General Population Balance Model of Dissolution of Polydisperse Particles

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Dissolution of solid particles in liquids is commonly encountered in the chemical process industry. Solids possessing wide distributions of particle sizes appear in most dissolution processes (e.g., crystallization: Randolph and Larson, 1971) and shrinkage processes (e.g., combustion: Dickinson and Marshall, 1986). Models formulated in terms of the average particle size can lead to objectionably large errors in predicting the behavior of a realistic dissolution process (LeBlanc and Fogler, 1987). Errors of this origin can be eliminated through the use of the population balance method. This fact has been demonstrated by LeBlanc and Fogler (1987) for the special cases of rate-limiting regimes, namely, the regimes of mass-transfer control and surface-reaction control. No general analyses of the transition regime, however, have been reported until now, for the situations with either the surface-reaction control or the bulk-liquid reaction control as the kinetic asymptote. Even the simpler rate-limiting regime of bulk-liquid reaction control for a polydisperse system has apparently remained unanalysed so far. Recent work on the concept of kinetic invariance (Bhaskarwar, 1987) has led to some useful approximate analytical solutions describing the dissolution behaviour of small particles. The purpose of the present paper is to combine these two approaches in order to generate a population balance theory of a dissolution process which is valid not only for the rate-limiting regimes of mass-transfer control and bulk-liquid reaction control, but also for the general transition regime. In essence, it is a generalization of an analysis which, while being analogous to that of LeBlanc and Fogler (1987), describes the dissolution accompanied by a bulk-liquid reaction.

To cope with the variety of influences of the different methods of particulate production on the size distribution, a number of distribution models and parameters have been analysed allowing also for the distribution shift with reaction.

Model Development for the Transition Regime

A differential population balance on a diameter increment from D to $D + \Delta D$ of the dissolving solid particles in a batch slurry reactor may be written as:

$$R(D)\, F(D,t)|_{D} - R(D)\, F(D,t)|_{D+\Delta D} = \frac{\partial}{\partial t}[F(D,t)\Delta D] \quad (1)$$

where

$$R(D) = \frac{dD}{dt} = \text{particle growth rate, and}$$

$$F(D,t) = \text{number distribution function.}$$

The first two terms of Eq. 1 represent the number of particles growing into and out of D to $D + \Delta D$, respectively. The right hand side of the equation describes the rate of accumulation of particles in the size range D to $D + \Delta D$. The limiting form of Eq. 1 is the following expression for the population balance:

$$-\frac{\partial}{\partial D}[R(D)\, F(D,t)] = \frac{\partial}{\partial t}[F(D,t)] \quad (2)$$

From the kinetic invariant model of the dissolution process (Bhaskarwar, 1987), we have

$$E(1 - \omega^{2/3}) + B(1 - \omega) = \theta \quad (3)$$

where

$$E = \frac{\alpha}{1+\alpha}; \qquad B = 1 - E; \qquad \alpha = \frac{D_g^2 K_r Z_o \rho}{8 M \mathcal{D} C_o}$$

and

$$\theta = \frac{t}{\tau}$$

It may be noted here that the rate-limiting expression resulting from Eq. 3 corresponds to the shrinking-particle expression given by Levenspiel (1972) under the conditions of diffusion control. For the special case of kinetic control, however, the expression deduced from Eq. 3 differs from that of Levenspiel (1972), owing to the inevitable differences in the governing equations which appropriately account for the bulk and surface reactions, respectively. The kinetic invariant function, ω, is related to the particle diameter by

$$D = D_g \omega^{1/3} \tag{4}$$

Substitution of ω from Eq. 4 into Eq. 3, and subsequent differentiation of the resulting equation with respect to t, yields the fol-

Table 1. Approximate Analytical Solutions of the Population Balance Model

Distribution $f(\bar{D}, 0)$	Transition Regime $\Phi(\bar{D}, \theta)$	Diffusion Control $\Phi(\bar{D},\theta)$ $(B = 0, E = 1)$	Kinetic Control $(B = 1, E = 0)$
Normal: $\frac{1}{\sigma_g\sqrt{2\pi}}\exp\left(-\frac{D_g^2(\bar{D}-1)}{2\sigma_g^2}\right)$	$\bar{D}(2E+3B\bar{D})\cdot\frac{D_g}{\sigma_g\sqrt{2\pi}}\frac{\exp\left(-\frac{D_g^2(\bar{D}'-1)^2}{2\sigma_g^2}\right)}{\bar{D}'(2E+3B\bar{D}')}$	$\frac{\bar{D}}{(\theta+\bar{D}^2)^{1/2}}\cdot\frac{D_g}{\sigma_g\sqrt{2\pi}}\exp\left[-\frac{D_g^2}{2\sigma_g^2}[(\theta+\bar{D}^2)^{1/2}-1]^2\right]$	$\frac{\bar{D}^2}{(\theta+\bar{D}^3)^{2/3}}\frac{D_g}{\sigma_g\sqrt{2\pi}}\exp\left[-\frac{D_g^2[(\theta+\bar{D}^3)^{1/3}-1]^2}{2\sigma_g^2}\right]$
Lognormal: $\frac{1}{D_g\bar{D}\ln\sigma_g\sqrt{2\pi}}\exp\left(-\frac{[\ln(\bar{D})]^2}{2(\ln\sigma_g)^2}\right)$	$A\cdot\bar{D}\cdot(2E+3B\bar{D})\cdot\exp\frac{(-B'[\ln\bar{D}']^2)}{\bar{D}'^2(2E+3B\bar{D}')}$	$\frac{A\bar{D}}{(\theta+\bar{D}^2)}\cdot\exp(-B'[\ln(\theta+\bar{D}^2)^{1/2}]^2)$	$\frac{A\bar{D}^2}{(\theta+\bar{D}^3)}\cdot\exp(-B'\cdot[\ln(\theta+\bar{D}^3)^{1/3}]^2)$
Rosin-Rammler: $\frac{n}{D_g}\bar{D}^{n-1}\cdot\exp(-\bar{D}^n)$	$\frac{\bar{D}(2E+3B\bar{D})n\bar{D}'^{n-2}}{(2E+3B\bar{D}')}\exp(-\bar{D}'^n)$	$\bar{D}\cdot n\cdot(\theta+\bar{D}^2)^{n-2/2}\cdot\exp(-[\theta+\bar{D}^2]^{n/2})$	$\bar{D}^2 n(\theta+\bar{D}^3)^{n-3/3}\cdot\exp(-[\theta+\bar{D}^3]^{n/3})$
Gamma: $(\lambda' = \lambda D_g) > 0$; $r = 1, 2, \ldots$; $\frac{\lambda'}{D_g(r-1)!}\cdot(\lambda'\bar{D})^{r-1}e^{-\lambda'D}$	$\frac{\bar{D}(2E+3B\bar{D})}{\bar{D}'(2E+3B\bar{D}')}\frac{\lambda'}{(r-1)!}(\lambda'\bar{D}')^{r-1}\exp(-\lambda'\bar{D}')$	$\frac{\bar{D}(\lambda')^r}{(r-1)!}(\theta+\bar{D}^2)^{r-2/2}\exp(-\lambda'[\theta+\bar{D}^2]^{1/2})$	$\frac{\bar{D}^2(\lambda')^r}{(r-1)!}(\theta+\bar{D}^3)^{r-3/3}$
Cauchy: $-\infty < \alpha < \infty$; $\beta > 0$; $\beta' = \beta/D_g$; $\alpha' = \alpha/D_g$; $\frac{1}{D_g\pi\beta'\left[1+\left(\frac{\bar{D}-\alpha'}{\beta'}\right)^2\right]}$	$\frac{\bar{D}(2E+3B\bar{D})}{\bar{D}'(2E+3B\bar{D}')\pi\beta'\left[1+\left(\frac{\bar{D}'-\alpha'}{\beta'}\right)^2\right]}$	$\frac{\bar{D}}{(\theta+\bar{D}^2)^{1/2}\pi\beta'\left[1+\left(\frac{(\theta+\bar{D}^2)^{1/2}-\alpha'}{\beta'}\right)^2\right]}$	$\frac{\bar{D}^2}{(\theta+\bar{D}^3)^{2/3}\pi\beta'\left(1+\left[\frac{(\theta+\bar{D}^3)^{1/3}-\alpha'}{\beta'}\right]^2\right)}$
Rayleigh: $\alpha > 0$; $\alpha' = \alpha/D_g$; $\frac{\bar{D}}{D_g\alpha'^2}\exp\left(-\frac{1}{2}[\bar{D}/\alpha']^2\right)$	$\frac{\bar{D}(2E+3B\bar{D})}{\alpha'^2(2E+3B\bar{D}')}\exp\left(-\frac{1}{2}(\bar{D}'/\alpha')^2\right)$	$\frac{\bar{D}}{\alpha'^2}\exp\left(-\frac{(\theta+\bar{D}^2)}{2\alpha'^2}\right)$	$\frac{\bar{D}^2}{\alpha'^2(\theta+\bar{D}^3)^{1/3}}\exp\left(-\frac{1}{2}\left[\frac{(\theta+\bar{D}^3)^{1/3}}{\alpha'}\right]^2\right)$
Maxwell: $\alpha' = \alpha/D_g > 0$; $\frac{4}{\sqrt{\pi}}\frac{1}{D_g}\frac{\bar{D}^2}{\alpha'^3}\exp(-\bar{D}^2/\alpha'^2)$	$\frac{4\bar{D}(2E+3B\bar{D})\bar{D}'}{\pi\alpha'^3(2E+3B\bar{D}')}\exp\left(-\frac{\bar{D}'^2}{\alpha'^2}\right)$	$\frac{4}{\sqrt{\pi}\alpha'^3}\bar{D}(\theta+\bar{D}^2)^{1/2}\exp\left(-\frac{(\theta+\bar{D})}{\alpha'^2}\right)$	$\frac{4}{\sqrt{\pi}\alpha'^3}\bar{D}^2\exp\left(-\left[\frac{(\theta+\bar{D}^3)^{1/3}}{\alpha'}\right]^2\right)$
Exponential: $\lambda' = \lambda D_g > 0$; $\frac{\lambda'}{D_g}\exp(-\lambda'\bar{D})$	$\frac{\bar{D}(2E+3B\bar{D})\lambda'\exp(-\lambda'\bar{D}')}{\bar{D}'(2E+3B\bar{D}')}$	$\frac{\lambda'\bar{D}\exp(-\lambda'[\theta+\bar{D}^2]^{1/2})}{(\theta+\bar{D}^2)^{1/2}}$	$\frac{\lambda'\bar{D}^2\exp[-\lambda'(\theta+\bar{D}^3)^{1/3}]}{(\theta+\bar{D}^3)^{2/3}}$
Beta: a, b > 0, $0 < \bar{D} < 1$; $\frac{1}{\bar{B}(a,b)}\bar{D}^{a-1}(1-\bar{D})^{b-1}$	$\frac{\bar{D}(2E+3B\bar{D})\bar{D}'^{(a-2)}(1-\bar{D}')^{(b-1)}}{\bar{B}(a,b)(2E+3B\bar{D}')}$	$\frac{\bar{D}(\theta+\bar{D}^2)^{(a-2)/2}(1-[\theta+\bar{D}^2]^{1/2})^{(b-1)}}{\bar{B}(a,b)}$	$\frac{\bar{D}^2(\theta+\bar{D}^3)^{(a-3)/3}}{\bar{B}(a,b)}(1-[\theta+\bar{D}^3]^{1/3})^{(b-1)}$
Chi: $\sigma' = \frac{\sigma}{D_g} > 0$; $n = 1, 2, \ldots$; $(n/2)^{n/2}\frac{1}{D_g}\frac{\bar{D}^{n-1}}{\sigma'^n}\frac{\exp[-(n/2\sigma'^2)\bar{D}^2]}{\Gamma(n/2)}$	$\frac{2(n/2)^{n/2}\bar{D}(2E+3B\bar{D})\bar{D}'^{(n-2)}\cdot\exp[-(n/2\sigma'^2)\bar{D}'^2]}{\sigma'^n(2E+3B\bar{D}')\Gamma(n/2)}$	$\frac{2\bar{D}(n/2)^{n/2}(\theta+\bar{D}^2)^{(n-2)/2}}{}\cdot\frac{\exp\left[-\frac{n(\theta+\bar{D}^2)}{2\sigma'^2}\right]}{\sigma'^n\Gamma(n/2)}$	$\frac{2(n/2)^{n/2}\bar{D}^2(\theta+\bar{D}^3)^{(n-3)/3}}{\sigma'^n\Gamma(n/2)}\cdot\exp\left(-\frac{n(\theta+\bar{D}^3)^{2/3}}{2\sigma'^2}\right)$

lowing expression for the particle growth rate:

$$R(D) = -\frac{D_g^3}{\tau D[2ED_g + 3BD]} \quad (5)$$

To prove that the growth expression, Eq. 5, although obtained from Eq. 3 derived originally for a monodisperse system, is compatible with the population balance modeling of the polydisperse system, it is sufficient to demonstrate that for any arbitrarily chosen particle of size D, the more general expression, Eq. 5, reduces to that of LeBlanc and Fogler (1987) under the conditions of diffusion control; diffusion control brings out the effects of particle size more significantly than any other condition. With the incorporation of $E = 1$, $B = 0$ and $\tau = \rho D_g^2/8C^*M\mathcal{D}$, Eq. 5 yields

$$-R(D) = \frac{4C^*M\mathcal{D}}{\rho D} \quad (6)$$

This is identical with the expression of LeBlanc and Fogler (1987) in whose notation $\rho_s = \rho/M$ and $C = C^*$.

Combination of Eq. 2 and 5 leads to

$$\frac{D_g^3}{\tau}\left[\frac{2[ED_g + 3BD]}{D^2[2ED_g + 3BD]^2}\right]F(D,t) - \frac{D_g^3}{\tau}\cdot\left[\frac{1}{D[2ED_g + 3BD]}\right]\frac{\partial F(D,t)}{\partial D} = \frac{\partial F(D,t)}{\partial t} \quad (7)$$

Nondimensionalisation of Eq. 7 may be based on the following choice of variables:

Dimensionless Diameter:

$$\bar{D} = D/D_g \quad (8)$$

Dimensionless Time:

$$\theta = t/\tau \quad (9)$$

Dimensionless Distribution Function

$$\Phi = \frac{D_g F(D,t)}{N(O)} \quad (10)$$

Using Eqs. 7–10, we obtain

$$\frac{1}{\bar{D}(2E + 3B\bar{D})}\frac{\partial\Phi}{\partial\bar{D}} - \frac{\partial\Phi}{\partial\theta} = \frac{2(E + 3B\bar{D})}{\bar{D}^2(2E + 3B\bar{D})^2}\Phi \quad (11)$$

The dimensionless population balance equation, Eq. 11, is a quasilinear hyperbolic partial differential equation. It may be solved by means of the method of characteristics (Hildebrand, 1976; Kovach, 1982). According to this method, the ordinary differential equations corresponding to Eq. 11 are

$$\frac{d\bar{D}}{1/\bar{D}(2E + 3B\bar{D})} = \frac{d\theta}{(-1)} = \frac{d\Phi}{2(E + 3B\bar{D})\Phi/\bar{D}^2(2E + 3B\bar{D})^2} \quad (12)$$

Treating the equalities in Eq. 12 as a set of simultaneous ordinary differential equations, one obtains the following solution to the population balance equation:

$$\Phi(\bar{D},\theta) = \bar{D}(2E + 3B\bar{D}) \cdot H(E\bar{D}^2 + B\bar{D}^3 + \theta) \quad (13)$$

where H is an arbitrary function. At $\theta = 0$, the solution of the population balance equation is

$$\Phi(\bar{D},0) = \bar{D}(2E + 3B\bar{D}) \cdot H(E\bar{D}^2 + B\bar{D}^3) \quad (14)$$

The functional form of H is determined by comparing Eq. 14 with a rearranged form of the initial distribution function which resembles Eq. 14 in the coefficient term. The exact expression for H is then arrived at by replacing $\bar{D}$ with an equivalent expression obtained from the transient argument. The solutions for a number of distribution functions are presented in Table 1. The general solution for a transition regime involves a parameter, $\bar{D}'$, given by

$$E\bar{D}'^2 + B\bar{D}'^3 = E\bar{D}^2 + B\bar{D}^3 + \theta \quad (15)$$

The implicitly defined value of $\bar{D}'$ may be calculated using a simple iterative procedure like the Newton-Raphson method. The special cases of the rate-limiting regimes are also displayed in Table 1.

The mathematical machinery involved in the kinetic invariance analysis is somewhat heavier than that in the conventional approach. As a consequence, it is comparatively more difficult to include a complex kinetics in this approach. Nevertheless, this difficulty should not diminish its original purpose and merit of incorporating the bulk-liquid reaction and the general transition regime into the framework of the population balance theory.

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Notation

- a = parameter in beta distribution
- A = constant in lognormal distribution $(1/\ln\sigma_g\sqrt{2\pi})$
- b = parameter in beta distribution
- B = constant in Eq. 3 for kinetic invariant function
- C_o = equivalent concentration of initial loading of solid, kmol/m^3
- D = particle diameter, m
- $\mathcal{D}$ = diffusivity of dissolving reactant, m^2/s
- D_g = geometric mean diameter, m
- $\bar{D}$ = particle diameter
- $\bar{D}'$ = parameter, Eq. 15
- E = constant, Eq. 3
- $F(D, t)$ = number distribution at any time t, m^{-1}
- $H(\cdot)$ = arbitrary function accruing from method of characteristics
- K_r = reaction rate constant, m^3/kmol · s
- n = parameter in Rosin-Rammler and chi-distribution
- $N(O)$ = total number of particles present at time, $t = 0$
- r = parameter in gamma distribution
- $R(D)$ = particle growth rate, m/s
- t = time of operation, s
- Z_o = concentration of the catalyst or liquid-phase-reactant species, kmol/m^3

Greek letters

- α = constant, Eq. 3; parameter in Cauchy, Rayleigh, Maxwell distributions

α' = parameters, Rayleigh distribution
β, β' = parameters, Cauchy distribution
$\Gamma(\cdot)$ = gamma function
Δ = increment
λ, λ' = parameters in gamma and exponential functions
ω = kinetic invariant function
ρ = density of solid particle, kg/m^3
τ = time of complete conversion of solid reactant, s
θ = time
Φ = number distribution
σ, σ' = parameters, chi-distribution
σ_g = geometric standard deviation

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