Sep 25 report

1 Atom-diatom collision

Minimum translational energy required:

$$E_t = G = \frac{1-\sqrt{\alpha}}{(1+\sqrt{\alpha})\cos^2\gamma_1\cos^2\gamma_2}\left(\frac{\sqrt{D-E_v\sin^2\varphi}+\sqrt{E_v}\cos\varphi}{(1-\sqrt{\alpha})\cos\theta}-\sqrt{E_v}\cos\theta\cos\varphi-\sqrt{E_r}\cos\beta\sin\theta\right)^2 \tag{1}$$

Simplified:

$$E_t = G = \frac{1-\sqrt{\alpha}}{(1+\sqrt{\alpha})\cos^2\gamma_1\cos^2\gamma_2}\left(\frac{\sqrt{D^*-E_v\sin^2\varphi}+\sqrt{E_v}\cos\varphi}{(1-\sqrt{\alpha})\cos\theta}-\sqrt{E_v}\cos\theta\cos\varphi\right)^2 \tag{2}$$

Threshold line:

$$\gamma_1 = \gamma_2 = \theta = 0 \tag{3}$$

$$\cos\varphi = \begin{cases} -1 & if E_v \leq \alpha D^* \\ -\sqrt{\dfrac{\alpha(D^*-E_v)}{(1-\alpha)E_v}} & if E_v > \alpha D^* \end{cases} \tag{4}$$

Threshold function:

$$E_t = F(E_v) = \begin{cases} \dfrac{(\sqrt{D^*}-\sqrt{\alpha E_v})^2}{1-\alpha} & if E_v \leq \alpha D^* \\ D^* - E_v & if E_v > \alpha D^* \end{cases} \tag{5}$$

Taylor expansion of G :

1.1 For $E_v < \alpha D$

$$\begin{aligned} G^{(2)}_{\gamma_1,\gamma_2} &= 2F \\ G^{(2)}_{\theta} &= \frac{2D}{1-\alpha}\left(1-\sqrt{\frac{\alpha E_v}{D}}\right)\left(1-(2-\sqrt{\alpha})\sqrt{\frac{E_v}{D}}\right) \\ G^{(2)}_{\varphi} &= \frac{2}{1-\alpha}D\sqrt{\frac{\alpha E_v}{D}}\left(1-\sqrt{\frac{\alpha E_v}{D}}\right)\left(1-\sqrt{\frac{E_v}{\alpha D}}\right) \\ G^{(4)}_{\varphi} &= 6D\alpha(1-\alpha) \end{aligned} \tag{6}$$

1.2 For $E_v > \alpha D$

Follow the similar procedure,

$$\begin{aligned} G^{(2)}_{\gamma_1,\gamma_2} &= 2F \\ G^{(2)}_{\theta} &= \frac{1-\sqrt{\alpha}}{1+\sqrt{\alpha}}\cdot 2F \\ G^{(2)}_{\varphi} &= 2(E_v-\alpha D) \end{aligned} \tag{7}$$

1.3 Monte Carlo Process

We can also get the probability by **Monte Carlo sampling**, which should be more accurate and we won't have any singularity:

procedure CHECK_REACTION(E_t,E_r,E_v)
    Generate phase angles $\gamma_1, \gamma_2, \theta, \varphi$ randomly with suitable $p.d.f$
    Compute effective dissociation energy $D_{ef} = D_{ef}(E_r)$
    Compute threshold of reaction $E_{th} = F(\gamma_1, \gamma_2, \theta, \varphi, D_{ef}, E_v)$
    if $E_t \geq E_{th}$ **then**
        Reaction occurs (i.e. $P = 1$)
    else
        Reaction doesn't occur (i.e. $P = 0$)
    end if
end procedure

2 Derivation for diatom-diatom collision

A different set of geometry angles are used here. These angles are fully decoupled.

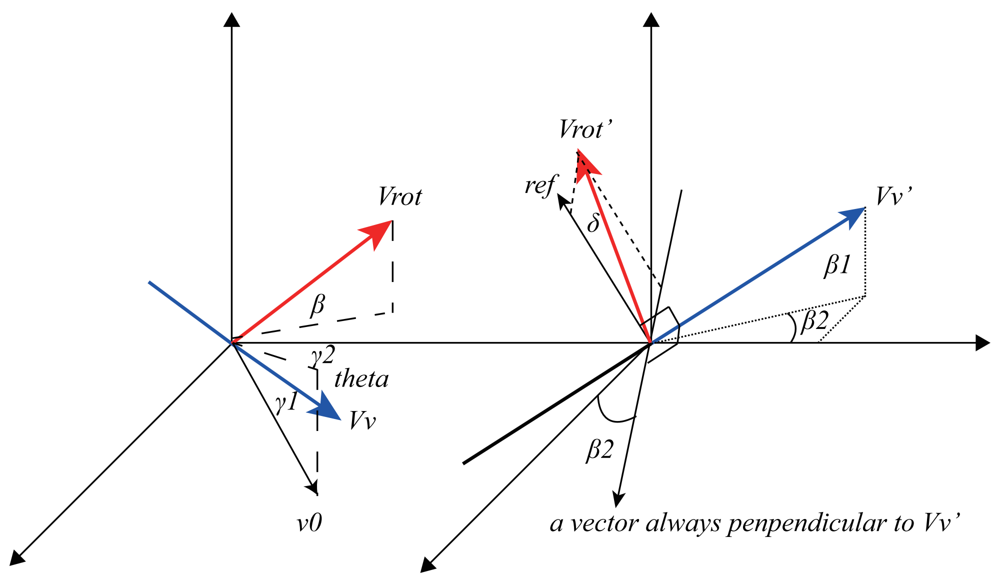

Figure 1: Collision geometry

Assume a collision between diatom(N_1N_2) and diatom(N_3N_4), N_2 and N_3 are the atoms which collide. A body fitted right-hand-side coordinate system is formulated by unit vectors:

$$
\begin{aligned}
\hat{v_x'} &= \begin{bmatrix}\cos\beta_2, & \sin\beta_2, & 0\end{bmatrix}^T \\
\hat{v_v'} &= \begin{bmatrix}-\cos\beta_1\sin\beta_2, & \cos\beta_1\cos\beta_2, & \sin\beta_1\end{bmatrix}^T \\
\hat{v_{ref}'} &= \begin{bmatrix}\cos\beta_2, & \sin\beta_2, & 0\end{bmatrix}^T \times \hat{v_v'} = \begin{bmatrix}\sin\beta_1\sin\beta_2, & -\sin\beta_1\cos\beta_2, & \cos\beta_1\end{bmatrix}
\end{aligned}
\tag{8}
$$

Two rotational operation can transform the coordinates from original coordinates to the new one:

$$
\begin{bmatrix}x'\\y'\\z'\end{bmatrix} = R_x(\beta_1)\cdot R_z(\beta_2)\begin{bmatrix}x\\y\\z\end{bmatrix} = \begin{bmatrix}1 & 0 & 0\\ 0 & \cos\beta_1 & \sin\beta_1\\ 0 & -\sin\beta_1 & \cos\beta_1\end{bmatrix}\cdot\begin{bmatrix}\cos\beta_2 & \sin\beta_2 & 0\\ -\sin\beta_2 & \cos\beta_2 & 0\\ 0 & 0 & 1\end{bmatrix}\begin{bmatrix}x\\y\\z\end{bmatrix} \tag{9}
$$

Thus we can get:

$$
\begin{bmatrix}x\\y\\z\end{bmatrix} = R_z(-\beta_2)\cdot R_x(-\beta_1)\begin{bmatrix}x'\\y'\\z'\end{bmatrix} = \begin{bmatrix}\cos\beta_2 & -\cos\beta_1\sin\beta_2 & \sin\beta_1\sin\beta_2\\ \sin\beta_2 & \cos\beta_1\cos\beta_2 & -\cos\beta_2\sin\beta_1\\ 0 & \sin\beta_1 & \cos\beta_1\end{bmatrix}\begin{bmatrix}x'\\y'\\z'\end{bmatrix} = A\begin{bmatrix}x'\\y'\\z'\end{bmatrix} \tag{10}
$$

Then we have:

$$\begin{aligned}
\hat{v'_v} &= A\left[0, \quad 1, \quad 0\right]^T \\
\hat{v'_{ref}} &= A\left[0, \quad 0, \quad 1\right]^T \\
\hat{v'_r} &= A\left[-\sin\delta, \quad 0, \quad \cos\delta\right]^T = \begin{bmatrix} -\cos\beta_2\sin\delta + \sin\beta_1\sin\beta_2\cos\delta \\ -\sin\beta_2\sin\delta - \sin\beta_1\cos\beta_2\cos\delta \\ \cos\beta_1\cos\delta \end{bmatrix}
\end{aligned} \tag{11}$$

Velocity vector for diatom(N_1N_2)-diatom(N_3N_4) collision:

$$\vec{v_2}^T = \begin{bmatrix} -\cos\beta\cos\theta & \sin\theta & \cos\gamma_1\sin\gamma_2 \\ \cos\beta\sin\theta & \cos\theta & \cos\gamma_1\cos\gamma_2 \\ \sin\beta & 0 & -\sin\gamma_1 \end{bmatrix} \begin{bmatrix} v_r \\ v_v \\ v \end{bmatrix} \tag{12}$$

$$\vec{v_3}^T = \begin{bmatrix} -\cos\beta_2\sin\delta + \sin\beta_1\sin\beta_2\cos\delta & -\cos\beta_1\sin\beta_2 & -\cos\gamma_1\sin\gamma_2 \\ -\sin\beta_2\sin\delta - \sin\beta_1\cos\beta_2\cos\delta & \cos\beta_1\cos\beta_2 & -\cos\gamma_1\cos\gamma_2 \\ \cos\beta_1\cos\delta & \sin\beta_1 & \sin\gamma_1 \end{bmatrix} \begin{bmatrix} v'_r \\ v'_v \\ \frac{m}{M}v \end{bmatrix} \tag{13}$$

Pre-collision component of velocity on $y - axis$:

$$\begin{aligned}
v_{2y} &= v\cos\gamma_1\cos\gamma_2 + v_r\cos\beta\sin\theta + v_v\cos\theta \\
v_{3y} &= -\frac{m}{M}v\cos\gamma_1\cos\gamma_2 - v'_r\left(\sin\beta_1\cos\beta_2\cos\delta + \sin\beta_2\sin\delta\right) + v'_v\cos\beta_1\cos\beta_2
\end{aligned} \tag{14}$$

The minimum velocity v to make post-vibrational energy equal to D:

$$\begin{aligned}
v = \frac{1}{\cos\gamma_1\cos\gamma_2}\Bigg[&\frac{1}{\cos\theta}\left(\frac{\sqrt{D - mv_0^2\sin^2\varphi_0}}{\sqrt{m}} + \frac{m + M\sin^2\theta}{M+m}v_0\cos\varphi_0\right) \\
&- \frac{M}{m+M}\left(v'_r\left(\sin\beta_1\cos\beta_2\cos\delta + \sin\beta_2\sin\delta\right) - v_1\cos\varphi_1\cos\beta_1\cos\beta_2\right) \\
&- \frac{M}{m+M}\left(v_r\cos\beta\sin\theta\right)\Bigg]
\end{aligned} \tag{15}$$

Noted that the following term is the projection of velocity on y axis:

$$\boxed{v'_r\left(\sin\beta_1\cos\beta_2\cos\delta + \sin\beta_2\sin\delta\right) - v_1\cos\varphi_1\cos\beta_1\cos\beta_2} \tag{16}$$

Then we can get the threshold $E_t = \frac{2}{\mu}(mv)^2$:

$$\begin{aligned}
E_t = \frac{2m^2/\mu}{\cos^2\gamma_1\cos^2\gamma_2}\Bigg[&\frac{M}{(m+M)\sqrt{m}}\left(\frac{\sqrt{D - E_v\sin^2\varphi_0} + \sqrt{E_v}\cos\varphi_0}{\cos\theta(M/(m+M))} - \sqrt{E_v}\cos\varphi_0\cos\theta - \sqrt{E_r}\cos\beta\sin\theta\right) \\
&- \frac{\sqrt{M}}{m+M}\left(\sqrt{E'_r}\left(\cos\delta\cos\beta_2\sin\beta_1 + \sin\beta_2\sin\delta\right) - \sqrt{E'_v}\cos\varphi_1\cos\beta_1\cos\beta_2\right)\Bigg]^2
\end{aligned} \tag{17}$$

Again, define $\alpha = (m/(M+m))^2$, then we have:

$$\frac{m}{M+m} = \sqrt{\alpha}; \ \frac{M}{M+m} = 1 - \sqrt{\alpha} \tag{18}$$

$$\frac{m}{M} = \frac{\sqrt{\alpha}}{1-\sqrt{\alpha}}; \ \frac{M}{m} = \frac{1-\sqrt{\alpha}}{\sqrt{\alpha}}; \tag{19}$$

Then:

$$E_t = \frac{1-\sqrt{\alpha}}{\cos^2\gamma_1\cos^2\gamma_2}\left[\frac{\sqrt{D-E_v\sin^2\varphi_0}+\sqrt{E_v}\cos\varphi_0}{\cos\theta(1-\sqrt{\alpha})} - \sqrt{E_v}\cos\varphi_0\cos\theta - \sqrt{E_r}\cos\beta\sin\theta \right.$$
$$\left. - \left(\frac{\sqrt{\alpha}}{1-\sqrt{\alpha}}\right)^{1/2}\left(\sqrt{E_r'}\left(\cos\delta\cos\beta_2\sin\beta_1+\sin\beta_2\sin\delta\right) - \sqrt{E_v'}\cos\varphi_1\cos\beta_1\cos\beta_2\right)\right]^2 \tag{20}$$

Again, we use $D_{eff} = D - E_r + \frac{2E_r^{3/2}}{3(3bD)^{1/2}}$ to replace E_r

$$\boxed{\begin{aligned} E_t = \frac{1-\sqrt{\alpha}}{\cos^2\gamma_1\cos^2\gamma_2}&\left[\frac{\sqrt{D_{eff}-E_v\sin^2\varphi_0}+\sqrt{E_v}\cos\varphi_0}{\cos\theta(1-\sqrt{\alpha})} - \sqrt{E_v}\cos\varphi_0\cos\theta \right. \\ &\left. - \left(\frac{\sqrt{\alpha}}{1-\sqrt{\alpha}}\right)^{1/2}\left(\sqrt{E_r'}\left(\cos\delta\cos\beta_2\sin\beta_1+\sin\beta_2\sin\delta\right) - \sqrt{E_v'}\cos\varphi_1\cos\beta_1\cos\beta_2\right)\right]^2 \end{aligned}} \tag{21}$$

The term $[\cos\delta\cos\beta_2\sin\beta_1+\sin\beta_2\sin\delta]$ can be replaced by $\cos\alpha_1\cos\alpha_2$, in which α_1 and α_2 are azimuth and polar angle for $\vec{v_r'}$

The original one in the paper:

$$\boxed{\begin{aligned} E_t = \frac{1-\sqrt{\alpha}}{\cos^2\gamma_1\cos^2\gamma_2}&\left[\frac{\sqrt{D_{eff}-E_v\sin^2\varphi_0}+\sqrt{E_v}\cos\varphi_0}{\cos\theta(1-\sqrt{\alpha})} - \sqrt{E_v}\cos\varphi_0\cos\theta \right. \\ &\left. - \left(\frac{\sqrt{\alpha}}{1-\sqrt{\alpha}}\right)^{1/2}\left(\sqrt{E_r'}\left(\cos\delta\cos\beta_2\sin\beta_1+\sin\beta_2\sin\delta\right) + \sqrt{E_v'}\cos\varphi_1\cos\beta_1\cos\beta_2\right)\right]^2 \end{aligned}} \tag{22}$$

Optimum configuration and threshold function are same as the ones in original paper.

$$\gamma_1 = \gamma_2 = \theta = \beta_1 = \varphi_1 = 0; \quad \delta = \frac{\pi}{2}; \quad \beta_2 = \pi - \arctan(\sqrt{E_r'/E_v'}) \tag{23}$$

3 DSMC recipe

There are 8 angles to be sampled. The range of sampling are:

$$\begin{aligned} \text{Phase angle}: \varphi_0, \varphi_1 &\in [0, 2\pi] \\ \text{Polar angle}: \gamma_2, \beta_2 &\in [0, 2\pi] \\ \text{Azimuth angle}: \gamma_1, \beta_1 &\in [0, \pi] \\ \text{Reference angle}: \theta, \delta &\in [0, 2\pi] \end{aligned} \tag{24}$$

The region can be reduced by considering terms in Eq. 21.
First, the phase angles only appear in $\sin^2\varphi$ or $\cos\varphi$, thus:

$$\text{Phase angle}: \varphi_0, \varphi_1 \in [0, \pi] \tag{25}$$

Next, polar angle γ_2 appears as $\cos^2\gamma_2$. The reason is that only projection of velocity influences, thus $\gamma_2 \in [0, \pi]$ has no difference compared to $\gamma_2 \in [\pi, 2\pi]$

$$\text{Polar angle}: \gamma_2 \in [0, \pi] \tag{26}$$

Next, if we expand Eq. 21, we will find that θ only appears in $\cos\theta, \cos^2\theta, \cos^3\theta, \cos^4\theta$. Thus In summary:

$$\boxed{\begin{aligned} &\varphi_0, \varphi_1, \gamma_2, \beta_1, \gamma_1 \in [0, \pi] \\ &\beta_2, \theta, \delta \in [0, 2\pi] \end{aligned}} \tag{27}$$

4 Matlab recipe

We can also obtain the same results by Monte-Carlo sampling in Matlab.

for $E_v = E_v(0), ..., E_v(end)$ **do**

  Sample E_t from $f(\frac{E_t}{T}) = \frac{1}{\Gamma[5/2-\bar{\omega}]}\left(\frac{E_t}{T}\right)^{3/2-\bar{\omega}} \exp(-\frac{E_t}{T})$

  Sample E_r, E_r' from $f(\frac{E_r}{T}) = \exp(-\frac{E_r}{T})$

  Sample E_v' from $P(E_v') = \frac{\exp(-E_v'/T_v)}{\sum_j \exp(-E_v'(j)/kT_v)}$

  Sample angles

  Calculate reaction probability $P(v)$

end for

Calculate VHS collision rates $k_{coll}(T)$

Reaction rates $k(T, T_v) = k_{coll}(T)\frac{\sum_j P(j)\exp(-E_v(j)/T_v)}{\sum_j \exp(-E_v(j)/kT_v)}$

This method is much faster than DSMC (2 min v.s. 2 hours). It can also obtain rates for extreme low temperature since vibrational state-specific rates are directly calculated with the method.

Appendix:

1. Volume 1

$$\sum_{i=1}^{n}\left(\frac{x}{R_i}\right)^2 = 1 \tag{28}$$

$$V = \frac{\Pi^{n/2}\prod_i R_i}{\Gamma[n/2+1]} \tag{29}$$

2. Volume 2

$$\sum_{i=1}^{n-1}\left(\frac{x}{R_i}\right)^2 + \left(\frac{x}{R_n}\right)^4 = 1 \tag{30}$$

$$V = \frac{2\pi^{n/2-1}\Gamma[\frac{5}{4}]}{\Gamma\left[\frac{3}{4}+\frac{n}{2}\right]}\prod_i R_i \tag{31}$$