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Analytical time-stepping solution of the discretized population balance equation

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Abstract

The prediction of the particle-size distribution (PSD) of the particulate systems in chemical engineering is very important in a variety of different contexts, such as parameter identification, troubleshooting, process control, design, product quality, production economics etc. The time evolution of the PSD can be evaluated by means of the population balance equation (PBE), which is a complex integro-differential equation, whose solution in practical cases always requires sophisticated numerical methods that may be computationally tedious. In this work, we propose a novel technique that tackles this issue by using an analytical time-stepping procedure (ATS) to resolve the PSD time dependency. The ATS is an explicit time integrator, taking advantage of the linear or almost linear time dependency of the discretized population balance equation. Thus, linear approximation of the source term is a precondition for the ATS simulations. The presented technique is compared with a standard variable step time integrator (MATLAB ODE15s stiff solver), for practical examples e.g. emulsion, ageing cellulose process, cooling crystallization, reactive dissolution, and liquid-liquid extraction. The results show that this advancing in time procedure is accurate for all tested practical examples, allowing reproducing the same results given by standard time integrators in a fraction of the computational time.

1 Introduction

Population Balance Model (PBM) is an important modelling framework for particulate systems. PBM is used to describe the evolution of the particle size distribution (PSD), accounting for particle behaviors, such as breakage, agglomeration, growth and nucleation. Typical applications of the PBM are, e.g, in dissolution, precipitation, cooling crystallization, polymerization, emulsion, gas-liquid and liquid-liquid separation and reaction processes, etc. (Zhao et al., 2018&2012; Ma et al., 2008; Zhen et al., 2011; Becker et al., 2014; Buffo et al., 2012; Alopaeus, V., 2014; Nauha et al., 2018) The PSD in the so-called Population Balance Equation (PBE) is expressed as the number density n(t, x; L) function with respect to the external (the spatial location, *x* and time, t) and internal (particle properties, *L*, e.g. size or concentration) coordinates. Such definition leads to the following general expression for the PBE:

$$\frac{\partial n(t, \boldsymbol{x}; L)}{\partial t} + \nabla_{\boldsymbol{X}} \cdot (v(t, \boldsymbol{x}; L)n(t, \boldsymbol{x}; L)) + \nabla_{r} \cdot (\dot{R}(t, \boldsymbol{x}; L)n(t, \boldsymbol{x}; L)) = h(t, \boldsymbol{x}; L)$$
(1)

where v is the particle velocity, \dot{R} is the time rate of change along the internal variable L due to continuous processes (e.g., mass transfer), and h(t, x; L) is the source term that describes the collisional phenomena in the particulate process.

The complexity of the source term in Eq. (1) determines the method adopted for the solution of the PBE. The method of characteristics can be adopted when the source term is constant or linear with respect to probability distribution function (PDF) (Courant & Hilbert, 1956; Rhee et al., 1986). When h(t, x; L) is instead expressed as an integral function, which is the case when breakage and/or aggregation are considered, the PBE becomes a nonlinear

integro-partial differential equation, hence no general analytical solution is possible with the exception of a few very simplified cases. Lage (2002) and Patil (1998) presented non-closed Laplace transformation based analytical solution for PBE, when the total number density and coalescence kernel are constant. McCoy and Madras (2003) introduced a more general asymmetric solution for the systems where the rates of the breakage and agglomeration processes are not the same. Nevertheless, the solutions found with these methods are valid only for a very limited subset of possible breakage and aggregation models. Thus, these analytical solutions are not useful for real applications, but they are mainly used for validating numerical methods. For this reason, several numerical approaches are developed during the years to tackle very general PBE formulations.

These numerical approaches can be classified into different categories, such as, for instance, the method of moments (MOM) (McGraw, 1997; Marchisio et al., 2003a & 2003b; Alopaeus et al., 2006a; Buffo et al., 2012; Petitti et al., 2013; De Bona et al. 2016; Gao et al., 2016), the method of classes (MC) (i.e. sectional methods) (Alopaeus et al., 2006b; Kumar and Ramkrishna, 1997, 1996; Laakkonen et al., 2007; Dorao et al., 2006; Zhu et al., 2008; Kostoglou et al., 2004; Kostoglou, 2007; Kostoglou et al., 2009), Monte Carlo methods (MCM) (Smith et al., 1998; Zhao et al., 2007). Each approach has its pros and cons, i.e. when the knowledge of the shape of the PSD is of interest for the particular system under investigation, the MC are often used to solve the PBE. However, if the shape of the distribution is needed with very high precision, the computational costs can be excessive especially for the large and complex multiphase systems. The reduction of the computational time is often a top

priority, especially, for an online process control, parameter estimation, or coupled solution of the PBM within a Computational Fluid Dynamics (CFD) platform.

The MOM and MC are based on transformation of the integrals into their counterparts and the discretization of the hyperspace generated by all the possible values of the internal and external coordinates. Time integration in these approaches has been done with standard time integrators, e.g. ode15s of the Matlab software. Alternatively, in probability-based methods (MCM), time step size is sometimes connected to the given probabilities.

In this work, we propose a method for MC in which the system's evolution in time is not followed by numerical integration of a system of ODEs, but by integrating the time dependent discretized PBE analytically and advancing in time in relatively long discrete intervals. Via a number of practical examples, it will be shown that the present method can be applied to a broad range of problems: five practical tests cases taken from the literature are considered, i.e., the emulsification (Becker et al., 2014), ageing cellulose process (Ahmad et al., 2015), cooling crystallization (Choong and Smith, 2004), reactive dissolution (Zhao et al., 2018), and liquid-liquid extraction (Buffo et al., 2016). Although these examples are totally distinct from each other, the source terms in PBE have fundamentally different nature: in the four first cases aggregation of particles can be neglected. Two first cases are rather simple, where the source term is also time invariant. Thus, there is an analytical solution if the MC is used. Third and fourth cases contain various time invariances which require special attention during time integration. The fifth case contains nonlinear source term (agglomeration). Properties of the five test cases are summarized in Table 1.

Table 1 List of the different practical test cases and physical phenomena considered. Thetime dependency and linearity of the source terms with respect to particle size of thesecases are presented.

Process	Breakage	Agglomeration	Growth	Nucleation	Chemical reaction
Case 1 Ageing cellulose	Yes (Time invariant and linear)	-	-	-	-
Case 2 Emulsion	Yes (Time invariant and linear)	-	-	-	-
Case 3 Cooling crystallizati on	Yes (Time invariant and linear)	-	Yes (Time depende nt and linear)	Yes (Time dependent and linear)	-
Case 4 Reactive dissolution	Yes (Time invariant and linear)	-	Yes (Time depende nt and linear)	-	Yes (Time dependent and linear)
Case 5 Liquid- liquid extraction	Yes (Time invariant and linear)	Yes (Time invariant and non-linear)	-	-	-

Nevertheless, where the source term in the PBE contains growth or nucleation terms, that are inherently time dependent, it is not possible anymore to apply the analytical formula. This technique is based on the simple idea of discretizing of the time space in intervals, in order to allow the solver to update the time dependent source term of the PBE at each discrete time, while the PBE is solved consecutively in each discrete time interval using the analytical formula. In this way, the time dependent source term in the PBE is evaluated before every time iteration and considered constant within time iteration. Therefore, the ATS can be seen as an explicit time integrator for PBE, when a MC is used. The goal of the ATS is to increase the computational speed by using much longer time steps in time integration compared to the state of art methods i.e. the Gear's method (ode15s stiff solver of Matlab). The batch cooling crystallization (Choong and Smith, 2004) and reactive dissolution (Zhao et al., 2018) presented in table 1, containing the time dependent growth and nucleation processes, are selected as practical cases to assess the performance of the ATS.

The only inherently non-linear term in the population balance equation is aggregation (coalescence) due to its second-order nature. Aggregation is hence non-linear even in the cases where the aggregation rate function would be constant. In order to make the proposed method (ATS) more universal, in chapter 2.1 the aggregation term is linearized with respect to particle size. Liquid-Liquid extraction process (Buffo et al., 2016) was in this case chosen as a practical test case. Correspondingly, the effect of the linearization on the ATS results is studied.

The practical test cases of the proposed method are based on one main assumption: homogeneous (well-mixed) condition with no spatial external variable dependency, namely the only external coordinate of the PBE is the time. This assumption is performed to simplify the solution of the problem without limiting the applicability of the method. The results, presented in the in chapter 4, from the comparison of the ATS and the state of art Gear's numerical time integrator introduced by Gear (1969), are showing that our method (ATS) is robust, accurate and fasts in broad practical chemical engineering applications.

2 Method

A generic PBE for a homogeneous (well-mixed) system with particle size as the only internal variable can be written as follows:

$$\frac{d(n(t,L))}{dt} = \int_{L}^{\infty} \beta(L,\lambda)g(\lambda)n(t,\lambda) d\lambda
+ \frac{L^{2}}{2} \int_{0}^{L} \frac{F((L^{3}-\lambda^{3})^{\frac{1}{3}},\lambda)n(t,(L^{3}-\lambda^{3})^{\frac{1}{3}})n(t,\lambda)}{(L^{3}-\lambda^{3})^{\frac{2}{3}}} d\lambda - g(t,L)n(t,L) \quad (2)
- n(t,L) \int_{0}^{\infty} F(L,\lambda)n(t,\lambda) d\lambda + \frac{\partial (G(t,L)n(t,L))}{\partial L} + B_{0}(t,L)$$

The meaning of each term in order from the left are: the variation of PSD with time, birth by breakage, birth by agglomeration, death by breakage, death by agglomeration, growth and primary nucleation.

By dividing the number density function into different categories (classes), it is possible to derive a discrete balance equation (Eq. (4)) for the number density of particles belonging to each category. Particle number density in category *i* is defined as follows:

$$Y_{i} = \int_{L_{-}}^{L_{+}} n(t, L) dL,$$
(3)

where Y_i represents the number of all the particle sizes belonging to the *i*-th category per unit volume and L_- and L_+ are the lower and upper bounds of *i*-th size category. Thus, by applying the CM of Alopaeus et. al. (2006b), the fully discretized PBE to the continuous equation (2) can be written as

$$\frac{\partial Y_{i}}{\partial t} = \sum_{j=1}^{NC} \beta(L_{i}, L_{j})g(L_{j})Y_{j} - g(L_{i})Y_{i}
+ \sum_{k=1}^{NC} \sum_{j=1}^{NC} \chi(L_{i}, L_{j}, L_{k})F(L_{j}, L_{k})Y_{j}Y_{k} - Y_{i} \sum_{j=1}^{NC} F(L_{i}, L_{j})Y_{j}
+ \sum_{j=1}^{NC} \frac{\xi(L_{i}, L_{j})}{\Delta L_{j}}G(L_{j})Y_{j} + \psi(L_{i})\Delta L_{i},$$
(4)

where $\beta(L_i, L_j)$ is a term that indicates the breakage of particle from category L_j to category L_i ; $g(L_i)$ is the breakage frequency; $\xi(L_i, L_j)$ is the growth term that counts the number of particles with size L_i after their growth from size L_j ; $G(L_j)$ is the growth rate; $\psi(L_i)$ is the distribution of primary nucleation. The terms $\beta(L_i, L_j)$, $\chi(L_i, L_j, L_j)$, $F(L_j, L_k)$ and $\xi(L_i, L_j)$ are referred as "tables", whose definition can be found elsewhere (Alopaeus et. al., 2006b): it is useful to mention that these terms do not depend on any physical parameter of the investigated problem, but only on the particular discretization scheme applied and on the choice of the particular set of moment to be preserved.

2.1 Analytical time stepping method

We start the derivation of the analytical time stepping method by looking at the linear terms in Eq. (4), i.e. those describing breakage, growth and primary nucleation. At this point, terms describing agglomeration (third and fourth on the right-hand side of Eq. 4) are neglected. Later, we will continue the method development also for agglomeration processes. With the linear terms only, the following discretized form for the PBE results in:

$$\frac{\partial Y_i}{\partial t} = \sum_{j=1}^{NC} \beta(L_i, L_j) g(L_j) Y_j - g(L_i) Y_i + \sum_{j=1}^{NC} \frac{\xi(L_i, L_j)}{\Delta L_j} G(L_j) Y_j + \psi(L_i) \Delta L_i$$
(5)

This can be expressed in a simple matrix form as:

$$\dot{Y} = HY + b, \tag{6}$$

where the matrix **H** contains the breakage and the growth terms ($H = H_{\beta} + H_{G}$). These two terms are:

$$\boldsymbol{H}_{\beta} = (\boldsymbol{\beta} \Delta \boldsymbol{L}) \operatorname{diag}(\boldsymbol{g}) - \operatorname{diag}(\boldsymbol{g}) = [\boldsymbol{A}]^{-1} (\boldsymbol{\mu}_{\beta}) \operatorname{diag}(\boldsymbol{g}) - \operatorname{diag}(\boldsymbol{g}), \tag{7}$$

$$\boldsymbol{H}_{G} = \boldsymbol{\xi}\boldsymbol{G} = [\boldsymbol{A}]^{-1}(\boldsymbol{m}_{G})\boldsymbol{G}. \tag{8}$$

The notation *diag*() stands for a diagonal matrix. The matrix [*A*] is a linear operator between discretized number distribution space and moment space (Alopaeus et al., 2006b):

$$A_{ij} = L^{\omega(j)}_{\nu(i)},\tag{9}$$

where v(j) and $\omega(i)$ are the vectors representing the categories into which the moments are distributed and the moment orders to be conserved, respectively. The meaning of

v(j) changes according to the different phenomena: for breakage, $v_i(j)$ defines the categories into which the daughter particles are distributed after the breakage of mother particles belonging to the *i*-th category; similarly, for growth $v_i(j)$ represents the distribution of the elements in consecutive categories. In breakage and growth, the smallest category $v_i(1)$ and the largest category $v_i(M)$ are calculated using the following scheme:

$$v_i(1) = i - floor\left(\frac{M}{2}\right) + Z,$$
(10)

$$v_i(M) = v_i(1) + M - 1, \tag{11}$$

where Z = 0 for breakage, Z = 1 for positive growth (*G*>0) and Z = -1 for negative growth (*G*<0). *M* is the number of preserved moments. Moreover, when *M*=2 and the conserved moments are the total number of particles and the total particle volume per unit volume, this method is similar to the fixed-pivot of Kumar and Ramkrishna (1996). For more information about the high order moment conserving discretization method applied here, see Alopaeus et al. (2006b, 2007).

Moments to be distributed in breakage ($\mu_{\beta i}$) and size dependent part of the growth table (m_{Gi}) in Eq. (7) and (8) are the following:

$$\mu_{\beta k i} = \int_{L_{-}}^{L_{+}} \beta(L, \lambda) L_{i}^{k} \mathrm{d}L, \qquad (12)$$

$$m_{Gi} = \omega(k) L_i^{\omega(k)-1}.$$
(13)

The vector *b*, in Eq. (6), contains the distribution of primary nucleates (ψ) (Alopaeus et al., 2007).

$$\boldsymbol{b} = \boldsymbol{\psi} = \boldsymbol{A}^{-1} (\frac{d\mu_B}{dt}) \tag{14}$$

$$\frac{d\mu_{Bk}}{dt} = \begin{cases} B_0 & for \ k = 0\\ 0 & for \ k > 0 \end{cases}$$
(15)

The matrix form in Eq. (6) is a first order linear differential equation system, which has the following analytical solution:

$$Y(t) = exp[Ht] Y_0 + H^{-1}b[exp(Ht) - I]$$
⁽¹⁶⁾

. . . .

The first term on the RHS of the Eq. (16) is the solution of the homogeneous part, and the second term is present only when nucleation occurs, namely when vector \boldsymbol{b} in Eq. (16) is not zero. It is important to remark that the Eq. (16) written above is strictly valid only if the matrix \boldsymbol{H} and vector \boldsymbol{b} are time independent. Otherwise, in the cases where time-dependent

growth and nucleation terms are considered, the matrices can be assumed constant over a certain time interval, that is

$$Y(t_{n+1}) = exp(H_n \Delta t_{n+1}) Y(t_n) + H_n^{-1} b_n [exp(H_n \Delta t_{n+1}) - I].$$
(17)

As previously mentioned, in the ATS, the continuous time space is replaced by discrete time intervals. In each time step the matrix **H** and vector **b** are considered time independent, then updated before (H_n) each time integration. In other words, time is advanced analytically within each time integration.

The present analytical time stepping is relatively straightforward to apply to processes without agglomeration. In those cases the source terms are linear with respect to the number densities, although there could be nonlinearities in the rate functions. In this respect, systems with noticeable agglomeration are more challenging. As already mentioned, for an analytical solution for the time propagation of the discretized PBM, it is essential that the source term of the PBE is linear with respect to the particle number density (**Y**). However, agglomeration term in the PBE is inherently of second order with respect to particle number density. Therefore, we propose to use a linear approximation of the agglomeration term in the present ATS framework. The discrete formulation of the PBE for the breakage and agglomeration processes is:

$$\frac{\partial Y_i}{\partial t} = \sum_{j=1}^{NC} \beta(L_i, L_j) g(L_j) Y_j - g(L_i) Y_i + \sum_{k=1}^{NC} \sum_{j=1}^{NC} \chi(L_i, L_j, L_k) F(L_j, L_k) Y_j Y_k - Y_i \sum_{j=1}^{NC} F(L_i, L_j) Y_j$$
(18)

The third and fourth terms in Eq. (18) are the birth (**C**) and death (**D**) rates by agglomeration, respectively. Linearized representations of these terms with respect to particle number density can be illustrated as:

$$C = J_1(Y - Y_0) + C_0$$
(19)
$$D = J_2(Y - Y_0) + D_0$$

Where $J_1 = \frac{\partial C_0}{\partial Y_0}$ and $J_2 = \frac{\partial D_0}{\partial Y_0}$ are the Jacobian matrixes for the birth and death by agglomeration, respectively. The C_0 and D_0 are the birth and death by agglomeration at the previous time step, respectively. Y_0 is the particle number density at the previous time step. The Jacobians are calculated at each linearized point in each time step as:

$$\frac{\partial D_i}{\partial Y_j} = \sum_{k=1}^{NC} [\chi (L_i, L_k, L_j) F(L_k, L_j) Y_k + \chi (L_i, L_j, L_k) F(L_j, L_k) Y_k]$$
(20)

$$\frac{\partial C_i}{\partial Y_j} = \begin{cases} F(L_i, L_j)Y_j & , when \ i \neq j \\ \sum_{j=1}^{NC} F(L_i, L_j)Y_j + F(L_i, L_i)Y_i & , when \ i = j \end{cases}$$
(21)

The ATS solution for breakage and agglomeration processes is

$$Y(t_{n+1}) = exp[(H_n + \frac{\partial C_n}{\partial Y_n} - \frac{\partial D_n}{\partial Y_n})\Delta t_{n+1}]Y_n + (H_n + \frac{\partial C_n}{\partial Y_n} - \frac{\partial D_n}{\partial Y_n})^{-1}(\frac{\partial D_n}{\partial Y_n}Y_n - \frac{\partial C_n}{\partial Y_n}Y_n + C_n - D_n)_n \left\{ exp[(H_n + \frac{\partial C_n}{\partial Y_n} - \frac{\partial D_n}{\partial Y_n})\Delta t_{n+1}] - I \right\}$$
(22)

It is worth mentioning that after linearization the Eq. (18) is separable in **Y**. Thus, the Eq. (22) is the ATS solution for a non-homogeneous system of ordinary differential equations (Eq. 18) over time interval Δt_{n+1} . In this solution there is no errors related to approximations of derivatives, such as truncation error. On the other hand, the linearization method is used to approximate the agglomeration near the **Y** = **Y** (t_{n+1}), which may introduce time step limitations.

The objective of the ATS is to increase the computational speed by using much less and longer time steps in time integration compared to the Gear's method, see Figure 1. The ATS is an explicit method, which uses the analytical solution of Eq. (16) within every time integration.



Figure 1 Time interval discretization in ATS and Gear's method.

3 Examples

The practical applications chosen in this work correspond to the different cases described in Table 1, highlighting which physical phenomena play a role in the studied process and should be considered in the modeling. In the first two cases, i.e., ageing process of cellulose (Case 1) and emulsions (Case 2), it is possible to apply the analytical formula expressed in Eq. (16), directly because the matrix **H** in the Eq. (7) and (8) is time independent. On the other hand, in the next two cases, i.e. cooling crystallization (Case 3) and dissolution (Case 4), the growth and nucleation terms are time dependent, which needs to be taken into account. This cases the ATS is implemented. The reader should notice that the vector **b** in the Eq. (6) exists only in Case 3, namely in the cooling crystallisation case, where nucleation is present. In the last liquid-liquid extraction case (case 5) the source term is linearized before employing the ATS. The sectional method used in the first four test cases is conserving two moments are, namely

the zeroth and the third, but in the last test case six first moments are conserved, making the sectional method high order.

The different closures for breakage, growth, agglomeration and nucleation used in the different test cases and their parameters are presented in Table 2 and 3.

Table 2 Closures adopted to describe the different physical phenomena in each test case.

	Case 1
Daughter size distribution, β	$\frac{90L_i^2}{L_i^2} (\frac{L_i^3}{L_i^2})^2 (1 - \frac{L_i^3}{L_i^2})^2$
	L_j^3 L_j^{3} L_j^{3}
Breakage rate, g	$k_1(L_i - 1)$
Agglomeration, F	-
Growth rate, G	-
Nucleation rate, B_n	-

Case 2			
Daughter size distribution, β	$\frac{2}{L}$		
Breakage rate, g	$A_1 \varepsilon^{\frac{1}{3}} erfc \left[\sqrt{A_2 \frac{\sigma}{\rho_C \varepsilon^{\frac{2}{3}} L_i^{\frac{5}{3}}} + A_3 \frac{\mu_d}{\sqrt{\rho_C \rho_d} \varepsilon^{1/3} L_i^{4/3}}} \right]$		
Agglomeration, F Growth rate, G	-		
Nucleation rate, B_n	-		

	Case 3
Daughter size distribution, β	$\frac{90L_i^2}{I_i^3} (\frac{L_i^3}{I_i^3})^2 (1 - \frac{L_i^3}{I_i^3})^2$
Breakage rate, g	$L_j = L_j$ L_j L_j
Agglomeration, F	-
Growth rate, G	$k_g[\mathcal{C}_s(t) - \mathcal{C}^*(t)]^g$
Nucleation rate, <i>B_n</i>	$k_p[C_s(t)-\bar{C}^*(t)]^p$

Ca	se 4
Daughter size distribution, β	$rac{A_7L_i^2}{L_i^3}(rac{L_i^3}{L_i^3})^2(1-rac{L_i^3}{L_i^3})^{A_6}$
Breakage rate, g	$A_4(\frac{L_i}{n})^{A5}\eta_T^{-1}$
Agglomeration, F	-
Growth rate, G	$N_i(L_i)A(L_i)v_i$
Nucleation rate, B_n	$\frac{3k_{v}L_{1}^{2}}{-}$

Case 5			
Daughter size distribution, β	$rac{90L_i^2}{L_j^3}(rac{L_i^3}{L_j^3})^2(1-rac{L_i^3}{L_j^3})^2$		
Breakage rate, g	$C_1 \frac{\varepsilon^{\frac{1}{3}}}{(1+\phi)L_i^{\frac{2}{3}}} \exp\left(-C_2 \frac{\sigma(1+\phi)^2}{\rho_D \varepsilon^{2/3} L_i^{5/3}}\right)$		
Agglomeration, F	$C_{3} \frac{\varepsilon^{\frac{1}{3}}}{1+\phi} \left(L_{i}+L_{j}\right)^{2} \left(L_{i}^{\frac{2}{3}}+L_{j}^{\frac{2}{3}}\right)^{\frac{1}{2}} \exp\left(-C_{4} \frac{\mu_{C}\rho_{C}\varepsilon}{\sigma^{2}(1+\phi)^{3}} \left(\frac{L_{i}L_{j}}{L_{i}+L_{j}}\right)^{4}\right)$		
Growth rate, G	_		
Nucleation rate, <i>B_n</i>	_		

Table 3 Model parameters used in all the tested cases.

Parameters	Numerical value
A ₁	2.1e ⁻³
A_2	4.16e ⁻²
A_3	1.059e ⁻¹
A_4	1.12e ⁻⁵
A_5	1
A ₆	1.35e ²
A_7	1.78e ⁸
<i>C</i> ₁	2.47e ⁻¹

<i>C</i> ₂	7.8e ⁻²
<i>C</i> ₃	3.51e ⁻²
<i>C</i> ₄	1.33e ¹¹
k_1	2.7e ⁻⁴
k_g	1e ⁻⁶
g	6.5e ⁻¹
k_p	1e ⁻⁷
р	3.54

In the comparison between the analytical/ATS and the Gear's method for time integration, identical internal coordinate discretization was chosen with 20, 22, 45, 50, and 50 size categories for liquid-liquid extraction, ageing process, emulsion, patch crystallization and dissolution, respectively. These size categories were chosen so that the internal coordinate discretization is no longer a major source of numerical error, but the number of categories is still reasonable for practical simulations. The ode15s stiff solver of Matlab commercial software based on Gear's method was chosen as the preference for the ATS. In the following, brief descriptions of the different test cases are given.

3.1 Case 1: Ageing process of cellulose

Ageing of cellulose in viscose process carries out at ≈ 50 °C to decrease the degree of polymerization (DP) of cellulose polymers. The control of DP of alkali cellulose (cellulose mixture with alkali and water) is desired to achieve the desired quality of final viscose fiber. Temperature and ageing time are manipulated parameters when controlling the decrease in DP. In this selected process, the alkali cellulose (containing 34-35 % cellulose, 15-16 % alkali and remaining water) was processed under typical ageing conditions i.e. at 50 °C. The

observed changes in molecular weight distributions (MWD) of cellulose resulting from ageing reactions corresponds to decrease in DP. In ageing, the decrease in DP of cellulose may result from polymer scission from random positions by oxidation and hydrolysis reactions from the reducing ends of polymer. Due to fast nature of oxidation reactions and insignificant change in DP due to hydrolysis, phenomenon is modelled by assuming only random scission of polymer chain. A population balance model can be used to predict evolution of MWD of cellulose during ageing process as can be seen in the work of Ahmad et al. (2015). The only physical phenomenon in this case is breakage that embodies the decrease in DP in the process.

3.2 Case 2: Emulsification

Emulsification is highly viscous and turbulent system, operating under dilute conditions, mechanically mixed and typically in the presence of surfactants. Therefore the process is breakage dominant, meaning that the coalescence can be assumed to be negligible in the modelling, when CM is used. The PBE for this case is the Eq. (6) without vector **b**, which has an analytical solution. The case setup introduced by Becker et al. (2014) is used as a test example in this work. A system of silicone oil and water, with mechanically mixed Tween 20 emulsifier in 0.1 diameter and 2 L stirred tank. The axial-flow Mixel-TT impeller and 4 equally sized baffles were used to generate sufficient mechanical mixing in the tank. The operating conditions assumed in modelling are shown in Table 4.

Surface tension, μ [mN/m]	10.1
Energy dissipation rate, ε [W/kg]	0.2
Dispersed phase hold-up, $oldsymbol{\phi}$ [%]	0.5

Table 4 Operation conditions used in this work.

3.3 Case 3: Cooling crystallization

Batch cooling crystallization is a common separation process when the solubility of a chemical species greatly increases with the temperature. It is widely used in small production plant to produce small-volume, high-value-added chemicals. The control of crystal size distribution (CSD) has a considerable influence on the efficiency of the down-stream operations. The cooling crystallization process of citric acid-water system is modelled by considering nucleation, breakage and growth phenomena. Initially the unseeded system is supersaturated. The supersaturation, namely the driving force of the crystallization, is manipulated by controlling the cooling temperature profile. Decreasing the temperature results in lower solubility, as shown in the following supersaturation formulas:

$$S(t) = C_{Cit}(t) - C_{Cit}^{*}(t)$$
(23)

Where C_{Cit}^* is the current citric acid solubility in water and C_{Cit} the current citric acid concentration. The solubility is a function of temperature as follows:

$$C_{Cit}^{*}(t) = N_0 + N_1 T(t) + N_2 T(t)^2 + N_3 T(t)^3$$
(24)

The temperature profile introduced by Nyvlt et al. (1973) with different exponent value of d, is used in this work:

$$T(t) = T_{in} - \frac{(t/t_{total})^d}{(T_{in} - T_{final})}$$
(25)

The temperature profile from the Eq. (25) is concave, convex or linear depending on the value of exponent *d*. In the optimized batch crystallization process, the cooling profile is mainly convex or concave (Nývlt et al., 1973), swinging (King et al., 2015) or combination of those. Examples of different cooling temperature profiles with respect to the cooling time can be seen in Figure 2.



Figure 2 Different temperature profiles in cooling crystallization according to different values of d in Eq. (25) (concave & convex) and to swinging profile.

Both growth (B) and nucleation (G) rates are function of the supersaturation. The following rate function were assumed here (Nielsen, 1964):

$$B = k_p S(t)^p \tag{26}$$

$$G = k_a S(t)^g \tag{27}$$

where k_p , k_g , p, and g are model constant, which values are reported in Table 5. The concentration change of the citric acid in the liquid phase is calculated via material balance, and dictated by the nucleation and growth processes, as follows:

$$\frac{dC_{cit}}{dt} = -k_v \frac{\rho_\infty}{M} BL_0^3 - k_s \frac{\rho_\infty}{2M} Gm_2,$$
(28)

where the ρ_{∞} is the density of the continuous phase, M is molecular weight of the citric, m_2 is the second-order moment with respect to the crystal size, which is proportional to the interfacial area of the crystal size distribution (CSD). Other parameters used are shown in Table 5.

Because the temperature is known in each time step, with the ATS a time-averaged solubility (time cell centred value) is used:

$$\bar{C}^*_{Cit}(t_{n+1}) = \frac{C^*_{Cit}(t_{n+1}) + C^*_{Cit}(t_n)}{2}$$
(29)

Therefore, the supersaturation and the concentration in the ATS becomes:

$$S(t_{n+1}) = C_{Cit}(t_{n+1}) - \bar{C}^*_{Cit}(t_{n+1})$$
(30)

$$C_{Cit}(t_{n+1}) = C_{Cit}(t_n) + \left[-k_v \frac{\rho_{\infty}}{M} B L_0^3 - k_s \frac{\rho_{\infty}}{2M} G m_2\right] \Delta t_{n+1}$$
(31)

The Eq. (31) and the PBE for CSD are solved by using the ATS subsequently in same time step. The time difference in Eq. (17) and (31) is the same. In each time iteration: (1) supersaturation is calculated, (2) the breakage, growth, and nucleation rates are updated, and then (3) the population balance is solved. The physical properties and parameter used in this case are reported in Table 5.

Parameters	Numerical value	Parameters	Numerical value
<i>N</i> ₀ [° <i>C</i>]	0.91176	d[-]	0.2,0.1,1,5,10
$N_{1}[-]$	0.0034875	p[-]	3.54
$N_2[^\circ C^{-1}]$	-2.8785e-4	g[-]	0.65
$N_3[^\circ C^{-2}]$	3.7228e-6	$k_p[\#/m3s]$	1e7
$oldsymbol{ ho}_\infty$ [kg/m3]	1540	$k_g[m/s]$	1e-6
M [kg/mol]	0.19212	$L_0[m]$	1e-10
<i>Τ_{in}</i> [° <i>C</i>]	60	<i>x</i> ₀ [kg/kgH20]	0.989
$T_{final}[^{\circ}C]$	40	<i>C</i> _{0,<i>Cit</i>} [mol/m3]	$\frac{x_0}{M} ho_w$
t _{total} [s]	8000	k_v, k_s	$\frac{\pi}{6}$, π

Table 5 Physical properties and other parameters.

3.4 Case 4: Dissolution

As a widely used industrial application, the solid-liquid reactive dissolution process is chosen as the next test case to study the performance of the ATS technique. Magnesium hydroxide (Mg(OH)₂) solids particles are introduced into a hydrochloric acid (HCl) solution (Zhao et al., 2016), contained in a stirred tank reactor equipped with one Ruston Turbine impeller and four equally sized baffles. As in a batch operation, 2.5L HCl solution (pH \approx 1) was first mixed in the reactor at 25°C. When the temperature and pH achieved stable values, 10 grams of solids were rapidly added into the solution. The dissolution rate can be tracked by monitoring the concentration of magnesium ion and pH of samples taken at different times. The mass transfer is the rate limiting step, since the reaction between Mg(OH)₂(s) and HCl(aq) is instantaneous. In the electrolyte solution, the shrinking particle model coupled with Nernst-Planck equation is used to calculate the mass transfer fluxes and satisfy the electroneutrality simultaneously. Meanwhile, the dynamic mass transfer area can be accurately captured by tracking the evolution of particle size distribution (PSD) by means of the population balance model.

The reactive dissolution of Mg(OH)₂ solids in aqueous HCl solution can be expressed as:

$$Mg(OH)_2(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + 2H_2O.$$
(32)

As a rate-limiting step, the mass transfer rates of the components between the solid-liquid interface and bulk solution determine the reactive dissolution rate. The liquid phase mass balance equation is:

$$\frac{dn_p}{dt} = N_p A_p \tag{33}$$

Where p is the index of chemical components (Mg2+, H+, Cl-, OH-); n_p is the moles of components dissolved in the liquid phase; N_p is the mass transfer fluxes; A_p is the total solid-liquid mass transfer area. The solid-liquid mass transfer flux can be calculated as (Zhao et al., 2016):

$$N_p = k_{s,p} \Delta c_p - k_{s,p} z_p \bar{c}_p \left[\frac{\sum_p (z_p k_{s,p} \Delta c_p)}{\sum_p (z_p^2 k_{s,p} \bar{c}_p)} \right]$$
(34)

Where $k_{s,p}$ is the size dependent solid-liquid mass transfer coefficient; *z* are the charges of the cationic and anionic species; Δc_p and \bar{c}_p are the concentration difference and average concentration between the solid-liquid interface and the bulk solution respectively. The first term on the RHS of the Eq. (34) is the typical mass transfer flux, while the second term on the RHS is derived from the Nernst-Planck equation to preserve the electroneutrality of mass transfer flux during the dissolution of particles in the electrolyte solution.

In the bulk concentration calculations, the hydrazine and hydroxide water dissociation is taken into account, making the model stiff due to the fast dissociation reactions. Therefore, the ordinary differential equations for the bulk concentrations are integrated in time with the Gear's method (the MATLAB solver ode15s) within each ATS time step.

3.5 Case 5: Liquid-liquid extraction

One-compartment section in a pilot scale RDC extractor column presented by Buffo el al. (2016) for toluene-acetone-water (European Federation of Chemical Engineering test system) was chosen as the last test case. The compartment is considered to be well mixed. The operation conditions and other used parameters are shown in table 6 & 7.

Table 6 Operation conditions. (Test case 5)

Energy dissipation rate, ϵ [W/kg]	0.00075, 0.0015, 0.0035
Dispersed phase hold-up, ϕ [%]	5

Table 7 physical properties. (Test case 5)

Physical property	$ ho_c$ (kg/m ³)	ρ_d (kg/m ³)	η_c (10 ⁻³ kgm/s)	η_d (10 ⁻³ kgm/s)	σ (10 ⁻³ N/m)
Toluene-	992	863.3	1.134	0.566	24.41
acetone-water					

Binary breakage is assumed for the daughter size distribution. Six first moments are conserved constructing the size distribution tables, χ , β and F in Eq. (18), for breakage and agglomeration, respectively. The well known Coulaloglou and Tavlarides (1977) models are chosen for the breakage and coalescence closures. The empirically adjustable parameters, shown in Table 3, optimized by Jidleh et. al. (2015), are used in the modeling.

4 Results and discussion

The sectional method proposed by Alopaeus et al. (2006b) and in its multivariate form by Buffo and Alopaeus (2016a) are used in this work to discretize internal coordinate of the PBE in the process of deriving the analytical and ATS formulas. The sectional method with a high number of categories and very small tolerances of the time integrator (the MATLAB solver ode15s) is known to provide a solution that is very close to the real solution of the problem; therefore the results provided by this method are used to compare the results given by the analytical and the ATS formulas. All models in this work are implemented in MATLAB and run on a CPU *Intel Xeon E3-1230 v5 @ 3.4 GHz*.

4.1 Case 1: Ageing process of cellulose

In the ageing cellulose process, the time evolution of the molecular weight distribution is important to predict the degree of polymerization (DP) of cellulose polymers. In this case, the analytical formula presented in Eq. (16) can be used to evaluate the time needed to get a desired molecular weights. Figure 3 shows a comparison between the two different strategies to predict the time evolution of the distribution: analytical formula and the Gear's time integrator at different ageing times. As previously mentioned, after preliminary sensitivity tests we chose only 22 size categories. As it is possible to see, the distributions at different aging times, obtained with different numerical methods, are perfectly overlapping. However, this is expected, as the source terms in this case are linear and time invariant.

The analytical formula is able to provide the results in a fraction (6%) of the computational time compared to the numerical time integrator, for this particular test case, in which we are interested in the evolution of the PSD after long time.



Figure 3 The molecular weight distribution from the analytical formula and Gear's method calculation at different aging time for Case 1.

4.2 Case 2: Emulsification

In emulsification process, when the disperse phase is diluted and therefore the droplet coalescence can be neglected, the PBE has a pseudo-equilibrium solution, due to low breaking rates, that can be calculated from Eq. (16). The comparison between the volumetric droplet distributions from the analytical formula and Gear's method, with 45 size categories, is presented in Figure 4. As in the Case 1, the two methods give the same results. Both methods predict the formation of large number of small droplets caused by the breakage induced by turbulent fluctuations in the vessel. The droplet distribution is concentrated into small droplet sizes, unlike the wider initial distribution. Also in this case, the computational

time is significantly less by using the proposed method, which is 1 % of the the Gear's method.



Figure 4 The volumetric droplets distribution from analytical formula and Gear's method calculations for Case 2.

4.3 Case 3: Cooling crystallization

In this case, ATS based on the preliminary estimation of the cooling profile is implemented to provide an accurate and efficient solution for the PBM in order to optimize the batch cooling crystallization process. The cooling profile is chosen to be concave (d=5), convex (d=0.1), and swinging, as mentioned in the previous section. As the ATS requires a discretization of the time space, a uniform discretization scheme (noted here as A1) is first chosen. Figures 5-10 show that with 100 time steps the prediction of the concentration and volumetric CSD given by the ATS is very close to one given by the numerical time integrator

(Gear's method). In this case, we can consider the one given by the time integrator as a reference solution, since the tolerances adopted are very tight and the time stepping procedure used by Gear's method is adaptive. Therefore, if we define the relative error of the citric acid concentration between ATS and Gear's method predictions as follows:

Relative error
$$\theta(i) = \frac{|\phi_{Gear}(i) - \phi_{ATS}(i)|}{\phi_{Gear}(i)}$$
 (37)

with the index *i* indicating the *i*-th solution time step, it is possible to see in Figure 5 that the maximum relative error is around 1.45 % for the convex cooling profile. The maximum relative error for the other two cases (concave and swinging) are one order of magnitude smaller than the concave cooling profile, see Figure 7 and Figure 9. Local relative error is highest in the area where the absolute slope value of the citric acid concentration profile is high, indicating that a different choice of the time step in ATS is needed in the region where the gradient of concentration is large. Moreover, another way to quantify the difference between the ATS and the Gear's method is through the following definition:

The L² relative error norm =
$$\frac{\sum_{i}^{N} (\phi_{Gear}(i) - \phi_{ATS}(i))^{2}}{\sum_{i}^{N} \phi_{Gear}(i)^{2}}$$
(38)

where the index *i* may refer to the different time steps (in case of the time evolution of citric acid concentration) or to different size categories (in case of the volumetric CSD after 100 time steps).

The normalized sum of relative error (L2) for the different cooling profiles is reported in Table 8. As it is possible to note, the larger error for both acid concentration and volumetric CSD is obtained in the case of convex cooling.



Figure 5 Above: comparison between the time evolution of citric acid concentration for A1 time discretization for different time integration methodologies (Cooling parameter d = 0.1). Below: time evolution of the relative error (θ) between ATS and Gear's method defined in Eq. (37)



Figure 6 Comparison between ATS and Gear's method in terms of the volumetric crystal size distribution for A1 discretization (Cooling parameter d = 0.1).



Figure 7 Above: comparison between the time evolution of citric acid concentration for A1 time discretization for different time integration methodologies (Cooling parameter d = 5). Below: time evolution of the relative error (θ) between ATS and Gear's method defined in Eq. (37)



Figure 8 Comparison between ATS and Gear's method in terms of the volumetric crystal size distribution for A1 discretization (Cooling parameter d = 5).



Figure 9 Above: comparison between the time evolution of citric acid concentration for A1 time discretization for different time integration methodologies (swinging.). Below: time evolution of the relative error between (θ) ATS and Gear's method defined in Eq. (36)



Figure 10 Comparison between ATS and Gear's method in terms of the volumetric crystal size distribution for A1 discretization (swinging).

The effect of number of analytical time steps was further studied in the case showing largest errors, namely the convex cooling. The results in terms of time evolution of the citric acid concentration and volumetric CSD is reported in Figure 11-12. The strategy adopted to refine the time space discretization is the following (noted here as A2): we divided the whole time integration interval into two uniformly discretized subintervals, namely 96 steps between 0-40 min and only 4 steps between 40 and the final time (133 min). The maximum relative percentage error, for citric acid for convex cooling profile, is reduced from 1.45 % to 0.45 %, seen in Figure 5 and 11. Table 8 shows that the value of the normalized sum of relative error decreases from 0.0038 to 0.0017 for the citric acid concentration and from 0.2290 to 0.1232 for

the CSD. This indicates that the difference between ATS and Gear's method results get smaller by using A2 discretization scheme, in which the time interval is better refined.



Figure 11 Above: comparison between the time evolution of citric acid concentration for A2 time discretization for different time integration methodologies (Cooling parameter d = 0.1). Below: time evolution of the relative error (θ) between ATS and Gear's method defined in Eq. (37)



Figure 12 Comparison between ATS and Gear's method in terms of the volumetric crystal size distribution for A2 discretization (Cooling parameter d = 0.1).

Table 8 The normalized sum of relative error defined in Eq. (37) between ATS and Gear'	S
method for different simulations.	

Case	Concentration Citric acid [kmol/m3]	Volumetric crystal size distribution
A1, d =0.1	0.0038	0.2290
A1, d= 5	0.0017	0.1232
A1, swinging	0.0016	0.1853
A2, d =0.1	0.0020	0.0660

As far as the CPU time is concerned, the time needed to perform the simulations with the different methods is reported in Table 9. As one may notice, the ATS is two order of magnitude faster than the Gear's method. Moreover, the discretization A2 is not only more accurate comparing to the A1, but also faster.

Case	A2 discretization CPU time [s]	A1 discretization CPU time [s]	Gear's method CPU time [s]
d = 0.1	0.3	0.4	9.0
d = 5	-	0.2	11.2
swinging		0.3	10.5

Table 9 CPUs in cooling crystallization.

4.4 Case 4: Dissolution

As previously mentioned, a particle dissolution process can be modeled considering only the particle shrinkage and the particle breakage. In this case, in fact, the particle size distribution (PSD) shifts towards smaller sizes as time evolves. As in Case 3, firstly 100 equal-sized time steps are used to divide the whole time interval (denoted there as B1) in ATS. The size discretization was composed of 50 size categories for both ATS and Gear's method to make the results comparable.

By using the same as in the previous cases definitions for the relative error (Eq. 37) and the L2 norm error (Eq. 38), it is possible to observe that this case shows high relative errors for the magnesium concentration (see Figure 13), due to very low magnesium concentration at the beginning. However, the normalized sum of relative error is relatively moderate comparing to cooling crystallization case (see Table 5 and Table 8). Figure 13 shows that

both modeling results (from ATS and Gear's method) provide good predictions with respect to the experiment data, even though the main focus is on the comparison between different time integration methods and not on the model itself. Dividing the whole time integration into subintervals by using different strategies, as done in Case 3, can highlight the influence of the time discretization. ATS is predicting accurately the CSD at the last time step (see Figure 14) and pH evolution (see Figure 15), with low *L*2 errors reported in Table 8. The relative error in the pH prediction is highest in the region of high absolute slope.



Figure 13 Comparison between ATS, Gear's method and experiment in terms of magnesium concentration for B1 discretization.



Figure 14 Comparison between ATS and Gear's method in terms of the CSD for B1 discretization.



Figure 15 Above: comparison between ATS, Gear's method and experiment in terms of pH for B1 discretization. Below: time evolution of the relative error (θ) between ATS and Gear's method defined in Eq. (37)

For this test case, other two time-stepping strategies are investigated here: (1) geometric discretization (noted here as B2) of the type $t_{n+1} = 2^{1/q} t_n$ with q = 0.8, and (2) the time interval is divided into two uniformly divided intervals (noted here as B3), 96 steps between 0-200 min and only 4 steps between 200-600 min.

Table 7 shows high *L*2 errors for magnesium concentration, volumetric CSD, and pH predictions from B2 discretization comparing to B1 discretization. The difference between model predictions from ATS and Gear's method, shown in Figure 16-18, are larger than in B1 discretization (Figure 13-15). The reason of such behavior is due to the fact that the discrete

time interval from B2 scheme is coarser in the area where the slope of the pH profile is the highest (Figure 18), causing significant relative and *L*2 errors.



Figure 16 Comparison between ATS, Gear's method and experiment in terms of magnesium concentration for B2 discretization.



Figure 17 Comparison between ATS and Gear's method in terms of the CSD for B2 discretization.



Figure 18 Above: comparison between ATS, Gear's method and experiment in terms of pH for B2 discretization. Below: time evolution of the relative error (θ) between ATS and Gear's method defined in Eq. (37)

Figures 19-21 show that the relative errors are moderate with the B3 discretization scheme. For the CSD, as shown in Figures 19, the agreement between ATS and Gear's method predictions are very good. Overall, the *L*2 errors for the magnesium concentration and CSD are relatively low in B3 comparing to other discretization schemes, as shown in Table 10.



Figure 19 Comparison between ATS, Gear's method and experiment in terms of magnesium concentration for B3 discretization.



Figure 20 Comparison between ATS and Gear's method data in terms of the CSD for B3 discretization.



Figure 21 Above: comparison between ATS, Gear's method and experiment in terms of pH for B3 discretization. Below: time evolution of the relative error (θ) between ATS and Gear's method defined in Eq. (37)

The difference in terms of CPU times between ATS and Gear's method modelling are smaller in this reactive dissolution case than in cooling crystallization process. The main reason for this outcome can be found in the usage of Matlab ODE solver (ode15s) to solve the reactant mass balances in both ATS and and Gear's method. Table 11 shows that CPU time in all ATS discretization schemes are around the same, even though B3 is the slowest and the most accurate.

Case	Concentration	Volumetric crystal	рН [-]
	Magnesium [mol/m3]	size distribution [-]	
B1	0.0082	0.0036	0.0134
B2	0.0114	0.0259	0.0449
B3	0.0056	0.0015	0.0229

Table 10 The normalized sum of relative error between ATS and Gear's method.

Case	ATS CPU time [s]	Gear's method CPU time [s]
B1	6.4	9.3
B2	5.5	9.3
B3	7.7	9.3

4.5 Case 5. Liquid-liquid extraction

In this last practical test case, the ATS is applied to solve population balance equation with both breakage and agglomeration. In this case, the agglomeration term is linearized with respect to number density (**Y**). It is well known that generally linear approximation for a particular nonlinear function (f (**Y**)) is sufficiently accurate only near the linearization point of interest (**Y**= Y_o). Moreover, in this case the point of interest, i.e. the number density in the previous time step, is not constant but changing with respect to time during the solution of the PBE. Thus, in every time iteration the point of interest is getting closer to final linearized point.

As previously showed for other test cases, our aim is to compare the results obtained with the ATS with the Gear's method, using the results of Gear's method as reference. The effect of the linear approximation on PSD and especially on Sauter mean diameter is investigated here for a liquid-liquid extraction system. The chosen operating condition parameters are shown in Table 6.







Figure 23 The Sauter mean diameter from the Gear's method and ATS simulation at different energy dissipation rates.

Figures 22 and 23 show the initial and final distributions and Sauter diameters evolution for liquid-liquid extraction system in different operation conditions, respectively. The volume fraction of the dispersed phase is kept constant (5%), but different energy dissipation rate values ($\varepsilon = 0.00075$ W/kg, 0.0015 W/kg, 0.0035 W/kg) were used. Identical size discretization methods with 20 categories were chosen for both ATS and Gear's method. Correspondingly, unlike in the previous cases in this case the discrete time interval from automatic time discretization schemes of Gear's method were saved and used in the ATS modeling, so the two methods are comparable. Figures 22 and 23 show that with identical time and size discretization PSD and Sauter mean diameter evolution results from ATS and Gear's method are equally accurate. The results indicate that the time-steps adopted in the ATS procedure are small enough to minimize error caused by the linearization approximation. It is well known, that reasonable approximation with the explicit method requires relatively small time-steps. Therefore, two coarse discrete time intervals (G2 and G3) are compared with the one (G1) used in the Figures 22 and 23. The G1 time discretization is from adaptive Gear's method, where the number of time-steps for the G2 is half of the one in G1 and in the G3 it is half of the one in G2, see Figures 24. The operating condition is exactly the in Figures 22 and 23, except the energy dissipation rate is kept constant ($\varepsilon = 0.0015$ W/kg) and different discrete time intervals are employed (G1, G2 and G3).



Figure 24 The Sauter mean diameter evolution from the Gear's method and ATS simulation and the corresponding time steps with different discrete time intervals.

For the three different discrete time intervals (G1, G2 and G3), the simulation results are shown in Figure 24. One can see that Sauter mean diameters evolution fist increase rapidly and then level off, due to droplet agglomeration process. Good predictions were achieved for G1, G2, and G3 discrete time intervals with relative deviations of 0.085%, 0.17% and 0.35%, respectively, with respect to Gear's method. Although, the number of time-steps and computational time in G3 are a one-quarter and 50% of the one in the G1 respectively, the relative deviation between the Sauter mean diameters results from these two is less than 0.3%.

5 Conclusion

As the accuracy of the measurement techniques in multiphase systems are developing, increasingly more phenomenological models are validated to predict underlying complex physics. Thus, the role of the PBE in modelling of particulate systems has become very important. Although numerical techniques for discretizing internal coordinate of the PBE have been studied heavily in the literature, time integration options have received much less attention, although they affect to the computational time and accuracy determining the quality of the numerical method.

A novel analytical time stepping method is presented in this work to evaluate the variation in time of the discretized PBE. These time-advancing methods are here tested numerically for a number of well-mixed systems. Practical examples from chemical engineering e.g. cellulose aging process, emulsification, cooling crystallization, reactive dissolution, and liquid-liquid extraction are chosen as test cases for the presented methods. As the results show, the proposed methods are capable of predicting the time evolution of the particle size distribution for a wide range of chemical engineering processes, showing very similar results compared to the standard numerical time integrators. Our method is effective and precise for breakage and agglomeration processes, where the details of the breakage mechanisms do not depend on the time. On the other hand, fewer and longer time steps are required for ATS to model accurately more complex processes with time depending mechanisms, namely growth and nucleation as in cooling crystallization or reactive dissolution. The CPU times in ATS comparing to Gear's method are faster for all test cases. This is a remarkable result, since the speed and accuracy of the modeling approach are crucial to contain the computational costs, and this is particularly true for the modeling of complex multiphase systems.

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6 Nomenclature

<i>A</i> ₁₋₅	constants in breakage model, dimensionless [-]
Atot	total mass transfer area, [m ²]
В	nucleation rate, [1/ m ⁴ s]
С	concentration, $[mol/m^3]$
С*	solubility, [mol/m ³]
F	agglomeration rate between particles of size λ and <i>L</i> , [m ³ /s]
g	breakage rate, [1/s]
G	growth rate, [m/s]
k_g	crystal growth rate constant, [m/(s (kg=kg)g)]
k_p	primary nucleation rate constant, [#/((kg=kg)p kg H2O s)]
ks	Surface shape factor, [-]
k_{ν}	volume shape factor, [-]
Ksp	solubility product, [mol ³ /m ⁹]
L	internal coordinate (particle size), [m]
L ₀	characteristic crystal length of a newly formed [m]
m_k	k- th moment of the PSD, $[1/m^{k-3}]$
М	molecular weight, [kg/mol]
n	density of particle size distribution, $[\#/m^4]$
Ν	mass transfer flux, [mol/(m ² s)]
N ₀	zero order solubility constant, [kg/(kg H2O)]
<i>N</i> ₁	first order solubility constant, [kg/(kg H2O °C)]
<i>N</i> ₂	second order solubility constant, [kg/(kg H2O °C2)]
<i>N</i> ₃	third order solubility constant, [kg/(kg H20 °C3)]
NC	total number of categories, [-]
S	supersaturation, $[mol/m^3]$

t	time, [s]
Т	temperature, [°C]
Vm	molar volume of solid, [m ³ /mol]
Y	particle number density, [#/m ³]
Ζ	charge of the cationic and anionic, [-]

Greek letters

β	daughter particle size distribution; probability that a particle of size Li is born when Lj breaks, $[1/m]$
λ	Internal coordinate (particle size), [m]
ξ	growth distribution: a table that determines the distribution to category of size L_i due to growth of particle of size L_j , [-]
X	coalescence product distribution table, [-]
ρ	density, [kg m^3]
σ	surface tension, [N m ⁻¹]
ψ	distribution of primary nucleates, [-]
ε	energy dissipation rate[W kg ⁻¹]
μ	viscosity [kg m ⁻¹ s ⁻¹]
Н	Kolmogorov length scale, [m]
$\eta_{ m T}$	Kolmogorov time scale, [s]
θ	Relative error, [-]

Superscripts

G	crystal growth rate exponent, dimensionless
Р	primary nucleation rate exponent, dimensionless
D	exponent for controlled cooling expression

Subscripts

Cit	Citric acid
in	Initial
d	dispersed phase
c	continuous phase
i, j	Indices of particle size category

Abbreviations

MOM	method of moments
MC	method of classes
QMOM	quadrature method of moments
DQMOM	direct quadrature method of moments
CQMOM	conditional quadrature method of moments
PSD	particle size distribution
PBE	population balance Eq.
НММС	higher order moment conserving method of classes
NDF	number density function
SMOM	sectional quadrature method of moments

7 References

- Ahmad, W., Kuitunen, S., Sixta, H., Alopaeus, V., 2015. Population balance based modeling of changes in cellulose molecular weight distribution during ageing. Cellulose 22, 151– 163.
- Alopaeus, V., Koskinen, J., Keskinen, K.I., 1999. Simulation of the population balances for liquid-liquid systems in a nonideal stirred tank. Part 1 Description and qualitative validation of the model. Chemical Engineering Science 54, 5887–5899.
- Alopaeus, V., Laakkonen, M., Aittamaa, J., 2006a. Numerical solution of moment-transformed population balance equation with fixed quadrature points. Chemical Engineering Science 61, 4919–4929.
- Alopaeus, V., Laakkonen, M., Aittamaa, J., 2006b. Solution of population balances with breakage and agglomeration by high-order moment-conserving method of classes. Chemical Engineering Science 61, 6732–6752.
- Alopaeus, V., Laakkonen, M., Aittamaa, J., 2007. Solution of population balances with growth and nucleation by high order moment-conserving method of classes. Chemical Engineering Science 62, 2277–2289.
- Alopaeus, V., 2014. Analysis of concentration polydispersity in mixed liquid–liquid systems. Chemical Engineering Research and Design 92, 612-618.
- Attarakih, M., Drumm, C., Bart, H., 2009. Solution of the population balance Eq. using the sectional quadrature method of moments (SQMOM). Chemical Engineering Science 209–214.
- Attarakih, M.M., Bart, H.J., Faqir, N.M., 2006. Numerical solution of the bivariate population balance Eq. for the interacting hydrodynamics and mass transfer in liquid-liquid extraction columns, in: Chemical Engineering Science. pp. 113–123.

- Becker, J., Puel, F., Jakobsen, H.A., Sheibat-Othman, N., 2014a. Development of an improved breakage kernel for high dispersed viscosity phase emulsification. Chemical Engineering Science 109, 326–338.
- Bhaskarwar, A.N., 1989. General population balance model of dissolution of polydisperse particles. AIChE Journal 35, 658–661.
- Bohlin, M., Rasmuson, A.C., 1992. Application of controlled cooling and seeding in batch crystallization. The Canadian Journal of Chemical Engineering 70, 120–126.
- Buffo, A., Alopaeus, V., 2016a. Solution of bivariate population balance equation with highorder moment-conserving method of classes. Computers and Chemical Engineering 87, 111–124.
- Buffo, A., Jama, M. A., Alopaeus, V., 2016b. Liquid–liquid extraction in a rotating disc column: Solution of 2D population balance with HMMC. Chemical Engineering Research and Design 115, Part B, 270-281.
- Buffo, A., Vanni, M., Marchisio, D.L., 2012. Multidimensional population balance model for the simulation of turbulent gas-liquid systems in stirred tank reactors. Chemical Engineering Science 70, 31–44.
- Chen, X. Z., Luo, Z. H., Yan, W. C., Lu, Y. H., & Ng, I-S. (2011). Three-dimensional CFD-PBM coupled model of the temperature fields in fluidized-bed polymerization reactors. *AIChE Journal*, *57*(12), 3351-3366.
- Choong, K.L., Smith, R., 2004. Optimization of batch cooling crystallization. Chemical Engineering Science 59, 313–327.
- Chung, S.H., Ma, D.L., Braatz, R.D., 1999. Optimal seeding in batch crystallization. The Canadian Journal of Chemical Engineering 77, 590–596.
- Coulaloglou, C. A., & Tavlarides, L. L. (1977). Description of interaction processes in agitated liquid-liquid dispersions. Chemical Engineering Science, 32(11), 1289-1297.
- Courant, R.; Hilbert, D., 1962. Methods of Mathematical Physics, Vol. 2, Wiley: New York, NY

- De Bona, J., Buffo, A., Vanni, M., Marchisio, D.L., 2016. Limitations of simple mass transfer models in polydisperse liquid-liquid dispersions. Chemical Engineering Journal 296, 112-121.
- Dorao, C. A., Jakobsen, H.A., A least square method for the solution of population balance problems, Comput. Chem. Eng. 30 (2006) 535–547.
- Fox, R.O., Laurent, F., Massot, M., 2008. Numerical simulation of spray coalescence in an Eulerian framework: Direct quadrature method of moments and multi-fluid method. Journal of Computational Physics 227, 3058–3088.
- Gao, Z., Li, D., Buffo, A., Podgorska, W., Marchisio, D.L., 2016. Simulation of droplet breakage in turbulent liquid-liquid dispersions with CFD-PBM: Comparison of breakage kernels. Chemical Engineering Science 142, 277–288.
- Gear, C. W., 1969. The automatic integration of stiff ordinary differential equations. Information Processing 68, A. J. H. Morrell, Ed., North Holland, Amsterdam, 187-193
- Genck, W.J., D'Aquino, R.L., 2000. Better growth in batch crystallizers. Chemical Engineering (New York) 107, 90–95.
- Jildeh, B. Hanin, 2015, Liquid-Liquid Extraction Columns: Parameter Estimation, PhD thesis, Vom Fachbereich Maschinenbau und Verfahrenstechnik der Technischen Universität Kaiserslautern
- Jones, A.G., Mullin, J.W., 1974. Programmed cooling crystallization of potassium sulphate solutions. Chemical Engineering Science 29, 105–118.
- King, J.C., Li, H., Grover, M.A., Kawajiri, Y., Rousseau, R.W., 2015. Optimization of two-stage cooling profile in unseeded batch crystallization, in: IFAC-PapersOnLine. 297–302.
- Kostoglou M. and Karabelas A.J., 2004. "Optimal low order methods of moments for solving the fragmentation equation". Powder Technology 143-144, 280-290.
- Kostoglou M., 2007. "Extended cell average technique for the solution of coagulation equation" Journal of Colloid and Interface Science 306,72-81.

- Kostoglou, M. and Karabelas, A.J., 2009. "On sectional techniques for the solution of the breakage equation" Computers and Chemical Engineering 33, 112-121.
- Kumar, S., Ramkrishna, D., 1997. On the solution of population balance Eq.s by discretization
 III. Nucleation, growth and aggregation of particles. Chemical Engineering Science 52, 4659–4679.
- Kumar, S., Ramkrishna, D., 1996. On the solution of population balance Eq.s by discretization—I. A fixed pivot technique. Chemical Engineering Science 51, 1311–1332.
- Laakkonen, M., Moilanen, P., Alopaeus, V., Aittamaa, J., 2007. Modelling local bubble size distributions in agitated vessels. Chemical Engineering Science 62, 721–740.
- Lage, P L C., 2002. Comments on the "An analytical solution to the population balance Eq. with coalescence and breakage—the special case with constant number of particles" by DP Patil and JRG Andrews [Chemical Engineering Science 53 (3) 599–601]. Chemical Engineering Science 57 (19), 4253-4254
- Leblanc, S.E., Fogler, H.S., 1987. Population balance modeling of the dissolution of polydisperse solids: Rate limiting regimes. AIChE Journal 33, 54–63.
- Ma, C.Y., Wang, X.Z., Roberts, K:J., 2008. Morphological population balance for modeling crystal growth in face directions. AIChE Journal. 54, 209-222.
- Ma, D.L., Tafti, D.K., Braatz, R.D., 2002. Optimal control and simulation of multidimensional crystallization processes. Computers & Chemical Engineering 26, 1103–1116.
- Marchisio, D.L., Fox, R.O., 2005. Solution of population balance Eq.s using the direct quadrature method of moments. Journal of Aerosol Science 36, 43–73.
- Marchisio, D.L., Vigil, R.D., Fox, R.O., 2003a. Implementation of the quadrature method of moments in CFD codes for aggregation breakage problems. Chemical Engineering Science 58, 3337–3351.
- Marchisio, D.L., Vigil, R.D., Fox, R.O., 2003b. Quadrature method of moments for aggregationbreakage processes. Journal of Colloid and Interface Science 258, 322–334.

- McCoy, B., Madras, G., 2003. Analytical solution for a population balance Eq. with aggregation and fragmentation. Chemical Engineering Science 58, 3049–3051.
- McGraw, R. (1997). Description of aerosol dynamics by the quadrature method of moments. Aerosol Science and Technology, 27(2), 255–265.
- Mullin, J.W., Nývlt, J., 1971. Programmed cooling of batch crystallizers. Chemical Engineering Science 26, 369–377.
- Nauha, E. K., Alopaeus, A., Modeling method for combining fluid dynamics and algal growth in a bubble column photobioreactor. Chem. Eng. J., 229 (2013), pp. 559-568.
- Nauha, E.K., Kálal, Z., Jama, M.A., Alopaeus, V., 2018. Compartmental modeling of large stirred tank bioreactors with high gas volume fractions Chemical Engineering Journal 334, 2319-2334.
- Nguyen, T.T., Laurent, F., Fox, R.O., Massot, M., 2016. Solution of population balance Eq.s in applications with fine particles: Mathematical modeling and numerical schemes. Journal of Computational Physics 325, 129–156.
- Nielsen, A., 1964. Kinetics of precipitation, 1st ed. Pergamon Press, Oxford.
- Nopens, I., Torfs, E., Ducoste, J., Vanrolleghem, P.A., Gernaey, K. V., 2015. Population balance models: A useful complementary modelling framework for future WWTP modelling. Water Science and Technology 71, 159–167.
- Nývlt, J., Kočová, H., Černý, M., 1973. Size distribution of crystals from a batch crystallizer. Collection of Czechoslovak Chemical Communications 38, 3199–3209.
- Patil, D.P., Andrews, J.R.G., 1998. An analytical solution to continuous population balance model describing floc coalescence and breakage - A special case. Chemical Engineering Science 53, 599–601.
- Petitti, M., Vanni, M., Marchisio, D.L., Buffo, A., Podenzani, F., 2013. Simulation of coalescence, break-up and mass transfer in a gas-liquid stirred tank with CQMOM. Chemical Engineering Journal 228, 1182–1194.

- Puel, F., Févotte, G., Klein, J.P., 2003. Simulation and analysis of industrial crystallization processes through multidimensional population balance Eq.s. Part 2: A study of semibatch crystallization. Chemical Engineering Science 58, 3729–3740.
- Qamar, S., Elsner, M.P., Angelov, I.A., Warnecke, G., Seidel-Morgenstern, A., 2006. A comparative study of high resolution schemes for solving population balances in crystallization. Computers and Chemical Engineering 30, 1119–1131.
- Rhee, H.-K., Aris, R., Amundson, N. R., First-Order Partial Differential Eq.s: Vol. Z. Theory and Applications of Single Eq.s; Prentice-Hall: Englewood Cliffs, NJ, 1986.
- Smith M, Matsoukas T., 1998. Constant-number Monte Carlo simulation of population balances. Chemical Engineering Science 53(9), 1777–1786.
- Zhao, H., Maisels, A., Matsoukas, T., Zheng, C., 2007. Analysis of four Monte Carlo methods for the solution of population balances in dispersed systems. Powder Technology 173, 38-50.
- Zhao, W., Han, B., Jakobsson, K., Louhi-Kultanen, M., Alopaeus, V., 2016. Mathematical model of precipitation of magnesium carbonate with carbon dioxide from the magnesium hydroxide slurry. Computers and Chemical Engineering 87, 180–189.
- Zhao, W., Jama, M.A., Buffo, A., Alopaeus, V., 2018. Population balance model and experimental validation for reactive dissolution of particle agglomerates. Comput. Chem. Eng. 108, 240–249.