The Nonequilibrium Distribution function

- If a distribution changes with time, then it is an non-equilibrium distribution.
- Consider the following:
  - Gas confined to the center of a large container.
  - The confining walls are removed.
  - The gas expands to fill the container.
  - The gas reaches equilibrium with the new volume.
  - What are the properties of the distribution before equilibrium is reached?
  - What role do collisions play in the evolution of the nonequilibrium distribution?
- Like the equilibrium distribution, the nonequilibrium distribution depends on:
  - velocity
  - position
- In addition the distribution depends on time.

- Thus the nonequilibrium distribution function, f^* may be written as:

  $$f^*(v_x, v_y, v_z, x, y, z, t)\ dv_x\ dv_y\ dv_z\ dx\ dy\ dz$$

  which may be interpreted that a molecule at time t is in the volume $dx\ dy\ dz$ located at (x, y, z) with velocity in the range $dv_x\ dv_y\ dv_z$ at (v_x, v_y, v_z).

  - Note that the nonequilibrium distribution function, f^*, depends explicitly on t as well as through the coordinates (x, y, z) and velocities (v_x, v_y, v_z).

- The derivative of f^* with respect to time is:

  $$\frac{df^*}{dt} = \frac{\partial f^*}{\partial v_x}\frac{dv_x}{dt} + \frac{\partial f^*}{\partial v_y}\frac{dv_y}{dt} + \frac{\partial f^*}{\partial v_z}\frac{dv_z}{dt}$$

  $$+\frac{\partial f^*}{\partial x}\frac{dx}{dt} + \frac{\partial f^*}{\partial y}\frac{dy}{dt} + \frac{\partial f^*}{\partial z}\frac{dz}{dt} + \frac{\partial f^*}{\partial t}$$

- Consider the three terms involving the coordinates:

  $$\frac{\partial f^*}{\partial x}\frac{dx}{dt} + \frac{\partial f^*}{\partial y}\frac{dy}{dt} + \frac{\partial f^*}{\partial z}\frac{dz}{dt}$$

- Note that $dx/dt = v_x$, $dy/dt = v_y$, and $dz/dt = v_z$
- Note that $\partial f^*/\partial x$, $\partial f^*/\partial y$, and $\partial f^*/\partial z$ are the spatial gradients of f^*.
- This can be written in vector short hand notation:
$$\frac{\partial f^*}{\partial x}\frac{dx}{dt} + \frac{\partial f^*}{\partial y}\frac{dy}{dt} + \frac{\partial f^*}{\partial z}\frac{dz}{dt} = \nabla f^* \cdot \mathbf{v}$$
where $\nabla = \partial/\partial x + \partial/\partial y + \partial/\partial z$, $\mathbf{v}$ is the velocity vector and $\cdot$ means the vector dot product. (∇ may be read as "nabla" or "grad".)
- Now consider:
$$\frac{\partial f^*}{\partial v_x}\frac{dv_x}{dt} + \frac{\partial f^*}{\partial v_y}\frac{dv_y}{dt} + \frac{\partial f^*}{\partial v_z}\frac{dv_z}{dt}$$
  - Note that dv_x/dt, dv_y/dt, and dv_x/dt are the components of acceleration vector $\mathbf{a}$ and that $\mathbf{F_{ext}} = m\mathbf{a}$. Therefore:

$$\frac{\partial f^*}{\partial v_x}\frac{dv_x}{dt} + \frac{\partial f^*}{\partial v_y}\frac{dv_y}{dt} + \frac{\partial f^*}{\partial v_z}\frac{dv_z}{dt} = \nabla_v f^* \cdot \frac{\mathbf{F_{ext}}}{m}$$

- Therefore:
$$\frac{df^*}{dt} = \nabla f^* \cdot \mathbf{v} + \nabla_v f^* \cdot \frac{\mathbf{F_{ext}}}{m} + \frac{\partial f^*}{\partial t}$$

- When
$$\frac{\partial f^*}{\partial t} = 0$$
the system is in a steady state or at equilibrium.
    - In a steady state, the properties of the system at a particular point in space do not change with time.
- When
$$\nabla_v f^* \cdot \frac{\mathbf{F_{ext}}}{m} = 0$$
There are no external forces on the system.
- When something is being transported
$$\nabla f^* \cdot \mathbf{v} \neq \ 0$$

The Molecular Basis of f^*

- Recall that f^* is proportional to a probability.
    - We are concerned with molecular concentrations or number density.
- If the system is not at equilibrium, then we are concerned with number densities that depend on position and N/V is an insufficient description.

$$
\begin{aligned}
dN &= n(x,y,z,t)(f^*(v_x,v_y,v_z,x,y,z,t)d^3\mathbf{v}d^3\mathbf{r} \\
&= F^*(v_x,v_y,v_z,x,y,z,t)d^3\mathbf{v}d^3\mathbf{r}
\end{aligned}
$$

where

  - dN is the number of molecules at time t in the six-dimensional volume element defined by the velocity and position coordinates $d^3\mathbf{v}d^3\mathbf{r} = dv_x\ dv_y\ dv_z\ dx\ dy\ dz$.
  - F^* is the number density distribution function, $F^* = nf^*$.

- Consider the evolution of the number density distribution function through the time interval dt.
  - Molecules move due to their velocity and any acceleration caused by external forces.
  - Positions change from $\mathbf{r}$ to $\mathbf{r}' = \mathbf{r} + \mathbf{v}\ dt$
  - Velocities change from $\mathbf{v}$ to $\mathbf{v}' = \mathbf{v} + \mathbf{a}\ dt$
  - The number, dN', in $d^3\mathbf{v}\ d^3\mathbf{r}$ at $\mathbf{r}'$ and $\mathbf{v}'$ is:

$$
dN' = F^*(\mathbf{v}', \mathbf{r}', t + dt)d^3\mathbf{v}\ d^3\mathbf{r}
$$

- But collisions may cause molecules to enter or leave the volume element $d^3\mathbf{v}\ d^3\mathbf{r}$. The contribution this makes is dN_{coll}

  $$dN' - dN = dN_{coll}$$

  Therefore

$$dN_{coll} = \left[F^*(\mathbf{v}', \mathbf{r}', t+dt) - F^*(\mathbf{v}, \mathbf{r}, t)\right] d^3\mathbf{v}\ d^3\mathbf{r}$$

  But

$$\left[F^*(\mathbf{v}', \mathbf{r}', t+dt) - F^*(\mathbf{v}, \mathbf{r}, t)\right] = dF^* = \frac{dF^*}{dt}dt$$

  Therefore

  $$dN_{coll} = \frac{dF^*}{dt}dt\ d^3\mathbf{v}\ d^3\mathbf{r}$$

  Analogous to the treatment of f^*:

  $$\frac{dF^*}{dt} = \nabla F^* \cdot \mathbf{v} + \nabla_v F^* \cdot \frac{\mathbf{F_{ext}}}{m} + \frac{\partial F^*}{\partial t}$$

  and

$$dN_{coll} =$$

$$\left(\nabla F^* \cdot \mathbf{v} + \nabla_v F^* \cdot \frac{\mathbf{F_{ext}}}{m} + \frac{\partial F^*}{\partial t}\right) dt\ d^3\mathbf{v}\ d^3\mathbf{r}$$

- Now collisions must be considered explicitly.
    - dN_{coll} is the net change of molecules scattered in and out of $d^3\mathbf{v}\ d^3\mathbf{r}$ in time dt.
    - The rate of change of this with time is:

$$\frac{dN_{coll}}{dt} = (\text{time rate of change of F}^*) d^3\mathbf{v}\ d^3\mathbf{r}$$

- Finding the time rate of change is difficult. The result is the *Boltzmann Transport Equation* which is difficult to solve.
    - Need to use approximations instead.
- Consider a system sufficiently close to equilibrium that $F^* \cong F$.
    - F is the equilibrium number density distribution function Nf/V.
    - If the system is isolated, F^* should go smoothly and quickly toward F.
- Consider Ar(g) at equilibrium at 300 K.
    - Alter the equilibrium by taking half the molecules at v_x=250 m s^{-1} and reverse their direction.

  - The distribution will be the equilibrium distribution except for spikes at $v_x = \pm 250$ m s^{-1}.
  - The system then *relaxes* smoothly toward equilibrium.
- Consider first the spike at v_x =-250 m s^{-1}.
  - $f^* > f$ or $f^* - f > 0$. Therefore $df^*/dt < 0$.
  - The spike drops until equilibrium is reached.
- For the spike at v_x =+250 m s^{-1}.
  - $f^* < f$ or $f^* - f < 0$. Therefore $df^*/dt > 0$.
  - The spike rises until equilibrium is reached.
- Thus it can be shown that df^*/dt dF^*/dt, and dN_{coll}/dt have the same sign and that the sign is opposite to that of $(f^* - f)$ or $(F^* - F)$.
- When F^* is not far from F it may be assumed that dN_{coll}/dt is directly proportional to the difference between F^* and F

$$\text{(time rate of change of F}^*) \propto \ (F^* - F)$$

  - This is known as the *linear response regime.*

  - What affects the proportionality factor?
  - Since it is collisions that cause the relaxation, the average time between collisions τ_{coll} will be involved. If it is assumed that this is the proportionality factor, then:

$$\frac{dN_{coll}}{dt} = \frac{F^* - F}{\tau_{coll}} d^3\mathbf{v}\ d^3\mathbf{r}$$

- Thus, in the linear response regime, the Boltzmann transport equation become linearized:

$$\nabla F^* \cdot \mathbf{v} + \nabla_v F^* \cdot \frac{\mathbf{F_{ext}}}{m} + \frac{\partial F^*}{\partial t} = -\frac{F^* - F}{\tau_{coll}}$$

What is τ_{coll}?

- Consider λ, the mean free path or the average distance travelled between collisions.
- Consider the cross section σ
  - A cross section may be determined for **any** type of interaction potential.
  - For most potentials, the cross section varies with relative speed of the collision partners.

  - Collision cross sections for slow speeds can be larger than those for faster speeds since the molecules have more time to interact under the influence of the interaction potential.

- A velocity-specific free path needs to be considered.

$$\lambda(\mathbf{v}) = v\tau_{coll}(\mathbf{v})$$

  where:

  - $\lambda(\mathbf{v})$ is the free path of a molecule with velocity $\mathbf{v}$,
  - v is the speed corresponding to velocity $\mathbf{v}$,
  - $\tau_{coll}(\mathbf{v})$ is the time between collisions for a molecule with velocity $\mathbf{v}$.
  - $v\tau_{coll}(\mathbf{v})$ is the distance travelled at speed v before the next collision.
  - We must now get the average of $\tau_{coll}(\mathbf{v})$ over all velocities.

- The collision rate is the reciprocal of τ_{coll}, i.e. τ_{coll}^{-1}

- To determine the collision rate:
  - Consider molecules with velocity $\mathbf{v}_1$ colliding with molecules of velocity $\mathbf{v}$.
  - The relative speed of these molecules is $g = |\mathbf{v}_1 - \mathbf{v}|$
  - The collision cross section is $\sigma(g)$
  - n is the number density of target molecules with velocity $\mathbf{v}$.
  - The flux of molecules with velocity $\mathbf{v}_1$ toward the collision partners is gn.
- The collision rate for molecules with velocity $\mathbf{v_1}$ is the product of flux and cross section.

$$\tau_{coll}^{-1}(\mathbf{v_1}) = gn\sigma(g)$$

- Consider (see Figure 25.2) a frame of reference in which the target molecules are still (i.e. both the frame of reference and the target molecules are moving with velocity $\mathbf{v}$).
- The unit area holding the target molecules is considered as the end of a solid of length $g\ dt$.
  - The target molecules take up a fraction of this unit area.

  - The solid defines a volume containing a flux of molecules that are moving with uniform speed g
  - In the time, dt, all the molecules contained in the volume moving with speed g will move through the unit area unless they collide with a target molecule.
- We can find the average collision rate for one molecule of type 1:

$$z_1 = \tau_{coll}^{-1} = \int g\ \sigma(g)\ F^*(\mathbf{v}) d^3\mathbf{v} = n\ \langle g\sigma \rangle$$

  - If a system is at equilibrium, this is a constant.
  - If a system is not at equilibrium, then n depends on time and space.
- Recall that:

$$\lambda(\mathbf{v}) = v\tau_{coll}(\mathbf{v})$$

- Thus at conditions of equilibrium:

$$\lambda = \int \lambda(\mathbf{v}) f(\mathbf{v}) d^3\mathbf{v} = \frac{\langle v \rangle}{n\langle g\sigma \rangle}$$

  - If σ is independent of velocity then $\langle g\sigma\rangle = \langle g\rangle\sigma$ and $\langle g\rangle = \sqrt{2}\langle v\rangle$
  - At equilibrium $n = N/V$, therefore:

    $$\lambda = \frac{\langle v\rangle V}{N\sqrt{2}\langle v\rangle\sigma} = \frac{V}{\sqrt{2}N\sigma}$$

    (which is the equation we previously derived).

- The mean collision rate gives an upper limit on reaction rates.
  - Why don't all collisions lead to reaction?

Collisions between Unlike Molecules

- The cross section for a collision depends specifically on the types of molecules undergoing collision.
- Consider a binary mixture of gases 1 and 2.
  - σ_{11} is the cross section for collision of a type 1 molecule with another molecule of type 1.
  - σ_{22} is the cross section for collision of a type 2 molecule with another molecule of type 2.
  - σ_{12} is the cross section for collision of a type 1 molecule with another molecule of type 2.

- With hard sphere molecular diameters of d_1 and d_2, the cross sections are:

$$\sigma_{11} = \pi d_1^2$$

$$\sigma_{22} = \pi d_2^2$$

$$\sigma_{12} = \frac{\pi(d_1 + d_2)^2}{4}$$

- The mean collision rate for molecules of type 1 with molecules of type 2.

$$z_{12} = n_2 \langle g \rangle \sigma_{12} = n_2 \left(\frac{8 k_B T}{\pi \mu_{12}} \right)^{1/2} \sigma_{12}$$

  where μ_{12} is the reduced mass of molecule 1 with molecule 2.

  - Note the dependence of this rate on the number density of molecule 2, the target molecule.

Total Collision Rate per Unit Volume

- The total collision rate per unit volume is the collision rate per molecule times the number density for that molecule.

- If there is one component in the gas:

  $$Z_{11} = \frac{1}{2} n z_1 = \frac{1}{2} \langle g\sigma \rangle n^2 = \frac{\sigma \langle v \rangle}{\sqrt{2}} n^2$$

  where the factor of 1/2 ensures that collisions are not double counted.

- If there are two components in the gas, then:

  $$Z_{12} = n_1 z_{12} = n_2 z_{21} = \langle g\sigma \rangle n_1 n_2$$

  where $\langle g\sigma \rangle \cong \langle g \rangle \sigma_{12}$

- See the summary in table 25.1

Macroscopic Non-equilibrium Phenomena

- We will consider
  - Diffusion
  - Thermal conduction
  - Electrical conduction
  - Viscosity
- The evolution of nonequilibrium systems is governed by the Second Law of Thermodynamics.
  - In an isolated system, a spontaneous process will continue until maximum entropy is reached subject to the constraints of the system.

  - Nonequilibrium thermodynamics may be considered in terms of the time dependence of entropy.

- Recall the formulation of chemical potential (μ) in terms of the minimization of the potential and the maximization of entropy.
  - Chemical potential gradients will drive the system toward equilibrium.
  - These gradients are of macroscopic parameters such as temperature, concentration, or density.

- For a system at equilibrium:

$$\mu(T, P) = \mu^\circ(T) + RT \ln \left(\frac{P}{1 \text{ bar}} \right)$$

- Consider a closed system with a temperature gradient in the x direction and with uniform pressure.
  - The chemical potential gradient is:

$$\frac{\partial \mu}{\partial x} = \frac{\partial \mu}{\partial T} \frac{\partial T}{\partial x} = \frac{\partial(\mu^\circ + RT \ln P)}{\partial T} \frac{\partial T}{\partial x}$$

  - The spatial derivative of thermodynamic potential (in this case $\partial T / \partial x$) act as the forces that drive transport phenomena.

  - The mathematical formulation of diffusion, thermal conduction, electrical conduction, and viscosity are all similar.

- Recall the wall collision rate, J_x, or flux of molecules moving through a plane in the gas.
  - All transport phenomena may be treated in terms of the vector flux of a transported quantity.

$$\text{Flux} = \mathbf{J}(\text{something})$$
$$= \frac{\text{amount of something moving in given direction}}{(\text{unit area})(\text{unit time})}$$

- This may be applied to:
  - diffusion - transport of matter
  - thermal conduction - transport of energy
  - electrical conduction - transport of charge
  - viscosity - transport of linear momentum
- Flux increases, the further a system is from equilibrium.
  - Distance from equilibrium may be measured by the magnitude of simple gradients of macroscopic parameters.

$$\mathbf{J}(\text{something}) = -(\text{phenomenological coefficient})$$

$$\times(\text{gradient of a macroscopic parameter})$$

Diffusion

- Consider the diffusion of matter, where z is the direction of the flux of matter.

$$J_z = -D\left(\frac{\partial n}{\partial z}\right)$$

  where:

  - D is the diffusion coefficient
  - $(\partial n/\partial z)$ is the density gradient.
  - The negative sign indicates that the flux is in the direction opposite that of the gradient.
  - This equation is known as Fick's first law.

- This equation applies if the system is not far from equilibrium (i.e. in the linear response regime.)

- If the system is far from equilibrium, then the situation is more complex.
- Consider binary diffusion:
  - For example a drop of dye in water. The dye diffuses through the water until the composition is uniform.
  - Binary diffusion is defined in terms of two distinquishable species moving through each other.
- Self diffusion involves only one species.
  - May be monitored experimentally by isotopic labelling.
  - May be monitored by optical properties such as light scattering.
  - May be monitored by nuclear spin properties (NMR).
- Consider a density gradient in the z direction:
  - The flux into a region from z to $z + dz$ is given by Fick's first law evaluated at z:

$$J_{n,z} = -D\left(\frac{\partial n(z)}{\partial z}\right)$$

- The flux out of this region is given by Fick's first law evaluated at $z + dz$:

$$J_{n,z+dz} = -D\left(\frac{\partial n(z+dz)}{\partial z}\right)$$

$$= -D\left[\left(\frac{(\partial n(z)}{\partial z}\right) + \left(\frac{\partial^2 n(z)}{\partial z^2}\right)dz\right]$$

where:

$$n(z+dz) = n(z) + dn(z) = n(z) + \left(\frac{\partial n(z)}{\partial z}\right)dz$$

- The difference between flux in and flux out, per unit distance, is:

$$\frac{J_{n,z} - J_{n,z+dz}}{dz} = \frac{\partial n(z)}{\partial t}$$

- Substitution for $J_{n,z}$ and $J_{n,z+dz}$ gives:

$$\frac{\partial n(z,t)}{\partial t} = D\left(\frac{\partial^2 n(z,t)}{\partial z^2}\right)$$

which is Fick's second law.

- Fick's second law accounts for nonlinear concentration gradients.
  - If a gradient were perfectly linear and stable in time, then

    $$\left(\frac{\partial^2 n(z,t)}{\partial z^2}\right) = 0; \left(\frac{\partial n}{\partial t}\right) = 0$$

  - Spontaneous fluctuations characterized by large values of $\left(\partial^2 n(z,t)/\partial z^2\right)$ which change rapidly with time.
- Solutions to Fick's second law depend strongly on the initial conditions.

An Example of Diffusion

- Initially the solute is contained in a yz plane at $x = 0$ and $t = 0$.
- Let it diffuse from $x = 0$ to $x = \pm\infty$
- Experimentally this may be achieved by coating a thin plate on both sides with the solute and inserting it into the solvent.
- The solution to Fick's second law is:

  $$n(x,t) = \frac{N_0}{A\sqrt{4\pi Dt}} e^{-x^2/4Dt}$$

- Conservation of the number of molecules gives the normalization condition:

$$\int_{-\infty}^{\infty} n(x,t)dx = \frac{N_0}{A}$$

- Note also that this solution of Fick's second law is in the form of the Gaussian function, i.e.:

$$\exp\left[-\left(\frac{\text{distance}}{\text{width}}\right)^2\right]$$

  - In this case width$= (4Dt)^{1/2}$.
  - Note the dependence on the square root of time.
  - As the concentration gradients lessen, diffusion slows down.

- The solution to Fick's second law may be thought of in terms of a time dependent distribution function with the fraction of molecules at a particular time and position given by:

$$f(x,t) = \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/4Dt}$$

- The rms spread in x may be determined:

$$x_{rms} = \left[\int_{-\infty}^{\infty} \frac{x^2}{\sqrt{4\pi D t}} e^{-x^2/4Dt} dx\right]^{1/2}$$

$$= \left[\frac{4Dt}{\sqrt{\pi}} \int_{-\infty}^{\infty} y^2 e^{-y^2} dy\right]^{1/2} = (2Dt)^{1/2}$$

Diffusion as a Stochastic Process

- In 1905, Einstein and van Smoluchowski independently explained Brownian motion as a stochastic or random process.
    - Diffusion is one consequence of Brownian motion.
    - Individual molecules collide and as a result the molecules change direction randomly.
    - This may be simulated by a random walk.
- Consider a one dimensional random walk.
    - The initial position is $x = 0$.
    - The particle may move randomly by $x = \pm 1$ each time step.

- What is the probability that the particle has moved X units after N time steps?
- Since there are two choices at each step, there are 2^N possibilities.
- Denote the number of steps in the positive direction as N_+.
- Denote the number of steps in the negative direction as N_-.
  - The final position is:

$$X = N_+ - N_-$$

  - Since the total number of steps taken is $N = N_+ + N_-$,

$$X = N_+ - (N - N_+) = 2N_+ - N$$

or

$$N_+ = \frac{1}{2}(N + X)$$

- The number of ways, W, that N_+ may be achieved are:

$$W = \frac{N!}{N_+!N_-!} = \frac{N!}{N_+!(N - N_+)!}$$

  - In terms of position and total number of moves, this becomes:

$$W = \frac{N!}{\left[\frac{1}{2}(N+X)\right]!\left[\frac{1}{2}(N-X)\right]!}$$

- Therefore the probability of arriving X steps from the origin after N steps is:

$$P = \frac{W}{2^N} = \frac{N!}{2^N\left[\frac{1}{2}(N+X)\right]!\left[\frac{1}{2}(N-X)\right]!}$$

- Recall Stirling's Approximation:

$$\ln N! = \left(N + \frac{1}{2}\right)\ln N - N + \ln(2\pi)^{1/2}$$

- Rewriting the probability P in logarithmic form gives:

$$\ln P = \ln N! - N\ln 2 - \ln\left\{\left[\frac{1}{2}(N+X)\right]!\right\}$$

$$-\ln\left\{\left[\frac{1}{2}(N-X)\right]!\right\}$$

Therefore:

$$\ln P = \left(N + \frac{1}{2}\right) \ln N - N + \ln(2\pi)^{1/2} - N \ln 2$$

$$-\left(\left\{\left[\frac{1}{2}(N+X)\right] + \frac{1}{2}\right\} \ln \left[\frac{1}{2}(N+X)\right]\right.$$

$$\left. - \left[\frac{1}{2}(N+X)\right] + \ln(2\pi)^{1/2}\right)$$

$$-\left(\left\{\left[\frac{1}{2}(N-X)\right] + \frac{1}{2}\right\} \ln \left[\frac{1}{2}(N-X)\right]\right.$$

$$\left. - \left[\frac{1}{2}(N-X)\right] + \ln(2\pi)^{1/2}\right)$$

Rearranging gives:

$$\ln P = \left(N + \frac{1}{2}\right) \ln N - \ln(2\pi)^{1/2}$$

$$-\left(\left[\frac{1}{2}(N+X+1)\right] \ln \frac{1}{2}\right.$$

$$\left. + \left[\frac{1}{2}(N+X+1)\right] \ln \left[N\left(1 + \frac{X}{N}\right)\right]\right)$$

$$-\left(\left[\frac{1}{2}(N-X+1)\right]\ln\frac{1}{2}\right.$$

$$\left.+\left[\frac{1}{2}(N-X+1)\right]\ln\left[N\left(1-\frac{X}{N}\right)\right]\right)$$

Further rearrangement gives:

$$\ln P=\left(N+\frac{1}{2}\right)\ln N-\ln(2\pi)^{1/2}$$

$$-\left[\frac{1}{2}(N+X+1)\right]\ln\frac{1}{2}-\left[\frac{1}{2}(N-X+1)\right]\ln\frac{1}{2}$$

$$-\left[\frac{1}{2}(N+X+1)\right]\ln N-\left[\frac{1}{2}(N-X+1)\right]\ln N$$

$$-\left[\frac{1}{2}(N+X+1)\right]\ln\left(1+\frac{X}{N}\right)$$

$$-\left[\frac{1}{2}(N-X+1)\right]\ln\left(1-\frac{X}{N}\right)$$

which simplifies to:

$$\ln P=\ln\left(\frac{2}{\pi N}\right)^{1/2}-\left[\frac{1}{2}(N+X+1)\right]\ln\left(1+\frac{X}{N}\right)$$

$$-\left[\frac{1}{2}(N-X+1)\right]\ln\left(1-\frac{X}{N}\right)$$

- This with the the power series for e^x and the fact that X/N is sma!ll gives:

$$P = \left(\frac{2}{\pi N}\right)^{1/2} e^{-X^2/2N}$$

  which is an unnormalized Gaussian function.

- Normalization (i.e. integration over all space gives 1) yields:

$$\frac{1}{2}\left(\frac{2}{\pi N}\right)^{1/2} e^{-X^2/2N} = \left(\frac{1}{4\pi Dt}\right)^{1/2} e^{-x^2/4Dt}$$

- If it is assumed that a random step covers the distance $x_\circ$ such that $Xx_\circ = x$ and the time between steps is τ (i.e.$N = t/\tau$) then:

$$\frac{X^2}{2N} = \frac{x^2\tau}{2x_\circ^2 t} = \frac{x^2}{4Dt}$$

  Therefore:

$$D = \frac{x_\circ^2}{2\tau} = \frac{\lambda^2}{2\tau}$$

- Recall that:

$$\langle \tau_{coll} \rangle = \frac{\lambda}{\langle v \rangle}$$

  where $\langle v \rangle$ is the mean speed.

  - Therefore:

$$D = \frac{\langle v \rangle \lambda}{2}$$

- Therefore the diffusion is faster the larger the mean free path is.
  - The diffusion coefficient, D, increases as the square of the mean free path.
- Random walks may be studied by computer simulation (Fig. 25.6).
  - The difference between the simulation and theory varies as $\sqrt{N}$ where in this case N is the number of simulations.

Concentration Gradients

- What drives diffusion or any other transport process, are chemical potential gradients.
  - A concentration gradient is just one example of a chemical potential gradient.

  - Nonideal systems may have gradients in chemical potential which give rise to concentration gradients.

Diffusion in Solids

- Defects in the crystalline structure are important (See section 16.4 of Winn).
  - Defects can affect how diffusion occurs in a solid.
  - Defect sites themselves can diffuse through the solid.
  - Annealing or tempering is a way to minimize defects in a solid.
- Small molecules such as H_2 or He can diffuse through the interstitial sites in a crystalline solid.
  - Reactions of the solid with the diffusing molecules can change the properties of the solid (i.e. poisoning of a catalyst).
- Consider two pure metals or alloys, A and B

- A and B are a diffusion couple which initially have a distinct interface and diffuse into each other.
- If one metal diffuses into the other much more rapidly, then the Hartley-Kirkendall may be observed.
- Let B be the faster moving metal.
- As diffusion proceeds, the interface of the AB region appears to move towards B.
- Vacancies appear in B as the atoms move into A and diffusion may be interpreted as the movement of the vacancies themselves.
- The mutual diffusion coefficient, D_{AB} is proportional to $x_A D_B + x_B D_A$ where x_A and x_B are mole fractions and D_A and D_B are the self-diffusion coefficients.
- If B diffuses quickly then $D_B >> D_A$ and as B moves into A, $x_A >> x_B$.
  - Then $D_{AB} \cong \; D_B$
- A is moving slowly into B and from that perspective, $D_{AB} \cong \; D_A$
- The interface moves toward B and as B depletes, vacancies form.

Thermal Conduction

- Encounter it frequently in our day-to-day life.
  - Insulation of walls
  - Heat loss through different types of windows
  - Styrofoam food containers
- Temperature gradient transports energy.

$$J_{q,z} = -k \left(\frac{\partial T}{\partial z} \right)$$

  where k is thermal conductivity (W m^{-1} K^{-1})
  - This equation is known as "Fourier's Law".
- What affects the value of k?
  - For elements, k reflects periodic trends.
  - Metals typically have k between 10-300 W m^{-1} K^{-1} (for example Ag has k= 430 W m^{-1} K^{-1}) .
  - Diamond has k= 1370 W m^{-1} K^{-1}.
  - Graphite has k= 129 W m^{-1} K^{-1}.

- Molecular solids have lower k.
    - Red phosphorous k= 13.2 W m^{-1} K^{-1}.
    - White phosphorous k= 0.44 W m^{-1} K^{-1}.
- What affects the ability of of solids to conduct heat:
    - The physical state of the system (i.e. polycrystalline or single crystal)
    - Anisotropy of physical structure.
    - Lattice vibrations (phonons), especially insulating materials.
    - Electron mobility in metals and semiconductors (more important than phonons in conducting materials.
- How do liquids conduct heat?
    - Liquids generally have lower conductivity than solids.
    - k= 0.03 W m^{-1} K^{-1} for liquid He at 4.2 K.
    - k= 0.10-0.15 W m^{-1} K^{-1} for most molecular liquids.

  - k= 0.61 W m^{-1} K^{-1} for water.
  - $k > 10$ W m^{-1} K^{-1} for liquid metals.
- The mechanism for heat transfer is energy transfer in molecular collisions and is related to the speed of sound in the liquid.
  - Therefore thermal conductivity in a liquid is related to heat capacity.
- Thermal conductivity in gases is related to the pressure of the gas.
- Thermal conductivity usually increases with temperature at temperatures above room temperature.
  - The temperature dependence of thermal conductivity in single crystal solids in very nonlinear at low temperature.

Electrical Conduction

- Metals conduct electricity well.
- Insulators do not conduct electricity.
- Semiconductors can conduct electricity, but not as well as metals.

- The high conductivity of metals can be interpreted in terms of the structure of the metals and the mobility of the conduction elections in the conducting band.
- Ohm's Law is the flux gradient equation for charge transport:

  $$J_{e,z} = -\sigma_e \left(\frac{\partial \phi}{\partial z} \right)$$

  where:

  - $J_{e,z}$ is the electron flux in C m^{-2} s^{-1} or A m^{-2}
  - σ_e is the electical conductivity in S m^{-1} or A^2 s^3 kg^{-1} m^{-3}. (S stands for siemens where 1 S = 1 A V^{-1} and is the reciprocal of the ohm.)
  - ϕ is the potential difference in V or J C^{-1}
  - z is distance in m.
- A variant of Ohm's Law is $E = IR$ where:
  - E is the electomotive force or voltage.
  - I is the current

  - R is the resistance (which is the reciprocal of the conductance.)
- The relationship between resistance and conductivity is:

$$\sigma_e = \frac{1}{R}\frac{\text{length}}{\text{area}}$$

  - Thus the bulk resistance of something depends on its size.
- Consider a sample of area A
  - The current I is constant
  - The voltage difference over a distance Δz (in the direction of the current flow) is $V_2 - V_1$.
  - Therefore the resistance is:

$$R = \frac{E}{I} = \frac{V_2 - V_1}{I}$$

  - The flux of electrons $J_{e,z}$ or the current density is:

$$J_{e,z} = \frac{I}{A} = \frac{\sigma_e |V_2 - V_1|}{\Delta z}$$

  - Resistance R, resistivity ρ_e, and conductivity σ_e, are all related by:

$$R = \frac{\Delta z}{\sigma_e A} = \frac{\rho_e \Delta z}{A}$$

- Electrical conductivities (S m^{-1}) span over 24 orders of magnitude for ordinary substances (not superconductors).
- Metals have high values:
  - Ag 6.3×10^7 S m^{-1}
  - Cu 5.85×10^7 S m^{-1}
  - Stainless steel 0.14×10^7 S m^{-1}
- Conductivity of carbon depends on the form:
  - Graphite 10^5 S m^{-1}
  - Diamond 10^{-8} S m^{-1}
- Semiconductors span several orders of magnitude:
  - Si 2.52×10^{-4} S m^{-1}
  - Ge 1.45 S m^{-1}
  - “gray” Sn 136 S m^{-1}

- Other elements
    - Iodine 7.7×10^{-8} S m^{-1}
    - Sulphur 5×10^{-16} S m^{-1}
- Polymers are often poor conductors:
    - Polyethylene 10^{-15} S m^{-1}
    - Polytetrafluoroethylene 10^{-17} S m^{-1}
- Conductivities of solutions depend strongly on the composition (i.e. electrolytes) of the solution.
- Conductivities of gases are extremely low unless the gas is subject to a high electric field that can ionize atoms and molecules.
- Conductivity and resistivity are temperature dependent.

Viscosity

- There are various types of viscosity. We will focus on shear viscosity.
- Viscosity is related to the flux of momentum.

- Newton's viscous law is:

$$J_{mv,zx} = -\eta \left(\frac{\partial v_x}{\partial z} \right)$$

    - Flux, $J_{mv,zx}$, has units of momentum per unit time per unit area.
    - However flux is easily interpreted as pressure because although momentum per unit time is a force, the direction of the force is parallel to the area and not perpendicular to it.
    - Viscosity, η, has units of Pa s or poise (1 P = 0.1 Pa s)
    - Hydrodynamics treats viscosity in great detail.

- Consider shear viscosity (Figure 25.9).
    - Consider an xz plane in a fluid.
    - Move a large thin plate (xy plane) in the x direction with velocity v_x.
    - A thin layer of fluid in contact with the plate moves with velocity v_x.

- The layer of fluid in contact with the fixed container is moving with zero velocity.
- This produces a velocity gradient in the z direction.
- If the container is not fixed and the fluid sufficiently viscous, then the motion of the plate will cause the container to move.
- This means that x momentum has been transferred along the z direction.
- This is an example of a shear force.
- This type of viscosity is called shear viscosity.

Some Representative Viscosities

- Cold molasses ≈ 1 Pa s
- Gylcerol ≈ 1.5 Pa s
- Water $\approx 10^{-3}$ Pa s
- Viscosity may also be expressed in units of poise (P).
  - 1 Pa s = 1 kg m^{-1} s^{-1}
  - 1 P = 1 g cm^{-1} s^{-1}, therefore 1 P = .1 Pa s; 1 cP = 10^{-3} Pa s; 1 μ P = 10^{-7} Pa s.

Measuring Viscosity

- The Ostwald viscosimeter is a convenient instrument for measuring the viscosity of a liquid.
- Includes a vertical capillary tube.
    - The flow of a fluid through a tube is subject to a radial velocity gradient and flows fastest in the center.
    - Flow through a capillary is subject to laminar (non-turbulent) flow.
    - The viscous force is a friction.
    - If this friction is balanced by a hydrostatic head providing pressure, then steady-state flow results.
- The viscosity of the incompressible fluid is η.
- The tube is of length L and radius R.
- ΔP is the pressure difference between the top and bottom of the tube.
- r is the distance from the center of the tube.
    - The force pushing the fluid at r is $\Delta P \pi r^2$
- The contact area is $2\pi L r$.

- The force per unit contact area is given by $(\Delta P \pi r^2)/(2\pi r L) = (\Delta P r)/(2L)$
- This force is exactly balanced by radial flux of z momentum. Therefore:

$$J_{mv,rz} = -\frac{\Delta P r}{2L} = -\eta \frac{\partial v_z}{\partial r}$$

- Thus the velocity v may be found as a function of r:

$$v_z(r) = \int_{v_z(R)}^{v_z(r)} dv_z = -\frac{\Delta P}{2L\eta} \int_R^r r dr$$

$$= \frac{\Delta P}{4L\eta} \left(r^2 - R^2\right)$$

  - The flow rate per unit time for an incompressible fluid becomes:

$$\frac{dV}{dt} = \frac{\Delta P \pi R^4}{8L\eta}$$

  - The flow rate per unit time for a compressible fluid becomes:

$$\frac{dV}{dt} = \frac{\pi R^4}{16L\eta} \frac{P_i^2 - P_f^2}{P_0}$$

where

  - P_i is the pressure at the tube's inlet,
  - P_f is the pressure at the tube's outlet,
  - P_0 is the pressure at which the volume is measured.

- The Ostwald viscometer is designed to exploit these equations.
  - Fill viscometer bulb with fluid of interest.
  - Draw fluid through capillary into calibrated bulb of volume V to above start mark.
  - Measure the time between the start and finish mark.
  - Calculate viscosity from:

$$\eta = \left(\frac{\pi R^4}{8L} \right) \frac{\rho g \langle \Delta h \rangle}{V} \Delta t$$

where ρ is the density of the fluid, g is gravitational acceleration, and $\langle \Delta h \rangle$ is the time average height difference:

$$\langle \Delta h \rangle = \frac{\Delta h_{start} - \Delta h_{finish}}{\ln \left(\Delta h_{start} / \Delta h_{finish} \right)}$$

Microscopic Transport Coefficients

- Recall the linearized Boltzmann transport equation.
  - The solution gives the non-equilibrium number density distribution function, F^*.
  - Of more interest are the transport coefficients.
- Consider flux:

$$\text{flux} = \int \begin{pmatrix} \text{quantity} \\ \text{transported} \\ \text{per} \\ \text{molecule} \end{pmatrix} \begin{pmatrix} \text{molecular} \\ \text{speed in} \\ \text{transport} \\ \text{direction} \end{pmatrix} . \\ F^*(\mathbf{v}, \mathbf{r}, t)\ dv_x dv_y dv_z$$

  - Applied to diffusion this becomes:

$$J_{n,z} = \int v_z F^*(\mathbf{v}, \mathbf{r}, t)\ dv_x dv_y dv_z = -D \left(\frac{\partial n}{\partial z} \right)$$

  - Applied to thermal conductivity this becomes:

$$J_{q,z} = \int \frac{mv^2}{2} v_z F^*(\mathbf{v}, \mathbf{r}, t)\ dv_x dv_y dv_z = -k \left(\frac{\partial T}{\partial z} \right)$$

  - Applied to electrical conductivity this becomes:

$$J_{e,z} = \int Q v_z F^*(\mathbf{v}, \mathbf{r}, t)\ dv_x dv_y dv_z = -\sigma_e \left(\frac{\partial \phi}{\partial z} \right)$$

- Applied to viscous flux of x momentum, this becomes:

$$J_{mv,zx} = \int m v_x v_z F^*(\mathbf{v}, \mathbf{r}, t)\ dv_x dv_y dv_z$$
$$= -\eta \left(\frac{\partial v_x}{\partial z} \right)$$

- From each of these it is possible to derive the transport coefficient, since each flux expression imposes constraints on the Boltzmann transport equation.

The Diffusion Coefficient

- Assumptions:
  - Steady state, thus

$$\frac{\partial F^*}{\partial t} = 0$$

  - No external forces, thus
$$\nabla_v F^* \cdot \frac{\mathbf{F_{ext}}}{m} = 0$$
  - The concentration gradient is only in the z direction, thus:
$$\nabla F^* \cdot \mathbf{v} = \left(\frac{\partial F^*}{\partial z}\right) v_z$$

- Under these conditions, the Boltzmann equation becomes:
$$\frac{\partial F^*}{\partial z} v_z = -\frac{F^* - F}{\tau_{coll}}$$
- Further assume that F^* is close to F. Define the difference F':
$$F^*(\mathbf{r}) = F(\mathbf{r}) + F'(\mathbf{r})$$
- Also assume that the spatial derivative of F' is negligible.
$$\left(\frac{\partial F^*}{\partial z}\right) \cong \left(\frac{\partial F}{\partial z}\right)$$
- With these further assumptions, the Boltzmann equation becomes:
$$\frac{\partial F}{\partial z} v_z = -\frac{F'}{\tau_{coll}}$$

- Isolating F' gives:

$$F' = -\tau_{coll}\frac{\partial F}{\partial z}v_z = -\tau_{coll}v_z\frac{\partial F}{\partial n}\frac{\partial n}{\partial z}$$

$$= \frac{-\tau_{coll}v_z F}{n}\frac{\partial n}{\partial z}$$

- Substituting $F + F'$ for F^* gives:

$$J_{n,z} = \int v_z F(\mathbf{v}, \mathbf{r}, t)\ dv_x dv_y dv_z$$

$$+ \int v_z F'(\mathbf{v}, \mathbf{r}, t)\ dv_x dv_y dv_z$$

$$= 0 + - \left(\frac{\tau_{coll}}{n}\int v_z^2 F d\mathbf{v}\right)\left(\frac{\partial n}{\partial z}\right)$$

- Therefore:

$$D = \frac{\tau_{coll}}{n}\int v_z^2 F d\mathbf{v} = \frac{\tau_{coll}}{n}\left(\frac{nk_BT}{m}\right) = \frac{\tau_{coll}k_BT}{m}$$

since $F = nf$ and $\langle v_z \rangle = k_BT/m$.

- Recalling that $\tau_{coll} = \lambda/\langle v \rangle$:

$$D = \frac{\lambda k_B T}{m\langle v\rangle} = \frac{1}{4n\sigma}\left(\frac{\pi k_B T}{m}\right)^{1/2}$$
$$= \left(\frac{\pi}{m}\right)^{1/2}\frac{(k_b T)^{3/2}}{4P\sigma}$$

where σ is the collision cross section and P is the pressure.

- Therefore:
    - Molecules with larger σ diffuse more slowly than ones with smaller σ.
    - Diffusion slows as P increases
    - Diffusion is faster at higher T

Thermal Conductivity

- A temperature gradient at constant pressure means that there is a density gradient.

  $$P = nk_B T$$

  where n is the density N/V

    - If $\partial T/\partial z \neq 0$ then $\partial n/\partial z \neq 0$ to maintain constant P.

- This means that the local equilibrium distribution function explicitly depends on z through $n(z)$ and $T(z)$:

$$F(z) = n(z)\left(\frac{m}{2\pi k_B T(z)}\right)^{\frac{3}{2}} e^{-m\left(v_x^2+v_y^2+v_z^2\right)/2k_B T(z)}$$

- Following the same procedure as we used for diffusion, the Boltzmann transport equation becomes:

$$F' = -v_z \tau_{coll}\left(\frac{\partial F(z)}{\partial z}\right)$$

and

$$\frac{\partial F(z)}{\partial z} = \frac{F}{T}\left(\frac{mv^2}{2k_B T} - \frac{5}{2}\right)\left(\frac{\partial T}{\partial z}\right)$$

- Thus $J_{q,z}$ becomes:

$$J_{q,z} = \int \left(\frac{mv^2}{2}\right) v_z F' d\mathbf{v}$$

$$= -\left[\frac{\tau_{coll}}{T}\int\left(\frac{mv^2}{2}\right) v_z^2 \left(\frac{mv^2}{2k_B T} - \frac{5}{2}\right) F d\mathbf{v}\right]\left(\frac{\partial T}{\partial z}\right)$$

- Integration yields:

$$k = \frac{5}{2}\frac{\tau_{coll} n k_B^2 T}{m}$$

- Using $\overline{C}_v = 3N_A k_B/2$ for an ideal monatomic gas, this becomes:

$$k = \frac{5}{2}\frac{\lambda n k_B^2 T}{m\langle v\rangle} = \frac{5}{2}\frac{k_B^{3/2}}{4\sigma}\left(\frac{\pi T}{m}\right)^{1/2}$$

$$= \frac{5}{12}\frac{\overline{C}_V}{\sigma N_A}\left(\frac{\pi k_B T}{m}\right)^{1/2}$$

- Thus thermal conductivity k
  - decreases for heavier molecules
  - increases with temperature
  - is independent of pressure, but the expression breaks down at low pressures and extremely high pressures.
- At intermediate pressures, the P dependence of λ is cancelled out by the P dependence of n.
- If the pressure is so low that λ is greater than the thickness of the gas layer through which the heat is conducted, then k becomes P dependent and the heat transfer does not depend on collisions.
- At high pressures, multiple collisions become an important means of heat transfer.

Electrical Conductivity

- Consider a weakly ionized gas (i.e. a plasma)
  - n_+ is the number density of positively charged ions, each with a charge of Q_+.
  - Sufficient electrons or anions are present to balance the charge and assure that the plasma is electrically neutral.
- While the net current is due to motion of all charged species, the movement of positive charges will be initially considered.
- Impose on a plasma a small potential gradient,

$$\frac{\partial \phi}{\partial z} = -E_z$$

  due to the z component of the external electric field.

  - Thus the flux gradient equation becomes:

$$J_{e,z} = \sigma_e E_z$$

- Assume that ions and neutrals have the same f^*.

  - This is reasonable because of collisions.
- Assume that $n_+ << n$
  - For the positive ions, $F^* = n_+ f^*$.
  - For the neutrals $F^* = n f^*$.
- Assume that the deviation, F' from equilibrium is small.

$$F^* = F + F'$$

- The Boltzmann equation has no spatial gradient term ($\nabla F^* = 0$), but is subject to an external force ($F_{ext,z} = Q_+ E_z$).
- Thus:

$$\nabla F^* \cdot \mathbf{v} + \nabla_v F^* \cdot \frac{\mathbf{F_{ext}}}{m} + \frac{\partial F^*}{\partial t} = -\frac{F^* - F}{\tau_{coll}}$$

  becomes:

$$\frac{\partial F}{\partial v_z} \frac{Q_+ E_z}{m} = -\frac{F'}{\tau_{coll}}$$

  which rearranges to:

$$F' = -\frac{\tau_{coll} Q_+ E_z}{m} \frac{\partial F}{\partial v_z}$$

- Since F is the equilibrium distribution,

$$\frac{\partial F}{\partial v_z} = -\frac{m v_z}{k_B T} F$$

$$F' = \frac{\tau_{coll} Q_+ E_z}{k_B T} v_z F$$

- Because $F' << F$, the electric field, E_z is small.
- The expression for flux becomes:

$$J_{e,z} = Q_+ \int v_z F' d\mathbf{v} = \left(\frac{\tau_{coll} Q_+^2}{k_B T} \int v_z^2 F d\mathbf{v} \right) E_z$$

where

$$\sigma_e = \frac{\tau_{coll} Q_+^2}{k_B T} \int v_z^2 F d\mathbf{v} = \frac{n_+ \tau_{coll} Q_+^2}{m}$$

- If it is assumed that the ions have the same cross section as the neutrals, then a substitution may be made for τ_{coll}:

$$\sigma_e = \frac{\lambda n_+ Q_+^2}{m \langle v \rangle} = \frac{n_+}{n} \frac{Q_+^2}{4\sigma} \left(\frac{\pi}{m k_B T} \right)^{1/2}$$

  - Note that the charge term is squared so that σ_e is always positive.

- It is necessary to consider other ions and other charges that are present in the solution.
  - The concept of ion mobility u is useful.
  - u is the ions' drift velocity per unit electrical field or conductivity per unit of charge concentration.

$$u_+ = \frac{\text{conductivity}}{\text{unit charge concentration}} = \frac{\sigma_e}{n_+ Q_+}$$

$$= \frac{\tau_{coll} Q_+}{m} = \frac{Q_+}{4n\sigma}\left(\frac{\pi}{mk_B T}\right)^{1/2}$$

- For two species of opposite charge with ion mobilities of u_+ and u_-, the net conductivity is:

$$\sigma_e = \sigma_+ + \sigma_- = n_+ Q_+ u_+ + n_- Q_- u_-$$

- The ratio of mobility to the diffusion coefficient is:

$$\frac{u_+}{D} = \frac{\tau_{coll} Q_+}{m} \frac{m}{\tau_{coll} k_B T} = \frac{Q_+}{k_B T}$$

Viscosity

- Consider a gas with a slow *bulk flow* in the x direction and a flow gradient in the z direction.
- The flow speed is u_x is additive to the velocity vectors of the molecule, yielding local velocity components (U_x, U_y, U_z) with respect to the *flowing* frame of reference:

$$U_z = v_z, \quad U_y = v_y, \quad U_x = v_x - u_x$$

- Assume
  - A steady state flow
  - That the distribution is slightly perturbed from equilibrium such that:

$$F^* = F + F'$$

- Thus, it can be shown that:

$$F' = -\tau_{coll} v_Z \frac{\partial F}{\partial z} = -\tau_{coll} v_Z \left(\frac{\partial F}{\partial U_x}\right)\left(\frac{\partial U_x}{\partial z}\right)$$

$$= -\tau_{coll} v_Z \left(\frac{\partial F}{\partial u_x}\right)\left(\frac{\partial u_x}{\partial z}\right)$$

- The flux expression becomes:

$$J_{mx,zx} = \int (mU_x) U_z F' d\mathbf{U} = m \int U_x v_z F' d\mathbf{U}$$

$$= \left[\tau_{coll}\ m \int \left(\frac{\partial F}{\partial U_x} \right) U_x v_z^2 d\mathbf{U} \right] \left(\frac{\partial u_x}{\partial z} \right)$$

- Thus:

$$\eta = -\tau_{coll}\ m \int \left(\frac{\partial F}{\partial U_x} \right) U_x v_z^2 d\mathbf{U}$$

$$= -\tau_{coll}\ m \int \left(-F \frac{mU_x}{k_B T} \right) U_x v_z^2 d\mathbf{U}$$

$$= \frac{\tau_{coll}\ m^2}{k_B T} \int F U_x^2 v_z^2 d\mathbf{U} = \frac{\tau_{coll}\ m^2}{k_B T} n \left(\frac{k_B T}{m} \right)^2$$

$$= n \tau_{coll} k_B T$$

- And substituting for τ_{coll} yields:

$$\eta = \frac{n \lambda k_B T}{\langle v \rangle} = \frac{(\pi k_B T m)^{1/2}}{4\sigma}$$

- Thus for a gas:
  - η increases with temperature.
  - η is independent of pressure.