Physics 467/667: Thermal Physics **Spring 2019**

Lecture 24: Ideal Gas Model in Boltzmann Statistics

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24.1 Partition Functions for Composite Systems

Consider a system of just two particles, 1 and 2. If these particles do not interact with each other, their energy is just simply $E1 + E2$, then

$$Z_{\text{total}} = \sum_s e^{-\beta[E_1(s)+E_2(s)]} = \sum_s e^{-\beta E1(s)} e^{-\beta E2(s)} \tag{24.1}$$

Where the sum runs over all states s for the composite system. If the two particles are *distinguishable*,

$$Z_{\text{total}} = \sum_{s1} \sum_{s2} e^{-\beta E1(s1)} e^{-\beta E2(s2)} \tag{24.2}$$

In this case, we split the total partition functions Z into separate $Z1$ and $Z2$.

$$Z_{\text{total}} = Z_1 Z_2 \tag{24.3}$$

If the two particles are indistinguishable, we have to apply 1/2 to reduce double counts.

$$Z_{\text{total}} = \frac{1}{2} Z_1 Z_2 \tag{24.4}$$

This formula is not precisely correct, because there are some terms **in the double sum in which both particles are in the same state when the system is very dense**.

Therefore, the generalization of the equation is the following

$$Z_{\text{total}} = Z_1 Z_2 Z_3 \cdots Z_N \tag{24.5}$$

$$Z_{\text{total}} = \frac{1}{N!} Z_1^N \tag{24.6}$$

24.2 The Partition Function of an Ideal Gas

An ideal gas should have the following partition function form,

$$Z_{\text{total}} = \frac{1}{N!} Z_1^N \tag{24.7}$$

To calculate Z_1, we must make the Boltzmann factor,

$$e^{-E(s)/kT} = e^{-E_{\mathrm{tr}}(s)/kT} e^{-E_{\mathrm{int}}(s)/kT} \tag{24.8}$$

Since Z is additive,

$$Z_1 = Z_{\mathrm{tr}} Z_{\mathrm{int}} \tag{24.9}$$

Where

$$Z_{\mathrm{tr}} = \sum e^{-E_{\mathrm{tr}}/kT} \quad Z_{\mathrm{int}} = \sum e^{-E_{\mathrm{int}}/kT} \tag{24.10}$$

To calculate Z_{tr}, we can start with the case of a molecule confined to a one-dimensional box.

$$\lambda_n = \frac{2L}{n}, \qquad n = 1, 2, ..., \tag{24.11}$$

$$p_n = \frac{h}{\lambda_n} = \frac{hn}{2L} \qquad n = 1, 2, ..., \tag{24.12}$$

$$E_n = \frac{p_n^2}{2m} = \frac{h^2 n^2}{8mL^2} \tag{24.13}$$

Therefore,

$$Z_{1\mathrm{d}} = \sum_n e^{-E_n/kT} = \sum e^{\frac{-h^2 n^2}{8mL^2 kT}} \tag{24.14}$$

By doing integration

$$Z_{1\mathrm{d}} = \int_0^\infty e^{\frac{-h^2 n^2}{8mL^2 kT}} dn = \frac{\sqrt{\pi}}{2}\sqrt{\frac{8mL^2 kT}{h^2}} = \sqrt{\frac{2\pi mkT}{h^2}} L = \frac{L}{L_Q} \quad (L_Q : \text{ Quantum length}) \tag{24.15}$$

For 3 dimension,

$$E_{\mathrm{tr}} = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} \tag{24.16}$$

$$Z_{\mathrm{tr}} = \frac{L_x}{L_Q}\frac{L_y}{L_Q}\frac{L_z}{L_Q} = \frac{V}{V_Q} \quad (V_Q : \text{ Quantum Volume}) \tag{24.17}$$

$$Z_1 = \frac{V}{V_Q} Z_{\mathrm{int}} \tag{24.18}$$

where

$$Z = \frac{1}{N!}(\frac{VZ_{\mathrm{int}}}{V_Q})^N \tag{24.19}$$

and

$$\ln Z = N[\ln V + \ln Z_{\mathrm{int}} - \ln N - \ln V_Q + 1] \tag{24.20}$$

Knowing Z can help us to compute many quantities,

$$U = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta} \tag{24.21}$$

$$U = -N\frac{\partial \ln Z_{\text{int}}}{\partial \beta} + N\frac{1}{V_Q}\frac{\partial V_Q}{\partial \beta} = N\bar{E}_{\text{int}} + N\frac{3}{2\beta} = U_{\text{int}} + \frac{3}{2}NkT \tag{24.22}$$

$$C_V = \frac{\partial U}{\partial T} = \frac{\partial U_{\text{int}}}{\partial T} + \frac{3}{2}Nk \tag{24.23}$$

$$F = -kT\ln Z = -NkT[\ln V - \ln N - \ln V_Q + 1] + F_{\text{int}} \tag{24.24}$$

From this, it is easy to compute

$$P = -(\frac{\partial F}{\partial V})_{T,N} = \frac{NkT}{V} \tag{24.25}$$