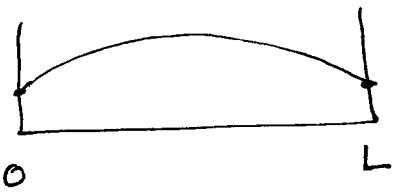
Microstates in monoatomic ideal gases

- no intermolecular interactions
- real gases approximate this as $\rho \to 0$



1 Particle in a box $-\frac{\hbar^2}{8\pi^2 m}\frac{d^2\psi}{\partial x^2} = \varepsilon\psi \Rightarrow \frac{d^2\psi}{\partial x^2} + k^2\psi = 0$

$k^2 = (8\pi^2 m\varepsilon/\hbar^2)$

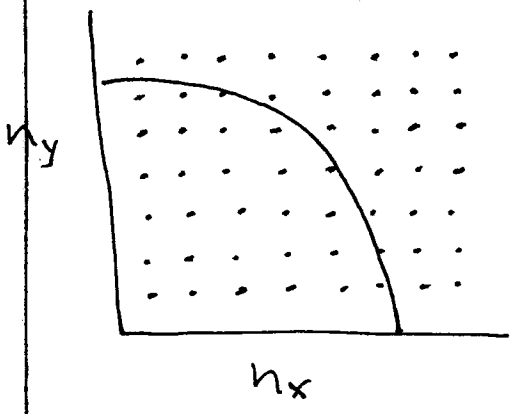
Boundary conditions $\psi(x=0)=0$ $\psi(x=L)=0$

$\Rightarrow \psi = A\sin(kL)$ with $kL = n_x\pi$

$\therefore \varepsilon = \frac{(n_x h)^2}{8mL^2}$ In 3D, $L\times L\times L$: $\varepsilon = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2)$

For multiple particles, same solution (non-interacting) with quantum numbers $\underbrace{n_{x1}, n_{x2} \cdots n_{xN}, n_{y1}, \cdots n_{zN}}_{3N}$

What is $\Omega(N, V, E)$?



Need to count states in $3N$-dimensional space such that

$\vec{n}^2\frac{\hbar^2}{8mL^2} \le E \Rightarrow \vec{n}^2 \le \frac{8mL^2E}{\hbar^2}$

$\vec{n} = \{n_{x1}, n_{x2} \cdots n_{zN}\}$

Number of states Φ with energy less than E?

Volume of hypersphere in d dimensions of radius R is $\frac{\pi^{d/2}}{\Gamma(d/2+1)}R^d$

We only take into account the positive quandrant:

$$\Phi = \left(\frac{1}{2}\right)^{3N} \frac{M^{3N/2} R^{3N}}{\Gamma(3N/2+1)} \simeq \frac{1}{(3N/2)!} \left(\frac{2\pi m L^2 E}{\hbar^2}\right)^{3N/2}$$

$\hookrightarrow \simeq (3N/2)!$ (Recall $R = (8mL^2E/\hbar^2)^{1/2}$)

$$\text{Now } \Omega = \frac{1}{N!}\frac{d\Phi}{dE} = \frac{3N/2}{N!\,(3N/2)!} \cdot \left(\frac{2\pi m L^2 E}{\hbar^2}\right)^{3N/2-1} \quad \text{neglect } N \gg 1$$

$$\ln \Omega = \ln \frac{3N}{2} - N\ln N + N - N\ln\left(\frac{3N}{2}\right)^{3/2} + \frac{3N}{2} + \frac{3N}{2}\ln\frac{2\pi m}{\hbar^2} + N\ln L^3 + N\ln E^{3/2}$$

(small - not prop. to N, neglect)

$$\simeq N\left[\ln\frac{1}{N} + 1 - \ln N^{3/2} + \ln\left(\frac{2}{3}\right)^{3/2} + \frac{3}{2} + \ln\left(\frac{2\pi m}{\hbar^2}\right)^{3/2} + \ln V + \ln E^{3/2}\right]$$

$$= N\left[\ln\left[\frac{V}{N}\cdot\left(\frac{E}{N}\right)^{3/2}\right] + \frac{5}{2} + \frac{3}{2}\ln\frac{4\pi m}{3\hbar^2}\right]$$ Sackur-Tetrode

This was obtained at the limits $N \to \infty$, $T \gg 0$

Thermodynamic Properties from $S = S(E,V,N) = k_B \ln \Omega$

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$$

$$1/T = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{\partial}{\partial E}\left[Nk_B \ln E^{3/2}\right] = \frac{3Nk_B}{2E} \Rightarrow$$

$$\boxed{E/N = 3k_BT/2}$$

$$P/T = \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{\partial}{\partial V}\left[Nk_B \ln V\right] \Rightarrow \boxed{PV = NK_BT}$$

$$\mu/T = \left(\frac{\partial S}{\partial N}\right)_{T,V} = k_B\left[\ln\left[\frac{V}{N}\left(\frac{E}{N}\right)^{3/2}\right] + \frac{5}{2} + \frac{3}{2}\ln\frac{4\pi m}{3\hbar^2} - N\frac{5}{2N}\right]$$

$$= -k_BT\ln\left[\left(\frac{2\pi m k_BT}{\hbar^2}\right)^{3/2}\frac{V}{N}\right] = -k_BT\ln\left(\frac{V}{\Lambda^3 N}\right)$$

$\Lambda \rightarrow$ DeBroglie wavelength

Λ in the μ expression is $\Lambda(T) = \left(\frac{h^2}{2\pi m k_B T}\right)^{1/2}$

has units of length.

If $\Lambda(T) << (V/N)^{1/3}$ (average interparticle distance)

→ quantum effects are not important

$A(T,V,N) = E - TS = -NK_BT\ln\left(\frac{V}{\Lambda^3 N}\right) - K_BT$

$G = \mu N$; need $\mu(P)$ to make it a F.E.

$\frac{V}{N} = \frac{K_BT}{P} \Rightarrow \mu = k_BT\ln P + \underbrace{\mu^\circ(T)}_{\text{contains } \Lambda(T)}$

For polyatomic molecules, E is no longer $3K_BT/2$, as there are contributions from internal motions.

However, $PV = NK_BT$, $\mu = K_BT\ln P + \mu^\circ(T)$

Ideal gas Mixtures

$\underline{O}(E,V,\{N\}) = \underline{O}_1(E_1,V,N_1) \times \underline{O}_2(E_2,V,N_2) \times \cdots$

since particles of each species are independent

$\therefore S(E,V,\{N\}) = S_1(E_1,V,N_1) + S_2(E_2,V,N_2) + \cdots$

mixing at const. volume has no entropic consequence

Thus, $A(T,V,\{N\}) = A_1(T,V,N_1) + A_2(T,V,N_2) + \cdots$

→ all species must be at <u>same</u> T.

Taking derivative w.r.t. volume V

$P = \underbrace{P_1 + P_2 + \cdots}_{\text{partial pressures}}$ $\qquad P_i = y_i P = \frac{N_i P}{N}$

$$\mu_i = \left.\frac{\partial A(T,V,\{N\})}{\partial N_i}\right)_{T,V,N_{j\neq i}} = \frac{\partial A_i(T,V,N_i)}{\partial N_i}$$

$$= -k_B T \ln\left(\frac{V}{\Lambda^3 N_i}\right) = \mu_i^\circ(T) - k_B T \ln\left(\frac{V}{N_i k_B T}\right)$$

Can convert to P using $P_i = \frac{N_i k_B T}{V} = y_i P$

$$\Rightarrow \mu_i = \mu_i^\circ(T) + k_B T \ln P_i = \mu_i^\circ(T) + k_B T \ln P + k_B T \ln y_i$$

Because μ_i is a function of y_i, mixing at const. P has entropic consequences:

$$\Delta G_{mix} = \underbrace{\sum_i N_i (\mu_i^\circ(T) + k_B T \ln P + k_B T \ln y_i)}_{\text{mixture}} - \underbrace{\sum_i N_i \mu_i(T,P)}_{\text{sum of pure}}$$

$\mu_i(T,P) = \mu_i^\circ(T) + k_B T \ln P$

$$\Rightarrow \boxed{\Delta G_{mix} = k_B T \sum_i N_i \ln y_i} < 0$$

Entropy of mixing at const. P:

$$\Delta S_{mix} = -\left.\frac{\partial \Delta G_{mix}}{\partial T}\right)_{P\{N\}} = -k_B \sum N_i \ln y_i = -N k_B \sum y_i \ln y_i$$

Non-Ideal Gases

Molecular attractions + repulsions → deviations from ideal behavior as $\rho > 0$.

By analogy to $\mu = \mu_i^\circ + k_B T \ln P$ (ideal)

$$\mu = \mu_i^\circ + k_B T \ln f \quad (\underline{\text{defines}}\ f)$$

Note that we have been taking logs of dimensional quantities by shifting terms to μ°, which depends on units