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 $\frac{\partial}{\partial t}\left[nf_o(c_i)\right]dV_c = 0$ ← *equilibrium PDF*
  - $f_o(c_i)$ = 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 collisions = rate replenishing collisions

Depleting Collision Rate

- Recall differential (binary) collision rate

$$d\zeta_{AB} = \frac{n_A n_B}{\delta_{AB}} f(c_i) f(z_i) g\sigma_{AB}(g,\chi) d\Omega dV_z dV_c$$

- Depleting collisions (with only one species)

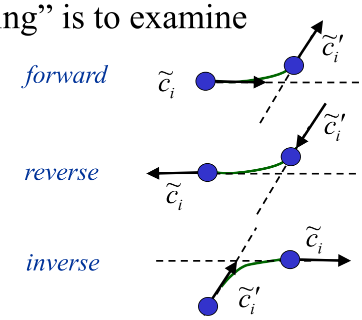
$$d\zeta_- = \frac{n^2}{2} f(c_i) f(z_i) g\sigma(g,\chi) d\Omega dV_z dV_c$$

- Total rate of depleting collisions

$$= \frac{n^2}{2}\left[\int_{-\infty}^{\infty}\int_{0}^{4\pi} f(c_i) f(z_i) g\sigma(g,\chi) d\Omega dV_z\right] dV_c$$

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



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Replenishing Collision Rate

- Analagous to previous result, replenishing rate is

$$d\zeta_+ = \frac{n^2}{2} f(c_i') f(z_i') g' \sigma(g', \chi) d\Omega' dV_{z'} dV_{c'}$$

- 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 collisions

$$= \frac{n^2}{2}\left[\int_{-\infty}^{\infty}\int_{0}^{4\pi} f(c_i') f(z_i') g \sigma d\Omega dV_z\right] dV_c$$

Net Collision Rate

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

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

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 for equilibrium is

$$\left[f_o(c_i')f_o(z_i') - f_o(c_i)f_o(z_i)\right] = 0$$

V&K IX.4: also necessary condition