

TURBULENCE-CHEMISTRY INTERACTIONS IN REACTIVE FLOWS WITH PARTICLE FORMATION

Stelios Rigopoulos

School of Mechanical, Aerospace and Civil Engineering,
The University of Manchester,
PO Box 88, Sackville Street,
Manchester M60 1QD, UK
stelios.rigopoulos@manchester.ac.uk

ABSTRACT

This paper discusses phenomena resulting from the interaction of turbulent flow, chemical species transport and particle formation encountered in problems such as soot formation and precipitation from solution. Such problems must be described by a combination of Navier-Stokes equations, scalar transport and reaction, and population balance equations (PBE) for the polydispersed particle phase. The latter was originally studied in a homogeneous environment, and first attempts at simulating flow problems with it assumed a straightforward coupling accomplished through conventional turbulence models within CFD codes. It is shown that this coupling gives rise to complex non-linear interactions resulting in terms that are unclosed under Reynolds averaging. Subsequently, a transported pdf formulation of the problem is proposed that overcomes these closure problems.

INTRODUCTION

The formation of a particulate phase through reaction in a gaseous or liquid environment is an important problem, both from the scientific and the applied point of view. Relevant industrial problems include the formation of soot particles in combustion engines (whose mitigation is an important environmental problem), of industrial nanoparticles via flame synthesis, and the precipitation of crystalline products in liquid-phase reactors.

For polydispersed particulates, the particle size distribution (PSD) essentially enters the analysis, both because it is an important property of the final product and because it is an essential variable of the model, on which important processes such as the growth rate depend. The PSD is described by the number density, $N(\varphi_1, \varphi_2, \dots, \varphi_k)$, where the φ_k variables describe the state of the particle (size, surface area etc. – in this work we shall use only particle volume, v), and N is the number of particles lying within a differentially small increment of φ_k per unit of φ_k .

Initially studies of polydispersed aerosols studied the PBE on its own; it was assumed that the hydrodynamic and chemical environment would be homogenised via intense turbulence. Most particulate processes, however, occur within a strongly heterogeneous environment. The coupling between the PBE and the equations of fluid dynamics and scalar advection has started to be explored relatively recently.

Most computational studies so far have sought to combine the PBE with a commercial CFD code. Such approaches proceed through discretising the PBE in the particle size domain, and subsequently treat the resulting equations for the discretised variables as additional scalars in the CFD code. While this approach seems intuitive and is indeed correct in a laminar flow, in a turbulent flow the coupling of turbulence, scalar transport/reaction and particle formation gives rise to several unique problems, as will be demonstrated below.

Early works (Drake, 1972; Friedlander, 2000) identified the need for closure in the PBE (or General Dynamic Equation, GDE, in the aerosol literature) in turbulent flows; however, no steps were taken at the time and it remained an unresolved problem. More recently, Baldyga and Orciuch (1997) employed a moment transformation of the PSD in conjunction with a presumed-shape pdf of the chemical species. Other researchers have pursued closure via transporting the joint species-moments pdf (Kollmann et al., 1994); and the Direct Quadrature Method of Moments (McGraw, 1994). Methods of moments proceed by means of an integral transformation of the PSD and predict its moments, which correspond to physical properties such as total number and mass.

In this work we attempt a full PDF closure of the equation. We do this introducing the joint pdf of both reactive scalars and particle number density and deriving a transport equation for it. It will be demonstrated that this approach overcomes the need for closure of the nucleation/growth terms, as well as being able to predict the full PSD. On the other hand, introduces a number of additional independent variables. However the problem is still tractable by means of a Monte-Carlo method. The objective of this paper is to formulate the pdf equations and demonstrate the existence and extent of the fluctuations induced.

REYNOLDS AVERAGING OF THE POPULATION BALANCE EQUATION

Let us assume that a turbulent flow is advecting several chemically reactive species, with potential to form a polydispersed aerosol. To view the problem in its simplest form we will assume incompressibility, no heat release (therefore no thermochemical coupling), uniform transport

properties and that the particles are small enough to follow the flow without differential drag force effects. Simplified though it may seem, this formulation can nevertheless describe practical problems such as the precipitation of solid particles in a liquid solution, a process used in the manufacture of crystalline products and pharmaceuticals. The basic equations are:

$$\nabla \cdot \mathbf{u} = 0 \quad (1)$$

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho(\mathbf{u} \cdot \nabla) \mathbf{u} = \mu \nabla^2 \mathbf{u} - \nabla P \quad (2)$$

$$\frac{\partial Y_a}{\partial t} + \nabla(\mathbf{u} \cdot Y_a) = D \nabla^2 Y_a + \dot{w}(Y_1, Y_2, \dots, Y_m) \quad (3)$$

This is the species transport equation, where Y_i denotes the chemical species' mass fractions while the last term is the reaction source. Finally, we have the population balance equation (PBE), written as:

$$\begin{aligned} & \frac{\partial N(\nu; \mathbf{x}, t)}{\partial t} + \nabla(\mathbf{u} \cdot N(\nu; \mathbf{x}, t)) + \\ & + \frac{\partial}{\partial \nu} (G(Y_1, Y_2, \dots, Y_m, \nu) \cdot N(\nu; \mathbf{x}, t)) = \\ & = D_p \nabla^2 N(\nu; \mathbf{x}, t) + B(Y_1, Y_2, \dots, Y_m, \nu) \cdot \delta(\nu - \nu_0) \end{aligned} \quad (4)$$

This is a transport equation for particle number density, $N(\nu; \mathbf{x}, t)$. As the particles are polydispersed, a measure of particle size is required and here we are using the particle volume, ν ; alternatively, mass can be also used, assuming uniform particle density. (Note that the use of a linear measure, such as diameter or radius, is not recommended for problems involving aggregation, which is a mass/volume conserving process, and while we will not study aggregation here, the approach to be developed anticipates application to aggregation processes). In a non-homogeneous hydrodynamic environment, number density is also going to be a field variable of space and time. Thus all \mathbf{x} , t and ν are dimensions of N , the first two denoting physical space/time, the last one phase space. Higher dimensional phase spaces have also been employed (to denote e.g. surface area or structure of particles) but for simplicity we will deal here with an 1-D phase space. Integration over the phase space yields the concentration of particles at any point in space/time (first moment):

$$M(\mathbf{x}, t) = \int_{\nu_0}^{\infty} N(\nu; \mathbf{x}, t) d\nu \quad (5)$$

For non-aggregating (or breaking) particles, the main processes affecting number density are:

- Convection/diffusion in physical space.
- Transport in phase space by means of growth or size reduction (e.g. particle growth via surface reactions, droplet condensation). This term is placed on the lhs of the PBE as it is of a convective nature (first-order derivative with respect to particle size). Growth rate is typically a function of the local composition, as the solution or vapour must be supersaturated to induce growth. It is also a function of the particle volume.
- Nucleation, which contributes a source of particles at the nuclei size, ν_0 . Like growth it is expressed by a

function of the local concentration/mass fractions; furthermore it is represented by a delta function because it contributes particles only at ν_0 .

This equation has been studied extensively in the literature assuming a homogeneous environment, where $N=N(\nu; t)$, or, more recently, in laminar flows. In a turbulent flow, however, $N(\nu; \mathbf{x}, t)$ is going to be a random variable, like everything else. If this randomness were due to the advection/diffusion processes alone, it could be treated by a straightforward extension of the techniques employed for scalar transport. More careful examination, however, reveals that it is not so.

The Reynolds decomposition of the number density is:

$$N(\nu, \mathbf{x}, t) = \langle N(\nu, \mathbf{x}, t) \rangle + N'(\nu, \mathbf{x}, t) \quad (6)$$

Let us now perform the Reynolds averaging on the PBE. Note that, in the interest of brevity, the spatial/temporal dependency of the number density will not be explicitly written from now on.

$$\begin{aligned} & \left\langle \frac{\partial N}{\partial t} \right\rangle + \langle \nabla(\mathbf{u} \cdot N) \rangle + \\ & + \left\langle \frac{\partial}{\partial \nu} (G(Y_1, Y_2, \dots, Y_m, \nu) \cdot N) \right\rangle = \\ & = \langle D_p \nabla^2 N \rangle + \langle B(Y_1, Y_2, \dots, Y_m, \nu) \cdot \delta(\nu - \nu_0) \rangle \end{aligned} \quad (7)$$

The first term needs no further treatment:

$$\left\langle \frac{\partial N}{\partial t} \right\rangle = \frac{\partial \langle N \rangle}{\partial t} \quad (8)$$

The second term, representing advection in physical space, gives rise to non-zero correlations, as we see below:

$$\begin{aligned} \langle \nabla(\mathbf{u} \cdot N) \rangle &= \nabla \langle (\langle \mathbf{u} \rangle + \mathbf{u}') \cdot (\langle N \rangle + N') \rangle = \\ &= \nabla(\langle \mathbf{u} \rangle \cdot \langle N \rangle) + \nabla \langle \mathbf{u}' \cdot N' \rangle \end{aligned} \quad (9)$$

Assuming that the particles are small and of zero inertia, this term can be treated in a manner similar to passive scalar advection, i.e. by the introduction of an eddy diffusivity:

$$\nabla \langle \mathbf{u}' \cdot N' \rangle = -\nu_p \nabla \langle N \rangle \quad (10)$$

The term representing particle diffusion can also be dealt with in a straightforward manner:

$$\langle D_p \nabla^2 N \rangle = D_p \nabla^2 \langle N \rangle \quad (11)$$

Coming to the growth term, if there is no dependency on the local species' mass fractions then there is no closure problem, as can be readily seen:

$$\begin{aligned} & \left\langle \frac{\partial}{\partial \nu} (G(\nu) \cdot N) \right\rangle = \\ & = \left\langle \frac{\partial}{\partial \nu} [G(\nu) \cdot (\langle N \rangle + N')] \right\rangle = \\ & = \langle N \rangle \cdot \frac{\partial G(\nu)}{\partial \nu} + G(\nu) \cdot \frac{\partial \langle N \rangle}{\partial \nu} \end{aligned} \quad (12)$$

Usually, however, growth depends on the local values of the reactive scalars. Two cases can now be identified:

- i) Size-independent growth with environment dependence. Size-independent growth can be physically possible when a linear measure of particle size is employed, under an assumption sometimes made in crystallization

processes known as McCabe's rule. If particle volume is employed, it can be easily seen that linear size-independent growth is volume-dependent (as $v \approx l^3$). Assume only one reactive scalar for simplicity:

$$\begin{aligned} \left\langle \frac{\partial}{\partial v} (G(Y) \cdot N) \right\rangle &= \quad (13) \\ &= \left\langle \frac{\partial}{\partial v} [G(\langle Y \rangle + Y') \cdot (\langle N \rangle + N')] \right\rangle \end{aligned}$$

The nature of the problem is similar to that encountered in turbulent reactive flows. Growth is usually a non-linear function of the scalars, so

$$\langle G(\langle Y \rangle + Y') \rangle \neq G(\langle Y \rangle) + \langle G(Y') \rangle \quad (14)$$

Thus:

$$\begin{aligned} \left\langle \frac{\partial}{\partial v} (G(Y) \cdot N) \right\rangle &= \left\langle \frac{\partial}{\partial v} (G(Y) \cdot (\langle N \rangle + N')) \right\rangle = \quad (15) \\ &= \langle N \rangle \cdot \left\langle \frac{\partial G(Y)}{\partial v} \right\rangle + \left\langle \frac{\partial G(Y)}{\partial v} \cdot N' \right\rangle \end{aligned}$$

Both terms would require a closure hypothesis, as there is no straightforward way of computing $\langle G(Y) \rangle$, let alone the correlation $\langle G(Y) \cdot N' \rangle$.

ii) Size-dependent growth with environmental dependence. This is the most complex case. Proceeding as before:

$$\begin{aligned} \left\langle \frac{\partial}{\partial v} (G(v, Y) \cdot N) \right\rangle &= \\ &= \left\langle \frac{\partial G(v, Y)}{\partial v} \cdot (\langle N \rangle + N') \right\rangle + \left\langle \frac{\partial (\langle N \rangle + N')}{\partial v} \cdot G(v, Y) \right\rangle = \\ &= \langle N \rangle \cdot \left\langle \frac{\partial G(v, Y)}{\partial v} \right\rangle + \left\langle \frac{\partial G(v, Y)}{\partial v} \cdot N' \right\rangle + \\ &+ \frac{\partial \langle N \rangle}{\partial v} \cdot \langle G(v, Y) \rangle + \left\langle \frac{\partial N'}{\partial v} \cdot G(v, Y) \right\rangle \quad (16) \end{aligned}$$

Once again, all terms require closure and there is no straightforward way of providing it.

The nucleation rate, in general, depends on the environment. This term can be written as:

$$\langle B(Y) \cdot \delta(v - v_0) \rangle = \langle B(Y) \rangle \cdot \delta(v - v_0) \quad (17)$$

The nucleation rate is usually a strongly non-linear function of the local concentrations. Especially in soot modelling, nucleation rates can assume very complex functional forms. Clearly the term cannot be elaborated any further, as the term $\langle B(Y) \rangle$ needs closure.

PDF FORMULATION

The previous section has clearly demonstrated that application of Reynolds averaging to the equations of particle formation/coagulation in turbulent flow results in a multitude of unclosed terms, which there is no straightforward way to model. In this section we will derive a PDF formulation for turbulent reactive flow with particle

formation, and show that these terms are naturally closed under this viewpoint.

Suppose that a reactive mixture of species with mass fractions Y_a and particles of various sizes – the measure of particle size used here is particle volume, v_i – characterised by a number density N with values $N(v_i)$ at each v_i , is present in a turbulent flow field. We would like to define the pdf of number density. To do this, it is necessary to determine whether the pdf will correspond to one or many values of the particle size. If only one-size pdfs were to be predicted, we would have no way of estimating the expected PSD at any point, for we would not know the correlation between number densities of different sizes. Therefore, we introduce the joint pdf of reactive scalars and particle number density at all sizes:

$$Y(\mathbf{x}, t) N(v_i, \mathbf{x}, t) \rightarrow f(y_1, y_2, \dots, y_m, n_1, n_2, \dots, n_n; \mathbf{x}, t) \quad (18)$$

The transport equation for the pdf will be derived by means of the fine-grained density, a concept introduced by Lundgren (1967):

$$F = \prod_{a=1}^M \delta(Y_a - y_a) \cdot \prod_{i=1}^N \delta(N_i - n_i) \quad (19)$$

The fine-grained density can be interpreted as the probability that, in a particular realisation of the flow, the scalars and number densities will assume values around y_a and n_i , respectively. The pdf is then obtained by ensemble averaging the fine-grained density:

$$f = \langle F \rangle \quad (20)$$

The transport equation we seek can, therefore, be obtained by taking the time derivative of the fine-grained density and subsequently averaging. The first step yields:

$$\frac{\partial F}{\partial t} = - \sum_{a=1}^M \frac{\partial F}{\partial y_a} \frac{\partial Y_a}{\partial t} - \sum_{i=1}^N \frac{\partial F}{\partial n_i} \frac{\partial N_i}{\partial t} \quad (21)$$

To proceed, we need a number of differential equations of the form:

$$\begin{aligned} \frac{\partial Y_a}{\partial t} &= f(Y_a, N_i, \mathbf{u}, \mathbf{x}, t) \quad (22) \\ \frac{\partial N_i}{\partial t} &= g(Y_a, N_i, \mathbf{u}, \mathbf{x}, t) \end{aligned}$$

The first set are provided by the species transport equations (eqs. 3). The second must be provided for the PBE which is, however, a transport equation for a continuous function of particle volume. To circumvent this obstacle, we first discretise the PBE in the particle volume domain, thus converting it into a set of PDEs in terms of the values nodal values of the number density. Several discretisation schemes have been proposed in the literature for the solution of the homogeneous PBE and they can be adapted for our purpose. The scheme employed here is due to Rigopoulos and Jones (2003) and results in discretised equations of the form:

$$\begin{aligned} \frac{\partial N_i}{\partial t} + \nabla(\mathbf{u} \cdot N_i) + \\ + G_1(Y_1, Y_2, \dots, Y_m) \cdot N_i + G_2 \cdot N_{i-1} = \quad (23) \\ = D_p \nabla^2 N_i + B_1(Y_1, Y_2, \dots, Y_m) \end{aligned}$$

where:

$$G_1 = G(Y_1, Y_2, \dots, Y_m, \nu) \cdot \frac{1}{\nu_i - \nu_{i-1}} + \frac{\partial}{\partial \nu} (G(Y_1, Y_2, \dots, Y_m, \nu_i)) \quad (24)$$

$$G_2 = -G(Y_1, Y_2, \dots, Y_m, \nu) \cdot \frac{1}{\nu_i - \nu_{i-1}}$$

$$B_1(Y_1, Y_2, \dots, Y_m) = \frac{B(Y_1, Y_2, \dots, Y_m)}{\frac{1}{2}(\nu_1 - \nu_0)} + \frac{B(Y_1, Y_2, \dots, Y_m)}{\frac{1}{2}(\nu_0 - 0)} \quad (25)$$

We will now proceed to show that the new formulation overcomes all of the closure issues associated with RANS closures. Particles and species' convection in physical space can be shown to yield:

$$\left\langle \sum_{i=1}^n \frac{\partial F}{\partial n_i} \cdot [-\nabla(\mathbf{u} \cdot N_i)] + \sum_{a=1}^m \frac{\partial F}{\partial y_a} \cdot [-\nabla(\mathbf{u} \cdot Y_a)] \right\rangle = \langle \nabla F \cdot (\bar{\mathbf{u}} + \mathbf{u}') \rangle = \bar{\mathbf{u}} \cdot \mathbf{f} + \langle \nabla(\mathbf{u}' \cdot F) \rangle \quad (26)$$

and can therefore be treated with a gradient transport hypothesis. The diffusion term can be decomposed into a term representing diffusional transport of the pdf in physical space, usually negligible compared with turbulent transport, and micromixing. Modelling of micromixing in pdf methods is largely an unresolved problem, and several reviews have been devoted to it (e.g. Kollmann, 1995). It is likely that additional considerations may be required for particle transport; here, however, we will employ the simplest micromixing model, the Linear Mean Square Closure (LMSE). The chemical reaction term appears in closed form (O'Brien, 1980).

It remains now to prove that the growth and nucleation terms are closed. The former can be written as:

$$\left\langle \sum_{i=1}^n \frac{\partial F}{\partial n_i} \cdot [-G_1(Y_1, \dots, Y_m) \cdot N_i - G_2 \cdot N_{i-1}] \right\rangle = -\sum_{i=1}^n \frac{\partial}{\partial n_i} \langle G_1(Y_1, \dots, Y_m) \cdot N_i \cdot F \rangle - \sum_{i=1}^n G_2 \frac{\partial}{\partial n_i} \langle N_{i-1} \cdot F \rangle = -\frac{\partial}{\partial n_i} \left[(G_1(y_1, \dots, y_m) \cdot n_i - G_2 \cdot n_{i-1}) \cdot f \right] \quad (27)$$

The growth term is thus closed, regardless of the growth mechanism (i.e. the function $G(Y, \nu)$), even if the latter depends on both the species' concentrations and particle size. This is a major advantage of the new pdf formulation. For the nucleation, we have:

$$\sum_{a=1}^m \frac{\partial F}{\partial n_i} [B_1(Y_1, \dots, Y_m)] = \frac{\partial}{\partial n_i} [B_1(y_1, \dots, y_m) \cdot f] \quad (28)$$

Like growth, this term is also closed and does not require further treatment. The joint size-species pdf transport equation is a PDE whose dimensions include: [number of size classes] + [number of species] + [space, time]. Clearly numerical solution with conventional methods (e.g. finite difference) must be excluded, as such methods scale exponentially with the dimensionality of the problem, and stochastic simulation (Monte-Carlo) methods must be pursued. Such methods have been devised for

turbulent reactive flows and have been applied mainly to combustion problems (see e.g. Pope, 1985). It is anticipated that their extension will allow the computation of this problem. In what follows, a stochastic method will be developed for solution of a simplified form of the pdf.

PRECIPITATION IN A PARTIALLY STIRRED REACTOR

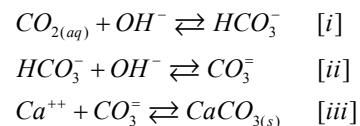
To demonstrate the above, we will employ the concept of a partially-stirred reactor (PSR). This is a system where the mean values of the convected scalars are uniform throughout, but not necessarily mixed at the molecular level. Such a state could occur if the turbulence is intense enough to homogenize the mixture at the macro level, but the micromixing timescale is not too short compared with the residence time. Such a system is an ideal test-bed for the method, because it provides us with the opportunity to test the new elements of the PDF method and to focus on the concentration-particle formation coupling, isolating it from the flow field whose computation can be performed in the same way as with other PDF methods.

The PDF transport equation describing the PSR can be derived from the full PDF transport equation by integrating over space (Chen, 1997). The final equation is shown below:

$$\begin{aligned} \frac{\partial f}{\partial t} = & \frac{f_{in} - f}{\tau_{res}} - \sum_{a=1}^m \sum_{b=1}^m D \frac{\partial^2}{\partial y_a \partial y_b} \langle \nabla Y_a \cdot \nabla Y_b \cdot F \rangle - \\ & - \sum_{i=1}^n \sum_{j=1}^n D_p \frac{\partial^2}{\partial n_i \partial n_j} \langle \nabla N_i \cdot \nabla N_j \cdot F \rangle - \\ & - \frac{\partial}{\partial y_a} [B_1(y_1, \dots, y_n) \cdot f] + \quad (29) \\ & + \frac{\partial}{\partial n_i} [(G_1(y_1, \dots, y_n) \cdot n_i - G_2 \cdot n_{i-1}) \cdot f] - \\ & - \sum_{i=1}^n \frac{\partial}{\partial n_i} \left[\left(\frac{1}{2} \sum_{j=1}^{i-1} a_{ij} n_j n_{i-j} \right) \cdot f \right] + \\ & + \sum_{i=1}^n \frac{\partial}{\partial n_i} \left[\left(n_i \sum_{j=1}^n a_{ij} N_j \right) \cdot f \right] \end{aligned}$$

where τ_{res} is the mean residence time and f_{in} the pdf of the input to the reactor. The only closure model required is a micromixing model, and here we will employ the simplest one, namely the Linear Mean Square Estimation (LMSE), (1975).

The reaction/particle formation system selected for the test case is the formation of CaCO_3 via reactive precipitation of $\text{Ca}(\text{OH})_2$ and $\text{CO}_{2(aq)}$. It is a good model system with simple kinetics that exhibits interesting behaviour. The kinetic data employed here is documented in Astarita (1967) and are summarised in table 1, together with the other parameters of the simulation. $\text{Ca}(\text{OH})_2$ is instantaneously dissociated into Ca^{++} and 2OH^- . Subsequently, the following reactions occur:



The last step, corresponding to particle formation, is described kinetically by the nucleation and growth functions, which are:

$$G_l = k_g \left(\frac{\sqrt{[Ca^{++}] \cdot [CO_3^-]} - 1}{K_{sp}} \right)^2 \quad (30)$$

$$B = k_n \left(\frac{\sqrt{[Ca^{++}] \cdot [CO_3^-]} - 1}{K_{sp}} \right)^6 \quad (31)$$

where G_l is the increase in particle radius, from which the volumetric growth rate can be calculated, k_g is a kinetic constant and K_{sp} is the solubility product.

Table 1: Kinetic data and parameters of the simulation.

Parameter	Value
K_{i1} , Equilb. const. of reaction [i] ($m^3 mol^{-1}$)	6.1×10^4
K_{i2} , Equilb. const. of reaction [ii] ($m^3 mol^{-1}$)	5.88
k_{i1} , kinetic const. of reaction [i] ($mol^{-1} m^3 s^{-1}$)	5.0
k_{i2} , kinetic const. of reaction [ii] ($mol^{-1} m^3 s^{-1}$)	1×10^4
K_{sp} , solubility product ($mol^2 m^{-6}$)	0.0047
k_g , growth constant (m/s)	6.2×10^{-11}
k_n , nucleation constant (s^{-1})	7.5×10^6
No. of nodes in particle size mesh	200
No. of particles	2000
τ_{res} , residence time (s)	1×10^{-3}
dt, time step (s)	$0.01 \times \tau_{res}$

To demonstrate the effects of turbulence-chemistry interaction in particle formation, the following levels of closure will be investigated, in increasing level of complexity:

- The joint pdf of species is calculated, but the particle formation terms are calculated on the basis of average number density. All correlations are thus neglected.
- The joint pdf of species is calculated, and with its aid the mean nucleation and growth terms are being averaged. In this model, correlations due to nonlinearities in the nucleation and growth functions ($\langle G(Y) \rangle, \langle B(Y) \rangle$) are accounted for.

However, the growth – number density correlations ($\langle G(Y) \cdot N' \rangle$) are neglected.

- The full species-number density pdf that was derived here is calculated.

The PSR is simulated by means of a Monte Carlo method. The statistics of the PSR are represented by an ensemble of stochastic particles. The PSR pdf equation is factorised into fractional steps for inflow/outflow, mixing, reaction and population balance. Inflow/outflow is simulated stochastically by removing a number of entities randomly selected, and inserting an equal number of entities featuring the input concentrations.

The main factor that determines the effect of mixing on the PSD is the ratio of the mixing timescale to a characteristic fluid dynamic timescale which, for the PSR, is the residence time (Chen, 1997). If mixing is instantaneous compared to the residence time, the reactor will be nearly homogeneous and the species/particle concentrations will

approach the average with all methods; otherwise, fluctuations are expected. Therefore a number of simulations were performed with varying ratios of mixing/residence time.

Figs. 1-3 show the mean particle size for each mixing timescale computed with all three methods, for three different initial concentrations of reactants. In all cases, as expected, the three methods coincide when $\tau_{mix}/\tau_{res} \ll 1$. At $\tau_{mix}/\tau_{res} > 0.1$, however, significant deviations appear. When only the correlations resulting from the terms $\langle G(Y) \rangle, \langle B(Y) \rangle$ are accounted for, the deviations are often higher than when with the full method and in the opposite direction. In fig. 3 we see that, for the lower initial concentration, the first two methods coincide, but the full species-number density pdf method deviates, indicating that only the correlations $\langle G(Y) \cdot N' \rangle$ are important here.

Clearly the strong non-linear interactions between turbulence, reactive scalars and number density have a strong and unpredictable effect on the mean particle size that cannot be neglected unless mixing is too fast. Finally, fig. 4 shows a comparison of the mass density distribution - $vN(v)$ - where the deviations are much more pronounced, due to the heavier weighting of the larger particles. Such deviations have a profound impact both on the mean particle size and on the quality of the product.

CONCLUSIONS

In problems involving chemical reaction and particle formation in a turbulent flow significant correlations appear in the population balance equation if dealt with a straightforward RANS approach, due to the non-linearity of the nucleation and growth terms. A new method based on a transport equation for the joint species-number density pdf was developed and it was shown that the terms giving rise to these correlations are closed under that formulation. The method was demonstrated by means of a Partially Stirred Reactor (PSR) and it was shown that, when the mixing timescale is of a similar order to the characteristic fluid dynamic timescale, significant deviations can occur in the PSD if these correlations are not taken into account.

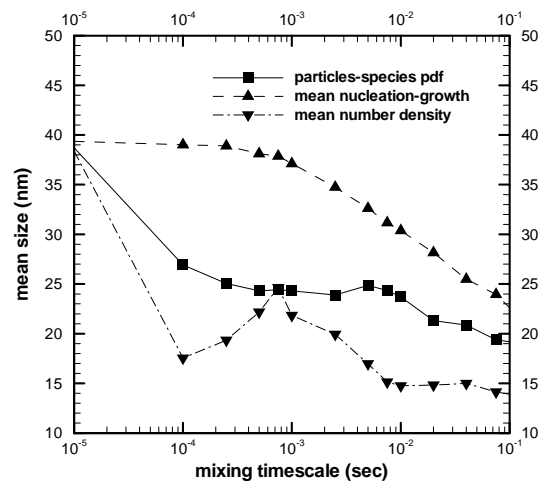


Figure 1: Comparison of the three methods, initial concentration is $1 \times 10^3 mol/m^3$

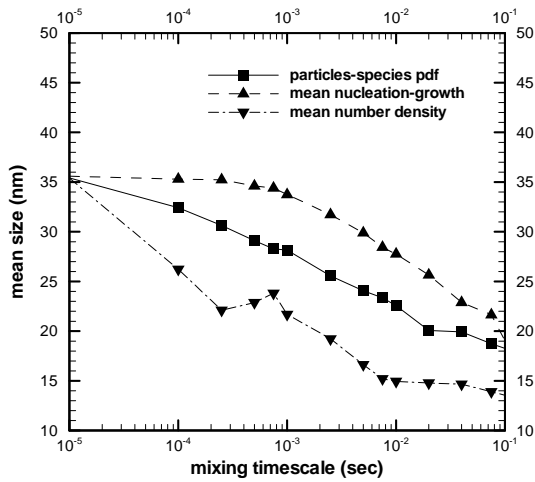


Figure 2: Comparison of the three methods, initial concentration is $5 \times 10^2 \text{ mol/m}^3$

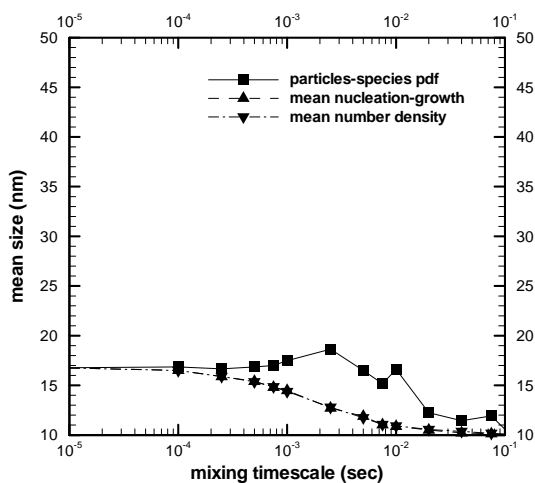


Figure 3: Comparison of the three methods, initial concentration is $5 \times 10^1 \text{ mol/m}^3$

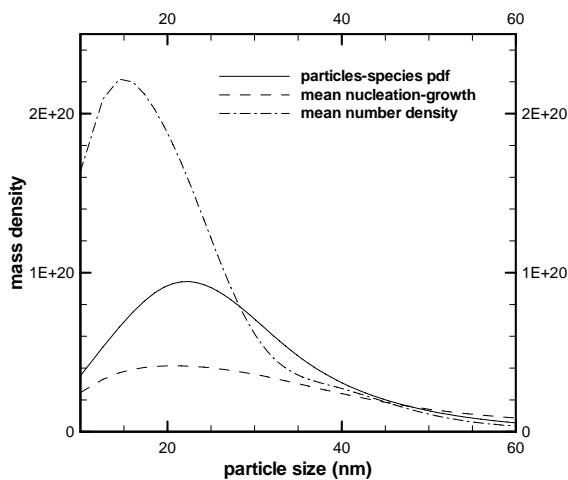


Figure 4: Comparison of the mass density distribution, initial concentration is $5 \times 10^2 \text{ mol/m}^3$, $\tau_{\text{mix}} = \tau_{\text{res}}$.

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