Chapter 14

The Classical Statistical Treatment of an Ideal Gas

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14.1 Thermodynamic Properties from the Partition Function

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

$$S = k \ln W$$

$$\sum g_j e^{-\varepsilon_j/kT}$$

6×10^{23} molecules

Partition function

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

cf. $dF = -SdT - PdV + \mu dN$

$$\mu = \left.\frac{dF}{dN}\right)_{T,V} \qquad \mu = -kT(\ln Z - \ln N)$$

14.1 Thermodynamic Properties from the Partition Function

(1) Internal energy

$$U = \sum N_j \varepsilon_j = \boxed{\sum g_j \frac{N}{Z} e^{-\varepsilon_j/kT}}\, \varepsilon_j$$

Partition function $Z = \sum g_j e^{-\varepsilon_j/kT}$

$$\left.\frac{\partial Z}{\partial T}\right)_V = \sum g_j \frac{\varepsilon_j}{kT^2} e^{-\varepsilon_j/kT}$$

ε_j fixed

$$\therefore \quad U = \frac{N}{Z} kT^2 \left.\frac{\partial Z}{\partial T}\right)_V = NkT^2 \left.\frac{\partial \ln Z}{\partial T}\right)_V$$

14.1 Thermodynamic Properties from the Partition Function

(2) Gibbs function

$$G = \mu N = -NkT(\ln Z - \ln N)$$

(3) Enthalpy

$$H = G + TS$$

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

$$= U + NkT$$

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

14.1 Thermodynamic Properties from the Partition Function

(4) Pressure

$$P = -\left.\frac{dF}{dV}\right)_{T,N} = NkT \left.\frac{\partial \ln Z}{\partial V}\right)_T$$

cf. $dF = -SdT - PdV + \mu dN$

14.2 Partition Function for a Gas

- **Partition function**

$$Z = \sum g_j e^{-\varepsilon_j/kT}$$

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

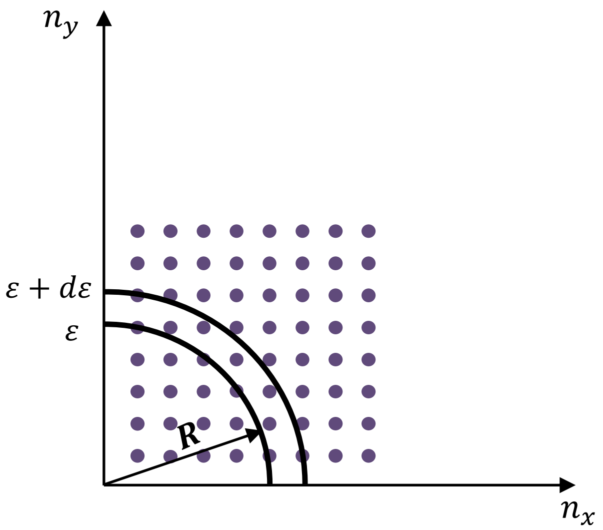
$$= \frac{4\sqrt{2}\pi V}{h^3} m^{3/2} \int_0^\infty \underbrace{\varepsilon^{1/2} e^{-\varepsilon/kT} d\varepsilon}_{\frac{kT}{2}\sqrt{\pi kT}}$$

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

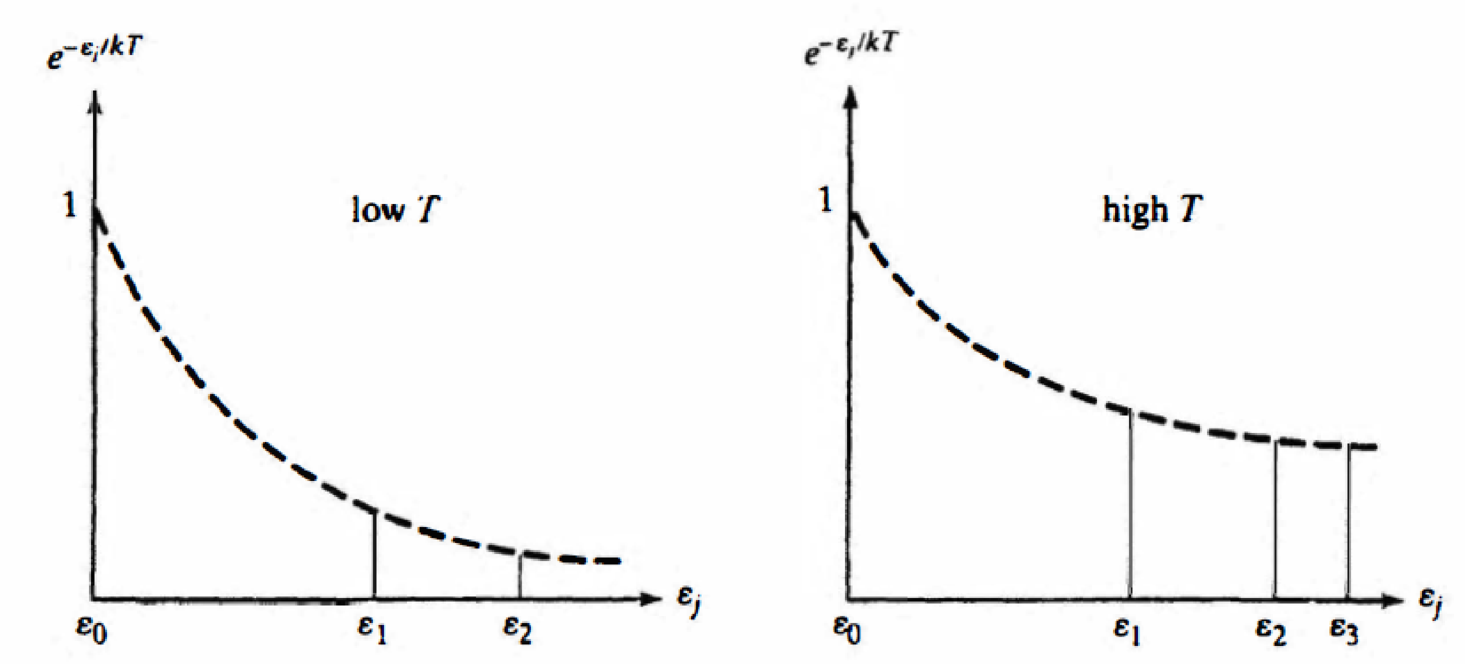
cf.

$g(\varepsilon)d\varepsilon$: number of quantum state $\varepsilon < \quad < \varepsilon + d\varepsilon$

$$\mathrm{g}(\varepsilon)d\varepsilon = \frac{\pi}{6} V \left(\frac{2^{9/2} m^{2/3}}{h^3}\right) \frac{3}{2} \varepsilon^{\frac{1}{2}} d\varepsilon = \frac{4\sqrt{2}\pi V}{h^3} m^{\frac{3}{2}} \varepsilon^{\frac{1}{2}} d\varepsilon$$



14.2 Partition Function for a Gas



(a) (b)

Successive terms of the partition function sum for (a) low temperature; and (b) high temperature. The energy level spacings are comparatively large for a small volume.

14.3 Properties of a Monatomic Ideal gas

The partition function depends on both volume and temperature

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

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

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = NkT\frac{\partial \ln Z}{\partial V}\bigg)_T = \frac{NkT}{V} \quad \Rightarrow \quad PV = NkT$$

$$U = NkT^2\frac{\partial \ln Z}{\partial T}\bigg)_V = NkT^2\frac{3}{2T} \quad \Rightarrow \quad U = \frac{3}{2}NkT$$

14.3 Properties of a Monatomic Ideal gas

The calculation of entropy

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

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

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

Sackur-Tetrode Equation

14.3 Properties of a Monatomic Ideal gas

Statistical approach

$$s = S/n, \qquad Nk = n\bar{R} \qquad c_v = \frac{3}{2}R$$

$$s = c_v \ln T + R \ln v + s_0$$

Classical approach

$$Tds = du + Pdv$$

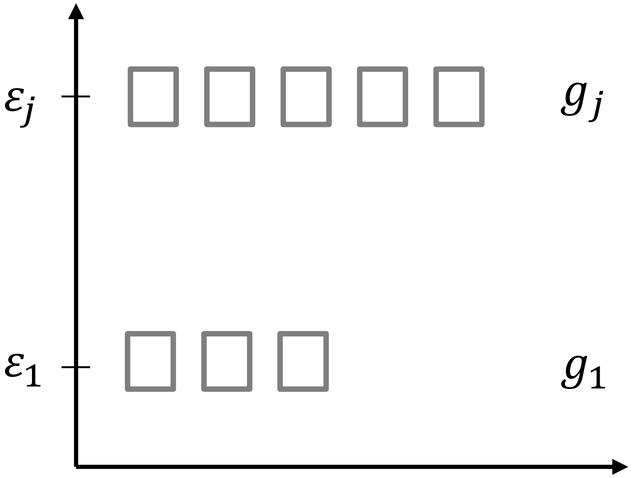
$$ds = c_v \frac{dT}{T} + R\frac{dv}{v}$$

14.4 Applicability of MB Distribution

Maxwell-Boltzmann distribution: valid under dilute gas

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

$$g_j \gg N_j$$



Maxwell-Boltzmann distribution

$$\frac{N_j}{g_j} = \frac{N}{Z}e^{-\varepsilon_j/kT} = \left(\frac{N}{V}\right)\frac{1}{n_Q}e^{-\varepsilon_j/kT}$$

14.4 Applicability of MB Distribution

For Helium,

$$m = 6.65 \times 10^{-27}\ \text{kg}$$

$$T = 273\ \text{K}$$

$$\text{k} = 1.381 \times 10^{-23}\ \text{J/K}$$

$$h = 6.626 \times 10^{-34}\ \text{J·s}$$

➡ $n_Q = 7 \times 10^{30}\ m^{-3}$

Number of particles per unit volume $\dfrac{N}{V} = \dfrac{6 \times 10^{26}}{22.4\ \text{m}^3} \approx 3 \times 10^{25}\ m^{-3}$

$$\frac{N_j}{g_j} = \frac{N}{Z} e^{-\varepsilon_j/kT} = \left(\frac{N}{V}\right)\frac{1}{n_Q} e^{-\varepsilon_j/kT} \sim 4 \times 10^{-6}$$

14.5 Distribution of Molecular Speed

$$f(\varepsilon) = \frac{N(\varepsilon)}{g(\varepsilon)} = \frac{N}{Z} e^{-\varepsilon_j/kT}$$ Maxwell-Boltzmann distribution

$N(\varepsilon)d\varepsilon$: # of particles $\varepsilon < \quad < \varepsilon + d\varepsilon$

For an ideal gas,

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

The density of states is given by

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

14.5 Distribution of Molecular Speed

$$N(\varepsilon)d\varepsilon = \frac{Ne^{-\varepsilon/kT}}{V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}} \cdot \frac{4\sqrt{2}\pi V}{h^3} m^{3/2}\varepsilon^{1/2}d\varepsilon$$

$$= \frac{2\pi N}{(NkT)^{3/2}}\varepsilon^{1/2}e^{-\varepsilon/kT}d\varepsilon$$

ε is the single particle kinetic energy. Thus

$$\varepsilon = \frac{1}{2}mv^2, \ \ d\varepsilon = mvdv$$

$$\varepsilon^{1/2}d\varepsilon = \frac{(mv^2)^{1/2}}{\sqrt{2}}mvdv = \frac{1}{\sqrt{2}}m^{3/2}v^2dv$$

14.5 Distribution of Molecular Speed

$N(v)dv$: # of particles $v < \quad < v + dv$

$$N(v)dv = \frac{2\pi N}{(2\pi kT)^{3/2}} \cdot \frac{1}{\sqrt{2}} m^{3/2} v^2 dv \cdot e^{-mv^2/2kT}$$

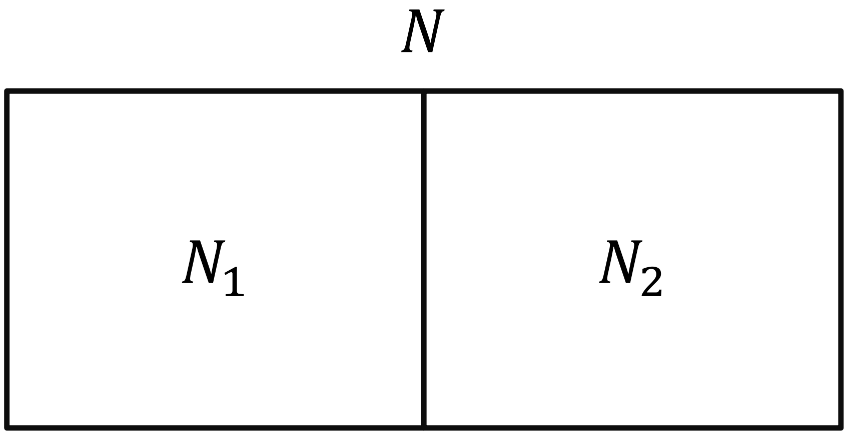
$$= 4\pi N \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT} dv$$

cf. from kinetic theory,

$$dN_v = \underbrace{\left(N\alpha^3 e^{-\beta^2 v^2}\right)}_{\rho} \times \underbrace{(4\pi v^2 dv)}_{V} = 4\pi N\alpha^3 v^2 e^{-\beta^2 v^2} dv$$

$$dN_v = 4\pi N\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT} dv$$

14.7 Entropy Change of Mixing



$$\Delta S = -n\bar{R}(x_1 \ln x_1 + x_2 \ln x_2)$$

- **Effect of mixing**

$$\Delta W = \frac{N!}{N_1!\,N_2!} = \frac{N!}{(x_1 N)!\,(x_2 N)!}$$

14.7 Entropy Change of Mixing

$$\Delta S = k \ln W = k[\ln \mathrm{N}! - \ln(x_1 N)! - \ln(x_2 N)!]$$

$$\frac{\Delta S}{k} = N \ln N - N - \{x_1 N \ln(x_1 N) - x_1 N\} - \{x_2 N \ln(x_2 N) - x_2 N\}$$

$$= -N(x_1 \ln x_1 + x_2 \ln x_2)$$