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.
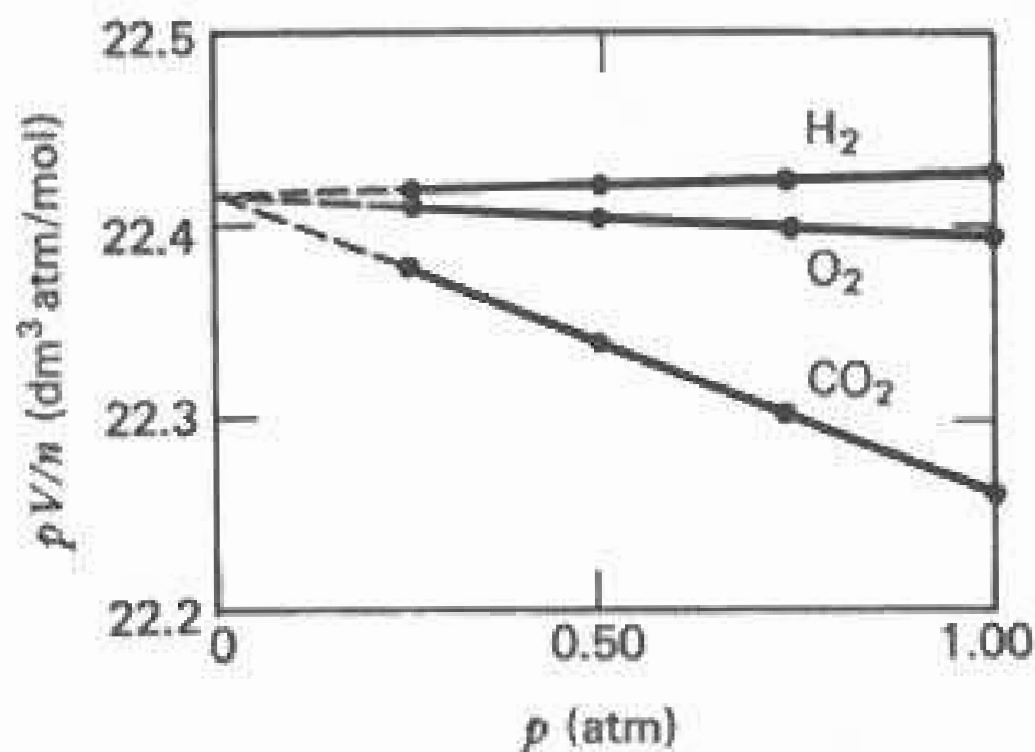
UNITS ARE YOUR FRIENDS!!

EQUATIONS OF STATE

- "An equation of state is the mathematical relationship among the relevant thermodynamic variables of an equilibrium system."

- Examples (from gas behaviour):
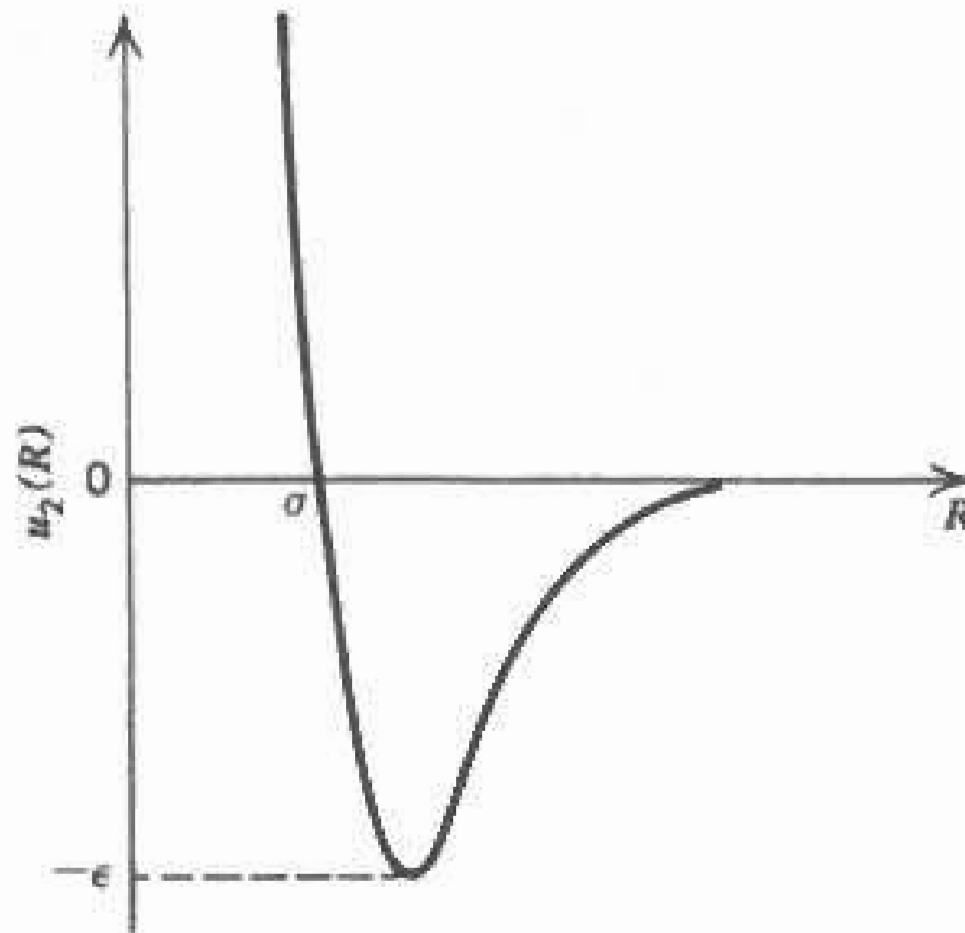 - Ideal Gas Equation of State

$$pV = nRT$$

  - van der Waals Equation of State

$$p = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

Figure 21.1 The pV product for three gases, showing the universal approach to the ideal gas value as the pressure tends to zero. From R. H. Cole and J. S. Coles, *Physical Principles of Chemistry* (Freeman, San Francisco, 1964).

Figure 21.6 A representation of the intermolecular potential between a pair of molecules as a function of the distance between them.

- Berthelot Equation of State

$$p = \frac{RT}{\overline{V} - b} - \frac{a}{T\overline{V}^2}$$

- Virial Equation of State

$$\frac{p\overline{V}}{RT} = 1 + \frac{B(T)}{\overline{V}} + \frac{C(T)}{\overline{V}^2} + \dots$$

THERMODYNAMIC VARIABLES

- Intensive
- Extensive
- Relation to Equation of State
- Description of Equilibrium

COMPRESSIBILITY

- Recommended Reading: Chapter 21 of Berry *et al.*
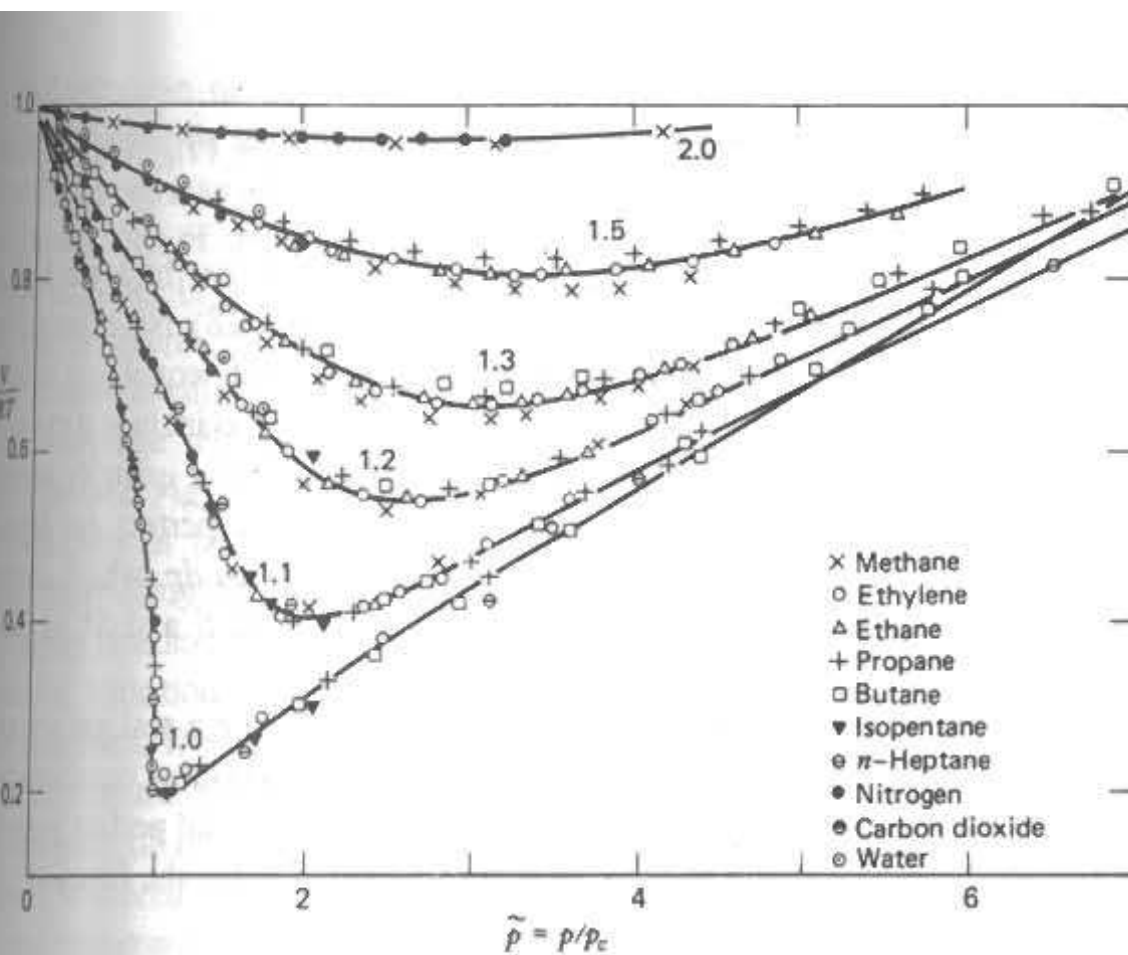- The compressibility factor, Z, may be defined:

$$Z \equiv \frac{\overline{V}(\text{real})}{\overline{V}(\text{ideal})} = \frac{p\overline{V}}{RT}$$

- Ideal gas

$$Z \equiv \frac{p\overline{V}}{RT} = 1$$

- van der Waals

$$Z \equiv \frac{p\overline{V}}{RT} = \frac{\overline{V}}{\overline{V} - b} - \frac{a}{RT\overline{V}}$$

Figure 21.5 The compressibility factor pV/nRT for several gases plotted as a function of the reduced pressure p/p_c. The curves are for different values of T/T_c. From G. J. Su, *Ind. Eng. Chem.* **38**, 803 (1946).

- Virial equation

$$Z \equiv \frac{p\overline{V}}{RT} = 1 + \frac{B(T)}{\overline{V}} + \frac{C(T)}{\overline{V}^2} + \dots$$

- For more equations of state, see Table 21.2 on page 553 of Berry *et al.*

- Deviation from 1 of the value of Z, the compressibility factor, is a measure of the nonideal behaviour of a gas.

- $B(T)$, the second virial coefficient, has units of molar volume (m^3 mol^{-1}) and is the first term in the description of deviation from ideal behaviour.

- $C(T)$, the third virial coefficient, has units of the square of molar volume (m^6 mol^{-2}) and is the second term in the description of deviation from ideal behaviour.
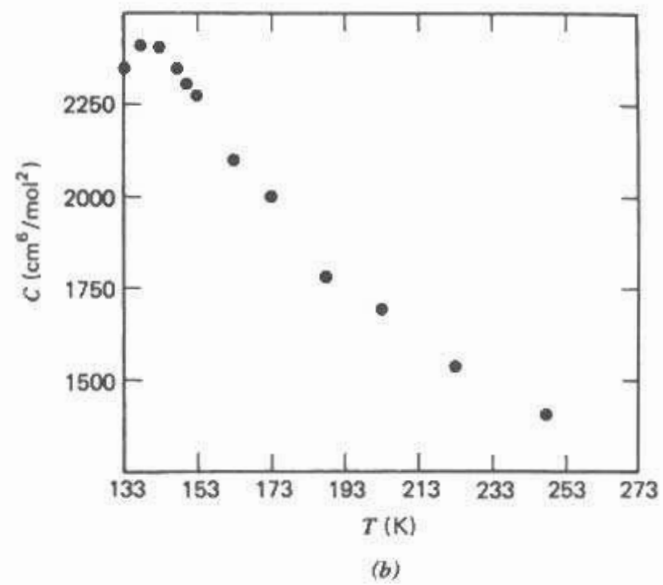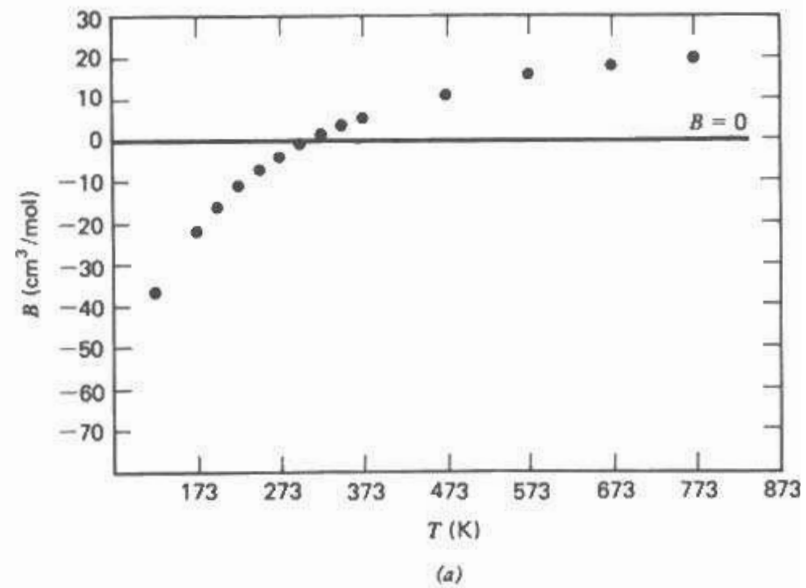
Figure 21.7 The second and third virial coefficients of Ar.

Significance of the second virial coefficient, $B(T)$

- $B(T)$ is temperature dependent
  - At high T repulsions are expected to be important.
  - At low T attractions are expected to be important.

- Consider the van der Waals equation of state written in virial form:

$$Z = 1 + \left(b - \frac{a}{RT} \right) \frac{1}{\overline{V}} + \frac{b^2}{\overline{V}^{\,2}} + \ldots$$

or:

$$Z \equiv \frac{p\overline{V}}{RT} = 1 + \frac{B(T)}{\overline{V}} + \frac{C(T)}{\overline{V}^{\,2}} + \ldots$$

where:

$$B(T) = b - \frac{a}{RT} \; ; \;\; C(T) \;=\; b^2$$

- If T is large, $B(T) \to b$, which is positive.
  - Repulsion accounts for most of the deviation from ideal behaviour.
- If T is small, $B(T)$ becomes negative.

$$B(T) \to -\frac{a}{RT}$$

  - Attraction accounts for most of the deviation from ideal behaviour.
- When $B(T) = 0$, the corresponding temperature is the Boyle temperature, T_B.

$$B(T) = 0 = b - \frac{a}{RT_B}; T_B = \frac{a}{Rb}$$

- A physical interpretation of the Boyle temperature, T_B, is that temperature at which the average attractive and repulsive forces are balanced.

- The second virial coefficient depends on the interaction potential between molecules of the gas of interest.
  - See section 21.7 of Berry et $al.$

- For a van der Waals gas, the Boyle temperature, T_B, allows us to define a dimensionless temperature scale in terms of multiples of the Boyle temperature.

$$B(T) = 0 = b - \frac{a}{RT_B}$$

- Dividing both sides of the equation by b gives:

$$\frac{B(T)}{b} = 1 - \frac{a}{RbT} = 1 - \frac{T_B}{T}$$

- This means:
  - that any temperature can be expressed as a multiple of of the Boyle temperature, T_B;
  - and that the second virial coefficient, $B(T)$, can be expressed as a multiple of the second van der Waals parameter b.
- Dimensionless scales allow the convenient comparison of a number of different gases described by the van der Waals equation.
- To set up scales of $\overline{V}$ and P, combinations of parameters that have the "right" dimensions are need.
  - The van der Waals parameter b has units of molar volume, which are the same units as $\overline{V}$.
 - The term $a/\overline{V}^2$ has the same units as pressure.

- Thus, one system of scaled variables is:
  - $\mathcal{T} = \dfrac{T}{T_B} = \dfrac{RbT}{a}$
  - $\mathcal{V} = \dfrac{\overline{V}}{b}$
  - $\mathcal{P} = \dfrac{pb^2}{a}$
- The van der Waals equation may be rewritten as:

$$\mathcal{P} = \frac{\mathcal{T}}{\mathcal{V} - 1} - \frac{1}{\mathcal{V}^2}$$

- This contains the same information as the original form of the van der Waals equation:
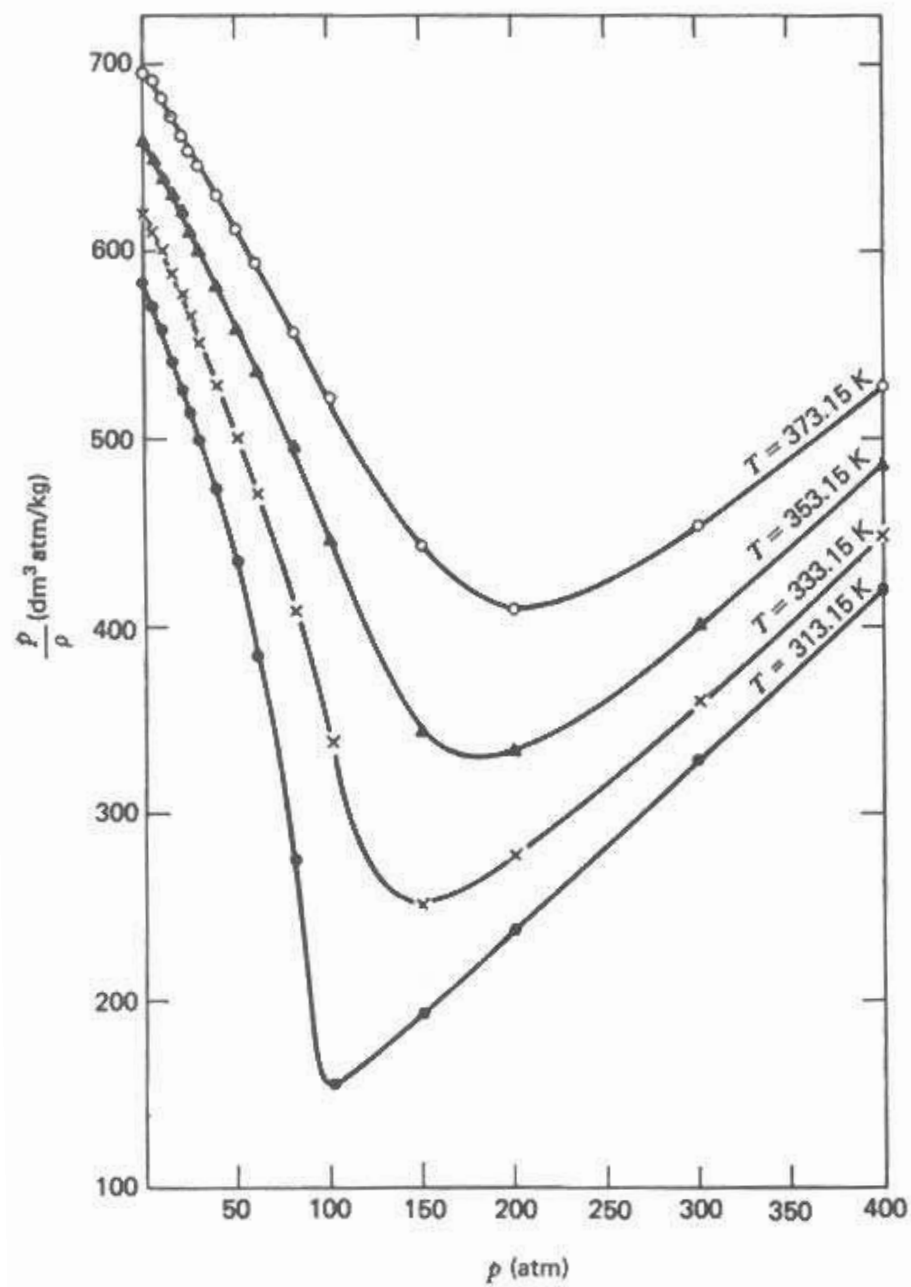
$$p = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

- Consider $p\overline{V}$ isotherms of the van der Waals equation.
  - At high temperature, the curve has neither a maximum nor a minimum.
  - At lower temperature, the curve has both a maximum and a minimum.
  - As temperature is increased from this lower temperature, the maximum and minimum move closer together.
  - There exists a temperature such that the minimum and maximum meet in an inflection point.
    - This temperature is the critical temperature.
  - An inflection point has the properties that the first and second derivatives of the curve are 0.
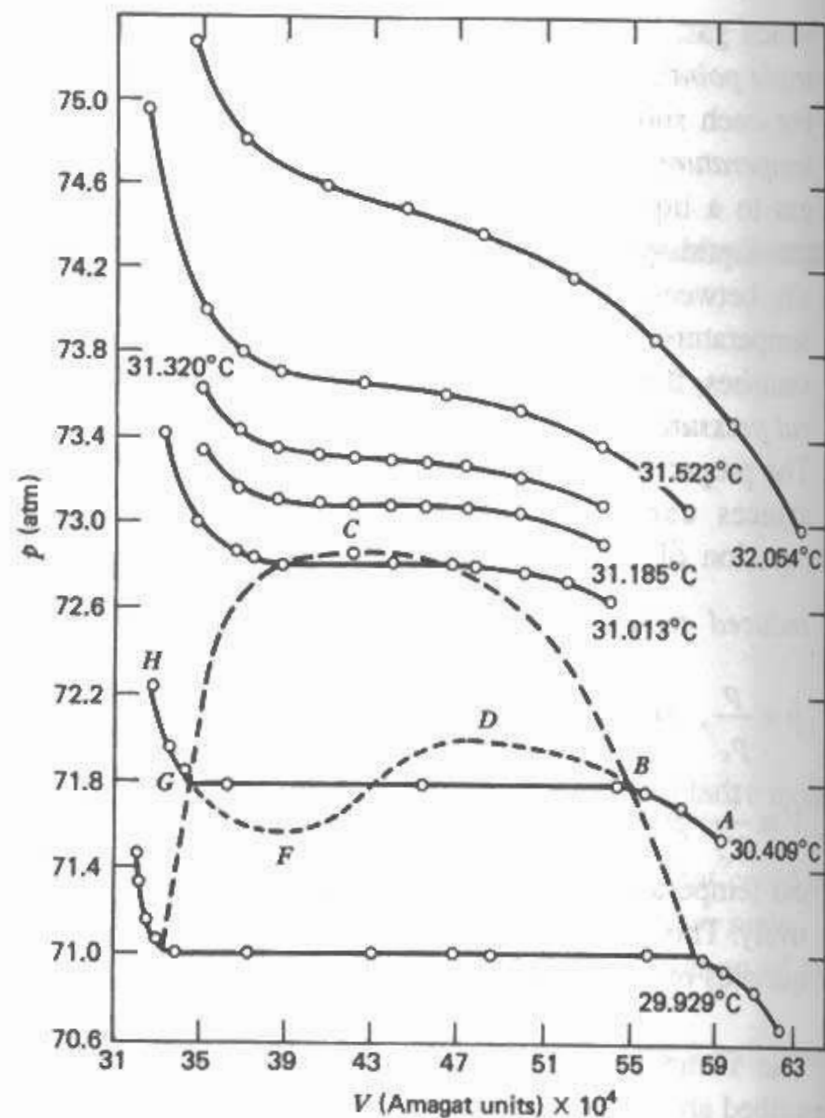
Figure 21.3 Some isotherms of CO_2 in the immediate vicinity of the critical temperature. From E. A. Moelwyn-Hughes, *Physical Chemistry* (Cambridge University Press, Cambridge, 1940); data from A. Michels, B. Blaisse, and C. Michels, *Proc. Roy. Soc.* **A160,** 367 (1937). One Amagat unit of volume for CO_2 is 2.2398×10^4 cm³/mol.

Figure 21.2 Some isotherms of CO_2 for temperatures above the critical temperature.

- Thus there are three simultaneous equations that can be solved for p_c, T_c, and $\overline{V}_c$.

$$p = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

$$\left(\frac{\partial p}{\partial \overline{V}}\right)_{T=T_c} = 0 = \frac{-RT}{(\overline{V} - b)^2} + \frac{2a}{\overline{V}^3}$$

$$\left(\frac{\partial^2 p}{\partial \overline{V}^2}\right)_{T=T_c} = 0 = \frac{2RT}{(\overline{V} - b)^3} - \frac{6a}{\overline{V}^4}$$

- To solve for $(p_c, \overline{V}_c, T_c)$:
  - Isolate T_c in the first and second derivatives.
  - Combine the resulting two equations and isolate $\overline{V}_c$

- Continued:
  - Substitute $\overline{V}_c$ into one of the equations and evaluate T_c.
  - Substitute $\overline{V}_c$ and T_c in the van der Waals equation to get p_c.
  - This gives:

$$\overline{V}_c = 3b; \quad T_C = \frac{8a}{27Rb}; \quad p_C = \frac{a}{27b^2}$$

- The critical variables provide another way to scale $(p, \overline{V}, T)$. (See section 21.1 of Berry *et al.*)
- The resulting set of scaled variables are known as *the reduced variables,* $(\tilde{p}, \tilde{V}, \tilde{T})$.
- Different gases described by the same set of reduced variables are in *corresponding states.*

- Something to try on your own (between now and the first term test):
  - Write the van der Waals equation in terms of reduced variables.

Some useful properties of partial derivatives

- Consider some function $z(x, y)$.

$$\left(\frac{\partial x}{\partial z}\right)_y = \left(\frac{\partial z}{\partial x}\right)_y^{-1}$$

  if z is a continuous function of x.
  - Most thermodynamic functions are continuous functions.

- An application of this would be for a van der Waals gas of the evaluation $\left(\partial \overline{V}/\partial p\right)_T$.

The Cyclic Rule

- Another useful property of partial derivatives.
- Again consider the function $z(x, y)$. The cyclic rule is:

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

- This in combination with the previous property allows us to find one of the derivatives given the other two.
- An application of this would be the evaluation for a van der Waals gas of

$$\left(\frac{\partial \overline{V}}{\partial T}\right)_p$$

- The cyclic rule is a consequence of the chain rule.

The Chain Rule

- Consider function $f(x_1, x_2)$ such that
  - $x_1 = x_1(y_1, y_2)$
  - $x_2 = x_2(y_1, y_2)$
- Then the chain rule is:

$$\left(\frac{\partial f}{\partial x_1}\right)_{x_2} =$$

$$\left(\frac{\partial f}{\partial y_1}\right)_{y_2} \left(\frac{\partial y_1}{\partial x_1}\right)_{x_2} + \left(\frac{\partial f}{\partial y_2}\right)_{y_1} \left(\frac{\partial y_2}{\partial x_1}\right)_{x_2}$$

- Consider the case where

$$x_1 = T, \; x_2 = p, \; y_1 = T, \; y_2 = V$$

- Then the chain rule becomes:

$$\left(\frac{\partial f}{\partial T}\right)_p = \left(\frac{\partial f}{\partial T}\right)_V \left(\frac{\partial T}{\partial T}\right)_p + \left(\frac{\partial f}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

- If $f = p$ then this becomes:

$$0 = \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial T}\right)_p + \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

- From this the cyclic rule may be derived:

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

- which can be rearranged as:

$$-1 = \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_V$$

State Functions and Path Functions (see Chapter 13 of Berry)

- Consider a system initially at equilibrium in state 1.

- The system undergoes a change and comes to a new equilibrium at state 2.

- The value of a **state function** at state 2 is **independent of the path** taken from state 1 to state 2.

- The value of a **path function** at state 2 is **dependent on the path** taken from state 1 to state 2.
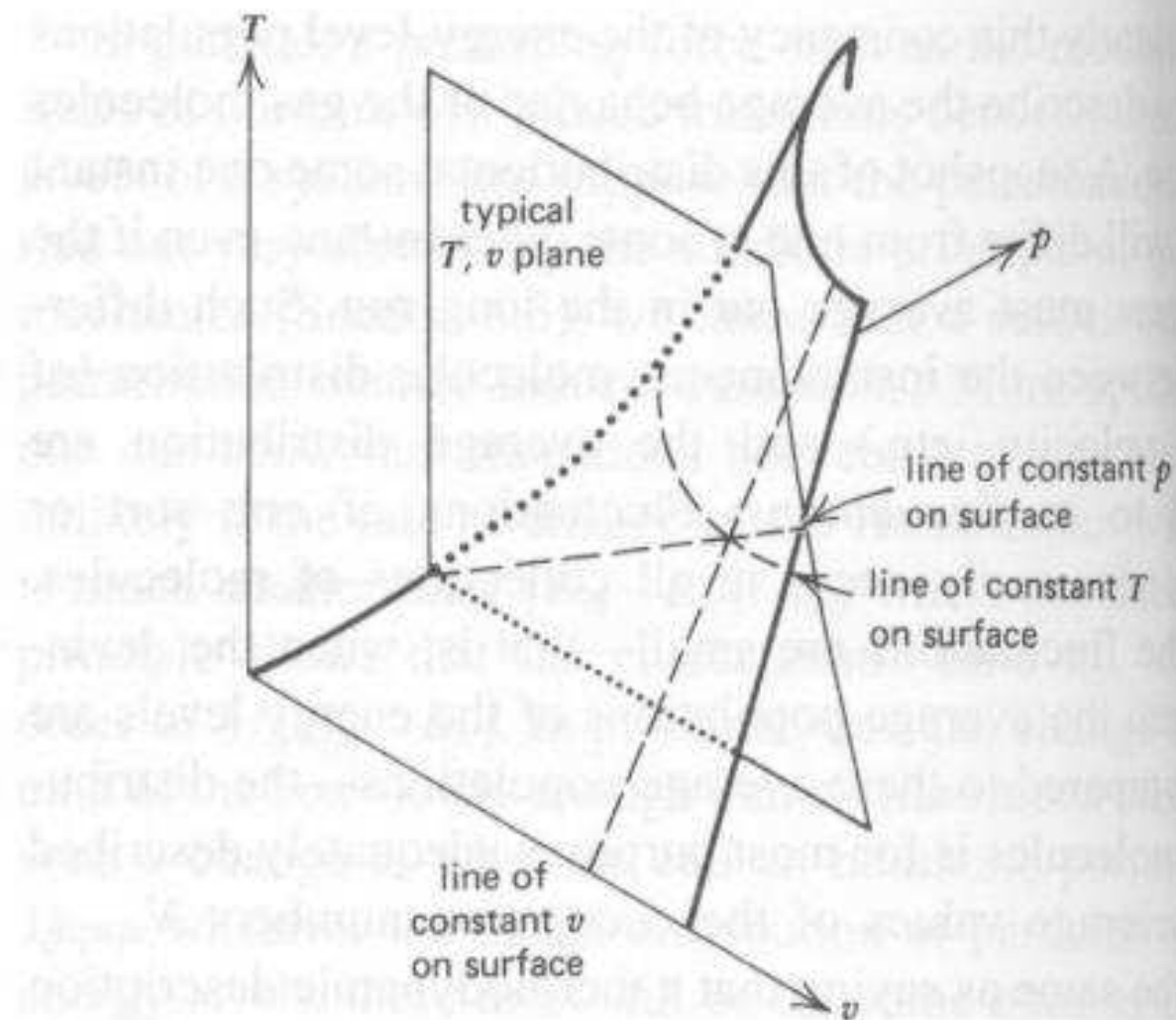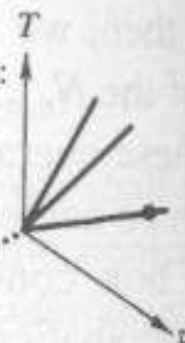
Figure 13.1 Part of a surface representing the equation of state in (p, v, T) space. The particular surface shown is for the perfect gas, with the equation of state $pv = RT$. The lines of constant p, T, and v on the surface are the loci of the intersections of the surface with typical (T, v), (p, v), and (T, p) planes, respectively. A typical (T, v) plane is shown; the others are omitted for clarity.
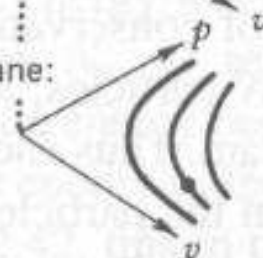
Figure 13.2 Intersections of the perfect gas surface of Fig. 13.1 with planes on which v, p, or T is constant. (a) (T, P) plane—each line in this plane is the locus of the intersection of the p, v, T surface and a plane on which v is constant. (b) (T, v) plane—each line in this plane is the locus of the intersection of the p, v, T surface and a plane on which p is constant. (c) (p, v) plane—each curve (hyperbola) in this plane is the locus of the intersection of the p, v, T surface and a plane on which T is constant.

Exact and Inexact Differentials

- An infinitesimal change on a path for a state function between state 1 and state 2 is described by an exact differential.

- An infinitesimal change on a path for a path function between state 1 and state 2 is described by an inexact differential.

- Consider some function z such that:

$$dz = f_x(x, y)dx + f_y(x, y)dy$$

where functional forms are chosen arbitrarily for f_x and f_y. For example:

$$f_x(x, y) = xy \text{ and } f_y(x, y) = x^2y^2$$

- Does there exist some function $z(x, y)$ such that dz is the total derivative?
    - If there does, then z is a state function.
    - If there does not, then z is a path function.

How to Test for State Functions

- If z is a state function, it must pass the cross derivative equality test.

- If the state function $z(x, y)$ exists then:

$$\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right) = \left(\frac{\partial^2 z}{\partial x \partial y}\right) = \frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right) = \left(\frac{\partial^2 z}{\partial y \partial x}\right)$$

- Applied to $dz = f_x(x, y)dx + f_y(x, y)dy$, the test becomes whether:

$$\frac{\partial f_y(x,y)}{\partial x} = \frac{\partial f_x(x,y)}{\partial y}$$

- Applied to $dz = xydx + x^2y^2dy$, we see that the cross derivative equality test is failed because:

$$\frac{\partial xy}{\partial y} = x$$

and

$$\frac{\partial (x^2y^2)}{\partial x} = 2xy^2$$

Therefore in this case z is a path function.

Energy, Work, and Heat

- Consider energy and molecules.
  - Energy affects how molecules react. In particular the distribution of energy within a molecule influences how it behaves both chemically and physically.
- How do molecules have energy?
  - In chemical bonds. The more energy required to break a bond, the stronger the bond is.
  - In internal motions (such as vibration and rotation) and electronic excitations.
  - As kinetic energy of motion. Temperature is a way of measuring the average kinetic energy of a system of molecules at equilibrium.

Energy (from a Thermodynamic Perspective)

- Consider the exothermicity of a chemical reaction.
  - Food Calories
  - Fuel Combustion
  - Corrosion
  - Decomposition
- Energy is considered on a scale related to changes, not an absolute scale.
- In thermodynamics, two particular forms of energy transfer are considered:
  - q heat
  - w work

What is energy?

- What are the properties of energy?
  - Cannot be created or destroyed
  - Can only change form such as be converted to heat, work, or internal energy.
- This will be examined initially from the perspective of the perfect gas.

The Perfect Gas (See Chapter 12 of Barry)

- 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.
  - 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.
  - Even though macroscopic properties of the system are stable, the microscopic positions and velocities of the individual molecules are constantly changing.

- Continued:
  - 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 and the gas is at rest in its container with no flows or currents.

- Continued:
  - Measurements of intensive variables such as pressure and temperature are the same regardless of where in the system they are made.
  - 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:

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

- 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.
- In the time between two collisions with S, the molecule must move $2l$ (to the other end of the box and back).
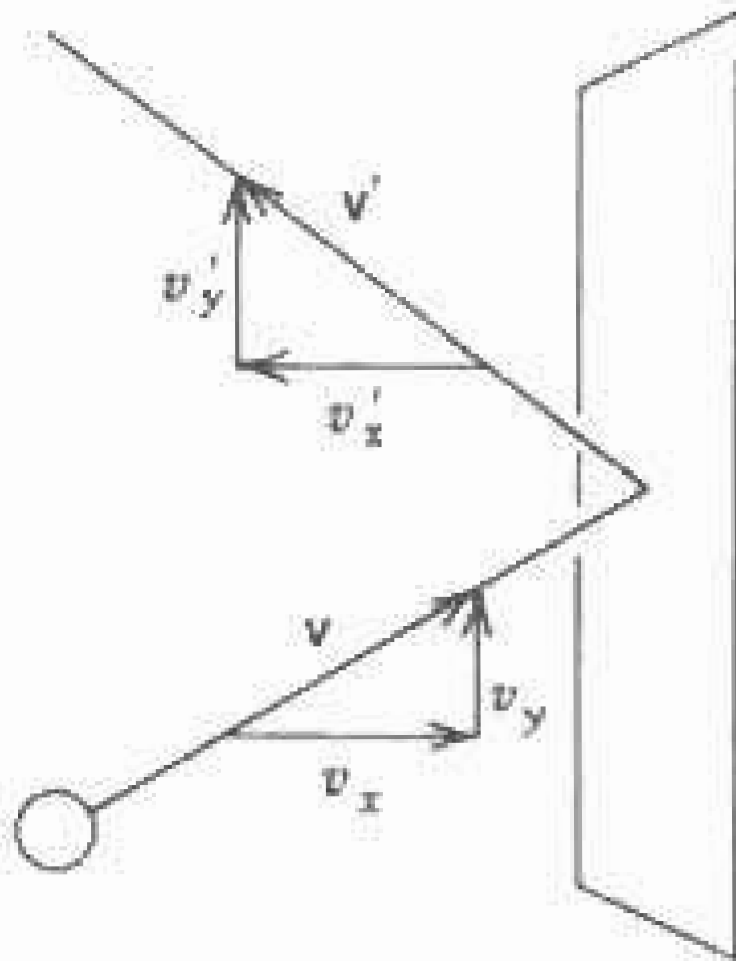
Figure 12.1 Elastic reflection of a particle from the wall of a box. The initial velocity is **v**, with components v_x perpendicular to the wall and v_y parallel to the wall. After reflection the velocity is **v'**, with components $v_x' = -v_x$ and $v_y' = v_y$.

- 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 with all molecules having 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

$$pl^2 = nml^2v_z^2 \text{or } p = nmv_z^2$$

- 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.

- It may be useful to have 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 $f(\mathbf{v}) \to 0$ as $\mathbf{v} \to \infty$
- 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

- 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:
$$f(v) = 4\pi v^2 f(\mathbf{v})$$
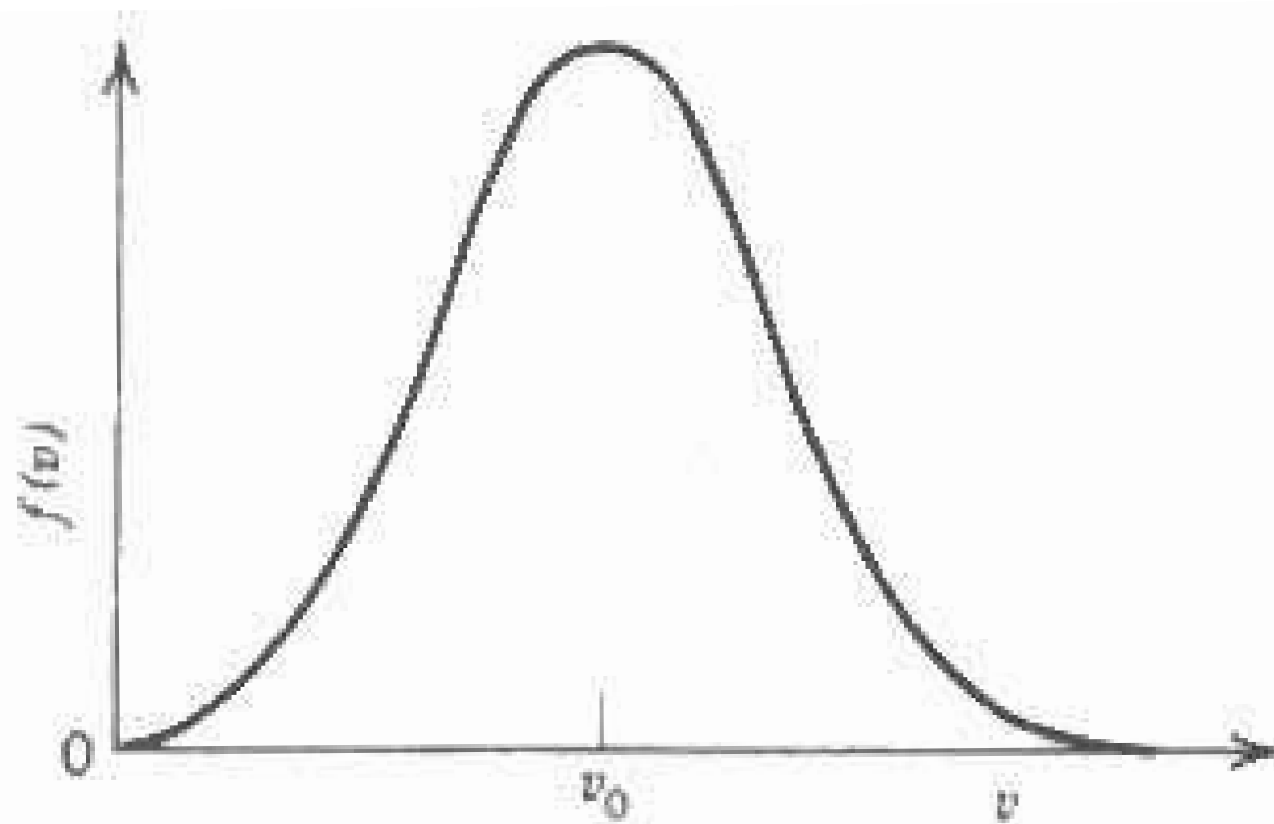
Figure 12.2 The distribution of molecular speeds, $f(v)$. The speed v_0, which is the most probable, is the *mode* of the distribution.

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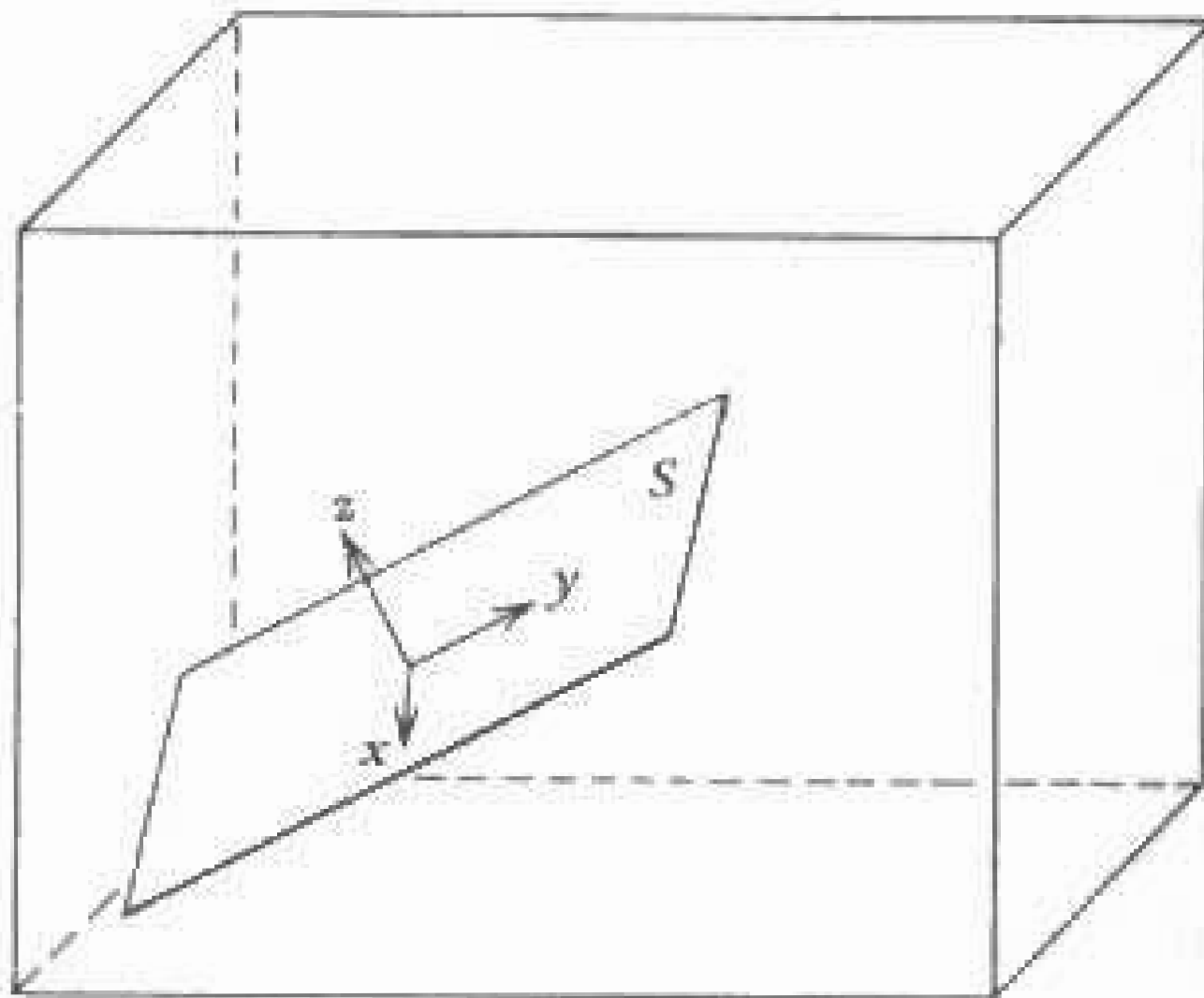
Figure 12.3 The plane surface S is fixed at an arbitrary position in a container of gas. The xyz coordinate system is defined so that the z axis is normal to S.

- 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.

- 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.
- $F(\theta, v)d\theta dv$ 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.
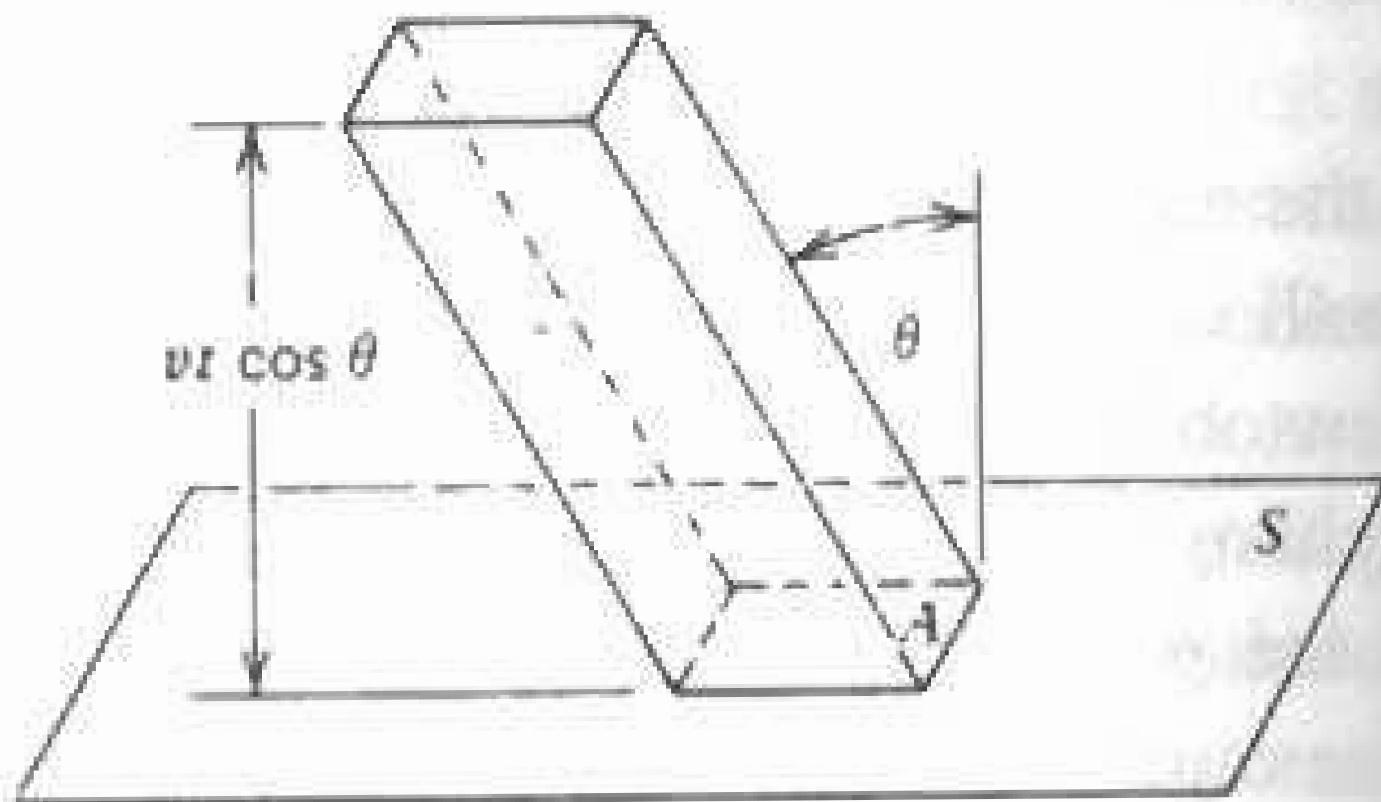
Figure 12.4 All the molecules within the inclined prism that have velocity **v** in the direction θ will strike the area A within time t. The volume of the prism is $A\,vt\cos\theta$.

- 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 $dv d\theta$ 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.
  - 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 $v + dv$.

- Thus:

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

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

  - Note also that $f(\theta, v) d\theta dv$ 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 $2\pi \sin \theta d\theta$
    - Therefore:

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

- 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 $u = \cos\theta$ 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.