A. The BGK Equation:

- The Kramer-Klein (K-K) equation

\[
\frac{\partial W}{\partial t} + v \frac{\partial W}{\partial x} = \frac{\partial}{\partial v} \left( v - \frac{F(x)}{\tau} \right) + \frac{k_B T}{\tau M} \frac{\partial}{\partial v^2} W
\]  

is a basic equation for calculating transport properties (e.g.: viscosity, thermal conductivity, etc.) in dilute gases. The K-K equation can be rearranged to

\[
\frac{dW}{dt} = \frac{\partial W}{\partial t} + v \frac{\partial W}{\partial x} + \frac{F(x)}{M} \frac{\partial W}{\partial v} = \frac{1}{\tau} \left[ \frac{\partial}{\partial v} v + \frac{k_B T}{M} \frac{\partial}{\partial v^2} \right] W
\]  

- In (12.2) \( dW/dt \) is sometimes called the hydrodynamic derivative.

- In gas phase theory distribution functions are normalized to equal the number density, unlike \( W \) which is normalized to 1. For example, the relationship for the equilibrium velocity distribution conventions is

\[
f_{eq}(v) = \rho W_{eq}(v) = \rho \left( \frac{m}{2\pi kT} \right)^{3/2} \exp \left( -\frac{m(v-\bar{v})^2}{2kT} \right)
\]

where \( \rho = N/V \)

- We will use the \( f \) convention in the following discussion in which case the K-K equation is

\[
\frac{df}{dt} = \frac{\partial f}{\partial t} + v \frac{\partial f}{\partial x} + a \frac{\partial f}{\partial v} = \frac{1}{\tau} \left[ \frac{\partial}{\partial v} v + \frac{k_B T}{M} \frac{\partial}{\partial v^2} \right] f
\]

- The rhs of equation (12.4) is called the collision operator

\[
L_{coll} = \frac{1}{\tau} \left[ \frac{\partial}{\partial v} v + \frac{k_B T}{M} \frac{\partial}{\partial v^2} \right]
\]

- Equation (12.4) and its close relative the Boltzmann equation (see McQ Ch. 18) are difficult to solve. But we do know that in the field-free stationary limit \( df/dt=0 \) and the solution to (12.4) is (12.3). Using this bit of knowledge, an approximation to (12.4) can be derived that is far easier to solve.

- Assume that as a result of bimolecular collisions, the system relaxes to a local equilibrium distribution, described by a function \( f_{loc} \). This distribution function has the form
\[
\frac{m}{2\pi k T(r,t)}^{3/2} \exp \left( -\frac{m(v-\bar{v}(r,t))^2}{2kT(r,t)} \right)
\]

(12.6)

- Note the similarity to the equilibrium distribution function in (12.3) but constant quantities in (12.3) like the density, temperature and mean velocity are functions of \( r \) and \( t \) in (12.6).
- For a system at local equilibrium we get relationships analogous to equilibrium expressions…
\[
\rho(r,t) = \int d^3v f_{\text{loc}}(r,v,t) = \langle v \rangle_{\text{loc}}
\]
\[
\bar{v}(r,t) = \frac{1}{\rho(r,t)} \int d^3v v f_{\text{loc}}(r,v,t) = \frac{\langle v \rangle_{\text{loc}}}{\rho(r,t)}
\]
\[
\bar{E}(r,t) = \frac{1}{m} \int d^3v \left( \frac{C(r,t)^2}{2} \right) f_{\text{loc}}(r,v,t) = \frac{\langle C(r,t)^2 \rangle_{\text{loc}}}{2\rho(r,t)}
\]

where \( \bar{v}(r,t) \) is the internal energy density per unit mass and \( C(r,t) = v - \bar{v}(r,t) \), which is the velocity of a molecule relative to the bulk fluid velocity. The local temperature can be defined from the local energy density equation…
\[
\bar{E}(r,t) = \frac{3k_B T(r,t)}{2m}
\]

(12.8)

- In BGK theory the collision operator assumes the simple linear form
\[
\frac{df}{dt} = \frac{\partial f}{\partial t} + v \cdot \frac{\partial f}{\partial r} + a \cdot \frac{\partial f}{\partial v} = -\frac{f - f_{\text{loc}}}{\tau}
\]

(12.9)

- This equation is based on the idea that as a result of intermolecular collisions, the velocity distribution \( f \) will relax to a local equilibrium distribution in a time \( \tau \), the relaxation time, which is on the order of the inverse of the average collision rate. Equation (12.9) is called the BGK equation.
- An important use of (12.9) is to obtain \( f(r,v,t) \) which in turn is used to calculate transport coefficients. Before doing so, we briefly review the idea of transport, concentrating on viscosity.

B. Transport

- Transport properties are characteristic of a system not at equilibrium. In the present context they express the response of a dilute gas to mild displacements from equilibrium. Transport occurs when a physical property of the system varies over space, for example. In response to a gradient in a property, the system transports mass, heat, momentum, etc. Transport equations have the form of a “current”, i.e. a quantity transported per unit time, expressed as being proportional to the gradient. The constant of proportionality to called a transport coefficient. Examples include:
- Heat Conduction: In response to a temperature gradient in the z direction, heat is transported. \( h = -\lambda \frac{dT}{dz} \) where \( h \) is the heat current density and \( \lambda \) is the thermal conductivity coefficient.

- Diffusion: In response to a density gradient, mass is transported according to \( i = -D \frac{dn}{dz} \) where \( i \) is the mass current density and \( D \) is the diffusion coefficient.

- Electrical current: In response to a gradient in the electrostatic potential \( V \) a charge current \( I \) will occur according to \( I = V/R \), where \( R \) is the electrical resistance and \( 1/R \) is the electrical conductivity.

- Viscosity: In response to a velocity gradient a shearing stress \( \pi \) appears which physically corresponds to a momentum current density. The shearing stress is related to the velocity gradient by \( \pi = \eta \frac{dc}{dz} \) where \( \eta \) is the viscosity coefficient.

C. Shearing Stress & Momentum Transport

- Viscosity is manifested when a fluid flows over a surface. The fluid lamina closest to the surface are assumed to move at a lower velocity than the lamina farthest from the surface. Suppose a fluid is constrained between two flat, parallel plates. Assume the normal to the plates is the z direction. Now one plate is translated at velocity \( c_0 \) relative to the other and in the y direction. Now the fluid closest to the mobile plate will be carried along at a velocity \( c_0 \). But because the fluid lamina closest to the immobile plate are also immobilized, a velocity gradient is created. As a result of the gradient in the y velocity...also called a momentum gradient, y momentum must be transported in the z direction from right to left.

- The rate at which molecules traveling in the z direction at velocities
between \(v_z\) and \(v_z + dv_z\) cross the barrier at \(z\) in unit time is \(v_z f(v) dv_z\). If the gradient in \(v_y\) is linear in the \(z\) direction the rate of momentum transport over the barrier per unit volume is then

\[
\rho m (v_y - \gamma z) v_z f(v) dv_z
\]  

(12.10)

where \(\rho = \frac{N}{V}\) and \(\gamma = \frac{\partial c_0}{\partial z}\). The total momentum transport is then

\[
\pi_{yz} = -\rho m \int dv_x \int dv_y (v_y - \gamma z) \int dv_z v_z f(v)
\]  

(12.11)

where \(\pi_{yz}\) is the \(yz\) component of the stress tensor. Diagonal elements of the stress tensor are called pressures. Off-diagonal elements are called shearing stresses. That is

\[
\pi = \begin{pmatrix}
p_{xx} & \pi_{xy} & \pi_{xz} \\
\pi_{yx} & p_{yy} & \pi_{yz} \\
\pi_{zx} & \pi_{zy} & p_{zz}
\end{pmatrix}
\]  

(12.12)

At equilibrium shearing stresses are zero and \(p_{xx} = p_{yy} = p_{zz} = P\), so (12.12) assumes scalar form and \(\pi\) is called the equilibrium pressure

\[
\pi = P \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]  

(18.10)

D. Solution of the BGK Equation

- To calculate a transport coefficient we first assume that displacement from equilibrium is slight. The field-free BGK equation has the approximate form

\[
\frac{df}{dt} = \frac{\partial f}{\partial t} + v \cdot \nabla f \approx v \cdot \nabla f = -\frac{f - f_{\text{loc}}}{\tau}
\]  

(12.13)

- Now the key assumption...if displacement from local equilibrium is slight, we assume

\[
f(v, r) = f_{\text{loc}} \left(1 + g(v_x, v_y, -\gamma z, v_z)\right)
\]

\[
= \rho \left(\frac{m}{2\pi kT}\right)^{3/2} \exp \left(-m \frac{v_x^2 + (v_y - \gamma z)^2 + v_z^2}{2kT}\right) \times \left(1 + g(v_x, v_y, -\gamma z, v_z)\right)
\]  

(12.14)

where the function \(g\) is zero at local equilibrium. Putting (12.14) into (12.13) we can determine the form of \(g\)...
\[ g(v) = -\frac{\gamma m v_z}{kT} (v_y - \gamma z)v_z \]  

(12.15)

- We now take the form for \( f \) given in (12.14) and (12.15) and substitute it into (12.11)...

\[
\pi_{yz} = \left( \frac{\rho m^2 \gamma \tau}{kT} \right)^{3/2} \int dv_z \int dv_y (v_y - \gamma z)^2 \int dv_x v_x^2 \exp \left\{ -m v_x^2 + \left( v_y - \gamma z \right)^2 + v_z^2 \right\} \]

(12.16)

- If you like doing integrals the task of solving (12.16) is a real joy, and in any case yields...

\[
\pi_{yz} = \rho \tau kT \times \gamma
\]

(12.17)

- The relaxation time \( \tau \) is approximated by the inverse of the collision rate...which is ...

\[
\tau \approx \frac{1}{\bar{R}} = \frac{1}{\sqrt{2\bar{v} \rho \sigma}} \ldots \text{where } \bar{v} = \sqrt{\frac{8kT}{\pi m}}
\]

(12.18)

and \( \sigma \) is the collision cross section.

- Substituting (12.18) into (12.17)...note that \( \pi = \eta \frac{dc}{dz} = \eta \gamma \)

\[
\pi_{yz} = \frac{\pi}{4\sigma} \sqrt{\frac{m kT}{\pi}} \gamma = \eta \gamma \Rightarrow \eta \approx (0.78) \frac{1}{\sigma} \sqrt{\frac{m kT}{\pi}}
\]

(12.19)

- More “rigorous” treatments of the Boltzmann equation yield viscosity values in the range

\[
\eta = \frac{\kappa}{\sigma} \sqrt{\frac{m kT}{\pi}} \ldots \text{where } \kappa = 0.78 \rightarrow 1.47
\]

(12.20)

**References:** This is a tough subject. The most comprehensive recent text I have seen is by Liboff, entitled “Kinetic Theory...”. This is an advanced physics-oriented text and is not for the faint-of-heart. Zwanzig’s text ”Non-equilibrium Statistical Mechanics” includes a brief and clear discussion of the BGK equation. I would avoid McQuarrie who, except for a few text problems, fails to even mention the BGK equation. But for readability, Wannier’s somewhat-dated text ”Statistical Physics” is preferred, and I used it in designing these notes.