Microstates in monoatomic ideal gases

- no intermolecular interactions
- real gases approximate
  thus as \( p \to 0 \)

1 Particle in a box

\[
- \frac{\hbar^2}{8m^2} \frac{d^2 \psi}{dx^2} = E \psi = \frac{\hbar^2}{8m^2} \frac{d^4 \psi}{dx^4} + k^2 \psi = 0
\]

\[k^2 = \left( \frac{8\pi^2 mE}{\hbar^2} \right)\]

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

\[\Rightarrow \psi = A \sin(kx) \quad \text{with} \quad kL = n_x \pi \]

\[\varepsilon = \frac{(n_x \pi)^2}{8mL^2} \quad \text{in 3D}\]

\[\varepsilon = \frac{\hbar^2}{8mL^2} \left( n_x^2 + n_y^2 + n_z^2 \right) \]

For multiple particles, same solution (non-interacting) with quantum numbers \( n_{x1}, n_{x2}, \ldots, n_{xN}, n_{y1}, \ldots, n_{yN} \)

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

\( 3N \)

Need to count states in 3N-dimensional space

Such that

\[ \frac{n^2 \pi^2}{8mL^2} \leq E \Rightarrow \frac{n^2}{\pi^2} \leq \frac{8mL^2E}{\hbar^2} \]

\[n^2 = \{ n_{x1}, n_{x2}, \ldots, n_{xN} \} \]

Number of states \( \Phi \) with energy less than \( E \)?

Volume of hypersphere in \( d \) dimensions

\[ \text{of radius} \ R \text{ is} \ \frac{\pi^{d/2} R^d}{\Gamma(d/2 + 1)} \]
We only take into account the positive quadrant:
\[ \Phi = \left( \frac{1}{2} \right)^{3N} \frac{R^{3N}}{\Gamma(3N/2 + 1)} \approx \frac{1}{(3N/2)!} \left( \frac{2\pi m L^2 E}{\hbar^2} \right)^{3N/2} \]

Now \[ \frac{d\Phi}{dE} = \frac{3N/2}{N! (3N/2)!} \left( \frac{2\pi m L^2 E}{\hbar^2} \right)^{3N/2 - \frac{1}{2}} \]

\[ \ln \Phi = \frac{3N}{2} - N \ln N + N - N \ln \left( \frac{3N}{2} \right) + \frac{3N}{2} + \frac{3N}{2} \ln \left( \frac{2\pi m}{\hbar^2} \right) + N \ln 4 + N \ln \left( \frac{2\pi m}{\hbar^2} \right) \]

Small, not prop. to \( N \), neglect

\[ \frac{\partial}{\partial N} \ln \Phi = \ln \left( \frac{3N}{2} \right) + \frac{3}{2} \ln \left( \frac{4\pi m}{3\hbar^2} \right) \]

This was obtained at the limits \( N \to \infty \), \( T \to 0 \)

**Thermodynamic Properties**

from \( S = S(E, V, N) \)

\[ dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{k}{T} dN \]

\[ \frac{1}{T} = \frac{\partial S}{\partial E} \bigg|_{V,N} = \frac{\partial}{\partial E} \left[ Nk \ln E^{3/2} \right] = \frac{3Nk}{2E} \]

\[ \frac{E}{N} = \frac{3kT}{2} \]

\[ \frac{P}{T} = \frac{\partial S}{\partial V} \bigg|_{E,N} = \frac{\partial}{\partial V} \left[ Nk \ln V \right] \Rightarrow P/V = NkT \]

\[ \frac{N}{T} = \frac{\partial S}{\partial N} \bigg|_{V} = k \left[ \ln \left( \frac{V}{N} \right)^{3/2} \right] + \frac{5}{2} + \frac{3}{2} \ln \left( \frac{4\pi m}{3\hbar^2} \right) - \frac{N}{2N} \]

\[-kT \ln \left( \frac{2\pi m k^2 T}{\hbar^2} \right)^{3/2} \]

De Broglie wavelength
\[ \Lambda \text{ in the } \mu \text{ expression is } \Lambda(T) = \left( \frac{\hbar^2}{2\pi m k_B T} \right)^{1/2} \]

has units of length.

If \( \Lambda(T) \ll (v/N)^{1/3} \) (average interparticle distance)

\[ \Rightarrow \text{quantum effects are not important} \]

\[ A(T; V, N) = E - TS = -Nk_B T \ln \left( \frac{V}{\Lambda^3 N} \right) - k_B T \]

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

\[ \frac{V}{N} = \frac{E_0 T}{P} \Rightarrow \mu = k_B T \ln P + \mu^0(T) \]

\[ \text{contains } \Lambda(T) \]

For polyatomic molecules, \( E \) is no longer \( 3k_B T/2 \),
as there are contributions from internal motions.

However, \( PV = Nk_B T \), \( \mu = k_B T \ln P + \mu^0(T) \)

**Ideal gas Mixtures**

\[ O(E; V; XN_3) = O_1(E_1; V, N_1) \times O_2(E_2; V, N_2) \times \cdots \]

Since particles of each species are independent

\[ S(E; V; XN_3) = S_1(E_1; V, N_1) + S_2(E_2; V, N_2) + \cdots \]

mixing at const. volume has no adiabatic consequence

Thus,

\[ A(T; V; XN_3) = A_1(T; V, N_1) + A_2(T; V, N_2) + \cdots \]

\[ \Rightarrow \text{all species must be at same } T. \]

Taking derivative w.r.t. volume \( V \)

\[ P = P_1 + P_2 + \cdots \]

\[ P_i = y_i P = \frac{N_i P}{N} \]

partial pressures
\[ \frac{T_i}{N_i} = \frac{\frac{\partial A(T, \nu, \nu N_i^3)}{\partial N_i}}{\frac{\partial A(T, \nu, \nu N_i^3)}{\partial N_i}} = \frac{\partial A; (T, \nu, N_i)}{\partial N_i} = -k_B T \ln \left( \frac{\nu}{N_i^3} \right) = T_i^0 (T) - k_B T \ln \left( \frac{\nu}{N_i^3} \frac{1}{k_B T} \right) \]

Can convert to P using \( P_i = \frac{N_i k_B T}{\nu} = y_i P \)

\[ \Rightarrow T_i = T_i^0 (T) + k_B T \ln P_i = T_i^0 (T) + k_B T \ln P + k_B T \ln y_i \]

Because \( T_i \) is a function of \( y_i \), mixing at constant \( P \) has entropic consequences:

\[ \Delta G_{\text{mix}} = \sum_{i} N_i \left( T_i^0 (T) + k_B T \ln P_i + k_B T \ln y_i \right) - \sum_{i} N_i T_i (T, P) \]

\[ \Rightarrow \Delta G_{\text{mix}} = k_B T \sum_{i} N_i \ln y_i < 0 \]

Entropy of mixing at constant \( P \):

\[ \Delta S_{\text{mix}} = -\frac{\partial \Delta G_{\text{mix}}}{\partial T} = k_B \sum_{i} N_i \ln y_i = N k_B \sum_{i} \ln y_i \]

Non-Ideal Gases

Molecular attractions and repulsions \( \rightarrow \) deviations from ideal behavior as \( P \to 0 \).

By analogy to \( T_i = T_i^0 + k_B T \ln P \) (ideal)

\[ T = T_i^0 + k_B T \ln P \]

Note that we have been taking logs of dimensional quantities by shifting terms to \( T_i^0 \) which depends on \( y_i \).