5 Transport phenomena

Gas not in equilibrium => distribution fct. different from Maxwell-Boltzmann distribution

temperature, density, and average velocity are not constant throughout the gas

Reaching equilibrium implies: transport of energy, mass, and momentum from one part of the gas to another

Average distance over which molecular properties can be transported in one collision is the mean free path.

Mean free path : average distance traveled by an atom / molecule between successive collisions.

Solve Boltzmann transport equation for some initial conditions $\Rightarrow$ $\underbrace{f(\vec{r}, \vec{p}, t) \text{ as a fct. of time}}_{\text{in general non-trivial}}$

Some dynamical quantities are rigorously conserved. We will look at mass, momentum, and energy.

see text (not in notes)

↳ get three conservation theorems

↳ the idea is that some equations related to the conservation theorems are easier to solve than the Boltzmann transport equation

Collision taking place at $\vec{r}$:

$$\{\vec{p}_1, \vec{p}_2\} \longrightarrow \{\vec{p}_1{}', \vec{p}_2{}'\}$$

Let χ be a quantity with the following property:

$$\boxed{\chi(\vec{r}_1, \vec{p}_1) + \chi(\vec{r}_2, \vec{p}_2) = \chi(\vec{r}_1{}', \vec{p}_1{}') + \chi(\vec{r}_2{}', \vec{p}_2{}')}$$

χ: "conserved property"

↳ like mass, energy, ...

It can be shown : $\boxed{\int \chi(\vec{r}, \vec{p}) \left(\frac{\partial f(\vec{r}, \vec{p}, t)}{\partial t}\right)_{coll} d^3\vec{p} = 0}$

See pages 308a - 308c

So, we can multiply both sides of the Boltzmann transport equation by χ and then integrate over $d^3\vec{p}$:

$$\Rightarrow \frac{\partial}{\partial t} \int \chi f \, d^3\vec{p} + \sum_i \frac{\partial}{\partial x_i} \int \chi \overset{v_i}{\frac{p_i}{m}} f \, d^3\vec{p} - \sum_i \int \frac{\partial \chi}{\partial x_i} \overset{v_i}{\frac{p_i}{m}} f \, d^3\vec{p}$$

$$+ \underbrace{\sum_i \int \frac{\partial}{\partial p_i}(\chi F_i f) \, d^3\vec{p}}_{\substack{\to 0 \text{ provided} \\ f(\vec{r}, \vec{p}, t) \to 0 \text{ as } |\vec{p}| \to \infty}} - \sum_i \int \frac{\partial \chi}{\partial p_i} F_i f \, d^3\vec{p} - \sum_i \int \chi \frac{\partial F_i}{\partial p_i} f \, d^3\vec{p}$$

$$= 0$$

A bit more detail on last eq. of page 308:

We start with: $\left(\frac{\partial}{\partial t} + \frac{1}{m}\vec{p}\cdot\vec{\nabla}_r + \vec{F}\cdot\vec{\nabla}_{\vec{p}}\right) f(\vec{r},\vec{p},t) = \left(\frac{\partial f(\vec{r},\vec{p},t)}{\partial t}\right)_{coll}$

Multiply by χ:

$$\chi\frac{\partial}{\partial t} f + \frac{1}{m}\chi\,\vec{p}\cdot\vec{\nabla}_r f + \chi\vec{F}\cdot\vec{\nabla}_p f = \chi\left(\frac{\partial f(\vec{r},\vec{p},t)}{\partial t}\right)_{coll}$$

Integrate over $d^3\vec{p}$:

using that χ is conserved

$$\underbrace{\int \chi \frac{\partial}{\partial t} f\, d^3\vec{p}} + \frac{1}{m}\int \chi\,\vec{p}\cdot\vec{\nabla}_r f\, d^3\vec{p} + \int \chi\,\vec{F}\cdot\vec{\nabla}_{\vec{p}} f\, d^3\vec{p} = 0$$

χ is indep. of time

$$\Rightarrow\ = \frac{\partial}{\partial t}\int \chi f\, d^3\vec{p}$$

$$= \frac{1}{m}\int \sum_{i=1,2,3} \chi\, p_i \frac{\partial}{\partial x_i} f\, d^3 p$$

chain rule

$$= \frac{1}{m}\sum_i \frac{\partial}{\partial x_i}\int \chi\, p_i f\, d^3 p$$

$$- \frac{1}{m}\int \frac{\partial \chi}{\partial x_i} p_i f\, d^3 p$$

$$- \frac{1}{m}\int \chi \underbrace{\frac{\partial p_i}{\partial x_i}}_{=0} f\, d^3 p$$

$$\int \chi \sum_i F_i \frac{\partial}{\partial p_i} f\, d^3\vec{p}$$

$$= \sum_i \int \frac{\partial}{\partial p_i}\left(F_i \chi f\right) d^3\vec{p}$$

$$- \sum_i \int \frac{\partial F_i}{\partial p_i} \chi f\, d^3\vec{p}$$

$$- \sum_i \int F_i \frac{\partial \chi}{\partial p_i} f\, d^3\vec{p}$$

Recall:

Boltzmann transport equation

$$\left(\frac{\partial}{\partial t} + \frac{1}{m}\vec{p}\cdot\vec{\nabla}_{\vec{r}} + \vec{F}\cdot\vec{\nabla}_{\vec{p}}\right) f(\vec{r},\vec{p},t) = \left(\frac{\partial f}{\partial t}\right)_{coll}$$

$$\left(\frac{\partial f}{\partial t}\right)_{coll} = \int \delta(\vec{P}' - \vec{P})\,\delta(E-E')\,|T_{fi}|^2$$

$$\left[f(\vec{r},\vec{p}_1',t)\,f(\vec{r},\vec{p}_2',t) - f(\vec{r},\vec{p},t)\,f(\vec{r},\vec{p}_2,t)\right] d^3\vec{p}_2\, d^3\vec{p}_1'\, d^3\vec{p}_2'$$

Let's look at an example:

$$\chi(\vec{r},\vec{p}) = \frac{\vec{p}^{\,2}}{2m}$$

So: $\chi(\vec{r}_1,\vec{p}_1) = \frac{\vec{p}_1^{\,2}}{2m}$

$$\chi(\vec{r}_2,\vec{p}_2) = \frac{\vec{p}_2^{\,2}}{2m}$$

$$\chi(\vec{r}_1',\vec{p}_1') = \frac{\vec{p}_1^{\,\prime 2}}{2m}$$

$$\chi(\vec{r}_2',\vec{p}_2') = \frac{\vec{p}_2^{\,\prime 2}}{2m}$$

Want to show: $\int \chi(\vec{r},\vec{p}) \left(\frac{\partial f(\vec{r},\vec{p},t)}{\partial t}\right)_{coll} d^3\vec{p} = 0$

Let's write it out:

$$\int \chi(\vec{r},\vec{p}_1)\left(\frac{\partial f(\vec{r},\vec{p}_1,t)}{\partial t}\right)_{coll} d^3\vec{p}_1$$

← I'm now using $\vec{p}_1$ to make the Eq. more symmetric

$$= \int \chi(\vec{r},\vec{p}_1)\,\delta(\vec{P}'-\vec{P})\,\delta(E-E')\,|T_{fi}|^2$$

$$\left[f(\vec{r},\vec{p}_1{}',t)f(\vec{r},\vec{p}_2{}',t) - f(\vec{r},\vec{p}_1,t)f(\vec{r},\vec{p}_2,t)\right]d^3\vec{p}_1\,d^3\vec{p}_2\,d^3\vec{p}_1{}'\,d^3\vec{p}_2{}'$$

$\vec{p}_1$ and $\vec{p}_2$ are "fully symmetric" in all green underlined terms → since we are integrating over all momentum coordinates, we can replace $\chi(\vec{r},\vec{p}_1)$ by $\underbrace{\frac{1}{2}\chi(\vec{r},\vec{p}_1)+\frac{1}{2}\chi(\vec{r},\vec{p}_2)}$

this does not change the integrand

note: E depends on $\vec{p}_1$ and $\vec{p}_2$

I'm only concerned about $\vec{p}$-dep.

$$= \frac{1}{2}\int\left(\chi(\vec{r},\vec{p}_1)+\chi(\vec{r},\vec{p}_2)\right)\delta(\vec{P}'-\vec{P})\,\delta(E-E')\,|T_{fi}|^2$$

$$\left[f(\vec{r},\vec{p}_1{}',t)f(\vec{r},\vec{p}_2{}',t) - f(\vec{r},\vec{p}_1,t)f(\vec{r},\vec{p}_2,t)\right]d^3\vec{p}_1\,d^3\vec{p}_2\,d^3\vec{p}_1{}'\,d^3\vec{p}_2{}'$$

we also see that $\vec{p}_1{}'$ and $\vec{p}_2{}'$ are fully symmetric in the green underlined terms

Moreover: the two orange underlined terms have opposite sign

To break $\frac{1}{2}(\chi(\vec{r},\vec{p}_1)+\chi(\vec{r},\vec{p}_2))$ up into four pieces (two four unprimed and two for primed coordinates), we need a minus sign

$$= \frac{1}{4}\int \left[\chi(\vec{r},\vec{p}_1)+\chi(\vec{r},\vec{p}_2)-\chi(\vec{r},\vec{p}_1{}')-\chi(\vec{r},\vec{p}_2{}')\right]\delta(\underline{P}'-\underline{P})\delta(E-E')$$

$$|T_{fi}|^2\left[f(\vec{r},\vec{p}_1{}',t)f(\vec{r},\vec{p}_2{}',t)-f(\vec{r},\vec{p}_1,t)f(\vec{r},\vec{p}_2,t)\right]d^3\vec{p}_1\,d^3\vec{p}_2\,d^3\vec{p}_1{}'\,d^3\vec{p}_2{}'$$

We should also change the variables in f-fcts. -> only gives $(-1)^4$ factor

by our assumption, the term in the orange circle is equal to zero!

$$=0$$

So: if $\chi(\vec{r},\vec{p}_1)+\chi(\vec{r},\vec{p}_2)$ are conserved,

then $\int \chi(\vec{r},\vec{p})\left(\frac{\partial f(\vec{r},\vec{p},t)}{\partial t}\right)_{coll} d^3\vec{p} = 0$

Let's define:
$$\langle A\rangle = \frac{\int A f\, d^3p}{\int f\, d^3p} = \frac{1}{n}\int A f\, d^3\vec{p}$$

$f = f(\vec{r}, \vec{p}, t)$

$$n(\vec{r},t) = \int f(\vec{r},\vec{p},t)\, d^3\vec{p}$$

With this notation, we have

$$\boxed{\frac{\partial}{\partial t}\langle n\chi\rangle + \sum_i \frac{\partial}{\partial x_i}\langle n v_i \chi\rangle - \sum_i n\left\langle v_i \frac{\partial \chi}{\partial x_i}\right\rangle - \frac{n}{m}\sum_i\left\langle F_i \frac{\partial\chi}{\partial v_i}\right\rangle - \underbrace{\frac{n}{m}\sum_i\left\langle\frac{\partial F_i}{\partial v_i}\chi\right\rangle}_{\to 0 \text{ for velocity-indep. external force}} = 0}$$

Conservation theorem

Let $\chi = m$:

m is constant (pull out of integral) → only the first two terms contribute

$$\frac{\partial}{\partial t}(m\,n) + \sum_i \frac{\partial}{\partial x_i}\langle m\, n\, v_i\rangle = 0$$

or: $\rho(\vec{r},t) = m\, n(\vec{r},t) \mathrel{\hat{=}}$ mass density

$$\Rightarrow \boxed{\frac{\partial \rho(\vec{r},t)}{\partial t} + \vec{\nabla}\cdot\big(\rho(\vec{r},t)\,\vec{u}(\vec{r},t)\big) = 0}$$

continuity eq. for the mass

where $\vec{u}(\vec{r},t) = \langle\vec{v}\rangle$

Note: If we use $\chi = 1$, we get a very similar result:

$$\frac{\partial n(\vec{r},t)}{\partial t} + \underbrace{\vec{\nabla}_{\vec{r}} \cdot \langle n\vec{v} \rangle}_{\vec{\nabla}_{\vec{r}} \cdot \underbrace{\int \vec{v}\, f(\vec{r},\vec{p},t)\, d^3\vec{p}}_{\text{this is sometimes called particle current } \vec{j}_N(\vec{r},t)}} = 0$$

Let $\chi = \varepsilon(\vec{p}) = \frac{\vec{p}^{\,2}}{2m}$:

assuming: no external force

$$\frac{\partial}{\partial t} \langle n \underbrace{\frac{\vec{p}^2}{2m}}_{\varepsilon(\vec{p})} \rangle + \vec{\nabla}_{\vec{r}} \cdot \langle n \vec{v} \underbrace{\frac{\vec{p}^2}{2m}}_{\varepsilon(\vec{p})} \rangle = 0$$

$$\partial \frac{\varepsilon(\vec{p})}{\partial t} + \vec{\nabla}_{\vec{r}} \cdot \underbrace{\int \vec{v}\, f(\vec{r},\vec{p},t)\, \varepsilon(\vec{p})\, d^3\vec{p}}_{\text{this is sometimes called energy current } \vec{j}_E} = 0$$

$$\partial \frac{\varepsilon(\vec{p})}{\partial t} + \vec{\nabla}_{\vec{r}} \cdot \vec{j}_E = 0$$

Note : a more comprehensive analysis will look at

$$K = \frac{1}{2} m \left| \vec{v} - \langle \vec{v} \rangle \right|^2$$

See text pages 98 - 100.