Chapter 3. Ideal Gases

In this chapter we discuss such basic notions of statistical physics including probability, statistical ensembles, probability density, and density matrix. Then we use the basic statistical hypothesis, as formulated for the microcanonical ensemble, to define entropy. After that we use the notion of canonical ensemble to derive the Gibbs distribution (which is the central point of statistics). After that we discuss the partition function and the grand canonical ensemble.

3.1. Ideal Classical Gas: The Maxwell Distribution

Definitions:

"Ideal": no interactions

"Classical": average occupancy $n_k << 1$ for all particle energy levels n.

Since no interactions (explicit or Pauli-principle), we may apply the Gibbs distribution to a ensemble of single particles, so that $E \rightarrow \varepsilon$, and the Gibbs distribution turns into

$$n_k = C \exp\{-\varepsilon_k / T\}$$

- the *Boltzmann distribution*. Constant C should be found from the normalization condition:

$$\sum_k n_k = N.$$

At no external forces, no internal degrees of freedom:

$$\varepsilon_k = \frac{p_x^2 + p_y^2 + p_z^2}{2m}.$$

Essentially continuous variables. *Maxwell distribution*:

$$dw = c \exp\left\{-\frac{p_x^2 + p_y^2 + p_z^2}{2m}\right\} dp_x dp_y dp_z,$$

or equivalently

$$dw' = c \exp\left\{-\frac{p^2}{2m}\right\} 4\pi p^2 dp.$$

Normalization:

$$\frac{N}{V} = 4\pi c \int_0^\infty \exp\left\{-\frac{p^2}{2m}\right\} p^2 dp$$

gives:

$$c = (2\pi mT)^{-3/2}.$$

Average energy per particle:

$$\langle \varepsilon \rangle = \int\limits_{p\,space} dw = 4\pi c \int\limits_0^\infty \frac{p^2}{2m} \exp\left\{-\frac{p^2}{2m}\right\} p^2 dp = 3\int\limits_{-\infty}^{+\infty} dp_x \frac{p_x^2}{2m} \left[\int\limits_{-\infty}^{+\infty} dp_y \int\limits_{-\infty}^{+\infty} dp_z \frac{dw}{dp_x dp_y dp_z}\right] = \frac{3}{2}T.$$

This means that the r.m.s. velocity of the particles is

$$\langle v^2 \rangle^{1/2} = (3\frac{T}{m})^{1/2}.$$

For a typical gas (say, N_2): $m \sim 30\ m_p \sim 6\times10^{-26}$ kg at 300K ($E = k_B T_K \approx 4\times10^{-21}$ J), this velocity is about 4.5 km/s, about 10 times faster than a typical handgun bullet.

Explicit calculation of work for the Maxwell's Demon system (Fig. 2.3):

$$\langle v_x^2 \rangle = \frac{T}{m}.$$

Momentum transferred at single collision with the partition: $2mv_x$. Average pressure force:

$$\langle F \rangle = \left\langle \frac{2mv_x}{\tau} \right\rangle = \left\langle \frac{2mv_x}{2x/v_x} \right\rangle = \frac{m}{x}\langle v_x^2 \rangle = \frac{T}{x},$$

where x is the length of the cylinder's part containing the molecule. Work:

$$\int\limits_{L/2}^L \langle F \rangle dx = \int\limits_{L/2}^L \frac{T}{x} dx = T\ln 2.$$

(Confirms our general result for this particular case.)

Gas in an external field:

$$\varepsilon_k = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + U(x,y,z).$$

Distribution:

$$dw = c\exp\left\{-\frac{p_x^2 + p_y^2 + p_z^2}{2mT} - \frac{U(x,y,z)}{T}\right\} dxdydz\ dp_x dp_y dp_z.$$

If we are not interested in momentum distribution:

$$dw = c\exp\left\{-\frac{U(x,y,z)}{T}\right\} dxdydz \int \exp\left\{-\frac{p^2}{2mT}\right\} d^3p = c'\exp\left\{-\frac{U(x,y,z)}{T}\right\} dxdydz.$$

Example: Earth's gravity field: $U = mgz +$ const. Density of molecules (number per unit volume $dV = dxdydz$):

$$n \equiv \frac{dw}{dV} = n_0 \exp\left\{-\frac{mgz}{T}\right\} = n_0 \exp\left\{-\frac{z}{z_0}\right\}.$$

(the "barometric formula"). For a typical gas (N_2) at $T_K = 300$K, $z_0 \equiv k_B T_K / mg \approx 7$ km. This gives the right order of magnitude of the Earth atmosphere's thickness, though the exact law differs from Eq. (?) because of the drop of temperature with height.

3.2. Ideal Classical Gas: Thermodynamics

Independent particles (no interaction energy):

$$E = \sum_{j=1}^{N} \varepsilon_{k(j)}$$

Apparent (but wrong) formula:

$$Z = \sum_{n} \exp\left\{-\frac{E_n}{T}\right\} = \left(\sum_{k} \exp\left\{-\frac{\varepsilon_k}{T}\right\}\right)^{N}.$$

"Correct Boltzmann counting":

$$Z = \frac{1}{N!}\left(\sum_{k} \exp\left\{-\frac{\varepsilon_k}{T}\right\}\right)^{N}.$$

Taking into account the internal degrees of freedom:

$$\varepsilon_k = \frac{p^2}{2m} + \varepsilon_k'.$$

As a result,

$$F = -T \ln Z = -NT \ln \frac{eV}{N} + Nf(T),$$

with

$$f(T) = -T \ln\left[\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2} \times \sum_{k} \exp\left\{-\frac{\varepsilon_k}{T}\right\}\right].$$

If the internal degrees of freedom are "frozen" ($T \ll \varepsilon_1$) then the last sum equals 1.

Now using thermodynamics, we get:

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{NT}{V},$$

i.e. regardless of $f(T)$, we have the equation of state

$$pV = NT.$$

Next,

$$S = -\left(\frac{\partial F}{\partial V}\right)_T = N\left[\ln\frac{eV}{N} - f'(T)\right].$$

(Without the "correct Boltzmann counting", would give a wrong result under the logarithm, leading to the Gibbs mixing paradox.)

$$E = F + TS = N[f(T) - Nf'(T)]$$

The average energy per molecule, $\langle \varepsilon \rangle = E/N$ is a function of temperature alone.

$$W = E + pV = N[f(T) - Tf'(T) + T]$$

$$c_p - c_V = \left(\frac{\partial W}{\partial T}\right)_p - \left(\frac{\partial E}{\partial T}\right)_V = \frac{\partial(NT)}{\partial T} = N.$$

$$G = F + pV = N[T \ln p + \chi(T)],$$

i.e.

$$\mu = T \ln p + \chi(T),$$

where

$$\chi(T) = f(T) - T \ln T.$$

In particular, for a gas with the internal degrees of freedom frozen,

$$\mu = T \ln \left[\frac{N}{V} \left(\frac{2\pi\hbar^2}{mT} \right)^{3/2} \right].$$