gas

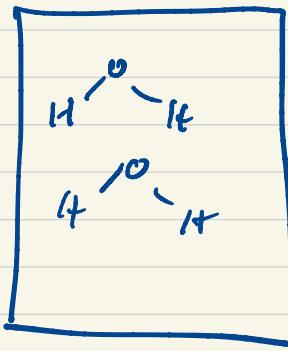
simple interaction



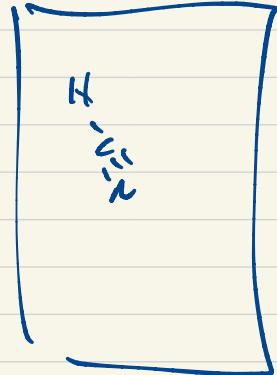
\rightsquigarrow vdW EOS



molecular liquids



H-bonding



dipolar