Monatomic Gases

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Monatomic Gases

- For monatomic gases we will need the translational and electronic partition functions, as those are the two modes of energy storage available.

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The Translational Partition Function

To evaluate q_{tr} we need the energy:

$$\varepsilon_{tr} = \frac{h^2}{8m}\left\{\left(\frac{n_x}{l_x}\right)^2 + \left(\frac{n_y}{l_y}\right)^2 + \left(\frac{n_z}{l_z}\right)^2\right\}$$

If the motions in the three coordinate directions are independent, then

$$q_{tr} = q_x q_y q_z = \sum_{n_x} e^{-\frac{\beta h^2}{8m}\frac{n_x^2}{l_x^2}} \sum_{n_y} e^{-\frac{\beta h^2}{8m}\frac{n_y^2}{l_y^2}} \sum_{n_z} e^{-\frac{\beta h^2}{8m}\frac{n_z^2}{l_z^2}}$$

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The Continuum Approximation

Because we are dealing with such large quantum numbers we can approximate the sum in the partition function with an integral:

$$q_x = \sum_{n_x} e^{-\frac{\beta h^2}{8m}\frac{n_x^2}{l_x^2}} \cong \int_0^\infty e^{-\frac{\beta h^2}{8m}\frac{n_x^2}{l_x^2}} dn_x$$

If we let

$$x = \left(\frac{\beta h^2}{8m}\right)^{1/2} \frac{n_x}{l_x}$$

Then

$$q_x \cong \left(\frac{8m}{\beta h^2}\right)^{1/2} l_x \int_0^\infty e^{-x^2} dx$$

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The definite integral has the value $\sqrt{\pi}/2$

So that

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

where $V = l_x l_y l_z$

This will be the only place where the volume appears and is due to the dependency of translational quantum states on the volume.

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Translational Degeneracy

Recall that the translational states are degenerate. Therefore, if we are interested in energy rather, than state, we need to account for the degeneracy.

If we define $f(\varepsilon)d\varepsilon$ as the fraction of particles in the interval ε to $\varepsilon + d\varepsilon$, and dg as the degeneracy for the energy increment $d\varepsilon$, then

$$f(\varepsilon)d\varepsilon = \frac{e^{-\beta\varepsilon_k}}{\sum_k e^{-\beta\varepsilon_k}} dg$$

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To relate $d\varepsilon$ to dg first consider that

$$\varepsilon = \frac{h^2}{8mV^{2/3}} n^2$$

where n is the total translational quantum number equal to

$$n = \sqrt{n_x^2 + n_y^2 + n_z^2}$$

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Therefore, n is the radius of a one-eighth sphere in the positive octant of translational quantum number space. All states on the surface of the sphere have the same energy. Therefore, each state with energy between ε + $d\varepsilon$ occupies the one-eighth spherical shell between n and $n + dn$. The volume of this shell is

$$dg = \frac{4\pi n^2 dn}{8}$$

Differentiating ε with respect to n and substituting we get:

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

Since $\varepsilon = \frac{mc^2}{2}$ $d\varepsilon = mcdc$

(where c is the molecular translational speed)

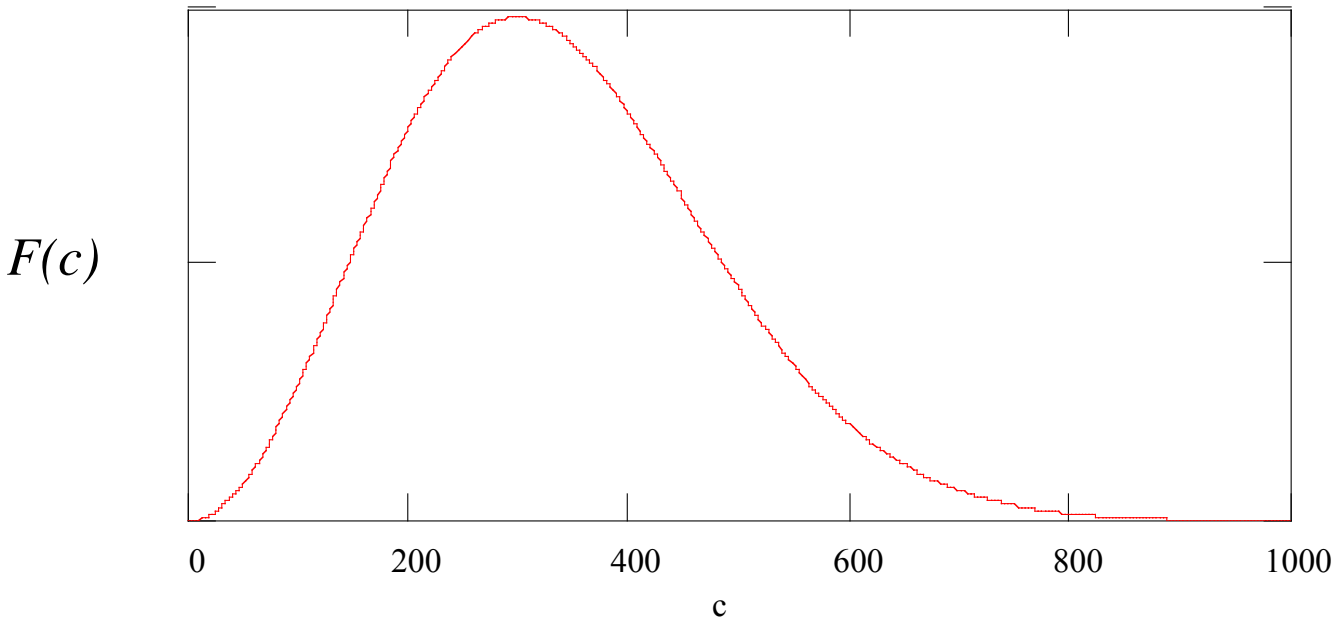
And we must have $f(\varepsilon)d\varepsilon = f(c)dc$

$$f(c) = \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{m}{kT}\right)^{3/2} c^2 e^{-mc^2/2kT}$$

Maxwellian Speed Distribution

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Speed Distribution



Average speed $$\overline{c} = \int_0^\infty c f(c) dc = \left(\frac{8kT}{\pi m} \right)^{1/2}$$

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The Electronic Partition Function

- Electronic motion is degenerate, thus the partition function becomes:

$$q_e = \sum_k g_k e^{-\beta \varepsilon_k}$$

- Sum is over energy states rather than quantum states

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The Boltzmann Ratio

Recall that $N_k = e^{-\gamma} e^{-\beta\varepsilon_k}$

and since $N = e^{-\gamma} \sum_k e^{-\beta\varepsilon_k}$

the probability of finding a particle in a given state is thus

$$\frac{N_k}{N} = \frac{e^{-\beta\varepsilon_k}}{\sum_k e^{-\beta\varepsilon_k}}$$

This is called the Boltzmann ratio.

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Population of Electronic States

- For Nitrogen, $\varepsilon_1 = 19{,}227$ cm^{-1}, and g_0 and $g_1 = 4$ and 10 respectively. If the temperature is 300 K, then

$$\frac{N_1}{N_0} = \frac{g_1 e^{-\varepsilon_1/kT}}{g_0 e^{-\varepsilon_0/kT}} \frac{10 e^{-\frac{19227\,hc}{kT}}}{4} = 1.67x10^{-40}$$

This is a pretty small number!

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- Thus we can ignore electronic energies above the ground state, then

$$q_e = g_e$$

- Otherwise we just have to perform the sum.

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- Thus the fundamental relation becomes (ignoring excited electronic states:

$$S\left[\frac{1}{T},\frac{-\mu}{T}\right] = ke^{-\frac{\mu}{kT}}\left(\frac{2\pi mkT}{h^2}\right)^{3/2} Vg_e$$

- Recall

$$dS\left[\frac{1}{T},\frac{-\mu}{T}\right] = -Ud\frac{1}{T} + \frac{P}{T}dV + Nd\frac{\mu}{T}$$

- And the Euler relation:

$$S = \frac{1}{T}U + \frac{P}{T}V - \sum_{i=1}^{r}\frac{\mu_i}{T}N_i$$

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Equations of State

$$U = \frac{-\partial S\left[\frac{1}{T}, \frac{-\mu}{T}\right]}{\partial \frac{1}{T}} = \frac{3}{2} TS\left[\frac{1}{T}, \frac{-\mu}{T}\right] = \frac{3}{2} PV = \frac{3}{2} NkT$$

$$\frac{P}{T} = \frac{\partial S\left[\frac{1}{T}, \frac{-\mu}{T}\right]}{\partial V} = \frac{1}{V} S\left[\frac{1}{T}, \frac{-\mu}{T}\right] = \frac{P}{T}$$

$$N = \frac{\partial S\left[\frac{1}{T}, \frac{-\mu}{T}\right]}{\partial \frac{-\mu}{T}} = \frac{1}{k} S\left[\frac{1}{T}, \frac{-\mu}{T}\right] = \frac{PV}{kT}$$

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- The average energy per atom is:

$$u = \frac{U}{N} = \frac{3}{2}kT$$

- The entropy is

$$S = S\left[\frac{1}{T}, \frac{-\mu}{T}\right] + U\frac{1}{T} - N\frac{\mu}{T} = k\left\{N + U\frac{1}{T} - N\frac{\mu}{T}\right\} = k\left\{\frac{5}{2} - \frac{\mu}{kT}\right\}$$

- Specific heat

$$c_v = \frac{\partial u}{\partial T}\Big)_V = \frac{3}{2}k$$

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Useful Energy Units

- Electron volt - Energy to move an electron through a potential of one volt
  - 1 ev = 1.602×10^{-19} J
- Inverse centimeter - Energy of photon
  - $E = h\nu = hc/\lambda, \quad \lambda' = 1/\lambda, \quad \lambda' = E/hc$
  - 1 ev = 8066 cm^{-1}
- Temperature - kT
  - 1 ev = 11,600 K

1 ev = 8066 cm^{-1} = 11,600 K = 1.602×10^{-19} J

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Recall the Maxwell-Boltzmann Limit

Must have

$$\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \frac{kT}{P} g_e >> 1$$

For H_2 at 300 K and 1 atmosphere, the left hand side has a value of 40,747, clearly satisfying the inequality.

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