

## 6.2: Translational Partition Function

First, we derive the density of states that we had already used in computing the distribution functions for quantum gases. We consider a quantum particle in a three-dimensional cubic box with edge length  $a$ . The energy is quantized with integer quantum numbers  $n_x$ ,  $n_y$ , and  $n_z$  corresponding to the three pairwise orthogonal directions that span the cube,

$$\epsilon_{\text{trs}} = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2) \quad (6.2.1)$$

$$= \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) . \quad (6.2.2)$$

It follows that momentum is also quantized with  $|p_i| = (h/2a)n_i$  ( $i = x, y, z$ ). It is convenient to consider momentum in a Cartesian frame where  $h/2a$  is the unit along the  $x$ ,  $y$ , and  $z$  axes. Each state characterized by a unique set of *translational quantum numbers*  $(n_x, n_y, n_z)$  'owns' a small cube with volume  $h^3/8a^3$  in the octant with  $x \geq 0$ ,  $y \geq 0$ , and  $z \geq 0$ . Since momentum can also be negative, we need to consider all eight octants, so that each state owns a cell in momentum space with volume  $h^3/a^3$ . In order to go to phase space, we need to add the spatial coordinates. The particle can move throughout the whole cube with volume  $a^3$ . Hence, each state owns a phase space volume of  $h^3$ .

By rearranging Equation 6.2.1 we can obtain an equation that must be fulfilled by the quantum numbers,

$$\frac{n_x^2}{\left(\frac{a}{h}\sqrt{8m\epsilon}\right)^2} + \frac{n_y^2}{\left(\frac{a}{h}\sqrt{8m\epsilon}\right)^2} + \frac{n_z^2}{\left(\frac{a}{h}\sqrt{8m\epsilon}\right)^2} = 1 \quad (6.2.3)$$

and by using Equation 6.2.2 we can convert it to an equation that must be fulfilled by the components of the momentum vector,

$$\frac{p_x^2}{\left(\frac{1}{2}\sqrt{8m\epsilon}\right)^2} + \frac{p_y^2}{\left(\frac{1}{2}\sqrt{8m\epsilon}\right)^2} + \frac{p_z^2}{\left(\frac{1}{2}\sqrt{8m\epsilon}\right)^2} = 1 . \quad (6.2.4)$$

All states with quantum numbers that make the expression on the left-hand side of Equation 6.2.3 or Equation 6.2.4 smaller than 1 correspond to energies that are smaller than  $\epsilon$ . The momentum associated with these states lies in the sphere defined by Equation 6.2.4 with radius  $\frac{1}{2}\sqrt{8m\epsilon}$  and volume  $\frac{\pi}{6}(8m\epsilon)^{3/2}$ . With cell size  $h^3/a^3$  in momentum space the number of cells with energies smaller than  $\epsilon$  is

$$\mathcal{N}(\epsilon) = \frac{8\sqrt{2}}{3}\pi \frac{V}{h^3} (m\epsilon)^{3/2} , \quad (6.2.5)$$

where we have substituted  $a^3$  by volume  $V$  of the box. The number of states in an energy interval between  $\epsilon$  and  $\epsilon + d\epsilon$  is the first derivative of  $\mathcal{N}(\epsilon)$  with respect to  $\epsilon$  and is the sought density of states,

$$D(\epsilon) = 4\sqrt{2}\pi \frac{V}{h^3} m^{3/2} \epsilon^{1/2} . \quad (6.2.6)$$

### Partition Function and Accessible States

This density of states is very high, so that we can replace the sum over the quantum numbers  $n_i$  in the partition function of the canonical ensemble by an integral ,

$$Z_{\text{trs},i} = \int_0^\infty e^{-\beta n_i^2 h^2 / 8ma^2} dn_i \quad (i = x, y, z) \quad (6.2.7)$$

$$= \sqrt{\frac{2\pi m}{\beta}} \frac{a}{h} . \quad (6.2.8)$$

The contributions along orthogonal spatial coordinates are also independent of each other and factorize. Hence,

$$Z_{\text{trs}} = Z_{\text{trs},x} \cdot Z_{\text{trs},y} \cdot Z_{\text{trs},z} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V , \quad (6.2.9)$$

where we have again substituted  $a^3$  by  $V$  and, as by now usual, also  $\beta$  by  $1/k_B T$ . The corresponding molar partition function is

$$z_{\text{trs}} = \frac{1}{N_{\text{Av}}!} \left[ \left( \frac{2\pi m k_{\text{B}} T}{h^2} \right)^{3/2} V \right]^{N_{\text{Av}}} \quad (6.2.10)$$

At this point it is useful to introduce another concept:

The molecular canonical partition function  $Z$  is a measure for the number of states that are accessible to the molecule at a given temperature. [concept:accessible\_states]

This can be easily seen when considering

$$P_i = \frac{N_i}{N} = \frac{g_i e^{-\epsilon_i/k_{\text{B}}T}}{Z} \quad (6.2.11)$$

and  $\sum_i P_i = 1$ . If we consider a mole of  $^4\text{He}$  (bosons) at 4.2 K, where it liquifies, we find that  $z_{\text{trs}}/N_{\text{Av}} \approx 7.5$ , which is not a large number. This indicates that we are close to breakdown of the regime where Bose-Einstein statistics can be approximated by Boltzmann statistics.

For  $T \rightarrow 0$  only the  $g_0$  lowest energy states are populated. In the absence of ground-state degeneracy,  $g_0 = 1$ , we find  $Z = 1$  and with an energy scale where  $U(T=0) = 0$  we have  $S(0) = 0$  in agreement with Nernst's theorem.

An expression for the translational contribution to the entropy of an ideal gas can be derived from Equation 6.2.9, Equation ???, and Equation ???). We know that  $u = 3Nk_{\text{B}}T/2$ , so that we only need to compute  $\ln z_{\text{trs}}$ ,

$$\ln z_{\text{trs}} = \ln \frac{1}{N!} Z_{\text{trs}}^N \quad (6.2.12)$$

$$= -\ln N! + N \ln Z_{\text{trs}} \quad (6.2.13)$$

$$= -N \ln N + N + N \ln Z_{\text{trs}} \quad (6.2.14)$$

$$= N \left( 1 + \ln \frac{Z_{\text{trs}}}{N} \right), \quad (6.2.15)$$

where we have used Stirling's formula to resolve the factorial. Thus we find

$$s = \frac{u}{T} + k_{\text{B}} \ln z \quad (6.2.16)$$

$$= \frac{3}{2} N k_{\text{B}} + k_{\text{B}} N \left( 1 + \ln \frac{Z_{\text{trs}}}{N} \right) \quad (6.2.17)$$

$$= N k_{\text{B}} \left( \frac{5}{2} + \ln \frac{Z_{\text{trs}}}{N} \right) \quad (6.2.18)$$

By using Equation 6.2.9 we finally obtain the **Sackur-Tetrode equation**

$$s = N k_{\text{B}} \left\{ \frac{5}{2} + \ln \left[ \left( \frac{2\pi m k_{\text{B}} T}{h^2} \right)^{3/2} \frac{V}{N} \right] \right\}. \quad (6.2.19)$$

To obtain the molar entropy  $S_{\text{m}}$ ,  $N$  has to be replaced by  $N_{\text{Av}}$ . Volume can be substituted by pressure and temperature, by noting that the molar volume is given by  $V_{\text{m}} = RT/p = N_{\text{Av}}V/N$ . With  $N_{\text{Av}}k_{\text{B}} = R$  and the molar mass  $M = N_{\text{Av}}m$  we obtain

$$S_{\text{m}} = R \left\{ \frac{5}{2} + \ln \left[ \left( \frac{2\pi M k_{\text{B}} T}{N_{\text{Av}} h^2} \right)^{3/2} \frac{RT}{N_{\text{Av}} p} \right] \right\} \quad (6.2.20)$$

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