Treating collisions in the lab and centre of mass frames

In the gas or liquid phase, a typical molecule undergoes billions of collisions every second. Such collisions may be grouped into three types:

1. Elastic – kinetic energy is conserved
2. Inelastic – kinetic energy is not conserved, and energy is converted between different forms e.g. translational to rotational or vibrational, or vice versa.
3. Reactive – chemical bonds are made or broken (this is actually a special case of an inelastic collision).

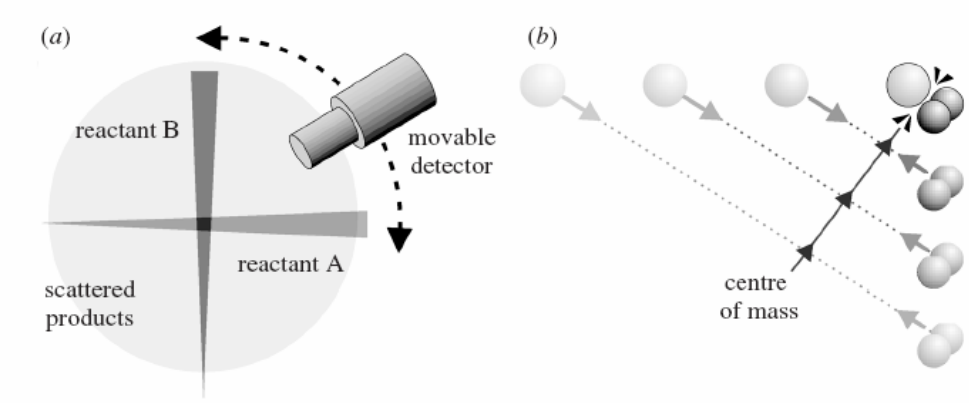
Collisions lie at the heart of chemistry. Reactive collisions are the processes in which chemical change occurs, while inelastic collisions are often the means by which molecules gain enough energy to overcome activation barriers so that subsequent collisions may lead to reaction. Because of their central role in chemistry, it is important that you understand the basic physics describing collisions, and can carry out simple calculations on the energetics and dynamics of these processes.

Why do we need a centre of mass frame?

One of the aspects of such calculations that seems to cause the most confusion is the concept of 'lab' and 'centre of mass' frames. The following example might help illustrate why two reference frames are necessary.

Imagine you are carrying out an experiment in which you observe single reactive collisions and measure the angles at which the product molecules scatter (this is not just a thought experiment – it is perfectly possible to make these measurements using currently available experimental techniques). The direction in which the products scatter results from the forces acting in the transition state region of the reaction, and the product angular distribution is therefore a sensitive probe of the detailed chemical rearrangement occurring during the reactive collisions. Another way of thinking about it is that the product scattering distribution provides a 'fingerprint' for a reaction in the same way as a spectrum provides a fingerprint for a molecule. Some reactions scatter products forwards relative to the relative velocity of the reactants, some scatter products backwards, and some show a complicated mixture of the two.

Now think about how we would go about measuring the scattering distribution. One way of doing it is shown in Figure a) below. The two reactants are prepared in molecular beams (these literally are beams of molecules formed by expanding a gas through a small hole into a vacuum). The beams are allowed to cross at right angles, and reactive collisions occur at the crossing point. A detector then measures the number of product molecules scattered into each angle, thereby determining the angular distribution.



The fact that the beams cross at right angles in this example is fairly arbitrary. We could have crossed them at a different angle, in which case conservation of momentum and energy would mean that the scattering distribution would look different. We could have carried out a different experiment entirely, in which case the scattering distribution would look different again. However, no matter what experiment we choose to do, we are looking at the same chemical process. We said above that the scattering distribution depends only on the chemical rearrangement occurring during the collision, so there must be some way in which we can compare the scattering distributions from different experiments and obtain chemically meaningful information. It turns out that what we need to do is transform the results into the centre of mass (CM) frame. This is simply a frame of reference in which the observer is travelling along with the centre of mass of the system. The total momentum in this frame is zero, and the reactants appear to undergo a head on collision at the position of their centre of mass (this is illustrated in Figure b) above). The CM frame is independent of experimental geometry, allowing results from different types of experiments to be compared, and also provides a much more intuitive picture of the collision dynamics. As an example, 'forward' and 'backward' scattering is always defined relative to the CM frame, whereas in the lab frame these terms can be ambiguous to say the least.

An analogy that some people find helpful in thinking about the lab and CM frames comes from NMR spectroscopy. The natural units for displaying any kind of spectrum are frequency units (or equivalently, wavelength or energy units). However, in NMR spectroscopy the transition frequencies depend on the magnetic field strength inside the spectrometer. No two spectrometers will have exactly the same magnet, with the result that two spectra of the same molecule measured on different spectrometers would not match. To get around this problem, NMR spectroscopists have defined 'chemical shift' units of ppm, which are independent of the spectrometer. The CM frame in the treatment of collisions serves the same purpose as the 'chemical shift' units in NMR, allowing the results of different experiments to be compared.

Calculations on collisions

For simplicity, we will only consider calculations involving elastic collisions here. It is straightforward to extend the following to inelastic or reactive collisions – all you have to do is add or subtract the appropriate energy change from the energy of the collision products. Note that in the general case all of the velocities are vector quantities, though often you will only be concerned with motion in one dimension (e.g. a head on collision or collision involving a stationary particle in the lab frame), in which case they may be treated as scalars.

Usually, we know the velocities of the two particles before the collision, $\mathbf{v_1}$ and $\mathbf{v_2}$. These are our 'lab frame' velocities. The kinetic energies of the two particles are $K_1 = \frac{1}{2} m_1 \mathbf{v_1}^2$ and $K_2 = \frac{1}{2} m_2 \mathbf{v_2}^2$, and the total kinetic energy is

$$K = K_1 + K_2 = \frac{1}{2} m_1 \mathbf{v_1}^2 + \frac{1}{2} m_2 \mathbf{v_2}^2 \qquad \text{(lab frame)}$$

At some point we will need to determine the velocities in the CM frame – call them u_1 and u_2 to differentiate them from the lab frame velocities. This is a simple calculation to do. Remember that the centre of mass frame is just the frame in which we are travelling along with the centre of mass. This means that all we have to do to go from lab frame to CM frame velocities is subtract the velocity of the centre of mass.

$$\mathbf{u_1} = \mathbf{v_1} - \mathbf{v_{CM}}$$
$$\mathbf{u_2} = \mathbf{v_2} - \mathbf{v_{CM}}$$

We can determine $\mathbf{v_{CM}}$ by recalling that in the CM frame, the total momentum is zero. The total momentum may be written either as the momentum of the centre of mass, or as the sum of the momenta of the two individual particles.

$$M\mathbf{v_{CM}} = m_1\mathbf{v_1} + m_2\mathbf{v_2} \quad \Rightarrow \quad \mathbf{v_{CM}} = \frac{m_1\mathbf{v_1} + m_2\mathbf{v_2}}{M}$$

Above, we have defined a momentum associated with the motion of the centre of mass. We can also define the kinetic energy associated with this motion.

$$K_{CM} = \tfrac{1}{2} M\mathbf{v_{CM}}^2$$

Note that because the total momentum of the system has to be conserved, the velocity, momentum, and kinetic energy of the centre of mass are conserved throughout the collision (this is true for any type of collision, including inelastic and reactive ones). Energy 'tied up' in the motion of the centre of mass is therefore not available for the collision. For a reactive collision, this energy does not help overcome any activation barrier that might be present.

We have now defined the total kinetic energy and the kinetic energy associated with the centre of mass. The remaining kinetic energy is the energy associated with relative motion of the two particles. This energy *is* available for the collision, and consequently, it is often called the 'collision energy', or sometimes the 'CM frame kinetic energy'.

$$K_{rel} = \tfrac{1}{2} \mu\mathbf{v_{rel}}^2$$

In the above, m is the reduced mass of the two particles, $\mu = m_1m_2/M$, and $\mathbf{v_{rel}}$ is their relative velocity.

$$\mathbf{v_{rel}} = \mathbf{v_2} - \mathbf{v_1}$$

We have now determined all of the relevant parameters involving the reactants. The product velocites may be determined by requiring that momentum and kinetic energy (or total energy in the case of an inelastic collision) are conserved during the collision. Usually it is most straightforward to do this calculation in the CM frame, though it should work just as well in the lab frame.

$$m_1\mathbf{u_1} + m_2\mathbf{u_2} = m_1\mathbf{u_1}' + m_2\mathbf{u_2}'$$
$$\tfrac{1}{2} m_1\mathbf{u_1}^2 + \tfrac{1}{2} m_2\mathbf{u_2}^2 = \tfrac{1}{2} m_1\mathbf{u_1}'^2 + \tfrac{1}{2} m_2\mathbf{u_2}'^2$$

We therefore have two equations in the two unknowns $\mathbf{u_1}'$ and $\mathbf{u_2}'$ (the final CM frame velocities) Remember that in the CM frame the total momentum is zero both before and after the collision – this will simplify solving these equations considerably, since the first equation becomes simply $m_1\mathbf{u_1}' + m_2\mathbf{u_2}' = 0$.

Once we have determined the CM frame velocities after the collision, we can find the equivalent lab frame velocities simply by adding on the velocity of the CM (which, remember, stays constant throughout the collision).

$$\mathbf{v_1}' = \mathbf{u_1}' + \mathbf{v_{CM}}$$
$$\mathbf{v_2}' = \mathbf{u_2}' + \mathbf{v_{CM}}$$