Georgia Tech College of Engineering School of Aerospace Engineering

Collisions – Requirement for Equil.

- Consider pure perfect gas (single species)
- At equilibrium
  - rate of change of number of molecules in class C_i must be zero $\frac{\partial}{\partial t}\left[nf\left(C_i\right)\right]dV_C = 0$
  - $f(C_i)$ = constant
- Two kinds of collisions, those that:
  - **deplete** C_i (C_i molecule collides, goes to new vel.)
  - **replenish** C_i class (another class molecule has collision and ends up in C_i)

$$rate\,depleting\,coll. = rate\,repleneshing\,coll.$$

Collision Rate and Equilibrium-1

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Depleting Collision Rate

- Recall differential (binary) collision rate

$$dz_{AB} = n_A n_B\, f\left(C_i\right) f\left(Z_i\right) g\sigma_{AB}\left(g,\chi\right) d\Omega dV_Z dV_C$$

- Depleting collisions (only one species)

$$dz_{-} = n^2\, f\left(C_i\right) f\left(Z_i\right) g\sigma\left(g,\chi\right) d\Omega dV_Z dV_C$$

- Total rate depleting collisions

$$= n^2\left[\int_{-\infty}^{\infty}\int_{0}^{4\pi} f\left(C_i\right) f\left(Z_i\right) g\sigma\left(g,\chi\right) d\Omega dV_Z\right] dV_C$$

Collision Rate and Equilibrium-2

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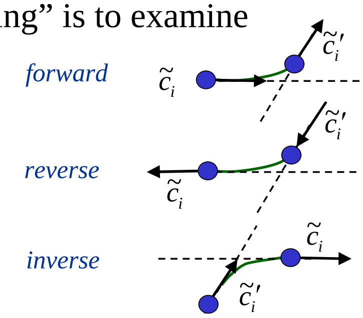
Replenishing Collisions

- Now determine rate at which all non-C_i class molecules become C_i through collisions
- Need to consider all possible collisions between all other classes of molecules except C_i
- Simplest way of "bookkeeping" is to examine the **inverse** collision of our depleting collision
  - $C_i' \rightarrow C_i$ and $Z_i' \rightarrow Z_i$
  - *not a reverse collision* would change the molecule's direction



Replenishing Collision Rate

- Analagous to previous result, replenishing rate is

$$dz_+ = n^2 \; f(C_i')f(Z_i')g'\sigma(g',\chi)d\Omega' dV_{Z'}dV_{C'}$$

- Already showed $g'=g$
- Differentials are essentially dummy variables (what we will intergrate over
  - $d\Omega' \rightarrow d\Omega$
  - $dV_{Z'} \rightarrow dV_Z$
  - $dV_{C'} \rightarrow dV_C$
- Total rate replenishing coll.

$$= n^2 \left[\int_{-\infty}^{\infty} \int_{0}^{4\pi} f(C_i') f(Z_i') g \sigma d\Omega dV_Z \right] dV_C$$

Net Collision Rate

- Combining depleting and replenishing rates (and canceling dV_C term)

$$0=\frac{\partial}{\partial t}\left[nf\left(C_i\right)\right]=n^2\int_{-\infty}^{\infty}\int_{0}^{4\pi}\left[f\left(C_i'\right)f\left(Z_i'\right)-f\left(C_i\right)f\left(Z_i\right)\right]g\sigma d\Omega dV_z$$

replenish   deplete

- Result is special case of **principle of detailed balancing**
  - at equilibrium, each molecular process and its inverse occur at (on average) the same rate
- In our case, when is net rate zero?
  - from above, sufficient condition is

$$\boxed{\left[f\left(C_i'\right)f\left(Z_i'\right)-f\left(C_i\right)f\left(Z_i\right)\right]=0}$$

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also necessary condition