

Plasma Primer Part II (Boltzmann's Equation and Conservation Laws)

Boltzmann's Equation – Continuum Conservation Laws:

Boltzmann's Equation governs temporal and spatial variations in each species distribution function. Several approaches to deriving this central relationship are possible. The following is probably the easiest to understand since it uses a generalized conservation argument (See Alternative Argument in Tien & Leinhard, Statistical Thermodynamics, Hemisphere 1979).

Since $f_s = f_s(\bar{x}, \bar{w}, t) = f_s(x_1, x_2, x_3, w_1, w_2, w_3, t)$ then we can consider f as being defined in a G-dimensional space (phase space) in which the independent variables are $x_1, x_2, x_3, w_1, w_2, w_3$. Boltzmann argues that the total time rate of change of f_s must be due to collisions between particles. In other words:

$$\frac{df_s}{dt} = \left. \frac{\partial f_s}{\partial t} \right|_c \quad (1)$$

Where $\left. \frac{\partial f_s}{\partial t} \right|_c$ denotes the net rate of change in f_s due to collisions. We will go into more detail on this term later (when deriving continuum equations). Now, since $f_s = f_s(x_1, x_2, x_3, w_1, w_2, w_3, t)$ then by chain rule:

$$\frac{df_s}{dt} = \sum_{i=1}^3 \frac{\partial f_s}{\partial x_i} \frac{dx_i}{dt} + \sum_{i=1}^3 \frac{\partial f_s}{\partial w_i} \frac{dw_i}{dt} + \frac{\partial f_s}{\partial t} \quad (2)$$

The term $\frac{dx_i}{dt}$ is just the absolute velocity component w_i , while $\frac{dw_i}{dt}$ is the particle acceleration which we can determine using Newton's Second Law:

$$\frac{dw_i}{dt} = \frac{1}{m_s} F_i \quad (3)$$

Where F_i is the net force on s particles (i^{th} component). In a plasma, the dominant force is the electromagnetic body force, which is given by:

$$\bar{F} = ez_s [\bar{E} + \bar{w} \times \bar{B}] \quad (4)$$

Where $\bar{E}$ is the electric field, z_s is free charge on species s , and $\bar{B}$ is the magnetic field. The first form on the right represents the coulomb force while the second follows from ampere's law. Thus (3) becomes:

$$\frac{dw_i}{dt} = \frac{ez_s}{m_s} [\bar{E}i + (\bar{w} \times \bar{B})i] \quad (5)$$

Inserting (5) into (2) and using $\frac{dx_i}{dt} = dw_i$ we obtain Boltzmann's equation:

$$\frac{\partial f_s}{\partial t} + \sum_{i=1}^3 w_i \frac{\partial f_s}{\partial x_i} + \sum_{i=1}^3 \frac{e z_s}{m_s} [\bar{E} i + (\bar{w} \times \bar{B}) i] \frac{\partial f_s}{\partial w_i} = \left(\frac{df_s}{dt} \right)_c \quad (6)$$

=Boltzmann's Equation for species s in a plasma

Notes

- 1) Under nominally collisionless conditions, the collision term $\left(\frac{df_s}{dt} \right)_c = 0$.
- 2) Under equilibrium conditions (i.e. no velocity gradients, no temperature gradients, and no specie gradients) the distribution functions for each species does not change with time. In other words collisions do not change f_s . Thus under equilibrium conditions $\left(\frac{df_s}{dt} \right)_c = 0$. (Note that collisions do occur under equilibrium conditions they do not affect f_s , however.)
- 3) We will find that the collision term $\left(\frac{df_s}{dt} \right)_c$ gives rise to a mass source term (due to chemical reactions) when deriving the continuum conservation of mass. Similarly, this term gives rise to a dynamical friction terms in the species momentum equation. (Note: Viscous forces will come out of the stress tensor $[J_s]$ we discussed earlier.)
- 4) In flows where collision between particles are elastic (typically true in non-plasma gas flows) it can be shown that the collision term equals zero.
- 5) Under steady-state conditions $\frac{df_s}{dt} = 0$.

Derivation of Conservation Laws (Continuum):

First, multiply (6) by a molecular property θ_s and integrate with respect to dw_1, dw_2, dw_3 $F d\bar{w}$:

$$\int \theta_s \frac{\partial f}{\partial t} d\bar{w} + \int \theta_s (\bar{w} \cdot \nabla) f_s d\bar{w} + \int \theta_s \left(\frac{\bar{F}}{m_s} \cdot \nabla w \right) f_s d\bar{w} = \int \theta_s \left(\frac{\partial f}{\partial t} \right)_c d\bar{w} \quad (7)$$

Where

$$\begin{aligned}
(\vec{w} \cdot \nabla) f_s &= \sum_{i=1}^3 w_i \frac{\partial f_s}{\partial x_i} \\
\left(\frac{\vec{F}}{m_s} \cdot \nabla w \right) f_s &= \sum_{i=1}^3 F_i \frac{\partial f_s}{\partial w_i} \\
\nabla w &= \sum_{i=1}^3 \mathbf{e}_i \frac{\partial}{\partial w_i} \\
d\vec{w} &= dw_1 dw_2 dw_3
\end{aligned}$$

Now:

$$\begin{aligned}
\int \theta_s \frac{\partial f_s}{\partial t} d\vec{w} &= \frac{\partial}{\partial t} \int \theta_s f_s d\vec{w} - \int \frac{\partial \theta_s}{\partial t} f_s d\vec{w} \\
&= \frac{\partial}{\partial t} (n_s \langle \theta_s \rangle) - n_s \left\langle \frac{\partial \theta_s}{\partial t} \right\rangle
\end{aligned} \tag{7a}$$

$$\begin{aligned}
\int \theta_s (\vec{w} \cdot \nabla) f_s d\vec{w} &= \nabla \cdot \int \theta_s \vec{w} f_s d\vec{w} - \int \nabla (\theta_s w) f_s d\vec{w} \\
&= \nabla \cdot (n_s \langle \theta_s \vec{w} \rangle) - n_s \langle \nabla (\theta_s w) \rangle \\
&= \nabla \cdot (n_s \langle \theta_s \vec{w} \rangle) - n_s \langle \vec{w} \cdot \nabla \theta_s \rangle
\end{aligned} \tag{7b}$$

$$\begin{aligned}
\int \theta_s \left(\frac{\vec{F}}{m} \cdot \nabla w \right) f_s d\vec{w} &= \int \nabla_w \cdot (\vec{F}_s \theta_s f_s) d\vec{w} - \int f_s \nabla_w \cdot (\vec{F}_s \theta_s) d\vec{w} \\
&= \oint_{S_\infty} (\vec{F}_s \theta_s f_s) \hat{n}_o \cdot d\mathbf{s} - n_s \langle \nabla_w \cdot (\vec{F}_s \theta_s) \rangle
\end{aligned} \tag{7c}$$

Note that in the last step we used a generalized form of the divergence theorem to convert 1st ‘volume’ integral in the 1st line to a ‘surface’ integral in the second line (i.e. we’ve done integration by parts). $\hat{n}_o$ is a generalized unit normal on surface S_∞ , and S_∞ is the surface that n lies at $w_1 = \pm\infty, w_2 = \pm\infty, w_3 = \pm\infty$ since $f_s \rightarrow 0$ for large velocities then the $\oint$ term = 0.

Exercise: Show that

$$\langle \nabla_w \cdot (\vec{F} \theta_s) \rangle = \langle \vec{F}_s \cdot \nabla_w \theta_s \rangle \tag{7d}$$

for $\vec{F} = e z_s [\vec{E} + (\vec{w} \times \vec{B})]$. Using (7a)-(7d) in (7) we obtain:

$$\begin{aligned}
&\frac{\partial}{\partial t} (n_s \langle \theta \rangle_s) - n_s \left\langle \frac{\partial \theta}{\partial t} \right\rangle_s + \nabla \cdot (n_s \langle \theta \vec{w} \rangle_s) - n_s \langle \vec{w} \cdot \nabla \theta \rangle_s - \frac{n_s}{m_s} (\vec{F} \cdot \nabla_w \theta)_s \\
&= \int \theta \left(\frac{df}{dt} \right)_c d\vec{w}
\end{aligned} \tag{8}$$

This is called Maxwell’s Transport Equation.

Conservation of Species $\Rightarrow \theta_s = m_s$ = mass of species s. For $\theta_s = m_s$:

$$\begin{aligned}
\langle \langle \theta \rangle_s \rangle_s &= m_s \\
\left\langle \frac{\partial \theta_s}{\partial t} \right\rangle_s &= \left\langle \frac{\partial m_s}{\partial t} \right\rangle_s = 0 \\
n_s \langle m_s \bar{w} \rangle_s &= n_s m_s \langle \bar{w} \rangle_s = \rho \bar{v} \Rightarrow \nabla \cdot (n_s \langle m_s \bar{w} \rangle_s) = \nabla \cdot (\rho_s \bar{v}_s) \\
n_s \langle \bar{w} \nabla \theta \rangle &= 0 \text{ Since } m_s = \text{constant} \\
\langle \bar{F} \nabla_w m_s \rangle &= 0 \text{ Since } m_s = \text{constant}
\end{aligned}$$

Thus (8) becomes:

$$\begin{aligned}
&\frac{\partial}{\partial t}(\rho_s) + \nabla \cdot (\rho_s \bar{v}_s) \\
&= \int \theta \left(\frac{df}{dt} \right) \bigg|_c d\bar{w}
\end{aligned} \tag{9}$$

IN words, L.H.S. states that local rate of change of specie $\frac{\text{mass}}{\text{volume}}$ + net flux of

$\frac{\text{mass}}{\text{volume}}$ with and through an infinitesimal volume of space = R.H.S. Thus, R.H.S. is interpreted as a mass source form (of species s), which in Boltzmann's picture, arises due to collisions. Therefore, R.H.S. is written as $\dot{\rho}_s$ where s is created by chemical reactions or ionization or recombination.

$$\frac{\partial}{\partial t}(\rho_s) + \nabla \cdot (\rho_s \bar{v}_s) = \dot{\rho}_s = \text{Conservation of Species s} \tag{9}$$

Overall Mass Conservation

Sum up all species conservation equations:

$$\begin{aligned}
&\sum_s \frac{\partial \rho_s}{\partial t} + \sum_s \nabla \cdot (\rho_s \bar{v}_s) = \sum_s \dot{\rho}_s \\
&\text{or} \\
&\frac{\partial}{\partial t} \sum_s \rho_s + \nabla \cdot \sum_s (\rho_s \bar{v}_s) = 0
\end{aligned} \tag{10}$$

$\sum_s \dot{\rho}_s = 0$ since there can be no net course or sink of mass during chemical reactions, ionizations and/or recombination. Note that (10) is exactly the equation we derive when doing a mass balance on an infinitesimal volume, i.e., it's the same conservation of mass equation we use in fluid mechanics.

Conservation of Species Momentum

Let $\theta_s = m_s \bar{w}_s$. The transport equation (8) becomes:

$$\begin{aligned}
& \frac{\partial}{\partial t} (n_s \langle m_s \bar{w}_s \rangle_s) - n_s \left\langle m_s \frac{\partial \bar{w}_s}{\partial t} \right\rangle + \nabla \cdot (n_s \langle m_s \bar{w} \bar{w} \rangle_s) \\
& - n_s \langle \bar{w} \nabla m_s \bar{w} \rangle_s - \frac{n_s}{m_s} \left(\langle \bar{F} \nabla_w \rangle m_s \bar{w} \right)_s \\
& = \int m_s \bar{w} \left(\frac{df}{dt} \right)_c d\bar{w} \\
& \frac{\partial}{\partial t} (n_s \langle m_s \bar{w}_s \rangle_s) = \frac{\partial}{\partial t} (\rho_s \bar{v}_s)
\end{aligned} \tag{11}$$

Since $\bar{w}$ are independent variables, then are not functions of time, thus:

$$n_s \left\langle m_s \frac{\partial \bar{w}}{\partial t} \right\rangle = 0$$

0

$$\nabla \cdot (n_s m_s \langle \bar{w} \bar{w} \rangle_s) = \nabla \cdot (\rho_s \langle \bar{w} \bar{w} \rangle_s)$$

But,

$$\begin{aligned}
\langle \bar{w} \bar{w} \rangle_s &= \langle (\bar{v} + \bar{c})(\bar{v} + \bar{c}) \rangle \\
&= \langle \bar{v} \bar{v} \rangle_s + \langle \bar{c} \bar{v} \rangle_s + \langle \bar{v} \bar{c} \rangle_s + \langle \bar{c} \bar{c} \rangle_s \\
&= \bar{v} \bar{v} + \bar{v}_s \bar{v} + \bar{v} \bar{v}_s + \frac{1}{\rho_s} [P]_s
\end{aligned}$$

$$\begin{aligned}
n_s \langle (\bar{w} \nabla) m_s \bar{w} \rangle_s &= \rho_s \langle (\bar{w} \nabla) \bar{w} \rangle_s \\
&= n_s \left\langle F_1 \frac{\partial}{\partial w_1} (w_1 \hat{e}_1 + w_2 \hat{e}_2 + w_3 \hat{e}_3) + F_2 \frac{\partial}{\partial w_2} (w_1 \hat{e}_1 + w_2 \hat{e}_2 + w_3 \hat{e}_3) \right. \\
&\quad \left. + F_3 \frac{\partial}{\partial w_3} (w_1 \hat{e}_1 + w_2 \hat{e}_2 + w_3 \hat{e}_3) \right\rangle_s \\
&= n_s \langle F_1 \hat{e}_1 + F_2 \hat{e}_2 + F_3 \hat{e}_3 \rangle_s \\
&= n_s \langle \bar{F} \rangle_s
\end{aligned}$$

$$\langle \bar{F} \rangle_s = z e_s \left[\langle \bar{E} + \bar{w} \times \bar{B} \rangle_s \right]$$

Thus, collecting all of these into equation (11) we obtain:

$$\begin{aligned}
& \frac{\partial}{\partial t} (\rho_s \bar{v}_s) + \nabla \cdot \left[\rho_s \left(\bar{v} \bar{v} + \bar{v}_s \bar{v} + \bar{v} \bar{v}_s + \frac{1}{\rho_s} [P]_s \right) \right] - n_s z e_s \langle \bar{F} \rangle_s = z e_s \langle \bar{E} + \bar{w} \times \bar{B} \rangle_s \\
& = \int m_s \bar{w} \left(\frac{df}{dt} \right)_c d\bar{w}
\end{aligned} \tag{12}$$

Specie conservation of linear momentum. Note that the term on right side represents a momentum source term associated with collisions of s with other species and with itself. We'll consider this term in detail later.

Overall Conservation of Linear Momentum

Sum all terms in equation (12) over all species.

$$\sum_s \frac{\partial}{\partial t} (\rho_s \bar{\mathbf{v}}_s) = \frac{\partial}{\partial t} \sum_s (\rho_s \bar{\mathbf{v}}_s) = \frac{\partial}{\partial t} (\rho \bar{\mathbf{v}})$$

$$\sum_s \nabla \cdot (\rho_s \bar{\mathbf{v}} \bar{\mathbf{v}}) = \nabla \cdot \sum_s (\rho_s \bar{\mathbf{v}} \bar{\mathbf{v}}) = \nabla \cdot (\rho \bar{\mathbf{v}} \bar{\mathbf{v}})$$

Now $\bar{\mathbf{v}} \bar{\mathbf{v}}$ is a diadic, which can be expressed in indicial notation as:

$$\bar{\mathbf{v}} \bar{\mathbf{v}} = v_i v_j \hat{\mathbf{e}}_i \otimes \hat{\mathbf{e}}_j$$

The divergence of a diadic can be calculated as follows:

$$\begin{aligned} \nabla \cdot (\bar{\mathbf{v}} \bar{\mathbf{v}}) &= \hat{\mathbf{e}}_e \frac{\partial}{\partial x_e} (v_i v_j \hat{\mathbf{e}}_i \otimes \hat{\mathbf{e}}_j) \\ &= \hat{\mathbf{e}}_e \frac{\partial}{\partial x_e} (v_{i,e} v_j + v_i v_{j,e}) (\hat{\mathbf{e}}_e \cdot \hat{\mathbf{e}}_i) \hat{\mathbf{e}}_j \\ &= (v_{i,i} v_j + v_i v_{j,i}) \hat{\mathbf{e}}_j \\ &= (\nabla \cdot \bar{\mathbf{v}}) \bar{\mathbf{v}} + (\bar{\mathbf{v}} \cdot \nabla) \bar{\mathbf{v}} \end{aligned}$$

Thus:

$$\begin{aligned} \nabla \cdot (\rho \bar{\mathbf{v}} \bar{\mathbf{v}}) &= \hat{\mathbf{e}}_e \frac{\partial}{\partial x_e} (\rho v_i v_j \hat{\mathbf{e}}_i \otimes \hat{\mathbf{e}}_j) \\ &= ((\rho v_i)_{,e}) v_j + \rho v_i v_{j,e} (\delta_{ei} \hat{\mathbf{e}}_j) \\ &= ((\rho v_i)_{,i}) \bar{\mathbf{v}} + \rho (\bar{\mathbf{v}} \cdot \nabla) \bar{\mathbf{v}} \\ &= [\nabla \cdot (\rho \bar{\mathbf{v}})] \bar{\mathbf{v}} + \rho (\bar{\mathbf{v}} \cdot \nabla) \bar{\mathbf{v}} \\ \sum_s \bar{\mathbf{v}} \cdot (\rho_s \bar{\mathbf{v}}_s \bar{\mathbf{v}}) &= \nabla \cdot (\sum_s \rho_s \bar{\mathbf{v}}_s \bar{\mathbf{v}}) \\ &= \nabla \cdot \left[(\sum_s \rho_s \bar{\mathbf{v}}_s) \bar{\mathbf{v}} \right] \\ &= \nabla \cdot \left[(\sum_s \rho_s (\bar{\mathbf{v}}_s - \bar{\mathbf{v}})) \bar{\mathbf{v}} \right] \\ &= \nabla \cdot \left[(\sum_s \rho_s (\bar{\mathbf{v}}_s) \bar{\mathbf{v}} - \bar{\mathbf{v}} \bar{\mathbf{v}} \sum_s \rho_s) \right] \\ &= \nabla \cdot [\rho \bar{\mathbf{v}} \bar{\mathbf{v}} - \rho \bar{\mathbf{v}} \bar{\mathbf{v}}] = 0 \end{aligned}$$

Similarly,

$$\sum_s \nabla \cdot (\rho_s \bar{\mathbf{v}}_s \bar{\mathbf{v}}_s) = 0$$

$$\begin{aligned}
\sum_s (\nabla[\rho_s]) &= \sum_s [\nabla[J_s] + P_s[I]] \\
&= \nabla \left(\sum_s [J_s] + (\sum_s P_s)[I] \right) \\
&= \nabla[J + P[I]] \\
&= \nabla[J] + \hat{e}_k \frac{\partial}{\partial x_k} (P \delta_{ij} \hat{e}_i \otimes \hat{e}_j) \\
&= \nabla[J] + \frac{\partial P}{\partial x_k} \delta_{ij} \delta_{ik} \hat{e}_j \\
&= \nabla[J] + \frac{\partial P}{\partial x_i} \hat{e}_i \\
&= \nabla[J] + \nabla P
\end{aligned}$$

$$\begin{aligned}
\sum_s n_s \langle \vec{E}_s \rangle &= n \vec{E} \quad (\vec{E} \text{ is not a function of } \vec{w}) \\
e \sum_s n_s z_s \langle \vec{w} \times \vec{B} \rangle &= e \sum_s z_s \left[\int \langle \vec{w} \times \vec{B} \rangle f_s d\vec{w} \right] \\
&= e \sum_s \left[z_s \int (\vec{c} + \vec{v}) \times \vec{B} f_s(\vec{c}, \vec{x}, t) d\vec{c} \right] \\
&= e \sum_s z_s \left[\int (\vec{c} \times \vec{B}) \hat{f} d\vec{c} + \int (\vec{v} \times \vec{B}) \hat{f} d\vec{c} \right] \\
&= e \sum_s z_s \left[\int E_{ijk} c_j B_k \hat{e}_i \hat{f} d\vec{c} + (\vec{v} \times \vec{B}) \int \hat{f} d\vec{c} \right] \\
&= e \sum_s z_s (E_{ijk} B_k \hat{e}_i \langle c_j \rangle_s) + \sum_s e n_s (\vec{v} \times \vec{B}) z_s \\
&= e \sum_s n_s z_s \vec{v}_s \times \vec{B} + \rho_e (\vec{v} \times \vec{B}) \\
\rho_e &= \sum_s e n_s z_s = \text{Free charge density}
\end{aligned}$$

We will call

$$\vec{j} = \sum_s e n_s z_s \vec{v}_s$$

the conductive current. Physically it's the electric conduction component due to the charged particle diffusion. Thus:

$$\sum_s e n_s z_s \langle \vec{w} \times \vec{B} \rangle_s = \vec{j} \times \vec{B} + \rho_e \vec{v} \times \vec{B}$$

Due to the mobility of electrons with in plasmas, and positive charge is rapidly neutralized by a swarm of electrons. The result is that free charge density, ρ_e , tends to be negligible (except for near boundaries, where the rapidly moving electrons can pass preferentially into or away from the solid; in these regions,

called sheaths, non-negligible ρ_e 's do exist). Finally we interpret $\int m_s \bar{w} \left(\frac{df}{dt} \right) \bigg|_c d\bar{w}$

as a momentum source term in the momentum balance for species s (due to collisions between particles). Due to conservation of momentum during collisions, the sum of all s momentum source terms equals 0. Thus the overall conservation of momentum equation is given by:

$$\begin{aligned} & \frac{\partial}{\partial t}(\rho \bar{v}) + \bar{v}(\bar{v} \cdot \nabla \rho \bar{v}) + \rho(\bar{v} \cdot \nabla) \bar{v} + \nabla[J] + \nabla P \\ & = \rho e(\bar{E} + \bar{v} \times \bar{B}) + \bar{j} \times \bar{B} \end{aligned} \quad (13)$$

= overall conservation of momentum within plasma

Equation (13) can be simplified by use of overall conservation of mass, equation (10), and by defining:

$$\begin{aligned} \bar{J} & \equiv \rho e \bar{v} + \bar{j} = \text{current density} \\ & (= \text{current due to bulk flow} + \text{current due to diffusion}) \end{aligned}$$

Thus,

$$\begin{aligned} & \rho \frac{\partial \bar{v}}{\partial t} + \rho(\bar{v} \cdot \nabla) \bar{v} + \bar{v} \left(\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \bar{v}) \right) + \nabla[J] + \nabla P \\ & = \rho_e \bar{E} + \bar{J} \times \bar{B} \end{aligned}$$

Or

$$\rho \frac{D\bar{v}}{Dt} + \nabla[J] + \nabla P = \rho_e \bar{E} + \bar{J} \times \bar{B} \quad (14)$$

= Overall conservation of momentum

Note that the only difference between (14) and the Navier-Stokes equation is the body force term on the R.H.S. In the Navier-Stokes equation, this is $\rho \bar{g}$ (we've neglected gravitational force in our derivation; no real need to, gravity is typically much smaller than the electromagnetic forces).

Note: To actually solve (14) or (13) we need explicit expressions for $[J]$ and $\bar{j}$ (shear stress tensor and conduction current). We might try to obtain the shear stress tensor.

By letting $[J_s] = \theta_s$ in the transport equation (8). Unfortunately, since

$[J_s] = \rho_s \langle \bar{c} \bar{c} \rangle_s - \rho_s [I]$, then the term $\langle \theta_s (\bar{w} \cdot \nabla) \bar{f}_s \rangle$ in (7) leads to a term

$\langle c^2 \bar{c} \rangle_{s1}$ which (in analogy with the $\langle c^2 \bar{c} \rangle_s$ term that arises in the momentum

equations) is unknown. To obtain a closed problem, we return to the Boltzmann

equation (6) $\left(\frac{\partial \bar{f}_s}{\partial t} + (\bar{w} \cdot \nabla) \bar{f}_s + \frac{e \bar{z}_s}{m_s} [(\bar{E} + \bar{w} \times \bar{B}) \cdot \nabla] \bar{f}_s = \frac{\partial \bar{f}_s}{\partial x} \bigg|_c \right)$ and derive approximate

relationships for $\frac{\partial \bar{f}_s}{\partial x} \bigg|_c$ involving only distribution functions (of both s and other

species). This leads to N coupled Boltzmann Equations in N distribution

functions (where N=number of species). Once these N equations are obtained, then the usual procedure is to assume that each distribution functions is nearly maxwellian (isotropic) (which arises when each specie is in equilibrium). Each distribution function is the expanded as:

$$f_s = f_{s0} + \beta f_{s1} + \beta^2 f_{s2} \dots$$

Where f_{s0} is the (known) Maxwell distribution, β is a small (perturbation) parameter, and $f_{s1}, f_{s2} \dots$ are higher order corrections to f_{s0} , this perturbation approach leads to f_{s1}, f_{s2} etc. Once f_s is thus obtained, then terms like

$$\langle \bar{c}\bar{c} \rangle_s = \langle (\bar{w} - \bar{v})(\bar{w} - \bar{v}) \rangle = \frac{1}{n_s} \int (\bar{w} - \bar{v})(\bar{w} - \bar{v}) f_s d\bar{w} \text{ can be explicitly calculated.}$$

Using this approach, it is that:

$$J_{ij} = -\mu \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) + \frac{2}{3} \mu \delta_{ij} \nabla \cdot \mathbf{v} \quad (15)$$

Which is the well-known constitution relation for Newtonian Fluids (i.e. fluids in which shear strain rate $\frac{\partial v_i}{\partial x_j}$).

The relationship for $\bar{j}$ will either be derived or given later.

Species Energy Equation

$$\theta_s = \varepsilon = \frac{1}{2} m_s w^2 + \varepsilon_{\text{int}} = \frac{1}{2} m_s \bar{w}\bar{w} + \varepsilon_{\text{int}} = \text{Total energy of an individual particle}$$

Referring to equation (8) lets obtain expressions for each term:

$$\langle \theta \rangle_s = \left\langle \frac{1}{2} m_s w^2 + \varepsilon_{\text{int}} \right\rangle_s$$

Follow the same procedures as before and express everything in terms of mass average velocity $\bar{v}$ and diffusion velocity $\bar{v}_s$:

$$n_s \left\langle \frac{1}{2} m_s w^2 + \varepsilon_{\text{int}} \right\rangle_s = \int \frac{1}{2} m_s (\bar{v} + \bar{c}) (\bar{v} + \bar{c}) \hat{f}_s d\bar{c} + \langle \varepsilon_{\text{int}} \rangle_s$$

$$(\text{Where } \hat{f}_s = \hat{f}_s(\bar{c}, \bar{x}, t))$$

$$= \int \frac{m_s}{2} (v^2 + 2\bar{v} \cdot \bar{c} + c^2) \hat{f}_s d\bar{c} + \langle \varepsilon_{\text{int}} \rangle_s$$

$$= \frac{m_s n_s}{2} v^2 + \bar{v} \cdot \left[\int m_s \bar{c} \hat{f}_s d\bar{c} + \int m_s \bar{c} \hat{f}_s d\bar{c} \right] + \langle \varepsilon_{\text{int}} \rangle_s$$

$$= \frac{\rho_s}{2} v^2 + \bar{v} \cdot (n_s m_s \langle \bar{c} \rangle) + \frac{m_s n_s}{2} \langle c^2 \rangle_s + \langle \varepsilon_{\text{int}} \rangle_s$$

$$= \frac{\rho_s}{2} v^2 + \rho_s \bar{v} \cdot \bar{v}_s + \frac{3}{2} P_s + \langle \varepsilon_{\text{int}} \rangle_s$$

(where we have used $\frac{1}{3}\rho_s \langle c^2 \rangle_s = P_s$) using $P_s = n_s k T_s$ (Ideal gas law applied to species s). We obtain:

$$n_s \left\langle \frac{1}{2} m_s w^2 + \varepsilon_{\text{int}} \right\rangle_s = \frac{\rho_s}{2} v^2 + \rho_s \bar{v} \cdot \bar{v}_s + \frac{3}{2} n_s k T_s + n_s \langle \varepsilon_{\text{int}} \rangle_s \quad (16)$$

$$\left\langle \frac{\partial \theta_s}{\partial t} \right\rangle_s = \left\langle \frac{\partial G_{\text{int},s}}{\partial t} + \frac{1}{2} m_s \frac{\partial w^2}{\partial t} \right\rangle_s = 0 + 0$$

Since a particles internal energy and velocity aren't explicitly functions of t.

$$\begin{aligned} n_s \langle \theta w_s \rangle_s &= \int (t_{\text{int},s} + \frac{m_s w^2}{2}) \bar{w} f_s d\bar{w} \\ \int \frac{m_s w^2}{2} f_s d\bar{w} &= \int \frac{m_s}{2} (\bar{v} + \bar{c}) (\bar{v} + \bar{c}) (\bar{v} + \bar{c}) \hat{f}_s d\bar{c} + \int \frac{m_s}{2} (v^2 + 2\bar{v} \cdot \bar{c} + c^2) \bar{c} \hat{f}_s d\bar{c} \\ &= \frac{n_s m_s}{2} v^2 \bar{v} + n_s m_s (\bar{v} \cdot \hat{v}_s) \bar{v} + \bar{v} \frac{n_s m_s}{2} \langle c^2 \rangle_s + \frac{n_s m_s}{2} v^2 \hat{v}_s \\ &\quad + v_i \hat{e}_i \left[\int m_s c_i \hat{e}_j \hat{e}_j \hat{f}_s d\bar{c} \right] + \int \frac{m_s}{2} (c^2) \bar{c} \hat{f}_s d\bar{c} \\ &= \frac{\rho_s}{2} v^2 \bar{v} + \rho_s (\bar{v} \cdot \hat{v}_s) \bar{v} + \frac{3}{2} n_s k T_s \bar{v} + \frac{\rho_s}{2} v^2 \hat{v}_s \\ &\quad + v_i \hat{e}_i \left[\int m_s c_i c_j \hat{e}_i \otimes \hat{e}_j \hat{f}_s d\bar{c} \right] + \frac{n_s m_s}{2} \langle c^2 \bar{c} \rangle \end{aligned}$$

Now

$$\begin{aligned} &+ v_i \hat{e}_i \left[\int m_s c_i c_j \hat{e}_i \otimes \hat{e}_j \hat{f}_s d\bar{c} \right] = \bar{v} \int m_s \bar{c} \bar{c} \hat{f}_s d\bar{c} \\ &= \bar{v} \rho_s [P_s] \frac{1}{\rho_s} \\ &= \rho_s \bar{v} [P_s] \frac{1}{\rho_s} \\ &= \frac{\rho_s}{\rho_s} \bar{v} ([J_s] + P_s [I]) \end{aligned}$$

Also we define the best flux vector $\bar{E}_s$ as

$$\bar{E}_s = n_s \left\langle \bar{c} \left(\frac{m_s c^2}{2} + \varepsilon_{\text{int},s} \right) \right\rangle$$

Physically, the term in parentheses is the particle energy associated with its random motion and its internal energy. Thus $\bar{q}_s$ is a measure of the molecular energy transport due to random molecular motion (i.e. diffusion of molecular energy).

Finally to complete the evaluation of $n_s \langle \theta \bar{w} \rangle_s$, we have to include $\int \bar{v} \varepsilon_{\text{int},s} \hat{f}_s d\bar{c}$.

Thus:

$$n_s \langle \theta \vec{w} \rangle_s = \frac{\rho_s}{2} v^2 \vec{v} + \frac{3}{2} n_s k T_s \vec{v} + \frac{\rho_s}{2} v^2 \vec{v}_s + \vec{v} [J_s] + P_s \vec{v} + \vec{q}_s + \vec{v} n_s \langle \varepsilon_{\text{int}} \rangle_s \quad (17)$$

$$\vec{v} [I] = v_k \hat{e}_k \delta_{ij} \hat{e}_i \otimes \hat{e}_j$$

$$= v_k \delta_{ij} \delta_{ki} \hat{e}_j$$

$$(\text{where we have used } = v_i \delta_{ij} \hat{e}_j \quad)$$

$$= v_j \hat{e}_j$$

$$= \vec{v}$$

$$n_s \langle \vec{w} \cdot \nabla \theta \rangle = \int (\vec{w} \cdot \nabla) \varepsilon_{\text{int},s} + \frac{1}{2} m_s w^2 f_s d\vec{w} = 0$$

Since $\varepsilon_{\text{int},s}$ and $\frac{1}{2} m_s w^2$ aren't explicit functions of position

$$\frac{n_s}{m_s} \langle \vec{F} \cdot \nabla_w \theta \rangle_s = \frac{1}{m_s} \int F_i \frac{\partial}{\partial w_i} (\varepsilon_{\text{int},s} + \frac{m_s}{2} w_j w_j) f_s d\vec{w}$$

$$= \frac{1}{2} \frac{m_s}{m_s} \int F_i (\delta_{ij} w_j + w_j \delta_{ij}) f_s d\vec{w}$$

$$= \frac{2}{2} \int F_i w_i f_s d\vec{w}$$

$$\int F_i w_i f_s d\vec{w} = \int \mathbf{e} z_s (\vec{E} + \vec{w} \times \vec{B}) \cdot \vec{w} f_s d\vec{w}$$

$$= \int \mathbf{e} z_s \vec{E} \cdot \vec{w} f_s d\vec{w}$$

$$= \int \mathbf{e} z_s \vec{E} \cdot (\vec{v} + \vec{c}) f_s d\vec{w}$$

$$= \mathbf{e} z_s n_s \vec{E} \cdot \vec{v} + \mathbf{e} z_s n_s \vec{E} \cdot \vec{v}_s$$

$$= \vec{E} \cdot (\mathbf{e} z_s n_s \vec{v} + \vec{j}_s)$$

$$\int F_i w_i f_s d\vec{w} = \vec{E} \cdot \vec{j}_s = \text{Joule heating term due to motion of species } s$$

$$= \langle \vec{F} \cdot \nabla_w \theta \rangle_s \frac{n_s}{m_s} \quad (18)$$

Using (16), (17) and (18) in the transport equation (8) we obtain:

$$\begin{aligned} & \frac{\partial}{\partial t} \left(\frac{\rho_s}{2} v^2 + \rho_s \vec{v} \cdot \vec{v}_s + \frac{3}{2} n_s k T_s + n_s \langle \varepsilon_{\text{int}} \rangle_s \right) \\ & + \nabla \cdot \left[\frac{\rho_s}{2} v^2 + \rho_s v^2 \vec{v}_s + \frac{3}{2} n_s k T_s + P_s + n_s \langle \varepsilon_{\text{int}} \rangle_s \right] \vec{v} \\ & + \frac{\rho_s}{2} v^2 \vec{v}_s + \vec{v} [J_s] - \vec{E} \cdot \vec{j}_s = \int \sum_s \left(\frac{\partial f_s}{\partial t} \right)_c d\vec{w} \end{aligned} \quad (19)$$

This is the specie energy equation.

Overall energy equation

Let's use the following definition of the average specie internal energy e_s :

$$e_s \equiv \frac{1}{m_s} \langle \varepsilon_{\text{int}} \rangle_s + \frac{3}{2} \frac{kT_s}{m_s} \equiv \frac{\langle \varepsilon_{\text{int}} \rangle_s}{m_s} + \frac{1}{2} \langle \bar{c} \cdot \bar{c} \rangle \quad (20)$$

And rewrite (19):

$$\begin{aligned} & \frac{\partial}{\partial t} \left(\frac{\rho_s}{2} v^2 + \rho_s \bar{v} \cdot \bar{v}_s + \rho_s e_s \right) + \\ & + \nabla \cdot \left[\left(\frac{\rho_s}{2} v^2 + \rho_s v^2 \bar{v}_s + n_s k T_s + \rho_s e_s \right) \bar{v} \right] \\ & + \nabla \cdot \left[\frac{\rho_s}{2} v^2 \bar{v}_s \right] + \bar{v} (\bar{v} \cdot [J_s]) - \nabla \cdot \bar{E}_s - \bar{E} \cdot \bar{J}_s = \varepsilon_s \left(\frac{\partial f_s}{\partial t} \right)_c d\bar{w} \end{aligned} \quad (19a)$$

= Species energy equation

Now sum each term in (19a) over all species:

$$\begin{aligned} \sum_s \left(\frac{\partial}{\partial t} \frac{\rho_s}{2} v^2 \right) &= \frac{\partial}{\partial t} \left(\sum_s \frac{\rho_s}{2} v^2 \right) = \frac{\partial}{\partial t} \frac{\rho}{2} v^2 \\ \sum_s \left(\frac{\partial}{\partial t} \rho_s \bar{v} \cdot \bar{v}_s \right) &= \frac{\partial}{\partial t} \left(\sum_s \rho_s \bar{v} \cdot \bar{v}_s \right) = \frac{\partial}{\partial t} (\bar{v} \cdot \sum_s \rho_s \bar{v}_s) = 0 \\ \sum_s \left(\frac{\partial}{\partial t} \rho_s e_s \right) &= \frac{\partial}{\partial t} \left(\sum_s \rho_s e_s \right) = \frac{\partial}{\partial t} (\rho e) \end{aligned}$$

Where :

$$e = \sum_s \frac{\rho_s e_s}{\rho}$$

Similar manipulations can be used on the 4th through the 7th terms in (19a):

$$\nabla \cdot \left[\bar{v} \left(\frac{\rho_s}{2} v^2 + 0 + P + \rho e \right) \right] \quad (\text{where we have used } \sum_s n_s k T_s = \sum_s P_s = P = \text{total pressure})$$

Or

$$\nabla \cdot \left[\bar{v} \left(\frac{\rho_s}{2} v^2 + P + \rho e \right) \right]$$

$$\sum_s \nabla \cdot \left(\frac{\rho_s}{2} v^2 \bar{v}_s \right) = \nabla \cdot \left(\frac{v^2}{2} \sum_s \rho_s \bar{v}_s \right) = 0$$

$$\sum_s \nabla \cdot (\bar{v} [J_s]) = \nabla \cdot \bar{v} (\sum_s [J_s]) = \nabla \cdot \bar{v} (\sum_s [J_s]) = \text{Rate of work due to shear stresses}$$

$$\sum_s \nabla \cdot \bar{q}_s = \nabla \cdot \sum_s \bar{q}_s = \nabla \cdot \bar{q} = \text{net conduction heat transfer (into differential volume)}$$

$$\sum_s (\bar{E} \cdot \bar{J}_s) = \bar{E} \cdot (\sum_s \bar{J}_s) = \bar{E} \cdot \bar{J} = \text{Joule heating}$$

$$\sum_s \left(\int \bar{E}_s \left(\frac{\partial f_s}{\partial t} \right)_c d\bar{w} \right) = 0 \quad (\text{i.e. net energy transfer during collisions between all species is zero})$$

Thus, overall energy equation is:

$$\frac{\partial}{\partial t} \left(\frac{\rho_s}{2} v^2 + \rho e \right) + \nabla \cdot \left[\bar{v} \left(\frac{\rho_s}{2} v^2 + P + \rho e \right) \right] + \nabla \cdot (\bar{v} [J_s]) + \nabla \cdot \bar{q} = \bar{E} \cdot \bar{J} \quad (20)$$

Heat Flux Vector $\bar{q}$:

- 1) When all species temperatures T_s are equal to a single temperature, T , and when all f_s are Maxwellian (we'll describe this later), then

$$\bar{E} = -k \nabla T + \sum_s \rho \bar{v}_s h_s \quad (21)$$

Where k = the ordinary thermal conductivity = $fn(T)$

$$h_s = e_s + \frac{P_s}{\rho_s} = \text{specie specific enthalpy}$$

This version of k is sometimes called 'frozen' thermal conductivity.

- 2) In the case where all $T_s = T$, all $f_s = f_{\text{Maxwellian}}$, and $\bar{v}_s = fn$ (gradient in specie density) then:

$$\bar{q} = -k' \nabla T \quad (22)$$

Since $\bar{v}_s$ typically depends on other properties beside specie density gradients, (22) only applies under special conditions.

- 3) In cases where heavy particle temperatures = T'' , temperatures = T_e , then we can express k in terms of a heavy particle thermal conductivity, k'' , and an electron thermal conductivity, k_e ; in this case:

$$\bar{q} = -k'' \nabla T'' - k_e \nabla T_e + \sum_s \bar{v}_s \rho_s h_s \quad (23)$$

This expression reflects the fact that electron collisions with heavy particles (essentially) have no effect on the heavy specie distribution functions. The existence of (at least) two temperatures, a heavy particle temperature, T'' , and an electron temperature, T_e , is due to the much greater mobility of electrons (reflected in a higher $\langle c^2 \rangle_e$).

Exercise: Show that the overall energy equation (20) can be expressed as follows:

$$\rho \frac{De}{Dt} + P(\nabla \cdot \bar{v}) = -I - \nabla \cdot \bar{q} + \bar{E} \cdot \bar{J} - \bar{v} \cdot (\bar{j} \times B) \quad (24)$$

Where: $I = J_{ij} \frac{\partial v_i}{\partial x_j}$ = dissipation function

And $\bar{j} = \sum_s n_s e z_s \bar{v}_s$

Use continuity equation (10) and momentum equation (14).