COLLISION OF REAL MOLECULES : TRAJECTORY CALCULATIONS :

Collisions of real molecules differ significantly from the ideal "hard-sphere" model used in simple kinetic theory. While ideal models treat molecules as point masses or non-interacting spheres that change direction only upon impact, real molecules possess finite size, non-spherical shapes, and internal degrees of freedom (rotation, vibration). Furthermore, they interact through complex, distance-dependent potentials (attraction at long ranges, repulsion at short ranges).

The Trajectory calculations (often called Classical Trajectory Studies or Molecular Dynamics) are the computational methods used to simulate these complex encounters by solving Newton's equations of motion for molecules interacting on a Potential Energy Surface (PES).

The Key Features of Real Molecular Collisions are as follows -

- **Intermolecular Potentials:** Molecules experience van der Waals forces and electrostatic forces (dipoles, quadrupoles).
- **Non-Spherical Geometry:** Diatomic or polyatomic molecules possess shapes that make the collision outcome depend heavily on their orientation.
- **Internal Energy Transfer:** Collisional energy is not just translated; it is transferred between translational, rotational, and vibrational degrees of freedom.
- **Complex Collision Events:** Besides straightforward scattering, molecules can experience "orbiting" collisions, where they become trapped in a potential well and collide multiple times before separating.

The Trajectory Calculation Approach (Classical Dynamics)

The velocities of the reactant molecules relative to the centre of mass of the system. Thus, for a reaction $A + BC \longrightarrow AB + C$, an initial parameter is the relative velocity of A with respect to the centre of mass of BC.

The calculations involve-

- The vibrational energy of the reactant molecules.
- The vibrational phase of the reactant molecules relative to their approach.
- The rotational energy of the reactants.
- The rotational phase of the reactants.
- The impact parameter b.

This, is the closest distance of approach of A to the centre of mass of BC if the two molecules continued with their initial velocities without interacting with each other.

- **Computer Simulations:** The advent of digital computers allowed for more detailed studies, starting with Wall and co-workers, using London-Eyring-Polanyi (LEP) potential-energy surfaces.
- **Reaction Mechanisms:**
    - Calculations showed that for basin less potential-energy surfaces, the system passes directly through the activated state (a **direct** mechanism).
      On basinless potential-energy surfaces (PES), chemical reactions occur via a **direct mechanism** where the system moves smoothly from reactants to products without becoming trapped in a local minimum (intermediate). The trajectory passes directly through the **activated state**—or saddle point—corresponding to the maximum energy along the minimum energy path.
    - When a basin is present in the potential energy surface, the complex performs multiple vibrations before reacting (an **indirect** or complex-mode mechanism).

Trajectory calculations simulate the time-evolution of a collision pair or a collection of molecules. The method involves the following steps :

1. **Definition of Potential Energy Surface (PES):** A mathematical function describing the potential energy of the molecules as a function of their positions and orientations. Common models include Lennard-Jones (for dispersion/repulsion) and Morse potentials (for bond stretching).
2. **Initial Conditions Generation:** A large set of trajectories is initiated with random orientations, impact parameters (distance from the centre), and velocities corresponding to a specific temperature (Maxwell-Boltzmann distribution).
3. **Integration of Equations of Motion:** Newton's equations (F = m.a) are solved numerically using algorithms (e.g., Verlet algorithm) to move the particles over small time steps (e.g., femto seconds).
4. **Data Analysis:** The paths (trajectories) are analyzed to determine the outcome: elastic scattering, inelastic energy transfer, or chemical reaction (e.g., $H_2 + O_2$ reactions).

Errors and Reliability in Classical Methods:

Classical calculations involve errors, such as allowing reactions along paths inconsistent with quantum restrictions and neglecting quantum tunnelling, which is a serious issue for reactions involving hydrogen atoms.
Despite drawbacks, classical calculations offer a reliable guide to general reaction dynamics features, as quantum effects tend to be less significant in three-dimensional collisions.

Applications and Results

Trajectory calculations provide detailed microscopic information that experiments cannot easily measure.

- **Collision Cross-Sections:** Determining the effective area for collision as a function of relative velocity and orientation.
- **Energy Relaxation:** Calculating how fast vibrational or rotational energy is lost after a collision (e.g., water/Ar collision simulations).
- **Reaction Rates:** Calculating the probability of a reaction based on whether a trajectory passes through a reactive transition state.
- **Mean Free Path:** Recording the actual distance travelled between real, non-ideal collisions, which can be 40–50% smaller than calculated by simple theory.

Limitations and Specialized Methods

- **Classical vs. Quantum:** While classical trajectories are excellent for heavy atoms at high temperatures, they fail to account for quantum tunnelling or energy quantization at low temperatures.
- **Quasi-classical Trajectories (QCT):** To fix this, researchers often use QCT, where initial states (vibrational/rotational) are quantized, but the movement is classical.
- **Non-reactive vs. Reactive:** Standard trajectories assume molecules do not break apart. For reactions, "Reactive Force Fields" (like Reax FF) are used to handle bond breaking and forming.

Trajectory calculations are indispensable in chemical physics, plasma modelling, and atmospheric chemistry to bridge the gap between microscopic molecular behaviour and macroscopic thermodynamic properties.