ChE 512 General Population Balance

Consider a medium in Eulerian space consisting of an assembly of entities.

$\psi(x_1 x_2 x_3, \zeta_1 \zeta_2, \zeta_m)$ - probability density function (pdf) of an ensemble of entities

x_1, x_2, x_3 - spatial coordinates

ζ_i - i-th property of the entity (size, age, surface area, activity, etc.)

i = 1, 2...m

$\psi\, dx_1 dx_2 dx_3 d\zeta_1 d\zeta_2 ... d\zeta_m$ - (mass) fraction of the population contained around the point x_1, x_2, x_3 with properties in the neighborhood of $\zeta_1, \zeta_2, ... \zeta_m$

$$\int_{R_m} \psi\, dx_1 dx_2 dx_3, d\zeta_1 d\zeta_2 ... d\zeta_m = 1$$

ψ is number pdf (density) of the population.

We deal now with m+3 dimensional space.

Define

$$B = \frac{birth\ of\ entities}{(unit\ time)(unit\ geometric\ volume)(unit\ property\ change)}$$

$$D = \frac{death\ of\ entities}{(unit\ time)(unit\ geometric\ volume)(unit\ property\ change)}$$

Pick an arbitrary (volume) element in the (m + 3) D space $\Re(t)$

The conservation law requires

$$\frac{d}{dt} \int_{\Re(t)} \psi\, d\Re = \int_{\Re(t)} (B - D) d\Re$$

Now relate the "volume" element $d\Re$ at present to the volume element dR in some fixed reference configuration.

Recall that (Reynolds Transport Theorem) $d\Re$ = J dR where

J = det F_{iA} Jacobian of the transform

$$d\Re = dx_1 dx_2 dx_3, d\zeta_1 d\zeta_2 ... d\zeta_m$$

$$dR = dX_1 dX_2 dX_3, dZ, dZ_2 ... dZ_m$$

$$J = \frac{\partial(x_1 x_2 x_3, \zeta_1 ... \zeta_m)}{\partial(X_1, X_2, X_3, Z_1 ... Z_m)} = \begin{vmatrix} \frac{\partial x_1}{\partial X_1} \frac{\partial x_2}{\partial X_1} \frac{\partial x_3}{\partial X_1} \frac{\partial \zeta_1}{\partial X_1} \cdots \frac{\partial \zeta_m}{\partial X_1} \\ \frac{\partial x_1}{\partial X_2} \frac{\partial x_2}{\partial X_2} \frac{\partial x_3}{dX_2} \frac{\partial \zeta}{\partial X_2} \cdots \frac{\partial \zeta_m}{\partial X_2} \\ .... \\ .... \\ \frac{\partial x_1}{\partial Z_m} \frac{\partial x_2}{\partial Z_m} \frac{\partial \zeta_1}{\partial Z_m} \cdots \frac{\partial \zeta_m}{\partial Z_m} \end{vmatrix}$$

Thus

$$\frac{d}{dt}\int_R \psi\, J\, dR = \int_R (B-D) J\, dR$$

$$\int_R \left(\frac{\partial \psi}{\partial t} J + \sum_{i=1}^{3} \frac{\partial \psi}{\partial x_i} \frac{dx_i}{dt} J \sum^{m} \frac{\partial \psi}{\partial \zeta_i} \frac{d\zeta_i}{dt} J + \psi \frac{dJ}{dt} \right) dR = \int_R (B-D) J\, dR$$

We know that

$$\frac{dJ}{dt} = J\left[\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} + \sum_{i=1}^{m} \frac{\partial V_i}{\partial \zeta_i} \right] = J\left[\frac{\partial v_1}{\partial x_1} + \frac{\partial v_2}{\partial x_2} + \frac{\partial v_3}{\partial x_3} + \sum_{i=1}^{m} \frac{\partial V_i}{\partial \zeta_i} \right]$$

where

$$v_i = \frac{dx_i}{dt} - velocity\ component$$

$$V_i = \frac{d\zeta_i}{dt} - time\ rate\ of\ change\ of\ property\ \zeta_i$$

$$\int_R J \left\{ \frac{\partial \psi}{\partial t} + \sum_{i=1}^{3} V_i \frac{\partial \psi}{\partial x_i} + \sum_{i=1}^{m} V_i \frac{\partial \psi}{\partial \zeta_i} + \psi \sum_{i=1}^{3} \frac{\partial v_i}{\partial x_i} + \psi \sum_{i=1}^{m} \frac{\partial V_i}{\partial \zeta_i} - B + D \right\} dR = 0$$

$$\int_{\Re(t)} \left\{ \frac{\partial \psi}{\partial t} + \nabla(\vec{v}\,\psi) + \sum_{i=1}^{m} \frac{\partial}{\partial \zeta_i}(V_i \psi) - B + D \right\} d\Re = 0$$

Since choice of $\Re$ is arbitrary

$$\frac{\partial \psi}{\partial t} + \sum_{i=1}^{3} \frac{\partial}{\partial x_i}(\psi\, v_i) + \sum_{i=1}^{m} \frac{\partial}{\partial \zeta_i}(\psi\, V_i) - B + D = 0 \qquad (1)$$

is the general microscopic population balance.

Let us now introduce the volume averaged probability density

$$\overline{\psi} \equiv \frac{1}{V}\int_v \psi dV \ where\ dV = dx_1 dx_2 dx_3$$

Rewrite (1) and assume ψ independent of position in volume V except at the surface across which we have the inlet flow, S_{in} and the surface across which outlet flow occurs, S_{out}.

$$\frac{\partial \psi}{\partial t} + \nabla \cdot (\vec{v}\,\psi) + \sum_{i=1}^{m} \frac{\partial}{\partial \zeta_i}(\psi V_i) + D - B = 0 \qquad (1a)$$

$$\int_V \left[\frac{\partial \psi}{\partial t} + \nabla \cdot (\vec{v}\,\psi) \right] dV + \int_V \sum_{i=1}^{m} \frac{\partial}{\partial \zeta_i}(\psi V_i) dV + \int_V (D-B) dV = 0$$

$$\int_V \nabla \cdot (\vec{v}\,\psi) dV = \int_S \psi V_n dS = \sum_{i=1}^{T} v_{ext_i} \psi_{ext_i} S_i + \psi \frac{dV}{dt}$$

$$V \frac{\partial \overline{\psi}}{\partial t} - Q_{in}\psi_{in} + Q_{out}\psi_{out} + \overline{\psi}\frac{dV}{dt} + V \sum_{i=1}^{m} \frac{\partial}{\partial \zeta_i}(V_i \overline{\psi}) + V(\overline{D} - \overline{B}) = 0$$

After appropriate mathematical manipulations one gets the following macroscopic population balance

$$\frac{1}{V}\frac{\partial}{\partial t}(\overline{\psi}V) + \sum_{i=1}^{m}\frac{\partial}{\partial \zeta_i}(\overline{\psi}V_i) + \overline{D} - \overline{B} = \frac{1}{V}\left(Q_{in}\overline{\psi}_{in} - Q_{out}\overline{\psi}_{out}\right) \qquad (2)$$

where

$$\overline{V}_i = \frac{d\zeta_i}{dt}$$

At steady state

$$\sum_{i=1}^{m}\frac{\partial}{\partial \zeta_i}(\overline{\psi}\,\overline{V}_i) + \overline{D} - \overline{B} = \frac{1}{V}\left(Q_{in}\overline{\psi}_{in} - Q_{out}\overline{\psi}_{out}\right) \qquad (3)$$

Examples:

1. Take

$$\zeta_1 = \alpha - age\ of\ fluid\ element$$

$$m = 1$$

$$steady\ state \quad Q_{in} = Q_{out}$$

$$\frac{d}{d\alpha}\left(\overline{\psi}\frac{d\alpha}{dt}\right) + \overline{D} - \overline{B} = \frac{1}{V}\left(Q_{in}\delta(\alpha) - Q_{out}\overline{\psi}_{out}\right)$$

Let: $\overline{\psi}(\alpha) = I(\alpha) \qquad \overline{\psi}_{out} = E(\alpha)$

$$\frac{dI}{d\alpha} = \frac{1}{\bar{t}}\left[\delta(\alpha) - E(\alpha)\right]$$

$$\alpha \Rightarrow \infty \qquad I(\alpha) \to 0$$

$$\int_{o}^{I(\alpha)} dI = \frac{1}{\bar{t}}\int_{\infty}^{\infty}\left[\delta(\alpha) - E(\alpha)\right]d\alpha$$

$$I(\alpha) = +\frac{1}{\bar{t}}\left[\int_{\alpha}^{\infty}E(\alpha)d\alpha - \int_{\alpha}^{\infty}\delta(\alpha)d\alpha\right] = \frac{1}{\bar{t}}\left[1 - F(\alpha)\right]$$

2. Take $\zeta_1 = \lambda$ life expectation of fluid element

m =1

Steady state $Q_{in} = Q_{out}$

$$\frac{d}{d\lambda}\left(\overline{\psi}\frac{d\lambda}{dt}\right) + \overline{D} - \overline{B} = \frac{Q}{V}\left[\overline{\psi}_{in} - \overline{\psi}_{out}\right]$$

λ = -t + c

$$\frac{d\lambda}{dt} = -1$$

$$-\frac{d\overline{\psi}}{d\lambda} = \frac{1}{\bar{t}}\left[\overline{\psi}_{in}(\lambda) - \delta(\lambda)\right]$$

$$\frac{d\overline{\psi}}{d\lambda} = \frac{1}{\bar{t}}\left[\delta(\lambda) - \overline{\psi}_{in}(\lambda)\right]$$

Let: $\overline{\psi}_{in}(\lambda) = E(\lambda)$

Then it follows from the relationship of I and E curves that

$$\overline{\psi} = I(\lambda)$$

3. Segregated Flow Model

$$m = 1 \quad , \quad \zeta_1 = \alpha \quad , \quad \overline{\psi} = IC \quad , \quad \overline{\psi}_{out} = EC$$

$$\frac{d}{d\alpha}\left(IC\frac{d\alpha}{dt}\right) + r(C)I = -\frac{Q}{V}EC$$

$$C\frac{dI}{d\alpha} + I\frac{dC}{d\alpha} + r(C)I = -\frac{Q}{V}EC$$

But since $\frac{dI}{d\alpha} = -\frac{Q}{V}E$ the first term on the left hand side and the term on the right hand side cancel out. The remaining terms yield the batch kinetics.

$$\frac{dC}{d\alpha} = -r(C)$$

$$\alpha = 0 \quad C = C_o$$

The exit concentration is given by

$$\overline{C} = \int_o^\infty C(\alpha)E(\alpha)d\alpha$$

4. Maximum Mixedness Model

$$m = 1 \quad , \quad \zeta_1 = \lambda \quad , \quad \overline{\psi} = IC \quad , \quad \overline{\psi}_{in} = EC_o$$

$$\frac{d}{d\lambda}\left(IC\frac{d\lambda}{dt}\right) + r(C)I = \frac{Q}{V}EC_o$$

$$I\frac{dC}{d\lambda} + \frac{Q}{V}E(C_o - C) - r(C)I = 0$$

$$\frac{dC}{d\lambda} = r(C) - \frac{1}{\bar{t}}\frac{E}{I}(C_o - C)$$

$$\lambda \to \infty \quad \frac{dC}{d\lambda} = 0$$

5. Unsteady State RTD (Evolution of RTD)

Both I and E are now two place functions: I (α, t) a function of fluid element age, α, and actual time, t, and E (α, t), a function of fluid residence time, α, and actual time, t. Hence, m = 1, $\zeta_1 = \alpha$. Then from equation (2):

$$\frac{1}{V}\frac{\partial}{\partial t}(IV) + \frac{\partial}{\partial \alpha}(I) = \left[Q_{in}\delta(\alpha) - Q_{out}E(\alpha, t)\right]$$

Let V = const, $Q_{in} = Q_{out}$

Yet if state of the system is changed by some mechanism, the equation below describes the evolution of I (α, t)

$$\frac{\partial I}{\partial t}+\frac{\partial I}{\partial \alpha}=\frac{1}{\bar{t}}\left[\delta(\alpha)-E(\alpha,t)\right]$$

$$t=0 \quad I=I_o(\alpha) \quad E=E_o(\alpha)$$

Since in case of a CSTR, I = E, we can also write for a CSTR:

$$\frac{\partial E}{\partial t}+\frac{\partial E}{\partial \alpha}=\frac{1}{\bar{t}}\left[\delta(\alpha)-E\right] \tag{4}$$

By taking the Laplace Transform with respect to age α of equation (4), so that

$\bar{E}(s,t)=L\{E(\alpha,t)\}=\int_o^\infty E(\alpha,t)e^{-s\alpha}d\alpha$, we get

$$\frac{d\bar{E}}{dt}+s\bar{E}=\frac{1}{\bar{t}}\left[1-\bar{E}\right]$$

$$\frac{d\bar{E}}{dt}+(s+\frac{1}{\bar{t}})\bar{E}=\frac{1}{\bar{t}}$$

$$\frac{d}{dt}\left(e^{(s+\frac{1}{\bar{t}})t}\bar{E}\right)=\frac{1}{\bar{t}}e^{(s+\frac{1}{\bar{t}})t}$$

$$e^{(s+\frac{1}{\bar{t}})t}\bar{E}-\bar{E}_o=\frac{1}{\bar{t}(s+\frac{1}{\bar{t}})}\left(e^{\left(s+\frac{1}{\bar{t}}\right)}t-1\right)$$

$$\bar{E}(t,s)=\bar{E}_o(s)e^{-(s+\frac{1}{\bar{t}})t}+\frac{1}{\bar{t}(s+\frac{1}{\bar{t}})}\left[1-e^{-(s+\frac{1}{\bar{t}})t}\right]$$

Upon inversion into the (α,t) domain we get

$$E(t,\alpha)=e^{-t/\bar{t}}E_o(\alpha-t)+\frac{1}{\bar{t}}e^{-\alpha/\bar{t}}\left[H(\alpha)-H(\alpha-t)\right]$$

$$E_o(t,\alpha)=0 \quad t>\alpha$$

$$\lim_{t\to\infty}E(t,\alpha)=\frac{1}{\bar{t}}e^{-\alpha/t}$$

We could have instead used the Laplace transform in time on eq (4) with the following result:

$$s\bar{E}-E_o+\frac{d\bar{E}}{d\alpha}=\frac{1}{\bar{t}}\left[\frac{\delta(\alpha)}{s}-\bar{E}\right]$$

$$\frac{d\bar{E}}{d\alpha}+(s+\frac{1}{\bar{t}})\bar{E}=\frac{1}{\bar{t}s}\delta(\alpha)+E_o(\alpha)$$

$$\frac{d}{d\alpha}\left(e^{+(s+\frac{1}{\bar{t}})\alpha}\bar{E}\right)=\frac{1}{\bar{t}s}\delta(\alpha)e^{+(s+\frac{1}{\bar{t}})\alpha}+E_o(\alpha)e^{+(s+\frac{1}{\bar{t}})\alpha}$$

$$e^{+(s+\frac{1}{\bar{t}})\alpha}\bar{E}=\frac{1}{\bar{t}s}H(\alpha)+\int_o^\alpha E_o(\alpha')e^{+(s+\frac{1}{\bar{t}})\alpha'}d\alpha'$$

$$\bar{E}(s,\alpha)=\frac{1}{\bar{t}s}e^{-(s+\frac{1}{\bar{t}})\alpha}H(\alpha)+\int_o^\alpha E_o(\alpha')e^{-(s+\frac{1}{\bar{t}})(\alpha-\alpha')}d\alpha'$$

Inversion into the (t,α) domain produces:

$$E(t,\alpha) = \frac{1}{\bar{t}} e^{-\frac{\alpha}{\bar{t}}} H(t-\alpha)H(\alpha) + \int_o^{\alpha} E_o(\alpha')e^{-\frac{1}{\bar{t}}(\alpha-\alpha')}\delta(t-(\alpha-\alpha'))d\alpha'$$

$$= \frac{1}{\bar{t}} e^{-\frac{\alpha}{\bar{t}}} H(t-\alpha)H(\alpha) + E_o(\alpha-t)e^{-t/\bar{t}}$$

$$= e^{-t/\bar{t}} E_o(\alpha-t) + \frac{1}{\bar{t}} e^{-\frac{\alpha}{\bar{t}}}\left[H(\alpha) - H(\alpha-t)\right]$$

Of course the same final result is obtained.