

Let Q be any quantity associated with each particle.
The average value of Q is defined by

$$\langle Q \rangle = \frac{1}{n} \int d^3u Q f. \quad (2.36)$$

where

$$n = \int d^3u f$$

the number density per unit volume.

It follows that

$$\int d^3u Q f = n \langle Q \rangle$$

→ total amount of the quantity Q per unit volume.

Using the definition (2.36), the non-zero terms in (2.35) can be put in the form

$$\frac{\partial}{\partial t} (n \langle \chi \rangle) + \frac{\partial}{\partial x_i} (n \langle u_i \chi \rangle) - n \langle u_i \frac{\partial \chi}{\partial x_i} \rangle - \frac{n}{m} \langle F_i \frac{\partial \chi}{\partial u_i} \rangle - \frac{n}{m} \left\langle \frac{\partial F_i}{\partial u_i} \chi \right\rangle = 0 \quad (2.37)$$

→ how the volume density $n \langle \chi \rangle$ of any quantity χ conserved in binary collisions evolves in time.

P.30.

§ Exercises

02.1.

When $u_0 = 0$, the Maxwellian distribution (2.24) is

$$f(u) = n \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp \left(- \frac{m u^2}{2k_B T} \right)$$

$$(\because u^2 \rightarrow u^2, |u| = u = \sqrt{u_x^2 + u_y^2 + u_z^2})$$

then,

$$\begin{aligned} \langle u \rangle &= \frac{1}{n} \int d^3u u f(u) \\ &= \frac{1}{n} \int d^3u u n \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp \left(- \frac{m u^2}{2k_B T} \right) \\ &= 4\pi \int_0^\infty d^3u u^3 \exp \left(- \frac{m u^2}{2k_B T} \right) \end{aligned}$$

$$\begin{aligned} &(\because \int_0^\infty dx x^3 \exp(-Ax^2)) \\ &= \left[x^2 \cdot \left(-\frac{1}{2A} \right) \exp(-Ax^2) \right]_0^\infty \\ &\quad + \frac{1}{2A} \int_0^\infty 2x \exp(-Ax^2) dx \\ &= \frac{1}{A} \int_0^\infty x \exp(-Ax^2) dx \\ &= \frac{1}{A} \left[\left(-\frac{1}{2A} \right) \exp(-Ax^2) \right]_0^\infty \\ &= -\frac{1}{2A^2} (0 - 1) = \frac{1}{2A} \\ &= 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \cdot \frac{1}{2} \left(\frac{2k_B T}{m} \right)^2 \\ &= 2\pi \cdot \pi^{3/2} \left(\frac{m}{2k_B T} \right)^{3/2} \cdot \left(\frac{2k_B T}{m} \right)^2 \\ &= 2 \sqrt{\frac{2k_B T}{\pi m}} = \sqrt{\frac{8k_B T}{\pi m}} \end{aligned}$$

u_{rms}
根均方速度

The root mean square speed is given by

$$\begin{aligned}
 u_{rms} &= \sqrt{\langle u^2 \rangle} \\
 &= \sqrt{\frac{1}{n} \int d^3u u^2 f(u)} \\
 &= \sqrt{\frac{1}{n} \int d^3u u^2 \pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m u^2}{2k_B T}\right)} \\
 &= \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int d^3u u^2 \exp\left(-\frac{m u^2}{2k_B T}\right) \\
 &= 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_0^\infty du u^4 \exp\left(-\frac{m u^2}{2k_B T}\right) \\
 &\quad \left(\begin{aligned}
 &\because \int_0^\infty dx x^4 \exp(-Ax^2) \\
 &= \left[x^3 \cdot \left(-\frac{1}{2A}\right) \exp(-Ax^2) \right]_0^\infty \\
 &\quad + \frac{1}{2A} \int_0^\infty 3x^2 \exp(-Ax^2) dx \\
 &= \frac{3}{2A} \left[x \left(-\frac{1}{2A}\right) \exp(-Ax^2) \right]_0^\infty \\
 &\quad + \frac{3}{4A^2} \int_0^\infty \exp(-Ax^2) dx \\
 &= \frac{3}{4A^2} \cdot \frac{1}{2} \left(\frac{\pi}{A}\right)^{1/2} = \frac{3\pi^{1/2}}{8} \cdot A^{-5/2} \\
 &= 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \cdot \frac{3\pi^{1/2}}{8} \cdot \left(\frac{2k_B T}{m}\right)^{5/2} \\
 &= \frac{3}{2} \cdot \frac{2k_B T}{m} = \frac{3k_B T}{m} \\
 &\therefore u_{rms} = \sqrt{\frac{3k_B T}{m}}
 \end{aligned} \right)
 \end{aligned}$$

○ 2.2.

The number of collisions δn_c per unit volume per unit time is

$$\delta n_c = \sigma(u, u_2 | u_1, u_2') \cdot n(u - u_2) n_2 d\Omega \quad (2.6)$$

We write the differential scattering cross-section as a function of the scattering angle Ω between u and u' , so that

$$\begin{aligned}
 \delta n_c &= \sigma(\Omega) |u - u_2| f(u) f(u_2) d\Omega d^3u d^3u_2 \\
 &\quad (\because n = f(u) d^3u, n_2 = f(u_2) d^3u_2)
 \end{aligned}$$

and then integrating over Ω and u and u_2 , i.e.

$$N_{coll} = \int d^3u \int d^3u_2 \int d\Omega \sigma(\Omega) |u - u_2| f(u) f(u_2)$$

Now consider the molecules to be hard spheres of radius a so that the total scattering cross-section is πa^2 , the above integral for such molecules ~~is~~ ^{is} obtain

$$\begin{aligned}
 N_{coll} &= \int d^3u \int d^3u_2 \int d\Omega \underbrace{\sigma(\Omega)}_{\pi a^2} n \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m u^2}{2k_B T}\right) n \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m u_2^2}{2k_B T}\right) \\
 &= \pi a^2 n^2 \left(\frac{m}{2\pi k_B T}\right)^3 \int d^3u \int d^3u_2 \exp\left(-\frac{m(u^2 + u_2^2)}{2k_B T}\right) \\
 &\quad (\because u \rightarrow u_0 \rightarrow u, u_2 - u_0 \rightarrow u_2) \\
 &\quad \rightarrow \text{we go to a frame moving with velocity } u_0
 \end{aligned}$$

Transform from u and u_2

to the relative velocity $u_{rel} = u - u_2$

and the center-of-mass velocity $u_{cm} = \frac{u + u_2}{2}$

$$u = \frac{u_{rel} + 2u_{cm}}{2}, \quad u_2 = \frac{-u_{rel} + 2u_{cm}}{2}$$

$$\begin{aligned} u^2 + u_2^2 &= \left(\frac{u_{rel} + 2u_{cm}}{2} \right)^2 + \left(\frac{-u_{rel} + 2u_{cm}}{2} \right)^2 \\ &= \frac{u_{rel}^2 + 4u_{rel}u_{cm} + 4u_{cm}^2 + u_{rel}^2 - 4u_{rel}u_{cm} + 4u_{cm}^2}{4} \\ &= \frac{u_{rel}^2}{2} + 2u_{cm}^2 \end{aligned}$$

$$\text{Jacobian } \frac{\partial(u_1, u_2)}{\partial(u_{rel}, u_{cm})} = \begin{vmatrix} \frac{\partial u_1}{\partial u_{rel}} & \frac{\partial u_1}{\partial u_{cm}} \\ \frac{\partial u_2}{\partial u_{rel}} & \frac{\partial u_2}{\partial u_{cm}} \end{vmatrix}$$

$$= \begin{vmatrix} \frac{1}{2} & 1 \\ -\frac{1}{2} & 1 \end{vmatrix} = \frac{1}{2} - \left(-\frac{1}{2}\right) = 1$$

so that

$$N_{coll} = \pi n^2 a^2 \left(\frac{m}{2\pi k_B T} \right)^3 \int d^3 u_{rel} u_{rel} \exp\left[-\frac{m u_{rel}^2}{4k_B T}\right] \int d^3 u_{cm} \exp\left[-\frac{m u_{cm}^2}{k_B T}\right]$$

$$\therefore \int d^3 u_{rel} u_{rel} \exp\left[-\frac{m u_{rel}^2}{4k_B T}\right]$$

$$= 4\pi \int_0^\infty du_{rel} u_{rel}^3 \exp\left[-\frac{m u_{rel}^2}{4k_B T}\right]$$

$$= 4\pi \cdot \frac{1}{2} \left(\frac{4k_B T}{m} \right)^2 = 2\pi \left(\frac{4k_B T}{m} \right)^2$$

$$\int d^3 u_{cm} \exp\left[-\frac{m u_{cm}^2}{k_B T}\right]$$

$$= 4\pi \int_0^\infty du_{cm} u_{cm}^2 \exp\left[-\frac{m u_{cm}^2}{k_B T}\right]$$

$$\int_0^\infty dx x^2 \exp(-Ax^2)$$

$$= \left[x \cdot \left(-\frac{1}{2A}\right) \exp(-Ax^2) \right]_0^\infty$$

$$+ \frac{1}{2A} \int_0^\infty \exp(-Ax^2) dx$$

$$= \frac{1}{2A} \cdot \frac{1}{2} \left(\frac{\pi}{A} \right)^{1/2} = \frac{1}{4} \frac{\pi^{1/2}}{A^{3/2}}$$

$$\begin{aligned} &= 4\pi \cdot \frac{1}{2} \pi^{1/2} \left(\frac{k_B T}{m} \right)^{3/2} \\ &= \pi^{3/2} \left(\frac{k_B T}{m} \right)^{3/2} \end{aligned}$$

$$\begin{aligned} N_{coll} &= \pi n^2 a^2 \left(\frac{m}{2\pi k_B T} \right)^3 \cdot 2\pi \left(\frac{4k_B T}{m} \right)^2 \cdot \pi^{3/2} \left(\frac{k_B T}{m} \right)^{3/2} \\ &= n^2 a^2 \cdot \pi \cdot \frac{1}{8\pi^3} \cdot 2\pi \cdot 16 \cdot \pi^{3/2} \cdot \left(\frac{m}{k_B T} \right)^{3-2-\frac{3}{2}} \\ &= 4n^2 a^2 \left(\frac{\pi k_B T}{m} \right)^{3/2} \end{aligned}$$

The number of collisions taking place per unit time per unit volume per a particle is.

$$\frac{N_{coll}}{n} = 4n a^2 \left(\frac{\pi k_B T}{m} \right)^{3/2}$$

then,

$$\lambda \times \frac{N_{coll}}{n} = \langle u \rangle$$

($\because \lambda$: the mean free path)

i.e.,

$$\lambda = \langle u \rangle \times \frac{n}{N_{coll}}$$

$$= \sqrt{\frac{3k_B T}{\pi m}} \times \frac{1}{4n a^2} \left(\frac{m}{\pi k_B T} \right)^{3/2}$$

$$= \frac{1}{\sqrt{2} n \pi a^2}$$

Q 2.3.

The H function is

$$H = \int d^3u f \log f$$

so, that

$$\begin{aligned} H &= \int d^3u n \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mu^2}{2k_B T}\right) \log n \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mu^2}{2k_B T}\right) \\ &= n \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int d^3u \exp\left(-\frac{mu^2}{2k_B T}\right) \left[\log n \left(\frac{m}{2\pi k_B T}\right)^{3/2} + \left(-\frac{mu^2}{2k_B T}\right) \right] \\ &= 4\pi n \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int d^3u \left[\log n \left(\frac{m}{2\pi k_B T}\right)^{3/2} u^2 \exp\left(-\frac{mu^2}{2k_B T}\right) \right. \\ &\quad \left. - \frac{m}{2k_B T} u^4 \exp\left(-\frac{mu^2}{2k_B T}\right) \right] \\ &= 4\pi n \left(\frac{m}{2\pi k_B T}\right)^{3/2} \left[\log n \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int d^3u u^2 \exp\left(-\frac{mu^2}{2k_B T}\right) \right. \\ &\quad \left. - \frac{m}{2k_B T} \int d^3u u^4 \exp\left(-\frac{mu^2}{2k_B T}\right) \right] \end{aligned}$$

$$\begin{aligned} &\left(\begin{aligned} \therefore \int d^3u u^2 \exp\left(-\frac{mu^2}{2k_B T}\right) &= \frac{\sqrt{\pi}}{4} \left(\frac{2k_B T}{m}\right)^{3/2} \\ \int d^3u u^4 \exp\left(-\frac{mu^2}{2k_B T}\right) &= \frac{3\sqrt{\pi}}{8} \left(\frac{2k_B T}{m}\right)^{5/2} \end{aligned} \right) \\ &= 4\pi n \left(\frac{m}{2\pi k_B T}\right)^{3/2} \left[\log n \left(\frac{m}{2\pi k_B T}\right)^{3/2} \cdot \frac{\sqrt{\pi}}{4} \left(\frac{2k_B T}{m}\right)^{3/2} \right. \\ &\quad \left. - \frac{m}{2k_B T} \cdot \frac{3\sqrt{\pi}}{8} \left(\frac{2k_B T}{m}\right)^{5/2} \right] \\ &= n \left[4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \cdot \frac{\sqrt{\pi}}{4} \left(\frac{2k_B T}{m}\right)^{3/2} \log n \left(\frac{m}{2\pi k_B T}\right)^{3/2} \right. \\ &\quad \left. - 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \cdot \frac{3\sqrt{\pi}}{8} \left(\frac{2k_B T}{m}\right)^{5/2} \right] \\ &= n \left[\log n + \frac{3}{2} \log\left(\frac{m}{2\pi k_B T}\right) - \frac{3}{2} \right] \end{aligned}$$

The distribution function of an ideal monatomic gas is

$$\begin{aligned} Z &= \frac{1}{N! h^{3N}} \int \dots \int \exp\left[-\frac{1}{2mk_B T} (p_1^2 + p_2^2 + \dots + p_{3N}^2)\right] dx_1 \dots dx_{3N} dp_1 \dots dp_{3N} \\ &= \frac{1}{N! h^{3N}} \left[\int dx_1 dx_2 dx_3 \right]^N \left[\int \exp\left[-\frac{p^2}{2mk_B T}\right] dp \right]^{3N} \\ &= \frac{V^N}{N! h^{3N}} (2\pi mk_B T)^{\frac{3N}{2}} \end{aligned}$$

where V is volume, N is number of particles.

The Helmholtz free energy is given by

$$\begin{aligned} F &= -k_B T \log Z \\ &= -k_B T \left[\log\left(\frac{V^N}{N! h^{3N}}\right) + \frac{3}{2} N \log(2\pi mk_B T) \right] \end{aligned}$$

Then, the entropy per unit volume is

$$\begin{aligned} S &= \frac{1}{V} \left[-\left(\frac{\partial F}{\partial T}\right)_{N, V} \right] \\ &= \frac{k_B}{V} \left[\log\left(\frac{V^N}{N! h^{3N}}\right) + \frac{3}{2} N \log(2\pi mk_B T) \right] + \frac{k_B}{V} \cdot \frac{3}{2} N \cdot \frac{1}{T} \end{aligned}$$

 \therefore Stirling's approximation.

$$\begin{aligned} \log N! &= \log 1 + \log 2 + \dots + \log N \quad \left(\int_1^N \log x dx \right) \\ &\approx \int_1^N \log x dx \\ &= \left[x(\log x - 1) \right]_1^N \\ &= N \log N - N \end{aligned}$$

$$\begin{aligned} \therefore \log \frac{V^N}{N! h^{3N}} &\approx N \log V - \log N! - \log h^{3N} \\ &\approx N \log V - N \log N + N - \log h^{3N} \\ &= N \log \frac{V}{N} + N - \log h^{3N} \end{aligned}$$

so that.

$$\begin{aligned}
 S &= \frac{k_B}{V} \left[N \log \frac{V}{N} + N - \log h^{3N} + \frac{3}{2} N \log (2\pi m k_B T) + \frac{3}{2} N \right] \\
 &= \frac{N}{V} k_B \left[-\log \frac{N}{V} - \log h^3 + \frac{3}{2} \log (2\pi m k_B T) + \frac{5}{2} \right] \\
 &= n k_B \log \left[\frac{1}{n h^3} (2\pi m k_B T)^{\frac{3}{2}} e^{\frac{5}{2}} \right]
 \end{aligned}$$

also:

$$\begin{aligned}
 S &= -n k_B \left[\log n + \frac{3}{2} \log \left(\frac{1}{2\pi m k_B T} \right) - \frac{3}{2} \right] - n \log h^3 + n k_B \\
 &= -k_B \cdot n \left[\log n + \frac{3}{2} \log \left(\frac{m}{2\pi k_B T} \right) - \frac{3}{2} \right] - n k_B \log h^3 + n k_B \\
 &\quad + 3n k_B \log m \\
 &= -k_B H + \text{constant.}
 \end{aligned}$$