10.34, Numerical Methods Applied to Chemical Engineering
Professor William H. Green
**Lecture #32: Kinetic Monte Carlo and Turbulence Modeling.**

## Thermal Relaxation

$p_i(E,t)$

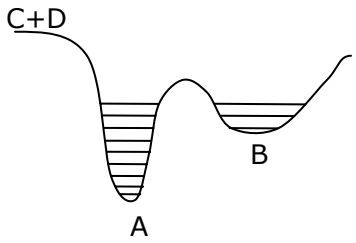



**Figure 1.** Energy diagram.

*Branching Fraction*: $\phi_{\frac{B}{C+D}}(t;T,P,p_A(\varepsilon,t=0)) \Rightarrow \dfrac{\int p_{i=B}(\varepsilon,t)d\varepsilon}{\int p_{i=C+D}(\varepsilon,t)d\varepsilon}$

One approach: $\dfrac{d}{dt}p_i(\varepsilon) = \ldots$ {track entire distribution}

Second approach: Kinetic Monte Carlo (Gillespie) {track individual molecule}

initial conditions: i = A; ε, t

$$\tau = \frac{1}{k_{isom}(E) + k_{disc}(E) + Z_{coll}} \quad t_{new} = t - \tau \ln(rand) = t - \Delta t$$

Pick rand2: if rand2 < $k_{isom}(E)\tau$

$i_{new}$ = B

$E_{new}$ = E

else if rand2 < $(k_{isom}(E)+k_{disc}(E))\tau$

$i_{new}$ = C+D

else $i_{new} = i_{old}$

random ΔE $E_{new} \leftarrow E + \Delta E$

Dilute in A so we can assume A does not interact with other molecules

## Problem Set 11

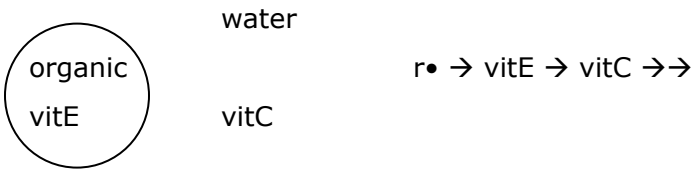
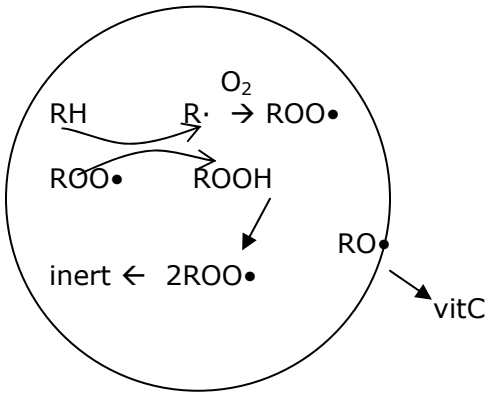



**Figure 2.** A droplet of organic solvent containing Vitamin E.

When a radical forms, Vitamin E picks up the radical. This radical is not as reactive. Some diffuses to the surface where Vitamin C picks up the radical. Enzymes then remove the radical.

Simplified model




$RH + O_2 (+ROO\cdot) \rightarrow ROOH (+ROO\cdot)$

$d[ROO\cdot]/dt = k[\ ]$

$d[ROOH]/dt = k\ldots[ROO\cdot]$

**Figure 3.** A model of the reactions inside the droplet.

Track one droplet using Gillespie

$N_{RH}$ $N_{O_2}$ T → are constant

t $N_{ROO\cdot}$ $N_{ROOH}$

When one has a small droplet, some droplets have no ROO·. How small is small? When will the continuum equation converge with the Gillespie algorithm? Your challenge is to write down the equations.

$$\tau = \frac{1}{k_{RH+O_2 \xrightarrow{(} ROOH}(N_{ROO}) + k_{ROOH \longrightarrow 2ROO}(N_{ROOH}) + k_{2ROO \longrightarrow inert}(N_{ROO}) + k_{ROO \longrightarrow bye-bye}(N_{ROO})}$$

The model: R· reacts with $O_2$ to make ROO·. The ROOH makes 2ROO· over several steps. Reactions are autocatalytic. The oxidation of the organic molecules leads to arteriosclerosis. With small droplets, there may not be many radicals so one needs to keep track of single molecules instead of simply using the mean value equations. This is where Gillespie's Algorithm applies.

A similar phenomenon occurs in emulsion polymerization where there may be only 1 radical in a droplet.

## Equation for Reacting Flow

probability density function (pdf) f($\underline{V}$, $\underline{\Psi}$; $\underline{x}$, t)

$\underline{V}$ = velocity. $\underline{\Psi}$ = all other state variables

$$p(\underline{\Psi})\frac{\partial f}{\partial t} + p(\underline{\Psi})\underline{V}\cdot\vec{\nabla}f + \sum_{\alpha=x,y,z}\left(p(\underline{\Psi})g_\alpha - \frac{\partial < p >}{\partial \alpha}\right)\frac{\partial f}{\partial V_\alpha} + \sum_{n=1}^{N_{solvent}}\frac{\partial}{\partial \Psi_m}\left[p(\underline{\Psi})S_n(\underline{\Psi})f\right] =$$

$$= \sum_{\alpha=x,y,z}\frac{\partial}{\partial V_\alpha}\left(\left\langle \sum_{\beta=x,y,z}\frac{\partial \tau_{\beta x}}{\partial \beta} + \frac{\partial(p - < p >)}{\partial \alpha}\middle| \underline{V},\underline{\Psi}\right\rangle f\right) + \sum_n \frac{\partial}{\partial \Psi_m}\left(\left\langle \sum_\alpha \frac{\partial J_\alpha^n}{\partial \alpha}\middle| \underline{V},\underline{\Psi}\right\rangle f\right)$$

S.B. Pope, Prog. Energy Combust. Science 11(2) 119-192 (1985) [Eq. 3.109]

Terms

$p(\underline{\Psi})\frac{\partial f}{\partial t} \Rightarrow$ Time dependence of probability density

$p(\underline{\Psi})\underline{V}\cdot\vec{\nabla}f \Rightarrow$ Convection

$\sum_{\alpha=x,y,z}\left(p(\underline{\Psi})g_\alpha - \frac{\partial < p >}{\partial \alpha}\right)\frac{\partial f}{\partial V_\alpha} \Rightarrow$ Buoyancy and Pressure-driven flow

$\sum_{n=1}^{N_{solvent}}\frac{\partial}{\partial \Psi_m}\left[p(\underline{\Psi})S_n(\underline{\Psi})f\right] \Rightarrow$ Chemical reaction source term

$$\sum_{\alpha=x,y,z} \frac{\partial}{\partial V_\alpha} \left( \left\langle \sum_{\beta=x,y,z} \frac{\partial \tau_{\beta x}}{\partial \beta} + \frac{\partial (p - < p >)}{\partial \alpha} \middle| \underline{V}, \underline{\Psi} \right\rangle f \right) \Rightarrow$$ Reynold's stress tensor and pressure fluctuation: expectation value for turbulence

$$\sum_n \frac{\partial}{\partial \Psi_m} \left( \left\langle \sum_\alpha \frac{\partial J_\alpha^n}{\partial \alpha} \middle| \underline{V}, \underline{\Psi} \right\rangle f \right) \Rightarrow$$ Diffusive mixing