The Classical Statistical Treatment of an Ideal Gas

(Lecture 14)

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Advanced Thermodynamics (M2794.007900)

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Thermodynamic Properties from the Partition Function

- Let's derive the thermodynamic properties of an ideal gas, based on the partition function.

  For a dilute gas, Maxwell-Boltzmann distribution is applied for an equilibrium state.

  We've already have the following equations:

$$S = \frac{U}{T} + Nk(\ln Z - \ln N + 1)$$

$$F = U - TS = -NkT(\ln Z - \ln N + 1)$$

$$\tilde{\mu} = -kT(\ln Z - \ln N) = kT \ln\left(\frac{N}{Z}\right)$$

We'll deal with other thermodynamic properties!

Thermodynamic Properties from the Partition Function

➔ Continue on.

1. Internal energy

$$U = \sum_{j=1}^{n} N_j \varepsilon_j = \frac{N}{Z}\sum_{j=1}^{n} g_j e^{-\frac{\varepsilon_j}{kT}} \varepsilon_j \quad \text{where} \quad Z = \sum_{j=1}^{n} g_j e^{-\frac{\varepsilon_j}{kT}}$$

$$\text{Here, } \left(\frac{\partial Z}{\partial T}\right)_V = -\sum_{j=1}^{n} g_j \varepsilon_j e^{-\frac{\varepsilon_j}{kT}} \frac{d}{dT}\left(\frac{1}{kT}\right) = \frac{1}{kT^2}\sum_{j=1}^{n} g_j \varepsilon_j e^{-\frac{\varepsilon_j}{kT}}$$

$$\rightarrow U = \frac{N}{Z}\sum_{j=1}^{n} g_j e^{-\frac{\varepsilon_j}{kT}} \varepsilon_j = \frac{N}{Z}\left(kT^2\right)\left(\frac{\partial Z}{\partial T}\right)_V = NkT^2\left(\frac{\partial \ln Z}{\partial T}\right)_V$$

2. Gibbs function (for a single component)

$$G = \tilde{\mu} N = -NkT\left(\ln Z - \ln N\right) = NkT \ln\left(\frac{N}{Z}\right)$$

Thermodynamic Properties from the Partition Function

➔ Continue on.

3. Enthalpy

$$G \equiv H - TS$$

$$\rightarrow H = G + TS = -NkT(\ln Z - \ln N) + T\left[\frac{U}{T} + Nk(\ln Z - \ln N + 1)\right] = U + NkT$$

$$= NkT\left[1 + T\left(\frac{\partial \ln Z}{\partial T}\right)_V\right]$$

4. Pressure

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \quad \text{and} \quad F = -NkT(\ln Z - \ln N + 1)$$

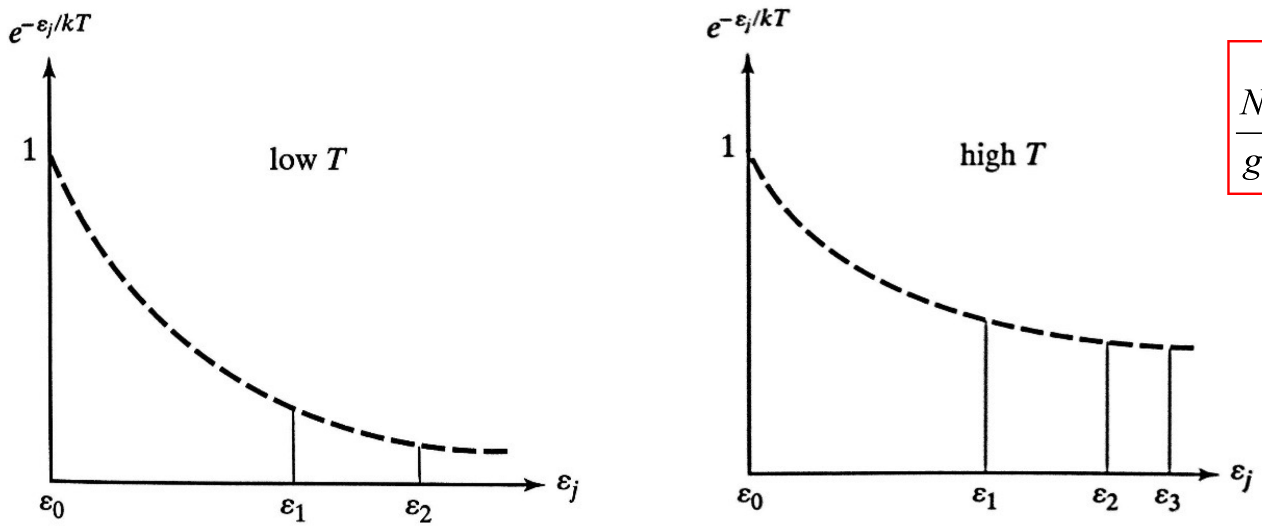
$$\rightarrow P = NkT\left(\frac{1}{Z}\frac{\partial Z}{\partial V}\right)_T = NkT\left(\frac{\partial \ln Z}{\partial V}\right)_T$$

Partition Function for a Gas

➔ Partition function is a measure of the states available to the system and is the essential link between the microscopic systems and the thermodynamic properties.

Suppose the system with $g_j = 1$ for all j.

$$Z = \sum_{j=0}^{n-1} g_j e^{-\frac{\varepsilon_j}{kT}} = 1 + e^{-\frac{\varepsilon_1}{kT}} + e^{-\frac{\varepsilon_2}{kT}} + \ldots \quad (\text{let } \varepsilon_0 = 0)$$



$$\frac{N_j}{g_j} = \frac{Ne^{-\frac{\varepsilon_j}{kT}}}{Z} \quad \text{or} \quad \frac{N_j}{N} = \frac{g_j e^{-\frac{\varepsilon_j}{kT}}}{Z}$$

Partition Function for a Gas

- Continue on.

For a sample of gas in a container of macroscopic size, the energy levels are closely spaced and can be regarded as a continuum. Then, the density of states was given by,

$$g(\varepsilon)d\varepsilon = \frac{4\sqrt{2}\pi V}{h^3} m^{3/2} \varepsilon^{1/2} d\varepsilon$$

for translational kinetic energy of bosons with zero spin

Then,

$$Z = \int_0^\infty g(\varepsilon) e^{-\varepsilon/kT} d\varepsilon = \frac{4\sqrt{2}\pi V}{h^3} m^{3/2} \int_0^\infty \varepsilon^{1/2} e^{-\varepsilon/kT} d\varepsilon$$

$$= \frac{4\sqrt{2}\pi V}{h^3} m^{3/2} \left(\frac{kT}{2} \sqrt{\pi kT} \right)$$

$$\rightarrow \quad Z = V \left(\frac{2\pi mkT}{h^2} \right)^{3/2}$$

Properties of a Monatomic Ideal Gas

- Let's evaluate the thermodynamic properties of a monatomic ideal gas with bosons of zero spin. → Consider translational kinetic energy only.

The partition function and the partial derivatives of its logarithm are,

$$Z = V\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \rightarrow \ln Z = \frac{3}{2}\ln T + \ln V + \frac{3}{2}\ln\left(\frac{2\pi mk}{h^2}\right)$$

$$\rightarrow \left(\frac{\partial \ln Z}{\partial V}\right)_T = \frac{1}{V} \quad \text{and} \quad \left(\frac{\partial \ln Z}{\partial T}\right)_V = \frac{3}{2}\cdot\frac{1}{T}$$

Then,

$$P = NkT\left(\frac{\partial \ln Z}{\partial V}\right)_T = NkT\left(\frac{1}{V}\right) \quad \text{or} \quad PV = NkT$$

$$U = NkT^2\left(\frac{\partial \ln Z}{\partial T}\right)_V = NkT^2\left(\frac{3}{2}\cdot\frac{1}{T}\right) = \frac{3}{2}NkT$$

This is the same with empirical statements in classical thermodynamics!

Properties of a Monatomic Ideal Gas

➔ Continue on.

For an entropy,

$$S = \frac{U}{T} + Nk(\ln Z - \ln N + 1) = \frac{3}{2}\cdot\frac{NkT}{T} + Nk\left[\frac{3}{2}\ln T + \ln V + \frac{3}{2}\ln\left(\frac{2\pi mk}{h^2}\right) - \ln N + 1\right]$$

$$= Nk\left\{\frac{5}{2} + \ln\left[\frac{V(2\pi mkT)^{3/2}}{Nh^3}\right]\right\}$$

← ***Sackur-Tetrode equation for the entropy of a monatomic gas***

or

$$S = Nk\left(\frac{3}{2}\ln T + \ln\frac{V}{N}\right) + S_0 \quad \text{where} \quad S_0 = Nk\left\{\frac{5}{2} + \ln\left[\frac{(2\pi mk)^{3/2}}{h^3}\right]\right\}$$

For specific entropy (per mole basis),

$$\bar{s} = \bar{c}_v \ln T + \bar{R}\ln\bar{v} + \bar{s}_0 \quad \text{where} \quad \bar{s} = S/n,\ \bar{c}_v = (3/2)\bar{R},\ \bar{R} = Nk/n,\ \bar{s}_0 \neq S_0/n$$

→ We can determine S_0 directly for an ideal gas, which was undetermined in classical thermodynamics!