EGEE 510 $\qquad$ $\bar{c}$ vs $\bar{c}_{rel}$: Clarification $\qquad$ Fall 2006

Here is a more complete (and more correct?) analysis of the relationship between <u>mean speed $\bar{v}_1$</u> vs. <u>mean relative speed $\bar{v}_{12}$</u> (or $\bar{c}$ vs. $\bar{c}_{rel}$) : $\boxed{\bar{c}_{rel} = \sqrt{2}\,\bar{c}}$

* Atkins-8 : "When the molecules are moving in the same direction, $\bar{c}_{rel} = 0$; it is $2\bar{c}$ when they are approaching each other ... A typical mean direction of approach is ... the most characteristic, so the mean speed of approach is $\sqrt{2}\bar{c}$.

90°

(Pythagoras, 45°)

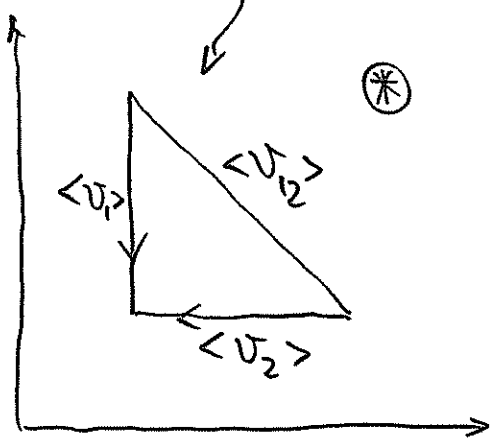
* An alternative, and more detailed, explanation is available in Silbey et al., PChem_4 (2005):

– average collision is at 90° ⊛

$$\langle v_{12} \rangle = \bar{c}_{rel} = \left(\frac{8k_BT}{\pi\mu}\right)^{0.5} \qquad \mu^{-1} \equiv \frac{1}{m_1} + \frac{1}{m_2}$$

(equal by def.)

$$\Rightarrow \langle v_{12} \rangle^2 = \frac{8k_BT}{\pi}\left(\frac{1}{m_1} + \frac{1}{m_2}\right) = \langle v_1 \rangle^2 + \langle v_2 \rangle^2 \qquad (\langle v \rangle \equiv \bar{c})$$



∴ For collision of <u>identical</u> particles

$$\langle v_{11} \rangle^2 = 2 \langle v_1 \rangle^2$$

$$\Rightarrow \langle v_{11} \rangle = \sqrt{2} \langle v \rangle$$

i.e. $\bar{c}_{rel} = \sqrt{2}\,\bar{c}$ (qed)

Closer to that of H_2 than of O_2 !?

Example: $\bar{c}_{rel}(H_2/O_2) = 1824 \frac{m}{s}$ at 298K (Check!) (See Exercise 1)