BEYOND THIS POINT BE DRAGONS

BEYOND THIS POINT BE EQUATIONS!

Some things to know from the prerequisites:

- **First Year Chemistry**
  - Significant figures
  - Manipulation of units
  - Fundamental units and derived units
  - The Ideal Gas Law
  - Van der Waals Gas Law
  - Enthalpy
  - Entropy
  - Free Energy
  - Hess's Law
  - Equilibrium Coefficients
  - Activity

Some things to know from the prerequisites (continued):

- **First Year Calculus (and High School Math)**
  - How to manipulate an equation algebraically
  - Derivatives of one variable
  - Integrals of one variable
  - Power series
  - Properties of logarithms and exponentials

What is Physical Chemistry?

- Physics of Chemistry

What is Thermodynamics?

- **THERMO** - heat, energy
- **DYNAMICS** - changes
- Consider

$$PV = nRT$$

  - Rewrite as:

$$P = \frac{nRT}{V}$$

- What can cause P to change?
  - V - volume

$$\left(\frac{\partial P}{\partial V}\right)_{n,T} = -\frac{nRT}{V^2}$$

  - n - number of moles of gas

$$\left(\frac{\partial P}{\partial n}\right)_{V,T} = \frac{RT}{V}$$

  - T - temperature

$$\left(\frac{\partial P}{\partial T}\right)_{n,V} = \frac{nR}{V}$$

How do we describe the change if all three are changing at once?

$$dP = \left(\frac{\partial P}{\partial V}\right)_{n,T} dV + \left(\frac{\partial P}{\partial n}\right)_{V,T} dn + \left(\frac{\partial P}{\partial T}\right)_{n,V} dT$$

- Note carefully the difference between ∂ and d
  - ∂ describes the partial change due to the change in a particular variable
  - d describes the total change
- Some other ways of describing changes (useful for numerical applications)
  - Δ - a finite change
  - δ - an infinitesimal change

UNITS

- Even when represented by a symbol, physical quantities have units.
  - Verification of units can help detect mistakes in a derivation.
- P - force per unit area. The SI unit is the Pascal (Pa).
  - 1 Pa = 1 N m^{-2} = 1 kg m s^{-2} m^{-2}
  - 1 Pa = 1 kg m^{-1} s^{-2} (fundamental units)
- V - volume
  - m^3 (fundamental units)
- n -number of moles
  - mol (fundamental units)

- R - Gas Constant
  - 8.314 J K^{-1} mol^{-1} = 8.314 kg m^{2} s^{-2} K^{-1} mol^{-1}
  - (1 J = 1 kg m^{2} s^{-2} (fundamental units))
  - (1 J = 1 Pa m^{3} or 1 Pa = 1 J m^{-3})
- T K (fundamental units)
  - temperature is on absolute Kelvin scale.

UNITS ARE YOUR FRIENDS!!

The Perfect Gas

- A dilute gas is the simplest type of matter.
  - Molecules are far apart.
  - Molecules do not interact with one another.
  - Properties observed are related to the properties of the individual gas molecules.
- An ideal gas is a perfect gas.
- In the limit of low pressure, real gases behave as perfect gases.
- The behaviour of a substance is described the equation of state.
  - The equation of state relates P, $\overline{V}$, and T.
  - Empirically determined for real substances.

The Kinetic Hypothesis

- The kinetic hypothesis assumes:
    - Individual molecules are continually in motion, even if the system as a whole is not in motion.
    - Individual motions are in all directions.
    - Individual motions are at a variety of speeds.
- The net effect is that the contributions of the individual molecules tend to cancel.
- Two consequences of molecular motion:
    - Kinetic energy of individual molecules contributes to the internal energy of the system.

- Continued:
    - The impact of the moving molecules on the wall of the container contributes to the pressure exerted by the system on the surroundings.
- In a dilute gas only the internal energy and pressure need to be considered at present.
- Consider the case of a monatomic gas such as He, Ne, or Ar.
    - No motions of the atoms internal to the molecule need to be considered.
    - Motions of the molecules are independent
    - Molecules exert no forces on each other, except at impact.

- Continued:
  - Collisions are elastic with momentum and kinetic energy being conserved.
  - If the extremely remote possibility of electronic excitation of the atom is ignored, then such a gas may be referred to as perfect.
- Most real gases at moderate pressures (such as atmospheric) are sufficiently dilute to behave as perfect gases.
- A perfect gas is also assumed to be at equilibrium.
  - Macroscopic properties of the system are not observed to change with time.

- Continued:
  - Even though macroscopic properties of the system are stable, the microscopic positions and velocities of the individual molecules are constantly changing.
  - Many different microscopic states (“microstates”) can correspond to one particular macroscopic state (“macrostate”).
  - Macroscopic properties such as P and T are related to averages of microscopic velocities.
  - In a particular macrostate, the values of the microscopic variables fluctuate negligibly about their average values.
  - Thus the equilibrium distribution of microscopic velocities is invariant with time.

- At equilibrium, in the absence of an external field, a gas is uniform throughout its container.
  - Measurements of intensive variables such as pressure and temperature are the same regardless of where in the system they are made.
  - Gas is at rest in its container with no flows or currents.
  - Kinetic energy per unit volume is the same in every volume element (that is sufficiently large to contain very many molecules).
    - Thus the distribution of velocities is the same everywhere.

- If the gas as a whole is at rest then:

$$<\mathbf{v}>=\frac{1}{N}\sum_{i=1}^{N}\mathbf{v}_i=0$$

and thus

$$\sum_{i=1}^{N}\mathbf{v}_i=0$$

  - The bold $\mathbf{v}_i$ indicates velocity which is a vector.
  - The average velocity of the system at rest is zero.
  - Recall that speed is a scalar and has magnitude only.
  - The average molecular speed is not zero.

- A density is any quantity per unit volume.
  - Mass density, ρ, is mass per unit volume.
  - Number density, n, is number per unit volume.
    - Consider N molecules of mass m in volume V:

$$n = \frac{N}{V} \quad \text{and} \quad \rho = nm$$

  - Energy density is energy per unit volume (and has units of pressure).
- What is the relationship between kinetic energy of molecules and the pressure of a gas?

- Consider a perfect gas contained in a cubical box of length l.
- Define a cartesian coordinate system with axes normal to the walls (and parallel to the sides) of the cube.
- The walls of the cube reflect molecules elastically.
  - If a molecule with velocity $\mathbf{v}$ and components v_x, v_y, v_z strikes a wall of the box, then the sign of the appropriate velocity component is reversed.
  - Therefore the velocity at some later time is described by $\pm v_x, \pm v_y, \pm v_z$.
- Consider motion in the z direction.
  - S is the face of the box perpendicular to z and has the area l^2.

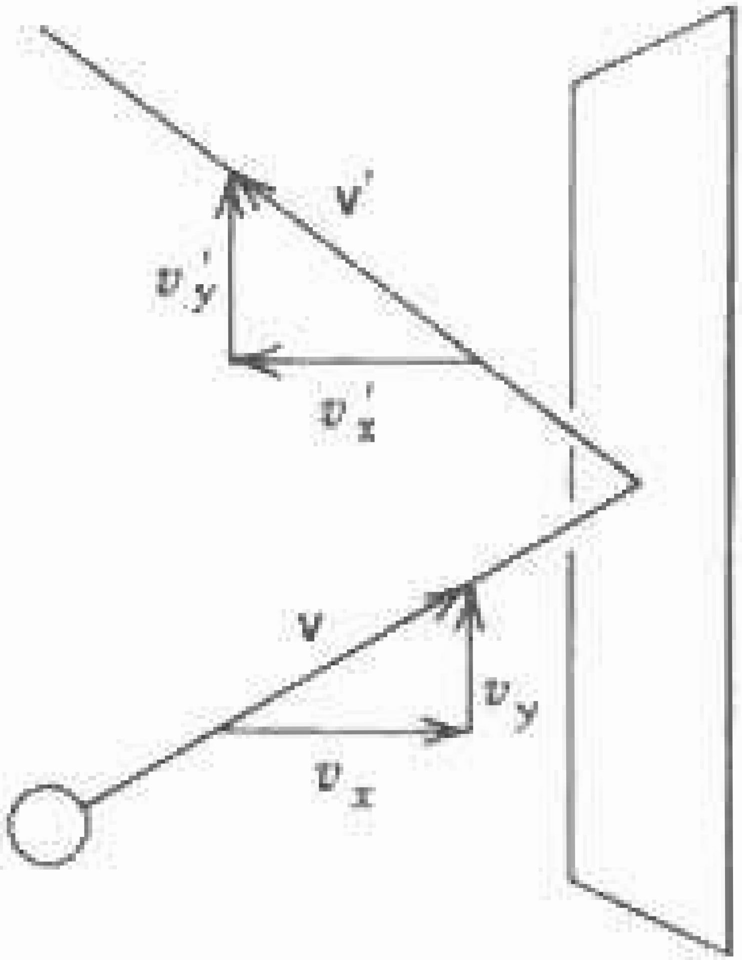


Figure 12.1 Elastic reflection of a particle from the wall of a box. The initial velocity is $\mathbf{v}$, with components v_x perpendicular to the wall and v_y parallel to the wall. After reflection the velocity is $\mathbf{v}'$, with components $v_x' = -v_x$ and $v_y' = v_y$.

- In the time between two collisions with S, the molecule must move to the other end of the box (a distance l away) and back, travelling a total of 2l between collisions.
- The velocity component perpendicular to S is v_z
- Therefore the time between collisions with S is $2l/v_z$
  - The frequency of collisions is $v_z/2l$
- When the molecule collides with S, its momentum changes from $+mv_z$ to $-mv_z$.
  - An equal and opposite momentum is transferred to the wall of the container.
- The total change in the z component of the momentum of a single molecule per unit time is:

$$\left[\frac{d(mv_z)}{dt}\right] = 2mv_z \cdot \frac{v_z}{2l} = \frac{mv_z^2}{l}$$

- Assume the simplest possible velocity distribution.
  - All molecules have the same velocity components, $\pm v_x, \pm v_y, \pm v_z$.
- There are N molecules in the volume $V = l^3$
  - Therefore the total change in momentum per unit time arising from all collisions with S is:

$$\left[\sum_{i=1}^{N} \frac{d(mv_z)}{dt}\right] = \frac{Nmv_z^2}{l} = \frac{nVmv_z^2}{l} = nml^2v_z^2$$

(Recall that n is number density.)

- Pressure is defined as force per unit area.
- Force is defined as the change in momentum per unit time.
- p is the pressure of the gas
    - pl^2 is the total force on S and

$$pl^2 = nml^2v_z^2$$

or

$$p = nmv_z^2$$

- The pressure of a gas is the same in all directions. Thus:

$$v_x^2 = v_y^2 = v_z^2 = \frac{1}{3}(v_x^2 + v_y^2 + v_z^2) = \frac{1}{3}v^2$$

  where v is the common speed of the molecules.
- This gives:

$$p = \frac{1}{3}nmv^2$$

- Since the kinetic energy of a single molecule is $mv^2/2$ and n is the number density of molecules, the pressure is $2/3$ of the kinetic energy density.

The Perfect Gas

- What is the relationship between pressure and energy?
- The previous treatment is restrictive.
  - Not all collisions with the wall are elastic.
  - Molecular speeds are not all the same.
  - Directions of motion are random.
  - The container is not a cube.
- A more general derivation of the relationship between the distribution of velocities and the pressure and energy of a gas.
  - In most cases the generalized distribution does not need to be known, but only some of its properties.

- Consider a perfect gas in equilibrium with N molecules in volume V.
  - The molecules will move with different velocities.
- Let $f(\mathbf{v})d\mathbf{v}$ be the number of molecules per unit volume with velocity between $\mathbf{v}$ and $\mathbf{v} + d\mathbf{v}$.
  - $f(\mathbf{v})$ is the velocity distribution function.
  - The total kinetic energy of all N molecules is finite. Therefore $f(\mathbf{v}) \rightarrow 0$ as $\mathbf{v} \rightarrow \infty$
  - If the sum of $f(\mathbf{v})d\mathbf{v}$ is taken over all possible velocities then n, the total number of molecules per unit volume is obtained.

- This may be written as:

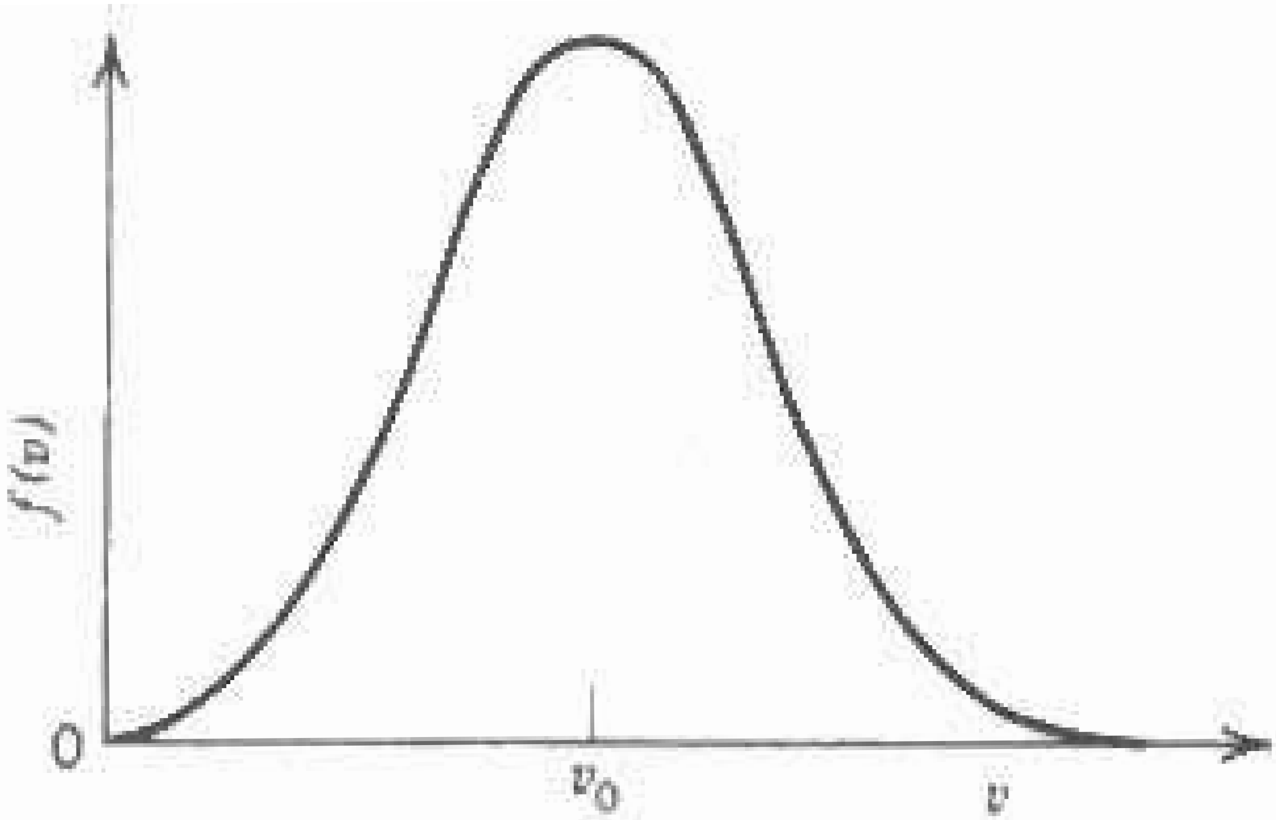
$$\int_{\mathbf{v}} f(\mathbf{v})d\mathbf{v} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f(\mathbf{v})dv_x dv_y dv_z = n$$

- Molecular motion at equilibrium is isotropic.
  - Equal numbers of molecules in any given speed interval must travel in any direction.
  - $f(\mathbf{v})$ is independent of direction.
  - $f(\mathbf{v})$ is a function only of its magnitude, the speed v.
  - Therefore, a distribution function in terms of v would be convenient.
- Consider $f(v)dv$ as the number of molecules per unit volume with speeds between v and $v + dv$.

- Consider the molecular velocity as a point in velocity space defined velocity coordinates, v_x, v_y, v_z
  - The volume element is $d\mathbf{v} = dv_x dv_y dv_z$
- But now the distribution is to be considered in terms of speed, not velocity.
  - What is the relationship between dv and $d\mathbf{v}$?
  - The molecules with the speed between v and $v + dv$ occupy a spherical shell of radius v and thickness dv.
  - The volume of this spherical shell is $4\pi v^2 dv$
- Therefore:

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

(The exact form of $f(v)$ is treated in great detail in Chem 300.)



igure 12.2 The distribution of molecular speeds, $f(v)$. The spee
v_0, which is the most probable, is the *mode* of the distribution.

- An important property of $f(v)$:
  - At equilibrium the gas is homogenous, therefore $f(v)$ is independent of the position within the gas.
  - This is true for real molecules if the energy of interaction is independent of velocity.
- What is the internal energy of a gas arising from molecular motion?
  - A molecule of mass m and speed v has kinetic energy of $mv^2/2$.
  - The total number of molecules with speed between v and $v + dv$ is given by $f(v)dv$.
  - Contributions from all values of v are summed.

- The total internal energy U is:

$$U = \int_V \int_{v=0}^{\infty} \frac{mv^2}{2} \, f(v) \, dv \, dV$$

  - Since $f(v)$ does not depend on the position, it is independent of the volume, therefore the integral over volume can be separated from the integral over speed:

$$U = \int_V \, dV \, \int_{v=0}^{\infty} \frac{mv^2}{2} \, f(v) \, dv$$

$$U = \frac{mV}{2} \int_{v=0}^{\infty} v^2 \, f(v) \, dv$$

- Note that this expression may break down for real gases.
  - For polyatomic molecules, there are contributions to the internal energy from the motions within the molecules.
  - Real molecules can have interactions between them which will also make a contribution to the internal energy.
- What is the relationship between internal energy and pressure?
  - Pressure has been defined as force exerted by the gas per unit area of the wall of the container, i.e. the rate at which momentum is transferred to the wall.

- But the gas is homogeneous and isotropic.
    - Therefore the pressure must be the same anywhere in the gas.
- Consider a plane surface S anywhere within the gas.
    - Molecules hit this surface in the same way as they hit the walls.
    - When a molecule with mv_z as the z component hits the surface, momentum $2mv_z$ is transferred to S.
    - The pressure on S is total momentum transmitted per unit time and per unit area of S.
    - The pressure is the same on both sides of S when the system is at equilibrium.

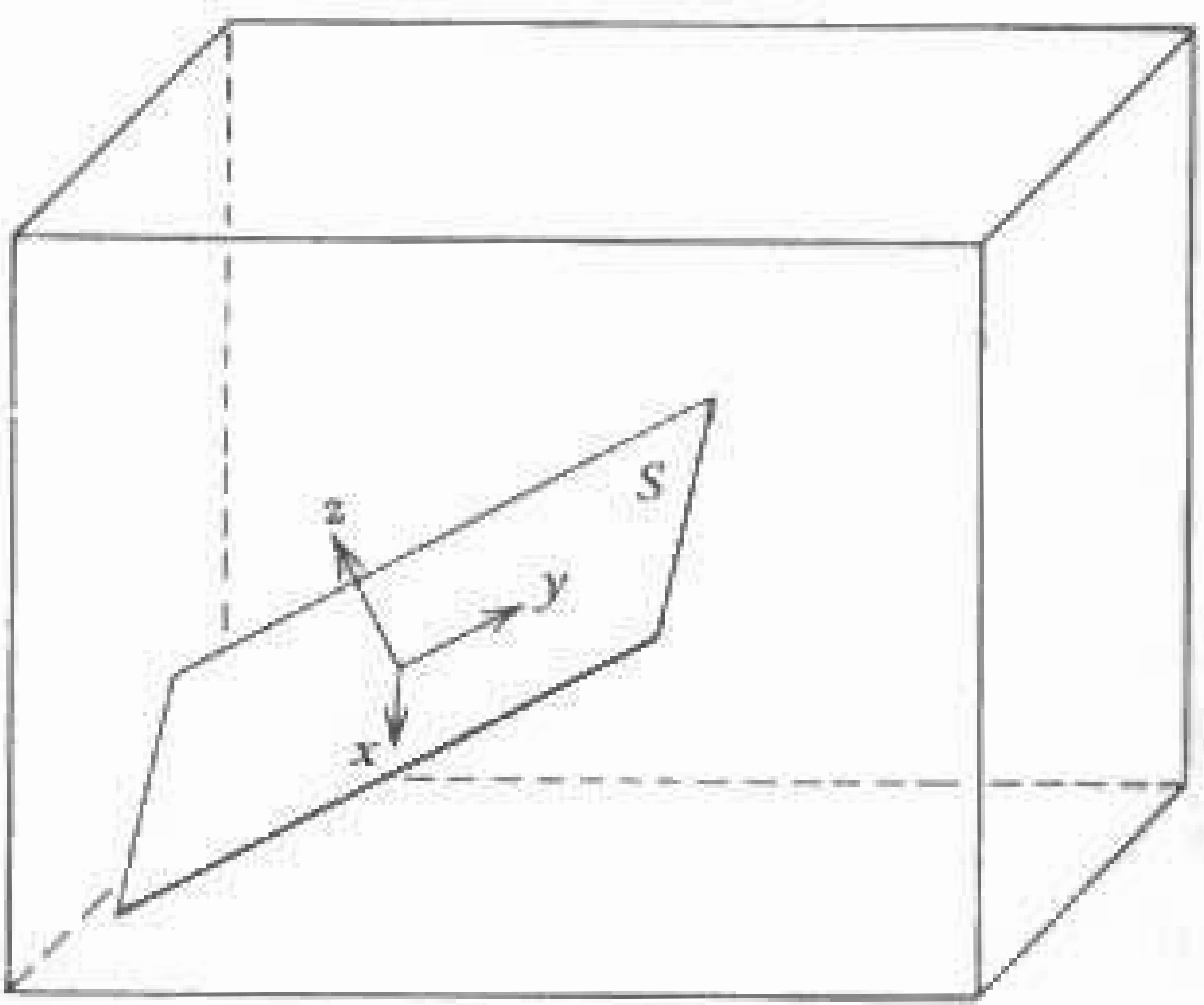
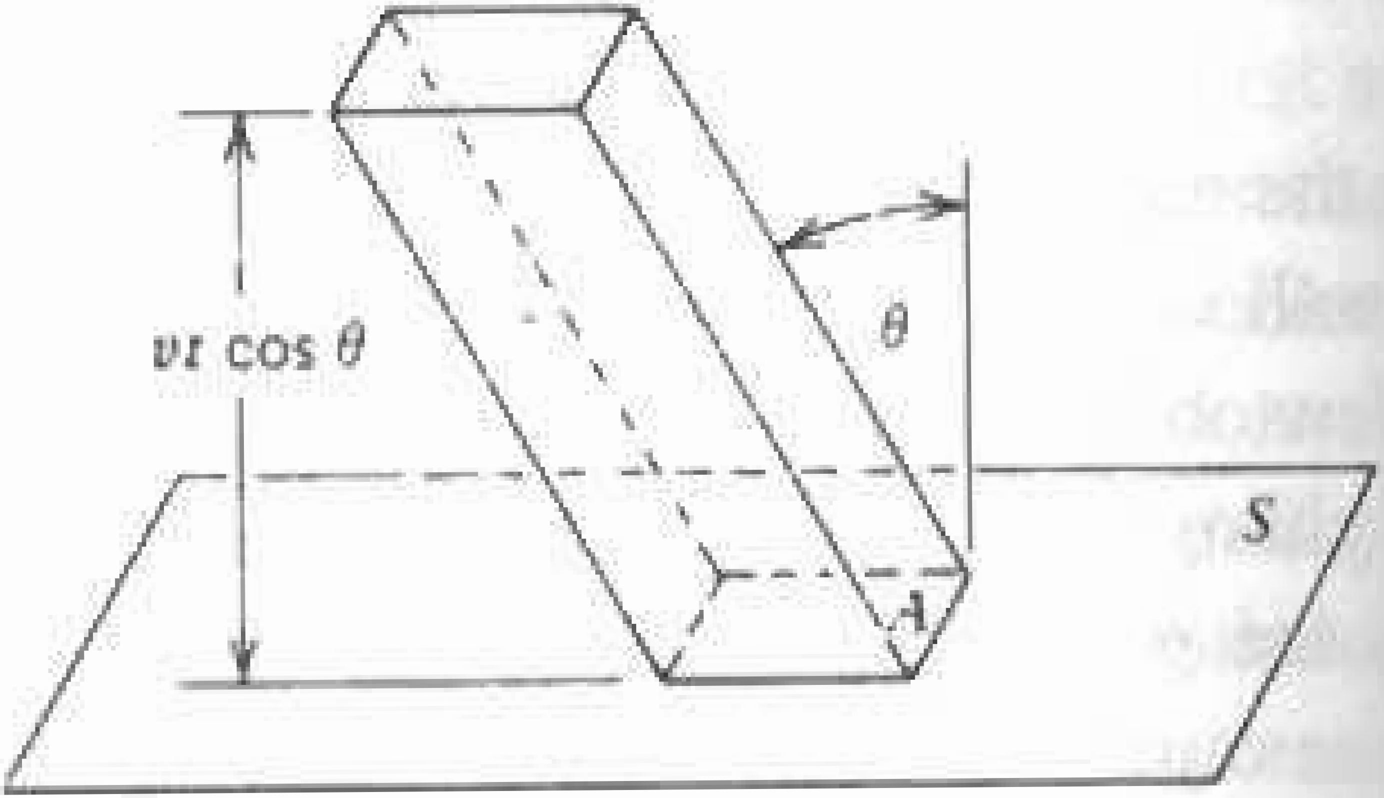


Figure 12.3 The plane surface S is fixed at an arbitrary position in a container of gas. The xyz coordinate system is defined so that the z axis is normal to S.

- Now replace S with an imaginary plane in the same position.
  - The molecules will cross this imaginary plane with momentum mv_z.
  - **By definition**, pressure is same whether the wall is there or not.
    - Thus the pressure normal to the imaginary plane S is twice the momentum transported from one side across S per unit time and per unit area.
- What is the rate of momentum transfer?
  - Consider those molecules crossing S in the positive z direction.
  - θ is the angle between the molecule's trajectory and S.



igure 12.4 All the molecules within the inclined prism that ha
elocity **v** in the direction θ will strike the area A within time t. T
olume of the prism is $A\,vt\cos\theta$.

- $F(\theta, v)d\theta dv$ is the number of molecules with speed between v and $v + dv$ that cross S per unit time and per unit area at angles between θ and $\theta + d\theta$.
- Each molecule has momentum mv with z component $mv\cos\theta$.
  - Only the z component contributes to the pressure.
  - The contribution of the other components of the motion cancel out due to the isotropy of the gas and make no net contribution to the pressure.
- Therefore the contribution to the pressure from the molecules in the range $dvd\theta$ is the number per unit time per units area multiplied by twice the z component of the momentum transported per molecule.

$$dp = 2mv\cos\theta F(\theta, v)d\theta dv$$

- This is integrated over all possible values of θ and v that represent molecules crossing z in the positive direction to give the total pressure:

$$p = \int_{v=0}^{\infty}\int_{\theta=0}^{\pi/2} 2mv\cos\theta F(\theta, v)d\theta dv$$

- What is $F(\theta, v)$? It is the product of:
  - the number of molecules per unit volume with speed between v and $v + dv$ moving with angles between θ and $\theta + d\theta$, i.e. $f(\theta, v)d\theta dv$.
  - The volume occupied by all molecules capable of crossing S per unit time, i.e. the volume of the prism.

- Continued:
  - The volume of the prism (Figure 12.4) is $Avt\cos\theta$ for a base of area A and time t, thus per unit area and per unit time, this becomes $v\cos\theta$

$$F(\theta, v)d\theta dv = v\cos\theta\ f(\theta, v)d\theta dv$$

  - Recall that $f(v)dv$ is the total number of molecules per unit volume with speeds between v and $v + dv$.

$$\int_\theta f(\theta, v)d\theta dv = f(v)dv$$

  - Recall also that molecular motion is isotropic. Therefore the integration is over the range of solid angles between θ and $\theta + d\theta$.

- Continued:
  - $f(\theta, v)d\theta dv$ and $f(v)dv$ are in the same relationship as are the solid angles between $\theta + d\theta$ and 4π.
    - The solid angle between θ and $\theta + d\theta$ is $2\pi \sin\theta d\theta$

$$\frac{f(\theta, v)d\theta dv}{f(v)dv} = \frac{2\pi \sin\theta d\theta}{4\pi} = \frac{1}{2} sin\theta d\theta$$

- Thus the pressure is:

$$p = \int_{v=0}^{\infty} \int_{\theta=0}^{\pi/2} (2mv\cos\theta)(v\cos\theta) \left(\frac{1}{2}\sin\theta d\theta\right) f(v)dv$$

$$p = m\int_{v=0}^{\infty} v^2 f(v)dv \int_{\theta=0}^{\pi/2} \cos^2\theta \sin\theta d\theta$$

- The angular integral is of the form:

$$\int u^2 du = \frac{u^3}{3} + C$$

where

$$u = \cos\theta \text{ and } du = -\sin\theta d\theta$$

Therefore

$$\int_{\theta=0}^{\pi/2} \cos^2\theta \sin\theta d\theta = -\frac{1}{3}\left(\cos^3(\pi/2) - \cos^3(0)\right)$$

$$= -\frac{1}{3}(0 - (1)^3) = \frac{1}{3}$$

- Therefore:

$$p = \frac{m}{3} \int_0^\infty v^2 f(v) dv$$

- Recall that:

$$U = \int_V \int_{v=0}^\infty \frac{mv^2}{2} \, f(v) \, dv \, dV$$

thus

$$p = \frac{2}{3} \frac{U}{V}$$

which is consistent with

$$p = \frac{1}{3} nmv^2$$

Some Comments about Thermodynamics

- Thermodynamics deals with relationships among the macroscopic properties of matter.
  - Equilibrium thermodynamics deals with relationships among macroscopic properties of matters at equilibrium.
- The laws of thermodynamics allow these relationships to be derived.
- The laws of thermodynamics are postulates.
  - These postulates conform with our observations of the world.
  - These postulates apply to systems containing a large number of molecules, i.e. a macroscopic system.

- Thermodynamics also permits us to interpret spontaneous processes.
  - Also aids in the understanding of “time’s arrow” and irreversible processes.
- The laws of thermodynamics make no assumptions about the microscopic structure of matter.
- The laws of thermodynamics allow the construction of a logically complete and internally self consistent theory.
  - The properties of real matter appear in the theory, but thermodynamics is only concerned about the relationships among these quantities.
  - These properties of real matter have the values that they do because of the microscopic interactions of the molecules.

- For example, the pressure of a gas may be given as a power series in n, the number density:

  $$P = a_0 + a_1 n + a_2 n^2 + a_3 n^3 + \cdots$$

  where a_i are experimentally determined. (This is also known as a virial equation.)
- From thermodynamics, relationships between pressure and other thermodynamic quantities such as internal energy, entropy, enthalpy, and free energy are known.
  - Thus these quantities may be determined in terms of the values of a_i.
  - The values of a_i depend on the interactions of the molecules.

- Continued:
    - If the molecular interaction potential is known, then a_i may be determined using the methods of statistical mechanics.
    - In principle, the interaction potential can be determined from quantum mechanics.
- The development of the principles of thermodynamics depends on some basic concepts.
- One of these basic concepts is the system.
    - A system is that part of the world under consideration.
        - Everything else is the surroundings.

- Systems may be classified according to their relationship to the surroundings.
  - An open system can exchange matter and energy with the surroundings.
  - A closed system can exchange energy but not matter with the surroundings.
  - An isolated system exchanges neither energy nor matter with the surroundings.
- A thermodynamic system is described by a set of macroscopic variables or “coordinates”.
- These macroscopic variables apply to measurements made for large number of molecules over a time period sufficiently long for many interactions of the molecules and at energies larger than individual quanta.

- The thermodynamic properties of the system can be completely describe by the set of macroscopic coordinates.
  - These variables are typically temperature, pressure, and volume.
- A macroscopic coordinate can be a constraint on the system when it is fixed in value by the boundary conditions that define the system.
  - A system can have constraints other than macroscopic coordinates.
- Classical thermodynamics deals with the properties of a system at equilibrium.
  - At equilibrium, none of the macroscopic coordinates changes with time.

- At equilibrium there is no net energy or matter flow through the system.
- The condition of equilibrium depends upon the constraints on the system.
  - These constraints must be specified.
  - There is only one true equilibrium state for a particular set of constraints.
- Metastable states can be observed not to change during the time of observation.
  - This is because the process that would take the system to equilibrium is so slow relative to the time of observation.
  - Nonequilibrium thermodynamics is a growing field.

- A complete set of thermodynamic coordinates uniquely determines the thermodynamic state.
  - If the mass is known, a complete set of thermodynamic coordinates is made up of those variables that can be independently specified.
  - For a one component system of fixed mass, two thermodynamic coordinates are needed.
  - For comparison, a microscopic system of N particles would need $6N - 6$ microscopic coordinates.
  - The number of thermodynamic coordinates needed varies with the number of components and the number of phases in the system.
- Consider a fluid which assumes the shape of its container such as a liquid or a gas.

- Continued:
    - The properties of a fluid are independent of its shape.
    - For a pure fluid (i.e. only one component) the thermodynamic state can be completely specified by just pressure and volume.
    - This means that any additional thermodynamic coordinates cannot be independent of the pressure and volume.
        - The relationship among pressure, volume, and thermodynamic coordinate X is the equation of state:
          $$f(p, V, X) = 0$$
          .

- What is the nature of X?
  - The thermodynamic coordinate X is more commonly known as temperature.
- The definition of the thermodynamic coordinate of temperature will be developed only in terms of those variables required to define the state of thermodynamic system, i.e. p and V or related quantities.
  - Temperature θ may be defined by an equation of the form:

    $$f(p, \rho, \theta) = 0$$

    where ρ is the density.
    - Note that density is related to the volume, but is intensive rather than extensive.
  - This equation defines θ.

- What properties should θ have?
  - Well behaved in that it is finite, continuous, and single-valued.
  - Have some relationship to intuitive notions of temperature.
  - Mathematically convenient.
- Many mathematical functions satisfy these conditions such as

$$\theta = p/\rho$$

$$\theta = (p/\rho)^2$$

$$\theta = \log{(p/\rho)}$$

or multiples thereof.

- To select an appropriate function, express this as a generality:

$$g(\theta) = \varphi(p, \rho)$$

- Now some concepts about temperature scales must be considered.
- Consider systems 1 and 2.
  - The systems consists of the same pure fluid.
  - Initially, the systems are isolated from each other and are separately at equilibrium at different temperatures, i.e.

$$\varphi(p_1, \rho_1) \neq \varphi(p_2, \rho_2)$$

- Continued:
  - The two systems are brought together so that they are isolated from the surroundings, but separated from each other by a rigid barrier B.
  - B is an adiabatic wall if the systems do not change from their initial states.
    - An adiabatic wall does not allow energy to cross.
    - Isolated systems are surrounded by adiabatic walls.
  - Suppose barrier B is rigid (so no work is done), but does allow energy to cross, i.e. it is diathermal.
    - The two systems will equilibrate to the same temperature, i.e. they will come into thermal equilibrium eventually.

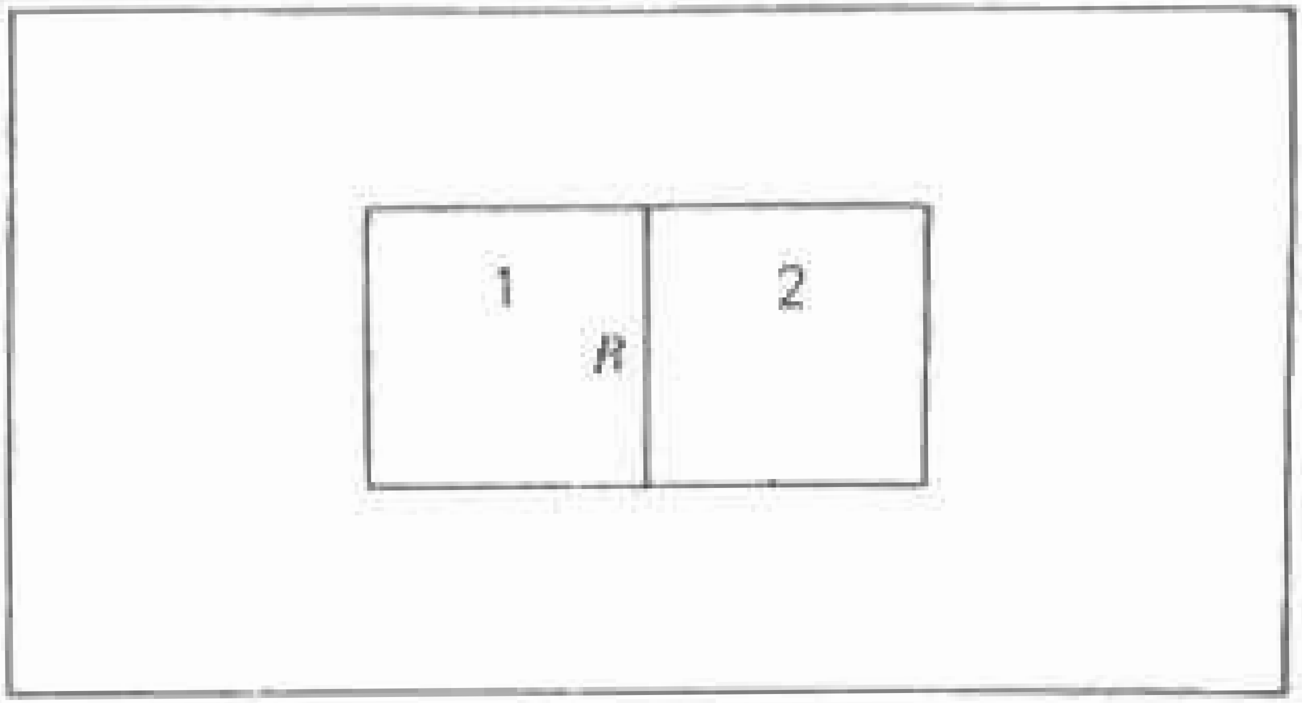


Figure 12.5 The two systems labeled 1 and 2 are separated by a rigid wall *B*. Both systems are isolated from the remainder of the universe.

- If the original isolated systems are separately in equilibrium, the constraint of isolation defines the equilibrium.
- If the constraint is altered, in this case by replacing the adiabatic wall with a diathermal wall, the system will move to a new equilibrium.
- If two systems have reached thermal equilibrium with each other, the state of one system cannot be changed without changing the other.
  - The overall equilibrium is described by a single relationship of the independent thermodynamics coordinates of each system:

$$F_{12}(p_1, \rho_1, p_2, \rho_2) = 0$$

- Continued:
    - The exact form of F_{12} depends on the nature of the fluids making up the systems and their individual equations of states.

The Zeroth Law of Thermodynamics

- Two systems, each separately in thermal equilibrium with a third system, are in thermal equilibrium with each other.
    - The third system is a thermometer.
    - This allows us to develop a universal definition of temperature.
    - This definition will be in terms of some property possessed by all objects “at the same temperature”.

- Consider fluids 1, 2, and 3, each described by their only independent variables, p and ρ.
- Fluids 1 and 2 are in mutual equilibrium and are described by:

$$F_{12}(p_1, \rho_1, p_2, \rho_2) = 0$$

- Fluids 1 and 3 are in mutual equilibrium and are described by:

$$F_{13}(p_1, \rho_1, p_3, \rho_3) = 0$$

- Both equations may be solved for p_1 yielding functions w_{12} and w_{13} :

$$p_1 = w_{12}(\rho_1, p_2, \rho_2) \text{ and } p_1 = w_{13}(\rho_1, p_3, \rho_3)$$

  - Therefore: $w_{12}(\rho_1, p_2, \rho_2) = w_{13}(\rho_1, p_3, \rho_3)$.

- But the Zeroth Law requires that if systems 1 and 2 are in thermal equilibrium and system 2 and 3 are in thermal equilibrium, then systems 2 and 3 are in thermal equilibrium.
  - Therefore there must exist some F_{23} such that:

    $$F_{23}(p_2, \rho_2, p_3, \rho_3) = 0$$

    which completely describes the equilibrium between systems 2 and 3.
- If this equation and $w_{12}(\rho_1, p_2, \rho_2) = w_{13}(\rho_1, p_3, \rho_3)$ is true, then the variable ρ_1 must disappear from w_{12} and w_{13}.
  - Therefore $w_2(p_2, \rho_2) = w_3(p_3, \rho_3)$, i.e. w_i depends only on the properties of system i.
  - Thus: $w_1(p_1, \rho_1) = w_2(p_2, \rho_2) = w_3(p_3, \rho_3)$

- Given the Zeroth Law, there exists at set of functions w_i which depend only on the state of fluid i and which have the same value of any number of fluids in equilibrium.
  - w_i must depend on some single property that all i systems have in equilibrium, regardless of the nature of the systems.
  - This single property is the thermodynamic temperature.
  - $w_i(p_i, \rho_i)$ is equivalent to $\varphi(p, \rho)$.
  - This means that $g(\theta)$ may be defined in terms of a property that all systems in thermal equilibrium have in common.
  - Thus a universal temperature scale may be constructed.

- Consider a particular system as the standard.
- Select one of the system’s temperature functions, $g(\theta)$.
- Define a numerical value of $g(\theta)$ as the temperature θ.
- This standard system is the thermometer.
- The function used to define the system is the thermometric property.

The Perfect Gas Temperature Scale

- How does this all relate to a usable temperature scale?
- Any property of a system that is “well-behaved” can be used to define the temperature scale.
  - The choice is arbitrary and is based on convenience.

- Since the choice of thermic properties is arbitrary, it is convenient that significant changes in the property can be measured accurately in small systems, i.e. the thermometer can come into equilibrium with the system without significantly changing the system.
  - Many thermometers are based on the volume of a liquid.
    - The expansion of the liquid is measured in a narrow tube attached to a reservoir.
  - Some thermometers are based on electrical resistance.
  - Thermocouples are based on the differential properties of bimetal strip as measured by electromotive force at the junction.

- Continued:
  - Pyrometers measure the intensity of radiation.
    - It is assumed that the emitted radiation follows the blackbody distribution.
- All of these are calibrated against a thermodynamic temperature scale.
- A thermodynamic temperature scale can be based on the properties of a very dilute gas.
  - Pressure and volume (or density) are easily measured.
  - The scale can be defined as proportional to the pressure or proportional to the volume.
  - Both thermometers (constant volume or constant pressure) converge to the same low pressure limit.

- The temperature scale needs a reference point.
    - The triple point of water is such a reference point.
        - Solid, liquid, and vapour coexist at a unique point in p, ρ, and temperature.
    - Consider a system in equilibrium with pure water at the triple point.
        - This system has pressure p_3 and temperature θ_3.
        - A constant volume temperature scale may be defined for this system in other conditions.

$$\theta(p) = \frac{p}{p_3}\theta_3$$

        - θ_3 is an arbitrary constant. By convention, θ_3 is 273.16 K.

- A constant pressure scale may also be defined with respect to the triple point.

$$\theta(V) = \frac{V}{V_3}\theta_3$$

- The actual empirical scales depend on the quantity and nature of the gas.
- In the limit of small quantity, both scales approach the same limiting temperature:

$$\lim_{p\rightarrow\ 0}\theta(p) = \lim_{V\rightarrow\ \infty}\theta(V) = \theta^*$$

- θ^* is the perfect gas temperature.

- Thermometers are calibrated with respect easily reproduced phase equilibria.
- Both the constant volume and the constant pressure temperature scales converge to the same limiting value.
  - This may be expressed as:

$$\lim_{p\rightarrow\ 0} \frac{pV}{n} = \beta\theta^*$$

where $\beta(\theta^*)$ is a function only of θ^*

- Limits at two different temperatures are proportional to the perfect gas temperature.

$$\frac{\beta(\theta_1^*)}{\beta(\theta_2^*)} = \frac{\theta_1^*}{\theta_2^*}$$

- Temperature scales had formerly been defined in terms of two fixed points.
  - The Celsius scale had been defined in terms of the freezing and boiling points of water at a pressure of 1 atm.
  - The Fahrenheit scale had been defined in terms of the freezing point of a saturated NaCl solution and the boiling point of pure water at a pressure of 1 atm.
- These scales can be related to the perfect gas scale.
  - For a constant volume thermometer, the Celsius temperature t^* may be defined by:

$$t^* = \lim_{p_0 \to 0} \frac{100(p - p_0)}{p_{100} - p_0}$$

- This can be related to the absolute temperature, θ^* by:

$$\theta^* = t^* + \theta_0^*$$

  where θ_0^* is the ice-point temperature, 273.15 K.
- The triple point temperature θ_3^* is by definition 273.16 K.
  - As a result the boiling point of water is 373.146 K. (This supersedes the previous definition of Celsius temperature.)
- There are other ways to establish thermodynamic temperature scales that do not depend on the properties of a substance.
  - It can be shown that these scales are equivalent to the perfect gas scale.

- T will be used to represent the perfect gas temperature.
  - The thermodynamic temperature T is equal to the perfect gas temperature θ.

Pressure Units

- The SI unit is the Pascal. 1 Pa = 1 N m^{-2}.
- Other units are:
  - In cgs (centimeter gram second), 1 dyne cm^{-2} = 0.1 Pa.
  - Common in meteorology is the bar, 1 bar = 10^{5} Pa.
  - Widely used is atm. By definition, 1 atm = 1.01325 $\times\ 10^5$ Pa.
  - The torr is defined as 1/760 atm or 1 mmHg.

- The perfect gas equation of state is:

  $$pV = nRT$$

  where n is number of moles of gas in volume V.
- The universal gas constant is evaluated by:

  $$R = \lim_{p \to 0} \frac{pV}{nT}$$

- R is related to the Boltzmann constant k_B:

  $$k_B = \frac{R}{N_A}$$

  where N_A is Avogadro's number.

- The perfect gas equation of state may be written:

  $$pV = Nk_BT$$

  where N is the number of molecules in volume V.
- Molar mass, M, may be determined by measuring p, ρ, and T

  $$M = RT \lim_{p \to 0} \frac{\rho}{p}$$

Microscopic and Macroscopic Approaches

- What are the essential features of each?
- What is general and what is specific to each approach?
- How are the two approaches to a perfect gas related?

The microscopic approach to the perfect gas

- The perfect gas is defined entirely in terms of the properties of the individual molecules that make up the gas.
- Already considered has been the case of monoatomic molecules which collide elastically with the walls.
  - What about polyatomic molecules?
  - What about molecules that interact with one another?
  - Statistical mechanics involves the adoption of a model of the molecular interactions.
    - Thus the results are specific to that model.

The macroscopic (or thermodynamic) approach to the perfect gas

- This is based on the properties of real gas in the limit of low pressure.
- No assumptions are necessary about the nature of the interactions of molecules with each other.
- This thermodynamic approach is tied directly to experiment.

How are the two approaches related?

- The microscopic approach and kinetic theory leads to

$$p = \frac{2}{3}\frac{U}{V}$$

where U is the total kinetic energy.

- The macroscopic approach involves only measurable variables:

$$p = \frac{nRT}{V}$$

- Combining these gives:

$$U = \frac{3}{2}nRT = \frac{3}{2}Nk_BT$$

  and the molecular kinetic energy per mole is proportional to absolute temperature.

  - This can be shown to be generally true for real gases.
  - The microscopic perfect gas has properties chosen to match those of the thermodynamic perfect gas.

- This basic approach is applicable to other systems.
- For a given mass of any fluid, two of p, V and T are independent.
  - That is, there exists an equation of state such that $f(p, V, T) = 0$.
- The corresponding molecular model must involve p, V and the molecular energy.
  - Intramolecular energy (vibrational, rotational, and electronic) as well as kinetic energy.
- Equations of state may be obtained by:
  - Direct measurement.
  - Extrapolation from a hypothetical system.
  - From statistical mechanics.

- Thermodynamics deals with relationships between the equation of state and measurable quantities and thermodynamic functions.
  - These relationships are general and apply regardless of the equation of state.
  - It can be shown that:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

is true for all systems, but its actual value depends on the equation of state.