PSAAP3 Project Notes

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Approximate treatment of the 3-body recombination reactions in MCC

Mass action kinetics for the recombination reaction

Consider the important recombination reaction

$$\mathrm{e} + \mathrm{Ar}^+ + \mathrm{e} \rightarrow \mathrm{Ar} + \mathrm{e} \quad (1)$$

This reaction is important in non-equilibrium discharges at pressures of ~1 Torr or higher.

From classical mass action kinetics, the rate of progress of this reaction can be written as

$$r = k_{recomb} n_{Ar^+} n_e^2 \quad (2)$$

The production rate of the neutral argon can be written as

$$\frac{dn_{Ar}}{dt} = r = k_{recomb} n_{Ar^+} n_e^2 \quad (3)$$

Monte-Carlo Collision background for binary collisions

Now let us consider the Monte-Carlo Collisions (MCC) algorithm for a particle method such as Particle-In-Cell (PIC). For any binary collision the MCC method depends on prescription of the collision cross section for each process (p) between any two collision partners a and b.

$$\mathrm{a} + \mathrm{b} \rightarrow \ldots \quad (4)$$

The collision frequency between partners a and b for a process p is given as

$$\nu_{ab}^p = n_b g_{ab} \sigma_{ab}^p(\varepsilon_{ab}) \quad (5)$$

Here, g_{ab} is the relative speed of collision between the partners and $\varepsilon_{ab} = \frac{1}{2} m_{ab} g_{ab}^2$ is the relative kinetic energy. In the MCC algorithm the probability of collision of a particle of species a with all possible collision partners for all possible processes in a time interval Δt is

$$P_a = 1 - \exp(-\nu_a \Delta t) \quad (6)$$

where ν_a is the total collision frequency of a and is given as

$$\nu_a = \sum_b \sum_p \nu_{ab}^p \quad (7)$$

where summation is over all processes (reactions) of a with all other species b and for all processes p for that collision partner combination. Hence,

$$P_a = 1 - \exp\left(-\sum_b \sum_p \nu_{ab}^p \, \Delta t\right) \quad (8)$$

Hence, the important input for MCC is the collision cross section for the process $\sigma_{ab}^p(\varepsilon_{ab})$.

Relation between reaction rate coefficient and the process collision cross section

We can now define a relation between the process cross section σ_{ab}^p and the corresponding reaction rate coefficient in mass action kinetics k_{ab}^p for the binary reaction

$$\mathrm{a} + \mathrm{b} \rightarrow \mathrm{c} + \mathrm{d} \quad (9)$$

The products in the above reaction are not important and are indicated above only to illustrate the approach. The production rate of the product species in the above reaction can be written in the mass action kinetics formulation as

$$\frac{dn_c}{dt} = k_{ab}^p n_a n_b \quad (10)$$

Using kinetic theory the collision frequency of a with b is

$$\nu_{ab}^p = n_b g_{ab} \sigma_{ab}^p \quad (11)$$

and the rate of collisions between of a with b is

$$R_{ab}^p = n_a \nu_{ab}^p = n_a n_b g_{ab} \sigma_{ab}^p \quad (12)$$

Hence, the production rate of the product species, say c is

$$\frac{dn_c}{dt} = n_a n_b g_{ab} \sigma_{ab}^p \quad (13)$$

Equating, the rates from kinetic theory with mass action kinetics

$$k_{ab}^p = g_{ab} \sigma_{ab}^p \text{ or } \sigma_{ab}^p = \frac{k_{ab}^p}{g_{ab}} \quad (14)$$

Treating 3-body recombination reaction in MCC

Now let's consider the recombination reaction (Eq. 1)

Assume that you can suppress the contribution of the 3rd body write as a two-body reaction

$$\mathrm{e} + \mathrm{Ar}^+ \; (+\,\mathrm{e}) \rightarrow \mathrm{Ar} + \mathrm{e} \quad (15)$$

The production rate of Ar in this "two-body" reaction can be written as

$$\frac{dn_{Ar}}{dt} = k'_{recomb} n_{Ar^+} n_e \quad (16)$$

where k'_{recomb} is the rate coefficient of this reaction (Eq. 15).

The corresponding binary collision cross section for the recombination reaction

$$\sigma'_{recomb} = \frac{k'_{recomb}}{g_e} \tag{17}$$

Now equating this production rate (Eq. 16) to the production rate of the original 3-body recombination reaction (Eq. 3) we can write

$$k'_{recomb} = k_{recomb} n_e \tag{18}$$

Hence,

$$\sigma'_{recomb} = \frac{n_e}{g_e} k_{recomb} \tag{19}$$

Since, we know the recombination reaction rate coefficient from general finite-rate mechanisms (put together from different sources), we can formulate the cross section for use in MCC. Note, unlike the traditional formulation where cross section is just a function of the relative collision energy ε_{ab}, here the cross section (we can call it a "pseudo cross section") is also a function of the local state of the gas, i.e. the electron (or any other 3rd body) density. From the mechanism we have the rate coefficient for reaction (Eq. 1) is $k_{recomb} = 9.75 \times 10^{-9} T_e^{-4.5}$ (cm^6/s), where T_e is in units of K.

Practical Note for MCC implementation:

In the MCC algorithm, make sure there are at least 2 electron particles in the collision cell. Once an electron is selected for collision, also randomly pick another electron from the cell and execute the collision using cross section σ'_{recomb}. Post collision destroy one of the electrons and destroy the ion. Then create a neutral Ar with the same velocity as the ion (since the only the heavy carries all the momentum and needs to be conserved). The product electron can be assigned velocity so that its kinetic energy is the left over energy from the collision.