Effects of More Realistic Single-Particle Rate Laws in the Eulerian Population-Balance Equation; Two Further Examples ('Growth' and Sintering)*

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ABSTRACT

Considerable insight has been obtained by introducing deliberately (over-) simplified rate laws (for suspended particle nucleation, coagulation, growth/dissolution, sintering, breakage,…) into the generally nonlinear integro-partial differential equation called the '*population balance' equation* (PBE). This approach has been justified by the complexity of this equation, and the need to satisfy it along with many other local PDE-balance principles in multi-dimensional transient flow environments. However, current requirements for process design, and the practical need to infer meaningful physico-chemical parameters based on accessible measurements on large populations rather than individual 'particles', make the introduction of more accurate rate laws an essential ingredient for the next generation of such process models. Following up on our earlier analyses of the effects of more accurate *collision frequency* rate laws for fractal-like aggregates, we further demonstrate this claim here by examining two further instructive linear, univariate examples, both in the context of a well-mixed steady-flow vessel:

E1 Non quasi-steady diffusion-controlled particle dissolution
E2 Non-relaxation type sintering (area-reduction) by surface-diffusion

In both cases our focus is on the systematic effects of introducing more realistic single-particle rate laws on the exiting particle population distribution functions---with respect to particle *volume* (Case E1) or particle *surface area* (Case E2). This is revealed by systematic shifts in the relevant moments of these distribution functions, displayed here for some cases of physical interest over a range of appropriate Damkohler numbers based on mean residence time.

The present results provide further support for our contentions that 1) the systematic introduction of more accurate rate laws (including nucleation, sintering, growth, ….) will be essential to meet the quantitative demands of the next-generation of simulation models for particulate processing/synthesis equipment, and, 2) QMOM-methods are capable of incorporating these more realistic rate laws into a PBE/CFD approach to particulate process simulation.

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1. INTRODUCTION AND OBJECTIVES

In our view, current requirements for the design of compact, safe and efficient chemical reactors, as well as the frequent need to infer meaningful physico-chemical parameters based on laboratory measurements on populations rather than individual ‘particles’, make the introduction of more accurate rate/transport laws essential for next-generation particle synthesis reactor models. While our group is currently active on each of the elementary rate processes mentioned above, we focus here on two of these generalizations in Section 2. One of these deals with the consequences of ‘non-power-law’ and non-quasi-steady (non-QS) dissolution (negative growth) behavior in liquids (see Rosner and Arias-Zugasti (2005) for a more detailed account). The second example (work still in progress) deals with non-relaxation-type sintering rate laws, and their PBE consequences.

Beyond this, additional experience is required with mathematical/numerical methods for solving such PBEs in the context of CFD reactor modeling---*ie*., methods which are computationally efficient, yet able to incorporate realistic single particle rate laws and faithfully generate their systematic effects on important ‘moments’ characterizing the reaction product joint distribution functions. These particular issues, our recent experience with so-called “Quadrature”-based moment methods (ie.:“QMOM”; McGraw,1997)---are summarized in Rosner *et al*. (2003,2005).

2. IMPROVED RATE/TRANSPORT LAWS FOR ISOLATED SPHERICAL PARTICLES AND 'DIMERS'

2.1 Dissolution of Isolated Spherical Particles

It appears that *all* previous applications of the PBE approach to particle populations evolving in the presence of either growth or dissolution (‘negative growth’, leading to disappearance from the particle phase) have made use of quasi-steady (QS-) power-law rate laws. This is not only true for deliberately idealized situations (such as growth proportional to (particle volume)$^{1/3}$ in a well-stirred nutrient containing vessel; Friedlander(2000), but also transient liquid fuel spray evaporation in a Diesel engine environment . But in such applications QS-power-law relations are often questionable even in the low particle volume fraction limit (negligible interparticle interactions). This is because the single particle diffusion-controlled mass transfer process even in a constant local environment can be intrinsically transient, leading to more complex dv/dt vs. v relationships (where v is the instantaneous particle volume).

We recently investigated the ‘test’ case of particle dissolution for small but non-zero values of a governing dimensionless parameter, ε, proportional to the square root of the product of the phase density ratio and the sphere solubility---*ie*.:

$$\varepsilon \equiv \{(2/\pi) \bullet (\rho_f/\rho_p) \bullet [\, ln\,(1 + B_m)]\}^{1/2} \qquad (1)$$

where, in terms of local solute mass fractions (see, *eg.,* Rosner(2000)):

$$B_m \equiv (\omega_{sat,w} - \omega_\infty)/(1 - \omega_{sat,w}). \qquad (2)$$

It is straightforward to generate typical values of the parameter ε for common pure inorganic salts dissolving in, say, 20C water (see, eg., Rosner(2005))---in this way one finds that, say $\varepsilon(NH4Cl)$ is 0.363 and $\varepsilon(SbCl3)$ is as high as 0.684 . Small ε perturbation results [Crespo and Linan(1975)] were used to conveniently predict the effects of non-QS, non power-law behavior on the PSD emerging from a well-stirred vessel (along with some of its dimensionless moments) into which particles of a single size are continuously admitted (Rosner and Arias Zugasti(2005), and Section 3.1 , below). As mentioned above, the non-zero parameter ε is associated with systematic departures from the well-known QS-continuum limit result that the individual particle *surface area* should fall off linearly with (dimensionless) residence time. However, to a first approximation $t_{life}(\varepsilon) = t_{life,QS}/(1+\varepsilon)$, with $t_{life}(\varepsilon)$ remaining proportional to $(d_{p,o})^2$------the familiar 'fingerprint' of an (external-) diffusion-controlled process (see, *eg.,* Rosner(2000)).

2.2 Surface-Diffusion-Controlled Sintering of Bi-sphere Aggregates

Motivated by our experimental observations on sintering populations of non-spherical alumina nano-particles (Rosner and Pyykonen (2002), Xing and Rosner(1999)) we have been examining, numerically, the sintering dynamics of bi-spheres, when the mechanism of atomic transport is surface diffusion. Not surprisngly, we find that the surface area vs. time relationship for any particular biosphere in an isothermal environment is far from the frequently assumed "relaxation"- (to $a_{min}(v)$) type. For this reason we are currently using our surface diffusion-based numerical integrations to develop robust correlations which will allow a more realistic sintering rate law to be inserted into the relevant PBE governing pdf(a), where a is the surface area of a particle of volume v.

3. IMPLICATIONS FOR PBE; PSD SHAPE- AND MOMENTS WITH IMPROVED RATE LAWS

Of course, our principal goal is to improve the accuracy of CRE/PBE modeling when many interacting phenomena may be occurring 'at the same time'. However, to understand the effects of systematically improved rate laws it is first prudent to study certain 'model' problems which are tractable and comparatively unambiguous.

3.1 Dissolution of a Particle Population in a Well-Stirred Vessel

How do the abovementioned non-QS dissolution rate effects influence the PSD of particles emerging from, say, a well-stirred solvent-containing vessel into which particles of a single size (volume v_o) are continuously fed? This instructive 'canonical'* problem can be solved by making use of the closed-form small ε-asymptotic results of Crespo and Linan (1975; *loc cit*). Of particular interest are the exit PSDs [ie., $\psi(\eta, Dam, \varepsilon)$ in dimensionless terms] at different mean residence times (see Fig. 2). Note the significant effect of non-QS behavior , especially at particle sizes near v_o, and at short vessel mean residence times.

Certain dimensionless moments of the exit PSD are also of considerable practical importance. Each is defined by and integral of the form:

$$\mu_k \equiv \int \eta^k \bullet \psi(\eta, Dam, \varepsilon) \bullet d\eta \quad \text{from } \eta = 0 \text{ to } 1 \qquad (3)$$

where the index(exponent) k need not be an integer and :

$$\eta \equiv v / v_o \quad , \quad \psi \equiv n(v) \bullet v_o/N_p \qquad (4a,b)$$

and N_p is the total particle number density.

For example, when k = 0.7653 this moment permits the calculation of the total mass deposition rate of suspended particles from this population across a Sc>>1 turbulent boundary layer (Rosner(1989)). The appreciable ε-dependence of this moment is shown in Fig.3, where, at *Dam*(QS) = 1 (*ie.* when the mean residence time in the vessel is equal to the QS-predicted particle lifetime in the prevailing solvent), the non-QS effect on $\mu_{0.7653}$ for $\varepsilon = 0.3$ is seen to be *ca.*50 pct.

3.2 Bi-sphere Sintering in a Well-Stirred Vessel

Of interest here are the PBE consequences of inserting a non-relaxation type rate law for sintering, of the type emerging from our rigorous surface-diffusion controlled calculations for bi-spheres (Zurita-Gotor and Rosner(2005)). The model problem consists of a mono-dispersed population of bi-spheres introduced into a well-stirred sintering vessel. At various mean residence times, what is the actual emerging pdf(a) and how does it compare to 'expectations' based on the use of the now-classical 'relaxation'-type rate law of the form $(-da/dt) = [a - a_{min}(v)]/t_{SD}$, where t_{SD} is the so-called characteristic sintering time. Similarly, how are certain important moments of pdf(a) modified, and can these changes be embraced by present QMOM techniques? These results are also needed to critically assess the credence currently being placed on sintering parameters previously extracted from measurements on complex populations with the help of PBE solutions in which relaxation type rate laws were deliberately introduced.

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*In the absence of coagulation and/or other complicating phenomena, the *linearity* of this problem permits this 'singular' solution to serve as a Greens function, enabling a superposition solution for the corresponding vessel fed with an *arbitrary* PSD. For further details about this particular study, see Rosner and Arias-Zugasti(2005).

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4. CONCLUSIONS, WORK-IN-PROGRESS

Our explicit discussion of improved rate laws appearing in the PBE dealt only with the 'unit processes' of (negative) '*growth*' (Section 2.1) and bi-sphere sintering by the mechanism of surface diffusion (Xing and Rosner(1999)). But progress is also being made in other areas important to CRE---including more accurate thermophoretic coefficients

(Zurita-Gotor(2005), and more realistic *coagulation* rate laws (Zurita-Gotor and Rosner(2004)). In each case our objective is to demonstrate the ability of QMOM-based PBE simulation methods to 'capture' these effects, without the closure problems associated with earlier moment methods.

Taken together, our present results provide further evidence that the systematic introduction of more accurate rate//transport laws will be essential to meet the quantitative demands of the next generation of such particulate process models. Moreover, these necessary rate-law refinements can evidently be accommodated using the QMOM methodology outlined in Rosner et al. (2005) and in the references cited therein.

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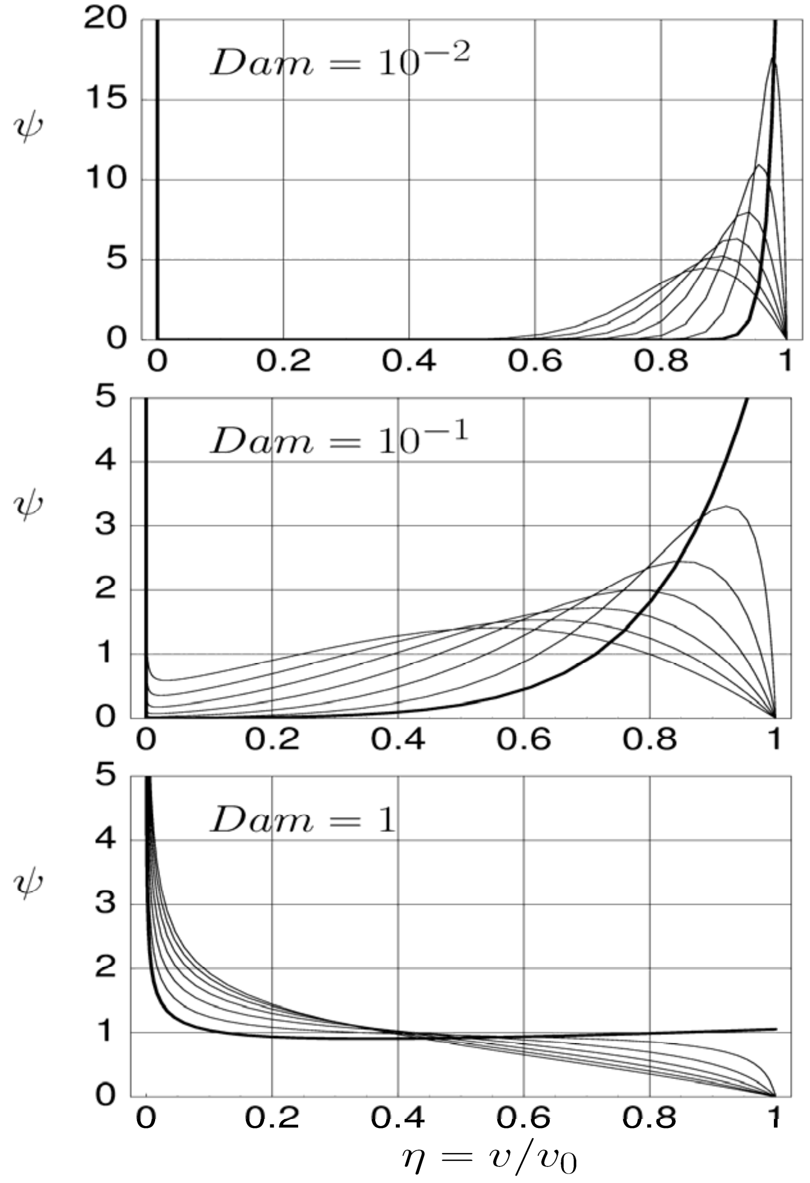
Figure Titles:

Figure 1 Effect of Non-Quasi-steady single particle dissolution rate law on emerging PSD at several vessel mean residence times (as multiple of characteristic particle dissolution time). Dilute, mono-size feed.

Figure 2. Effect of Non-QS dissolution rate law on an emerging PSD-moment over a range of Damkohler numbers ($<t_{residence}>/t_{life}(\varepsilon)$); (k=0.7653; Well-stirred vessel with Dirac function input at size v_o)



$Dam = 10^{-2}$
ψ
20
15
10
5
0
0.2
0.4
0.6
0.8
1
$Dam = 10^{-1}$
ψ
5
4
3
2
1
0
$Dam = 1$
ψ
$\eta = v/v_0$

Fig. 1 a,b,c

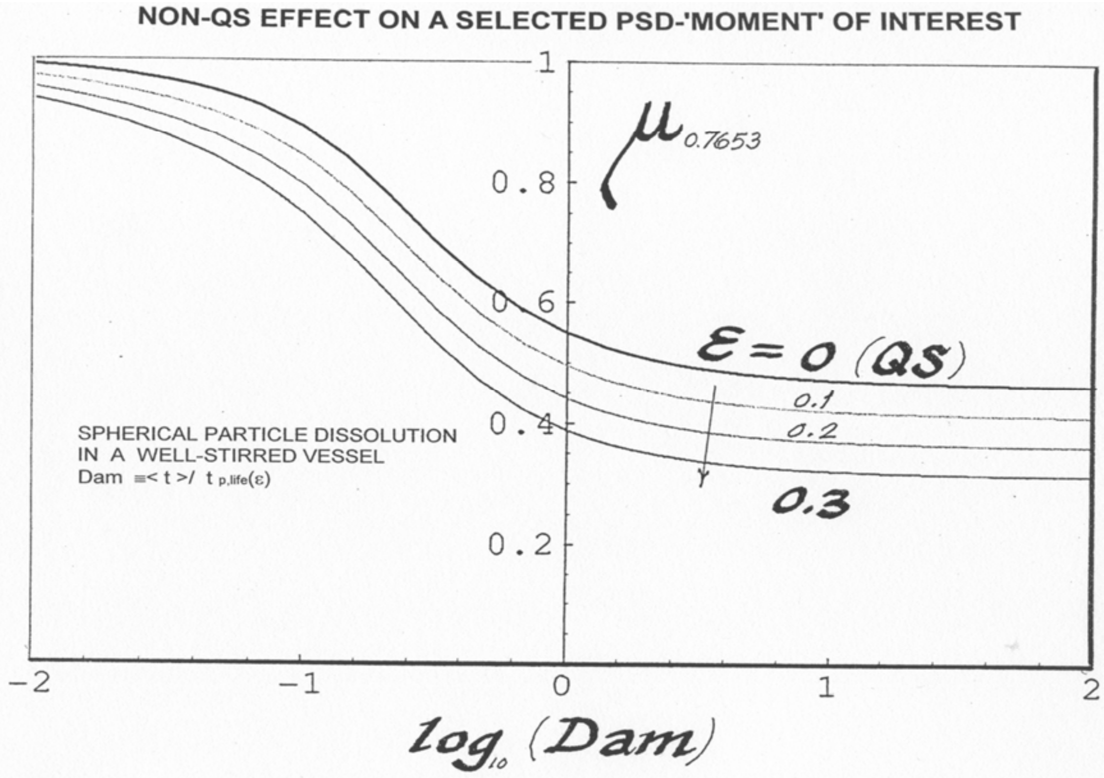

NON-QS EFFECT ON A SELECTED PSD-'MOMENT' OF INTEREST
$\mu_{0.7653}$
$\varepsilon = 0$ (QS)
0.1
0.2
0.3
SPHERICAL PARTICLE DISSOLUTION
IN A WELL-STIRRED VESSEL
Dam $\equiv \langle t \rangle / t_{p,\text{life}}(\varepsilon)$
1
0.8
0.6
0.4
0.2
−2
−1
0
1
2
$\log_{10}$ (Dam)

Fig. 2