

MIT OpenCourseWare
<http://ocw.mit.edu>

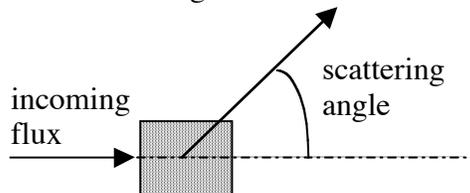
5.62 Physical Chemistry II
Spring 2008

For information about citing these materials or our Terms of Use, visit: <http://ocw.mit.edu/terms>.

Kinetic Theory of Gases: Collision Dynamics and Scattering

The goal of kinetic theory is to understand the collision process between a pair of molecules. In this lecture we give a simple description of the classical scattering process.

Although we cannot completely develop this subject, it is important to know that scattering experiments are an invaluable source of information about molecular interactions and that the results of scattering experiments can be used to predict transport coefficients for gases.



The typical scattering experiment consists in sending a flux of particles into a stationary target gas and observing the deflection of particles at a distance from the target region at various scattering angles.

We describe this process at the molecular level by considering a particular collision pair. We assume the following for the colliding pair: In center of mass coordinates the energy of the pair is given by:

$$E = \frac{\mu}{2} [\dot{x}(t)^2 + \dot{y}(t)^2] + V[r(t)] \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

and $r(t)$ is the distance between the colliding particles.

Only two components (x and y) are needed to characterize the collision because it is possible to show that two particle scattering is confined to a plane in the center of mass coordinate system.

The energy is the sum of the x and y kinetic energy of the fictitious particle with reduced mass μ . There is a potential energy, $V[r(t)]$, that depends only on the distance between the two centers. The collision is assumed to be “elastic,” which means that no energy is transferred into the internal modes of the two collision partners. In this case the total E is constant at every point along the trajectory.

In polar coordinates, $x(t) = r(t)\cos[\vartheta(t)]$, $y(t) = r(t)\sin[\vartheta(t)]$, and the energy is:

$$E = \frac{\mu}{2} \left[\dot{r}(t)^2 + r(t)^2 \dot{\vartheta}(t)^2 \right] + V[r(t)].$$

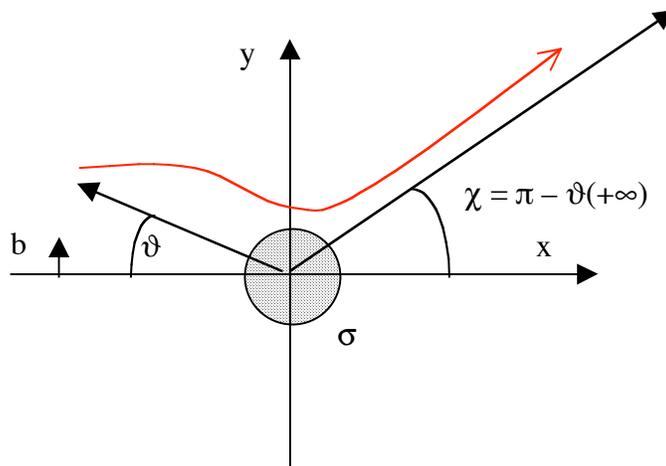
In addition, because the force is central there is conservation of angular momentum during the collision. The angular momentum is defined as $\vec{L} = \vec{r} \times \vec{p}$. Since

$$\vec{r} = (x, y, 0) = (r \cos \vartheta, r \sin \vartheta, 0) \quad \text{and} \quad \vec{p} = (\dot{r} \cos \vartheta - r \sin \vartheta \dot{\vartheta}, \dot{r} \sin \vartheta + r \cos \vartheta \dot{\vartheta}, 0)$$

and $L = L_z = xp_y - yp_x$, we obtain the result for the conserved, i.e. independent of time, angular momentum during the collision:

$$L = \mu r(t)^2 \dot{\vartheta}(t).$$

We imagine a collision process where the incoming particle approaches the target at $t = -\infty$ from $x = -\infty$; thus $r(-\infty) \approx +\infty$ and $\vartheta(0) = \frac{\pi}{2}$. We choose the coordinate system so that the initial particle velocity is in the x direction with value g ; thus $\dot{x}(-\infty) = g$ and $\dot{y}(-\infty) = 0$, and the particle position is at impact parameter “ b ” $y(-\infty) = b$. As the collision proceeds, the particle is attracted or repelled by the scattering center and eventually is scattered away so that at $t = +\infty$, the particle has been scattered at an angle $\chi = \pi - \vartheta(+\infty)$. This scattering angle is a function of the impact parameter, incoming relative velocity g , and of course of the scattering potential $V[r]$. The situation is diagrammed below:



The initial energy and angular momentum are:

$$E = \frac{\mu}{2} g^2 \quad \text{and} \quad L = \mu b g$$

and these two quantities are conserved throughout the collision.

Using the expression for the angular momentum to eliminate $\dot{\vartheta}(t)$ from the energy equation on the previous page, we find:

$$\frac{\mu}{2} g^2 = E = \frac{\mu}{2} \left[\dot{r}(t)^2 + \left(\frac{b g}{r(t)} \right)^2 \right] + V[r(t)]$$

and, solving for $\dot{r}(t)$,

$$\dot{r}(t)^2 = g^2 \left[1 - \left(\frac{b}{r(t)} \right)^2 \right] - \frac{2}{\mu} V[r(t)].$$

If we take the square root, we obtain;

$$\dot{r}(t) = \pm \sqrt{g^2 \left[1 - \left(\frac{b}{r(t)} \right)^2 \right] - \frac{2}{\mu} V[r(t)]}.$$

The +/- signs are important here.

In the collision process we are interested in the scattering and not the details of the trajectory over time. Thus we use the relation

$$\frac{dr}{d\vartheta} = \frac{\dot{r}(t)}{\dot{\vartheta}(t)}$$

to eliminate time in favor of the angle that describes the collision process. Since

$$\dot{\vartheta}(t) = \frac{\mu b g}{r(t)^2}, \text{ we have } \frac{dr}{d\vartheta} = \frac{\dot{r}(t)r(t)^2}{\mu b g}$$

and substituting for $\dot{r}(t)$ leads to the central equation to describe the scattering process:

$$\frac{dr}{d\vartheta} = \pm \frac{r(t)^2}{b g} \sqrt{g^2 \left[1 - \left(\frac{b}{r} \right)^2 \right] - \frac{2}{\mu} V[r]}$$

We divide the collision into the incoming part when the distance is decreasing and the angle is increasing. This continues until the distance of closest approach r_m is reached at angle ϑ_m . On the outgoing part of the trajectory both the angle and the distance increase. Thus:

$$\begin{aligned} \text{incoming: } & \dot{r}(t) < 0, \quad \dot{\vartheta}(t) > 0, \\ \text{outgoing: } & \dot{r}(t) > 0, \quad \dot{\vartheta}(t) > 0 \end{aligned}$$

Thus, we take the negative sign for $\left(\frac{dr}{d\vartheta} \right)$ on the incoming part of the trajectory and the positive sign for $\left(\frac{dr}{d\vartheta} \right)$ on the outgoing part of the trajectory; the distance of closest approach r_m divides the two regions. At the distance of closest approach $\dot{r}(t) = 0$ so

$$g^2 \left[1 - \left(\frac{b}{r_m} \right)^2 \right] = \frac{2}{\mu} V[r_m].$$

We are now in a position to integrate the scattering equation that we write as:

$$d\vartheta = \pm \frac{b dr}{r^2 \sqrt{\left[1 - (b/r)^2 \right] - (2/\mu g^2) V[r]}}$$

On the incoming part of the trajectory:

$$\int_0^{\vartheta_m} d\vartheta = -b \int_{\infty}^{r_m} \frac{dr}{r^2 \sqrt{\left[1 - (b/r)^2 \right] - (2/\mu g^2) V[r]}}.$$

On the outgoing part of the trajectory:

$$\int_{\vartheta_m}^{\pi-\chi} d\vartheta = +b \int_{r_m}^{\infty} \frac{dr}{r^2 \sqrt{[1 - (b/r)^2] - (2/\mu g^2)V[r]}}$$

Our final result for the scattering angle, χ , is:

$$\chi(g, b) = \pi + 2b \int_{\infty}^{r_m} \frac{dr}{r^2 \sqrt{[1 - (b/r)^2] - (2/\mu g^2)V[r]}}$$

where the distance of closest approach is found from the equation:

$$g^2 \left[1 - \left(\frac{b}{r_m} \right)^2 \right] = \frac{2}{\mu} V[r_m].$$

Hard spheres. For hard spheres $V(r) = \infty$, for $r < \sigma$, and $V(r) = 0$ for $r \geq \sigma$ where σ is the collision diameter. For $0 < b < \sigma$ the distance of closest approach is $r_m = \sigma$ and we have:

$$\chi(b) = \pi + 2b \int_{\infty}^{\sigma} \frac{dr}{r^2 \sqrt{[1 - (b/r)^2]}} \quad 0 < b < \sigma.$$

This integral is easy to evaluate. After a change of variables $x = b/r$:

$$\chi(b) = \pi + 2 \int_0^{b/\sigma} \frac{dx}{\sqrt{[1 - x^2]}} = \pi - 2 \sin^{-1}(x) \Big|_0^{b/\sigma} = \pi - 2 \sin^{-1} \left(\frac{b}{\sigma} \right) = 2 \cos^{-1} \left(\frac{b}{\sigma} \right) \quad 0 < b < \sigma$$

For a head on collision, $b = 0$, and $\chi(0) = \pi$.

If $b > \sigma$, there is no collision and the distance of closest approach is $r_m = b$. the resulting scattering angle is:

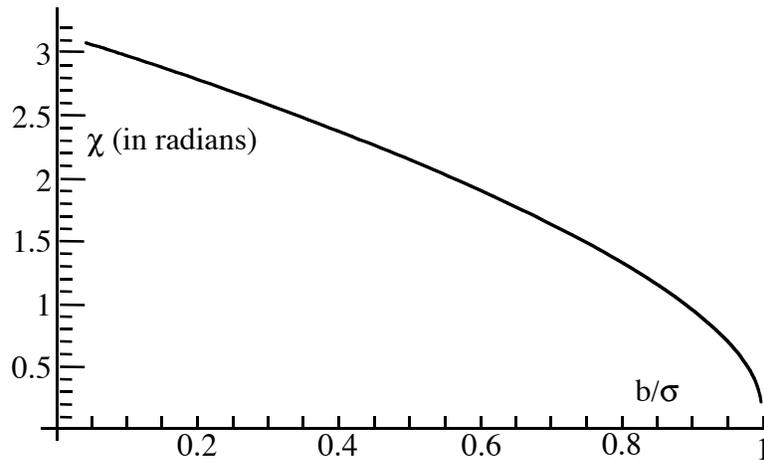
$$\chi(b) = \pi + 2b \int_{\infty}^b \frac{dr}{r^2 \sqrt{1 - (b/r)^2}} \quad b > \sigma.$$

Again after a change of variables $x = b/r$:

$$\chi(b) = \pi - 2 \int_0^1 \frac{dx}{\sqrt{1-x^2}} = \pi - 2 \sin^{-1}(x) \Big|_0^1 = \pi - 2 \frac{\pi}{2} = 0 \quad b > \sigma.$$

At these impact parameters there is no deflection.

Scattering angle from hard sphere of diameter σ



Coulomb interaction. For a Coulomb interaction of the form $V(r) = \frac{\alpha}{r}$ the deflection action can be found exactly. In this case the distance of closest approach is found from

$$g^2 \left[1 - \left(\frac{b}{r_m} \right)^2 \right] = \frac{2\alpha}{\mu r_m}.$$

The distance of closest approach is

$$\frac{r_m}{b} = \frac{u}{2} + \sqrt{\left(\frac{u}{2} \right)^2 + 1} \quad \text{where } u = \frac{2\alpha}{\mu g^2 b}.$$

The integration for the scattering angle can be done. The answer is:

$$\chi = \pi - 2 \cot^{-1} \left(\frac{\alpha}{\mu g^2 b} \right) = \pi - 2 \cot^{-1} \left(\frac{u}{2} \right).$$

Notice that this formula holds for both repulsive and attractive Coulombic potentials.

Inverse square potential. This potential can also be solved exactly

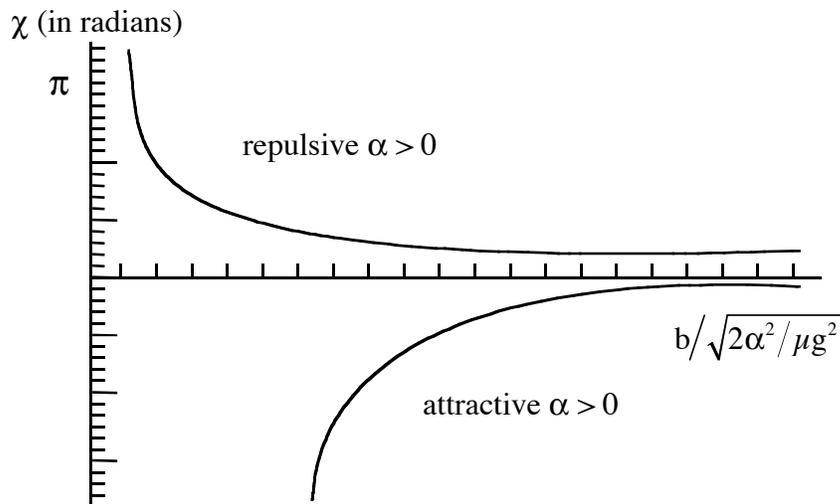
If $V(r) = \frac{\alpha}{r^2}$. We find for the distance of closest approach:

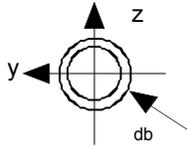
$$\left[1 - \left(\frac{b}{r_m} \right)^2 \right] = \frac{2}{\mu g^2} \frac{\alpha}{b^2} \left(\frac{b}{r_m} \right)^2 \quad \text{or} \quad \left(\frac{r_m}{b} \right) = \sqrt{1+v} \quad \text{where} \quad v = \frac{2}{\mu g^2} \frac{\alpha}{b^2}.$$

The result for the scattering angle is:

$$\chi = \pi - \pi(1+v)^{-\frac{1}{2}} = \pi - \pi \left(1 + \frac{2\alpha}{\mu g^2 b^2} \right)^{-\frac{1}{2}}.$$

Scattering from $V(r) = \alpha/r^2$



Scattering cross sections

The scattering takes place as shown in the figure as at the beginning of this lecture. Looking down the x-axis, the flux of incident particles is imagined to fall in a uniform fashion on a certain cross section. A differential cross section is the impacted area of size $2\pi b db$, as indicated in the figure on the left.

Thus we have for the differential scattering cross section $d\sigma$

$$d\sigma = 2\pi b db$$

The total cross section σ_T is found by integrating over the total area that the incident beam hits:

$$\sigma_T = \int_0^{b_{\max}} 2\pi b db = \pi b_{\max}^2 .$$

The scattering takes those particles in the incident beam which impact the target between b and $b+db$ into a particular scattering angle χ as described earlier. The measurement is made by placing a collector that intercepts the particles that are scattered into a small solid angle $d\Omega = 2\pi \sin \chi d\chi$. Since the collision dynamics connects this differential solid angle to a differential element of the impact parameter we have the relation:

$$\frac{d\sigma}{d\Omega} = b \left| \frac{db}{d\chi} \right| \frac{1}{\sin \chi} .$$

Or alternatively, in terms of the scattering function $S(\chi)$

$$d\sigma = 2\pi S(\chi) \sin \chi d\chi \quad \text{where} \quad S(\chi) = b \left| \frac{db}{d\chi} \right| \frac{1}{\sin \chi} .$$

Measurement of the scattering cross section gives information about the molecular parameters that characterize the interaction potential between the colliding partners.

Such measurements are an important tool for physical chemists who study collision dynamics in order to learn about transport properties or reaction dynamics.

The simplest example of cross section and scattering function is colliding hard spheres. Earlier in this lecture we determined for hard spheres:

$$\chi(b) = 2\cos^{-1}\left(\frac{b}{\sigma}\right) \text{ for } b < \sigma.$$

It follows that $\left|\frac{db}{d\chi}\right| = \frac{\sigma}{2} \sin\left(\frac{\chi}{2}\right)$ and hence

$$S(\chi) = b \frac{\frac{\sigma}{2} \sin\left(\frac{\chi}{2}\right)}{\sin \chi} = \frac{\frac{\sigma^2}{2} \cos\left(\frac{\chi}{2}\right) \sin\left(\frac{\chi}{2}\right)}{\sin \chi} = \left(\frac{\sigma}{2}\right)^2.$$

For hard spheres the scattering function is spherically isotropic. Its magnitude determines the collision diameter of the hard spheres σ . The differential scattering cross section for the hard spheres is:

$$d\sigma = \left(\frac{\sigma}{2}\right)^2 2\pi \sin \chi d\chi.$$