- The number of collisions per unit time for a single Ar atom with Xe atoms is:

$$\frac{Z_{12}}{n_1} = \pi d^2 n_2 \langle v_{12} \rangle$$

.

- Now consider the collision frequency in a pure gas.
  - $m_1 = m_2 = m$ so that $\mu_{12} = m/2$. Therefore

$$\langle v_{12} \rangle = \left[\frac{8\pi k_B T}{\pi(m/2)} \right]^{1/2} = \sqrt{2} \langle v \rangle$$

where $\langle v \rangle$ is the average speed in pure gas.
  - The number of collisions per unit time for a single atom is multiplied by the number density, then divided by 2 to avoid double counting collisions.

- The collision frequency for a pure gas is:

$$Z = \frac{\pi d^2}{\sqrt{2}} n^2 \langle v \rangle$$

- Consider a hard-sphere gas (see Figure 28.7):
  - As one atom moves through the gas with relative speed $\langle v_{12} \rangle$, it sweeps out a cylinder of cross-sectional area πd^2.
  - The volume swept out per second is $\pi d^2 \langle v_{12} \rangle$.
  - Any other atom within this volume will collide with the first atom.
  - If the density is n and the volume $\pi d^2 \langle v_{12} \rangle$, then the number of collisions per atom per unit time is $\pi d^2 n \langle v_{12} \rangle$.
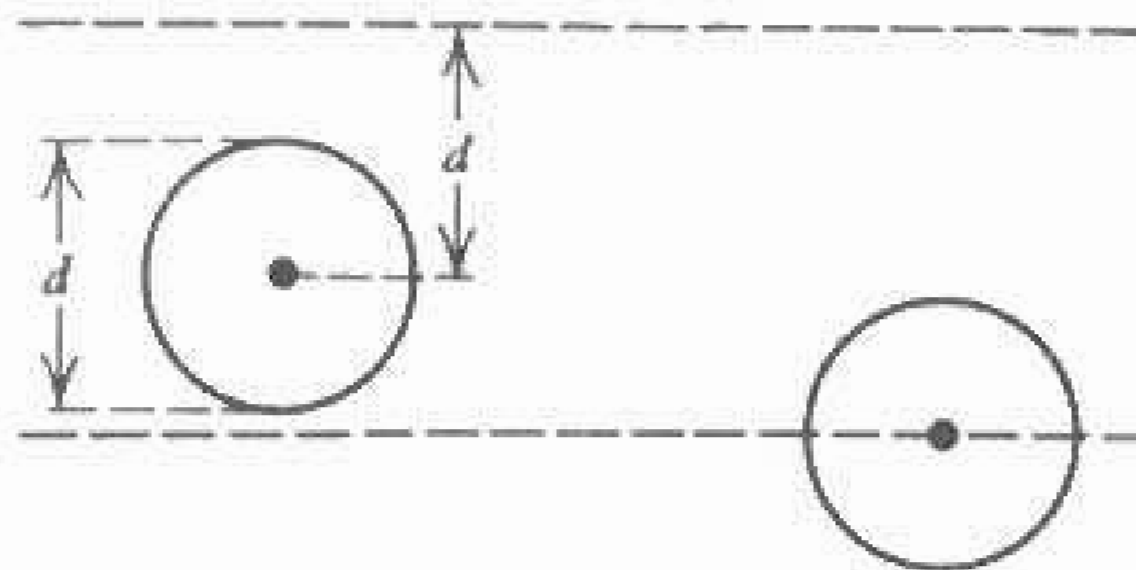
Figure 28.7 Illustrating the calculation of collision frequency for the molecular model of hard spheres.

- The mean free path is the overage distance that a molecule travels between collisions.
  - In time t an atom travels the distance $\langle v \rangle t$.
  - During time t, an atom undergoes $\pi d^2 n \langle v_{12} \rangle t$ collisions.
  - Therefore the mean free path l is:

  $$l = \frac{\langle v \rangle t}{\pi d^2 n \langle v_{12} \rangle t} = \frac{1}{\sqrt{2}\pi d^2 n}$$

  - Note that the mean free path is independent of temperature and decreases as the density increases.
  - The mean free path is not directly measurable.

Molecular Fluxes

- Three fluxes will be considered:
  - Density
  - Momentum Density
  - Energy Density
- A flux may be considered as the net flow of a physical quantity in a given direction.
- It is defined rigorously as the amount of a given quantity that flows across a surface area per unit time.
- The flux density is the flow per unit time per unit surface area.
  - Diffusion is the net flux of particles.
  - Viscous flow is produced by the net flux of momentum.
  - Thermal conduction is the flux of energy.

- Consider a hypothetical plane surface in a dilute gas.
  - The orientation of the plane is given by a perpendicular unit vector $\mathbf{k}$ pointing in the positive direction.
  - Molecules cross the planes in both directions.
  - The net flow of molecules per unit time per unit area is the quantity of interest.
- Consider molecules with velocity $\mathbf{v}$ with angle θ between $\mathbf{v}$ and $\mathbf{k}$
- In time dt a molecule with speed v moves vdt.
- Construct a parallelepiped of length vdt with base area A and inclination θ (see Figure 28.8).
  - The volume of the parallelepiped is $v\cos\theta \, dA \, dt$.
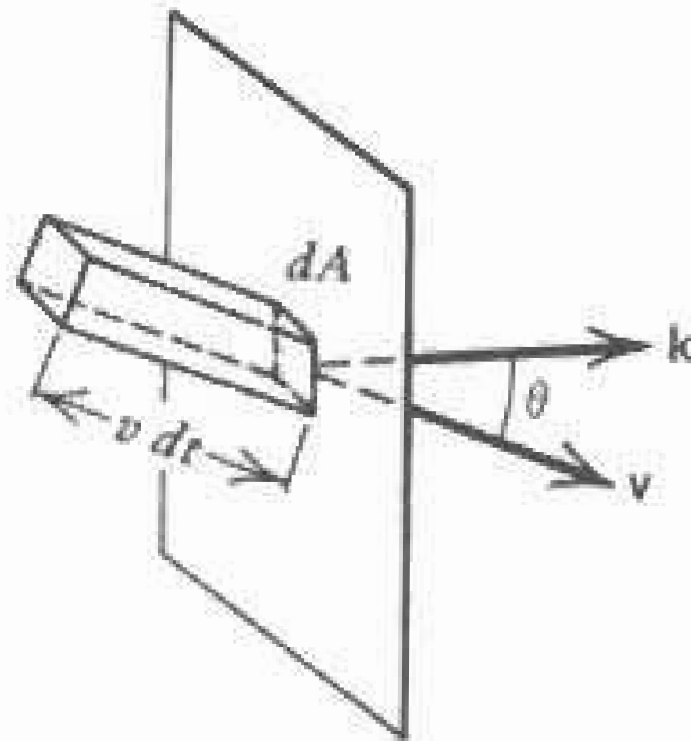 - All molecules within this volume will cross A in time dt.

Figure 28.8 Molecular flux across a plane surface. The orientation of the plane is given by the unit vector **k**, which is perpendicular to the plane.

- It is assumed that are no collisions between molecules within this volume.

- The number of molecules with velocity between $\mathbf{v}$ and $\mathbf{v} + d\mathbf{v}$ is $f(\mathbf{r}, \mathbf{v}, t)d\mathbf{v}$.

  - Therefore, the number of molecules with velocity between $\mathbf{v}$ and $\mathbf{v} + d\mathbf{v}$ that cross the plan per unit time is:
  $$v \cos \theta f(\mathbf{r}, \mathbf{v}, t)d\mathbf{v}$$

  - Integration of this over all velocities gives the number flux density, Γ_n

  $$\Gamma_n(\mathbf{r}, t) = \int_{\mathbf{v}} v \cos \theta f(\mathbf{r}, \mathbf{v}, t)d\mathbf{v}$$

  - The $\cos \theta$ factor is positive or negative depending on the direction of $\mathbf{v}$ relative to $\mathbf{k}$.

- $v \cos \theta$ may be rewritten as $\mathbf{v}\dot{\mathbf{k}}$ and keeps track of the *net* flow across the plane in the positive direction $\mathbf{k}$.

- The flux density vector is:

$$\boldsymbol{\Gamma}_n = \int_{\mathbf{v}} \mathbf{v} f(\mathbf{r}, \mathbf{v}, t) d\mathbf{v}$$

and the flux density in the $\mathbf{k}$ direction is given by:

$$\Gamma = \mathbf{k} \cdot \boldsymbol{\Gamma}_{\mathbf{n}}$$

which is a scalar.

- The flow of mass per unit time per unit area, $\boldsymbol{\Gamma}_m$ is sometimes denoted as $\mathbf{J^m}$ is:

$$\boldsymbol{\Gamma}_{\mathbf{m}} = m\boldsymbol{\Gamma}_{\mathbf{n}}$$

- Consider the flow of energy across the plane.
  - Recall the number of molecules with velocities between $\mathbf{v}$ and $\mathbf{v} + d\mathbf{v}$:

$$v \cos \theta f(\mathbf{r}, \mathbf{v}, t) d\mathbf{v}$$

.

  - Multiply this by the kinetic energy per molecule $\frac{1}{2}mv^2$ to yield:

$$\frac{1}{2}mv^2 v \cos \theta f(\mathbf{r}, \mathbf{v}, t) d\mathbf{v}$$

  as the kinetic energy flux density.
  - Thus the net energy carried by molecules across the unit area per unit time is:

$$\Gamma_E = \frac{1}{2}m \int_{\mathbf{v}} v^3 \cos\theta f(\mathbf{r}, \mathbf{v}, t) d\mathbf{v}$$

- The flow of energy per unit time per unit area is sometime denoted as $\mathbf{q}$. This is equivalent to the flux density vector $\mathbf{\Gamma}_E$ which is defined as:

$$\Gamma_E = \mathbf{k} \cdot \mathbf{\Gamma}_E$$

where

$$\mathbf{\Gamma}_E = \frac{1}{2}m \int_{\mathbf{v}} v^2 \mathbf{v} f(\mathbf{r}, \mathbf{v}, t) d\mathbf{v}$$

- Note that both mass and kinetic energy are scalars but that their fluxes are vectors.

- Momentum is a vector and the flux of momentum will be considered next.

- The flux of momentum is a tensor.
  - The flux density of momentum $\mathbf{\Gamma}_{m\mathbf{v}}$ is also denoted as J^P:

  $$\mathbf{\Gamma}_{m\mathbf{v}} = m \int_{\mathbf{v}} \mathbf{v}\mathbf{v} f(\mathbf{r}, \mathbf{v}, t) d\mathbf{v}$$

    which contains two vectors multiplied together.
  - In Cartesian space, this is a second rank tensor with nine components.
    - A vector is a first rank tensor with three components.
  - The components of $\mathbf{\Gamma}_{mv}$ are labelled by two subscripts denoting the Cartesian coordinates:

  $$(\mathbf{\Gamma}_{m\mathbf{v}})_{xy} = m \int_{\mathbf{v}} v_x v_y f(\mathbf{r}, \mathbf{v}, t) d\mathbf{v}$$

- Tensors are often represented as matrices.
  - If the indices are the same, then it is a diagonal component.
  - If the indices are different, then it is an off-diagonal component.
  - In this case the matrix is symmetric and $(\boldsymbol{\Gamma}_{m\mathbf{v}})_{xy} = (\boldsymbol{\Gamma}_{m\mathbf{v}})_{yx}$
- Consider now the physical interpretation of the elements of the momentum flux tensor.
  - Define a Cartesian coordinate system with an x axis parallel to the vector $\mathbf{k}$.
    - Thus $v_x = v\cos\theta$.
  - What is $(\boldsymbol{\Gamma}_{m\mathbf{v}})_{zz}$? (Note that the momentum component of the molecule is in the z direction.)

- It is the number of molecules of momentum mv_z with velocity between $\mathbf{v}$ and $\mathbf{v} + d\mathbf{v}$ crossing unit area of plane per unit time integrated over all velocities:

$$(\mathbf{\Gamma}_{m\mathbf{v}})_{zz} = m \int_{\mathbf{v}} v_z v_z f(\mathbf{r}, \mathbf{v}, t) d\mathbf{v}$$

- This gives the momentum in the z direction transferred across the plane per unit time and may be interpreted as a stress normal to the surface with the units of pressure:

$$\frac{1}{\text{area}} \frac{\Delta(mv)}{\Delta t} = \frac{\text{force}}{\text{area}}$$

- This is why $(\mathbf{\Gamma}_{m\mathbf{v}})$ is sometimes referred to as the pressure tensor or stress tensor.

- Now consider $(\mathbf{\Gamma}_{m\mathbf{v}})_{xz}$
  - The direction of flow is the x direction
  - The momentum is transferred in the z direction.
  - Thus, $(\mathbf{\Gamma}_{m\mathbf{v}})_{xz}$ may be considered in terms of the transfer of the total momentum in the x direction across a plane perpendicular to the z direction per unit area per unit time.

$$(\mathbf{\Gamma}_{m\mathbf{v}})_{xz} = m \int_{\mathbf{v}} v_x v_z f(\mathbf{r}, \mathbf{v}, t) d\mathbf{v}$$

- This is a sheer stress on the surface.
  - Consider a layer of gas flowing parallel to the plane with a smaller velocity in the x direction on one side of the plane than on the other.

- The molecular motion is in the x across the plane and there is a net transfer of momentum in the z direction from the faster moving to the slower moving layer.

- For a gas at equilibrium, the number of molecules with velocity between $\mathbf{v}$ and $\mathbf{v} + d\mathbf{v}$ is:

$$f(\mathbf{r}, \mathbf{v}, t)d\mathbf{v} = n\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2k_B T} d\mathbf{v}$$

- The distribution is independent of time and position since the gas is at equilibrium and is spatially uniform.

- Now consider this distribution and the flux density:

$$\Gamma_n(\mathbf{r}, t) = n\left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_{\mathbf{v}} \mathbf{v}e^{-mv^2/2k_B T} d\mathbf{v}$$

- Continued:
  - But it has already been shown that $\langle \mathbf{v} \rangle = 0$ for a gas at equilibrium.
  - Therefore there is not net flow of molecules at equilibrium.
  - Consequently the mass flow $\mathbf{\Gamma}_m$ is also zero.
  - This is to be expected for a gas at equilibrium.
- Consider now the energy flux density for a gas at equilibrium:

$$\Gamma_E = \frac{1}{2} mn \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_{\mathbf{v}} v^2 \mathbf{v} e^{-mv^2/2k_B T} d\mathbf{v}$$

- Since this is an odd function it will integrate to zero, which is the expected energy flux density for a gas at equilibrium.

- Consider now the off diagonal elements of the pressure or momentum flux density tensor which couples motion in two directions:

$$(\mathbf{\Gamma}_{m\mathbf{v}})_{xz} = mn \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_{\mathbf{v}} v_x v_z e^{-mv^2/2k_B T} dv_x dv_y dv_z$$

- When the integral is resolved into velocity components, two factors are odd and integrate to zero.

- This is consistent with the gas being at equilibrium.

- Consider now a diagonal component of the tensor.

$$(\mathbf{\Gamma}_{m\mathbf{v}})_{xx} = mn \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_{\mathbf{v}} v_x v_x e^{-mv^2/2k_B T} dv_x dv_y dv_z$$

- This is not zero.

- All the diagonal components are equivalent:

$$(\mathbf{\Gamma}_{m\mathbf{v}})_{xx} = (\mathbf{\Gamma}_{m\mathbf{v}})_{yy} = (\mathbf{\Gamma}_{m\mathbf{v}})_{zz}$$

and can be identified with the pressure.

$$p = \frac{1}{3}\left[(\mathbf{\Gamma}_{m\mathbf{v}})_{xx} + (\mathbf{\Gamma}_{m\mathbf{v}})_{yy} + (\mathbf{\Gamma}_{m\mathbf{v}})_{zz}\right]$$

- Thus:

$$p = \frac{1}{3}mn\left(\frac{m}{2\pi k_B T}\right)^{3/2}\int_{\mathbf{v}}(v_x^2 + v_y^2 + v_z^2)e^{-mv^2/2k_B T}\,dv_x dv_y dv_z$$

- Transforming to spherical coordinates gives:

$$p = \frac{1}{3}mn\left(\frac{m}{2\pi k_B T}\right)^{3/2}4\pi\int_{v=0}^{\infty}v^4 e^{-mv^2/2k_B T}\,dv$$

- Note that this has been integrated over all directions.
- Integrating over all speeds gives:

$$p = nk_B t$$

  (Recall $n = N/V$, the number density of the molecules.)
- Two assumptions in the derivation are now examined.
- One is the assumption that there collisions between molecules are ignored.
  - Collisions have the effect of increasing or decreasing the number of molecules with velocity $\mathbf{v}$.
  - If a gas is at equilibrium, then the opposing effects will cancel each other out and the assumption to ignore collisions is valid.

- The other assumption is that the net amount of particles crossing a given surface per unit time determines the flux density of particles, energy, and momentum.
  - This must be the case for molecular flux.
  - But it is not necessarily the case for transfer of energy or momentum because these can be transferred through momentum
  - Consider Figure 28.9 which shows a surface at which molecules collide.
  - Since molecules do not cross the surface, such collisions do not affect the molecular flux density.
  - Such collisions do affect the flux of momentum and energy since these can be transferred across the surface by molecular forces.
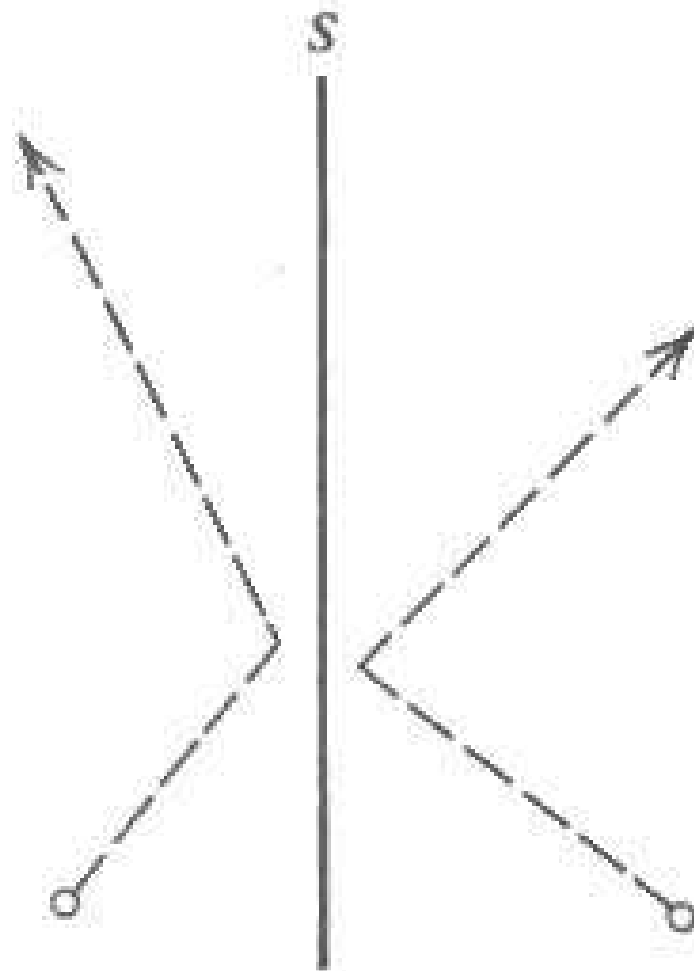
Figure 28.9 Collisional transfer across a surface S.

- The conditions for collisional energy transfer require the simultaneous presence of two molecules near surface S.

- The distance between the molecules must be within a range determined by the intermolecular forces.

- The importance of collisional transfer depends on the density of the gas.

- If the distance between the molecules is large, then the probability of collisional transfer is low and the gas may be considered at perfect gas.

- If the distance between the molecules is small, collisional transfer will dominate.

  - In a liquid, the dominant mechanism for energy or momentum transport is collisional transfer.

Effusion

- Consider the effusion of a gas.
  - A vessel is filled with gas at low pressure as in Figure 28.10.
  - The vessel has a small hole through which the gas escapes.
  - The vessel is surrounded by a vacuum chamber, which is maintained by a vacuum pump.
  - The pressure is the vacuum chamber is low enough that the probability of molecules moving from the vacuum chamber into the vessel is negligible.
  - Conditions need to be such that the molecules emerge independently through the hole.
    - This can be satisfied if the diameter of the hole is smaller than the mean free path.
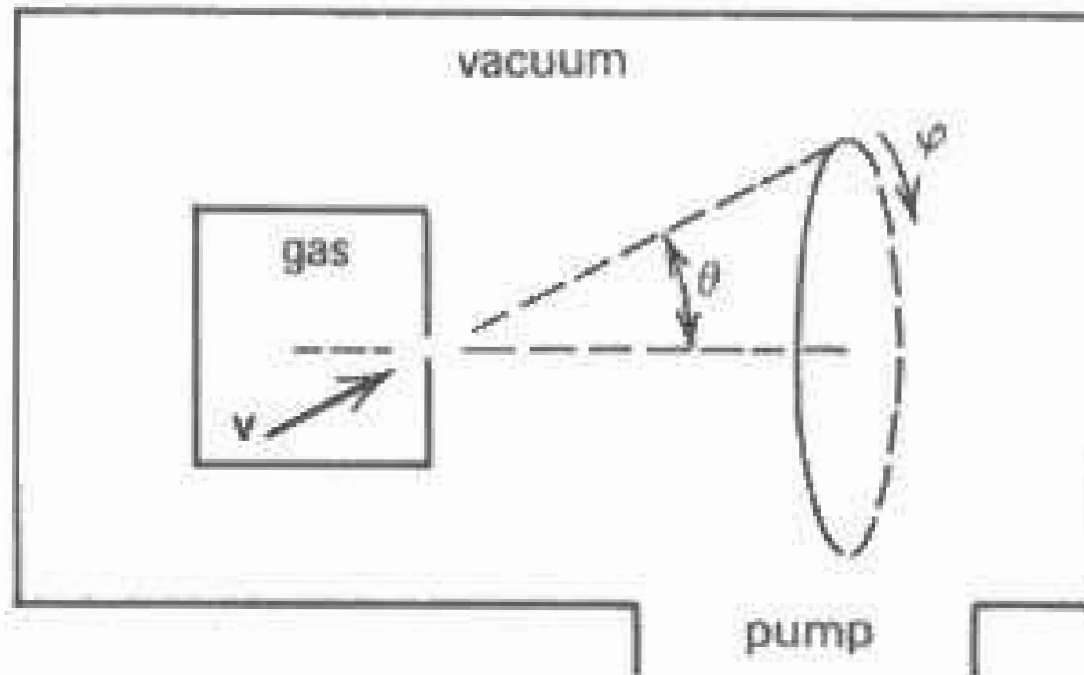   - This condition can be achieved if the density is low enough.

Figure 28.10 Simple experimental apparatus for the study of effusion.

- The plane of Figure 28.9 may be considered to contain the orifice.

- The number of molecules that cross a unit area of this surface with velocity between $\mathbf{v}$ and $\mathbf{v} + d\mathbf{v}$ per unit time is:

$$\Gamma_n(\mathbf{r}, \mathbf{v}, t) = v \cos\theta f(\mathbf{r}, \mathbf{v}, t) d\mathbf{v}$$

  - Recall that θ is the angle between the velocity vector and the normal to the surface.

- It is also assumed that the orifice is sufficiently small that the spatial uniformity and equilibrium velocity distribution are unaffected by molecules escaping through the hole.

  - These conditions define *effusion*.

- In spherical coordinates:

$$d\mathbf{v} = v^2 dv \ d\Omega \ = v^2 dv \ \sin\theta \ d\theta \ d\phi$$

  where θ is the polar angle and ϕ is the azimuthal angle as indicated in Figure 28.10.
- The total flux of molecules through the hole includes all possible speeds in the directions $0 \le \theta \le \pi/2$ and $0 \le \phi \le 2\pi$.
  - Note that the direction for θ does not include $\pi/2$ to π, as this would denote molecules moving back through the hole.
  - The range of θ is what ensures that the integral is non-zero.

- The total flux density is:

$$\Gamma_n(\mathbf{r}, t) = n \left(\frac{m}{2\pi k_B T} \right)^{3/2}$$

$$\times \int_{v=0}^{\infty} \int_{\theta=0}^{pi/2} \int_{\phi_0}^{2\pi} v \cos\theta e^{-mv^2/2k_B T} v^2 \sin\theta \; d\theta \; d\phi \; dv$$

- The angular integrals may be separated and evaluated:

$$\int_{\theta=0}^{\pi/2} \int_{\phi_0}^{2\pi} \cos\theta \; \sin\theta \; d\theta \; d\phi = 2\pi \int_0^1 x \; dx = \pi$$

- The integral over v is:

$$\int_{v=0}^{\infty} v^3 e^{-mv^2/2k_B T} dv$$

- This integral over v has been encountered previously in the calculation of average speed.

- Thus the flux density due to effusive flow may be recognized as:

$$\Gamma_n = \frac{1}{4} n \langle v \rangle$$

- Using $\langle v \rangle = (8k_B T/\pi m)^{1/2}$ and the equation for a perfect gas $p = nk_B T$ gives:

$$\Gamma_n = \frac{p}{(2\pi m k_B T)^{1/2}}$$

- Consider the situation in which it was desired to measure only part of the flux density, such as that the emerges in a given direction and hits a detector that subtends a solid angular element $d\Omega$.

- The number of molecules that escape the orifice per unit area of the orifice that strike the detector are:

$$n \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_{v=0}^{\infty} v \cos \theta e^{-mv^2/2k_B T} v^2 \; dv \; d\Omega = n \langle v \rangle \cos \theta \frac{d\Omega}{4\pi}$$

- It is possible to place a velocity selector in front of the detector and the number of molecules with speed from v to $v + dv$ encountering the detector may be determined.

$$n \left(\frac{m}{2\pi k_B T} \right)^{3/2} v \cos \theta e^{-mv^2/2k_B T} v^2 \; dv \; d\Omega$$

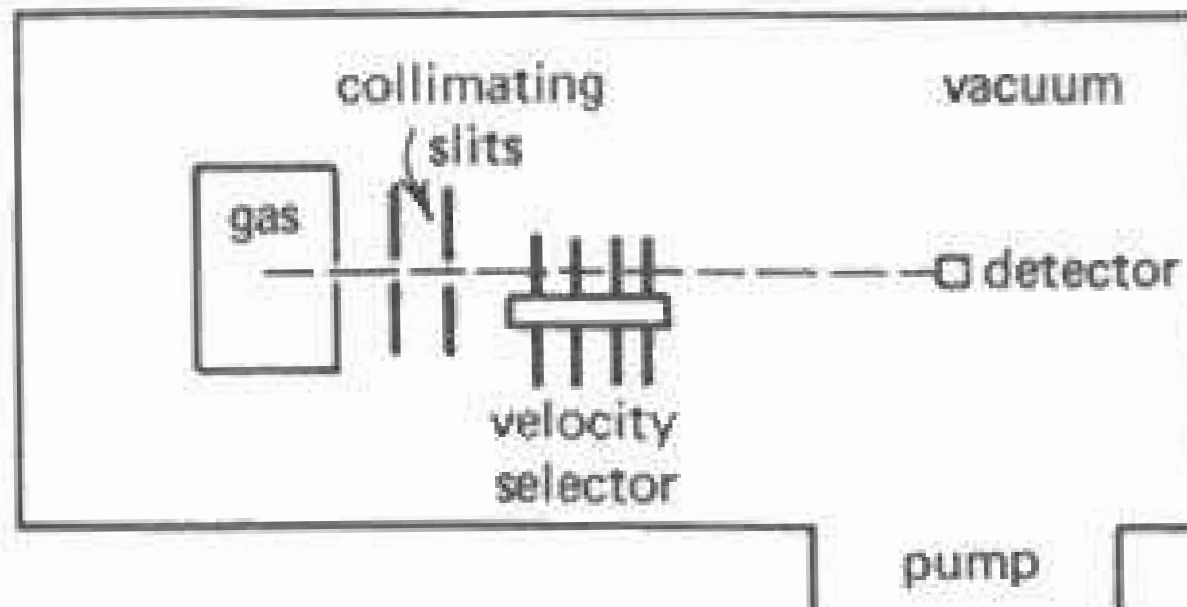- This permits experimental tests of the Maxwell-Boltzmann velocity distribution.

Figure 28.11 Schematic drawing of apparatus for experimental test of the Maxwell–Boltzmann velocity distribution.
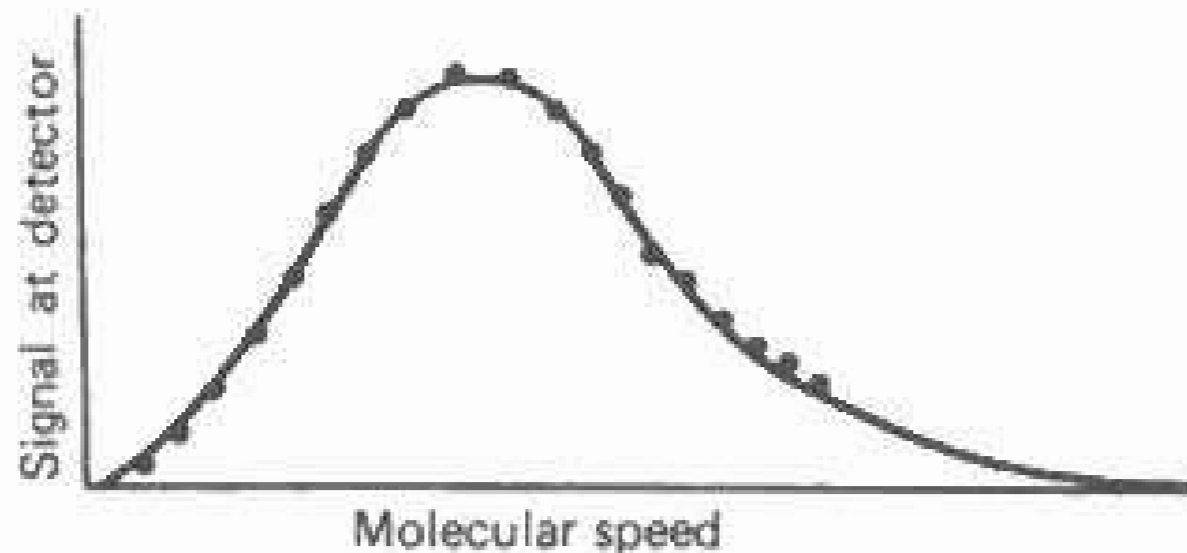
Figure 28.12 Experimental test of the Maxwell–Boltzmann veloc-ity distribution, not to scale. Solid line: predicted by the Maxwell–Boltzmann distribution. Points: experimental measure-ments [schematic, but cf. R. C. Miller and P. Kusch, *Phys. Rev.* **99**, 1314 (1955)].

- Effusion can be used to determine vapour pressures of liquids and solids, provided molecular mass is known.
  - Measurement of vapour pressure over a range of temperatures can be used to determine the heat of vaporization.

## Transport Properties of Gases

- Transfer from one part of a system to another of a physical property is known as a transport process.
  - A transport process involves physical systems in nonequilibrium states.
  - Understanding the mechanism of how the system evolves toward equilibrium is part of understanding transport processes.
  - This mechanism depends on intermolecular forces and thus structure and state of aggregation.

- Examples of transport processes will be considered from a macroscopic perspective and then from a microscopic perspective based on kinetic theory.

- Consider *diffusion*.

  - Consider two containers, one filled with argon and the other filled with neon.

  - When the two containers are connected to each other, a natural, irreversible process takes place as the two gases mix.

  - Each gas is observed to diffuse into the other gas until the gas mixture is uniform.

  - The process of diffusion reduces the concentration gradient until it disappears completely and the gas is at equilibrium.

  - The removal of a spatial gradient is *hydrodynamic relaxation*.

- In diffusion, it is molecular transport that is the macroscopic mass flow.

- Consider the experiment previously described carried out in two different ways.

- One way is to remove a large partition.
  - Consequently, the concentration at each point changes with time.
  - This process is not steady-state, but rather transient

- The other way is to connect the two containers with a capillary.
  - Consequently, the concentrations of each container varies slowly with time.

- Consider the limiting case where the containers are very large.
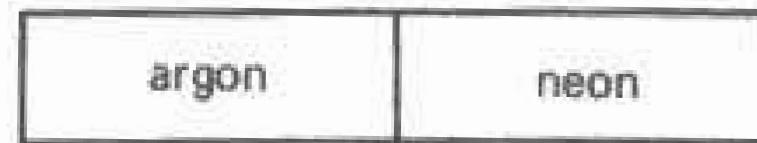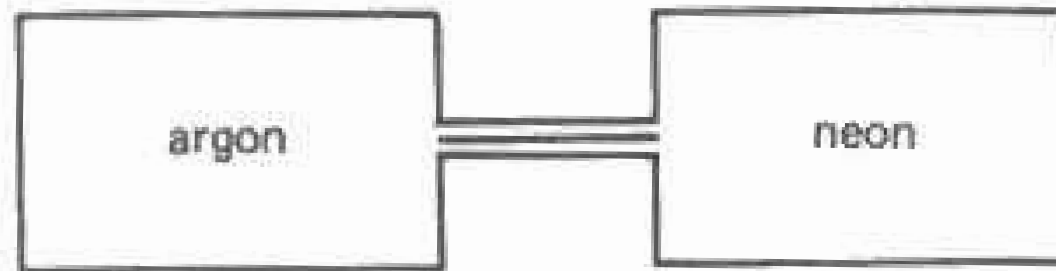
Figure 28.13 Diffusion experiments: (*a*) non-steady-state; (*b*) steady-state.

- In this case, the concentration in each vessel changes so slowly, the diffusion may be considered as occurring at fixed concentration.

- Diffusion proceeds as long as there is a concentration difference between the two vessels and there will be a concentration gradient in the capillary, although the concentration at any particular point may be regarded as invariant with time.

  - It is to be noted, however, that this steady state is not an equilibrium because mass is crossing through the capillary.

- Other transport processes and their associated gradients can be considered:

  - A temperature gradient is associated with the molecular transport of energy.

- A velocity gradient is associated with the molecular transport of momentum or viscosity.

- A potential gradient produced by an electrical field is associated with electric conduction.

- Transport processes may be coupled to each other.
  - Consider a uniform mixture of two gases in a vessel.
  - Impose and maintain a temperature gradient across the vessel.
  - This leads to the establishment of a concentration gradient and *thermal diffusion* occurs.
  - Thermal diffusion is the coupling of thermal conduction and diffusion.
  - Thermal diffusion also occurs as the result of a concentration gradient.

- Consider Figure 28.13(a) in which two gases are separated by a partition in a container that is thermally isolated from the surroundings.
  - When the partition is removed, there is a large concentration gradient which in turn gives rise to a temperature gradient.
  - The temperature gradient disappears as the concentration gradient disappears.
- Consider molecular transport of energy associated with a temperature gradient.
  - Energy is transferred by inelastic collisions.
  - In an inelastic collision, energy moves among internal degrees of freedom and the translational degree of freedom.

- Consider a set of quantum oscillators, which are all in the same quantum state, which are introduced to a bath of inert gas.

- The oscillators are uniformly distributed and no concentration gradients exist.

- The oscillators collide with the molecules.
  - The collisions may be elastic or inelastic.

- Inelastic collisions change the quantum states of the oscillators.

- The populations of the quantum states changes with time until a Boltzmann equilibrium distribution is reached.
  - The number of oscillators in state j is $g_j e^{-\epsilon_j/k_B T}$, where ϵ_j is the energy of the jth level and g_j is the degeneracy of the jth level.

- If the initial energy of the oscillators is larger than the average energy of the equilibrium distribution, then energy will be transferred to the bath gas.
  - This process is irreversible and is referred to as vibrational relaxation.
  - Relaxation can also involve electronic or rotational energy being transferred to translational energy.
- Chemical reactions may be considered as transport processes.
  - The atoms are transported from the conformation of the reactants to that of the products.
  - Equilibrium is attained when the free energy change of the reaction becomes zero.
  - A Gibbs free energy difference between reactants and products gives rise to an irreversible process.

- In a transport process, a flux occurs as the result of the existence of a gradient.

- If the gradient is not too large, then the flux is proportional to the gradient.

- The proportionality coefficients are:
  - D, the coefficient of diffusion
  - η, the coefficient of viscosity
  - λ, the coefficient of thermal conductivity.

- These are summarized in Table 28.1 on page 837.

- These coefficients have been found experimentally to depend on temperature.

- They are also independent of density for dilute gas.

- For higher densities, there is a strong dependence on density.

Table 28.1 Summary of Relations for Transport Processes (Gradients Taken to Be in the z Direction)

Molecular Flux Density	Transport Process	Gradient in z Direction	Macroscopic Law
Particles, Γ_n	Diffusion	Density, $\dfrac{dn}{dz}$	$(\Gamma_n)_z = -D\dfrac{dn}{dz}$
Momentum, Γ_{mv}	Viscosity	Average velocity, $\dfrac{d\langle v_y \rangle}{dz}$	$(\Gamma_{mv})_{yz} = -\eta\dfrac{d\langle v_y \rangle}{dz}$
Energy, Γ_E	Thermal conductivity	Temperature, $\dfrac{dT}{dz}$	$(\Gamma_E)_z = -\lambda\dfrac{dT}{dz}$

- Consider a transport process in a gas (see Figure 28.14) such as diffusion.

- Initially there are equal volumes of neon and argon at the same p and T in separate containers.

- At $t = 0$, the partition separating the two is removed and diffusion begins.
  - Figure 28.14 (a) shows the mole fraction of argon as a function of position at $t=0$.

- As diffusion occurs, a concentration gradient forms.
  - Figure 28.14 (b) shows this for argon.
  - A similar profile exists for neon in the opposite direction.

- The velocity distribution during diffusion is not the Maxwell-Boltzmann distribution, but rather a perturbation of it.
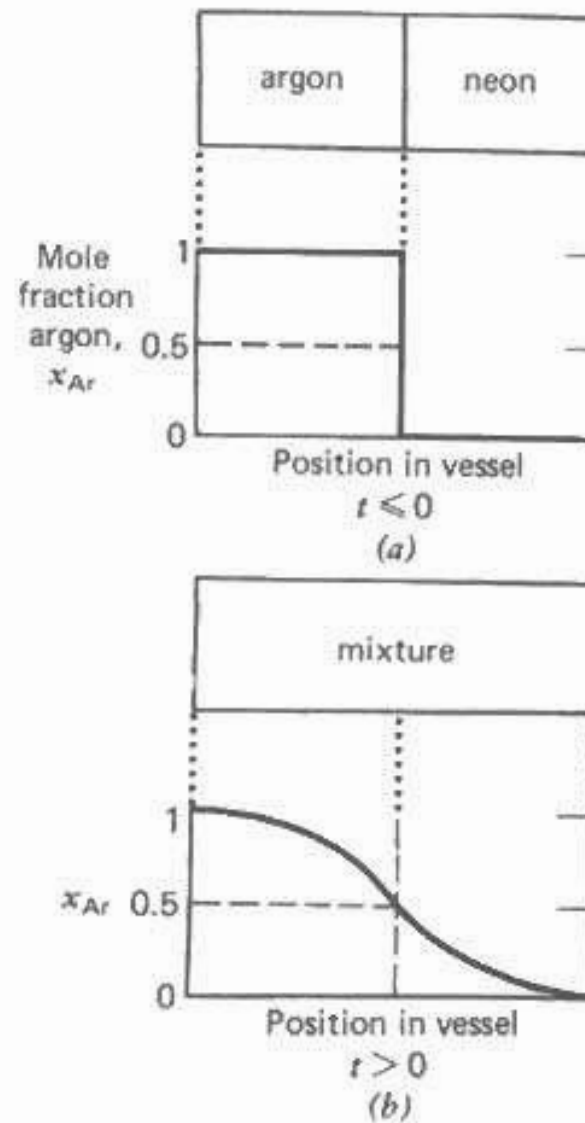
Figure 28.14 Concentration profile in diffusion experiment: (*a*) initially; (*b*) at a later time, but prior to attainment of equilibrium.

- Consider the nature of the perturbation of the Maxwell-Boltzmann distribution.

- Only the perturbation contributes to the transport process.

- It cannot be a large perturbation because it has been previously shown that the velocity relaxation time is short (10^{-8} to 10^{-9} seconds).

- The hydrodynamic relaxation time, the time required for macroscopic equilibrium (i.e. spatial homogeneity) to be attained, is much longer and can be of the order of seconds or minutes.

- It is the slow process of hydrodynamic relaxation that maintains the perturbation of the Maxwell-Boltzmann distribution.

- Consider a small volume element within the gradient.
- The velocity distribution within this element is nearly an equilibrium distribution and may be considered a *local equilibrium distribution*.
  - In a local distribution, variables within the velocity distribution may vary with position in accordance with the gradient of interest.
- The gradients are small enough that variation over distances comparable with the mean free path are negligible.
  - Thus for a volume element that is a few mean paths wide is sufficiently small for the assumption of local equilibrium to hold.
  - Thus information on the perturbation of the velocity distribution is needed.

- Because the perturbation is small, some approximations may be made.

  - Detailed solutions are beyond the scope of this course and may be found in the field of hydrodynamics.

- Consider the expression for flux density across a plane:

$$\Gamma_\psi = \int_{\mathbf{v}} v \cos\theta \, \psi f(\mathbf{r}, \mathbf{v}, t) d\mathbf{v}$$

  where ψ represents 1, $m\mathbf{v}$, or $\frac{1}{2}mv^2$ depending on whether it is the flux density of particles, momentum or energy that is under consideration.

- Consider now a one-dimensional transport process in the z direction as shown in Figure 28.15 and the net flux of density across the plane at $z = 0$.
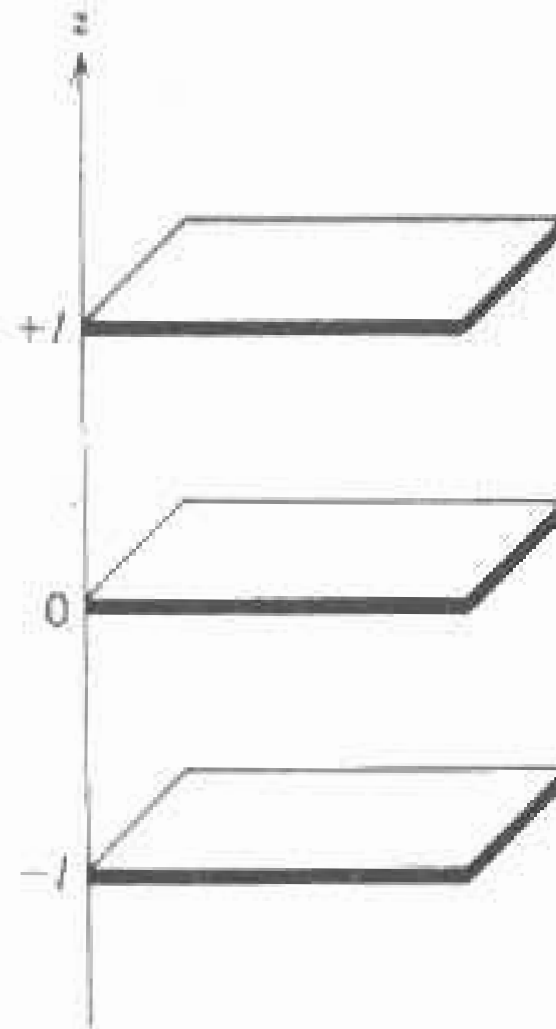
Figure 28.15 Calculation of flux across the plane $z = 0$ for eral transport process.

- The net flux across the plane $z = 0$ is the difference between the values of Γ_ψ on either side of this plane:

$$\Gamma_\psi = \Gamma_\psi^{+z} - \Gamma_\psi^{-z}$$

- Γ_ψ^{+z} may be written as:

$$\Gamma_\psi^{+z} = \int_v \int_{\theta,\phi} (n\psi \cos\theta) \frac{v}{n} f(\mathbf{r}, \mathbf{v}, t) d\mathbf{v}$$

  - Recall that θ is the angle between the velocity vector $\mathbf{v}$ and the positive z axis.
  - The range of integration is $0 \leq \theta \leq \pi/2$ for Γ_ψ^{+z} and $\pi/2 \leq \theta \leq \pi$ for Γ_ψ^{-z}.

- The next step is to make some approximations.

- The first approximation is that the term $n\psi\cos\theta$ is constant at an average value.
  - This allows the term to be taken outside the integral.
- The second assumption is that the actual velocity distribution deviates so little from the Maxwell-Boltzmann distribution adequately represents the local equilibrium.
  - Thus:

$$\frac{1}{n}f(\mathbf{r}, \mathbf{v}, t) \rightarrow \tilde{f}(\mathbf{v})$$

.
- The flux in the $+z$ direction may now be written as:

$$\Gamma_{\psi}^{+z} = \langle \psi n \cos\theta \rangle \int_{\mathbf{v}} v\tilde{f}(\mathbf{v})d\mathbf{v}$$

- This can be recognized as:

$$\Gamma_\psi^{+z} = \langle \psi n \cos\theta \rangle \langle v \rangle$$

- $\langle \psi n \cos\theta \rangle$ must be evaluated.
  - Consider the molecules as moving only along the axis.
  - Therefore $1/6$ will move in the $+z$ direction and $1/6$ will move in the $-z$ direction.
  - For the $+z$ direction $\cos\theta = 1$ and for the $-z$ direction $\cos\theta = $ -1.
  - Consider the molecules to be hard spheres.
  - A molecule that collides near $z = 0$ and contribute to the flux in the $+z$ direction will have last collided near $z = -l$ which is about one free path length away.

- Thus $\langle \psi n \cos\theta \rangle$ for Γ_ψ^{+z} should be evaluated at $z = -l$.

- Similarly, $\langle \psi n \cos\theta \rangle$ for Γ_ψ^{-z} should be evaluated at $z = +l$.

- Therefore:

$$\Gamma_\psi = \Gamma_\psi^{+z} - \Gamma_\psi^{-z}$$

becomes

$$\Gamma_\psi = \frac{\langle v \rangle}{6} \left(\langle \psi n \rangle_{-l} - \langle \psi n \rangle_{+l} \right)$$

where the subscripts indicate the positions where $\langle \psi n \rangle$ is evaluated.

- $\langle \psi n \rangle$ can be evaluated using a Taylor series:

$$\langle \psi n \rangle_{-l} = \langle \psi n \rangle_0 - l \left(\frac{d \langle \psi n \rangle}{dz} \right)_{z=0}$$

- Similarly:

$$\langle \psi n \rangle_{+l} = \langle \psi n \rangle_0 + l \left(\frac{d\langle \psi n \rangle}{dz} \right)_{z=0}$$

- Truncation at first order is justified because the gradient over the mean free path is small.

- This gives as the flux density, Γ_ψ:

$$\Gamma_\psi = -\frac{\langle v \rangle}{3} l \left(\frac{d\langle \psi n \rangle}{dz} \right)_{z=0}$$

- Recall the ψ is defined by the flux under consideration.
  - For diffusion $\psi = 1$.
  - For viscosity $\psi = m\mathbf{v}$
  - For thermal conductivity $\psi = \frac{1}{2}mv^2$.

- For diffusion, the flux density is:

$$\Gamma_n = -\frac{\langle v \rangle}{3} l \frac{dn}{dz}$$

and the diffusion coefficient is:

$$D = \frac{1}{3} \langle v \rangle l$$

- For viscous flow, the flux density in the z direction of the y component of momentum is:

$$(\Gamma_{mv})_{yz} = -\frac{1}{3} nm \langle v \rangle l \frac{dv_y}{dz}$$

and the viscosity coefficient is:

$$\eta = \frac{1}{3}nm\langle v\rangle l$$

- For thermal conduction, $\langle \psi n\rangle = nC_V T$ since $\langle \frac{1}{2}mv^2\rangle = \frac{3}{2}k_B T = C_V T$.
  - The energy flux density is:

$$\Gamma_E = -\frac{1}{3}\langle v\rangle ln C_V \frac{dT}{dz}$$

  and the coefficient of thermal conductivity is:

$$\lambda = \frac{1}{3}nC_V\langle v\rangle l$$

- Note that all these derivations assumed a spatial gradient small enough that the Taylor expansion can be truncated at first order.

- Thus the flux is proportional to the gradient.

- It was also assumed that there was local thermal equilibrium.

- The molecules were assumed to be hard spheres which gave rise to a mean free path.

- The molecules constitute a perfect gas with now forces of attraction between them.

- The effects of collisions were ignored.

- In Table 28.2, the results of these assumptions are compared with numerical solutions of the Boltzmann equation for hard spheres.

  - The differences are only in the numerical factors.
  - Temperature and density dependence are the same.

Table 28.2 Transport Coefficient for Hard Spheres

Transport Coefficient	Simple Theory	Rigorous Theory
Self-diffusion, D	$\dfrac{2}{3}\left(\dfrac{k_B T}{\pi m}\right)^{1/2}\dfrac{1}{\pi d^2 n}$	$\dfrac{3\pi}{8}\left(\dfrac{k_B T}{\pi m}\right)^{1/2}\dfrac{1}{\pi d^2 n}$
Viscosity, η	$\dfrac{2}{3}\left(\dfrac{m k_B T}{\pi}\right)^{1/2}\dfrac{1}{\pi d^2}$	$\dfrac{5\pi}{16}\left(\dfrac{m k_B T}{\pi}\right)^{1/2}\dfrac{1}{\pi d^2}$
Thermal conduction, λ	$\dfrac{2}{3}C_v\left(\dfrac{k_B T}{\pi m}\right)^{1/2}\dfrac{1}{\pi d^2}$	$\dfrac{25\pi}{32}C_v\left(\dfrac{k_B T}{\pi m}\right)^{1/2}\dfrac{1}{\pi d^2}$

- How do these transport coefficients compare to experiments?
  - The derivation predicts $T^{1/2}$ for all three.
  - The coefficients for viscosity and thermal conductivity are predicted to be independent of density while the diffusion coefficient is inversely proportional to the density.
  - In experimental regimes consistent with the assumptions of the derivations, these dependencies are confirmed.
- To advance on Maxwell's treatment requires the removal of one or more assumptions.
  - This took another 50 years.
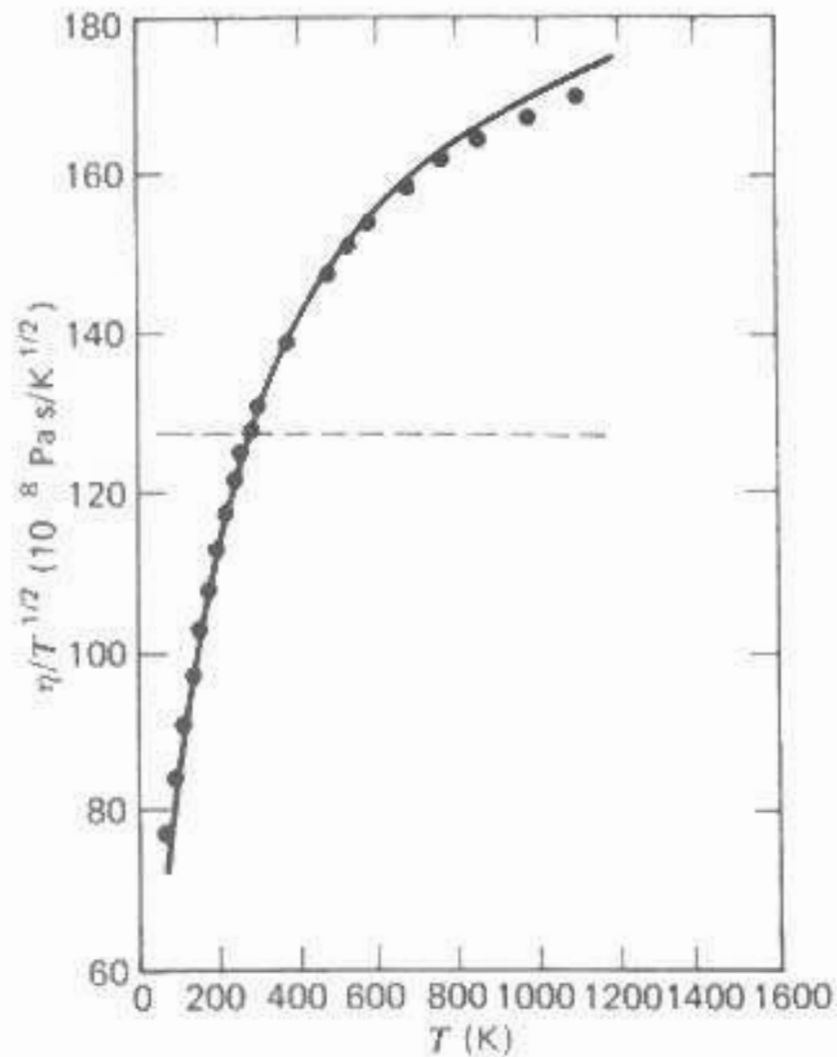- Theory and experiment are compared in Figure 28.16.

Figure 28.16 Temperature dependence of 1-atm viscosity for argon. Solid line: Lennard–Jones potential behavior. Dashed line: hard-sphere behavior (fitted to η for 273 K). The circles are experimental points.

- Note that the vertical axis is $\eta/T^{1/2}$.
  - Thus this quantity is constant for a hard sphere gas.
  - On the assumption of a hard sphere gas, molecular diameters may be estimated from experimental measurements.
- The experimental values of $\eta/T^{1/2}$ are not constant with temperature.
- Results of a model based on the Lennard-Jones potential give a reasonably good fit.
  - The Lennard-Jones potential includes short range repulsion and long range attraction.
  - At lower temperature attractions are important.
  - At higher temperature repulsions are important.

Energy Exchange Processes

- The previous discussion has be limited to structureless particles which can only undergo elastic collisions.

- Real molecules have internal degrees of freedom and can undergo inelastic collisions.

- Such molecules have internal energy and kinetic energy.

- The internal energy may be partitioned among vibration,rotation, and electronic energy.

  - The degrees of freedom are not rigorously separable.

  - Vibration and rotation are coupled and are sometimes referred to as rovibrational energy.

  - When electronic and vibrational states are coupled, they are referred to as vibronic and the Born-Oppenheimer approximation breaks down.

- Whether degrees of freedom may be treated separately is considered on a case by case basis.

- An increase in internal energy is referred to as excitation and occurs as the result of collisions or by absorption of a photon.

- In the gas phase, collisions are often binary.

- In the liquid phase, collisions may be multibody.

- Collisions may also occur with surfaces or within solids.

- Deexcitaion occurs as the result of collisions or by emission of a photon.

  - Which is most likely depends on the radiative lifetime relative to the time between collisions.

  - At standard temperature and pressure, the time between collisions is about 10^{-9} to 10^{-8} seconds.

- Radiative lifetimes depend upon the degree of freedom involved.
    - 10^{-8} to 10^{-6} seconds for allowed electronic transitions.
    - Up to 1 second for forbidden electronic transitions.
    - 10^{-3} to 10^{-1} seconds for vibrational states.
    - 10^{-1} seconds for rotational states.
- Rotational and vibrational deexcitation by radiation occurs only when the density of the gas is very low.
- The probability of energy transfer due to collisions is usually represented by energy transfer cross sections.
- Velocity relaxation occurs as the result of the transfer of translational energy from one molecule to another.
- There are also cross sections for the transfer of translational energy to internal energy.

- In order for internal energy changes to occur, the value of ΔE for the transition is usually small relative to $k_B T$, the thermal energy.
  - Energy spacings usually follows the order:

    $$\text{translation} < \text{rotation} < \text{vibration} < \text{electronic}$$

  - Thus the efficiency of energy transfer generally follows the order:

    $$\text{translation} > \text{rotation} > \text{vibration} > \text{electronic}$$

  - There are exceptions to this.
- Transfer of internal energy from one molecule to internal energy of another is also possible.
- Of particular interest is resonant or near-resonant energy transfer.

- Resonant energy transfer involves the conversion of internal energy from one form to another or from one molecule to another with little, if any, transfer to or from translation.

- Consider a N_2 molecule in the $v = 1$ state colliding with another N_2 molecule in the $v = 0$ state.
  - If the quantum of vibrational energy is transferred from one molecule to the other, resonant energy transfer has occurred.
  - The possibility of resonant energy transfer is high (in systems where the barrier to reaction is high).

- In other cases resonance is not likely to be exact.

- Consider:
$$N_2(v = 2) + N_2(v = 0) \rightarrow N_2(v = 1) + N_2(v = 1)$$
which is nearly resonant.

- Because N_2 is anharmonic, it is not exactly resonant and a small amount of energy needs to be transferred from translation.

- Consider the case of the polyatomic molecule, SF_6, which is excited by light under conditions where there is a low likelihood of collisions.

  - The density of states is shown in Figure 28.17.

  - At low energy, the density of states is sufficiently low, that the molecule may be regarded as having independent normal modes of vibration.

  - One mode can be excited by at photon and since there are no other states of the same energy, energy transfer within the molecule cannot occur and the energy stays in that mode until lost by radiation of a photon.
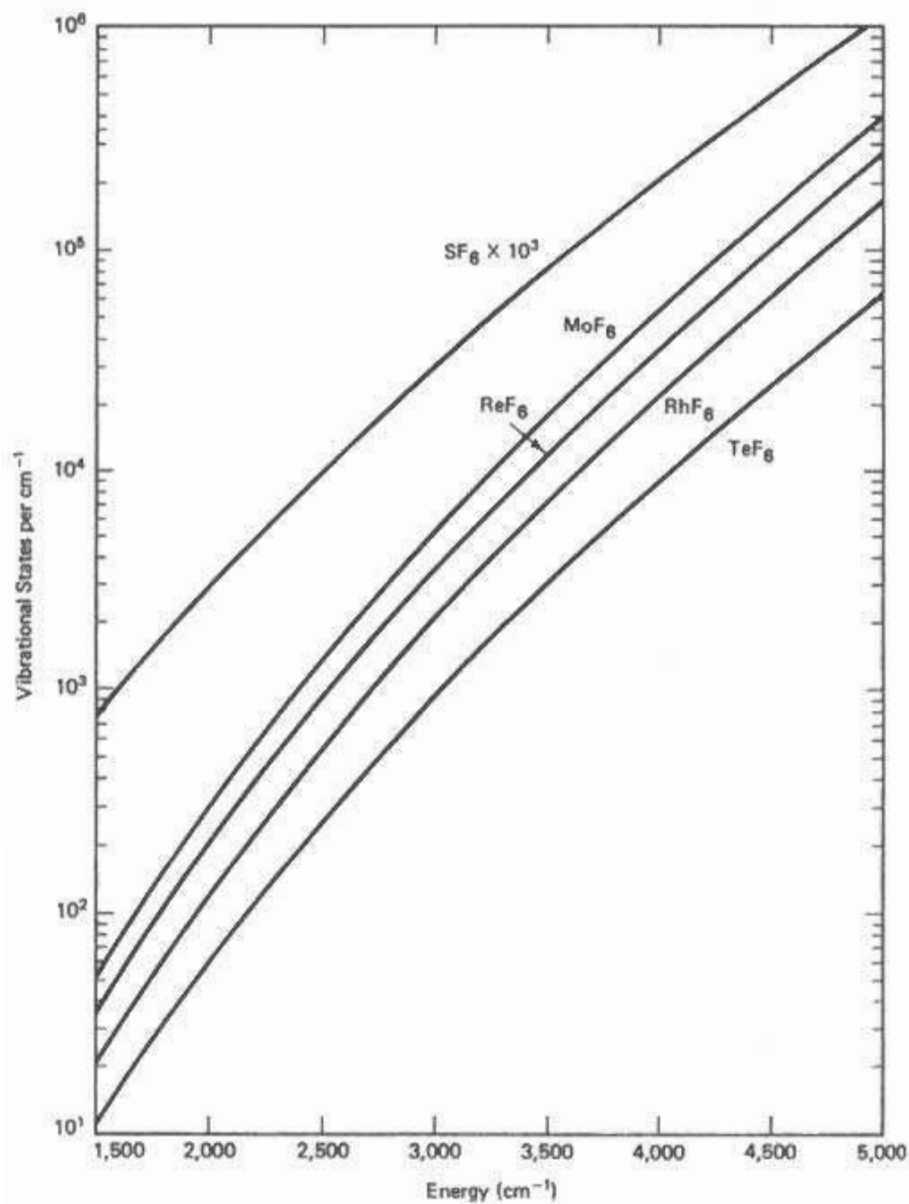
Figure 28.17 Density of vibrational states of some hexafluorides. From J. I. Steinfeld, J. S. Francisco, W. L. Hase, *Chemical Kinetics and Dynamics* (Prentice Hall, NJ, 1989).

- At higher energy, the density of states is higher, and if one mode is excited, that energy can be redistributed to many other modes.

- If such an excited SF_6 molecule were to collide with another SF_6 molecule in the ground state, near resonant energy transfer will occur.

- Consider now the relaxation of excited molecules.
  - If the excitation is the result of collisions or the absorption of blackbody radiation, the excitation in incoherent in that the vibrational phases are not related to each other.
  - If it is assumed that the temperature of the gas is low enough that collisions usually result in the transfer of energy from vibration to translation, the the population of the vibrational levels will relax to the final equilibrium distribution.

- Mathematically, this can be described by the relaxation equation:

$$\frac{d\left[c_n(t) - c_n(\infty)\right]}{dt} = \frac{c_n(t) - c_n(\infty)}{\tau}$$

- This can be recognized as a first order equation and has an exact solution:

$$c_n(t) - c_n(\infty) = \left[c_n(0) - c_n(\infty)\right] e^{-t/\tau}$$

- τ is the relaxation time for vibration and is related to the cross sections for the collisional processes leading to vibrational energy transfer.

- Consider now coherent excitation where the vibrational phase of all molecules is the same.
  - Elastic or inelastic collisions destroy coherence.

- Since elastic collisions are more common than inelastic collisions, dephasing of the coherence occurs more rapidly than vibrational relaxation.

- Energy transfer may be explored experimentally by a variety of techniques.

- With difficulty, energy transfer cross sections may be determined by molecular beam apparatus.

  - Consider a beam of O_2^+ ions prepared by velocity selection to have nearly the same translational energy somewhere in the range 10 - 20 eV.

  - The second beam of Ar atoms is prepared at a lower translational energy.

  - The two beams collide and the scattering of O_2^+ ions in measured as a function of angle and translational energy.

- If energy has been transferred from translation to internal energy, then the O_2^+ ions will be moving more slowly.

- Thus by measuring the translational energy, an "energy loss" spectrum may be determined (Figure 28.18) indicating which vibrational excitations have occurred.

- The cross section for a transition may be determined by summing scattering intensity over all angles.

- Kinetic spectroscopy is another technique.
  - I_2 vapour can be irradiated with an Ar^+ ion laser to produce a fluorescence spectrum.
  - The 514.5 nm line of the laser provides photons that can excite the I_2 molecule from $v = 0$ in the ground state to $v = 43$ in the first excited electronic state.
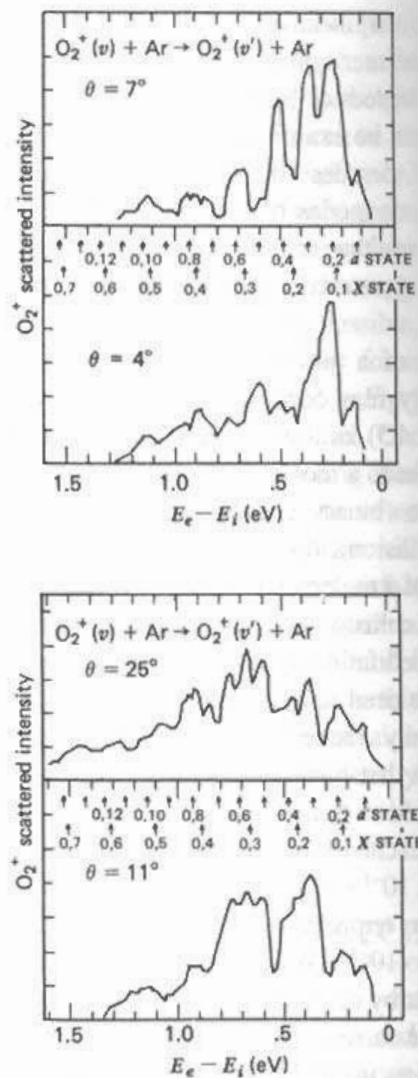
Figure 28.18 Measurements of conversion of translational to internal energy in O_2^+–Ar scattering. The intensity of scattered O_2^+ is plotted as a function of translational energy loss (from the initial value of 13.25 eV) at several angles. The energy losses corresponding to specific vibrational excitations are indicated by arrows: "0,1" refers to the transition $(v=0) \rightarrow (v=1)$, and so on. (The two sets of arrows refer to the $X^2\Pi_g$ and $a^4\Pi_u$ electronic states of O_2^+, both of which may be present in the beam.) From P. C. Cosby and J. F. Moran, *J. Chem. Phys.* **52,** 6157 (1970).

- The fluorescence spectrum is measured (Figure 28.19).

- Because a photon from the laser can be scattered elastically from the excited molecule, there is a large peak at 514.5 nm corresponding to the energy difference between $v = 0$ in the ground state and $v = 43$ in the first excited electronic state.

  - The rest of this peak is due to fluorescent emission from $v = 43$ in the first excited electronic state to $v = 0$ in the ground state.

  - Peaks at other positions are due to energy transfer upon collision with the excited molecule followed by fluorescent emission.

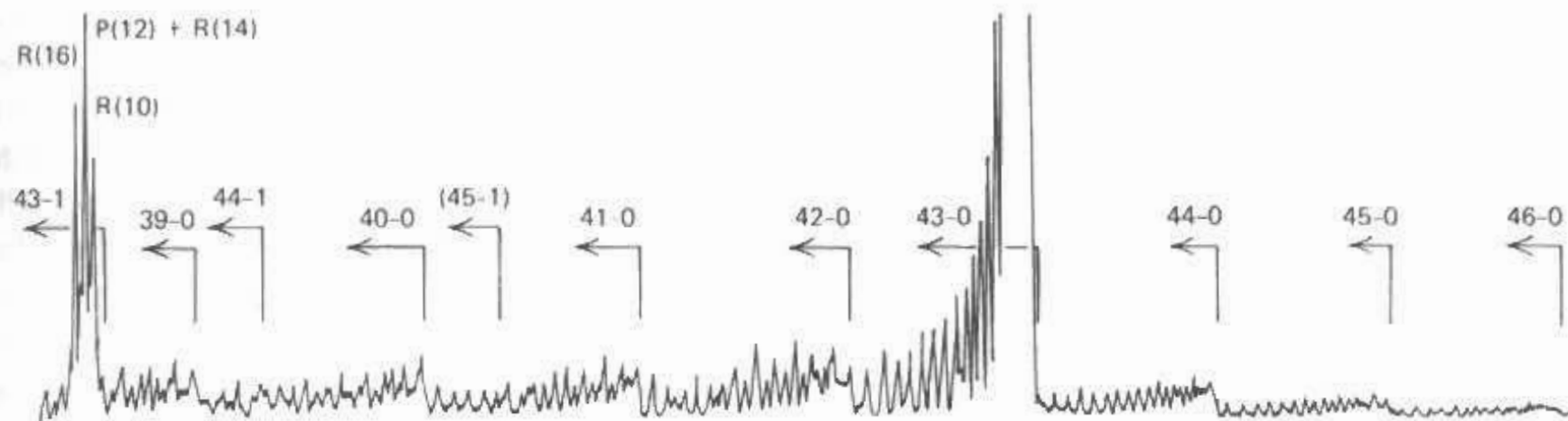- The spectrum is taken after a steady state has been reached.

Figure 28.19 Part of the fluorescence spectrum of I_2 vapor irradiated with the 514.5-nm line of an Ar^+ laser. The labels 43–0 and so on identify the peaks corresponding to various transitions: 43–0 is a drop from the 43rd excited vibrational level to the ground state. From R. B. Kurzel, J. I. Steinfeld, D. A. Hatzenbuhler, and G. E. Leroi, *J. Chem. Phys.* **55**, 4822 (1971).

- This steady state is NOT an equilibrium state because energy is being transferred into the system by the laser.
- The populations of the vibrational and rotational states are steady since the pumping of energy into the system is offset by collisional relaxation and fluorescent emission.
- Information about energy transfer cross sections may be obtained by such experiments.
- This type of experiment has been refined to use pulsed lasers which allows more direct determination of the cross sections.
  - Fluorescence is used to monitor the populations of excited states as a function of time.
- If a pulse of laser light is sufficiently intense, multiple absorptions may occur.
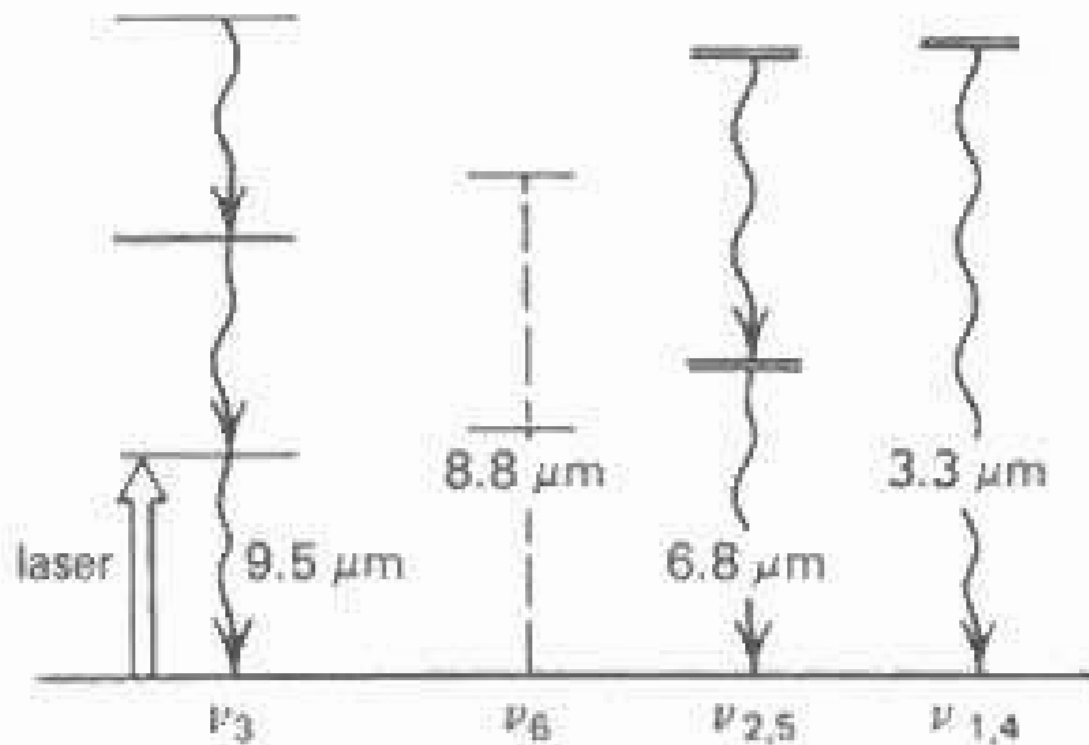
Figure 28.20 Some of the lower vibrational energy level
CH₃F. (See discussion in text.) From R. E. McNair, S. F. Fulgl
G. W. Flynn, M. S. Feld, and B. J. Feldman, *Chem. Phys. Let*
241 (1977).

- In CH_3F, there are a number of vibrational modes (Figure 28.20)
  - ν_3 is the C-F stretch.
  - ν_6 is the H-C-F bend.
  - $\nu_{2,5}$ is the H-C-H bend
  - $\nu_{1,4}$ is the C-H stretch.
- The energy levels for ν_3 are nearly evenly spaced.
  - Thus a CO_2 laser which emits photons at 9.6 μm can excite from $v = 0$ to $v = 1$ then from $v = 1$ to $v = 2$ then from $v = 2$ to $v = 3$ and so on.
- Within nanoseconds, collisions can cause vibration-vibration energy transfer and a steady state can be attained within microseconds.
- It takes milliseconds for vibrational-translational energy transfer to occur.

- Studies of phase relaxation require that coherent vibrations be prepared.
- This is done with lasers.
  - Radiation from a red laser at 9455 cm^{-1} is doubled by a frequency doubling device to produce green laser light at 18910 cm^{-1} which hits liquid nitrogen causing some of the N$_2$ molecules to undergo Raman scattering and be excited to $v = 1$.
  - The green laser at 18910 cm^{-1} is sufficiently intense to cause stimulated emission of a photon which is in phase with the original photon from the laser and leaves the N$_2$ molecules oscillating in phase.
  - The red laser can be used to probe the coherent vibrations after a few picoseconds.
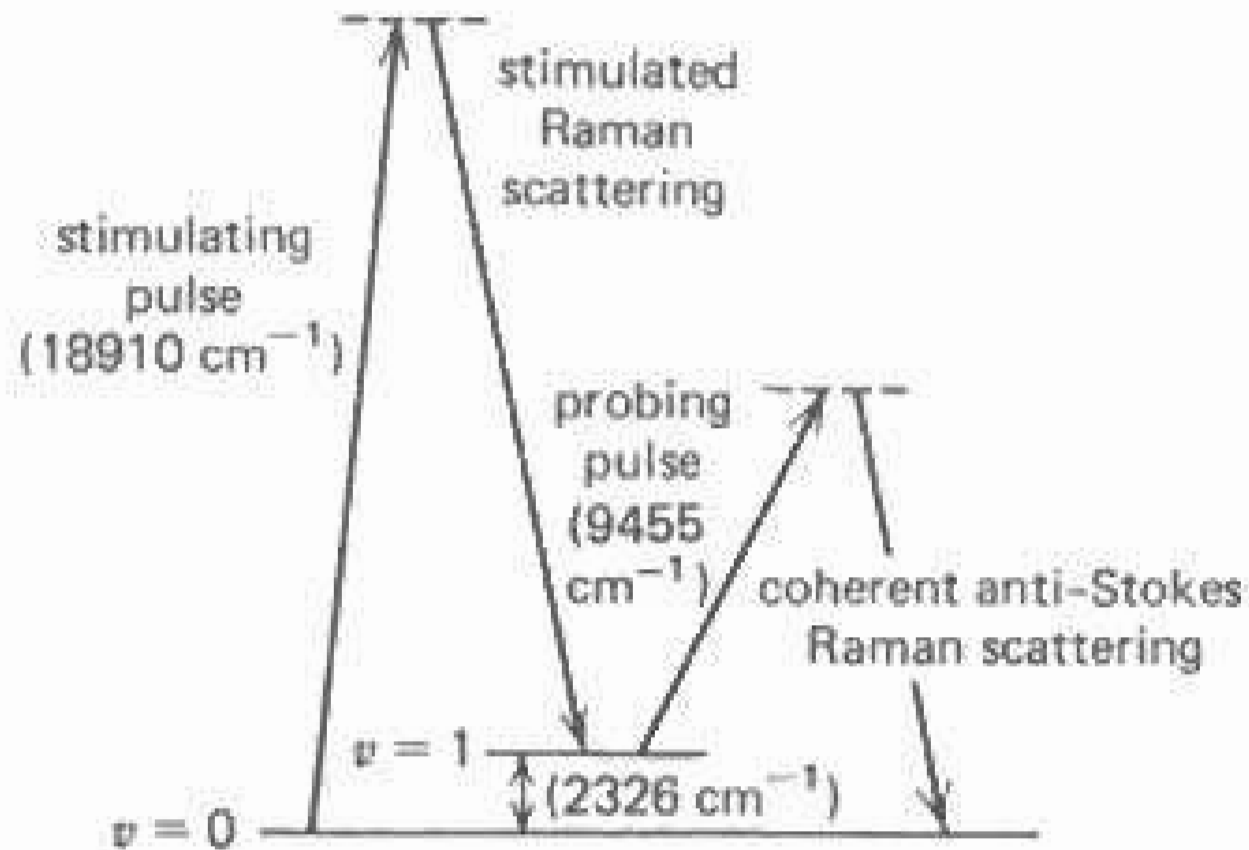 - The red laser produces CARS (coherent anti-Stokes Raman scattering) as shown in Figure 28.21.

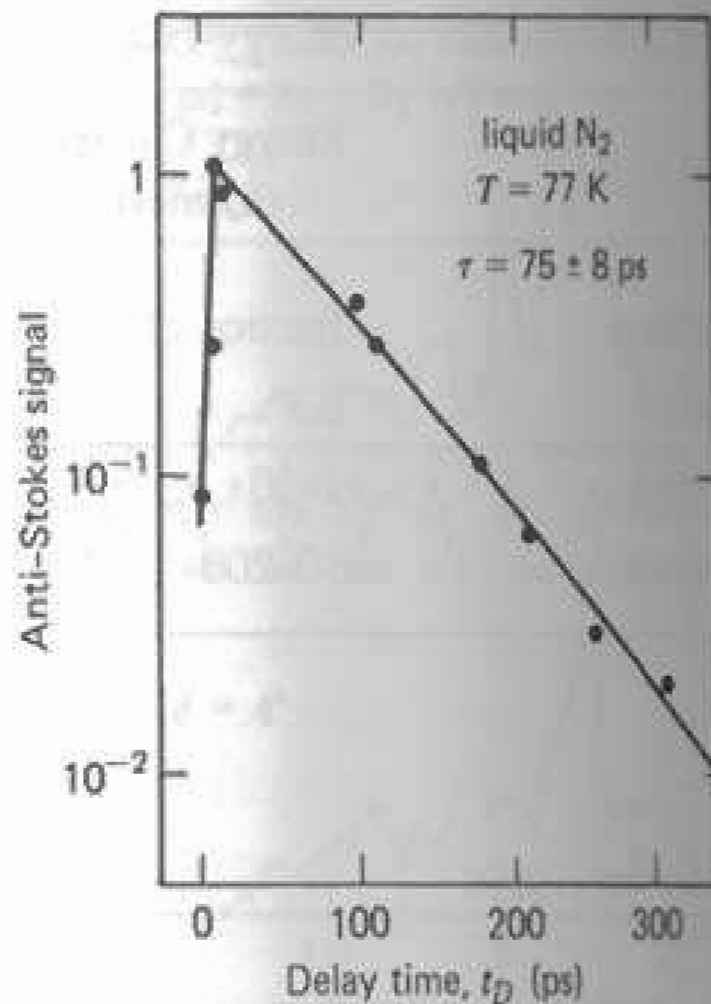**Figure 28.21** Schematic illustration of the process leading to CARS scattering (see text).

Figure 28.22 Intensity of CARS signal described in the text as a function of delay time between the stimulating and probing pulses. From A. Laubereau, *Chem. Phys. Lett.* **27**, 600 (1974).

- Collisions destroy the coherence of the vibrations.
- The decay of coherence is measures by changing the time between the pump (green) laser pulse and the probe (red) laser pulse.
- The phase relaxation time is found to be about 75 ps, must shorter than the 1.5 s required for vibrational to translational energy relaxation for liquid nitrogen.
- Relaxation times may be considered in terms of the number of collisions that it takes for them to occur.
  - The number of collisions required depends on the temperature and the nature of the interaction potential.
  - Translational relaxation takes a few collisions.
  - Rotational relaxation typically takes 5 to 10 collisions.

- Vibrational relaxation can take a few thousand collisions.

- Vibrational-vibrational energy transfer, especially near-resonant energy transfer is more rapid than vibrational relaxation.

- Because relaxation times vary by several orders of magnitude, "temperatures" can be associated with various degrees of freedom for a system not at equilibrium by assuming an internal equilibrium for those degrees of freedom.

  - A vibrational temperature, T_{vib} may be defined by a parameter characterizing a Boltzmann distribution function as $e^{-E_{vib}/kT_{vib}}$.

  - Similarly, rotational and electronic temperatures may be defined.

Sound Propagation and Absorption

- The speed of sound in a fluid depends on the ratio of heat capacity at constant pressure to the heat capacity at constant volume.

- The propagation and absorption of sound in a fluid can be used to study inelastic and reactive processes.

- Sound is a pressure or compression wave.

- Audible sound are those in the range of frequencies from 20 to 20,000 Hz (or s^{-1}).

- Consider sound with $\nu = 500$ Hz.

  - The speed of sound in air at 273 K is 300 m/s.
  - The wavelength is:

$$\lambda = \frac{c}{\nu} = \frac{300 \text{ m s}^{-1}}{500 \text{s}^{-1}} = 0.66 \text{ m}$$

- At 500 Hz, the time between a crest and a trough (half a period) is about 1 μs.
- This pressure variation occurs more quickly than heat may be transferred.
  - Therefore the compression and expansion of the fluid may be assumed to be near adiabatic.
- A sound wave is longitudinal.
  - This means that particles move back and forth in the propagating medium.
- Consider plane waves (Figure 28.23) in which the pressure varies only in the direction of propagation.
  - The pressure and its associated density perturbation is propagated by collisions between molecules.
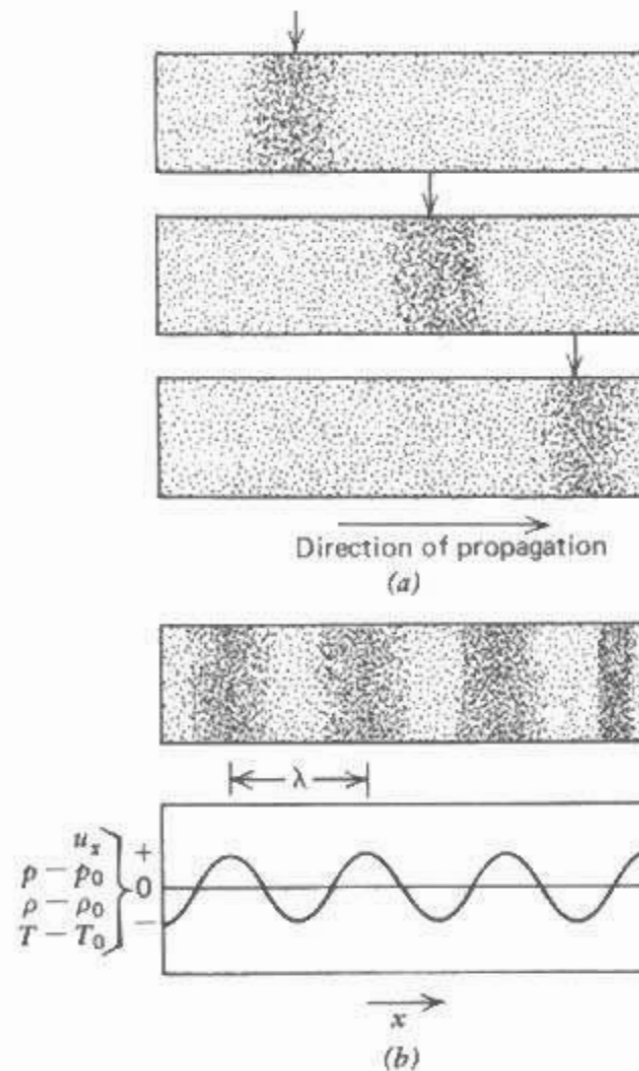 - Thus the speed of sound is proportional to the average molecular speed.

Figure 28.23 (*a*) Propagation of a pressure or density pulse (indicated by arrows) through a gas; the dots represent molecules. (*b*) Schematic representation of a periodic sound wave, in terms of molecules (density variation exaggerated) and of local variables: average velocity in the direction of propagation (*x* direction), excess pressure, excess density, excess temperature (p_0, ρ_0, T_0 are the equilibrium values); one can show (though we shall not) that all these variables are in phase.

- Consider a periodic wave, such as can be generated by a tuning fork, transmitted through a gas initially at rest.
- In the absence of a wave, the average molecular velocity is everywhere zero.
- As the wave propagates, the gas molecules oscillate about their equilibrium positions in the direction of propagation.
  - The local average velocity is $u(x; t)$, which is not the same as the speed of propagation c.
- The gas moves forward and backward in alternating regions of compression and rarefaction where the pressure is above or below the equilibrium pressure.
- The adiabatic compression is accompanied by a temperature increase.
  - Therefore temperature varies periodically.

- Setting up the oscillation associated with sound requires energy.

- the kinetic energy per unit volume is $\frac{1}{2}\rho u^2$ where ρ is the local density and u is the local average velocity.

- The potential energy is equivalent to the work of the pV compression which is nearly adiabatic.

- If the medium of propagation is perfectly elastic, the energy propagates with the wave and it never decreases with energy.

- In reality the medium is not elastic, the propagation is not perfectly adiabatic, and energy will dissipate as the wave is propagated.

- The main dissipative processes are thermal conduction and viscosity.