Chemical Kinetics

- Chemical kinetics complements thermodynamics:
  - Thermodynamics tells us if something can happen.
  - Kinetics tells us how long it takes.
- Together they enable us to predict:
  - Rates of reactions.
  - Preference for one reaction over another.
  - Reaction conditions that will produce desired result.
  - Explosions and other dangerous conditions.
- As in the case of thermodynamics, chemical kinetics connects the microscopic and the macroscopic.

Molecular Motion and Collisions (Chapter 27)

- Molecules are constantly in motion.
- Molecular motions are important in accounting for change with time of some observable physical or chemical properties:
  - Amount of liquid evaporating per unit time.
  - Change in translational temperature per unit time.
  - Change in concentration of chemical reactant per unit time.
- Collisions of molecules are the only way energy can be transferred from one degree of freedom to another.
  - Between vibration and translation
- Rates of chemical and physical processes depend on the detailed dynamics of molecular collisions.

Kinematics

- Consider a molecule as a point mass moving with a given velocity.
  - A collision between molecules is an event in which the velocity of each particle is changed.
  - An interaction occurs between the particles which must involve a force since the velocity is changed.
  - A change in velocity $d\mathbf{v}/dt$ is an acceleration that is proportional to force acting on the particle.
- Consider two point masses with masses m_1, m_2 and velocities $\mathbf{v}_1$,$\mathbf{v}_2$, respectively.
  - Conservation of mass may be stated as:

$$m_1 + m_2 = m_1' + m_2'$$

- Conservation of momentum may be stated as:

$$m_1\mathbf{v}_1 + m_2\mathbf{v}_2 = m_1'\mathbf{v}_1' + m_2'\mathbf{v}_2'$$

  where $\mathbf{v}$ is a vector.

- If no reaction has taken place, then $m_1 = m_1'$ and $m_2 = m_2'$.
  - Thus

$$m_1\mathbf{v}_1 + m_2\mathbf{v}_2 = m_1\mathbf{v}_1' + m_2\mathbf{v}_2'$$

- The third quantity to be conserved is energy:

$$\frac{1}{2}m_1v_1^2 + \frac{1}{2}m_2v_2^2 = \frac{1}{2}m_1v_1'^2 + \frac{1}{2}m_2v_2'^2$$

  where v is a scalar.

- A fourth quantity to be conserved is angular momentum, which will be considered later.
- The description of motion of two particles may be transformed into center of mass coordinates.
  - This is equivalent to the motion of one particle in a force field.
- Choose, initially, an arbitrary point for the origin.
  - Let $\mathbf{r}_1$ be the position of particle 1 and $\mathbf{F}_1$ the force exerted by particle 2 on particle 1.
  - Similarly $\mathbf{r}_2$ is the position of particle 2 and $\mathbf{F}_2$ the force exerted by particle 1 on particle 2.
- By Newton's Third Law:

$$\mathbf{F}_1 = -\mathbf{F}_2$$

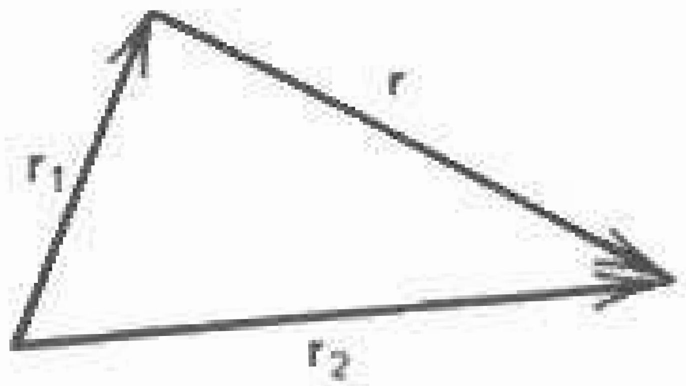


Figure 27.1 Definition of relative position vector **r**.

- By Newton's Second Law:

$$F_1 = m_1 \frac{d^2\mathbf{r}_1}{dt^2}, F_2 = m_2 \frac{d^2\mathbf{r}_2}{dt^2}$$

- These can be combined and rearranged to:

$$\frac{d^2\mathbf{r}_2}{dt^2} - \frac{d^2\mathbf{r}_1}{dt^2} = \frac{d}{dt}\left(\frac{dr_2}{dt} - \frac{dr_1}{dt}\right) = \left(\frac{1}{m_2} + \frac{1}{m_1}\right)\mathbf{F}_2$$

- The relative position and relative velocity may be defined:

$$\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1; \mathbf{v} = \mathbf{v}_2 - \mathbf{v}_1$$

- Define $\mathbf{F} = \mathbf{F}_2$ and the reduced mass μ as $\mu = \frac{m_1 m_2}{m_1 + m_2}$
    - $\mathbf{F}$ is the force between particles 1 and 2.

- This yields:

$$\mu\frac{d\mathbf{v}}{dt} = \mathbf{F}$$

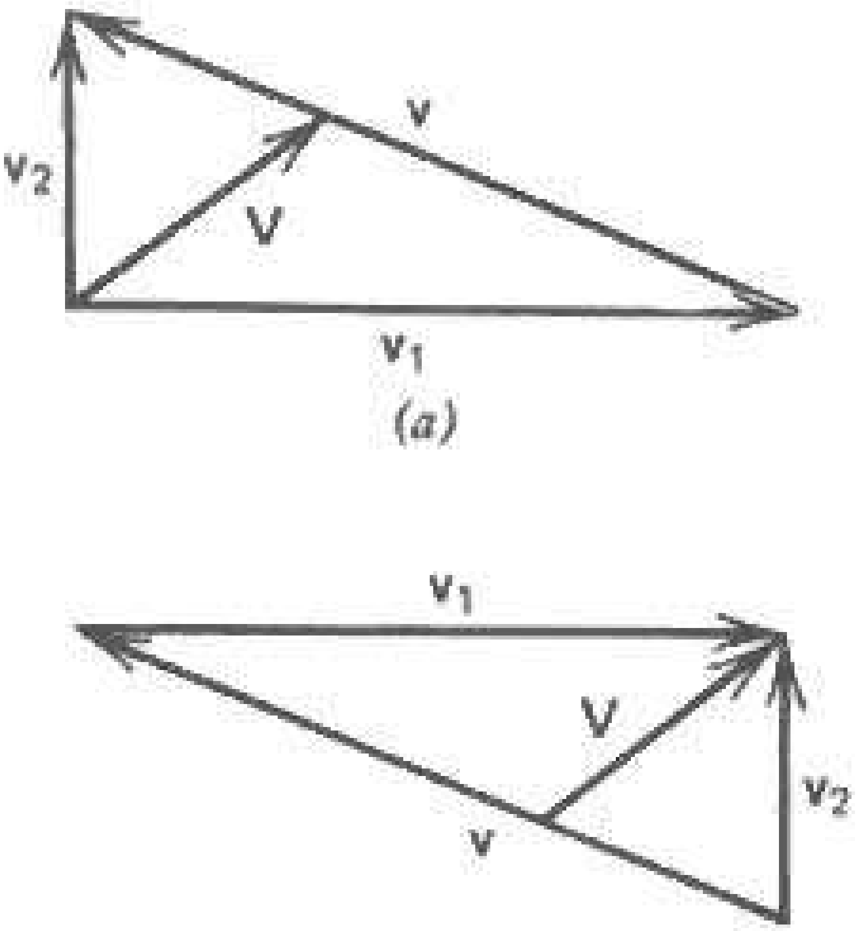
which is the equation of motion for a point mass μ in a force field $\mathbf{F}$.

- Conservation of momentum requires:

$$m_1\mathbf{v}_1 + m_2\mathbf{v}_2 = (m_1 + m_2)\mathbf{V}$$

where $\mathbf{V}$ is the velocity of the total mass.

- The motion of the two particles is now described in terms of the motion of the centre of mass and the relative motion of the two particles.
  - It is the relative motion between the two particles that is of interest in chemical kinetics.



(a)

(b)

Figure 27.2 Relation of laboratory velocities $\mathbf{v}_1$, $\mathbf{v}_2$ to center-of-mass velocity $\mathbf{V}$ and relative velocity $\mathbf{v}$; parts (*a*) and (*b*) are equivalent representations.

- The transformation from one set of velocity co-ordinates to the other (see figure 27.2). is:

$$\mathbf{v}_1 = \mathbf{V} - \frac{m_2}{m_1 + m_2}\mathbf{v}$$

$$\mathbf{v}_2 = \mathbf{V} + \frac{m_1}{m_1 + m_2}\mathbf{v}$$

- Recall the expression for total kinetic energy:

$$\frac{1}{2}m_1 v_1^2 + \frac{1}{2}m_2 v_2^2$$

where

$$v_1^2 = v_{1x}^2 + v_{1y}^2 + v_{1z}^2$$

$$v_2^2 = v_{2x}^2 + v_{2y}^2 + v_{2z}^2$$

- It can be shown that

$$\frac{1}{2}m_1v_1^2 + \frac{1}{2}m_2v_2^2 = \frac{1}{2}(m_1 + m_2)V^2 + \frac{1}{2}\mu v^2$$

- In molecular collisions (assuming that the molecules are point masses with no internal energy), relative kinetic energy is conserved:

$$\frac{1}{2}\mu v^2 = \frac{1}{2}\mu v'^2$$

  and $v = v'$, thus the magnitude, but not necessarily the direction, of the velocity is conserved.
    - Such collisions are elastic.
    - If the direction of relative motion has changed, then the collision has led to scattering.

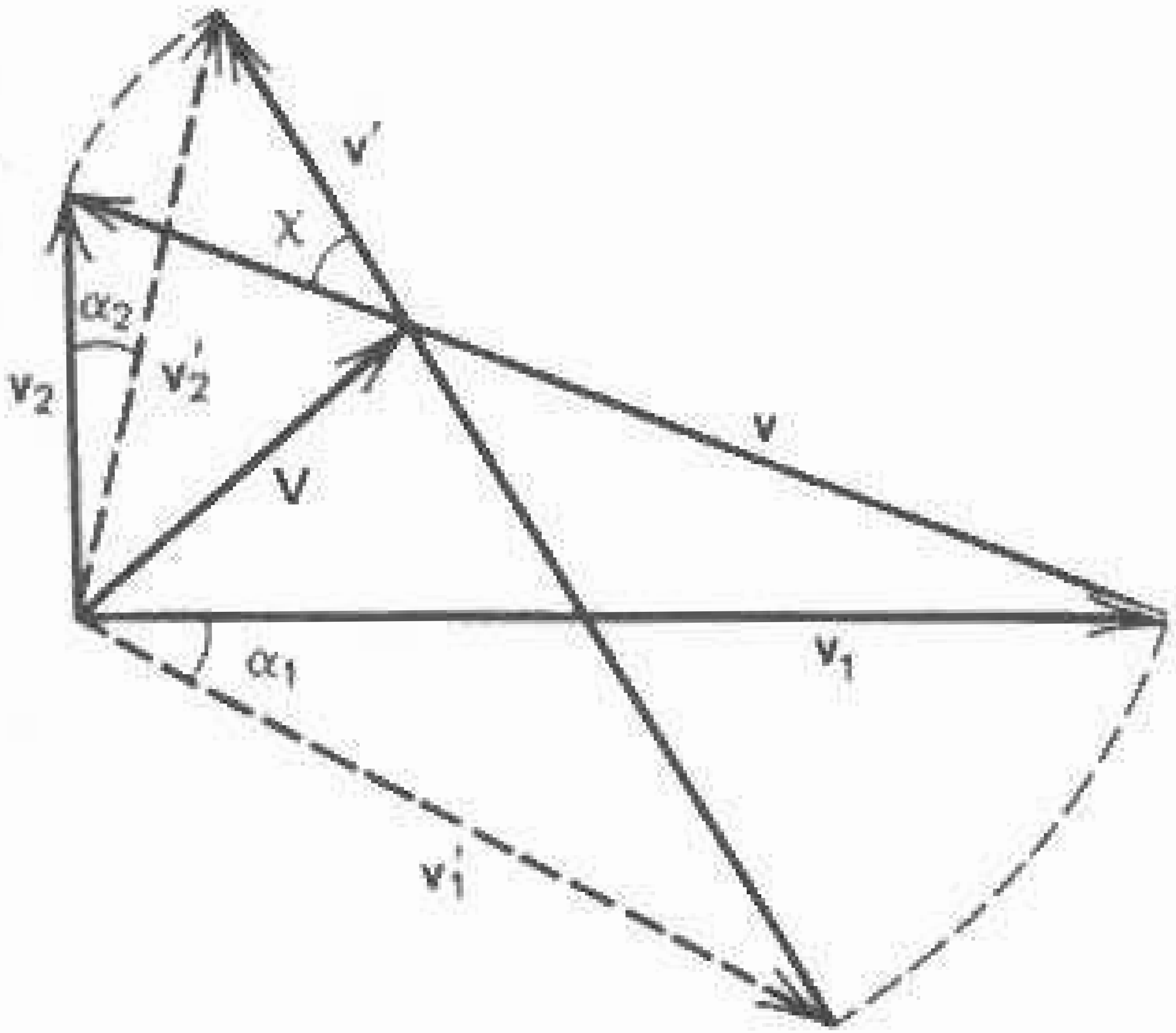


Figure 27.3 Velocities before and after an elastic collision.

- In the absence of forces of interaction, two particles will approach each other in a straight line.
  - The distance of closest approach is the impact parameter b.
- Angular momentum is conserved in a collision.
  - Before collision, the total angular momentum about the center of mass is $\mu v b$.
  - Since angular momentum is conserved in a collision and the speed is not changed, $b' = b$.
- For collisions of real molecules the impact parameter is important in determining the nature of the interaction.
  - If b is small, the interaction may be repulsive and a large deflection of their trajectory occurs.
  - If b is large, the interaction may be negligible and little if any deflection of the trajectory occurs.

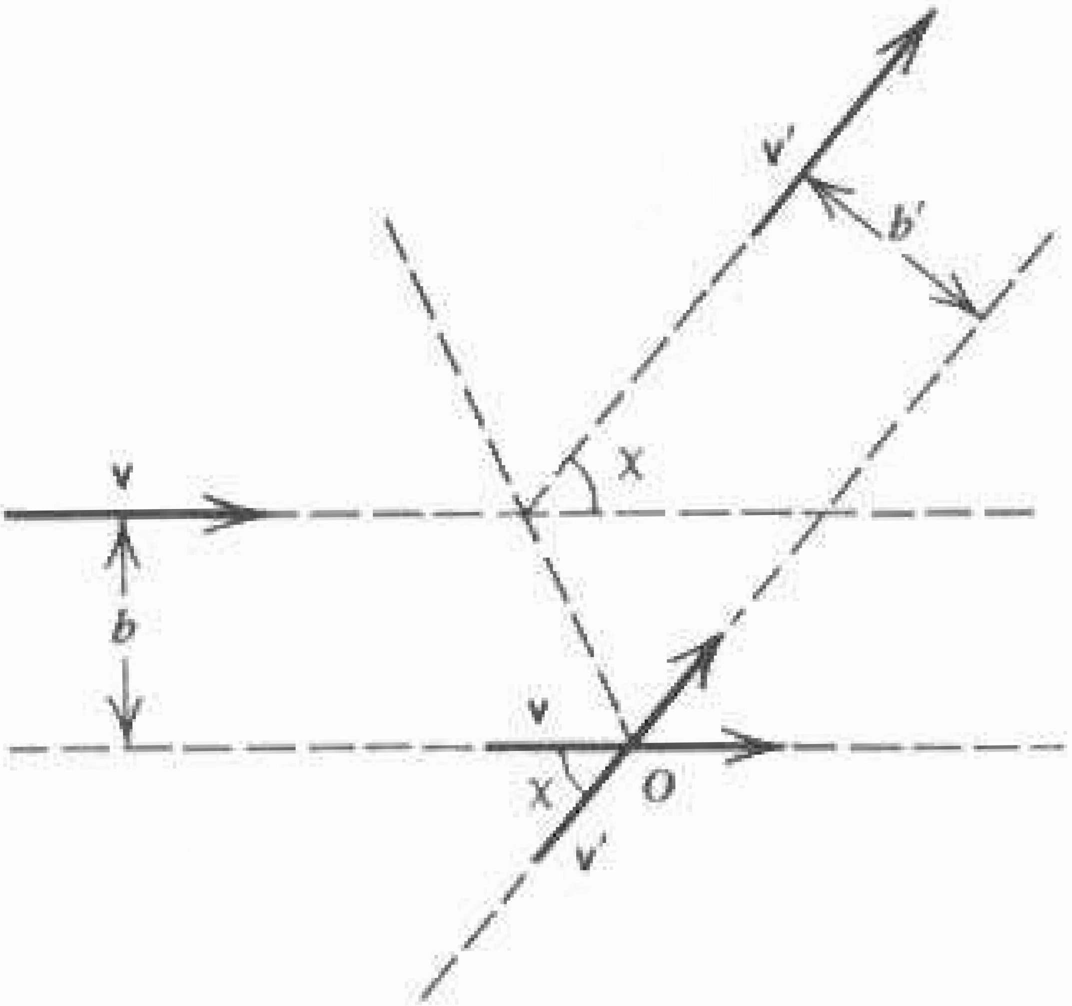


Figure 27.4 Relative velocity vector before (**v**) and after (**v**′) an elastic collision. The relative scattering angle is χ, and the impact parameter is b.

- Continued:
  - For intermediate values of b, attractive interactions may cause deflection of the trajectory.
  - The details of the deflection depends on the interaction potential which determines the forces of interaction (See Section 27.2 of Berry *et al.*)
- Consider the collision of two molecules interacting with a hard-sphere potential.
  - Consider two identical spheres of diameter d and mass m.
  - At impact, the centers of the molecules will be d apart, therefore the collision would be equivalent to a moving point mass bouncing off a stationary hard sphere of diameter d.
  - If the impact parameter b is greater than d, then no collision occurs.

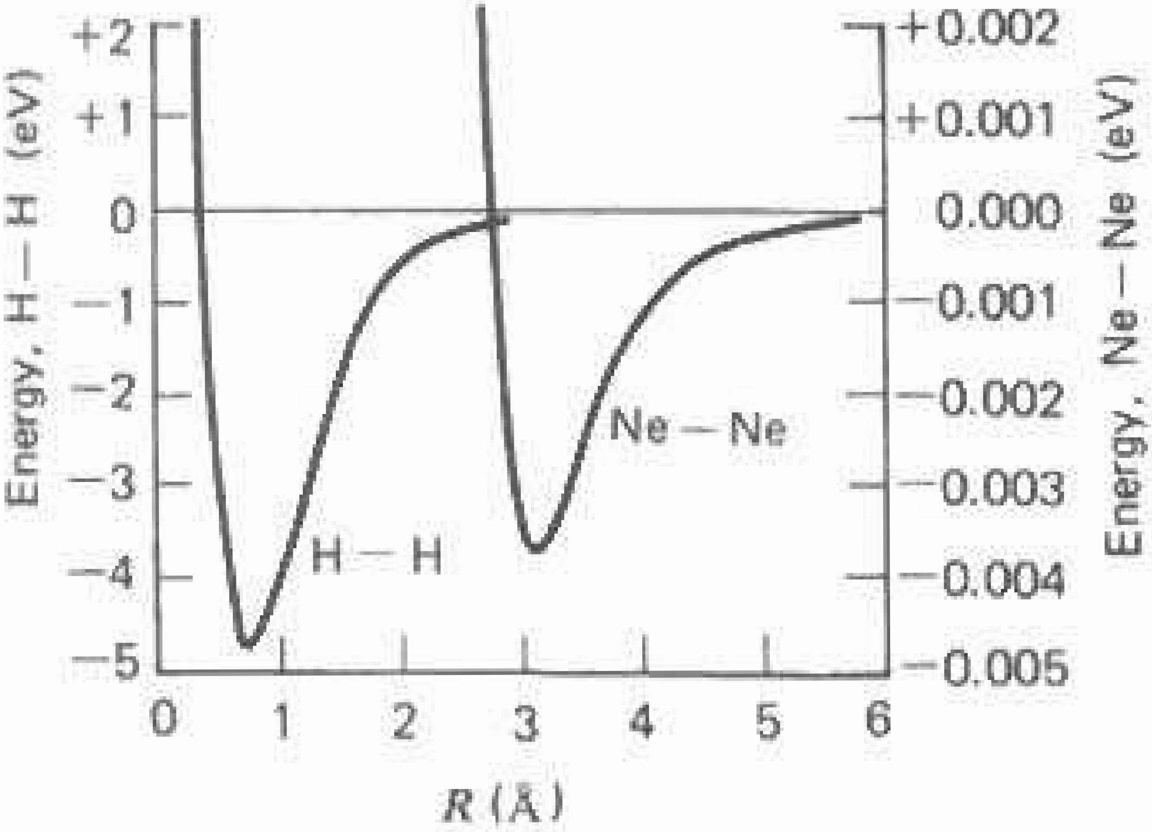


Figure 27.5 Potential energy curves for typical physical (Ne–Ne) and chemical (H–H) interactions. Note the difference in scale for the two curves.

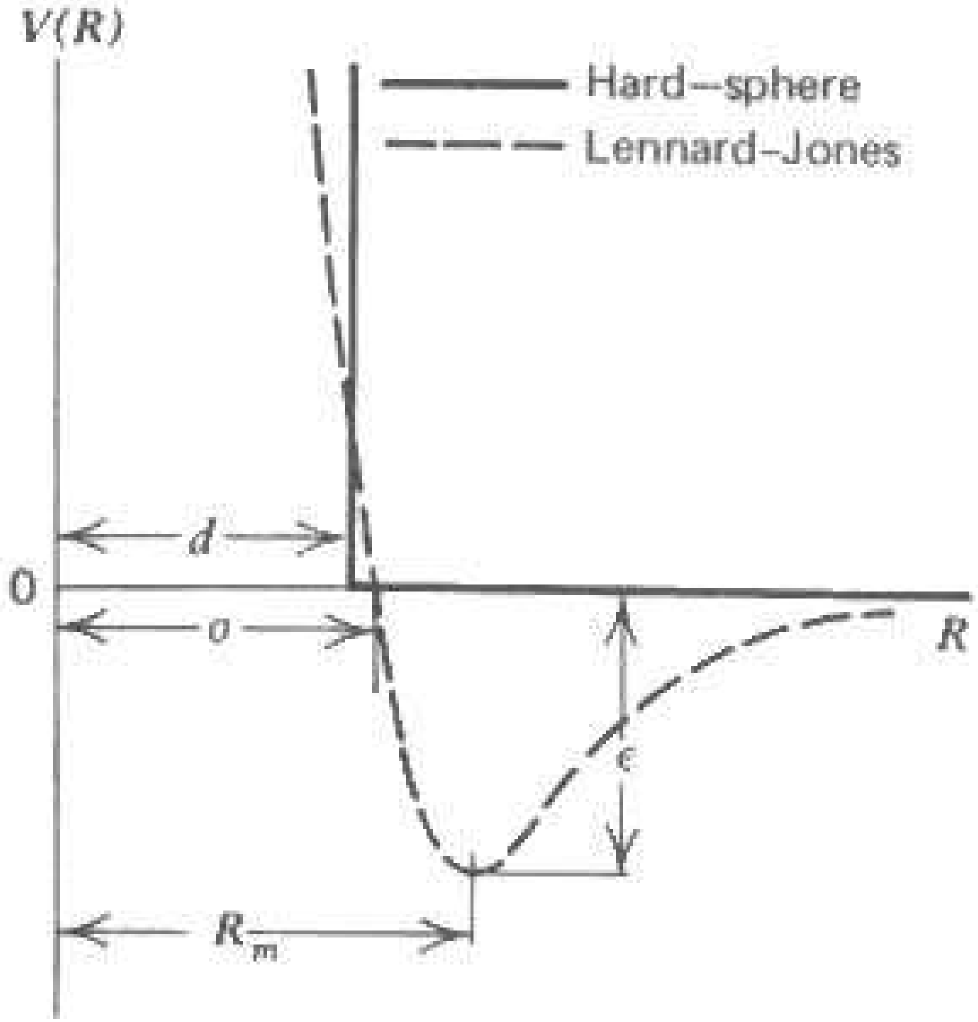


Figure 27.6 Comparison of hard-sphere potential and Lennard-Jones potential.

- Scattering of one hard sphere off the other is specular.
- If the impact parameter equals the hard-sphere diameter, then no deflection of the trajectory occurs.
- If the impact parameter is 0, then the trajectory rebounds and, χ, the angle between the initial and final path is π.
- If the impact parameter is between 0 and b, then the scattering angle, χ, is between 0 and π.

$$b = d \cos \frac{\chi}{2}$$

- If the interaction potential more complicated than the hard-sphere potential, then the relationship between the impact parameter and χ is more complicated.

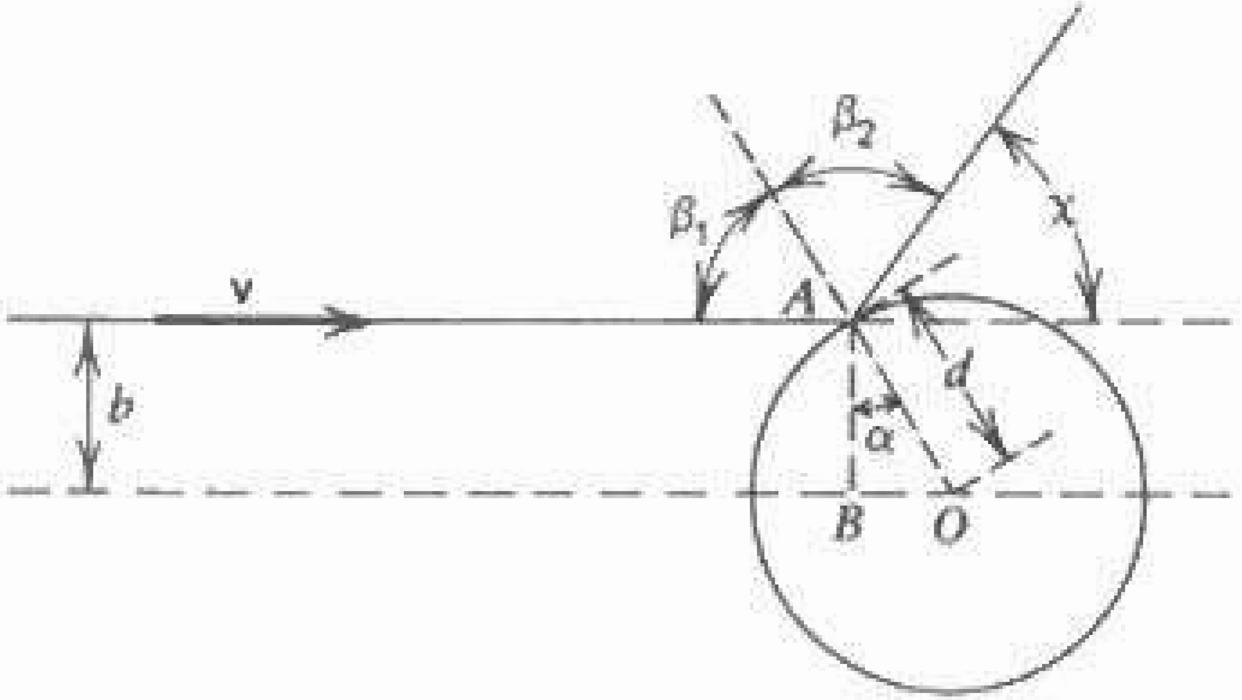


Figure 27.7 Scattering of hard spheres of diameter d, in relative coordinates.

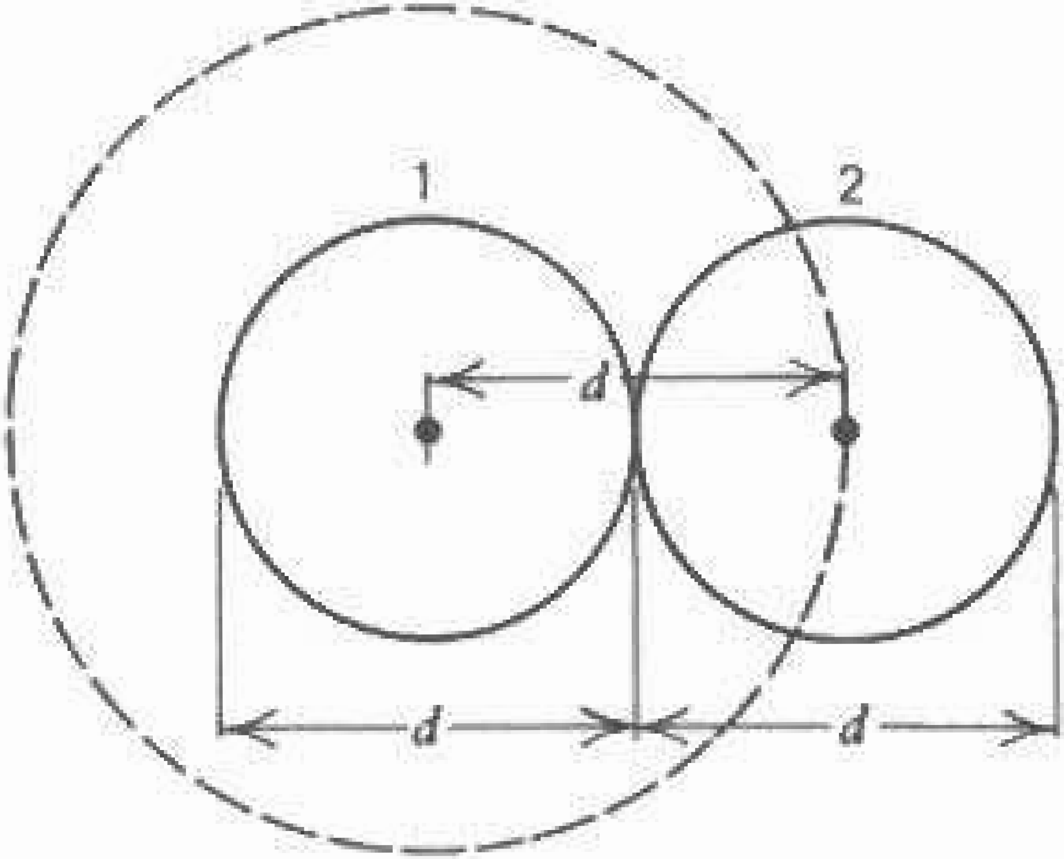


Figure 27.8 Impact between two hard spheres. The dashed line (circle of radius *d*) indicates the minimum distance to which the center of sphere 2 can approach the center of sphere 1.

- The interaction potential, V, depends on the separation, d, between the two molecules.
- Consider a hard-sphere collision (Figure 27.9) that changes the sign of one component of the relative velocity vector.
    - The velocity vector can be resolved into two components (OA) and (AC) which are, respectively, parallel and perpendicular to the line of centres at impact.
    - The collision changes the sign of v_{OA} but not v_{AC}.
- The kinetic energy at the instant of impact is:

$$\frac{1}{2}\mu v^2 cos^2\frac{\chi}{2}$$

- But energy is conserved.

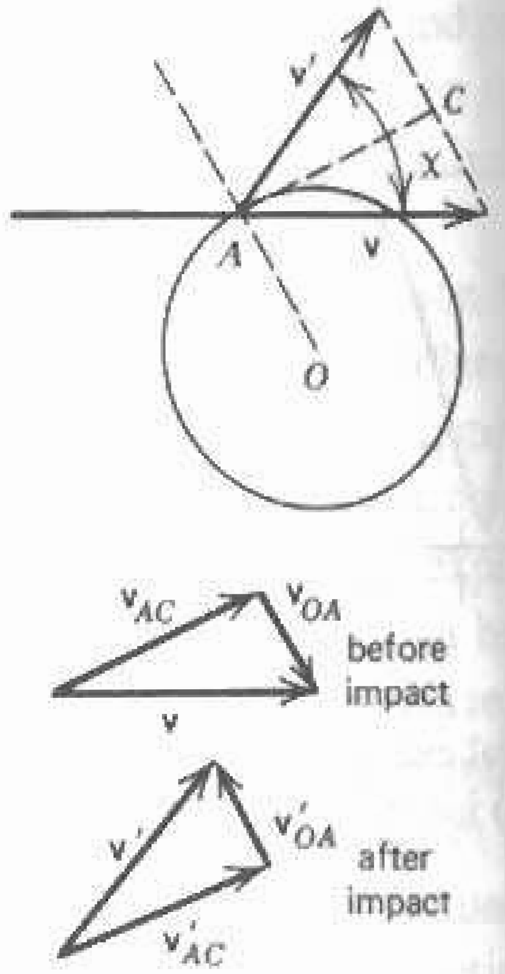


Figure 27.9 Relative velocity relationships at impact in an elastic hard-sphere collision.

- Therefore the energy at impact must still equal the original kinetic energy $E = \frac{1}{2}\mu v^2$.
  - Thus, at impact the potential energy is:

$$V(d) = \frac{1}{2}\mu v^2 - \frac{1}{2}\mu v^2 cos^2\frac{\chi}{2} = \frac{1}{2}\mu v^2 \left(1 - cos^2\frac{\chi}{2}\right)$$

$$= \frac{1}{2}\mu v^2 sin^2\frac{\chi}{2} = E\left(1 - \frac{b^2}{d^2}\right)$$

.

- For potentials other than hard-sphere, the relationship between the potential and the scattering angle is more complicated.
  - Scattering experiments can be used to obtain information about the potential.

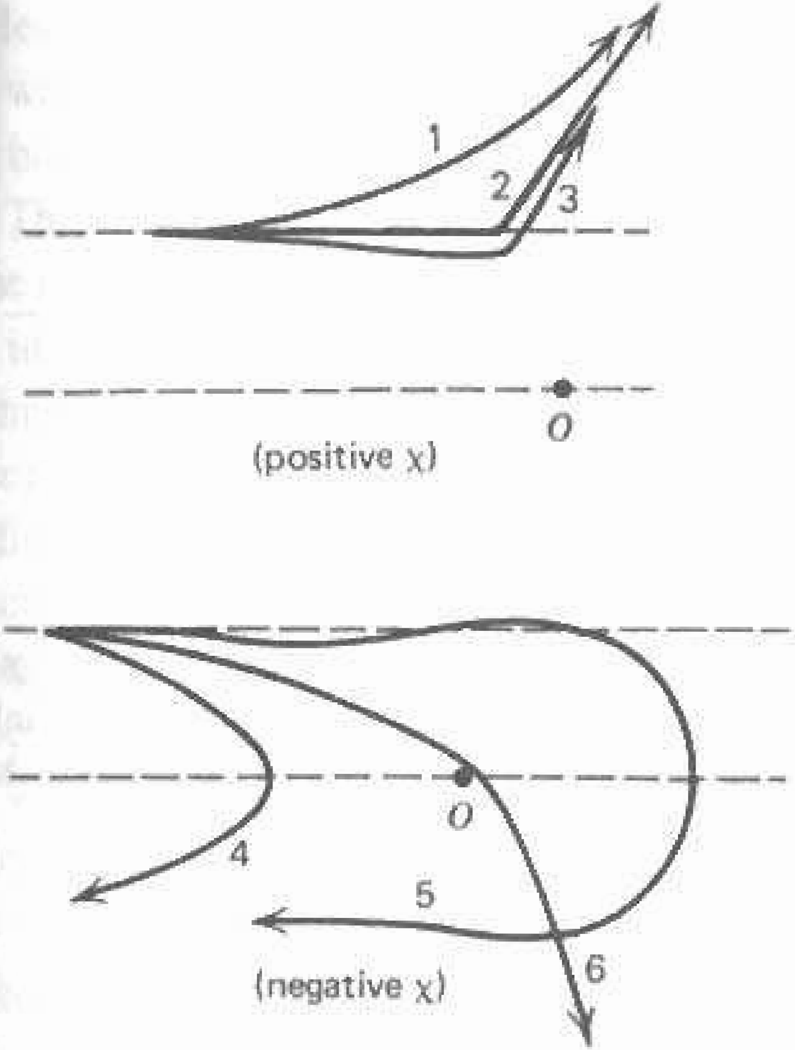


Figure 27.10 Typical collision trajectories for various types of interaction: 1, purely repulsive; 2, hard-sphere; 3, 4, 5, attractive at large distances, repulsive at small; 6, purely attractive.

- Consider the general case of an arbitrary interaction potential $V(R)$.
- Define the angle θ such that $\theta = (\pi - \chi)/2$.
- The distance of closest approach is R_0.
- The particle of reduced mass μ, initial relative velocity $\mathbf{v}$, with impact parameter b, is scattered with angle χ.
  - All motion takes place in a two dimensional plane, with coordinates R and θ.
  - The total kinetic energy is:

$$\frac{1}{2}\mu\dot{R}^2 + \frac{1}{2}\mu R^2\dot{\theta}^2$$

where $\dot{R} = dR/dt$ and $\dot{\theta} = d\theta/dt$.

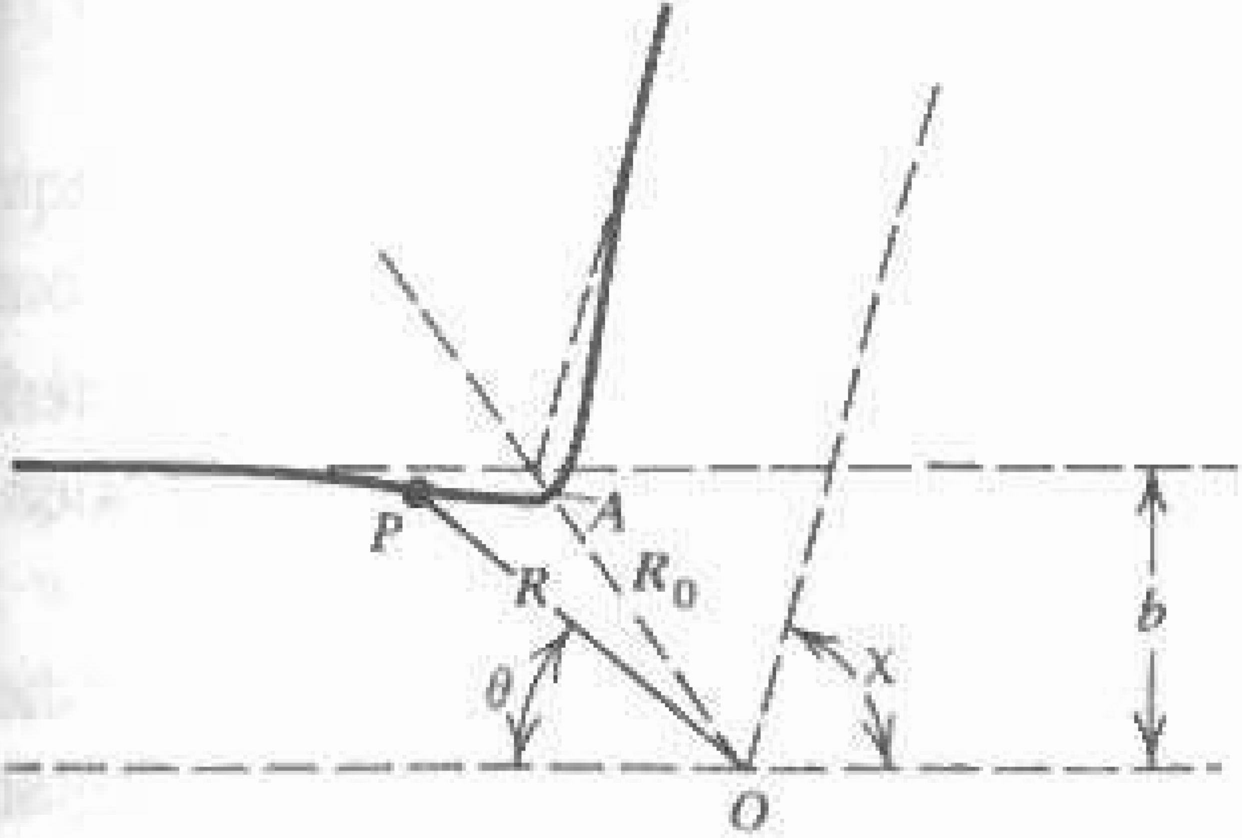


Figure 27.11 Coordinates used to describe a relative collision trajectory.

- Throughout the collision, the total energy must equal the initial kinetic energy.

$$E = \frac{1}{2}\mu v^2 = \frac{1}{2}\mu\dot{R}^2 + \frac{1}{2}\mu R^2\dot{\theta}^2 + V(R)$$

- Conservation of momentum requires:

$$p_\theta = \mu v b = \mu R^2\dot{\theta}$$

where $\mu R^2\dot{\theta}$ is the angular momentum at point R.

- Thus:

$$\dot{\theta} = \frac{d\theta}{dt} = \frac{vb}{R^2}$$

- Substituting into the expression for total energy yields:

$$E = \frac{1}{2}\mu v^2 = \frac{1}{2}\mu \dot{R}^2 + \frac{1}{2}\mu v^2 \frac{b^2}{R^2} + V(R)$$

- From this an expression for $\dot{R}$ may be derived:

$$\dot{R} = \frac{dR}{dt} = \sqrt{v^2 - v^2\frac{b^2}{R^2} - \frac{2V(R)}{\mu}}$$

- Dividing this into the expression for $d\theta/dt$ yields:

$$\frac{d\theta}{dR} = \frac{b}{R^2\sqrt{1 - \frac{b^2}{R^2} - \frac{2V(R)}{\mu v^2}}}$$

which describes the trajectory in terms of the relationship between θ and R.

- The collision trajectory must be symmetric about the line OA, which intersects with the trajectory at the distance of closest approach.
  - Define this extremum point as $R = R_0$.
  - At this turning point $dR/dt = 0$.
  - Thus:

$$1 - \frac{b^2}{R_0^2} = \frac{V(R)}{E}$$

- The scattering angle χ is determined by the angle between the initial and final path.
  - R is the magnitude of the separation of the two particles.
  - Therefore R varies from ∞ to R_0 and to ∞ again.
  - At the same time θ varies from 0 to $\pi - \chi$.

- Recalling that $E = \frac{1}{2}\mu v^2$, the expression for $d\theta/dR$ may be rewritten:

$$\int_0^{\pi-\chi} d\theta = 2\int_{R_0}^{\infty} \frac{b\ dR}{R^2\sqrt{1-\frac{b^2}{R^2}-\frac{V(R)}{E}}}$$

  where the factor of 2 arises from the symmetry of the trajectory.

- Thus the scattering angle is:

$$\chi = \pi - 2b\ \int_{R_0}^{\infty} \frac{dR}{R^2\sqrt{1-\frac{b^2}{R^2}-\frac{V(R)}{E}}}$$

  and χ depends on E and b.

- For the hard-sphere potential $R_0 = d$ and $V(R) = 0$ when $R > d$.

- The expression for the scattering angle becomes:

$$\chi = \pi - 2b \int_d^\infty \frac{dR}{R^2\sqrt{1-\frac{b^2}{R^2}}}$$

  as previously derived.

- When this is integrated analytically:

$$b = d\cos\frac{\chi}{2}$$

- Experimental measurements of scattering allow the nature of the potential to be probed.
- So far collisions between structureless particles have been considered, but real molecules can have internal structure and internal energy.

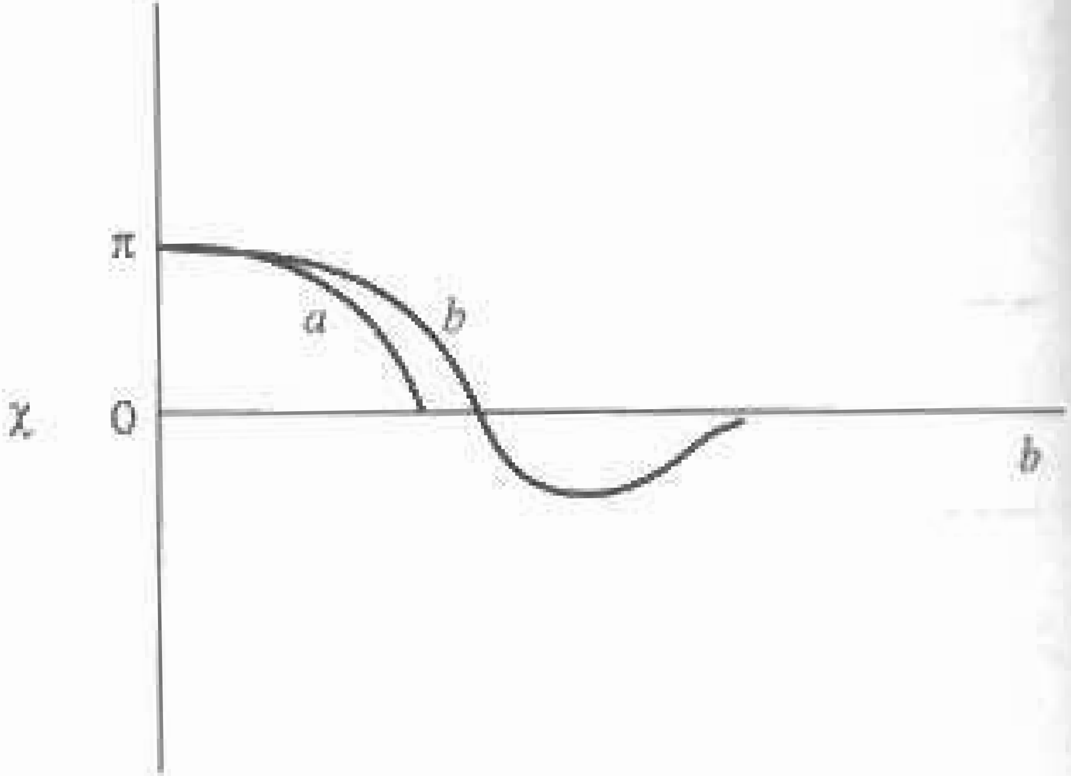


Figure 27.12 Variation of the scattering angle χ vs. impact parameter b for two spherically symmetric potentials: (a) hard-sphere potential, and (b) Lennard–Jones potential (schematic), see Fig. 27.6.

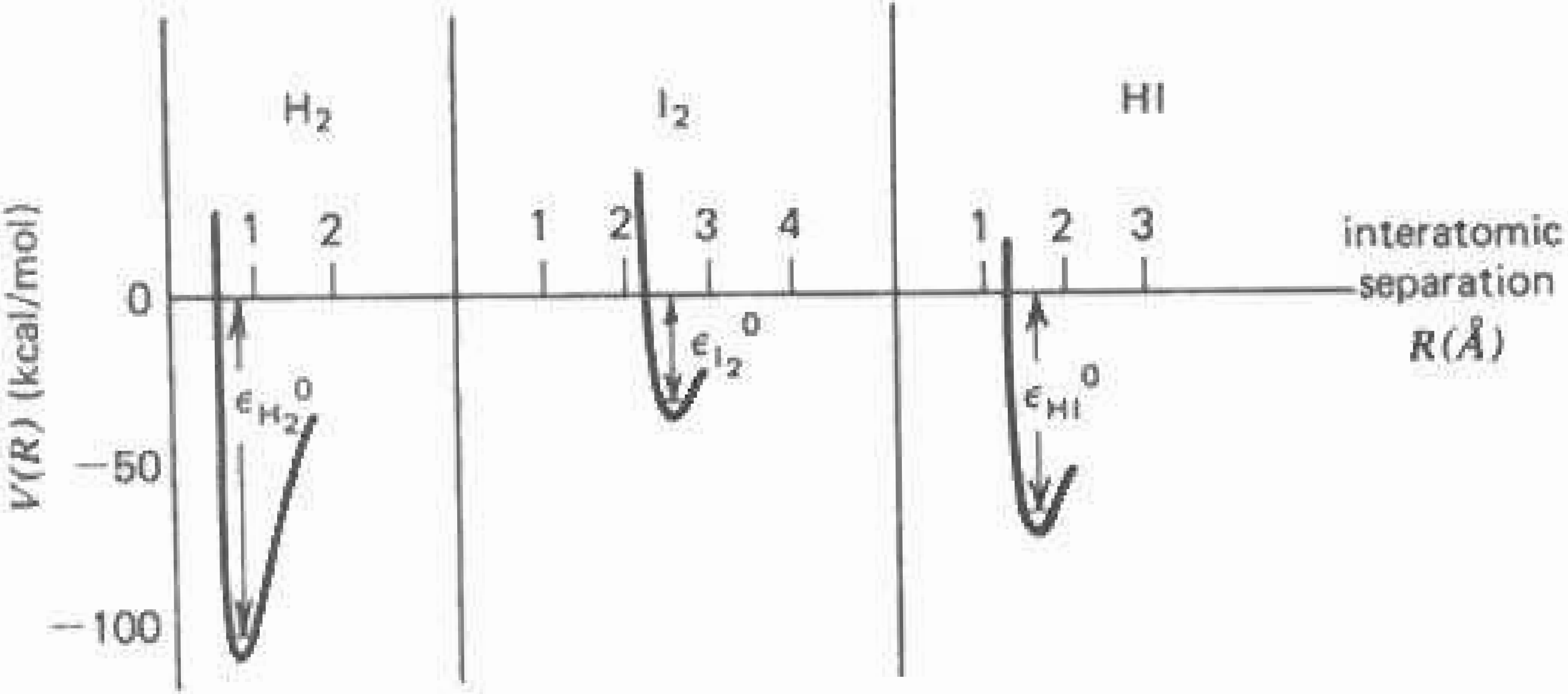


Figure 27.13 Potential energy curves for the molecules H$_2$, I$_2$, and HI.

Types of Collisions (See section 27.4 of Berry *et al.*)

- For molecules with internal structure, internal energy and internal angular momentum may be affected by a collision.
- Consider a diatomic molecule, such as N_2.
  - The internal state of the molecule is defined by rotational, vibrational, electronic, and nuclear quantum numbers.
  - Each degree of freedom has quantum number.
  - The complete set of quantum numbers defines an eigenstate.
  - The eigenstate representing the internal state of N_2 is denoted by i.
- Consider a collision of N_2 in state i moving with velocity v_1 with Ar moving with velocity v_2.

- An elastic collision would not change the state of the N_2 molecule:

  $$\mathrm{N}_2(\mathbf{v}_1,\, i) + \mathrm{Ar}(\mathbf{v}_2) \to \mathrm{N}_2(\mathbf{v}_1',\, i) + \mathrm{Ar}(\mathbf{v}_2')$$

  and the relative kinetic energy would not be altered.
- An inelastic collision does change the state of the N_2 molecule:

  $$\mathrm{N}_2(\mathbf{v}_1,\, i) + \mathrm{Ar}(\mathbf{v}_2) \to \mathrm{N}_2(\mathbf{v}_1',\, j) + \mathrm{Ar}(\mathbf{v}_2')$$

  and since the internal energy has been altered, so has the relative kinetic energy.
  - Conservation of energy requires:

    $$\varepsilon_i + \frac{1}{2}\mu v^2 = \varepsilon_j + \frac{1}{2}\mu v'^2$$

    where v and v' are initial and final relative speeds.
  - The change in state from i to j could include changes in any (or all) quantum numbers.

- Inelastic collisions can also involve the transfer of energy from one internal degree of freedom to another.
- Reactive collisions alter the chemical identity of one or more of the species involved in the chemical reaction.
  $\mathrm{I}_2(\mathbf{v}_1,\, i) + \mathrm{Ar}(\mathbf{v}_2) \rightarrow \mathrm{I}(\mathbf{v}_3, j\ ) + \mathrm{I}(\mathbf{v}_4, l) + \mathrm{Ar}(\mathbf{v}_2')$
  where:
  - i represents the initial internal state of I_2
  - j and l represent the electronic state of the iodine atoms produced by dissociation.
- Another type of reactive collision is the exchange or rearrangement collision:
  $\mathrm{H}_2(\mathbf{v}_1,\, i) + \mathrm{I}_2(\mathbf{v}_2,\, j) \rightarrow \mathrm{HI}(\mathbf{v}_3, l\ ) + \mathrm{HI}(\mathbf{v}_4, m)$
- As in all collisions, energy, linear momentum, and angular momentum must be conserved.

- Conservation of energy for this reactive collision may be rewritten as:

$$\varepsilon_{H_2,i} + \varepsilon_{I_2,j} + \frac{1}{2}m_{H_2}v_1^2 + \frac{1}{2}m_{I_2}v_2^2 =$$

$$\varepsilon_{HI,l} + \varepsilon_{HI,m} + \frac{1}{2}m_{HI}v_3^2 + \frac{1}{2}m_{HI}v_4^2$$

- Separating out the motion of the centre of mass yields:

$$\varepsilon_{H_2,i} + \varepsilon_{I_2,j} + \frac{1}{2}\mu v^2 = \varepsilon_{HI,l} + \varepsilon_{HI,m} + \frac{1}{2}\mu' v'^2$$

- When a chemical reaction has occurred, the reduced mass of the products can differ from the reduced mass of the reactants.
- The change in kinetic energy can be related to the endothermicity or exothermicity of the reaction.

- Consider a collision with both products and reactants in their ground states (denoted by ε^0).
  - ε^0 can be defined relative to infinite separation of the constituent atoms, in which case it has the value of the negative of the dissociation energy.
  - Thus:

    $$\Delta E_0^0 = 2\varepsilon^0_{HI} - (\varepsilon^0_{H_2} + \varepsilon^0_{I_2})$$

    which is the thermodynamic energy change at 0 K.
- In real experiments, both reactants and products are distributed over a number of quantum states.
  - Tabulated energies of reactions at a standard temperature reflect this.

Scattering Cross Sections

- Collisions between molecules depend on the forces between them.
- Consider a collision between single atoms in a molecular beam experiment (see Figures 27.14, 27.15, and 27.16).
- The first step in preparing a beam of atoms is formed by making a small hole in a container of gas which is surrounded by the vacuum.
  - The hole is small enough that only one atom can escape at a time, moving with any possible speed and direction.
  - This is the process of effusion and is known as Knudsen flow.
- The next step is to collimate the beam.

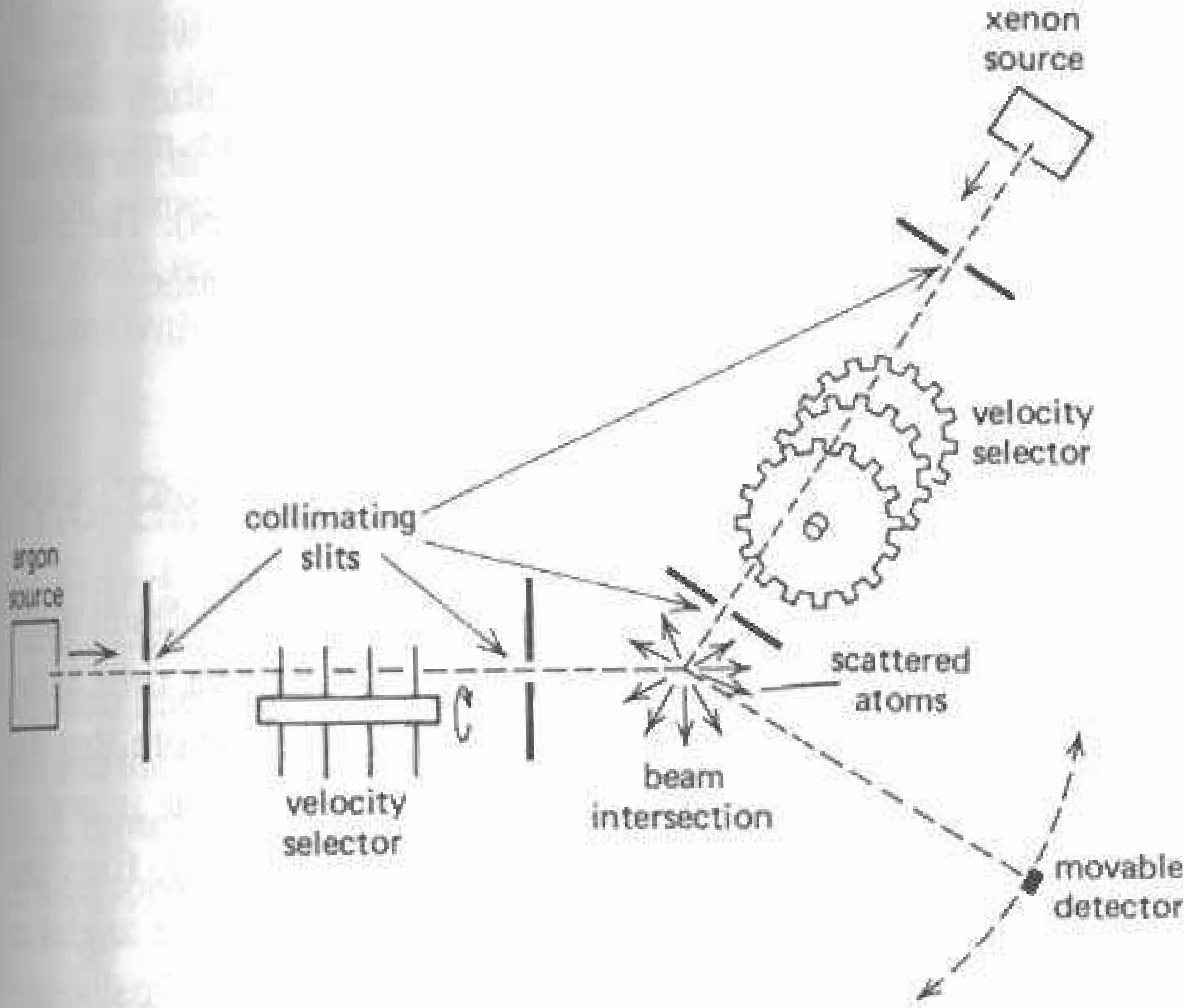


Figure 27.14 Experimental arrangement for a molecular-beam scattering experiment. All parts are in evacuated enclosures.

- Continued:
  - This is accomplished by a series of collimating slits which filter out any molecules moving in any direction not desired.
- The next step is to select the desired velocity.
  - The velocity selector consists of a set of slotted disks mounted on a shaft.
  - Either the relative orientation of the slots or the rotation of the shaft can be controlled.
  - Only the molecules with the velocity of interest will be able to pass though the slots. The rest of the molecules will be deflected.
- The result is a velocity selected, collision free, collimated beam with density $n_1(v_1)$ and flux density $v_1 n_1$.

- A second beam can be prepared with density $n_2(v_2)$ and flux density $v_2 n_2$.
- The two beams can be crossed such that they intersect in a volume element, τ, the scattering volume.
- A typical beam is about 1 cm^2 in cross sectional area, with a density of 10^9 atoms cm^{-3}, and flux density of 10^{13} atoms cm^{-3}.
  - Therefore τ is about 1 cm^3.
- Consider the case of one beam of Ar crossing a beam of Xe.
  - If an Ar atom collides with a Xe atom, it will be scattered. All directions are possible.
  - If an Ar atom crosses τ without colliding with a Xe atom, it will continue undeflected.

- Usually the density of the beams are chosen such that the probability of multiple collisions is negligible.
- A detector is able to determine the number of atoms scattered towards its location at distance L, at laboratory angles α and β. (See Figure 27.15).
    - The detector has an area A and subtends a solid angular element:

$$d\Omega' = \frac{A}{L^2}$$

    - In a spherical angular coordinate system with angles α and β:

$$d\Omega' = \sin\alpha \; d\alpha \; d\beta$$

- The scattering cross section can be determined by an experiment of this design.

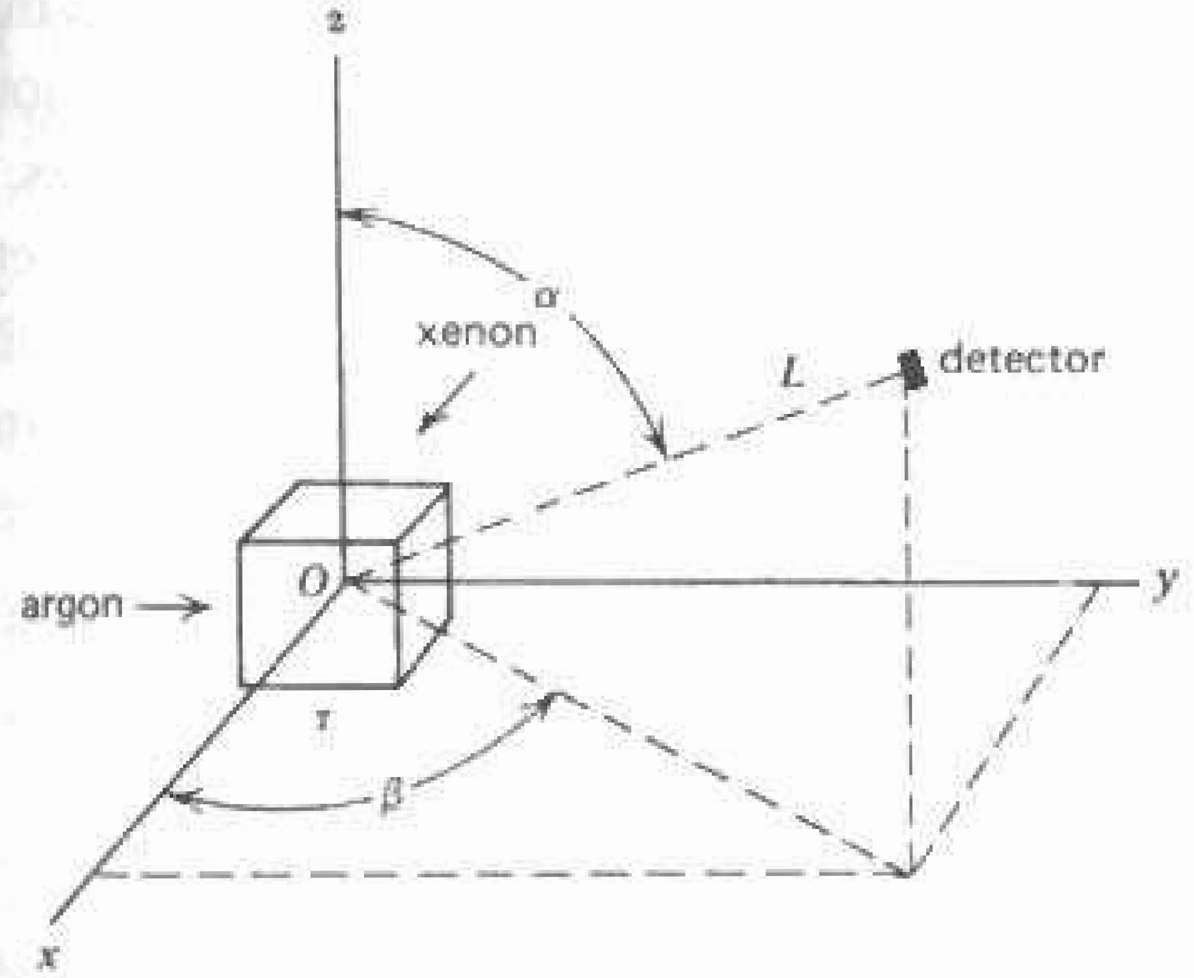


Figure 27.15 Laboratory coordinates for scattering from crossed molecular beams. It is assumed that $L >> \tau^{1/3}$, so that the angles α, β do not depend on the actual point of collision within the volume τ.

- $dN_{Ar}(\alpha, \beta)$ is the number of Ar atoms arriving at a detector per unit solid angle per unit time (second).
  - This is proportional to the number of collisions occurring per unit time.
  - This in turn is proportional to the densities of Xe and Ar and the collision volume τ, all of which can be controlled experimentally.
- The number of collisions per unit time is also related to the range of interaction between Ar and Xe.
  - More collisions occur if the range is large than if the range is small.
- The cross section σ is defined by:

$$dN_{Ar}(v, \alpha, \beta) = \sigma(v, \alpha, \beta)\ v\ n_1(v_1)\ n_2(v_2)\ \tau\ d\Omega'$$

where σ has units of cm^2 atom^{-1}.

- The cross section may be thought of as the effective area that the atoms present to each other, such that scattering into the angular volume of interest occurs.
- This cross section is in terms of quantities that can be controlled in the experiment.
- Scattering cross sections are measured in laboratory coordinates, but must be analyzed in terms of the center-of-mass coordinate system.
  - Note that any scalar quantity (i.e. a quantity that has magnitude but not direction) must be independent of the coordinate system in which it is measured.
    - The number of particles arriving at the detector per unit time is a scalar.
- The relative scattering angles are χ and ϕ (see Figure 27.16).

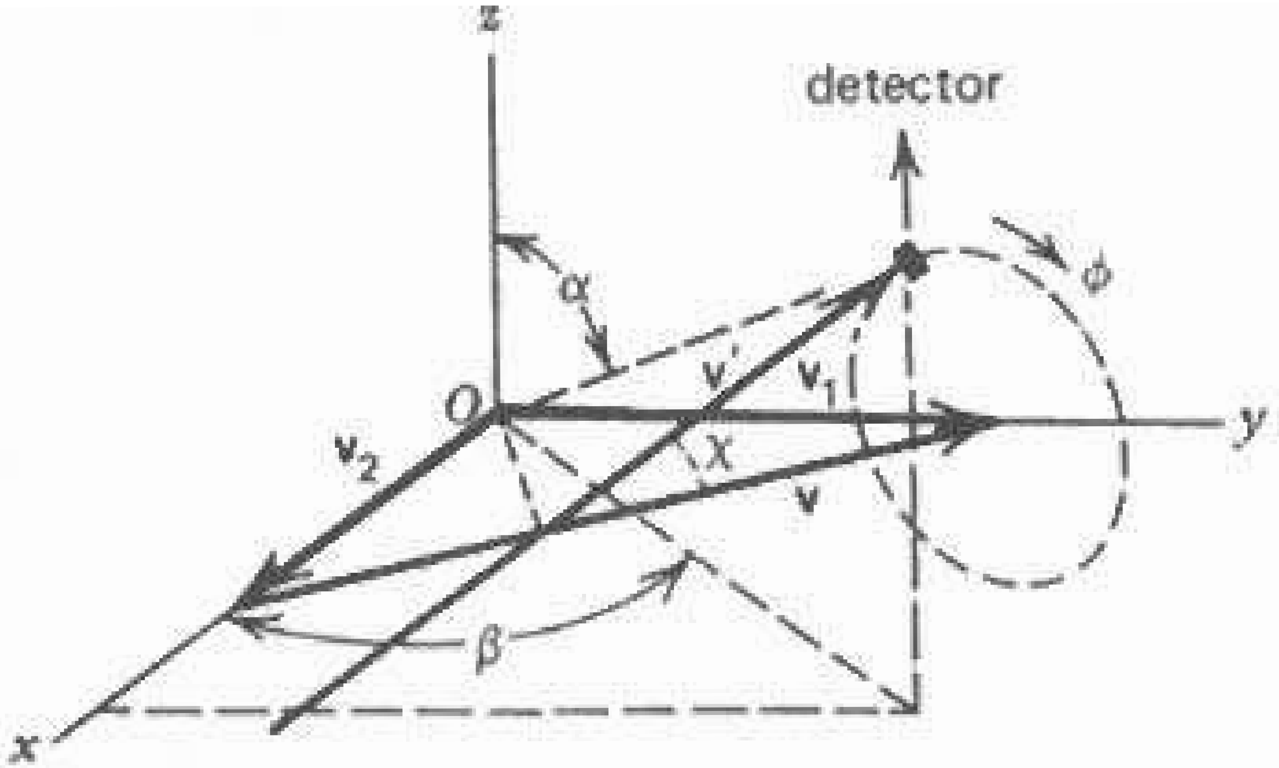


Figure 27.16 Relation between laboratory scattering angles α, β and relative scattering angles χ, ϕ.

atom approaches a xenon atom, and to the size of the beam-

- Thus:

$$dN_{Ar}(v,\chi,\phi) = \sigma(v,\chi,\phi)\ v\ n_1(v_1)\ n_2(v_2)\ \tau \sin\chi\ d\chi\ d\phi$$

- Because $dN_{Ar}(v,\chi,\phi) = dN_{Ar}(v,\alpha,\beta)$

$$\sigma(v,\alpha,\beta)\sin\alpha\ d\alpha\ d\beta = \sigma(v,\chi)\sin\chi\ d\chi\ d\phi$$

- Note that the relative azimuthal angle ϕ has been omitted as a variable of the relative cross section.
  - This is because the forces between the atoms is a central field and there is no external field.
  - Therefore there can be no dependence of the scattering cross section on ϕ.

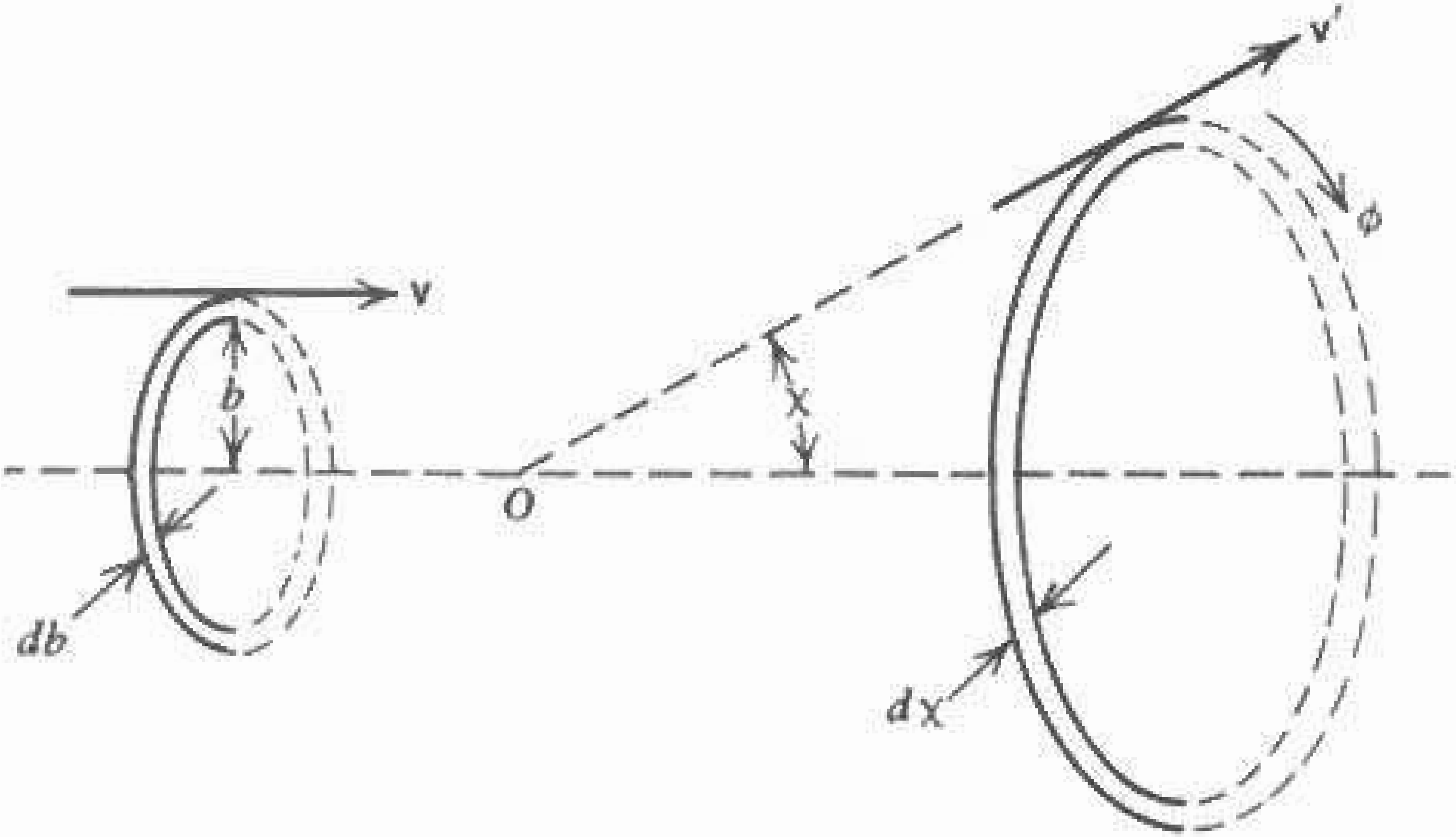


Figure 27.17 Relation of impact parameter b and relative speed v. The vectors $\mathbf{v}$ and $\mathbf{v}'$ define a plane with azimuthal angle ϕ, all values of ϕ being physically equivalent for a central force field.

- Consider a crossed beam experiment involving Ar atoms and N$_2$ molecules.

  $$\mathrm{N_2}(\mathbf{v}_1, V) + \mathrm{Ar}(\mathbf{v}_2) \rightarrow \mathrm{N_2}(\mathbf{v}_1', V') + \mathrm{Ar}(\mathbf{v}_2')$$

  where V and V' are the initial and final quantum numbers of the N$_2$
- A scattering cross section specific to the change in state can be measured:

  $$dN_{\mathrm{N_2}}(v, V', \alpha, \beta) = \sigma(V|V'; v, \alpha, \beta) v\, n_{\mathrm{N_2}}(v_1, V)\, n_{\mathrm{Ar}}(v_2)\, \tau\, d\Omega'$$

  where $\sigma(V|V'; v, \alpha, \beta)$ is “the cross section for conversion of V to V' with collision parameters v, α, β.”
  - The quantum state is now a variable for the cross section.

- Crossed beam experiments can also be used to determine reaction cross sections.

  $$\text{H}(\mathbf{v}_1,\,0) + \text{I}_2(\mathbf{v}_2,\,j) \rightarrow \text{HI}(\mathbf{v}_3, l\ ) + \text{I}(\mathbf{v}_4, 0)$$

  where an H atom in its ground state reacts with I_2 in quantum state j (as defined by rotational, vibrational, and electronic quantum numbers) to form HI in quantum state l and a ground state I atom.
- The cross section for this reaction is:

  $$dN_{HI}(v, l, \alpha, \beta) = \sigma_R(0, j|l, 0; v, \alpha, \beta)vn_H(v_1)n_{I_2}(v_2, j)\tau\, d\Omega'$$

  which does not depend on final velocity of either product.
  - Direction of final relative velocity is determined by α and β, while the magnitude is determined by conservation of energy.

- Experimental measurements may be carried out with varying detail.
  - It is now possible to detect final velocity and state as well as direction.
- The total scattering cross section may be determined by measuring all scattering at all laboratory angles.
  - This gives the total number of molecules scattered per unit time:

$$\int_{\alpha,\beta} dN(\alpha,\beta) = N$$

  - This is equivalent to:

$$N = \left[\int_{\Omega'} \sigma(v,\alpha,\beta)d\Omega'\right] v\ n_1(v_1)\ n_2(v_2)\tau$$

- Note that the integral depends only on v and thus is the integral cross section:

$$\sigma(v) = \int_{\alpha=0}^{\pi} \int_{\beta=0}^{2\pi} \sigma(v, \alpha, \beta) \sin\alpha \; d\alpha \; d\beta$$

  where $\sigma(v, \alpha, \beta)$ is the differential cross section.
- This can be related to the state specific cross section by summing over the states.

$$\sigma(v, \alpha, \beta) = \sum_j \sum_l \sigma_R(0, j|l; v, \alpha, \beta)$$

Elastic Scattering of Hard Spheres

- The previous will now be generalized to elastic scattering of hard spheres.

- The hard sphere scattering cross section is defined by:

  $$dN_1(\chi, \phi) = \sigma(v, \chi) v n_1(v_1) n_2(v_2) \tau \sin\chi d\chi d\phi$$

  where:
  - species 1 is the species for which the distribution is observed
  - species 2 is the scatterer.
- This may be integrated over all angles ϕ
- Thus the number of particles scattered between χ and $\chi + d\chi$:

  $$dN_1(\chi) = \int_{\phi=0}^{2\pi} dN_1(\chi, \phi) = 2\pi\sigma(v, \chi) v n_1(v_1) n_2(v_2) \tau \sin\chi d\chi$$

- What fraction of species 1 are scattered between χ and $\chi + d\chi$?

- At a given relative speed the scattering angle is determined by the impact parameter in accordance with:

$$\chi = \pi - 2b \int_{R_0}^{\infty} \frac{dR}{R^2\sqrt{1 - \frac{b^2}{R^2}}}$$

- Consider db as the range of b from which particles are scattered in $d\chi$.
    - The number of particles scattered into $d\chi$ is the product of flux density, $vn_1(v_1)$ and the differential area element $2\pi b db$. Thus:

      $$2\pi b \; db = 2\pi\sigma(v, \chi) \;\; \sin\chi \; d\chi$$

      relates the impact parameter to the differential cross section.

- This can be rearranged to:

$$\sigma(v,\chi) = \frac{b}{\sin\chi}\left|\frac{db}{d\chi}\right|$$

- But for hard spheres $b = d\cos(\chi/2)$ which is a single valued function of χ.
  - Therefore

$$\frac{db}{d\chi} = \frac{d}{2}\sin\frac{\chi}{2}$$

and

$$\sigma(v,\chi) = \frac{d^2}{2}\cos\frac{\chi}{2}\sin\frac{\chi}{2}\frac{1}{\sin\chi} = \frac{d^2}{4}$$

since

$$\cos\frac{\chi}{2}\sin\frac{\chi}{2} = \frac{1}{2}\sin\chi$$

- Note that the differential cross section does not depend either v or χ.
- The total cross section becomes:

$$\sigma(v) = 2\pi \int_0^\pi \sigma(v,\chi) \sin\chi d\chi$$

$$= \frac{\pi d^2}{2} \int_0^\pi \sin\chi d\chi$$

- Cross sections for real potentials will depend on relative speed and angle of collision.
- A cross section combined with velocity information will give information about the rate of collision.
  - The rate of collision is the upper limit on the rate of reaction.

solid line in Fig. 27.18. This maximum is called rainbow

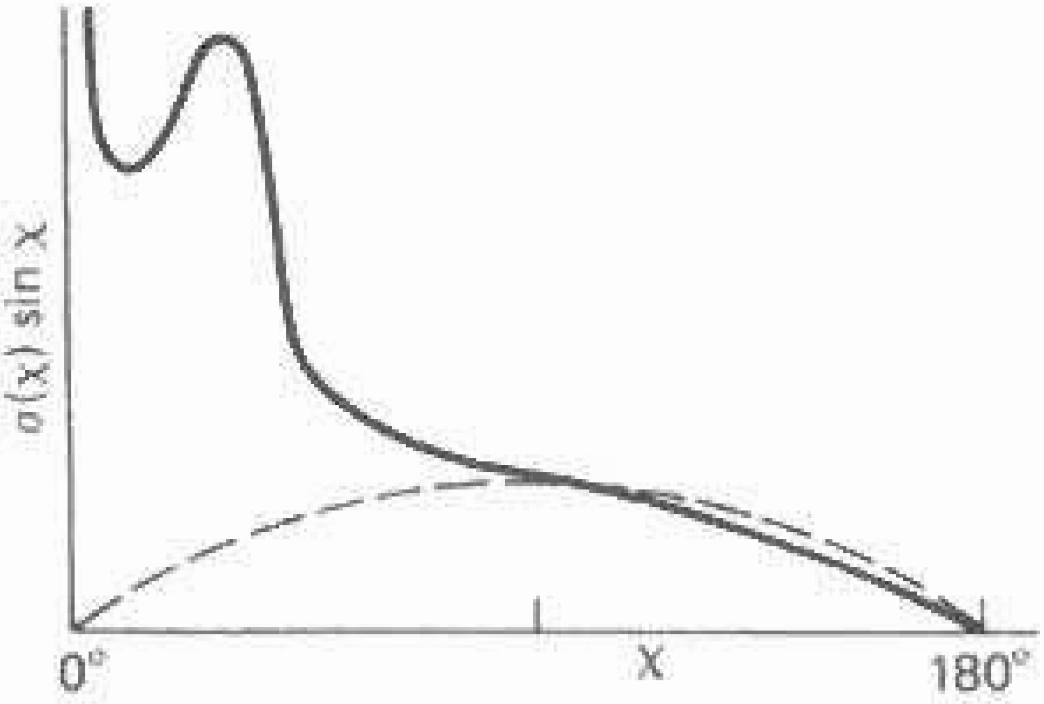


Figure 27.18 Elastic scattering cross section for K–Kr (solid line). The dotted line represents the same quantity for the model of hard spheres, fitted to the solid line (arbitrarily) at 90°.

Kinetic Theory of Gases

- The macroscopic properties of gases can be related to the averages of molecular motions and intermolecular forces.
- In thermodynamics we are concerned with equilibrium properties of systems such as pressure and temperature.
- In kinetics we are concerned with nonequilibrium properties such as fluxes.
    - Diffusion (flow of matter)
    - Viscosity (flow of momentum)
    - Thermal conductivity (flow of thermal energy)
    - Electrical conductivity (flow of charge)
- The kinetic theory of gases can be considered from the perspective of statistical mechanics.

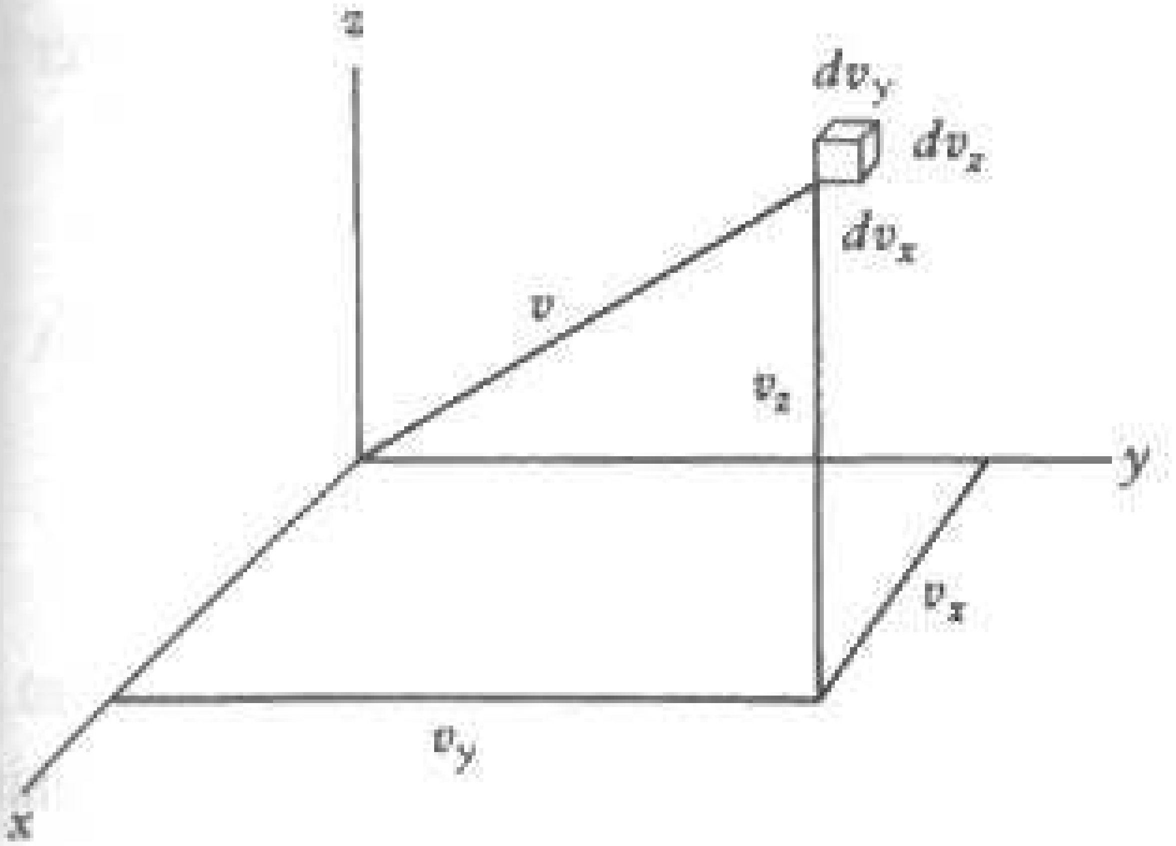


Figure 28.1 Cartesian coordinates in velocity space.

Distribution Functions

- Solving the equations of motion for a mole of molecules is not practical.
  - State-of-the-art high performance computers can do this for a few thousand molecules with a simple pairwise potential for a few ns.
  - This is not a feasible approach for macroscopic systems.
- We are interested in macroscopic phenomena such as the rate of change of some physical quantity with respect to time.
  - As in the case of thermodynamics, it is possible to move from a large number of variables to a small number of variables by the use of distribution functions.

- A volume element in three dimensional velocity space (figure 28.1) is:

$$d\mathbf{v} = dv_x \; dv_y \; dv_z$$

- The condition for equilibrium requires that the gas be homogeneous throughout the system and unchanging with time.
  - The distribution function $f(\mathbf{v})$ is independent of space and time.
- In the case of a nonequilibrium system there is dependence on space and time.
  - Thus the distribution function of interest is $f(\mathbf{r}, \mathbf{v}, t)$.
  - $f(\mathbf{r}, \mathbf{v}, t) d\mathbf{r} d\mathbf{v}$ is the total number of molecules with positions in spatial volume element $dx \; dy \; dz$ with velocities in $dv_x \; dv_y \; dv_z$.

- Thus $f(\mathbf{r}, \mathbf{v}, t)$ is a density with respect to phase space volume.
- The velocity distribution is the primary concern, therefore $f(\mathbf{r}, \mathbf{v}, t)$ is integrated over all space:

$$f(\mathbf{v}, t) = \int \int_V \int f(\mathbf{r}, \mathbf{v}, t)\ dx\ dy\ dz$$

  where V is the volume of the gas.
- The total number of molecules is obtained by integrating over all velocities:

$$N = \int_{v_x=-\infty}^{v_x=\infty} \int_{v_y=-\infty}^{v_y=\infty} \int_{v_z=-\infty}^{v_z=\infty} f(\mathbf{v}, t) dv_x\ dv_y\ dv_z$$

- Normalized distribution functions are convenient and can be achieved by division by N.

- Thus the normalized distribution function is:

$$\tilde{f}(\mathbf{v},t) = \frac{1}{N} f(\mathbf{v},t)$$

- When integrated, this becomes:

$$1 = \int_{v_x=-\infty}^{v_x=\infty} \int_{v_y=-\infty}^{v_y=\infty} \int_{v_z=-\infty}^{v_z=\infty} \tilde{f}(\mathbf{v},t) dv_x \; dv_y \; dv_z$$

  and $\tilde{f}(\mathbf{v},t)$ is a probability density.
  - $\tilde{f}(\mathbf{v},t)d\mathbf{v}$ is the probability of finding a molecule with a velocity between $\mathbf{v}$ and $\mathbf{v} + d\mathbf{v}$.
- With a coordinate transformation, this can be used to calculate the probability of finding a given speed v.
  - The new coordinates will be spherical coordinates.

Cartesian and Spherical Coordinates

- The relationship between cartesian and spherical coordinates in velocity space is:

$$v_x = v \sin\theta \cos\phi$$

$$v_y = v \sin\theta \sin\phi$$

$$v_z = v \cos\theta$$

- The relationship between the volume element in velocity space is:

$$d\mathbf{v} = dv_x\ dv_y\ dv_z\ \ = v^2 \sin\theta\ d\theta\ d\phi\ dv$$

- Therefore:

$$\tilde{f}(\mathbf{v}, t) d\mathbf{v} = \tilde{f}(v, \theta, \phi, t) v^2 \sin\theta\ d\theta\ d\phi\ dv$$

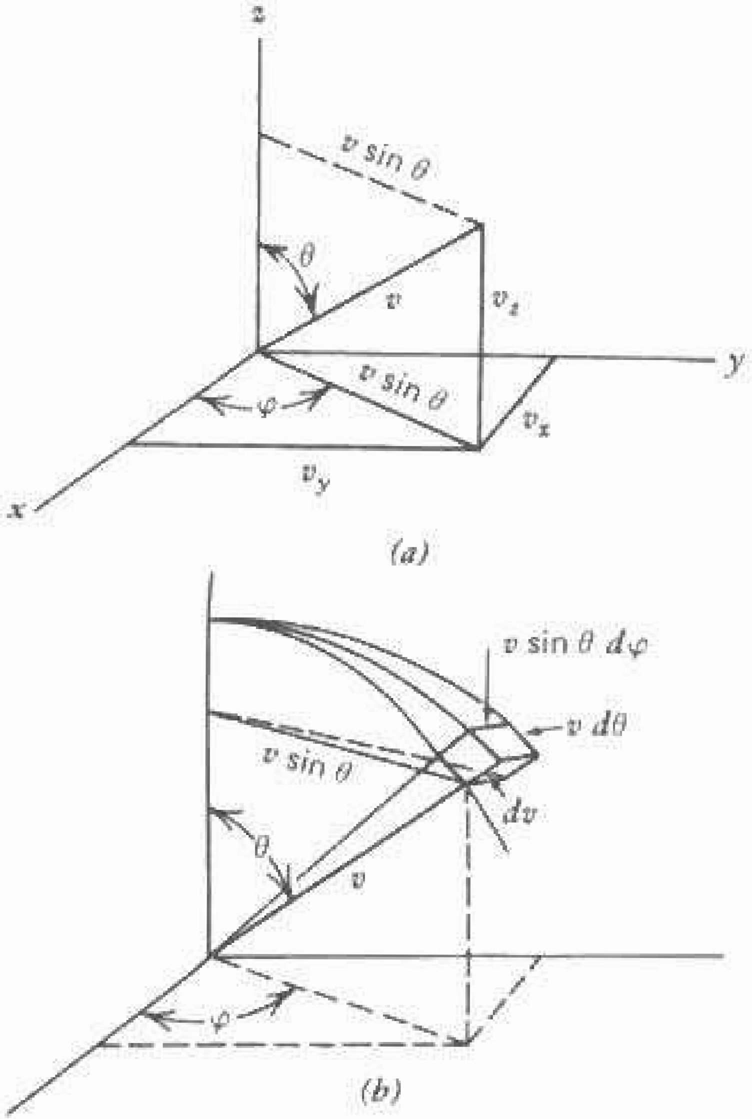


Figure 28.2 (*a*) Spherical coordinates in velocity space. (*b*) The differential volume element in velocity space in spherical coordinates. See Fig. 2A.2 for the analogous drawing of Fig. 28.2*b* in configuration space.

- This can be integrated over the angles θ and ϕ to give $f(v,t)dv$, the probability of finding a particle with speed between v and $v+dv$:

$$\tilde{f}(v,t) = \int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\tilde{f}(\mathbf{v},t)d\mathbf{v}$$

$$= v^2 dv\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\tilde{f}(v,\theta,\phi,t)\sin\theta\ d\theta\ d\phi$$

- The gas is isotropic, so $\tilde{f}(\mathbf{v}.t)$ is independent of the angular variables and

$$\tilde{f}(v,t) = v^2\tilde{f}(\mathbf{v},t)\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\sin\theta\ d\theta\ d\phi = 4\pi v^2\tilde{f}(\mathbf{v},t)$$

- The same approach may be taken with $f(\mathbf{r}, \mathbf{v}, t)$ where:

$$\tilde{f} = \frac{1}{N} f(\mathbf{r}, \mathbf{v}, t)$$

- Thus the normalization condition becomes:

$$1 = \int_{v_x=-\infty}^{v_x=\infty} \int_{v_y=-\infty}^{v_y=\infty} \int_{v_z=-\infty}^{v_z=\infty} \int \int_V \int \tilde{f}(\mathbf{r}, \mathbf{v}, t)$$

$$dv_x \; dv_y \; dv_z \; dx \; dy \; dz$$

  and $\tilde{f}(\mathbf{r}, \mathbf{v}, t)$ is the probability distribution in six dimensional phase (or position-velocity) space.

  - If a transport process is under consideration, this form of the distribution function is useful.

- Distribution functions are also associated with internal degrees of freedom:

$$N = \sum_{j=0}^{g-1} f(j,t)$$

  where there are N oscillators with g quantum states with quantum numbers $0, 1, 2, \ldots, g-1$.

- The normalized function is $N^{-1} f(j,t) = x(j,t)$ where $x(j,t)$ is the mole fraction of oscillators in state j at time t.
- Thus:

$$1 = \sum_{j} x(j,t)$$

Collision Frequency in a Dilute Gas

- In the kinetic theory, gas molecules move and collide with other molecules or the wall of the container.
- Consider a volume element away from the walls.
  - The spatial distribution is uniform.
  - The velocity distribution follows the Maxwell distribution.
- Now consider giving the molecules in this volume element a *nonequilibrium* velocity distribution.
  - How long will it take for the distribution to return to the equilibrium distribution?
  - Molecules can change velocity only as the result of collisions each other since the volume element under consideration is away from the walls.
  - What is the frequency with which collisions take place?

- This has been investigated by computer simulation in 1955 by Alder and Wainwright.
- 100 hard spheres of diameter d were distributed uniformly through volume V.
- All had the same initial speed, but the direction of motion was selected randomly.
- The motion of each particle was followed.
    - A collision occurs when the distance between two spheres is within d.
    - Since the position and coordinates of each particle are known, the outcome of the collision may be determined in terms of impact parameter, scattering angle, and direction and magnitude of velocity.
    - Distributions of velocity and speed may be determined at any time step in the simulation.

- The distribution of time and distance between collisions may also be determined.
    - The average time between collisions is the *mean free time*, τ_f.
    - The average distance travelled between collisions is the *mean free path*.
- After a few τ_f, the distribution of speed asymptotically approaches the equilibrium distribution.
- The *relaxation time* is a few τ_f.
- Consider now an experimental situation with the objective of deriving the collision frequency in a dilute gas.
    - Consider a uniform mixture of two gases, each of structureless particles.

T

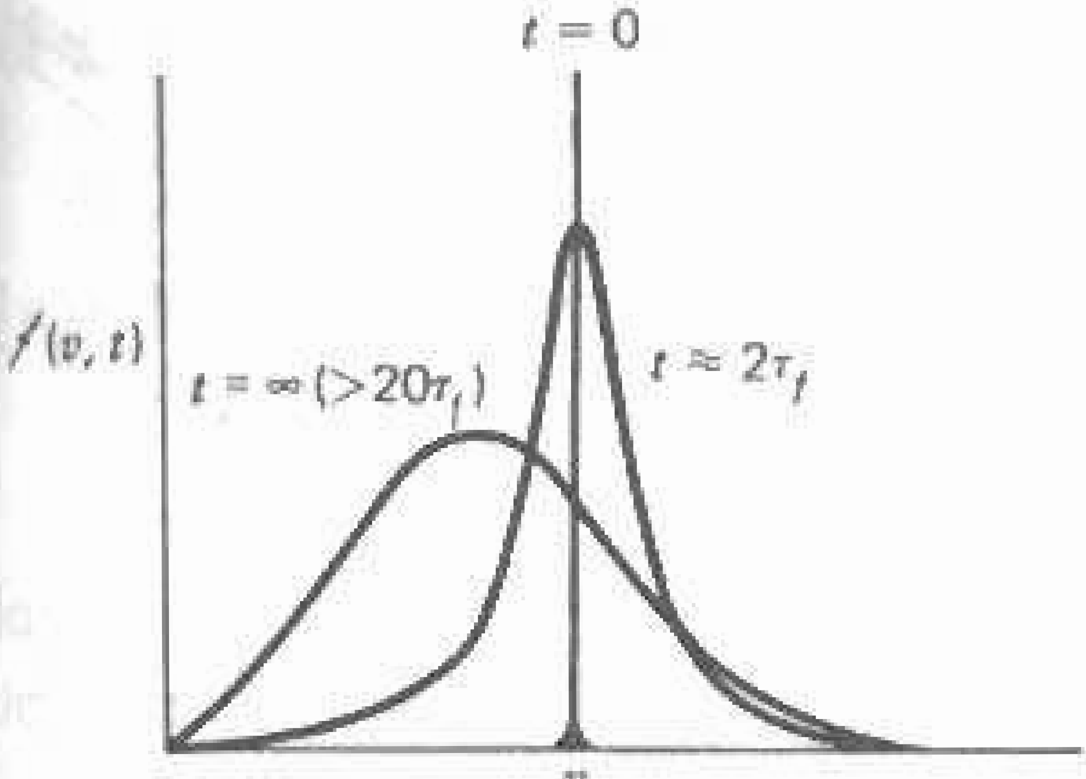


Figure 28.3 Calculated distribution of speeds as a function of time; τ_f is the average time between collisions. Schematic, after B. Alder and T. Wainwright. (Not to scale.)

of each sphere's velocity after the collision. Thus labor

- A real system that would approach these conditions would consist of Ar (1) and Xe(2).
  - The number densities are n_1 and n_2, respectively and are constant with time.
  - The velocity distributions are $\tilde{f}(\mathbf{v_1})$ and $\tilde{f}(\mathbf{v_2})$ and may be time dependent.
  - The number density of argon atoms with velocities between $\mathbf{v_1}$ and $\mathbf{v_1} + d\mathbf{v_1}$ is $n_1\tilde{f}(\mathbf{v_1})d\mathbf{v_1}$
- Recall collisions between molecules in molecular beams.
  - It is possible in a molecular beam to have all the molecules with the same velocity.
  - The number of collisions per unit time in a volume τ between Ar atoms with velocities between $\mathbf{v_1}$ and $\mathbf{v_1} + d\mathbf{v_1}$ of density $n_1\tilde{f}(\mathbf{v_1})d\mathbf{v_1}$ and Xe atoms with velocities between $\mathbf{v_2}$ and $\mathbf{v_2} + d\mathbf{v_2}$ of density

$n_2\tilde{f}(\mathbf{v_2})d\mathbf{v_2}$ is:

$$\tau Z_{12}(\mathbf{v_1},\mathbf{v_2}) =$$

$$2\pi v\int_{\chi=0}^{\pi}\sigma(v,\chi)n_1n_2\tilde{f}(\mathbf{v_1},t)\tilde{f}(\mathbf{v_2},\mathbf{t})\tau d\mathbf{v_1}d\mathbf{v_2}\sin\chi d\chi$$

where $v = |\mathbf{v_2} - \mathbf{v_1}|$ and is determined by the intersection angle in the beams.

- The overall collision rate is determined by summing over all possible values of $\mathbf{v_1}$ and $\mathbf{v_2}$.
- Implicit in this is the assumption that the atoms move freely and independently before collision and that the velocity of each atom is uncorrelated with the velocity of the collision partner.
- If the correlation existed then $\tilde{f}(v,t)$ for colliding atoms would be different from $\tilde{f}(v,t)$ for the bulk gas.

- The validity of this derivation will be restricted to situation where, on average, this condition is met.
  - This is true for the ideal gas, but would not be true in dense gases or liquids.
- The number of collisions per unit time per unit volume for Ar atoms with velocities between $\mathbf{v_1}$ and $\mathbf{v_1} + d\mathbf{v_1}$ is obtained by dividing the previous expression by the volume τ and integrating over all values of $\mathbf{v_2}$:

$$Z_{12}(\mathbf{v_1}) =$$

$$2\pi n_1 n_2 d\mathbf{v_1} \int_{\mathbf{v_2}} \int_{\chi=0}^{\pi} v\sigma(v,\chi) \tilde{f}(\mathbf{v_1}, t) \tilde{f}(\mathbf{v_2}, \mathbf{t}) d\mathbf{v_2} \sin\chi d\chi$$

- The total number of collisions per unit time per unit volume between Ar atoms of all velocities and Xe atoms of all velocities is:

$$Z_{12} = 2\pi n_1 n_2 \int_{\mathbf{v_1}} \int_{\mathbf{v_2}} \int_{\chi=0}^{\pi} v\sigma(v,\chi)\tilde{f}_1(\mathbf{v_1},t)\tilde{f}_2(\mathbf{v_2},t)d\mathbf{v_1}d\mathbf{v_2}\sin\chi d\chi$$

- Z_{12} is the collision frequency.
- Note that $\tilde{f}$ has yet to be specified.

The Evolution of Velocity Distributions in Time

- Consider a gas that initially has a *nonequilibrium* velocity distribution.
  - The velocity distribution evolves with time and asymptotically approaches equilibrium.
  - This time evolution of the velocity distribution is driven by molecular collisions.
  - The collision frequency will determine the rate of change of the distribution.

- $n\tilde{f}(\mathbf{v_1}, t)d\mathbf{v_1}$ gives the number of molecules per unit volume with velocities between $\mathbf{v_1}$ and $\mathbf{v_1} + d\mathbf{v_1}$
- If the gas is uniformly distributed in volume V, then n is a constant.
- Thus:

$$n\left[\frac{d\tilde{f}(\mathbf{v_1}, t)}{dt}\right]d\mathbf{v_1}$$

  describes the change per unit time in the number density of molecules with velocities between $\mathbf{v_1}$ and $\mathbf{v_1} + d\mathbf{v_1}$
- This change is the result of:
  - A molecule with velocity $\mathbf{v_1}$ before collision will have a different velocity after collision.
  - A molecule with a velocity outside the range of velocities between $\mathbf{v_1}$ and $\mathbf{v_1} + d\mathbf{v_1}$ before collision will have velocity within this range after collision.

- For a pure gas, the collision frequency for molecules at $\mathbf{v_1}$ with molecules of any value of $\mathbf{v_2}$ is:

$$Z_{12}(\mathbf{v_1}) = 2\pi n^2 d\mathbf{v_1} \int_\chi \int_{\mathbf{v_2}} v\sigma(v,\chi)\tilde{f}(\mathbf{v_1},t)\tilde{f}(\mathbf{v_2},t)d\mathbf{v_2}\sin\chi d\chi$$

- What is the corresponding expression for the number of collisions with $\mathbf{v_2}$?
  - Consider a collision occurring at velocities $\mathbf{v_1}, \mathbf{v_2}$ and scattering angle χ.
  - These conditions imply impact parameter b since for a given relative velocity and scattering angle, the impact parameter is determined.
  - The final velocities after the collision are $\mathbf{v_1'}, \mathbf{v_2'}$.
  - Since the particles are structureless, the collisions are elastic.

- Therefore the relative speed is unchanged and the final impact parameter b' is equal to b (see figure 27.4).
- Now consider a collision that starts with velocities $\mathbf{v_1'}, \mathbf{v_2'}$ and has scattering angle χ.
  - The only possible value of the velocities after the collision is $\mathbf{v_1}, \mathbf{v_2}$.
- The choice of which of $\mathbf{v_1}, \mathbf{v_2}$ and $\mathbf{v_1'}, \mathbf{v_2'}$ are initial or final is arbitrary.
- Thus the number of collisions between atoms of velocities $\mathbf{v_1'}, \mathbf{v_2'}$ leading to a scattering angle between χ and $\chi + d\chi$ is:

$$Z_{12}(\mathbf{v_1'}, \mathbf{v_2'}, \chi) = 2\pi n^2 v' \sigma(v', \chi) \tilde{f}(\mathbf{v_1'}, t) \tilde{f}(\mathbf{v_2'}, t)$$

$$d\mathbf{v_1'} d\mathbf{v_2'} \sin\chi d\chi$$

- Since the collision is elastic $v' = v$.
- It may be shown that

  $$d\mathbf{v_1'}d\mathbf{v_2'} = d\mathbf{V}'d\mathbf{v}'$$

  and

  $$d\mathbf{v_1}d\mathbf{v_2} = d\mathbf{V}d\mathbf{v}$$

  since the Jacobian is unity (see footnote on page 824).
- The center-of-mass vector $\mathbf{V}$ is unaffected by the collision.
  - Therefore $\mathbf{V} = \mathbf{V}'$ and $d\mathbf{V} = d\mathbf{V}'$
- It must now be shown that $d\mathbf{v} = d\mathbf{v}'$.
  - Consider Figure 28.4.
  - An apse line may be defined such that it lies in the plane defined by $\mathbf{v}, \mathbf{v}'$ and bisects the angle χ.

The

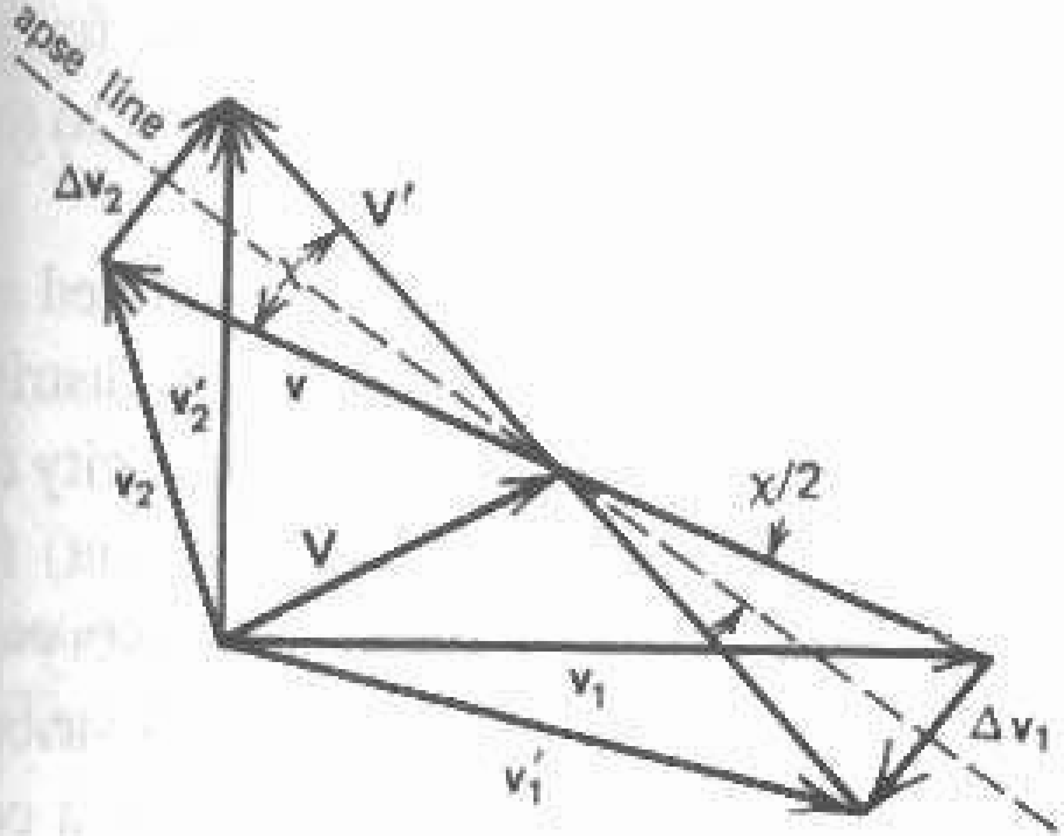


Figure 28.4 Velocity relationships for an elastic collision in a pure gas. (Note that in a pure gas **V** bisects **v**, as is apparent from Eqs. 27.15.)

- This apse line may be used to define an orthogonal coordinate system.
- The relative velocity vector may be resolved into two components: one parallel to and the other perpendicular to the apse line.
  - Recall that for hard spheres, the effect of a collision is to leave one component (i.e. the parallel) unchanged and the sign of the other (i.e. the perpendicular) reversed but the magnitude unchanged.
- Because the magnitude of the components are unchanged by the collision, the volume element is unchanged:

$$d\mathbf{v} = d\mathbf{v}'$$

- Thus:

$$d\mathbf{v_1'}d\mathbf{v_2'} = d\mathbf{v_1}d\mathbf{v_2}$$

  provided they are related as illustrated in Figure 28.4 which holds according the equation of motion for hard spheres for a given b or χ.

- To show this more clearly, consider

$$\mathbf{v_1'} = \mathbf{v_1} - \Delta\mathbf{v_1}(v,\chi)$$

$$\mathbf{v_2'} = \mathbf{v_2} + \Delta\mathbf{v_2}(v,\chi)$$

- Rewrite $Z_{12}(\mathbf{v_1'},\mathbf{v_2'},\chi)$:

$$Z_{12}(\mathbf{v_1}-\Delta\mathbf{v_1},\mathbf{v_2}-\Delta\mathbf{v_2},\chi) = 2\pi n^2 v\sigma(v,\chi)\tilde{f}(\mathbf{v_1}-\Delta\mathbf{v_1},t)$$

$$\times\tilde{f}(\mathbf{v_2}+\Delta\mathbf{v_2},t)d\mathbf{v_1}d\mathbf{v_2}\sin\chi d\chi$$

- Integration of this over all values of $\mathbf{v_2}$ and χ gives the total number of collisions per unit time per unit volume that one atom emerges from the collision with velocity between $\mathbf{v_1}$ and $\mathbf{v_1} + d\mathbf{v_1}$:

$$Z_{12}(\mathbf{v_1} - \Delta\mathbf{v_1}) = 2\pi n^2 d\mathbf{v_1} \int_\chi \int_{\mathbf{v_2}} v\sigma(v,\chi)\tilde{f}(\mathbf{v_1} - \Delta\mathbf{v_1}, t)$$

$$\times \tilde{f}(\mathbf{v_2} + \Delta\mathbf{v_2}, t) d\mathbf{v_2} \sin\chi d\chi$$

- Recall:

$$Z_{12}(\mathbf{v_1}) = 2\pi n^2 d\mathbf{v_1} \int_\chi \int_{\mathbf{v_2}} v\sigma(v,\chi)\tilde{f}(\mathbf{v_1}, t)\tilde{f}(\mathbf{v_2}, t) d\mathbf{v_2} \sin\chi d\chi$$

- The difference between these expressions is:

$$n\left[\frac{d\tilde{f}(\mathbf{v_1},t)}{dt}\right]_{\mathbf{v_1}} d\mathbf{v_1}$$

- Cancelling out $nd\mathbf{v_1}$ yields:

$$\left[\frac{d\tilde{f}(\mathbf{v_1},t)}{dt}\right]_{\mathbf{v_1}} = 2\pi n \int_\chi \int_{\mathbf{v_2}} v\sigma(v,\chi)\times$$

$$\left[\tilde{f}(\mathbf{v_1}-\Delta\mathbf{v_1},t)\tilde{f}(\mathbf{v_2}+\Delta\mathbf{v_2},t)-\tilde{f}(\mathbf{v_1},t)\tilde{f}(\mathbf{v_2},t)\right] d\mathbf{v_2}\sin\chi d\chi$$

- This is the Boltzmann equation, an integro-differential equation which has no general solutions.
  - For the special solution at infinite time:

$$\left[\frac{d\tilde{f}(\mathbf{v_1},t)}{dt}\right]_{\mathbf{v_1}} = 0$$

- A sufficient, but not necessary condition, for this to be true is:

  $$\tilde{f}(\mathbf{v_1} - \Delta\mathbf{v_1}(v,\chi))\tilde{f}(\mathbf{v_2} + \Delta\mathbf{v_2}(v,\chi)) - \tilde{f}(\mathbf{v_1})\tilde{f}(\mathbf{v_2}) = 0$$

  for all values of $\mathbf{v_1}, \mathbf{v_2}, \chi$.
- This is equivalent to the statement that there are as many collisions of the type:

  $$\mathbf{v_1}, \mathbf{v_2} \rightarrow \mathbf{v_1} - \Delta\mathbf{v_1}(v,\chi), \mathbf{v_2} + \Delta\mathbf{v_2}(v,\chi)$$

  as there are of the type:

  $$\mathbf{v_1} - \Delta\mathbf{v_1}(v,\chi), \mathbf{v_2} + \Delta\mathbf{v_2}(v,\chi) \rightarrow \mathbf{v_1}, \mathbf{v_2}$$
- This is a statement of the requirement of detailed balance between each possible collision and its inverse.

- Rearranging the equation and taking the natural logarithm of both sides yields:

$$\ln\tilde{f}(\mathbf{v_1}-\Delta\mathbf{v_1}(v,\chi))+\ln\tilde{f}(\mathbf{v_2}+\Delta\mathbf{v_2}(v,\chi)) = \ln\tilde{f}(\mathbf{v_1})+\ln\tilde{f}(\mathbf{v_2})$$

- This means that the sum of the logarithms of the velocities distribution is unchanged by the collision and is *invariant* or conserved.
- Previously encountered summational invariants for elastic collisions include:
    - mass
    - linear momentum
    - angular momentum
    - kinetic energy
- Thus $\ln\tilde{f}(\mathbf{v_1})$ must be a linear combination of at least some of the above.

- This function should depend only on the magnitude of $\mathbf{v_1}$.
  - Since linear and angular momentum depend on the direction they cannot be included in the function.
- Test the form:

$$\ln \tilde{f}(\mathbf{v_1}) = \alpha + \beta(\frac{1}{2}mv_1^2)$$

where α and β are constants independent of v_1.

  - $\beta = -1/k_BT$ according to section 15.5
  - Therefore:

$$\tilde{f}(\mathbf{v_1}) = Ae^{-mv^2/2k_BT}$$

where $A = e^{\alpha}$ and is determined by normalization.

- This is the Maxwell Boltzmann distribution.

- Thus an equation that describes the variation with time of the velocity distribution in a dilute, spatially homogeneous gas.
- At equilibrium, the integrand of the Boltzmann equation is zero.
    - Only the Maxwell-Boltzmann distribution satisfies this condition for a gas at rest.

The Maxwell-Boltzmann Distribution

- Properties of the Maxwell-Boltzmann distribution will now be considered.
- The probability density must be normalized:

$$\tilde{f}(\mathbf{v})d\mathbf{v} = 1$$

- This is satisfied when

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

- Recall that

$$\frac{1}{2}mv^2 = \frac{1}{2}m\left(v_x^2 + v_y^2 + v_z^2\right)$$

- Thus:

$$\int_{\mathbf{v}} \tilde{f}(\mathbf{v}) d\mathbf{v} = \left(\frac{m}{2\pi k_B T}\right)^{3/2}$$

$$\times \int_{v_x} \int_{v_y} \int_{v_z} e^{-m\left(v_x^2+v_y^2+v_z^2\right)/2k_B T} dv_x dv_y dv_z$$

- This may be factored into three integral factors:

$$\int_{\mathbf{v}} \tilde{f}(\mathbf{v})d\mathbf{v} = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \left[\int_{v_x=-\infty}^{+\infty} e^{-mv_x^2/2k_BT} dv_x\right]$$

$$\times \left[\int_{v_y=-\infty}^{+\infty} e^{-mv_y^2/2k_BT} dv_y\right] \left[\int_{v_z=-\infty}^{+\infty} e^{-mv_z^2/2k_BT} dv_z\right]$$

which may be considered are three identical factors of form:

$$\left(\frac{m}{2\pi k_B T}\right)^{1/2} \int_{u=-\infty}^{u=\infty} e^{-mu^2/2k_BT} du = 1$$

- Thus

$$\tilde{f}(\mathbf{v})d\mathbf{v} = \left[\tilde{f}(v_x)dv_x\right] \left[\tilde{f}(v_y)dv_y\right] \left[\tilde{f}(v_z)dv_z\right]$$

- where $\tilde{f}(v_x), \tilde{f}(v_y), \tilde{f}(v_z)$ are the probability densities for the velocity components.
- Thus the fraction of molecules with x component of velocity between v_x and $v_x + dv_x$ is:

$$\tilde{f}(v_x)dv_x = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-mv_x^2/2k_BT} dv_x$$

and similar for v_y and v_z

  - The distribution of velocity components in one direction is independent of the velocity distribution in the other directions.
  - It is symmetric about $u = 0$ (see Figure 28.5).
  - The maximum velocity is proportional to $T^{-1/2}$

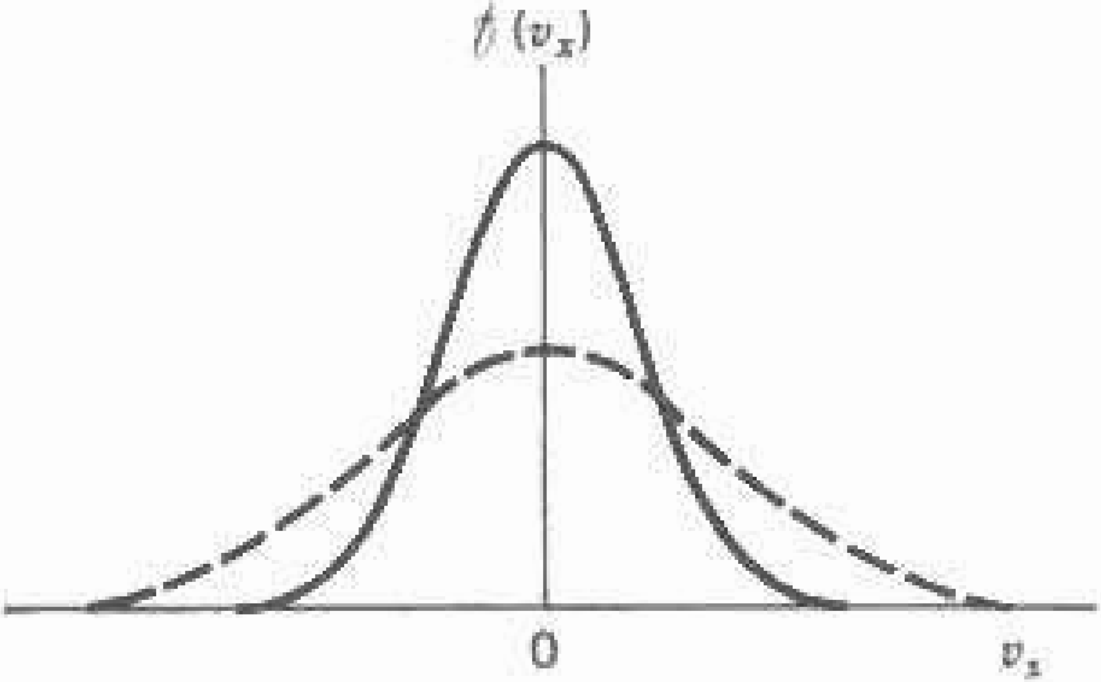


Figure 28.5 Probability density for velocity component in one dimension. Solid curve: $T = 300$ K; broken curve: $T = 1000$ K.

- Continued
  - The spread of the distribution is a function of both temperature and molecular mass.
  - For a given gas, as the temperature increases, the spread increases, but the area under the curve is still unity.
- The Maxwell-Boltzmann distribution has the same mathematical form as the Gaussian distribution, proportional to $e^{-a\delta^2}$, where δ is a measure of the deviation from the mean and a is a positive constant.
- Consider the average velocity of a gas at rest.
  - This involves determining the average value of each of the components.
  - Consider first $\langle v_x \rangle$.

- By definition:

$$\langle \mathbf{v} \rangle = \int_{\mathbf{v}} \mathbf{v} \tilde{f}(\mathbf{v}) d\mathbf{v}$$

.

- The x component is:

$$\langle v_x \rangle = \int_{v_x=-\infty}^{+\infty} \int_{v_y=-\infty}^{+\infty} \int_{v_z=-\infty}^{+\infty} v_x \tilde{f}(\mathbf{v}) dv_x dv_y dv_z$$

- Substituting the Maxwell-Boltzmann distribution for $\tilde{f}(\mathbf{v})$ gives:

$$\langle v_x \rangle = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_{v_x=-\infty}^{+\infty} \int_{v_y=-\infty}^{+\infty} \int_{v_z=-\infty}^{+\infty} v_x$$

$$\times e^{-m\left(v_x^2+v_y^2+v_z^2\right)/2k_BT} dv_x dv_y dv_z$$

- Factoring yields:

$$\langle v_x \rangle = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \left[\int_{v_x=-\infty}^{+\infty} v_x e^{-mv_x^2/2k_BT} dv_x\right]$$

$$\times \left[\int_{v_y=-\infty}^{+\infty} e^{-mv_y^2/2k_BT} dv_y\right] \left[\int_{v_z=-\infty}^{+\infty} e^{-mv_z^2/2k_BT} dv_z\right]$$

- Thus:

$$\langle v_x \rangle = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \left[\int_{v_x=-\infty}^{+\infty} v_x e^{-mv_x^2/2k_BT} dv_x\right]$$

  - Note that the integrand is an *odd* function of v_x.
  - Therefore $\langle v_x \rangle = 0$.
  - Similarly $\langle v_y \rangle = 0$ and $\langle v_z \rangle = 0$

- Consider a gas in motion in the x direction with speed v_{x0}
  - The Maxwell-Boltzmann distribution in v_x is no longer symmetric about $v_x = 0$, but instead about $v_x = v_{x0}$.
  - Thus the distribution becomes:

$$\tilde{f}(v_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-m(v_x - v_{x0})^2/2k_B T}$$

- Consider now the average speed.
  - Since only the magnitude and not the direction matter, consider the distribution function in spherical coordinates integrated over all angles.

$$\tilde{f}(v) = v^2 \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2k_B T} \sin\theta d\theta d\phi$$

- This yields:

$$\tilde{f}(v) = 4\pi v^2 \tilde{f}(\mathbf{v}) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-mv^2/2k_B T}$$

- This speed distribution is shown in Figure 28.6 and is not symmetric.
  - Therefore the average speed is not zero.

$$\langle v \rangle = \int_{v=0}^{\infty} v \tilde{f}(v) dv$$

$$= 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_{v=0}^{\infty} v^3 e^{-mv^2/2k_B T} dv = \left(\frac{8k_B T}{\pi m}\right)^{1/2}$$

  - The average speed in proportional to $T^{1/2}$.

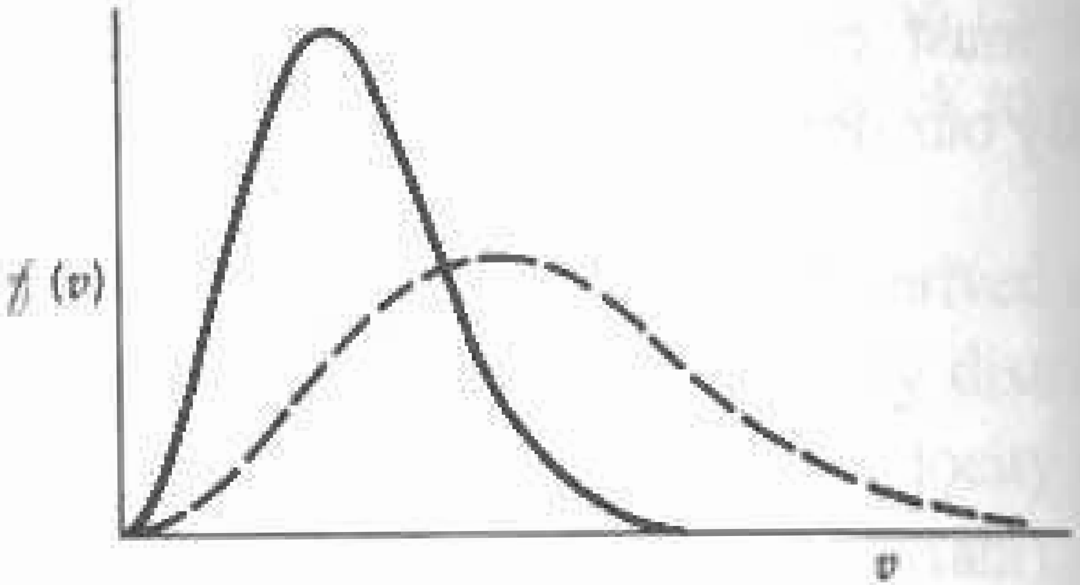


Figure 28.6 Equilibrium probability distribution of speeds in a gas at rest. Solid curve: $T = 300$ K; broken curve: $T = 1000$ K.

- $\langle v \rangle$ is also known as the first moment of the distribution.
  - Similarly $\langle v^2 \rangle$ and $\langle v^3 \rangle$ are known as the second and third moments of the distribution.
- The average kinetic energy is related to the second moment.

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

$$= \frac{3}{2} k_B T$$

- Expressed as energy per mole:

$$u = \frac{3}{2} N_A k_B T = \frac{3}{2} RT$$

- Previously shown (Equation 12.17) was that:

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

- Combining this with above yields:

$$pV = Nk_BT$$

Collision Frequency for Hard-Sphere Molecules

- What is Z_{12} for a hard-sphere gas at equilibrium?
  - An expression for this will be useful in predicting reaction rates.
- Recall collisions between argon and xenon:

$$Z_{12} = 2\pi n_1 n_2 \int_{\mathbf{v_1}} \int_{\mathbf{v_2}} \int_{\chi=0}^{\pi} v\sigma(v,\chi)\tilde{f}_1(\mathbf{v_1},t)\tilde{f}_2(\mathbf{v_2},t)d\mathbf{v_1}d\mathbf{v_2}\sin\chi d\chi$$

- For the hard-sphere gas, $\sigma(v, \chi) = d^2/4$ and is independent of both angle and relative speed.
  - Thus:

$$Z_{12} = \pi d^2 n_1 n_2 \left(\frac{m_1}{2\pi k_B T}\right)^{3/2} \left(\frac{m_2}{2\pi k_B T}\right)^{3/2}$$

$$\times \int_{\mathbf{v_1}} \int_{\mathbf{v_2}} v e^{-(m_1 v_1^2 + m_2 v_2^2)/2k_B T} d\mathbf{v_1} d\mathbf{v_2}$$

    (Recall that $\int_0^\pi \sin\chi d\chi = 2$)
  - In carrying out the integration over the velocities, care must be taken in the treatment of relative speed.
  - Convert to center-of-mass coordinates before integrating.

- Consider first the constant factors:

$$\left(\frac{m_1}{2\pi k_B T}\right)^{3/2}\left(\frac{m_2}{2\pi k_B T}\right)^{3/2}$$

$$= \left(\frac{m_1 m_2}{(m_1+m_2)2\pi k_B T}\right)^{3/2}\left(\frac{(m_1+m_2)}{2\pi k_B T}\right)^{3/2}$$

$$= \left(\frac{\mu_{12}}{2\pi k_B T}\right)^{3/2}\left(\frac{(m_1+m_2)}{2\pi k_B T}\right)^{3/2}$$

where

$$\mu_{12} = \frac{m_1 m_2}{(m_1+m_2)}$$

- It has been previously shown that:

$$\frac{1}{2}m_1v_1^2 + \frac{1}{2}m_2v_2^2 = \frac{1}{2}(m_1+m_2)V^2 + \frac{1}{2}\mu_{12}v^2$$

and

$$d\mathbf{v_1}d\mathbf{v_2} = d\mathbf{V}d\mathbf{v}$$

- Thus the expression for collision frequency becomes:

$$Z_{12} = \pi d^2 n_1 n_2 \int_{\mathbf{v}} \left[\int_{\mathbf{V}} \left(\frac{(m_1+m_2)}{2\pi k_B T} \right)^{3/2} e^{-(m_1+m_2)V^2/2k_BT} d\mathbf{V} \right]$$

$$\times \left(\frac{\mu_{12}}{2\pi k_B T} \right)^{3/2} v e^{-\mu_{12}v^2/2\pi k_BT} d\mathbf{v}$$

- Consider first the integral over $\mathbf{V}$.
  - This may be recognized as the normalized distribution function over $\mathbf{V}$ and thus integrates to unity.
- The integral over $\mathbf{v}$ is:

$$\langle v_{12} \rangle = \int_{\mathbf{v}} \left(\frac{\mu_{12}}{2\pi k_B T} \right)^{3/2} v e^{-\mu_{12} v^2 / 2\pi k_B T} d\mathbf{v} = \left(\frac{8 k_B T}{\mu_{12} \pi} \right)^{1/2}$$

- Thus:

$$Z_{12} = \pi d^2 n_1 n_2 \langle v_{12} \rangle = \pi d^2 n_1 n_2 \left(\frac{8 k_B T}{\mu_{12} \pi} \right)^{1/2}$$