# Polymer Moment Equations for Distributed Parameter Systems

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For conventional material balance problems in chemical engineering, either a mole or mass balance for the system is sufficient to characterize the concentration of the various components of interest. However, for polymerization systems, molecular weight determination of the product is generally necessary in addition to predicting the polymer concentration in order to assess the utility of a particular reactor scheme. For batch and continuous stirred-tank reactors, methods have been applied which allow satisfactory evaluation of performance; but for tubular reactors the method predominately used is to predict instantaneous molecular weights at any point in the tube and weight the contribution to the overall molecular weight according to the conversion that occurs at that point (Cintron-Cordero et al., 1968; Wallis, 1973). By neglecting diffusion and summing the weighted contributions over the reactor length for each radial position, the flow average or cross-sectional average molecular weight parameters at any distance down the tube are determined. Alternatively, a method has been developed based on the continuous blending approach which accounts for diffusion and predicts conversion as well as number and weight average chain lengths (Kwon and Evans, 1973).

This paper will show that by extending the derivation of mass and mole balances to other concentration systems, moment equations are derived which allow exact prediction of molecular weight characteristics in homopolymer systems in which both convection and diffusion are important. The derivation is general so that as many moments as are desirable can be calculated, but no more calculations are required than the previous methods to get the equivalent amount of information. This work follows the general format of Bird, Stewart, and Lightfoot (1960).

## DERIVATION OF MATERIAL BALANCE EQUATIONS

It can be shown that for a concentration $c_{ij}$ of type $i$ and species $j$ that a material balance gives

$$\frac{\partial c_{ij}}{\partial t} + \nabla \bullet \mathbf{N}_{ij} = R_{ij} \tag{1}$$

where $\mathbf{N}_{ij}$ is a flux of type $i$, species $j$ with respect to stationary coordinates while $R_{ij}$ is the reaction rate. Now, $\mathbf{v}_i$ is defined by

$$\mathbf{v}_i = \sum_{j=1}^{N} \frac{c_{ij}\mathbf{v}_j}{c_i} \tag{2}$$

The flux of species $j$ with respect to velocity $\mathbf{v}_i$ for a binary system is

$$\mathbf{J}^{*}_{ij} = c_{ij}(\mathbf{v}_j - \mathbf{v}_i) = - c_i D_{AB} \nabla x_{ij} \tag{3}$$

while that with respect to $\mathbf{v}_1$ is

$$\mathbf{J}_{ij} = c_{ij}(\mathbf{v}_j - \mathbf{v}_1) \tag{4}$$

It can be shown that

$$\mathbf{J}_{ij} = \frac{c_i(c_1 - c_{1j})}{c_1(c_i - c_{ij})} \mathbf{J}^{*}_{ij} \tag{5}$$

The flux with respect to stationary coordinates is

$$\mathbf{N}_{ij} = c_{ij}\mathbf{v}_j = c_{ij}\mathbf{v}_i - c_i D_{AB} \nabla x_{ij} \tag{6}$$

again for binary diffusion where

$$x_{ij} = \frac{c_{ij}}{c_i} \tag{7}$$

But it is desirable to reference all stationary coordinate fluxes relative to the same velocity $\mathbf{v}_1$. From (3) and (5)

$$\mathbf{J}_{ij} = \frac{- c_i(c_1 - c_{1j}) c_i}{c_1(c_i - c_{ij})} D_{AB} \nabla x_{ij} \tag{8}$$

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Therefore, the flux $\mathbf{N}_{ij}$ is given as

$$\mathbf{N}_{ij} = c_{ij}\mathbf{v}_j = c_{ij}\mathbf{v}_1 + \mathbf{J}_{ij} = c_{ij}\mathbf{v}_1 - \frac{c_i^2(c_1 - c_{1j})}{c_1(c_i - c_{ij})} D_{AB}\nabla x_{ij} \qquad (9)$$

Utilizing (9) and (1), then

$$\frac{\partial c_{ij}}{\partial t} + \nabla \bullet c_{ij}\mathbf{v}_1 = \nabla \bullet \frac{(c_1 - c_{1j})c_i^2}{(c_i - c_{ij})c_1} D_{AB}\nabla x_{ij} + R_{ij} \qquad (10)$$

Generally, $i = 1$ is chosen as the mass system since for constant density $\nabla \bullet \mathbf{v} = 0$ so

$$\frac{\partial c_{ij}}{\partial t} + \mathbf{v}_1 \bullet \nabla c_{ij} = \nabla \bullet \frac{(c_1 - c_{1j})c_i^2}{(c_i - c_{ij})c_1} D_{AB}\nabla x_{ij} + R_{ij} \qquad (11)$$

For constant density and molecular weight, this equation further simplifies to either a simple mass balance when $i = 1$ or a simple mole balance when $i = 0$.

## MOMENT EQUATIONS

If the moment approach of polymer characterization is examined, it is obvious that the zeroth moment is simply a mole balance on polymer while the first moment multiplied by the monomer molecular weight is a mass balance. Now, if $c_{0j}$ is defined as the molar concentration while $c_{1j}$ is the mass value, then the relations between the concentrations and the moments can be generalized to

$$c_{ij} = M^i \nu_{ij} \qquad (12)$$

While the definition of higher concentrations is not obvious, (12) also holds for the higher moments. For a system composed of only a single polymer type, $j = A$ for the monomer and $j = B$ for polymer. For monomer all the moments are equal so that a simple mass balance on monomer is sufficient.

$$\frac{\partial c_{1A}}{\partial t} + \nabla \bullet \mathbf{v}_1\, c_{1A} = \nabla \bullet D_{AB}\, c_1 \nabla x_{1A} + R_{1A} \qquad 13)$$

This relation follows from (10).

Now for polymer the first four moment equations derived from using (12) in (10) are

$$\frac{\partial \nu_{0B}}{\partial t} + \nabla \bullet \mathbf{v}_1\, \nu_{0B} = \nabla \bullet \frac{\nu_0^2}{\nu_1} D_{AB}\nabla x_{0B} + r_{0B} \qquad (14)$$

since

$$\nu_1 - \nu_{1B} = \nu_{1A} = \nu_{0A} = \nu_0 - \nu_{0B} \qquad (15)$$

Similarly

$$\frac{\partial \nu_{1B}}{\partial t} + \nabla \bullet \mathbf{v}_1\, \nu_{1B} = \nabla \bullet \nu_1 D_{AB}\nabla x_{1B} + r_{1B} \qquad (16)$$

$$\frac{\partial \nu_{2B}}{\partial t} + \nabla \bullet \mathbf{v}_1\, \nu_{2B} = \nabla \bullet \frac{\nu_2^2}{\nu_1} D_{AB}\nabla x_{2B} + r_{2B} \qquad (17)$$

$$\frac{\partial \nu_{3B}}{\partial t} + \nabla \bullet \mathbf{v}_1\, \nu_{3B} = \nabla \bullet \frac{\nu_3^2}{\nu_1} D_{AB}\nabla x_{3B} + r_{3B} \qquad (18)$$

Higher moments can be readily derived from (10). Now by ratioing the moments, the various weighted molecular weights are obtained,

$$M_n = (\nu_{1B}/\nu_{0B})M \qquad (19)$$

$$M_w = (\nu_{2B}/\nu_{1B})M \qquad (20)$$

$$M_z = (\nu_{3B}/\nu_{2B})M \qquad (21)$$

## DISCUSSION

The reaction rate terms in the moment expressions can be derived either empirically or by a more mechanistic approach. In either event, they will usually be nonlinear in concentration; for nonisothermal cases, they will also be nonlinear in temperature. These nonlinearities coupled with the nonlinear features of the diffusion terms require that the moments be evaluated by numerical methods for partial differential equations. Since numerical techniques are tedious to apply to complex expressions, the importance of diffusion should be assessed to determine whether an approximation would suffice.

If active polymer radicals with extremely short lives are considered, use of the approach outlined for radicals would be futile since diffusion and convection effects are inconsequential to their moment values. In addition, for numerical solutions, these species would generally be present in such low concentrations that errors would be significant. Therefore, the moments for such active polymer radicals must be found from the pseudo steady state assumption, while the values for dead polymer chains can be determined by the method presented.

If a tubular reactor is modeled in which the operating conditions are suddenly changed, the polymer moment profiles could be followed to assess the molecular weight characteristics of the output from the device. While the material near the centerline of the reactor will doubtless be swept out of the system rapidly, the polymer at the wall would remain indefinitely if diffusion did not occur. Similarly, if a stagnant layer exists, it would not be displaced without diffusion of polymer. If the existence of such stagnant material could jeopardize product quality or reactor operation due to adverse side reactions resulting from long residence times such as degradation, then the diffusion mechanism becomes a vital part of the model. Furthermore, the size of stagnant regions could change as polymer diffuses from these areas with a resultant change in the velocity profile (and residence time distribution) as well as the pressure drop.

## CONCLUSIONS

Moment equations have been derived which may be applied to distributed parameter systems to predict both the effects of diffusion and convection on polymer conversion and molecular weight distribution. These relations are derived from a conventional material balance approach by extending the method to concentrations not generally considered in typical engineering problems and then utilizing the relationships between these expressions and the polymer moments. Once appropriate simplifications for the system under study are incorporated into these moment equations, mathematical solutions (generally numerical) may be obtained to provide a detailed picture of the process.

## NOTATION

$c_i$ = total concentration of material in system $i$,

$$c_i = \sum_{J=1}^{n} c_{ij}$$

$c_{ij}$ = concentration of type $i$ for species $j$
$D_{AB}$ = diffusion coefficient of material $A$ in material $B$
$\mathbf{J}_{ij}$ = flux of species $j$ with respect to $\mathbf{v}_1$ for system $i$
$\mathbf{J}^{\circ}_{ij}$ = flux of species $j$ with respect to $\mathbf{v}_i$ for system $i$
$M$ = monomer molecular weight
$M_n$ = number average molecular weight
$M_w$ = weight average molecular weight
$M_z$ = $z$ average molecular weight
$\mathbf{N}_{ij}$ = flux vector of species $j$ with respect to stationary

coordinates for system $i$

$r_{ij}$ = reaction rate of moment $i$ for species $j$

$R_{ij}$ = reaction rate of species $j$ in concentration system $i$

$t$ = time

$\mathbf{v}_i$ = average velocity of material in system $i$

$\mathbf{v}_j$ = velocity of species $j$ with respect to stationary coordinates

$x_{ij}$ = fraction of species $j$ with respect to system $i$

**Greek Letters**

$\nu_{ij}$ = moment $i$ of species $j$

$\nu_i$ = total moment of system $i = \sum_{j=1}^{n} \nu_{ij}$

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