The Equilibrium Distribution and its Properties

In a previous lecture we derived the H theorem for a single species only, but it can be shown that the derivation also holds for mixtures of (non-reactive) species, for which the appropriate definition is,

$$H = \sum_{species} n_j \left\langle \ln f_j \right\rangle_j = \sum_{species} \left(\int f_j \ln f_j d^3 w \right)$$

If an equilibrium is reached ($dH/dt = 0$), H will then have attained its minimum value, consistent with the constraints that are implicit to the H theorem. These constraints are

(a) Conservation of the number of particles of each species (p.u. volume).

(b) Conservation of the overall momentum density (but species can exchange momentum, so it is not conserved species by species).

(c) Conservation of overall kinetic energy density (again, not for each species).

We therefore impose the following constraints:

$$E = \sum_i \int \frac{1}{2} m_i w^2 f_i(\vec{w}) d^3 w \quad \text{(one equation)}$$

$$\vec{P} = \sum_i \int m_i \vec{w} f_i(\vec{w}) d^3 w \quad \text{(three equations)}$$

$$n_i = \int f_i(\vec{w}) d^3 w \quad \text{(one equation per species)}$$

We adjoin Lagrange multipliers and minimize the functional:

$$\sum_i \int f_i (\ln f_i) d^3 w + \sum_i \alpha_i \int f_i d^3 w + \beta \sum_i \int \frac{1}{2} m_i w^2 f_i d^3 w + \vec{\gamma} \cdot \sum_i \int m_i \vec{w} f_i d^3 w$$
$$= \sum_i \int f_i \left(\ln f_i + \alpha_i + \beta \frac{1}{2} m_i w^2 + \vec{\gamma} \cdot m_i \vec{w} \right) d^3 w$$

Notice that a single Lagrange multiplier β is associated with the total sum of energies, and also a single vector $\vec{\gamma}$ is associated with the total sum of momenta; this is in fact the origin of the eventual fact that $\vec{u}_i = \vec{u}$ and $T_i = T$. Differentiation relative to f_i gives then,

$$\ln f_i + \alpha_i + \beta \frac{1}{2} m_i w^2 + \vec{\gamma} \cdot m_i \vec{w} + 1 = 0$$

$$f_i = e^{-(1+\alpha_i)} e^{-m_i \vec{\gamma} \cdot \vec{w} - \beta \frac{1}{2} m_i w^2}$$

$$= e^{-(1+\alpha_i) + \frac{m_i \gamma^2}{2\beta}} e^{-\frac{m_i \beta}{2} (\vec{w} + \frac{\vec{\gamma}}{\beta})^2}$$

where we have completed the square in the exponent.

The constants α_i, $\vec{\gamma}$ and β will now be determined from the constraint equations; before doing the detailed algebra however, one can readily see that the mean velocities and the temperatures must indeed be common to all species. For species i,

$$\vec{u}_i \;=\; \frac{1}{n_i}\int \vec{w} f_i d^3w \;=\; \frac{\int \vec{w} f_i d^3w}{\int f_i d^3w} \;=\; \frac{\int \vec{w} e^{-\frac{m_i\beta}{2}(\vec{w}+\frac{\vec{\gamma}}{\beta})^2} d^3w}{\int e^{-\frac{m_i\beta}{2}(\vec{w}+\frac{\gamma}{\beta})^2} d^3w}$$

where the common factor $e^{-(1+\alpha_i)+\frac{m_i\gamma^2}{2\beta}}$ has been dropped in the ratio. Change variable to $\vec{\zeta} = \vec{w} + \frac{\vec{\gamma}}{\beta}$:

$$\vec{u}_i \;=\; \frac{\int \vec{\zeta} e^{-\frac{m_i\beta}{2}\zeta^2} d^3\zeta - \frac{\vec{\gamma}}{\beta}\int e^{-\frac{m_i\beta}{2}\zeta^2} d^3\zeta}{\int e^{-\frac{m_i\beta}{2}\zeta^2} d^3\zeta} \;=\; \frac{-\vec{\gamma}}{\beta}$$

since the first integration vanishes by symmetry. This result is independent of i, and so $\vec{u}_i = \vec{u}$, the same for all i.

Similarly, once we know $\vec{u} = -\frac{\vec{\gamma}}{\beta}$ (and recall $\vec{c} = \vec{w} - \vec{u}$),

$$\frac{3}{2}kT_i \;=\; \frac{1}{2}m_i\left\langle c^2\right\rangle_i \;=\; \frac{1}{n_i}\int \frac{m_i(\vec{w}-\vec{u})^2}{2} f_i d^3w \;=\; \frac{\frac{m_i}{2}\int (\vec{w}-\vec{u})^2 e^{-\frac{m_i\beta}{2}(\vec{w}-\vec{u})^2} d^3w}{\int e^{-\frac{m_i\beta}{2}(\vec{w}-\vec{u})^2} d^3w}$$

and changing now to $\vec{y} = \sqrt{\frac{m_i\beta}{2}}(\vec{w}-\vec{u})$,

$$\frac{3}{2}kT_i \;=\; \frac{\frac{1}{\beta}\int y^2 e^{-y^2} d^3y}{\int e^{-y^2} d^3y}$$

The ratio of integrals turns out to be $\frac{3}{2}$, showing that,

$$T_i \;=\; \frac{1}{k\beta}$$

again independent of i. So with,

$$\beta = \frac{1}{kT} \qquad \text{and} \qquad \vec{\gamma} = -\frac{\vec{u}}{kT}$$

we have,

$$f_i(\vec{w}) \;=\; \underbrace{e^{-(1+\alpha_i)+\frac{m_i}{2}\frac{u^2}{kT}}}_{K} e^{-\frac{m_i(\vec{w}-\vec{u})^2}{2kT}}$$

$$n_i \;=\; \int f_i d^3w \;=\; K\int e^{-\frac{m_i(\vec{w}-\vec{u})^2}{2kT}} d^3w \qquad \text{with} \qquad \sqrt{\frac{m_i}{2kT}}\,(\vec{w}-\vec{u}) \;=\; y$$

then,

$$n_i \;=\; K\int_0^\infty \left(\frac{2kT}{m_i}\right)^{3/2} e^{-y^2} 4\pi y^2 dy$$

and noticing that,

$$y^2 \;=\; t \qquad\quad dy \;=\; \frac{1}{2}t^{1/2}dt$$

$$n_i \;=\; K\left(\frac{2kT}{m_i}\right)^{3/2}\frac{4\pi}{2}\underbrace{\int_0^\infty t^{1/2}e^{-t}dt}_{\Gamma(\frac{3}{2})=\frac{1}{2}\sqrt{\pi}} \;=\; K\left(\frac{2\pi kT}{m_i}\right)^{3/2}$$

Solving for K,

$$K = n_i\left(\frac{m_i}{2\pi kT}\right)^{3/2}$$

Therefore we find,

$$\boxed{f_i(\vec{w}) \;=\; n_i\left(\frac{m_i}{2\pi kT}\right)^{3/2} e^{-\frac{m_i(\vec{w}-\vec{u})^2}{2kT}}}$$

which is the Maxwellian or Equilibrium distribution function.

We could re-derive the Maxwellian limit using an alternative argument to the optimization procedure discussed above. During our discussion of the H-theorem, we obtained,

$$\frac{dH}{dt} \;=\; \frac{1}{4}\int d\Omega \iint (f'f_1' - ff_1)\ln\left(\frac{ff_1}{f'f_1'}\right) g\sigma d^3w d^3w_1 \leq 0$$

and the equality (equilibrium) can only be true if,

$$f'f_1' \;=\; ff_1 \qquad\qquad \text{for all } \vec{w}, \vec{w}_1, \vec{\Omega}$$

Hence the quantity,

$$\ln f(\vec{w}) \;+\; \ln f(\vec{w}_1)$$

is <u>conserved</u> in a collision between particles with velocities $\vec{w}, \vec{w}_1$. This is an <u>additive</u> quantity. What other additive quantities are conserved? The list is short; assuming zero momentum, they are:

(a) From number conservation, any constant quantity (the quantity 1, for instance)

(b) From energy conservation, the quantity $\frac{1}{2}mw^2$

Hence $\ln f$ must be a linear combination of these:

$$\ln f \;=\; \ln c_1 \;-\; c_3\frac{1}{2}mw^2$$

and therefore,

$$f \;=\; c_1 e^{-\frac{c_3}{2}mw^2}$$

If there is non-zero momentum, we should include it and write,

$$\ln f \;=\; \ln c_1 \;+\; \vec{c}_2\cdot m\vec{w} - c_3\frac{1}{2}mw^2$$

The values of c_1 and c_3 (and $\vec{c}_2$, if needed) come from imposing normalization such that,

$$\int f d^3w = n \qquad \int \vec{w} f d^3w = n\vec{u} \qquad \int \frac{1}{2} m w^2 f d^3 w = n\frac{3}{2}kT$$

The result, as with the minimization method, is,

$$\boxed{f(\vec{w}) \;=\; n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m(\vec{w}-\vec{u})^2}{2kT}}}$$

This method can be generalized to multi-species situations, although in that case, since there are several kinds of collisions, there will be more than one necessary conditions like $f'f'_1 \;=\; ff_1$, and some care must be exercised with terms arising from unlike particles.

Characteristic energies and velocities for a Maxwellian distribution

In a frame in which the gas is at rest ($\vec{u} = 0$), the mean vector velocity is zero. More generally, $\langle \vec{w} - \vec{u}\rangle_s = 0$, for any species s.

We generally define $\vec{c}_s = \vec{w} - \vec{u}_s$, the velocity of a particle with regard to the mean of its species. This is sometimes called the "diffusion velocity", but care must be taken not to confuse it with $\vec{c} = \vec{w} - \vec{u}$, where $\vec{u}$ is the mean mass velocity of all the species present. We see from the definition that $\boxed{\langle \vec{c}_s\rangle_s \equiv 0}$, but $\langle \vec{c}_s\rangle \equiv \vec{u}_s - \vec{u}$, which, in a non-equilibrium situation, can be non-zero.

An important velocity magnitude is $\bar{c}_s \equiv \langle c_s\rangle_s$, where the magnitude, and not the vector, is involved. For a Maxwellian,

$$\bar{c}_s \;=\; \frac{1}{\cancel{n_s}} \int c_s \cancel{n_s} \left(\frac{m_s}{2\pi kT_s}\right)^{\frac{3}{2}} e^{-\frac{m_s c_s^2}{2kT_s}} d^3c_s$$

Since only $|\vec{c}_s|$ appears, use spherical coordinates, where $d^3c_s = 4\pi c_s^2 dc_s$

$$\bar{c}_s \;=\; \int_0^\infty c_s \left(\frac{m_s}{2\pi kT_s}\right)^{\frac{3}{2}} e^{-\frac{m_s c_s^2}{2kT_s}} 4\pi c_s^2 dc_s$$

Define,

$$x^2 \;=\; \frac{m_s c_s^2}{2kT_s} \quad \rightarrow \quad c_s \;=\; \left(\frac{2kT_s}{m_s}\right)^{\frac{1}{2}} x \quad \text{and} \quad dc_s \;=\; \left(\frac{2kT_s}{m_s}\right)^{\frac{1}{2}} dx$$

The integral can be evaluated by changing $x^2 = t$, $x^3 dx = \frac{1}{2} t dt$, and its value is $\frac{1}{2}$. So,

$$\bar{c}_s \;=\; \frac{2}{\sqrt{\pi}}\left(\frac{2kT_s}{m_s}\right)^{\frac{1}{2}} \qquad \boxed{\bar{c}_s \;=\; \sqrt{\frac{8}{\pi}\frac{kT_s}{m_s}}}$$

Another important velocity is the RMS velocity, or $c_{RMS} = \sqrt{\langle c_s^2 \rangle_s}$. This can be calculated more easily, in fact, for any distribution, because,

$$\langle c_s^2 \rangle \equiv \frac{\not{2}}{m_s} \frac{3}{\not{2}} kT_s \quad \rightarrow \quad \boxed{c_{RMS} = \sqrt{3\frac{kT_s}{m_s}}}$$

Sometimes the distribution of interest is where particles are classified by either velocity magnitude or by energies. Looking at the first of these, we define a different distribution (assumed to be isotropic) by,

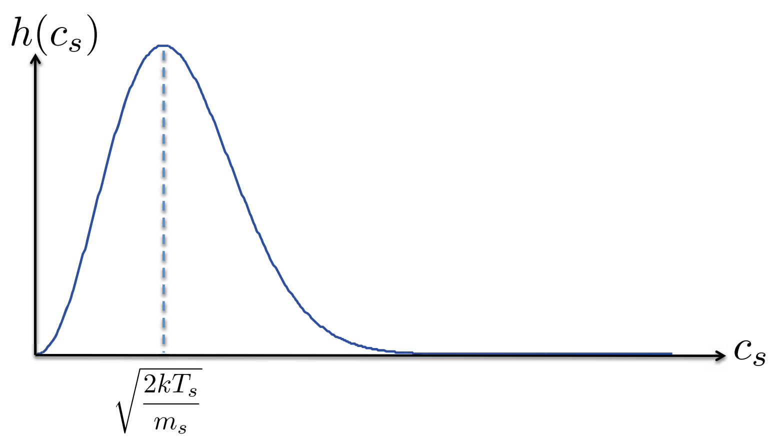
$$h(c_s)dc_s \;\equiv\; f(c_s)d^3c_s \;=\; f(c_s)4\pi c_s^2 dc_s \quad \rightarrow \quad h \;=\; 4\pi c_s^2 f$$

or

$$h(c_s) \;=\; 4\pi c_s^2 n_s \left(\frac{m_s}{2\pi kT_s}\right)^{\frac{3}{2}} e^{-\frac{mc_s^2}{2kT_s}}$$

The most probable velocity magnitude follows from,

$$\frac{d\ln h}{dc_s} \;=\; \frac{2}{c_s} - \frac{mc_s}{kT_s} \;=\; 0 \qquad \boxed{(c_s)_{\text{most probable}} \;=\; \sqrt{2\frac{kT_s}{m_s}}}$$



The other (related) definition is when particles are grouped by energies

$$E \;=\; \frac{mc_s^2}{2} \quad \rightarrow \quad c_s \;=\; \sqrt{\frac{2E}{m_s}} \quad \text{and} \quad dc_s \;=\; \frac{dE}{\sqrt{2m_sE}}$$

In this case,

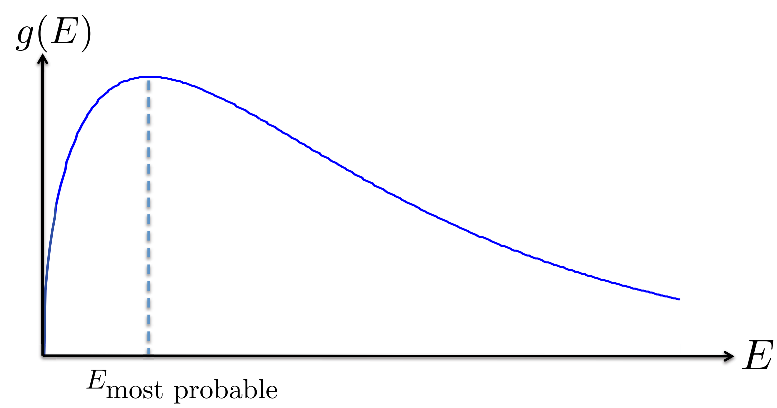
$$g(E)dE \;\equiv\; fd^3c_s \;=\; f4\pi c_s^2 dc_s \;=\; f\frac{4\sqrt{2}\pi}{m^{3/2}}E^{\frac{1}{2}}dE$$

and so,

$$g(E) \;=\; \frac{4\sqrt{2}\pi}{m^{3/2}}E^{\frac{1}{2}}f(E)$$

and for a Maxwellian,

$$f(E) \;=\; n_s\left(\frac{m_s}{2\pi kT_s}\right)^{\frac{3}{2}} e^{-\frac{E}{kT_s}}$$



we obtain,

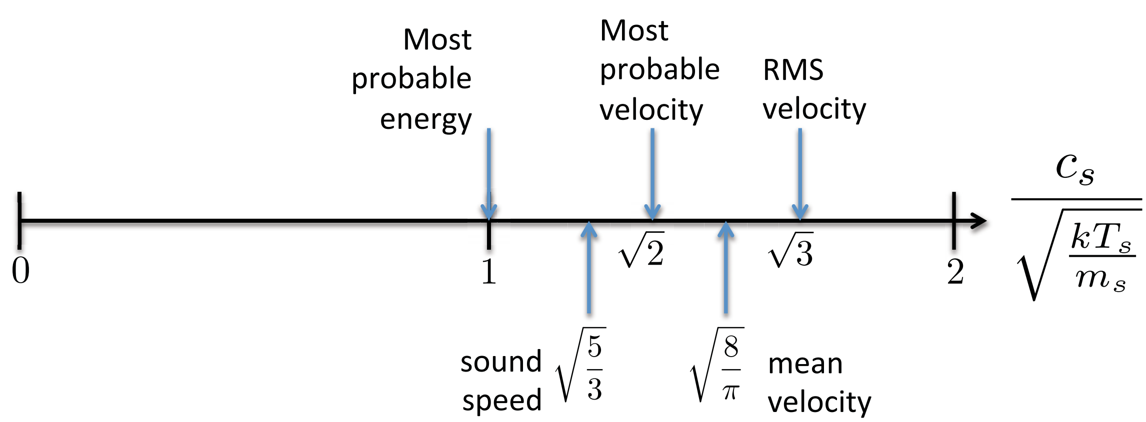
$$\boxed{g(E) \;=\; \frac{2n_s}{\sqrt{\pi}}\frac{E^{\frac{1}{2}}}{(kT_s)^{\frac{3}{2}}}e^{-\frac{E}{kT_s}}}$$

The most probable energy follows from,

$$\frac{d\ln g}{dE} \;=\; \frac{1}{2E} - \frac{1}{kT_s} \;=\; 0 \qquad \boxed{E_{\text{most prob.}} \;=\; \frac{kT_s}{2}} \quad , \quad \boxed{(c_s)_{\text{most prob. energy}} \;=\; \sqrt{\frac{kT_s}{m_s}}}$$

All these velocities are comparable to the speed of sound,

$$c_{\text{sound}} \;=\; \sqrt{\gamma\frac{kT_s}{m_s}} \;=\; \sqrt{\frac{5}{3}\frac{kT_s}{m_s}} \qquad \text{(for a monoatomic gas)}$$



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