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Statistical Thermodynamics

# Lecture 5: Ideal Monatomic Gas

Dr. Ronald M. Levy  
ronlevy@temple.edu

# Hamiltonian of Ideal Monatomic Gas:

Total Hamiltonian of monatomic gas is:

$$\hat{H} = \sum_{\alpha=1}^N \hat{h}_{\alpha} + V(\vec{r}_1, \vec{r}_2 \cdots \vec{r}_N)$$

$\hat{h}_{\alpha}$ : Atomic Hamiltonian

For ideal gas, we can neglect the potential energy because interatomic interaction is insignificant.

$$\hat{H} = \sum_{\alpha=1}^N \hat{h}_{\alpha}$$

The atomic Hamiltonian can be written:

$$\hat{h}_{\alpha} = \hat{h}_{\alpha}^{\text{translational}} + \hat{h}_{\alpha}^{\text{electronic}} + \hat{h}_{\alpha}^{\text{nuclearspin}}$$

From the time independent Schrodinger equation,

$$\hat{h}_{\alpha} \psi_i = E_i^{\alpha} \psi_i$$

$$E_i^{\alpha} \equiv \text{energy of atom } \alpha \text{ in state } i$$

## Distinguishable ideal gas:

For distinguishable particles,

$$\begin{aligned} Q(N, V, T) &= \sum_{i,j,k} e^{-\frac{(E_i^\alpha + E_j^\beta + E_k^\gamma + \dots)}{kT}} \\ &= \left( \sum_i e^{-E_i^\alpha / kT} \right) \left( \sum_j e^{-E_j^\beta / kT} \right) \left( \sum_k e^{-E_k^\gamma / kT} \right) \dots \\ &= q_\alpha \cdot q_\beta \cdot q_\gamma \dots \\ &= (q(V, T))^N \end{aligned}$$

Where  $q(V, T) = \sum_i e^{-E_i / kT}$ ,  $E_i$  are the atomic energy levels.

**But by Quantum Mechanics, Atoms are indistinguishable!**

# Indistinguishable ideal gas:

For indistinguishable particles,

$$Q(N, V, T) = \frac{[q(V, T)]^N}{N!}$$

Many body problem reduces to a 1 body problem because all particles are identical

Why N! in denominator?

1) To an excellent approximation, at room temperature, all the atoms are in different energy eigenstates. The reason is the number of energy states available at room temperature ( $\sim 10^{30}$ ), is much greater than number of atoms ( $\sim 10^{23}$ ). Thus  $i \neq j \neq k$ , indices for energies are all different

2) When  $i \neq j \neq k \neq \dots$ , There are N! ways to permute the indices of the N atoms among the possible energy eigenvalues, which correspond to a single state. For example, consider 3 atoms, the  $[q(V, T)]^3$  contains:

i	1	1	2	2	3	3
j	2	3	1	3	2	1
k	3	2	3	1	1	2

$$\begin{aligned}
 & e^{-E_i^1/KT} e^{-E_j^2/KT} e^{-E_k^3/KT} + e^{-E_i^1/KT} e^{-E_k^2/KT} e^{-E_j^3/KT} + \\
 & e^{-E_j^1/KT} e^{-E_i^2/KT} e^{-E_k^3/KT} + e^{-E_j^1/KT} e^{-E_k^2/KT} e^{-E_i^3/KT} + \\
 & e^{-E_k^1/KT} e^{-E_i^2/KT} e^{-E_j^3/KT} + e^{-E_k^1/KT} e^{-E_j^2/KT} e^{-E_i^3/KT} \\
 & = 6 \cdot e^{-E_i^1/KT} e^{-E_j^2/KT} e^{-E_k^3/KT}
 \end{aligned}$$

This should only be counted once instead of  $3!=6$  times in the partition functions.

## Indistinguishable ideal gas:

The atomic Hamiltonian is a sum of Hamiltonians of translational, electronic and nuclear spin:

$$\hat{h} = \hat{h}_{tr} + \hat{h}_{el} + \hat{h}_{ns}$$

Therefore, partition function is a product

$$q(V, T) = q_{tr}(V, T)q_{el}(V, T)q_{ns}(V, T)$$

So

$$Q(N, V, T) = (q_{tr}q_{el}q_{ns})^N / N!$$

# Thermodynamic Functions for Ideal Gas:

## a. Energy

$$\begin{aligned}
 \langle E \rangle &= kT^2 \frac{\partial \ln Q}{\partial T} = NkT^2 \frac{\partial \ln(q_{tr}q_{el}q_{ns})}{\partial T} \\
 &= NkT^2 \frac{\partial \ln q_{tr}}{\partial T} + NkT^2 \frac{\partial \ln q_{el}}{\partial T} + NkT^2 \frac{\partial \ln q_{ns}}{\partial T} \\
 &= \langle E_{Tr}(N, T) \rangle + \langle E_{el}(N, T) \rangle + \langle E_{ns}(N, T) \rangle
 \end{aligned}$$

## b. Heat capacity (canonical ensemble)

$$\begin{aligned}
 C_V(N, V, T) &= \frac{\partial \langle E(N, V, T) \rangle}{\partial T} \\
 &= C_{V,tr}(N, V, T) + C_{V,el}(N, T) + C_{V,ns}(N, T)
 \end{aligned}$$

## c. Helmholtz free energy

$$F(N, V, T) = -kT \ln Q = NkT \ln(q_{Tr} \cdot q_{el} \cdot q_{ns}) + kT \ln N!$$

## d. Pressure

$$\langle p \rangle = -\frac{\partial F}{\partial V} = kT \frac{\partial \ln Q}{\partial V} = NkT \frac{\partial \ln q_{tr}(V, T)}{\partial V}$$

The only contribution to the pressure is from the translational energy of the atoms – pressure is due to the atoms of the gas hitting the walls of the container.

## Thermodynamic Functions for Ideal Gas:

### e. Entropy:

$$\begin{aligned}
 S &= \frac{\langle E \rangle}{T} + k \ln Q \\
 &= \frac{\langle E_{tr} \rangle}{T} + \frac{\langle E_{el} \rangle}{T} + \frac{\langle E_{ns} \rangle}{T} + Nk \ln q_{tr} + Nk \ln q_{el} + Nk \ln q_{ns} - k \ln N!
 \end{aligned}$$

Note:  $-k \ln N! = -k(N \ln N - N) = Nk(1 - \ln N) = Nk \ln \left(\frac{e}{N}\right)$

Let  $S_{tr} \equiv \frac{\langle E_{tr} \rangle}{T} + Nk \ln q_{tr} + Nk \ln \left(\frac{e}{N}\right)$

Then

$$S = S_{tr}(N, V, T) + S_{el}(N, T) + S_{ns}(N, T)$$

### f. Chemical potential:

$$\begin{aligned}
 \mu(N, V, T) &= -kT \left( \frac{\partial \ln Q}{\partial N} \right)_{V, T} = \left( \frac{\partial A}{\partial N} \right)_{V, T} \\
 &= -kT \frac{\partial}{\partial N} \{ N \ln [q_{Tr} \cdot q_{el} \cdot q_{ns}] - \ln N! \} \\
 &= -kT \ln [q_{Tr} \cdot q_{el} \cdot q_{ns}] + kT \frac{\partial}{\partial N} \{ N \ln N - N \} \\
 &= -kT \ln \left[ \frac{q_{Tr} \cdot q_{el} \cdot q_{ns}}{N} \right]
 \end{aligned}$$

Now, we will evaluate translational, electronic, nuclear spin contributions to thermodynamic functions

## A. Translation partition function

For a particle in a cubic box of dimension 'a' on a side, the energy states are given by:

$$E_{n_x n_y n_z} = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2) \quad n_x, n_y, n_z = 1, 2, \dots$$

↑  
Mass of particle

$$q_{trans} = \sum_{n_x n_y n_z=1}^{\infty} e^{-\beta E_{n_x n_y n_z}} = \left( \sum_{n=1}^{\infty} \exp\left[-\frac{\beta h^2}{8ma^2} n^2\right] \right)^{\overbrace{3}^{1D}} \quad \leftarrow 3D$$

Now, we can approximate sum by integral,

$$\sum_{n=1}^{\infty} e^{-\beta h^2 n^2 / 8ma^2} \approx \underbrace{\int_0^{\infty} e^{-\beta h^2 n^2 / 8ma^2} dn}_{f(n)} \underbrace{1}_{"1"}$$

because the argument of the exponential is almost constant from n to n+1

$$\Delta = \frac{\beta h^2}{8ma^2} [(n+1)^2 - n^2] = \frac{\beta h^2 (2n+1)}{8ma^2}$$

For  $m = 10^{-22}$ g,  $a = 10$ cm,  $T = 300$ K, and  $n = 10^{10}$  ( $T = 300 \rightarrow \langle n_x \rangle \sim 10^{10}$ )

$$\Delta = 10^{-10}$$



So,  $q_{trans}(V, T) = \left( \int_0^\infty e^{-\beta h^2 n^2 / 8ma^2} dn \right)^3$

$= \left( \int_0^\infty e^{-\alpha n^2} dn \right)^3$     Where  $\alpha = \beta h^2 / 8ma^2$

$= \left[ \left( \frac{\pi}{4\alpha} \right)^{\frac{1}{2}} \right]^3$     Since  $\int_0^\infty e^{-\alpha n^2} = \left( \frac{\pi}{4\alpha} \right)^{1/2}$

$= \left[ \frac{2\pi mKT}{h^2} a^2 \right]^{3/2}$

$= \left[ \frac{2\pi mKT}{h^2} \right]^{3/2} \cdot V$     With  $V = a^3$

$= V / \Lambda^3$     With  $\Lambda = (h^2 / 2\pi m kT)^{1/2}$  units of length

$\Lambda \sim \frac{h}{\langle |p| \rangle}$    ← De Broglie wavelength of the atom

To prove this we calculate average translational energy  $\langle E_{trans} \rangle$

$$\langle E_{trans} \rangle = kT^2 \frac{\partial \ln q_{trans}}{\partial T} = kT^2 \frac{\partial}{\partial T} \ln T^{3/2} = \frac{3}{2} kT$$

Also  $\langle E_{trans} \rangle = \langle p^2 \rangle / 2m$     so,  $|p| = \langle p^2 \rangle^{1/2} = (3mkT)^{1/2}$

Therefore  $\Lambda = (h^2 / 2\pi m kT)^{1/2} \approx h / (2\pi m kT)^{1/2}$

$\sim \frac{h}{\sqrt{2}p} \sim \frac{h}{p}$  ← units of length

Classical or Boltzmann statistics to calculate  $q_{trans}$  (replace summation by integral) valid when,

$$\frac{V}{\Lambda^3} \gg 1$$

i.e. dimensions of the box are much greater than the De Broglie wavelength of the atom.

**In summary:**

$$q_{trans}(V, T) \sim V \cdot T^{\frac{3}{2}}$$

## B. Electronic and Nuclear partition functions for the ideal gas

For electronic and nuclear partition function, the gap between excited states and ground state is very large and contributes to partition function by excited states are very little.

$$q_n = \omega_{n1}$$

$$q_e = \omega_{e1}$$

Then for ground state ideal gas,

$$Q \approx \frac{q_{trans}^N}{N!} \sim \frac{[V \cdot T^{3/2}]^N}{N!}$$