Mathematical Relations

1. Integrals

- $\int_{-\infty}^{\infty} e^{-\alpha x^2}\,\mathrm{d}x = \sqrt{\frac{\pi}{\alpha}}$
- $\int_{-\infty}^{\infty} x^{2n} e^{-\alpha x^2}\,\mathrm{d}x = \frac{(2n)!}{n!2^{2n}}\sqrt{\frac{\pi}{\alpha^{2n+1}}}$. Obtained by differentiating both sides of the equation with respect to α a number of times.
- $\int_{-\infty}^{\infty} x^{2n+1} e^{-\alpha x^2}\,\mathrm{d}x = 0$ and $\int_{0}^{\infty} x^{2n+1} e^{-\alpha x^2}\,\mathrm{d}x = \frac{n!}{2\alpha^{n+1}}$
- $n! = \int_0^\infty x^n e^{-x}\,\mathrm{d}x$ and $\Gamma(n) = \int_0^\infty x^{n-1}e^{-x} = (n-1)!$ for integer n.

2. Approximations

- $\ln n! \approx n\ln n - n$ (Sitrling's Approximation)

3. Series

- Geometric progressions – $a\sum_{n=0}^{N-1} r^n = \frac{a(1-r^N)}{1-r}$
- Arithmetic progressions – $\sum_{n=1}^{n} a_1 + (n-1)d = \frac{n\left(a_1 + a_n\right)}{2} = \frac{n\left[2a_1 + (n-1)d\right]}{2}$
- Taylor Series
  - $\left(1+x\right)^n = 1 + nx + \frac{n(n-1)}{2!}x^2 + \frac{n(n-1)(n-2)}{3!}x^3 + \cdots$
  - $\sin x = x - \frac{x^3}{3!} + \frac{x^5}{5!} + \cdots$
  - $\cos x = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \cdots$
  - $\tan x = x + \frac{x^3}{3!} + \frac{2x^5}{15} + \cdots$
  - $\ln\left(1+x\right) = x - \frac{x^2}{2} + \frac{x^3}{3} + \cdots$

  - $\sinh(x) = x - \frac{x^3}{6} + \frac{x^5}{120} + \cdots$
  - $\cosh(x) = 1 + \frac{x^2}{2} + \frac{x^4}{24} + \cdots$
  - $\tanh(x) = x - \frac{x^3}{3} + \frac{2x^5}{15} + \cdots$
  - $\operatorname{sech}(x) = 1 - \frac{x^2}{2} + \frac{5x^4}{24} + \cdots$
  - $\operatorname{cosech}(x) = x^{-1} - \frac{x}{6} + \frac{7x^3}{360} + \cdots$
  - $\coth(x) = x^{-1} + \frac{x}{3} - \frac{x^3}{45} + \cdots$
- $\left[1 - (x / N)\right]^N = e^{-x}$, when N is very large.

4. Miscellaneous

- The volume of a hypersphere radius r in D-dimensions is

$$V_D = \frac{2\pi^{D/2} r^D}{\Gamma(\frac{1}{2} D + 1)}$$

Useful Thermodynamics Results

1. Microcanonical distribution

- $\omega(E)$ = Number of states with $\varepsilon < E$
- $\Omega(E) = \omega'(E)$ = Number of states with energy E
- $S = k \ln \Omega$
- $T = \left(\partial S / \partial E\right)^{-1}$
- $C = \left(\partial U / \partial T\right)_V$

2. Canonical distribution

- Z is the sum over all energies of $e^{-\beta E}$.
- The variance $\left\langle E^2 \right\rangle - \left\langle E \right\rangle^2 = \partial^2 \ln Z / \partial \beta^2$
- Define $Z = e^{-\beta F(\beta)}$ – F is the **Helmholtz Free Energy**.
- Quantities of interest
    - $U = -\partial \ln Z / \partial \beta$
    - $F = -k_B T \ln Z$
    - $S = -(\partial F / \partial T)_V$
    - $p = -(\partial F / \partial V)_T$
    - $H = U + pV$
    - $G = F + pV = H - TS$
    - $C_V = (\partial U / \partial T)_V$

3. Grand Canonical distribution

- The chemical potential is the amount of energy each new particle brings to the system – in other words

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} = \left(\frac{\partial F}{\partial N}\right)_{V,T} = \left(\frac{\partial G}{\partial N}\right)_{p,T}$$

- For two systems in thermal equilibrium, T must be the same. For two systems in particle-exchange equilibrium, μ must be the same.
- We define the grand potential by $Z_{\text{grand}} = e^{-\beta \Phi_G}$

- We then have the following relations
    - $S = -(\partial \Phi_G / \partial T)_{V,\mu}$
    - $p = -(\partial \Phi_G / \partial V)_{T,\mu}$
    - $N = -(\partial \Phi_G / \partial \mu)_{T,V}$

3. Maxwell Relations

$$\begin{aligned}\left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial p}{\partial S}\right)_V \\ \left(\frac{\partial T}{\partial p}\right)_S &= +\left(\frac{\partial V}{\partial S}\right)_p \\ \left(\frac{\partial S}{\partial V}\right)_T &= +\left(\frac{\partial p}{\partial T}\right)_V \\ -\left(\frac{\partial S}{\partial p}\right)_T &= \left(\frac{\partial V}{\partial T}\right)_p\end{aligned}$$

Kinetic Theory ~ The Boltzmann Equation

1. Basics

- Assumptions
  - Low density and high temperature → molecules can be considered as localised wavepackets. Requires de Broglie wavelength to be much smaller than inter-particle separation

$$\frac{\hbar}{\sqrt{2mkT}} \ll \sqrt[3]{\frac{V}{N}}$$

  - Molecules are distinguishable
  - Walls of the container are idealised surfaces.
- We define the **distribution function** f

$$\boxed{\begin{array}{l}\text{N}^\text{o}\text{ of molecules at } t \text{ with} \\ \text{position lying within } \mathrm{d}^3r \text{ about } \boldsymbol{r} \\ \text{and velocity within } \mathrm{d}^3v \text{ about } \boldsymbol{v}\end{array} = f\left(\boldsymbol{r},\boldsymbol{v},t\right)\mathrm{d}^3r\,\mathrm{d}^3v}$$

Notes

  - d^3r and d^3v large enough to contain a very large number of molecules, but small enough to be points macroscopically.
  - If there are N molecules in volume V

$$\int f(\boldsymbol{r},\boldsymbol{v},t)\,\mathrm{d}^3r\,\mathrm{d}^3v = N \qquad \int f(\boldsymbol{r},\boldsymbol{v},t)\,\mathrm{d}^3v = N\,/\,V$$

The second integral assumes the molecules are uniformly distributed through space (f does not depend on $\boldsymbol{r}$).

  - We call the 6-dimensional space of $\boldsymbol{r}$ and $\boldsymbol{v}$ μ-space.
- Our aim is to find f. As $t \to \infty$, f would then contain all the equilibrium properties of the system.

2. Finding an Equation of Motion for *f*

- Molecules continuously enter and leave a given volume element of μ-space, so f continuously changes with time.

- This happens because of **collisions** and because of any **external force** that might be acting on the system.
- Consider force the effect of the external force $\boldsymbol{F}$ only
    - A molecule with coordinates $\left(\boldsymbol{r}, \boldsymbol{v}\right)$ at t will have coordinates $\left(\boldsymbol{r} + \boldsymbol{v}\,\delta t, \boldsymbol{v} + (\boldsymbol{F} / m)\delta t\right)$ at the instant $t + \delta t$.
    - We therefore have that
    $$f\left(\boldsymbol{r} + \boldsymbol{v}\delta t, \boldsymbol{v} + \frac{\boldsymbol{F}}{m}\delta t, t + \delta t\right)\mathrm{d}^3 r\,\mathrm{d}^3 v = f\left(\boldsymbol{r}, \boldsymbol{v}, t\right)\mathrm{d}^3 r'\,\mathrm{d}^3 v'$$
    - Furthermore, by Liouville's Theorem, $\mathrm{d}^3 r\,\mathrm{d}^3 v = \mathrm{d}^3 r'\,\mathrm{d}^3 v'$.
    - As such
    $$f\left(\boldsymbol{r} + \boldsymbol{v}\delta t, \boldsymbol{v} + \frac{\boldsymbol{F}}{m}\delta t, t + \delta t\right) = f\left(\boldsymbol{r}, \boldsymbol{v}, t\right)$$
- If we are to also take collisions into account, we get
$$f\left(\boldsymbol{r} + \boldsymbol{v}\delta t, \boldsymbol{v} + \frac{\boldsymbol{F}}{m}\delta t, t + \delta t\right) = f\left(\boldsymbol{r}, \boldsymbol{v}, t\right) + \left(\frac{\partial f}{\partial t}\right)_{\text{coll}}\delta t$$
- Expanding the LHS to first order in δt, we get
$$\boxed{\left(\frac{\partial}{\partial t} + \boldsymbol{v}\cdot\nabla_{\boldsymbol{r}} + \frac{\boldsymbol{F}}{m}\cdot\nabla_{\boldsymbol{v}}\right)f\left(\boldsymbol{r}, \boldsymbol{v}, t\right) = \left(\frac{\partial f}{\partial t}\right)_{\text{coll}}}$$

3. Collisions – finding $\left(\partial f / \partial t\right)_{coll}$

- The collision term above is given by
$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll}}\delta t = \left(R_{\text{in}} - R_{\text{out}}\right)\delta t$$

  Where
    - $R_{\text{in}}\,\delta t\,\mathrm{d}^3 r\,\mathrm{d}^3 v$ = **number of collisions** occurring during $t \to t + \delta t$ in which one of the **final** molecules is in $\mathrm{d}^3 r\,\mathrm{d}^3 v$ about $(\boldsymbol{r}, \boldsymbol{v})$.
    - $R_{\text{out}}\,\delta t\,\mathrm{d}^3 r\,\mathrm{d}^3 v$ = **number of collisions** occurring during $t \to t + \delta t$ in which one of the **initial** molecules is in $\mathrm{d}^3 r\,\mathrm{d}^3 v$ about $(\boldsymbol{r}, \boldsymbol{v})$.

  The assumptions involved in this expression are
    - We assume that *any* collision involving a molecule in the volume will remove it from the volume.

  - In each case, we are assuming that only *one* of the molecules in each collision qualifies in either category.
- The next step in our journey is to analyse **binary collisions**, in which two molecules collide
  - Let velocities of incoming molecules be $\boldsymbol{v}_1, \boldsymbol{v}_2$ and that of the outgoing molecules $\boldsymbol{v}_1', \boldsymbol{v}_2'$. Further define

    $$\boldsymbol{V} = \tfrac{1}{2}\left(\boldsymbol{v}_1 + \boldsymbol{v}_2\right)$$
    $$\boldsymbol{u} = \boldsymbol{v}_2 - \boldsymbol{v}_1$$

    $\boldsymbol{V}$ is the centre-of-mass motion, and $\boldsymbol{u}$ is the relative motion. It is also clear that

    $$\mathrm{d}\,\boldsymbol{V}\mathrm{d}\boldsymbol{u} = \mathrm{d}\boldsymbol{v}_1\mathrm{d}\boldsymbol{v}_2$$
  - Conservation of momentum and energy requires that

    $$\boldsymbol{v}_1 + \boldsymbol{v}_2 = \boldsymbol{v}_1' + \boldsymbol{v}_2'$$
    $$\left|\boldsymbol{v}_1\right|^2 + \left|\boldsymbol{v}_2\right|^2 = \left|\boldsymbol{v}_1'\right|^2 + \left|\boldsymbol{v}_2'\right|^2$$

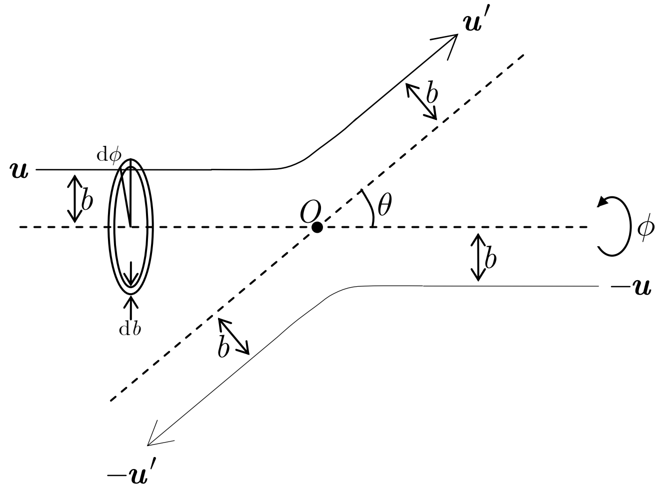
    Which gives

    $$\boldsymbol{V} = \boldsymbol{V}'$$
    $$\left|\boldsymbol{u}\right| = \left|\boldsymbol{u}'\right|$$

    As such, the collision can be reduced to a simple **rotation** of the vector $\boldsymbol{u}$. This means that

    $$\mathrm{d}\,\boldsymbol{V}\mathrm{d}\boldsymbol{u} = \mathrm{d}\,\boldsymbol{V}'\mathrm{d}\boldsymbol{u}'$$
  - Combining our two differential expressions, we get a fact that will be useful later:

    $$\mathrm{d}\boldsymbol{v}_1\mathrm{d}\boldsymbol{v}_2 = \mathrm{d}\boldsymbol{v}_1'\mathrm{d}\boldsymbol{v}_2'$$
  - We move to a frame in which $\boldsymbol{V} = 0$ (the **centre-of-mass frame**). The collision then looks as follows:



The effect of the collision is specified by θ and ϕ – describing the rotation of the vector $\boldsymbol{u}$ – which are collectively denoted by the solid angle Ω. b is called the **impact parameter**.

- It is clear that $\boldsymbol{v}_1$ and $\boldsymbol{v}_2$ do not uniquely define the collision because of possibly different impact parameters. In fact, given initial velocities specify a *class* of collisions, with all possible impact parameters. This can be thought of as a beam of particles velocity $\boldsymbol{u}$, uniformly spread out in space incident on O. We define the **incident flux**, I, as

$$I = \begin{array}{c}\text{Number of particles in beam crossing}\\ \text{unit area normal to the beam in 1 sec}\end{array}$$

- We then define, for the collision, the **differential cross section** $\sigma(\boldsymbol{v}_1, \boldsymbol{v}_2 \mid \boldsymbol{v}_1', \boldsymbol{v}_2') \equiv \sigma(\Omega)$, such that

$$I\sigma(\Omega)\,\mathrm{d}\Omega = \begin{array}{c}\text{Number of molecules deflected per sec into}\\ \text{direction lying within solid angle element } \mathrm{d}\Omega\end{array}$$

From the diagram above, it is clearly true that this number is also equal to $Ib\,\mathrm{d}b\,\mathrm{d}\phi$, and so

Number of molecules deflected per sec into direction lying within solid angle element $\mathrm{d}\Omega$	=	Number of molecules crossing area $\sigma(\Omega)\,\mathrm{d}\Omega$ per sec in incident beam

And the *total cross section* is

$$\sigma_{\text{tot}} = \int \sigma(\Omega)\,\mathrm{d}\Omega$$

    Both $\sigma(\Omega)$ and σ_{tot} can depend on $\boldsymbol{u}$.
  - The detailed form of σ depends on the potential, but we can derive some useful symmetry properties
    - Time reversal invariance
      $$\sigma(\boldsymbol{v}_1, \boldsymbol{v}_2 \mid \boldsymbol{v}_1', \boldsymbol{v}_2') = \sigma\left(-\boldsymbol{v}_1', -\boldsymbol{v}_2' \mid -\boldsymbol{v}_1, -\boldsymbol{v}_2\right)$$
    - Invariance under rotation and reflection
      $$\sigma(\boldsymbol{v}_1^*, \boldsymbol{v}_1^* \mid \boldsymbol{v}_1'^*, \boldsymbol{v}_2'^*) = \sigma(\boldsymbol{v}_1, \boldsymbol{v}_2 \mid \boldsymbol{v}_1', \boldsymbol{v}_2')$$
      Where * represents a combination of rotations and/or reflections.
    - Inverse collisions
      $$\sigma(\boldsymbol{v}_1, \boldsymbol{v}_2 \mid \boldsymbol{v}_1', \boldsymbol{v}_2') = \sigma(\boldsymbol{v}_1', \boldsymbol{v}_2' \mid \boldsymbol{v}_1, \boldsymbol{v}_2)$$
      This can be proved by noting that the inverse collision can be obtained from the original collision by a rotation followed by a reflection. [This is only true for quantum particles, though, which are completely defined by their position and total momentum].
- We're now ready to find R_{in} and R_{out}. The assumptions we will be doing this under are
  - Only binary collisions are taken into account [acceptable if gas is dilute].
  - The walls of the container are ignored [justified later].
  - The effect of external forces on σ is ignored.
  - The velocity of a molecule is uncorrelated with its position – this is the **assumption of molecular chaos** – and it allows us to states that in the spatial region $\mathrm{d}^3 r$, the number of pairs of molecules with respective velocities in $\mathrm{d}^3 v_1$ and $\mathrm{d}^3 v_2$ is
    $$\left[f\left(\boldsymbol{r}, \boldsymbol{v}_1, t\right)\mathrm{d}^3 r\, \mathrm{d}^3 v_1\right]\left[f\left(\boldsymbol{r}, \boldsymbol{v}_2, t\right)\mathrm{d}^3 r\, \mathrm{d}^3 v_2\right]$$
    [This is clearly a *possible* condition for the gas, but it is unclear whether it is the *general* condition – see later].

- A final point to bear in mind – we will *only* be considering molecules that are *already* in the region $\boldsymbol{r}$, and considering their changes in $\boldsymbol{v}$. This is justifiable if the time period under consideration is small enough.
- First, let's do R_{out}
    - Consider a given molecule in our region of μ–space. Let it have velocity $\boldsymbol{v}_1$ and position $\boldsymbol{r}$.
    - In the same spatial volume, *any* molecule of *any* velocity $\boldsymbol{v}_2$ poses an incident beam of molecules on the first molecule. The flux is given by

$$I = \left[f(\boldsymbol{r}, \boldsymbol{v}_2, t)\,\mathrm{d}^3 v_2\right]\left|\boldsymbol{v}_1 - \boldsymbol{v}_2\right|$$

    - The total number of collisions that will occur with this molecule in a time δt is then

$$I\sigma_{\text{tot}} = \left[f(\boldsymbol{r}, \boldsymbol{v}_2, t)\,\mathrm{d}^3 v_2\right]\left|\boldsymbol{v}_1 - \boldsymbol{v}_2\right| \int \sigma(\Omega)\,\mathrm{d}\Omega\,\delta t$$

    This is the total number of collisions of the form $\left\{\boldsymbol{v}_1, \boldsymbol{v}_2\right\} \rightarrow \text{other}$.

    - Finally, to get an expression for R_{out}, we integrate over all $\boldsymbol{v}_2$, and multiply by the original density of molecules in our region of μ–space

$$\boxed{R_{\text{out}} = f(\boldsymbol{r}, \boldsymbol{v}_1, \boldsymbol{t}) \iint f(\boldsymbol{r}, \boldsymbol{v}_2, t)\left|\boldsymbol{v}_1 - \boldsymbol{v}_2\right| \sigma(\Omega)\,\mathrm{d}^3 v_2\,\mathrm{d}\Omega}$$

- Next, we can find R_{in}
    - Consider *any* given molecule $\boldsymbol{v}_1'$ in $\boldsymbol{r}$, with a beam of molecules $\boldsymbol{v}_2'$ incident on it. The flux is

$$I = f\left(\boldsymbol{r}, \boldsymbol{v}_2', t\right)\mathrm{d}^3 v_2' \left|\boldsymbol{v}_1' - \boldsymbol{v}_2'\right|$$

    - The number of collisions within δt will therefore be

$$I\sigma_{\text{tot}}' = f\left(\boldsymbol{r}, \boldsymbol{v}_2', t\right)\mathrm{d}^3 v_2' \left|\boldsymbol{v}_1' - \boldsymbol{v}_2'\right| \int \sigma'(\Omega)\,\mathrm{d}\Omega\,\delta t$$

    - Integrating over all possible $\boldsymbol{v}_2'$ and multiplying by the density of $\boldsymbol{v}_1'$, we get the total number of collisions

$$f(\boldsymbol{r}, \boldsymbol{v}_1', t) \iint f\left(\boldsymbol{r}, \boldsymbol{v}_2', t\right)\left|\boldsymbol{v}_1' - \boldsymbol{v}_2'\right| \sigma'(\Omega)\,\mathrm{d}^3 v_2'\,\mathrm{d}\Omega\,\delta t$$

    This is the total number of collisions of the form $\left\{\boldsymbol{v}_1', \boldsymbol{v}_2'\right\} \rightarrow \text{other}$

    - However, the only collisions we are interested in are only those of the form $\left\{\boldsymbol{v}_1', \boldsymbol{v}_2'\right\} \rightarrow \left\{\boldsymbol{v}_1, \boldsymbol{v}_2\right\}$. This means that

    - $\left|\boldsymbol{v}_1' - \boldsymbol{v}_2'\right| = \left|\boldsymbol{v}_1 - \boldsymbol{v}_2\right|$
    - $\mathrm{d}^3 v_1 \mathrm{d}^3 v_2 = \mathrm{d}^3 v_1' \, \mathrm{d}^3 v_2'$
    - Fortuitously, these are precisely the inverse collisions to those of the form $\left\{\boldsymbol{v}_1, \boldsymbol{v}_2\right\} \to$ other we got when finding R_{out}. As such, $\sigma = \sigma'$.

This gives

$$\boxed{R_{\text{in}} = f(\boldsymbol{r}, \boldsymbol{v}_1', t) \iint f\left(\boldsymbol{r}, \boldsymbol{v}_2', t\right) \left|\boldsymbol{v}_1 - \boldsymbol{v}_2\right| \sigma(\Omega) \, \mathrm{d}^3 v_2 \, \mathrm{d}\Omega}$$

4. The Boltzmann Transport Equation

- Combining everything we have found so far, we obtain the **Boltzmann Transport Equation**

$$\boxed{\left(\frac{\partial}{\partial t} + \boldsymbol{v} \cdot \nabla_r + \frac{\boldsymbol{F}}{m} \cdot \nabla_v\right) f_1 = \iint \left(f_1' f_2' - f_1 f_2\right) \left|\boldsymbol{v}_1 - \boldsymbol{v}_2\right| \sigma(\Omega) \, \mathrm{d}^3 v_2 \, \mathrm{d}\Omega}$$

  Where

    - $\sigma(\Omega)$ is the differential cross section for $\left\{\boldsymbol{v}_1, \boldsymbol{v}_2\right\} \to \left\{\boldsymbol{v}_1', \boldsymbol{v}_2'\right\}$
    - $f_1 \equiv f\left(\boldsymbol{r}, \boldsymbol{v}_1, t\right)$
    - $f_2 = f\left(\boldsymbol{r}, \boldsymbol{v}_2, t\right)$
    - $f_1' = f\left(\boldsymbol{r}, \boldsymbol{v}_1', t\right)$
    - $f_2' = f\left(\boldsymbol{r}, \boldsymbol{v}_2', t\right)$

- If we had not used the *assumption of molecular chaos*, we would have obtained a series of N coupled differential equations relating an n-particle correlation function to an $(n + 1)$-particle correlation function. This is known as the Bogoliubov-Born-Green-Kirkwood-Yvon hierarchy.

Kinetic Theory ~ Equilibrium & The Boltzmann H-Theorem

1. Equilibrium

- An equilibrium distribution f_0 is a solution of the Boltzmann Transport Equation that is independent of time. We shall see that it is also the limiting form of the distribution function as $t \to \infty$.
- Assuming there is no external force, we can denote the equilibrium distribution $f_0(\boldsymbol{v}, t)$ and say that

  $$\frac{\partial}{\partial t} f(\boldsymbol{v}, t) = 0 \qquad \nabla_r \left(f_0\right) = 0$$

  Using the Boltzmann Transport Equation, therefore, we have that

  $$\iint \left[f_0(\boldsymbol{v}_1') f_0(\boldsymbol{v}_2') - f_0(\boldsymbol{v}_1) f_0(\boldsymbol{v}_2)\right] \left|\boldsymbol{v}_1 - \boldsymbol{v}_2\right| \sigma(\Omega)\, \mathrm{d}^3 v_2 \, \mathrm{d}\Omega = 0$$

  Where $\boldsymbol{v}_1$ is *any* given velocity.
- Clearly, a *sufficient* condition for this to happen is

  $$f_0(\boldsymbol{v}_1') f_0(\boldsymbol{v}_2') - f_0(\boldsymbol{v}_1) f_0(\boldsymbol{v}_2) = 0 \qquad (*)$$

  Where $\left\{\boldsymbol{v}_1, \boldsymbol{v}_2\right\} \to \left\{\boldsymbol{v}_1', \boldsymbol{v}_2'\right\}$ is *any* possible collision (ie: any collision with $\sigma \neq 0$).
- We show that this condition is also *necessary.* Consider

  $$\boxed{H(t) \equiv \int f(\boldsymbol{v}, t) \log f(\boldsymbol{v}, t)\, \mathrm{d}^3 v}$$

  Where $f(\boldsymbol{v}, t)$ is the distribution function at a time t satisfying

  $$\partial f / \partial t = \iint \left(f_1' f_2' - f_1 f_2\right) \left|\boldsymbol{v}_1 - \boldsymbol{v}_2\right| \sigma(\Omega)\, \mathrm{d}^3 v_2 \, \mathrm{d}\Omega$$

  Differentiating H, we get

  $$\frac{\partial H}{\partial t} = \int \frac{\partial f}{\partial t} \left[1 + \log f(\boldsymbol{v}, t)\right] \mathrm{d}^3 v$$

  As such, a **necessary condition** for $\partial f / \partial t = 0$ is $\partial H / \partial t = 0$. We then show, below, that $\partial H / \partial t = 0$ is the same statement as statement (*) above, and thus prove that it is *necessary.*
- This implies that $f_0(\boldsymbol{v})$ is **independent of** $\sigma(\Omega)$, provided that it is non-zero.

2. The Boltzmann H-Theorem

If f satisfies the Boltzmann Transport Equation, then $\partial H(t) / \partial t \leq 0$

- We showed above that

$$\frac{\partial H}{\partial t} = \int \frac{\partial f}{\partial t}\left[1 + \log f(\boldsymbol{v}, t)\right] \mathrm{d}^3 v$$

  Substituting the form of $\partial f / \partial t$ into this, we get

$$\frac{\partial H}{\partial t} = \iiint \left(f_1' f_2' - f_1 f_2\right)\left|\boldsymbol{v}_1 - \boldsymbol{v}_2\right| \sigma(\Omega)\left[1 + \log f_1\right] \mathrm{d}^3 v_1 \mathrm{d}^3 v_2 \, \mathrm{d}\Omega$$

- Now, interchanging $\boldsymbol{v}_1$ and $\boldsymbol{v}_2$ makes no difference to this integral, because σ is invariant to such changes. We can do this to obtain another expression for $\partial H / \partial t$.

$$\frac{\partial H}{\partial t} = \iiint \left(f_1' f_2' - f_1 f_2\right)\left|\boldsymbol{v}_1 - \boldsymbol{v}_2\right| \sigma(\Omega)\left[1 + \log f_2\right] \mathrm{d}^3 v_1 \mathrm{d}^3 v_2 \, \mathrm{d}\Omega$$

  Adding our two expressions and dividing by 2, we get

$$\frac{\partial H}{\partial t} = \frac{1}{2} \iiint \left(f_1' f_2' - f_1 f_2\right)\left|\boldsymbol{v}_1 - \boldsymbol{v}_2\right| \sigma(\Omega)\left[2 + \log f_1 f_2\right] \mathrm{d}^3 v_1 \mathrm{d}^3 v_2 \, \mathrm{d}\Omega$$

- This integral is invariant to the substitution $\left\{\boldsymbol{v}_1, \boldsymbol{v}_2\right\} \leftrightarrow \left\{\boldsymbol{v}_1', \boldsymbol{v}_2'\right\}$ because for every collision there exists an identical reverse collision. As such

$$\frac{\partial H}{\partial t} = \frac{1}{2} \iiint \left(f_1 f_2 - f_1' f_2'\right)\left|\boldsymbol{v}_1' - \boldsymbol{v}_2'\right| \sigma'(\Omega)\left[2 + \log f_1' f_2'\right] \mathrm{d}^3 v_1' \mathrm{d}^3 v_2' \, \mathrm{d}\Omega$$

  Noting that $\mathrm{d}v_1' \mathrm{d}v_2' = \mathrm{d}v_1 \mathrm{d}v_2$ and $\left|\boldsymbol{v}_1' - \boldsymbol{v}_2'\right| = \left|\boldsymbol{v}_1 - \boldsymbol{v}_2\right|$ and $\sigma' = \sigma$:

$$\frac{\partial H}{\partial t} = \frac{1}{2} \iiint \left(f_1 f_2 - f_1' f_2'\right)\left|\boldsymbol{v}_1 - \boldsymbol{v}_2\right| \sigma(\Omega)\left[2 + \log f_1' f_2'\right] \mathrm{d}^3 v_1 \mathrm{d}^3 v_2 \, \mathrm{d}\Omega$$

- Adding our two latest expressions for $\partial H / \partial t$ and dividing by 2

$$\boxed{\frac{\partial H}{\partial t} = \frac{1}{4} \iiint \left(f_1' f_2' - f_1 f_2\right)\left|\boldsymbol{v}_1 - \boldsymbol{v}_2\right| \sigma(\Omega)\left[\log f_1 f_2 - \log f_1' f_2'\right] \mathrm{d}^3 v_1 \mathrm{d}^3 v_2 \, \mathrm{d}\Omega}$$

- This integral is *never* positive, and so we have proved the theorem.
- As a corollary, we have shown that $\partial H / \partial t = 0$ only if (*) is true, as stated above.
- Note that at equilibrium (see next section) we obtain

$$H_0 = n\left\{\log\left[n\left(\frac{m}{2\pi kT}\right)^{3/2}\right] - \frac{3}{2}\right\}$$

Using the equation of state ($P = \frac{2}{3}n\varepsilon = nkT$), we get:

$$-kVH_0 = \tfrac{3}{2}Nk\log\left(PV^{5/3}\right) + \text{constant}$$

The RHS is the entropy of an ideal gas in thermodynamics. It follows, therefore, that if we define $H = -S / Vk$, the H-Theorem is simply the second law of Thermodynamics for an ideal gas.

3. The Maxwell-Boltzmann Distribution

- We have shown that the equilibrium distribution for our gas satisfies

$$f_0(\boldsymbol{v}_1')f_0(\boldsymbol{v}_2') - f_0(\boldsymbol{v}_1)f_0(\boldsymbol{v}_2) = 0$$
$$\ln f_0(\boldsymbol{v}_1) + \ln f_0(\boldsymbol{v}_2) = \ln f_0(\boldsymbol{v}_1') + \ln f_0(\boldsymbol{v}_2')$$

- This has the form of a conservation law – as such, if we find any quantity $\chi(\boldsymbol{v})$ such that $\chi(\boldsymbol{v}_1) + \chi(\boldsymbol{v}_2)$ is conserved in collisions, we have found a solution of this equation – namely

$$\log f_0(\boldsymbol{v}) = \chi(\boldsymbol{v})$$

  And the most general solution is a sum of all conserved quantities.

- For a free spinless particle conserved quantities are (1) energy (2) momentum in each dimension (3) a constant. As such

$$\log f_0(\boldsymbol{v}) = \alpha\boldsymbol{v}^2 + \boldsymbol{\beta}\boldsymbol{v} + \gamma$$
$$\log f_0(\boldsymbol{v}) = -A\left(\boldsymbol{v} - \boldsymbol{v}_0\right)^2 + \log C$$
$$f_0(\boldsymbol{v}) = C\exp\left(-A\left[\boldsymbol{v} - \boldsymbol{v}_0\right]^2\right)$$

  Where $\boldsymbol{v}_0$, C and A are five arbitrary constants.

- We now use a number of facts to find each constant
  - $\frac{N}{V} = \int f(\boldsymbol{v})\,\mathrm{d}^3v$ (from above) implies $C = \left(A / \pi\right)^{3/2} n$. Using our expression for A below, $\boxed{C = n\left(3m / 4\pi\varepsilon\right)^{3/2}}$.
  - The average velocity of any given molecule is given by $\left\langle \boldsymbol{v}\right\rangle = \int \boldsymbol{v}f_0(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v} \Big/ \int f_0(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v} = \boldsymbol{v}_0$. Thus, for a gas with no overall translational motion, we must have $\boxed{\boldsymbol{v}_0 = 0}$.

  - The average energy of any given molecule is given by $\left\langle \boldsymbol{v} \right\rangle = \int \frac{1}{2} m\boldsymbol{v}^2 f_0(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v} \Big/ \int f_0(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v} = 3m / 4A$, and so $\boxed{A = 3m / 4\varepsilon}$

- To calculate ε, we use the expression for pressure (calculated below) to find an equation of state:

$$P = 2n\varepsilon / 3$$

Experimentally, the equation of state is $P = nk_BT$, and so

$$\boxed{\varepsilon = 3k_BT / 2}$$

- As such

$$\boxed{f_0(\boldsymbol{v}) = n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{m(\boldsymbol{v}-\boldsymbol{v}_0)^2/2kT}}$$

This is the **Maxwell-Boltzmann distribution** for the probability

4. The Maxwell-Boltzmann Distribution – Useful Facts

- Individual distributions for each component of velocity can be calculated from the Boltzmann Distribution directly. We get

$$\boxed{g(v_x) = \sqrt{\frac{m}{2\pi k_BT}} e^{-mv_x^2/2k_BT}}$$

$$\left\langle v_x \right\rangle = 0$$

$$\left\langle \left| v_x \right| \right\rangle = 2\int_0^\infty v_x g(v_x)\,\mathrm{d}v_x = \sqrt{\frac{2k_BT}{\pi m}}$$

$$\left\langle v_x^2 \right\rangle = \int_{-\infty}^\infty v_x^2 g(v_x)\,\mathrm{d}v_x = \frac{k_BT}{m}$$

- For the full Maxwell-Boltzmann distribution

$$\boxed{f(v) = 4\pi v^2 g(v)}$$

$$\left\langle v \right\rangle = \sqrt{\frac{8k_BT}{\pi m}}$$

$$\left\langle v_x^2 \right\rangle + \left\langle v_y^2 \right\rangle + \left\langle v_z^2 \right\rangle = \left\langle v^2 \right\rangle = \frac{3k_BT}{m}$$

$$v_{\text{rms}} = \sqrt{\left\langle v^2 \right\rangle} = \sqrt{\frac{3k_BT}{m}}$$

5. Kinetic Theory Munched Up

- Number of molecules per volume with speeds $v \to v + \mathrm{d}v$ and at angles $\theta \to \theta + \mathrm{d}\theta$ is

$$n\ \overbrace{f(v)\,\mathrm{d}v}^{\text{Correct speed}}\ \overbrace{\tfrac{1}{2}\sin\theta\,\mathrm{d}\theta}^{\text{Correct orientation}}$$

The orientation comes from the fact that

$$\mathrm{d}\Omega = 2\pi\sin\theta\,\mathrm{d}\theta \Rightarrow \overbrace{\mathrm{d}\Omega\,/\,4\pi}^{\text{Fraction of total}} = \tfrac{1}{2}\sin\theta\,\mathrm{d}\theta$$

- The number of molecules hitting **unit area** of a wall in a time $\mathrm{d}t$ is equal to the number of molecules at a certain speed/direction multiplied by their velocities perpendicular to the wall $\mathrm{d}t$ [because lots of these molecules might make it in the interval $\mathrm{d}t$ – alternatively, because all molecules in a volume $v\cos\theta \times 1 \times 1$ will make it to the units area]. So it's given by

$$\overbrace{\int_0^\infty \mathrm{d}v}^{\substack{\text{Only those moving}\\ \textit{towards}\text{ the wall}}}\ \overbrace{\int_0^{\pi/2}\mathrm{d}\theta}^{\substack{\text{Since the solid}\\ \text{angle performs}\\ \text{a }2\pi\text{ rotation}\\ \text{round the }\perp\\ \text{axis anyway}}}\ v\cos\theta\, n\, f(v)\tfrac{1}{2}\sin\theta \qquad (*)$$

- As such, the pressure is equal to

$$\begin{aligned} P &= \int_0^\infty \mathrm{d}v \int_0^{\pi/2}\mathrm{d}\theta\ \overbrace{2mv\cos\theta}^{\substack{\text{Change of momentum}\\ \text{at each hit}}}\ v\cos\theta\, n\, f(v)\tfrac{1}{2}\sin\theta \\ &= \frac{1}{2}nm\left\langle v^2\right\rangle \end{aligned}$$

- Furthermore, the **molecular flux** [Number of molecules $\div$ (Area $\times$ Time)] is given by integrating expression (*). We get

$$\Phi = \tfrac{1}{4}n\left\langle v\right\rangle$$

$$\Phi = \frac{p}{\sqrt{2\pi m k_B T}}$$

As a result of the extra v in the expression for the number of molecules that hit a wall, the number of molecules leaving a hole will be something like

$$\propto v^3 e^{-mv^2/2k_B T}$$

And the average kinetic energies are

$$\begin{aligned}\left\langle \text{kinetic energy} \right\rangle &= \frac{1}{2} m \left\langle v^2 \right\rangle \\ &= 2k_B T\end{aligned}$$

6. Equilibrium in the presence of an external force

- In the presence of an external conservative force $\boldsymbol{F} = -\nabla\phi(\boldsymbol{r})$, the equilibrium distribution becomes

$$\boxed{f(\boldsymbol{r},\boldsymbol{v}) = f_0(\boldsymbol{v}) e^{-\phi(\boldsymbol{r})/kT}}$$

- We show that this is the case by showing that it satisfies the Boltzmann Transport Equation
  - It is certainly true that $\partial f / \partial t = 0$, because f does not depend on time.
  - It is also true that $\left(\partial f / \partial t\right)_{\text{coll}} = 0$, because the full integral form of $\left(\partial f / \partial t\right)_{\text{coll}}$ depends only on the $\boldsymbol{v}$ depends of f, which we already *know* has $\left(\partial f / \partial t\right)_{\text{coll}} = 0$ from the discussion above.
  - Finally, we need to show that $\left(\boldsymbol{v} \cdot \nabla_{\boldsymbol{r}} + \frac{\boldsymbol{F}}{m} \cdot \nabla_{\boldsymbol{v}}\right) f(\boldsymbol{r},\boldsymbol{v}) = 0$, which is trivial.
- We can, if we wish, absorb the potential into the density and write

$$f(\boldsymbol{r},\boldsymbol{v}) = n(\boldsymbol{r}) \left(\frac{m}{2\pi kT}\right)^{3/2} e^{m(\boldsymbol{v}-\boldsymbol{v}_0)^2/2kT}$$

$$\boxed{n(\boldsymbol{r}) = \int f(\boldsymbol{r},\boldsymbol{v})\,\mathrm{d}\boldsymbol{v} = n e^{-\phi(\boldsymbol{r})/kT}}$$

7. The H-Theorem in more Detail

- The H-Theorem only works given the assumption of molecular chaos, which in turn justifies the Boltzmann Transport Equation. In fact, the theorem states that *if, at a given instant t, the state of the gas satisfies the assumption of molecule chaos, then at the instant* $t + \varepsilon$:
  - $\mathrm{d}H / \mathrm{d}t \leq 0$
  - $\mathrm{d}H / \mathrm{d}t = 0$ if and only if $f(\boldsymbol{v},t)$ is the Maxwell-Boltzmann distribution.

- The key assumption here is that of molecular chaos – we first show that in a state of molecule chaos, H is at a local peak
    - Consider preparing a dilute gas in an initial condition at $t = 0$ that is invariant under time reversal, non-Maxwell-Boltzmann, and in "molecular chaos". According to the H-Theorem
    $$\mathrm{d}H / \mathrm{d}t\big|_{t=0^+} \leq 0$$
    - Now consider the gas prepared in the same state but with all velocities reversed. This gas must also be in molecular chaos and so have $\mathrm{d}H / \mathrm{d}t\big|_{t=0^+} \leq 0$. But the future of this gas is the past of the previous gas, and so
    $$\mathrm{d}H / \mathrm{d}t\big|_{t=0^-} \geq 0$$

  As such, H is at a local maximum.
- This implies that collisions can (a) create molecular chaos when there is none and (b) destroy molecular chaos when it exists.

Kinetic Theory ~ Transport Phenomena

1. Basics

2. Conservation Laws

- To investigate non-equilibrium phenomena, we must solve the Boltzmann Equation with given initial conditions. Some rigorous properties of any solution may be obtained from the fact that in any collision there are some properties that are rigorously conserved.
- Let $\chi(\boldsymbol{r},\boldsymbol{v})$ be any quantity such that in any collision $\left\{\boldsymbol{v}_1,\boldsymbol{v}_2\right\} \to \left\{\boldsymbol{v}_1',\boldsymbol{v}_2'\right\}$, we have $\chi_1+\chi_2=\chi_1'+\chi_2'$. For such quantities

$$\boxed{J_\chi(\boldsymbol{v},t)=\int \chi(\boldsymbol{r},\boldsymbol{v})\left[\frac{\partial f(\boldsymbol{r},\boldsymbol{v},t)}{\partial t}\right]_{\text{coll}} \mathrm{d}^3v=0}$$

  To prove this, first write the collision term out fully

$$J_\chi(\boldsymbol{v},t)=\iiint\left(f_1'f_2'-f_1f_2\right)\chi_1\left|\boldsymbol{v}_1-\boldsymbol{v}_2\right|\sigma(\Omega)\,\mathrm{d}^3v_1\,\mathrm{d}^3v_2\,\mathrm{d}\Omega$$

  We next perform the variable changes we used to obtain the H-Theorem (a) $\boldsymbol{v}_1\leftrightarrow\boldsymbol{v}_2$ (b) $\left\{\boldsymbol{v}_1,\boldsymbol{v}_2\right\}\leftrightarrow\left\{\boldsymbol{v}_1',\boldsymbol{v}_2'\right\}$ and we get

$$J_\chi(\boldsymbol{v},t)=\frac{1}{4}\iiint\left(f_1'f_2'-f_1f_2\right)\overbrace{\left(\chi_1+\chi_2-\chi_1'-\chi_2'\right)}^{=0}\left|\boldsymbol{v}_1-\boldsymbol{v}_2\right|\sigma(\Omega)\,\mathrm{d}^3v_1\,\mathrm{d}^3v_2\,\mathrm{d}\Omega$$

  This integral is always 0, as expected.
- Now, consider multiplying both sides of the Boltzmann Equation by χ and integrating over $\boldsymbol{v}$. The RHS vanishes because of the Theorem above, and so

$$\int \chi(\boldsymbol{r},\boldsymbol{v})\left(\frac{\partial}{\partial t}+\boldsymbol{v}\cdot\nabla_{r}+\frac{\boldsymbol{F}}{m}\cdot\nabla_{v}\right)f(\boldsymbol{r},\boldsymbol{v},t)\,\mathrm{d}\boldsymbol{v}=0$$

$$\int\left(\frac{\partial}{\partial t}+\boldsymbol{v}\cdot\nabla_{r}+\frac{\boldsymbol{F}}{m}\cdot\nabla_{v}\right)\left(\chi f\right)-f\left(\frac{\partial}{\partial t}+\boldsymbol{v}\cdot\nabla_{r}+\frac{\boldsymbol{F}}{m}\cdot\nabla_{v}\right)\chi\,\mathrm{d}\boldsymbol{v}=0$$

$$\frac{\partial}{\partial t}\int\chi f\,\mathrm{d}\boldsymbol{v}-\int f\frac{\partial\chi}{\partial t}\mathrm{d}\boldsymbol{v}+\int v_{i}\frac{\partial}{\partial x_{i}}\chi f\,\mathrm{d}\boldsymbol{v}-\int fv_{i}\frac{\partial\chi}{\partial x_{i}}\mathrm{d}\boldsymbol{v}$$

$$+\frac{1}{m}\int F_{i}\frac{\partial}{\partial v_{i}}\left(\chi f\right)\mathrm{d}\boldsymbol{v}-\frac{1}{m}\int fF_{i}\frac{\partial\chi}{\partial v_{i}}\mathrm{d}\boldsymbol{v}$$

$$\frac{\partial}{\partial t}\int\chi f\,\mathrm{d}\boldsymbol{v}-\int f\frac{\partial\chi}{\partial t}\mathrm{d}\boldsymbol{v}+\int v_{i}\frac{\partial}{\partial x_{i}}\chi f\,\mathrm{d}\boldsymbol{v}-\int fv_{i}\frac{\partial\chi}{\partial x_{i}}\mathrm{d}\boldsymbol{v}$$

$$+\frac{1}{m}\int\frac{\partial}{\partial v_{i}}\left(\chi fF_{i}\right)\mathrm{d}\boldsymbol{v}-\frac{1}{m}\int\chi f\frac{\partial F_{i}}{\partial v_{i}}-\frac{1}{m}\int fF_{i}\frac{\partial\chi}{\partial v_{i}}\mathrm{d}\boldsymbol{v}$$

The fifth term vanishes, since $f\to 0$ as $\boldsymbol{v}\to\infty$, and so

$$\frac{\partial}{\partial t}\left\langle n\chi\right\rangle-n\left\langle\frac{\partial\chi}{\partial t}\right\rangle+\frac{\partial}{\partial x_{i}}\left\langle nv_{i}\chi\right\rangle-n\left\langle v_{i}\frac{\partial\chi}{\partial x_{i}}\right\rangle-\frac{n}{m}\left\langle\frac{\partial F_{i}}{\partial v_{i}}\chi\right\rangle-\frac{n}{m}\left\langle F_{i}\frac{\partial\chi}{\partial v_{i}}\right\rangle=0$$

Where, in the third term, we have used the fact that velocity of a particular particle is independent of position, and where

$$\left\langle A\right\rangle=\frac{\int Af\,\mathrm{d}\boldsymbol{v}}{\int f\,\mathrm{d}\boldsymbol{v}}=\frac{1}{n}\int Af\,\mathrm{d}\boldsymbol{v}$$

Note that $\left\langle nA\right\rangle=n\left\langle A\right\rangle$, and that for velocity-independent forces, the second-last term above vanishes, giving

$$\boxed{\frac{\partial}{\partial t}n\left\langle\chi\right\rangle-n\left\langle\frac{\partial\chi}{\partial t}\right\rangle+\frac{\partial}{\partial x_{i}}n\left\langle v_{i}\chi\right\rangle-n\left\langle v_{i}\frac{\partial\chi}{\partial x_{i}}\right\rangle-\frac{n}{m}\left\langle F_{i}\frac{\partial\chi}{\partial v_{i}}\right\rangle=0}$$

- For simple molecules, the conserved quantities are particle number, momentum and energy, each of which leads to a hydrodynamic equation. We define $\boldsymbol{u}=\left\langle\boldsymbol{v}\right\rangle$.
  - $\boxed{\chi=\text{Particle number}=1}$

    The theorem above becomes

$$\frac{\partial}{\partial t} n\left\langle 1\right\rangle - n\left\langle \frac{\partial 1}{\partial t}\right\rangle + \frac{\partial}{\partial x_i} n\left\langle v_i 1\right\rangle - n\left\langle v_i \frac{\partial 1}{\partial x_i}\right\rangle - \frac{n}{m}\left\langle F_i \frac{\partial 1}{\partial v_i}\right\rangle = 0$$

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial x_i} n\left\langle v_i\right\rangle = 0$$

$$\boxed{\frac{\partial n(\boldsymbol{r},t)}{\partial t} + \nabla_r \cdot \left(n\boldsymbol{u}\right) = 0}$$

This is simply the statement that the variation in local particle density is due to a particle current.

- $\boxed{\chi = \text{Momentum} \propto \left(v_j - u_j\right) = c_j}$

$$\frac{\partial}{\partial t} n\left\langle c_j\right\rangle - n\left\langle \frac{\partial c_j}{\partial t}\right\rangle + \frac{\partial}{\partial x_i} n\left\langle v_i c_j\right\rangle - n\left\langle v_i \frac{\partial c_j}{\partial x_i}\right\rangle - \frac{n}{m}\left\langle F_i \frac{\partial c_j}{\partial v_i}\right\rangle = 0$$

We use the fact $\left\langle c_j\right\rangle = 0$ in the first term

$$\cancel{\frac{\partial}{\partial t} n\left\langle c_j\right\rangle} - n\left\langle \frac{\partial c_j}{\partial t}\right\rangle + \frac{\partial}{\partial x_i} n\left\langle v_i c_j\right\rangle - n\left\langle v_i \frac{\partial c_j}{\partial x_i}\right\rangle - \frac{n}{m}\left\langle F_i \frac{\partial c_j}{\partial v_i}\right\rangle = 0$$

Getting rid of v terms

$$-n\left\langle \frac{\partial c_j}{\partial t}\right\rangle + n\frac{\partial}{\partial x_i}\left\langle (u_i + c_i)c_j\right\rangle - n\left\langle (u_i + c_i)\frac{\partial c_j}{\partial x_i}\right\rangle - \frac{n}{m}\left\langle F_i \frac{\partial c_j}{\partial v_i}\right\rangle = 0$$

Now, we note that

$$\frac{\partial c_j}{\partial x_i} = \frac{\partial v_j}{\partial x_i} - \frac{\partial u_j}{\partial x_i} = -\frac{\partial u_j}{\partial x_i}$$

Where the second equality follows because individual velocities do not vary explicitly with position. It's just a number we're considering. We also note that

$$\frac{\partial c_j}{\partial v_i} = \frac{\partial v_j}{\partial v_i} + \frac{\partial u_j}{\partial v_i} = \delta_{ij}$$

Where the second inequality follows because individual average velocities are not affected by local velocities – u is explicitly a function of x and t. Finally, we note that

$$\left\langle \frac{\partial c_j}{\partial t}\right\rangle = \left\langle \frac{\partial v_j}{\partial t}\right\rangle - \left\langle \frac{\partial u_j}{\partial t}\right\rangle = -\frac{\partial u_j}{\partial t}$$

Again, because the initial velocity we consider is just a number. As such

$$\left\langle \frac{\partial u_j}{\partial t} \right\rangle + \frac{\partial}{\partial x_i}\left\langle (u_i + c_i)c_j \right\rangle + \left\langle (u_i + c_i)\frac{\partial u_j}{\partial x_i} \right\rangle - \frac{F_j}{m} = 0$$

All the u variables are averages, and so

$$\frac{\partial u_j}{\partial t} + \frac{\partial}{\partial x_i}\left\langle u_i c_j \right\rangle + \frac{\partial}{\partial x_i}\left\langle c_i c_j \right\rangle + \frac{\partial u_j}{\partial x_i}\left\langle u_i + c_i \right\rangle - \frac{F_j}{m} = 0$$

Making copious use of the fact that $\left\langle c_j \right\rangle = 0$

$$\frac{\partial u_j}{\partial t} + \frac{\partial}{\partial x_i}\left\langle c_i c_j \right\rangle + \frac{\partial u_j}{\partial x_i} u_i - \frac{F_j}{m} = 0$$

Finally, we write

$$\boxed{P_{ij} = mn\left\langle c_i c_j \right\rangle}$$

And so we get

$$\frac{\partial u_j}{\partial t} + u_i \frac{\partial u_j}{\partial x_i} = \frac{F_j}{m} - \frac{1}{mn}\frac{\partial}{\partial x_i} P_{ij}$$

$$\boxed{m\left(\frac{\partial}{\partial t} + \boldsymbol{u}\cdot\nabla_{\boldsymbol{x}}\right)\boldsymbol{u} = \boldsymbol{F} - \frac{1}{n}\nabla_{\boldsymbol{x}}\cdot\overleftrightarrow{\boldsymbol{P}}}$$

The LHS is the acceleration of an element of fluid (the convective derivative) and the RHS is equal to the total forces, due to external force and pressure differences.

- $\boxed{\chi = \text{Energy} = \varepsilon \propto \tfrac{1}{2} m\left(v_j - u_j\right)^2}$

The LHS is the acceleration of an element of fluid (the convective derivative) and the RHS is equal to the total forces, due to external force and pressure differences.

$$\frac{\partial}{\partial t} n\left\langle E \right\rangle - n\left\langle \frac{\partial E}{\partial t} \right\rangle + \frac{\partial}{\partial x_i} n\left\langle v_i E \right\rangle - n\left\langle v_i \frac{\partial E}{\partial x_i} \right\rangle - \frac{n}{m}\left\langle F_i \frac{\partial E}{\partial v_i} \right\rangle = 0$$

Now, we note that

$$\begin{aligned} \left\langle \frac{\partial E}{\partial t} \right\rangle &= \frac{1}{2} m \left\langle \frac{\partial}{\partial t}\left(v_j^2 + u_j^2 - 2u_j v_j\right) \right\rangle \\ &= \frac{1}{2} m \left\langle 2u_j \frac{\partial u_j}{\partial t} - 2\frac{\partial u_j}{\partial t} v_j \right\rangle \\ &= 0 \end{aligned}$$

And that

$$\begin{aligned}\left\langle v_i \frac{\partial E}{\partial x_i}\right\rangle &= \frac{1}{2} m \left\langle v_i \frac{\partial}{\partial x_i}\left(v_j^2 + u_j^2 - 2v_j u_j\right)\right\rangle \\ &= \frac{1}{2} m \left\langle v_i \left(2u_j \frac{\partial u_j}{\partial x_i} - 2v_j \frac{\partial u_j}{\partial x_i}\right)\right\rangle \\ &= 0\end{aligned}$$

And finally

$$\begin{aligned}\frac{n}{m}\left\langle F_i \frac{\partial E}{\partial v_i}\right\rangle &= \frac{n}{2}\left\langle F_i \frac{\partial}{\partial v_i}\left(v_j^2 + u_j^2 - 2v_j u_j\right)\right\rangle \\ &= \frac{n}{2}\left\langle F_i\left(2v_j\delta_{ij} - 2u_j\delta_{ij}\right)\right\rangle \\ &= n\left\langle F_i\left(v_j\delta_{ij} - u_j\delta_{ij}\right)\right\rangle \\ &= -n\boldsymbol{F}\cdot\boldsymbol{u}\end{aligned}$$

Where the last line follows for some reason. So we're left with

$$\frac{\partial}{\partial t} n\left\langle E\right\rangle + \frac{\partial}{\partial x_i} n\left\langle v_i E\right\rangle - n\boldsymbol{F}\cdot\boldsymbol{u} = 0$$

Next, write

$$v_i E = \left\langle (v_i - u_i)E\right\rangle + u_i\left\langle E\right\rangle$$

And get

$$\begin{gathered}n\frac{\partial}{\partial t}\left\langle E\right\rangle + \frac{\partial}{\partial x_i}\left(nu_i\left\langle E\right\rangle + n\left\langle (v_i - u_i)E\right\rangle\right) = n\boldsymbol{F}\cdot\boldsymbol{u} \\ n\frac{\partial}{\partial t}\left\langle E\right\rangle + \frac{\partial}{\partial x_i}\left(nu_i\left\langle E\right\rangle\right) + \frac{\partial}{\partial x_i}\left(n\left\langle (v_i - u_i)E\right\rangle\right) = n\boldsymbol{F}\cdot\boldsymbol{u}\end{gathered}$$

Now

$$\frac{\partial}{\partial x_i}\left(nu_i\left\langle E\right\rangle\right) = n\left(\frac{\partial u_i}{\partial x_i} + u_i\frac{\partial}{\partial x_i}\right)\left\langle E\right\rangle$$

Apparently, the first term vanishes, and so we're left with

$$n\frac{\partial}{\partial t}\left\langle E\right\rangle + nu_i\frac{\partial}{\partial x_i}\left\langle E\right\rangle + \frac{\partial}{\partial x_i}\left(n\left\langle (v_i - u_i)E\right\rangle\right) = n\boldsymbol{F}\cdot\boldsymbol{u}$$

Now, we define

$$\begin{gathered}q_\alpha = n\left\langle (v_\alpha - u_\alpha)\varepsilon\right\rangle = \text{local heat flux} \\ \Lambda_{\alpha\beta} = \tfrac{1}{2}\left(\frac{\partial u_\beta}{\partial x_\alpha} + \frac{\partial u_\alpha}{\partial u_\beta}\right)\end{gathered}$$

And after some magic, we get

$$\boxed{\left(\frac{\partial}{\partial t} + \boldsymbol{u}\cdot\nabla_{\boldsymbol{x}}\right)\boldsymbol{\varepsilon} = -\frac{1}{n}\nabla_{\boldsymbol{x}}\cdot\boldsymbol{q} - \frac{1}{n}\overleftrightarrow{\boldsymbol{P}}\cdot\overleftrightarrow{\boldsymbol{\Lambda}}}$$