Population Balance Modelling of Polydispersed Particles in Reactive Flows

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Abstract

Polydispersed particles in reactive flows is a wide subject area encompassing a range of dispersed flows with particles, droplets or bubbles that are created, transported and possibly interact within a reactive flow environment - typical examples include soot formation, aerosols, precipitation and spray combustion. One way to treat such problems is to employ as a starting point the Newtonian equations of motion written in a Lagrangian framework for each individual particle and either solve them directly or derive probabilistic equations for the particle positions (in the case of turbulent flow). Another way is inherently statistical and begins by postulating a distribution of particles over the distributed properties, as well as space and time, the transport equation for this distribution being the core of this approach. This transport equation, usually referred to as population balance equation (PBE) or general dynamic equation (GDE), was initially developed and investigated mainly in the context of spatially homogeneous systems. In the recent years, a growth of research activity has seen this approach being applied to a variety of flow problems such as sooting flames and turbulent precipitation, but significant issues regarding its appropriate coupling with CFD pertain, especially in the case of turbulent flow. The objective of this review is to examine this body of research from a unified perspective, the potential and limits of the PBE approach to flow problems, its links with Lagrangian and multifluid approaches and the numerical methods employed for its solution. Particular emphasis is given to turbulent flows, where the extension of the PBE approach is met with challenging issues. Finally, applications including reactive precipitation, soot formation, nanoparticle synthesis, sprays, bubbles and coal burning are being reviewed from the PBE perspective. It is shown that popualtion balance methods have been applied to these fields in varying degrees of detail, and future prospects are discussed.

[Keywords: Polydispersed Particles, Reactive Flows, Population Balance, Soot, Spray].

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1 Introduction

1.1 Modelling of Polydispersed Particles in Reactive Flows

The term 'polydispersed particles' refers to a population of entities such as solid particles, droplets or bubbles, characterised by one or more properties featuring a range of values - as opposed to a monodispersed phase where all the particles are identical. The property in question is usually a measure of the particle size such as particle volume, mass or an equivalent diameter/radius, but other properties may also be of relevance: e.g. a distribution of surface area or particle velocity (when inertial effects are important). The central problem of polydispersed particle dynamics is the determination of the dynamical evolution of the distribution of the characteristic property of the population. It is a problem relevant to a wide range of problems of both theoretical and applied interest; one can mention soot formation, nanoparticle material synthesis, spray combustion, crystallisation and precipitation, aerosol and cloud formation, and even astrophysics.

The theory of polydispersed particle dynamics has its origins in the early work of Smoluchowski - as early as 1916 [225], [226], see also Chandrasekhar [30] for an account in the English language - and his equation for coagulation of colloidal particles, known as the Smoluchowski equation. Subsequently, a large number of contributions were made by a diverse range of academic communities; as a result, results have often been derived independently by more than one researchers and presented with a different terminology. Most of the initial activity was carried out by the atmospheric science community, due to the relevance of this theory to a number of atmospheric problems such as aerosols and cloud formation. Early research in this community has been reviewed by Drake [53], while a more up-to-date account can be found in the book by Friedlander [73]. In this community the basic population dynamics equation is referred to as the General Dynamic Equation (GDE), and the focus is mainly on coagulation problems (relevant to cloud formation). The topic attracted the interest of the mechanical and chemical engineering community in the 1960's due to its relevance to important engineering problems such as soot formation, spray combustion, crystallisation and precipitation. In the work of Williams [259] on spray combustion, an equation was formulated for droplet population dynamics, commmonly referred to as the Williams spray equation. Hulburt and Katz [97] referred to the population dynamics equation derived in their paper as a Liouville equation, while Ramkrishna [193], [194] and Randolph and Larson [198] used the term 'Population Balance Equation' (PBE), a term that has become standard in the engineering community. Meanwhile, many problems of coagulation and fragmentation have been studied by the physics community, where the term 'Smoluchowski equation' is employed for the coagulation equation. In this paper, we will attempt to view this body of research from a unified perspective and employ the term 'population dynamics' to refer to this viewpoint in general, as well as the term 'population balance equation' (PBE) when referring to the equation as employed in the engineering literature, whose problems this review is primarily aimed at addressing, although fundamental work from other communities (particularly the atmospheric science community) will also be considered.

A large number of works formulate and solve the PBE within a spatially homogeneous system, with fluid flow being added in a simplified manner (i.e. fully mixed systems with flow or sequences of), and a number of excellent reviews on this topic exist in the literature - e.g. by Drake [53] or Ramkrishna [193], [194]. In most real-world situations, however, polydispersed particles are embedded within flow fields, resulting in an inhomogeneous spatial distribution of the particles. The flow field then exerts a significant influence on the particulate processes, acting as the 'stage' for them to take place. In particular, the flow determines the mixing of chemical species that react or condense resulting in particle formation and growth, changes the spatial distribution of larger and smaller particles and determines the collision mechanisms that result in coagulation or particle break-up through shear. In return, the presence of the particles may have

a feedback effect to the flow field: chemical species are being consumed with rates depending on total surface area (possibly with associated density changes) and in the case of large, inertial particles, modulation of the turbulence and even particle-particle mechanical ineractions may need to be considered. Clearly, the coupling between flow and particle dynamics lies at the heart of the issue. The problem was, however, considered intractable until relatively recently due to the complexity of the population balance (which is an integro-differential equation), which renders its coupling with the Navier-Stokes equations formidable, with the exception of a few asymptotic solutions that can be derived for idealised cases where major simplifications on the PBE itself, as well as on its boundary conditions, can be applied. During the last decade, advances in computational power have enabled us to approach the complete problem of PBE coupled with flow with the aid of numerical methods. This area is still very new, however, and significant theoretical issues pertain, especially regarding population dynamics in turbulent flows. The objective of this review is to examine this body of work and to present a hierarchy of mathematical formulations and numerical methods that can be employed to attack the problem of coupled fluid and population dynamics.

1.2 Scope and aims of the review

At this point we must stress that the (essentially statistical) population dynamics approach is not the only framework for the mathematical description of polydispersed particles in flows. An alternative approach is based on the Lagrangian equations of motion for the particles, either solved directly (in the context of a direct numerical simulation - DNS) or employed for the derivation of kinetic equations for the particle position in turbulent flow. This viewpoint has been explored by several number of researchers, such as Reeks [201], [203], [202], Hyland et al. [98], [99], Mashayek and Pandya [154], Pozorski and Minier [186] among others. A number of excellent reviews on this line of research exist in the literature, e.g. by Minier and Peirano [160], [172], [173], Mashayek and Pandya [154], Loth [140]. By contrast, population balance formulations proceed from the fundamental postulate of a particle continuum, which involves an inherent level of averaging over the Newtonian equations of motion, even in the case of laminar flow. Links between the two classs of approaches have been drawn by a number of researchers, such as Ramkrishna and Borwanker [195], [196], [197] Subramaniam [232], [233] and Laurent and Massot [128]. In this review, methods belonging to this class will not be discussed in detail, but references to them will be made at key points in order to establish links between these two kinds of modelling and to determine the classes of problems where they are more relevant.

The structure of this review is as follows. In the first part we will examine the foundations of the population dynamics approach and the formulation of the basic equations. The second part will briefly review methods of solution in homogeneous systems. This review is merited by the need to establish a basis for our discussion of population dynamics in flows; it will not be exhaustive or comprehensive, however, as this topic has been covered by reviews and books entirely devoted to it. The third part will examine population dynamics in flows and present a hierarchy of formulations and numerical methods of solution. In that part distinction will be made between laminar and turbulent flows, since in the case of the latter important issues, many of which still unresolved, are being raised. The last part is a review of relevant works where those methods have been developed or applied, classified according to their field of application (precipitation, soot and nanoparticles, bubbles and sprays).

2 Fundamentals of the Population Dynamics Approach for Polydispersed Particles

2.1 The Statistical Description of Polydispersed Particles

The most direct way to describe mathematically a dispersed system, whether polydispersed or not, is to write down the Newtonian equations of motion for every single particle in the system:

$$\frac{du_i}{dt} = f_i \tag{1}$$

where the right-hand side is the total force per unit mass applied to the particle. With particles embedded within a known flow field, the following formulation can be used:

$$\frac{du_{p,i}}{dt} = \frac{1}{\tau}(u_{p,i} - u_{f,i}) \tag{2}$$

where τ is the particle response time which depends on the physical problem - see [35] and $u_{p,i}, u_{f,i}$ the velocities of the particle and of the fluid phase, respectively. The analytical function for the response time depends on the forces applied to the particle. A number of works are devoted to the exact form of these forces and an established equation is that of Maxey and Riley [156] which describes the forces on a small rigid sphere in a nonuniform flow - see the reviews by Michaelides [159] and Crowe et al. [35] for more detail on this subject. For our purposes, however, it is safe to assume that the force will depend on the local fluid velocity and on the particle size (especially the drag force, which is usually the most important) - this is how polydispersity would enter the formulation. The carrier fluid velocity should, of course, be computed with the Navier-Stokes equations. So far, this formulation refers to motion of non-interacting particles whose motion has no effect on the flow field. The Newtonian method can be extended to problems including particle-particle collisions and coagulation, albeit with a considerable increase in complexity; flow and turbulence modulation, if present, renders the problem even more complicated.

This approach of Lagrangian tracking of individual particles according to the Newtonian equations of motion is mainly of use for DNS studies of ideal systems (e.g. [200], [253], [252], [266], [251] or for very small populations. For realistic systems containing large populations of particles, however, such a formulation would prove extremely costly as it would involve solving an enormous number of differential equations. For many systems of interest, such as soot and nanoparticles), the number of particles is very large ($\approx 10^6 - 10^8/cm^3$); in addition, the motion is chaotic and detailed boundary conditions corresponding to any particular experiment cannot be accurately prescribed. These facts clearly dictate the use of a statistical approach.

The statistical description of polydispersed particles draws essentially on the fundamental principles of kinetic theory. Assume a population of particles and a set of properties $q_1, q_2, ..., q_\alpha$ necessary to describe the state of each particle. These properties could include position (for systems that are spatially distributed), size (for particles polydispersed in size) etc., and we might call them generalised coordinates. For each of these coordinates a generalised velocity $(\dot{q}_1, \dot{q}_2, ..., \dot{q}_\alpha)$ can be defined; for example, with respect to the actual space dimensions this would correspond to the velocity in physical space, while with respect to particle size it would correspond to particle growth (soot, crystals) or evaporation (droplets).

The processes involved in polydispersed particles in flows to be discussed here are far from equilibrium, so we need to describe their dynamics using a transport equation. We now proceed in a way akin to the derivation of the Boltzmann transport equation (see e.g. Lifshitz and Pitaevskii [136] or Tolman [243]). The following distribution function can be defined:

$$N(q_1, ..., q_A, \dot{q}_1, ..., \dot{q}_A)$$

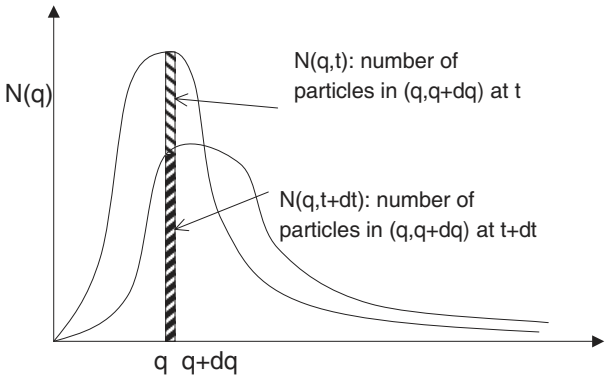


Figure 1: An one-dimensional distribution evolving in time

where $N dq_i ... d\dot{q}_A$ denotes the number of particles for which each property q_i has a value between q_i and $q_i + dq_i$ (i.e. N has dimensions of particles per unit of each property). The distribution does not normalise to 1 (as would a probability distribution), but to the total number of particles, which is its zeroth joint moment:

$$M_0 = \int_{-\infty}^{\infty} ... \int_{-\infty}^{\infty} N(q_i, \dot{q}_j) dq_1, ..., dq_A, \dot{q}_1, ..., \dot{q}_A = N_p \tag{3}$$

See fig. 1 for a representation of an one-dimensional distribution evolving in time. First or higher moments may also have a direct physical interpretation, depending on the case. Let us consider, for example, the case of a population of particles or droplets characterised by their volume v. In that case, the first moment would be the total volume of the particulate phase, per unit volume of the mixture, i.e. the volume fraction of the particulate phase, α_p:

$$M_1 = \int_0^{\infty} v N(v) dv = \alpha_p \tag{4}$$

If, on the other hand, a linear measure of particle size is employed, such as an equivalent diameter, then the second and third moment would express the total surface area and volume, respectively. If a distribution over an intrinsic coordinate, i.e. particle volume, and over velocity space, is being considered (e.g. for the description of inertial particles or droplets/bubbles), then the total volume of the particulate phase per unit volume of mixture is given by:

$$\alpha_p = \int_0^{\infty} \int_{-\infty}^{\infty} v N(v) dv d^3 u_i \tag{5}$$

while the joint first moment represents the flux of the particulate phase:

$$\alpha_p u_i = \int_0^{\infty} \int_{-\infty}^{\infty} v u_i N(v) dv d^3 u_i \tag{6}$$

An example of a population of solid particles exhibiting different sizes is shown in fig. 2. In fig. 2a the particles are practically monodispersed, while in 2b they exhibit a variety of sizes due to agglomeration. Figure 3 shows the particle size distribution during different stages of a precipitation experiment [207] (the simulation results have been obtained using one of the methods to be discussed in sec. 3). The objective of the field of population balance modelling is to develop methods that predict the dynamical evolution of the distribution.

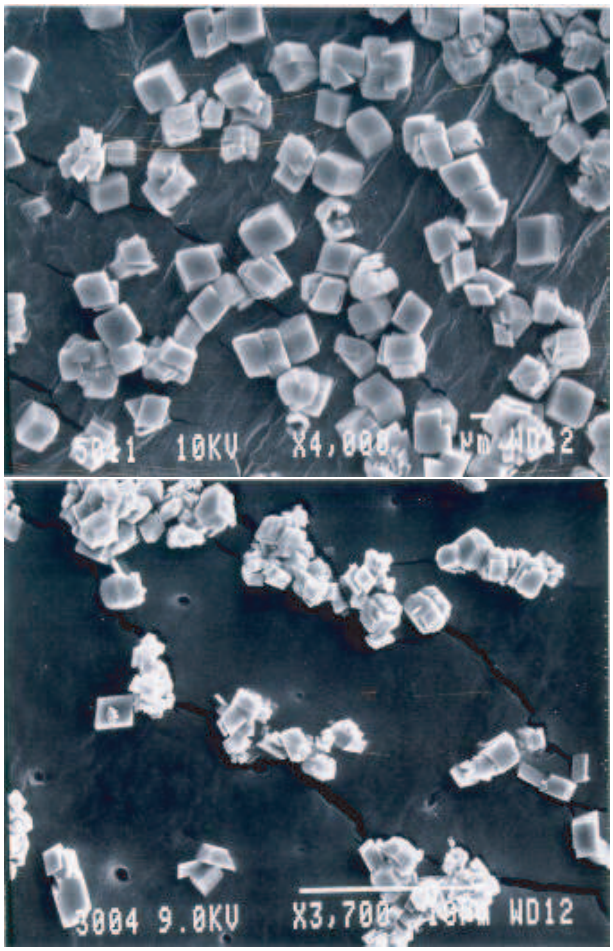


Figure 2: Scanning Electron Microscopy (SEM) of $CaCO_3$ crystals exhibiting different PSDs: a) mostly single crystals, b) mostly agglomerates - reprinted with permission from [207].

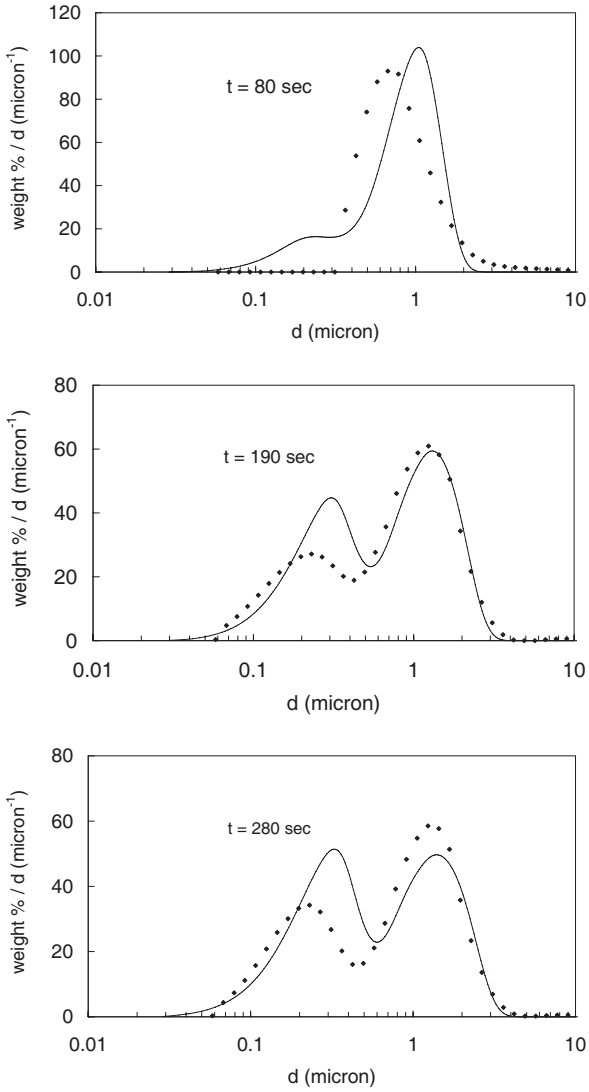


Figure 3: Experimental and simulated particle size distribution of $CaCO_3$ at three different stages of the process - reprinted with permission from [207].

2.2 Transport Equation Without Collisions and Sources

The transport equation we seek is simply a continuity equation in phase space. Assuming that the number density function is continuous and differentiable, the continuity equation in the case of non-interacting particles is:

$$\frac{\partial N}{\partial t} + \frac{\partial}{\partial q_a}(\dot{q}_a N) + \frac{\partial}{\partial \dot{q}_a}(\ddot{q}_a N) = 0 \tag{7}$$

where summation is implied over repeated indices. At this point we must note that, in applications of statistical mechanics to gases and plasmas, the phase space is defined over coordinates and momenta (Hamiltonian formulation) and eq. 7 is further simplified since the velocities have zero divergence [97]. This is not generally the case here, as the generalised velocities - such as the particle growth/evaporation, which represents the velocity with respect to particle size - can be of an entirely different nature to the physical velocity. In most physical systems, growth/evaporation is one-way - from smaller to larger in crystal growth, the reverse in droplet evaporation. Therefore we will leave the equation as it is, and it will be the starting point for the formulations that follow.

One more difference from the kinetic theory of gases and plasmas is that, whereas there each molecule can have its own individual velocity, in many problems in dispersed particle systems the generalised velocities are externally prescribed - i.e. the physical velocity may be following the streamlines of a flow field, while the particle growth rate is either constant or a fixed function of particle size. In these cases, the generalised velocities can be dropped from the list of independent coordinates. As an example of such an equation, we write the equation for crystal growth in a spatially homogeneous, stirred reactor - one of the first applications of population balance equations [97], [198]:

$$\frac{\partial N}{\partial t} + \frac{\partial}{\partial \upsilon}(G(\upsilon)N) = 0 \tag{8}$$

where we have only one independent dimension, and the growth function, $G(\upsilon)$, is in general a known function of particle volume.

Let us now consider the case of particles transported by a known flow field, strictly following its streamlines (i.e. without exercising slip). While the generality of eq.7 is not being questioned, there is some merit in separating the physical space and velocities from the remaining dimensions that are intrinsic to the particle (i.e. size). Assuming that the conjugate velocities of the intrinsic variables are known functions and therefore not independently varying from particle to particle (which is usually the case for particle growth), the relevant equation is:

$$\frac{\partial N}{\partial t} + \frac{\partial}{\partial q_a}(\dot{q}_a N) + \frac{\partial}{\partial x_i}(u_i N) = 0 \tag{9}$$

Like the growth function, physical velocity is a function of position in physical space. If the velocity field is not known a priori, it has to be computed from the continuity and Navier-Stokes equations for the carrier phase. This class of problems is appropriate for describing soot and nanoparticle growth and transport in gas flows (flames) and liquid flows (reactive precipitation) where particles are small enough to follow the flow, or for problems where the density of the particles does not differ significantly from that of the fluid phase.

The final case to consider is that of particles transported within a flow field while experiencing inertial effects. For this, particles must be of significant size or weight (quantified by the Stokes number) and have a significant momentum of injection, as in the case of sprays. In that case, a distribution over particle velocities must be considered:

$$\frac{\partial N}{\partial t} + \frac{\partial}{\partial q_a}(\dot{q}_a N) + \frac{\partial}{\partial x_i}(u_i N) + \frac{\partial}{\partial u_i}(f_i N) = 0 \tag{10}$$

where u_i now stands for the particle velocity, while f_i, the force per unit mass, is the particle acceleration - the generalised velocity conjugate to the particle velocity. An equation of this form was proposed by Williams [259] to describe spray combustion.

At first eq. 10 may appear overwhelming due to the large number of dimensions. A close inspection, however, reveals that a reduction of dimensionality is appropriate in most physical situations. The reasons why a distribution over velocity space is essential are that a) particles of different size experience different drag forces, and b) different particles may be have been injected with different initial velocities. If the flow field is assumed steady and known a priori, then the trajectory of an inertial particle within that field will be fully determined by its size, initial velocity and the flow field . This is clearly seen by eq. 2, whose integration will provide the trajectory of the particle. Thus we can write:

$$u_i = u_i(x_i, q_i, t, u_{i,0})$$

From this we can see that, in general, each particle will have its own individual velocity, and an elimination of the velocity as an independent dimension is not possible. In most practical cases, however, there is no reason to suppose that individual particles will be injected with a preferential velocity. In most particulate flows, particles are likely to start with the velocity of the fluid streamlines and deviate afterwards due to the effect of differential drag force, while in sprays the entire liquid phase is injected with a certain momentum. Therefore, under the assumption that particles do not differ in their initial velocity, their velocity at any instance will depend on their size and local field:

$$u_i = u_i(x_i, q_i, t)$$

This observation is very important, as it permits in principle the elimination of velocity from the list of independent coordinates of the number density. This is only a theoretical possibility since, in practice, the flow field is usually not known a priori and does not assume such a simple functional form anyway to permit this operation analytically. The functional dependence of u_i on particle properties and position, however, is of fundamental importance to the development of the theory, as it permits the derivation of the two-fluid and multi-fluid models. To see this, we integrate eq. 10 over velocity space, i.e. taking the zeroth moment with respect to velocity. The last term becomes:

$$\int_{-\infty}^{-\infty}\int_{-\infty}^{-\infty}\int_{-\infty}^{-\infty}\frac{\partial}{\partial u_i}(f_i N)du_1du_2du_3 = 0 \tag{11}$$

This term vanishes, assuming that the number density approaches zero at infinite velocity. Defining the velocity-averaged number density, N':

$$N' = \int_{-\infty}^{-\infty}\int_{-\infty}^{-\infty}\int_{-\infty}^{-\infty} N du_1du_2du_3 \tag{12}$$

and the average velocity of the particulate phase:

$$u_i' = \frac{1}{N'}\int_{-\infty}^{-\infty}\int_{-\infty}^{-\infty}\int_{-\infty}^{-\infty} u_i N du_1du_2du_3 \tag{13}$$

the velocity-averaged equation thus becomes:

$$\frac{\partial N'}{\partial t} + \frac{\partial}{\partial q_a}(\dot{q}_a N') + \frac{\partial}{\partial x_i}(u_i' N') = 0 \tag{14}$$

i.e. the velocity as an independent variable disappears by integration over velocity space.

Eq. 7 was derived simply on the basis of a particle continuum. An alternative derivation that demonstrates its relationship with the Newtonian equations of motion can be also be employed, again along the lines of the kinetic theory of gases and plasmas [168]. Suppose that, for every individual particle i, its orbit in the phase space is given by functions $Q_a^i(t)$ and $\dot{Q}_a^i(t)$ (for the coordinates in physical space, these would be the solutions of the Newtonian equations of motion, eq. 2). Then the following equation can be written for the number density of particles in the phase space:

$$N(q_a, \dot{q_a}, t) = \sum_i \left[\prod_a \left(\delta(q_a^i - Q_a^i) \delta(\dot{q_a^i} - \dot{Q_a^i}) \right) \right] \tag{15}$$

Taking the time derivative of this density, and using the identity

$$\frac{\partial f(q-Q)}{\partial q} = -\frac{\partial f(q-Q)}{\partial Q} \tag{16}$$

we obtain the following:

$$\frac{\partial N(q_a, \dot{q}_a, t)}{\partial t} = -\sum_i \left[\sum_{a'} \left(\frac{\partial}{\partial q_{a'}} \dot{Q}_{a'}^i \prod_{a \neq a'} \left(\delta(q_a - Q_a^i) \delta(\dot{q}_a - \dot{Q}_a^i) \right) \right) \right] - \sum_i \left[\sum_{a'} \left(\frac{\partial}{\partial \dot{q}_{a'}} \ddot{Q}_{a'}^i \prod_{a \neq a'} \left(\delta(q_a - Q_a^i) \delta(\dot{q}_a - \dot{Q}_a^i) \right) \right) \right] \tag{17}$$

Using now the identity

$$q\delta(q-Q) = Q\delta(q-Q) \tag{18}$$

and interchanging the summations, we obtain:

$$\frac{\partial N(q_a, \dot{q}_a, t)}{\partial t} = -\sum_{a'} \left[\frac{\partial}{\partial q_{a'}} \dot{q}_{a'} \sum_i \left(\prod_{a \neq a'} \left(\delta(q_a - Q_a^i) \delta(\dot{q}_a - \dot{Q}_a^i) \right) \right) \right] - \sum_{a'} \left[\frac{\partial}{\partial \dot{q}_{a'}} \ddot{q}_{a'} \sum_i \left(\prod_{a \neq a'} \left(\delta(q_a - Q_a^i) \delta(\dot{q}_a - \dot{Q}_a^i) \right) \right) \right] \tag{19}$$

which, given the definition of the number density from eq. 15, is exactly eq. 7. In the case of small populations, however, important complications arise; we refer the reader to Ramkrishna and Borwanker [195], [196], [197] or Subramaniam [232], [233] for a discussion of these.

2.3 Transport Equation with Collisions and Sources

The fact that there are no source terms on the right-hand side of the PBE so far implies that there are no interactions or external influences that can change the number of particles. Source terms can appear in the following cases:

- Particle formation (nucleation)
- Particle collisions, leading to aggregation
- Particle fragmentation (break-up)

New particles can be formed in cases such as soot nucleation and crystal precipitation. Nucleation rates are generally functions of environmental variables, such as reacting chemical species. Assuming a single particle size for the nuclei, nucleation rate is expressed mathematically by means of a delta function:

$$\dot{N}(q) = \delta(q - q_0) \tag{20}$$

where q is a variable associated with particle size, and q_0 is its value for the nuclei.

Collisions of particles can result in a redistribution of the properties and velocities. Elastic collisions result merely in the latter, but in particulate processes we are usually interested in collisions that result in aggregation (or coagulation or agglomeration, depending on the physicochemical mechanism involved - all of these processes share the same description from the mathematical point of view, in that they result in two smaller particles forming a single larger one, whose mass/volume is the sum of those of the single particles), forming particles of bigger sizes. Collisions are represented mathematically by integral terms, since all possible pairs of particles must be considered. For simplicity, assume a distribution over a single property q, $N(q)$. An aggregation event between a pair of particles with properties q, q' leads into a single particle with property q_1. We can expect that the number of collisions between particles with properties q, q' occurring will be proportional to the product of their number densities, $N(q)N(q')$, times a function, the kernel $K(q, q'; q_1)$ which may, in general, depend on the particle properties. The product $K(q, q'; q_1)N(q)N(q')$ thus represents the loss of particles of property q due to collisions with all other particles that result in formation of particles with properties q_1, i.e. it is a collision sink term. We also have to account for the increase of particles of property q due to collisions of other particles, q_1, q_1', via a source term; by following a similar reasoning as above, this term should be $K(q_1, q_1'; q,)N(q_1)N(q_1')$. The equation for aggregation, therefore, neglecting all other particulate processes except the collision source and sink, is:

$$\frac{dN}{dt} = \int\int \left[K(q_1, q_1', q)N(q_1)N(q_1')\right] dq_1 dq_1' - \int\int \left[K(q, q'; q_1)N(q)N(q')\right] dq' dq_1 \tag{21}$$

If more than one variables are distributed, then integration with respect to all of these variables must be considered. E.g. for aggregating particles with different inertia, integration must be carried out with respect to particle size and velocity. The integration is over the internal variables only, i.e. not in physical space. The kernel, K, encompasses all the physicochemical information regarding the mechanism of the collisions. The development of such constitutive relations is of major importance for the correct prediction of population dynamics.

When the independent variable is a measure of particle size (such as particle diameter, volume or mass) Eq. 21 is simplified due to a further constraint. The mass is conserved in aggregation events, which implies that a particle of mass m' can only aggregate with a particle of mass $m - m'$ if the collision is to result in the formation of a particle of size m. Marian Smoluchowski, who studied the coagulation of colloid particles ([225], [226]; see also Chandrasekhar, [30], Drake [53]) arrived at the following equation for the dynamics of a population where only discrete values of particle size are allowed, known as the Smoluchowski equation:

$$\frac{dN_i}{dt} = \frac{1}{2}\sum_{j=1}^{i-1} a_{j,i-j} N_j N_{i-j} - N_i \sum_{j=1}^{\infty} a_{ij} N_j \tag{22}$$

where N_i is the number density of particles of size i. This equation is a discrete form of eq. 21 and applies to a colloidal system where the population is evolving due to coagulation alone. The purpose of the factor $\frac{1}{2}$ in the source term is to prevent the double counting of aggregation pairs between particles smaller than i. The matrix a_{ij} is the kernel containing the aggregation frequences between all possible pairs i, j which, in general, may be variable (size-dependent). Smoluchowski obtained an analytical solution for the case of a constant kernel, which is a good

approximation for the Brownian motion kernel when the particle sizes do not differ very much (see below).

For systems where a continuous distribution of particle size must be considered, the equation for pure aggregation is an integral equation that can be written as follows:

$$\frac{\partial N(v,t)}{\partial t} = \frac{1}{2}\int_0^v \beta(v-v',v')N(v-v',t)N(v',t)dv' - \int_0^\infty \beta(v,v')N(v,t)N(v',t)dv' \quad (23)$$

To describe a problem involving simultaneous nucleation, particle growth and aggregation, the terms of eq. 23 must be combined with those of eqs. 9 and 20, resulting in an integro-differential equation.

The term $\beta(v,v')$ is the coagulation kernel and its dependence on the particle volume depends on hydrodynamics. The study of coagulation kernels is an extensive subject on its own, and a detailed discussion is out of the scope of this review. We will present only some basic results here; for an extensive treatment, the reader is referred to Drake [53], Friedlander [73] or Levich [134]. The kernel law depends on the nature of the physical phenomena that lead to aggregation and these can be very different for different fluid-particle systems. The main factors to be considered are the size of the particles and the nature of the flow (laminar, turbulent).

For tiny aerosol particles, the first point to consider is whether the particles are smaller or larger than the mean-free path of the gas molecules. This is quantified via the Knudsen number, which is the ratio of the mean free path to the particle diameter. For particles smaller than the mean free path, the kernel will be given by the kinetic theory of gases, which yields the following expression for collisions of particles behaving like elastic spheres [73]:

$$\beta(v,v') = \left(\frac{3}{4\pi}\right)^{\frac{1}{6}}\left(\frac{6kT}{\rho_p}\right)^{\frac{1}{2}}\left(\frac{1}{v}+\frac{1}{v'}\right)^{\frac{1}{2}}\left(v^{\frac{1}{3}}+v'^{\frac{1}{3}}\right)^2 \quad (24)$$

For particles larger than the mean-free path but still in the sub-micron range, aggregation is due to Brownian motion (perikinetic). Smoluchowski derived the following kernel for this case, assuming that the rate of collisions is diffusion limited:

$$\beta(v,v') = \frac{2kT}{3\mu}\left(\frac{1}{v^{\frac{1}{3}}}+\frac{1}{v'^{\frac{1}{3}}}\right)\left(v^{\frac{1}{3}}+v'^{\frac{1}{3}}\right) \quad (25)$$

The size-dependent part is approximately constant when the particle volumes do not differ significantly. By using this approximation, Smoluchowski was able to reduce eq. 25 to a size-independent kernel and obtain an analytical solution for the coagulation problem.

Another important mechanism is the collision of particles due to their relative motion in a shear flow field (orthokinetic). Smoluchowski also derived a hydrodynamic kernel for coagulation in a laminar shear flow:

$$\beta(v,v') = \frac{4}{3}\frac{du}{dx}(v^{\frac{1}{3}}+v'^{\frac{1}{3}})^3 \quad (26)$$

Other physical or chemical phenomena can induce aggregation such as gravitational settling, force fields etc.; the reader may refer to Friedlander for more information [73]. Several empirical kernels have also been proposed [53], [21]. Kernels for turbulent coagulation will be considered in sec. 5.3.

Finally, we will briefly consider particle fragmentation (breakage). The equation for fragmentation alone is:

$$\frac{\partial N(v,t)}{\partial t} = \int_v^\infty \beta_b(v')b(v/v')N(v',t)dv' - \beta_b(v)N(v,t) \quad (27)$$

where the functions $\beta(v/v')$ and $b(v/v')$ denote the rate of fragmentation and size distribution of daughter particles and are often merged in to a single function, $\beta'_b(v/v')$. The possibilities for this function are numerous. Uniform breakage implies that fragments of every size have the same probability to form. This situation may arise e.g. in polymer chains which, being one-dimensional, are as likely to break at any point. If the breakage is also binary, it can be represented by an following overall function $\beta'_b(v/v') = 2/v'$. Other possibilities are a parabolic "U-shape" function for the daughter paricle size distribution (rigid particles are more likely to break into unequal pieces); considerable work in this area has been contributed by Coulaloglou and Tavlarides [34], Prince and Blanche [191] and Luo and Zvendsen [142] For analytical solutions to fragmentation problems, the reader may also consult Ziff and McGrady [268] or Ziff [267] and references within.

3 Solution Methods for the Homogeneous Population Balance Equation

3.1 Overview

Before we consider the very complex problem of the coupled fluid dynamics - population balance equations, it is essential that we briefly review the methods employed for solution of the population balance in homogeneous systems. The reason is that they form the basis for the formulation of methodologies for the coupled problem. This is a subject that has been investigated for a long time and matured; by contrast, population balance in flows is a largely unexplored area. Detailed reviews of numerical methods for the homogeneous population balance have appeared in the literature at several times in the past; some pivotal ones have been contributed by Drake [53], Ramkrishna [193], [194] and Friedlander [73]. The treatment here will therefore be brief, the main objective being to prepare the ground for the analysis of flow systems that follows.

Even in homogeneous systems, the PBE including both growth/evaporation and aggregation/fragmentation is an integro-partial differential equation, the independent variables being the particle size (and/or possibly another characteristic variable) and time. Furthermore, it often has to be coupled with the mass balances for reactive species which react/condense to form the particulate phase. To further complicate things, the nucleation and growth terms are usually nonlinear. Clearly an analytical solution of the problem in the general case and for arbitrary boundary conditions must be ruled out, and even numerical approaches often have a limited range of validity, concentrating on a certain class of problems, since the range of physical problems that can be investigated under the general umbrella of the PBE is very wide.

In general, methods for solution of PBE fall into the following general categories:

- Analytical and perturbation methods
- Moment and approximate moment-based methods
- Discretisation and global approximation methods
- Monte Carlo methods

As mentioned, the PBE cannot be solved analytically in its general form. Solutions exist, however, for certain simplified problems with associated boundary conditions. As mentioned, solution to the discrete aggregation problem for constant kernel was first obtained by Smoluchowski. Further aggregation problems were solved by Scott [221]. The particle growth equation, in its simplest form, is an one-dimensional wave equation that can be solved with the method of characteristics. Randolph and Larson [198] showed solutions for steady-state size-independent

nucleation and growth, as well as for a special case of size-dependent growth; see also Hounslow for the time-dependent case [96]. Hostomsky [95] obtained a semi-analytical solution for a steady-state nucleation-aggregation problem while Ramabhadran et al [192] derived a solution for an aggregation-growth case. Further details of analytical and perturbation methods can be found in the review of Drake [53] as well as in the book by Ramkrishna [194]. All of these methods have a very limited range of validity, but they are of interest for the purpose of validating numerical approaches. Monte-Carlo methods proceed via a statistical sampling of particles undergoing the growth and interaction processes to simulate the evolution of the particle ensemble. Early work in that area was carried out in the aerosol community and a review of it can be found in [53]; recent work has applied these methods to nanoparticle production [239], [3], [82]. These methods are more suitable for the simulation of multidimensional PBEs, as they do not scale exponentially with dimensionality. They will not be covered here, but the reader can refer to Rosner et al. [211] for more detail.

In what follows we will briefly review moment and discretisation methods, as these will be of importance for the remainder of the article.

3.2 Moment-based methods

The method of moments is one of the earliest and most widespread methods for solving the PBE. It is also one of the most frequently employed in coupled PBE-CFD applications, its popularity being due to the fact that it transforms the original integro-partial differential equation into a set of ordinary differential equations, which are more easy to couple with fluid dynamics. It was developed by a number of researchers, seemingly independently; notably Hulburt and Katz [97] and , as well as Golovin [81] and Enukashvili [61]; see [53] for an English account of the latter works.

The essence of the method of moments is to transform the PBE into a set of ODEs for the dynamical evolution of the moments. Such an approach involves an inherent loss of information as the distribution is not to be retrieved, but only some integral properties of it. However, for many engineering applications, information about a few physical quantities represented by low-order moments (such as total number of particles, m_0, or total volume, m_1, in a distribution whose domain is the particle volume) would suffice, and therefore the prospect of such a formulation is attractive from a practical point of view, provided that the resulting system of equations is closed. Unfortunately, as we will see, the set of moment equations is unclosed in the general case and approximations are required to provide closure.

To apply the method of moments we have to apply the moment transformation to the PBE. We will demonstrate this first for a nucleation-growth PBE, where the method is directly applicable. For simplicity, we will also assume that the growth and nucleation functions are not functions of environmental variables (e.g. reacting species, temperature). Such terms, if present, can usually be taken out of the moment integrals. Moments up to order k are thus defined as:

$$m_k = \int_0^\infty \upsilon^k n(\upsilon) d\upsilon \tag{28}$$

The equation for nucleation and growth is:

$$\frac{\partial N}{\partial t} + \frac{\partial}{\partial \upsilon}\left[G(\upsilon)N\right] = \dot{N}\delta(\upsilon - \upsilon_0) \tag{29}$$

Multiplying eq. 29 by υ^k and integrating, we obtain:

$$\int_0^\infty \upsilon^k \frac{\partial N(\upsilon,t)}{\partial t} d\upsilon + \int_0^\infty \upsilon^k \frac{\partial}{\partial \upsilon}\left[G(\upsilon,t)N(\upsilon,t)\right] d\upsilon = \int_0^\infty \upsilon^k \dot{N}\delta(\upsilon - \upsilon_0) d\upsilon \tag{30}$$

which, after applying integration by parts to the growth term, yields:

$$\frac{\partial m_k(t)}{\partial t} - k \int_0^\infty \upsilon^{k-1} G(\upsilon, t) N(\upsilon, t) d\upsilon = \upsilon_0^k \dot{N} \tag{31}$$

Further progress depends on our ability to resolve the integral of the growth term in terms of the known moments. For the simplest case, that of size-independent growth, the result is readily obtained via integration by parts:

$$\frac{\partial m_k(t)}{\partial t} - k G m_{k-1}(t) = l_0^k \dot{N} \tag{32}$$

Thus the equation for kth moment involves the (k-1)th moment. The equation for the zeroth moment is straightforward:

$$\frac{\partial m_0(t)}{\partial t} = \dot{N} \tag{33}$$

i.e. the rate of change in the total number of particles is equal to the nucleation rate, and therefore the system of moment equations is closed.

In the general case where the growth is an arbitrary function of the particle size, however, eq. 31 cannot be further simplified since the integral of the growth term involves the unknown distribution $N(\upsilon, t)$. Size-independent growth is encountered in certain crystallisation problems, but only if the distribution is defined in terms of particle diameter, otherwise the growth term would depend on $\upsilon^{1/3}$. Apart from size-independent growth, closed forms can only be obtained for linear growth laws. This represents a severe limitation to the applicability of the method of moments, as in general the growth function is expected to be non-linear - e.g. diffusion controlled growth [157], volumetric description of growth for aggregation-growth problems, size-dependent evaporation etc..

Turning now our attention to aggregation, applying the moment transformation to the equation for pure aggregation (eq. 23) we have:

$$\int_0^\infty \upsilon^k \frac{\partial N(\upsilon, t)}{\partial t} d\upsilon = \frac{1}{2} \int_0^\infty \upsilon^k \int_0^\upsilon \beta(\upsilon - \upsilon', \upsilon') N(\upsilon - \upsilon', t) N(\upsilon', t) d\upsilon' d\upsilon$$
$$- \int_0^\infty \upsilon^k \int_0^\infty \beta(\upsilon, \upsilon') N(\upsilon, t) N(\upsilon', t) d\upsilon' d\upsilon \tag{34}$$

This equation can only be further elaborated if the aggregation kernel is constant. In that case, the following result can be derived ([97]):

$$\frac{\partial \mu_k}{\partial t} = \frac{1}{2} \beta \sum_{k'=0}^{k} \left(\begin{array}{c} k \\ k' \end{array} \right) \mu_{k'} \mu_{k'-k} - \beta \mu_0 \mu_k \tag{35}$$

This system of equations is closed for any number of moments we wish to retain, but again closure depended on a particularly simple assumption about the functional form of the kernel which, as we have seen, can only be considered as an approximation for Brownian coagulation.

So far, the limitations of the moment approach can be summarised as follows: a) the distribution is not being retrieved, but only its moments; b) the resulting set of equations is unclosed unless specific functional forms for the physical mechanisms of growth and aggregation (kernels) are assumed. These issues restrict the application of the basic moment method (which is exact, when it can be applied) to the simplest cases only. To obtain closure, approximations

must be made. Before we proceed, it must be observed that the two issues are closely related: they are both associated with the loss of information about the unknown distribution. If the distribution can be approximated in some sense, then the same approximation can be employed both to retrieve the distribution from the moments and to approximate the unknown integrands. Approximate moment methods generally proceed as follows: the unknown distribution is first approximated with a certain rule and subsequenty the parameters of the approximation are obtained from a closed set of moments.

The first suggestion for closure, to be found in both Hulburt and Katz [97] and Enukashvili [61], was to approximate the unknown distribution by a set of orthogonal polynomials. In both works, Laguerre polynomials were employed, in which case only the first 3 moments are needed. Approximating a distribution by a low-order polynomial parametrised by its moments is equivalent to presuming a certain functional form for it - in the case of the Laguerre series with 3 moments it is the Γ-pdf. Clearly, this representation is somewhat rigid, especially in cases where we have no knowledge about the shape of the distribution, or it may change its shape during the process. Nevertheless, the method gives adequate results in simple cases [16].

A more recent development that has found widespread application is the Quadrature Method of Moments (QMOM) proposed by McGraw [157]. QMOM approximates the unknown distribution in a way that allows more flexibility than a universal polynomial approximation. It is based on the concept of Gaussian quadrature, which is the approximation of an integral according to the following rule:

$$\int_{-1}^{1} w(x)f(x) \simeq \sum_{i=1}^{n} w_i f_i \tag{36}$$

i.e. the integral of an function $f(x)$ times a weight function $w(x)$ is approximated by a number of unevenly spaced function values multiplied by approximate weights, the parameters of the approximation being the abscissas and the weights - thus an n point approximation involves $2n$ parameters. A certain procedure [190] can be followed for determining the abscissas and weights, which will be the same for every integral whose integrand can be factored into a product with the same weight function. In our problem, however, the distribution function is unknown. What QMOM does is to regard the distribution as the weight function, and the kernel as the function to be integrated. Let us demonstrate this with the growth integral:

$$k \int_{0}^{\infty} \upsilon^{k-1} G(\upsilon, t) n(\upsilon, t) d\upsilon \simeq \sum_{i=1}^{n} w_i \upsilon_i^{k-1} G(\upsilon_i, t) \tag{37}$$

In this approximation the quadrature parameters w_i, υ_i are unknown. However, if they could be somehow determined, it would be possible to approximate all integrals involving the unknown distribution (e.g. the moments) with the same parameters:

$$\int n(\upsilon, t) \upsilon^k d\upsilon \simeq \sum_{i=1}^{n} w_i \upsilon_i^k \tag{38}$$

QMOM determines the quadrature parameters so as to be consistent with a finite number of moments. If the initial distribution is known, then the initial moments up to any order can be calculated. Knowledge of $2n$ such moments thus permits the calculation of the parameters for an n-point quadrature. At subsequent time steps the distribution will change, however, and therefore these parameters will change. The original procedure of QMOM is to integrate the moments for a single time step using the parameter values at t_i, and update the values of these parameters from the computed moments at $t_i + \delta t$. Computationally, such an algorithm relies on an efficient method for inverting the moments to obtain the quadrature parameters.

McGraw employed the product-difference (PD) algorithm [83] to construct a Jacobi matrix, the eigenvalues and eigenvectors of which yield the parameter values - the procedure is described in [157]. QMOM was originally demonstrated by McGraw [157] on a problem of diffusion controlled growth, the kernel being proportional to the inverse of the particle size measure, and compared with Laguerre quadrature, the results showing a notable improvement. It was subsequently applied to problems involving aggregation [16] and aggregation-breakage [151].

The implementation of the quadrature method of moments exhibits some problems, mainly associated with its two-stage process - the inversion of a matrix to obtain quadrature parameters from the moments and the integration of the moments. Apart from the possibility that the matrix may be ill-conditioned, this makes the method difficult to extend into multi-dimensional PBE formulations or to couple with transport equations. For these reasons, Marchisio and Fox [148] have proposed an improved algorithm, the Direct Quadrature Method of Moments (DQMOM). The main point of DQMOM is to derive the ordinary differential equations for the quadrature parameters themselves, rather than for the moments, thus eliminating the need for the intermediate step. DQMOM is based on the following representation of the distribution (also referred to as finite-mode PDF [67]:

$$n(\upsilon) = \sum_{i=1}^{n} w_i \delta(\upsilon - \upsilon_i) \tag{39}$$

This is equivalent to the Gaussian quadrature, eq. 36, as can be readily seen:

$$\int f(\upsilon) \sum_{i=1}^{n} w_i \delta(\upsilon - \upsilon_i) d\upsilon = \sum_{i=1}^{n} f_i w_i \tag{40}$$

This representation allows the explicit introduction of the abscissas into the equations. By substituting eq. 39 into the PBE and manipulating, a system of differential equations can be derived for the evolution of the υ_i, w_i. These equations can be found in [148] for cases involving growth, nucleation, aggregation and breakage, while the book by Fox [67] presents the DQMOM equations for a reactive flow. The main advantage of the DQMOM formulation is that it provides a system of ODEs in terms of a closed set of parameters from which the moments can be reconstructed, bypassing the intermediate step in the original QMOM. This makes the method more convenient for coupling with fluid dynamics, as the ODEs can easily become PDEs in an inhomogeneous system by including the convection terms. DQMOM can also be described as a represenation of the distribution using a finite number of delta functions; in this sense, it is also been referred to as the 'multi-environment PDF' and can be compared with presumed PDF methods (to be reviewed in sec. 5.2). However, the ensemble of delta functions cannot be expected to generally converge to the distribution resulting from the PBE solution [231]. Moreover, it is not clear that the method will maintain positive values for the weights and realizable values of the conditional means under all circumstances [108], [109].

Another class of methods for closing the moment equations without assuming the shape of the distribution operates on the discrete population balance (eq. 22, with the possible addition of nucleation and surface growth terms for soot formation). These methods originate in the work of Frenklach and Harris [71] who initially proposed two methods of closure. The first method is based on a Taylor expansion of the aggregation kernel and relies on the assumption that the distribution is narrow. Only the first two terms are retained and results for the model problems were obtained very fast for the cases where the method was applicable. The second method is an interpolation that approximates directly the rate of change of the moments and is of wider applicability. This method was further developed and applied to a number of problems; it was later called the 'Method of Moments with Interpolative Closure' (MOMIC). This work has been recently reviewed by Frenklach [70]. Diemer and Olson [48], [46], [47], also presented a moment

method and investigated the reconstruction of the distribution from the moments. Their studies were focussed on steady-state population balance formulations with coagulation and breakage.

3.3 Discretisation methods

We will now look at methods that compute the entire distribution, rather than certain integral properties of it. This can generally be accomplished in two ways: either by approximating the distribution globally via a polynomial whose coefficients are to be determined, or by discretising the domain of the distribution and employing a local approximation. The former approach is in essence similar to the quadrature method of moments and found several applications in the early stages of population balance research. For a review of these methods, such as the method of weighted residuals, one is referred to Ramkrishna [193], [194]. Methods belonging to the second class, to be referred to as the discretisation methods, are among the most flexible and widely applied for solving the PBE. Due to their importance in the second part of the review, these methods will be described in detail here. It must be noted that the literature in this area is very extensive, with many new methods being proposed and improved, although most of them have so far been used only in homogeneous systems. Our treatment here will focus on the fundamentals in order to prepare the ground for application to flows, rather than attempt to provide a comprehensive review; for the latter, the interested reader is referred to [121], [131], [193], [194], [249], [214],[4], among others.

One may wonder why so many special numerical techniques have been developed for the PBE. The reason for this is the integro-differential nature of the equation. For nucleation-growth problems, the appropriate PBE is a first-order hyperbolic partial differential equation, which can indeed be solved numerically using standard methods. On the other hand, the PBE for aggregation or fragmentation is an integral equation which requires a completely different treatment. The simultaneous presence of these phenomena is responsible for the unique features of the PBE and the formulation of a single numerical method able to accommodate all of these is a major challenge. Nucleation-growth problems can exhibit shocks, as is evident from the hyperbolic nature of the equation; aggregation problems can result in rapid changes of the shape of the distribution. Many methods are tailored to specific problems and have a limited range of validity.

In general, two classes of discretisation methods can be identified. In the first one, the domain of the independent variable is discretised into a number of 'bins', over which the distribution is assumed to have a single value (the mean value in that bin). Essentially, this is equivalent to fitting a piecewise constant function to the distribution. Methods belonging to this category are customarily referred to in the literature as 'Methods of Classes' or 'Discretised Population Balances' (DPB). In the second approach, the distribution is approximated by local functions (piecewise linear or spline) defined over a few neighbouring nodes, the coefficients of which can be written in terms of the nodal values. These methods are variations of the finite element method.

A very important issue with discretisation methods is the choice of grid. Aggregation problems can rapidly shift the distribution towards bigger sizes, resulting in a variation over several orders of magnitude. A uniform grid would thus require in an enormous number of nodal points. On the other hand, rapid variations can occur around the nucleation point, or at the point of growth where the distribution can even become discontinuous (for the size-independent nucleation-growth problem). Early literature focussed on aggregation problems, and one of the first ideas to be introduced, by Bleck [26], was the geometric grid. Employing a geometric progression of (2^j), the number of combinations of particles that must be considered to evaluate the aggregation terms is substantially reduced.

The method of Bleck was one of the first DPB methods. A major challenge, however, is

to make these methods consistent with low-order moments, which represent important physical quantities such as total number and mass of particles. Batterham et al. [17] modified this approach so that it conserves exactly the first moment with respect to volume (i.e. the total mass) by dividing particles that were created at non-nodal points into fragments whose volume would lie at the nearby nodal points. This artificial way of conserving mass, however, introduced errors in all the other moments, as well as in the predicted population density. Hounslow et al. [96] developed a method capable of conserving exactly both total mass and number of particles, as well as accommodating simultaneous growth and aggregation. All these methods are, however, constrained with respect to the choice of grid, as they are based on exploiting the properties of the geometric progression. More recent works by Litster et al. [138] and Kumar and Ramkrishna ([124], [125]) have succeeded in extending the concept of DPBs to finer grids; the latter also offers the advantage of conserving any two chosen moments. In [126] a method particularly suited to problems with growth involving discontinuities was shown, based on the method of characteristics. The method of classes, due to Marchal et al. [145], treats the aggregation process as a set of chemical reactions. A number of works, such as Hill and Ng [93] have concentrated on fragmentation problems.

The application of the finite element method to the PBE has its origin in the work of Gelbard and Seinfeld [80]. Steemson and White [229] used spline collocation to solve steady state problems of nucleation, growth and size dispersion; Eyre et al. [62] also employed spline collocation, complemented with an adaptive grid. Nicmanis and Hounslow [169] solved the steady-state PBE with nucleation, growth, aggregation and breakage using collocation and Galerkin finite elements with cubic Lagrangian trial functions. Liu and Cameron [139] employed wavelets to represent the solution, and focussed on accurate prediction of discontinuities. Rigopoulos and Jones [209] proposed a finite element method that focusses on the accurate evaluation of the aggregation terms by applying corrections to eliminate the errors in conservation of mass arising from the use of a non-uniform grid. Roussos et al. [214] developed a Galerkin on finite elements approach. Reciting in detail the discretised equations that result from all of these methods is out of the scope of this review, but some general features of the formulation can be described for use in sections 4, 5. Considering a monovariate distribution in terms of particle volume, the domain is discretised into a number of points, or nodes, with corresponding nodal values of the number density:

$$N(v) \approx \{N(v_1), N(v_2), ..., N(v_n)\} = \{N_1, N_2, ..., N_n\} \tag{41}$$

In the case of DPBs, these are the values of the number density in each size bin, while in the case of finite element methods they are the nodal values at the element boundaries or interior points. Considering now a homogeneous PBE with nucleation, growth and aggregation, the growth term is approximated as:

$$\frac{\partial}{\partial v}\left(G(v)n(v)\right) \approx G_d(N_{i-k}..., N_{i-1}, N_i, N_{i+1}, ..., N_{i+k}) \tag{42}$$

where G_d is typically a polynomial function whose coefficients depend on the discretisation method, and which approximates the first-order derivative of the number density at point v_i. Usually at most two neighbouring values will be involved (central difference). The method e.g. by Rigopoulos and Jones [209] employs only one adjacent value, to reflect the upwind nature of growth - particles grow from smaller to bigger sizes only, with the reverse occurring in evaporation. Nucleation poses no problem as it is usually a delta function depending on a single particle size. Aggregation birth and death terms will be approximated as:

$$B \approx \frac{1}{2}\sum_{j=1}^{i-1} a_{i-j,j}(v_{i-j}, v_j)N_{i-j}N_j \tag{43}$$

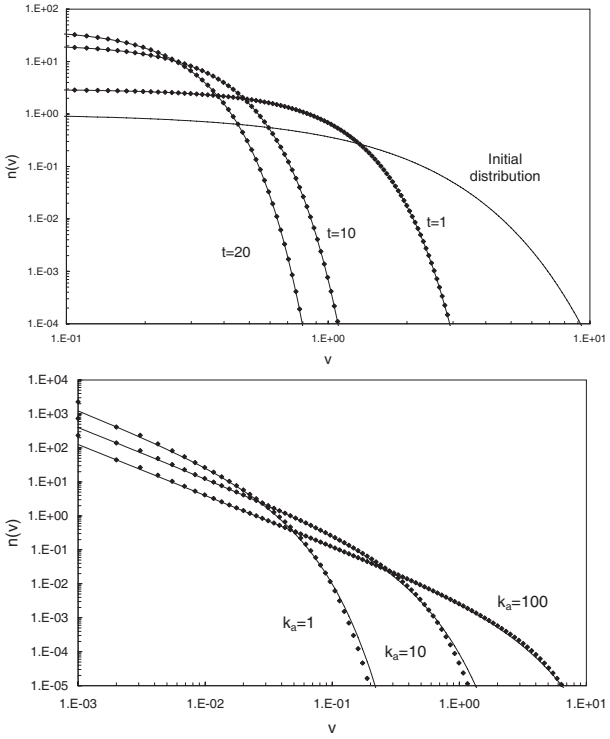


Figure 4: Comparison of the numerical method of [209] with analytical solutions - a) pure aggregation, comparison with the solution of [221], b) aggregation-nucleation, comparison with solution of [95]. Reprinted with permission from [209].

$$D \approx N_i \sum_{j=1}^{n} a'_{ij}(v_i, v_j) N_j \tag{44}$$

Therefore the continuous PBE is converted to a number of ODEs for the nodal values of the number density:

$$\begin{aligned} \frac{\partial N_i}{\partial t} + \frac{\partial}{\partial x_k}(u_k N_i) + G_d(N_{i-k}..., N_{i-1}, N_i, N_{i+1}, ..., N_{i+k}) = D_p \frac{\partial^2 N_i}{\partial x_k^2} + B\delta(v_i - v_0) \\ + \frac{1}{2}\sum_{j=1}^{i-1} a_{i-j,j}(v_{i-j}, v_j) N_{i-j} N_j - N_i \sum_{j=1}^{n} a'_{ij}(v_i, v_j) N_j \end{aligned} \tag{45}$$

In some cases, these may be differential-algebraic equations. Fig. 4 shows comparison of the numerical simulation with the method of [209] with analytical solutions from model problems.

With a proliferation of methods for solving the PBE, a number of comparative studies have attempted to assess their performance and domain of validity. Barret and Webb [16] compared moment Laguerre quadrature methods, QMOM and a finite element method based on linear trial functions for a aggregation problem with different kernels. They found that, while for the Brownian kernel moment methods - even the simpler Laguerre quadrature - gave a good estimate, complex kernels for processes such as the gravitational settling and turbulent coagulation require the finite element method. Grosch et al. [89] conducted a systematic study of various

QMOM formulations and concluded that QMOM is efficient for simpler problems involving non-local, smooth phenomena, but less applicable to problems with a range of interacting and local processes (i.e. acting within a localised range of the particle size distribution) and recommended that its use on unknown problems must be validated against reference solutions. Several studies show comparisons between different discretisation methods, either for coagulation only [121], coagulation-fragmentation [249], or simultaneous nucleation, growth and aggregation [4], [5]. It must be remembered that the majority of these studies focus on the PBE for homogeneous systems; coupling of these numerical methods with fluid dynamics raises further issues that render some approaches more or less practical than others. For example, some of these approaches require solution of algebraic as well as differential equations or intermediate inversion of matrices, while moving grid techniques continuously change the dependent variables.

4 Population Dynamics in Laminar Flow

4.1 Population dynamics for non-inertial particles

Having reviewed the development of population dynamics in homogeneous systems, we now turn to flow systems. The approaches to be covered involve a coupling of the population balance with the equations of fluid dynamics. The presence of turbulence poses important complications, so we will begin by considering laminar flow. The presence or not of inertial forces is another important issue. The effect of inertia on the particle motion can be quantified with the aid of the Stokes number, defined as:

$$St = \frac{\tau_V}{\tau_F} \tag{46}$$

where τ_V is the momentum response time and τ_F is a flow characteristic time (see Crowe et al., [35] - it can also be defined in terms of characteristic lengths [73]). The Stokes number expresses the response of the particle to changes in the flow imposed by an obstacle or change in boundary conditions and implies that, with $St << 1$, the particles will follow the streamlines of the flow. This assumption is acceptable for smaller particles, and is usually made in problems such as soot formation, nanoparticle production, precipitation and sometimes in sprays where the droplets are not too large or have significantly different momentum. We will consider this case first.

The mathematical model for non-inertial particles in a flow field is a population balance equation with no slip. We will write the equation in terms of a single internal coordinate which will be a measure of particle size, as this is the case with most flow problems that have been investigated. We choose particle volume (as opposed to a linear dimension such as radius or diameter) as the variable of choice, since it facilitates the analysis of aggregation problems (aggregation is volume preserving).

$$\frac{\partial N(v;x_j,t)}{\partial t} + \frac{\partial}{\partial x_j}\left(u_j \cdot N(v;x_j,t)\right) = -\frac{\partial}{\partial v}\left(G(v)N(v;x_j,t)\right) + \frac{\partial}{\partial x_i}\left(D_N \frac{\partial N(v;x_j,t)}{\partial x_j}\right)$$
$$+ \frac{1}{2}\int_0^v \beta(v-v',v')N(v-v';x_j,t)N(v';x_j,t)dv' - \int_0^\infty \beta(v,v')N(v';x_j,t)N(v;x_j,t)dv' \tag{47}$$

Compared to the homogeneous population balance equation, the only addition to this equation is transport in physical space. This is divided into two terms, one for the convective contribution to the flux and one for the diffusive contribution. The latter term expresses diffusion of particles due to Brownian motion, where D_N is the diffusivity of particles given by the Stokes-Einstein law [73]. The PBE must be coupled with the continuity and Navier-Stokes

equations, shown below for reference:

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_j}(\rho u_j) = 0 \tag{48}$$

$$\frac{\partial u_j}{\partial t} + u_j \frac{\partial u_j}{\partial x_j} = \frac{\partial \tau_{ij}}{\partial x_j} - \frac{1}{\rho}\frac{\partial P}{\partial x_j} \tag{49}$$

as well as by the scalar transport and reaction equation for any chemical species contributing to the growth and, possibly, aggregation processes:

$$\frac{\partial \rho Y_\alpha}{\partial t} + \frac{\partial}{\partial x_j}(\rho u_j Y_\alpha) = \frac{\partial j_{\alpha,j}}{\partial x_j} + \dot{\omega}(Y_1, Y_2, ...Y_m, N(\upsilon; x_j, t)) \tag{50}$$

where Y_α are the species' mass fractions, $j_{\alpha,j}$ is the diffusive flux and $\dot{\omega}(Y_1, Y_2, ...Y_m)$ is the reaction source term. An energy equation may have to be added if heat release is of importance. The reaction source term in eq. 50 would depend only on the species in a combustion process; in a particulate process, however, it will also depend on the particle size distribution, as rates of reactions that involve the particles will depend on their total surface area. For problems such as soot and nanoparticles, the volume fraction is usually too small to require a source term in the continuity equation; for bubbles and droplets this may not be so, but these are more likely to be inertial particles.

The population balance, therefore, is of higher dimensionality than the remaining equations, due to the presence of the phase space dimensions (here particle volume). Solution of the coupled PBE-fluid dynamics/species transport equations therefore must involve two steps:

1. Transformation of the PBE into an equivalent PDE system where the dependent variables are space and time only.

2. Coupling of the dependent variables with the flow/transport equations.

Step 1 can be carried out either with the method of moments or with a discretisation scheme, as explained in the previous section, the only difference being that the equations are PDEs rather than ODEs due to the addition of the spatial dimension. The transformed variables are either the moments or the nodal values of the discretised distribution. This procedure permits straightforward implementation of population balance modelling into CFD codes, as the transformed variables of the PBE appear as additional scalars, while the particle formation and interaction mechanisms appear as source terms.

The method of moments has the advantage that it involves only a few additional variables, thereby minimising the number of equations to be coupled with the CFD code. On the other hand, it cannot be employed but in the simplest of cases. To deal with size-dependent growth functions and aggregation kernels, an approximate method of moments (e.g. Laguerre quadrature, QMOM/DQMOM, MOMIC) must be employed. These methods were described in sec. 3.

The alternative approach, which completely overcomes the need for closure, is the use of a discretised PBE. The discretised PBE will introduce at least 20-30 variables (number densities at the nodal points) which, in the context of a flow problem, must be stored and solved for every point in the domain. As a result the computational and memory requirements are higher, but feasible with today's computational resources. Discretisation methods also overcome the need for inverting matrices or similar operations inherent in QMOM and its variants. The scalar transport equations for the discretised number densities will be of the form:

$$\frac{\partial N_i}{\partial t} + \frac{\partial u_j N_i}{\partial x_j} = \frac{\partial}{\partial x_j}\left(D_p \frac{\partial N_i}{\partial x_j}\right) + S(N_i, Y_a) \tag{51}$$

with the source term provided by the discretisation method and, in general, depending on the whole range of values of N_i (for aggregation or fragmentation problems that involve integral terms) and on the values of the reactive scalars (for particle formation and growth). We conclude that the dynamics of non-inertial particles in laminar flows can be studied numerically with a straightforward extension of the methods presented in sec. 3, where the moments or discretised nodal values of the number density are treated as additional scalar variables in a CFD code.

4.2 Population dynamics of inertial particles

If $St >> 1$, particles of different size will experience a different drag force and therefore exhibit different velocity. The most general way of taking this effect into account within a population balance approach is to add the particle velocity to the phase space. This poses a major complication, as it increases the phase space to a degree that it becomes intractable for straightforward techniques. A spatially distributed population balance involving size alone is a 3-D (for axisymmetric geometries) or 4-D problem, apart from the time dependency and the integral terms. If velocity components are added to the phase space the number of dimensions increases to 5-7, meaning that alternative solution techniques must be sought. A simplification of the problem is possible, however, by exploiting the relationship between particle size and velocity.

A large amount of research in this area has been contributed by the spray and bubble flow modelling community, as droplets/bubbles often exhibit large sizes and/or are injected with considerable initial momentum. The subject is still evolving, both in terms of numerical methods and theoretical foundations. Existing approaches can be broadly classified into three categories:

- Direct solution of the population balance equation within the complete phase space (including velocity components).
- Two-fluid and multi-fluid methods.
- Lagrangian particle tracking.

The first approach is fundamentally based on the population balance and allows for rigorous modelling of population dynamics such as coagulation, collisions etc. at the cost of computational complexity. The second approach can be regarded as an approximation to the first under certain assumptions and renders the problem more computationally tractable. The third one is based on the Newtonian equations of motion rather than on the PBE and will therefore not be reviewed here, but we will note that links between the Lagrangian approach and PBE/multi-fluid methods have been established in the recent literature [128].

Population balance methods for inertial particles can be traced to the early work of Williams and his spray equation ([259],[260]; see also [262], [261]). Williams based his equation on the following number density function:

$$N(r, u_{p,j}; x_j, t)$$

where r is the radius of the droplets in the spray and $u_{p,j}$ is the velocity of the individual droplets which, for inertial particles/droplets, may differ from the fluid velocity. He subsequently postulated the following equation:

$$\frac{\partial N}{\partial t} = -\frac{\partial}{\partial r}\dot{r}N - \frac{\partial}{\partial x_j}u_j N - \frac{\partial}{\partial v_j}F_j N + Q + \Gamma \tag{52}$$

where the functional dependence of N has been omitted for the sake of clarity. The equation is consistent with the general form of the kinetic equation (10) shown in sec. 2.2. Q here accounts for formation of new droplets (nucleation in the terminology of this paper) while Γ accounts for

the effects of droplet collisions and break-up which redistribute the number density in terms of both size and velocity. Williams obtained solution for some simplified cases via an asymptotic method. Numerical solution of the equation in the general case was impossible at that time, however, and it took some time to follow the work of Williams.

Direct numerical solutions to Williams' equation were sought by Westbrook [256], Gany et al. [76] and Sutton et al. [236]. These methods involve a discretisation of the domain of the pdf in all independent variables, i.e. position, velocity and droplet size, with dimensionality potenially rising to 7, and clearly the applications of finite difference methods is likely to meet its limitations as soon as the mesh reaches any appreciable dimensions. Gupta and Bracco [90] proposed an approach where the spray is simulated as ensemble of a discrete number of sprays, each one injected at a different time with a certain initial distribution. This permits converting the boundary value problem posed by the original equation into a number of initial value problems. Overall, however, direct solutions to the Williams equation are limited to idealised initial/boundary conditions for the distribution, idealised carrier phase flow fields (where the dispersed phase exhibits no feedback effect) and do not take into account the integrals of collision/coagulation or sources. As Gupta and Bracco acknowledged, the main value of this approach is for validating the results of comprehensive models.

Meanwhile, an alternative approach to dispersed phase modelling had been developed by the multiphase flow community. This approach describes a multiphase flow as the flow of two continuous phases ('interpenetrating continua'), each phase being characterised by its volume fraction. Therefore a minimum of two equations per phase are required: a continuity equation for the volume fraction and a momentum equation for the average phase momentum. This approach is fundamentally related to the population balance, as it amounts to solving equations for the first and second joint moments of the number density distribution with respect to particle size and velocity, and these quantities correspond to the phase volume fraction and average momentum. The equations of this 'two fluid' approach were not originally derived from the PBE, but rather via volume or ensemble averaging of the conservation equations (e.g. Ishii, [101], Drew [54] or Drew and Passman [55]); its relation to the PBE and its potential derivation from it was, however, noted by researchers such as Gupta and Bracco [90] and Sirignano [223]. This approach also allows for straightforward implementation of the two-way exchange of momentum between the continuous and dispersed phases, which is important in dense flows - this is also possible with the population balance approach, but requires integration of the distribution to obtain the momentum of the dispersed phase. While polydispersity information is lost in this approach, later research showed that the two approaches can be reconciled via the extension to 'multifluid' models.

The key point in linking multifluid models to the population balance is the realisation that, while the PBE for inertial particles requires a phase space comprising of both particle size and velocity, these two variables are functionally related via the drag force - unlike the kinetic theory of gases, where particles can have independent velocities. If inertial non-interacting particles of various sizes are injected into a steady flow with the same initial velocity, then every particle will follow a deterministic trajectory that depends on its size and the ambient flow field - this fact forms the basis of the 'trajectory method' (Crowe et al. [35]). In a dynamic flow field, the velocity of each particle will depend on its size and on the instantaneous local fluid velocity. Thus particles of the same size will follow the same set of trajectories and it should be possible, in principle, to eliminate the particle velocity from the list of independent variables by treating all particles of the same size as an ensemble, in the sense that their velocity exhibits the same functional form. In a steady-state flow field, this functional form can in principle be determined, although its analytical derivation would be impossible in any practical case. In an unsteady flow, the instantaneous velocity should be determined by solving a momentum equation for the phase-average velocity, which is the first joint moment of the distribution. Thus the problem

can be reduced to a set of discretised equations along the size coordinate, together with a set of momentum equations for each size node or section. The number of discretised equations and variables is thus reduced from $N_x^3 N_s N_u^3$ (where N_x^3, N_s, N_u^3 are the number of nodes along the space, size and velocity coordinates) to $(N_x^3 N_s + N_s)$. This conclusion is not always valid, however: if, for instance, we allow for the particles to be injected with different initial velocities, then no single momentum value can be assigned to a size class, at least in the initial period. This assumption has been discussed recently by Laurent and Massot [128], and we will soon return to this point.

Greenberg et al. [87] first derived the multi-fluid method as a discretised population balance. They regarded their work as an extension to that of Tambour et al. [238] whose 'sectional method' was essentially a discretised population balance for non-inertial droplets). Greenberg et al. sought to reconcile the method of Tambour with the Williams spray equation. By integrating the (inertial) spray equation with respect to the velocity coordinate and subsequently discretising into a number of size classes, they obtained a set of equations for the volume fraction and average momentum of each class. In addition, they considered coagulation via a sum over the discretised classes. No solutions or applications were presented; however, their formulation demonstrated the link between population balance and multi-fluid methods and also accounted for both inertial forces and coagulation.

The alternative to the (essentially Eulerian) population balance approach is the tracking of sample particle paths by solving the Lagrangian equations of motion. More recently, the links and relationships between the two approaches were examined in the work of Laurent and Massot [128] who sought to link the sectional approaches of Tambour and Greenberg et al. to the Lagrangian approach. They first discussed the derivation of the sectional approach from the kinetic equation of Williams via taking moments, in a manner similar to [87], and provided equations for the phase average energy in addition to mass and momentum. Subsequently, they drew an equivalence with the Lagrangian approach by introducing a sampling over the Eulerian distribution. Laurent and Massot also drew attention to the fact that, while the sectional approach involves the implicit assumption that particles within the same size class move with the same velocity (which is valid if they were injected with the same initial velocity), the Lagrangian approach does not. This limitation, however, is not implicit in the original population balance (which includes particle velocity as an independent coordinate, thereby allowing particles with arbitrary velocities), but only in its discretised formulation derived after averaging in velocity space.

Multi-fluid methods have also been employed in the context of bubble flows by Jakobsen, Svendsen, et al. [91], [102] and Dorao et al. [52] - see the recent review by Jakobsen et al. [103] - as well as chemical reactors such as fluidised beds [100]. The multi-fluid approach is fully consistent with population balance formulations for inertial particles (such as the Williams equation), apart from the fact that the latter allows for particles of the same size, at the same position and time instance, to have a distribution of velocities. It can be concluded that the latter is of greater generality, but this generality is mainly of theoretical value. For most applications, a simplified initial velocity profile allows for the application of the multi-fluid method.

5 Population Dynamics in Turbulent Flow

5.1 Interaction of turbulence and polydispersed particle dynamics

The coupling of the population balance equation with fluid dynamics in a turbulent flow is a very complex problem, but also a very practically relevant one, as most real-world applications involve turbulence. Turbulent flows represent a chaotic and unsteady state of fluid motion which is, nevertheless, still described by the same instantaneous equations as laminar flow. Numerical

solution of these equations for turbulent flow is practically unattainable, though, due to the chaotic nature of the flow and the presence of a very wide range of space and time scales - except for very simple, academic problems (and even then it requires formidable computational resources). As a result, equations for statistical quantities need to be derived; these equations are always unclosed, and various models have been applied to obtain closure (see e.g. [127], [257], [185] for turbulence modelling, or [161], [162], [241], [155], [57], [40] among others for a more general review of turbulence).

In what follows, we will be assuming fully developed turbulence. In that case all quantities, including the number density, can be assumed to be random variables - i.e. their instantaneous value would be different in any individual experiment, regardless of our efforts to reproduce the experimental conditions, and a probability density function (pdf) can be associated with them. Following the convention in the theory of stochastic processes, we shall be representing the instantaneous values of these variables with a capital letter, to distinguish it from the domain of the pdf - e.g. $U(x,t) \rightarrow f(u;x,t)$, which is the one-point pdf of U. Note that an extensive body on research has been devoted to the non-linear dynamics of isolated particles (or small groups of them) in transitional and weak turbulence regimes, and to the identification of coherent structures; this line of work lies out of the scope of the review, which deals with essentially statistical approaches.

Before proceeding, it is worthwhile to distinguish between two levels of randomness and averaging that are present when applying the population balance to a turbulent flow. At the first place, the PBE is an averaged equation in itself; it describes the number density of particles exhibiting certain properties at a certain point in space and time, and results from averaging of the equations of motion over a very large ensemble of individual particles. This assumption of a particle continuum constitutes the first level of averaging and is inherent in the PBE description of any polydispersed system, turbulent or not. The second level of averaging is required when the population of particles is embedded in a turbulent flow. There, if we focussed our attention to an individual fluid element containing a certain population of particles, in any particular experiment we would observe a different particle size distribution (at the same point in space/time). Two kinds of distribution can therefore be defined: the particle number density distribution (which is not a probability density function, as it is not normalised) and the probability distribution of the (essentially random) number density of particles of any size at any point in space and time.

Let us now enquire about the physical mechanisms through which randomness enters the PSD (fig. 5). To begin with, turbulent transport of particles will result in fluctuations in the particle number density. This problem is much more complex for inertial particles, where particles of different size experience a different drag force. For very dense flows, such as fluidised beds, the fluid-particle interaction is two-way - i.e. the flow is experiencing a feedback effect (turbulence modulation). Another mechanism, present in reactive flows with particle production such as soot formation and reactive precipitation, is the following: the randomness in the field of the reactive species results in random formation and growth of particles in different parts of the domain. Feedback occurs via the consumption of the reactive species associated with these particle production processes, while in the case of combustion the changes in the species' field affect the flow via the associated heat release and density change. Another mechanism is related to coagulation, which involves non-linear interactions between particles of different sizes and depends on local shear. These phenomena give rise to non-linear correlations associated with the coupling of the reactive species' field and the population density, and have been studied very little so far. The analysis of the closure problems resulting from them will be the subject of the following sections. Turbulent dispersion of inertial particles, on the other hand, has been the subject of a large number of studies, mostly from the Lagrangian point of view or using the two-fluid model. As this body of research is very extensive, we will not discuss it in any detail here and refer the interested reader to a number of excellent reviews [154], [160], [172]. The

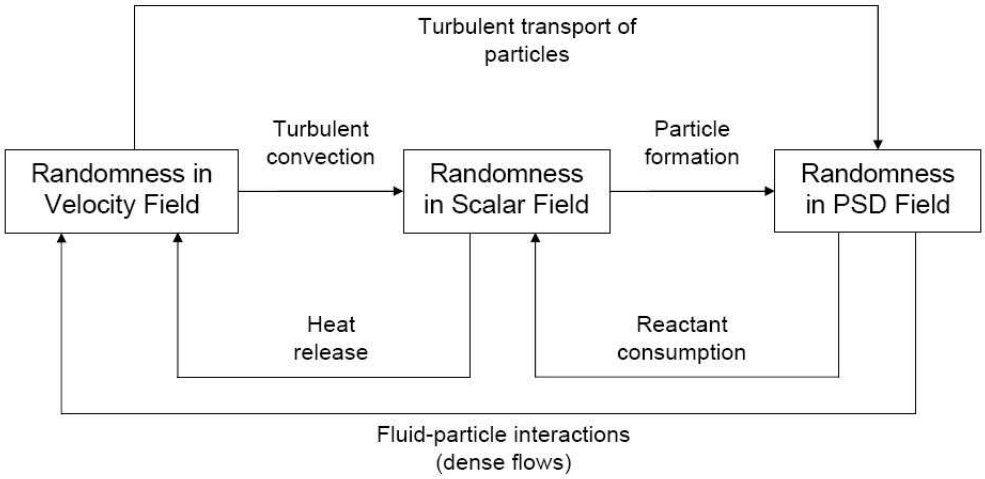


Figure 5: Interactions between turbulence and particulate processes

main focus of this review is on population balance modelling approaches, and therefore only works from that point of view will be covered extensively.

5.2 The closure problem for particle formation

Turbulence modelling approaches are based on the concept of Reynolds' decomposition, which consists of decomposing each random variable into a mean and a fluctuating component. This results in equations for the mean values which are unclosed, as they involve higher order moments, and phenomenological models are applied to obtain closure. An alternative approach is Large Eddy Simulation (LES), where a spatial average over a coarse grid is employed, and again a model is employed for the unclosed sub-grid terms. Apart from providing closure for the Reynolds (or sub-grid) stresses, these models can also provide closure for the transport of scalars due to the fluctuating velocity components. This modelling would suffice for turbulent transport of non-inertial particles.

The presence of particle formation, however, results in further unclosed terms arising from the non-linear particle formation terms. This is a problem similar to the closure of reaction source terms in combustion, where one is faced with the need for averaging a strongly non-linear function of concentrations which are random due to turbulence. Turbulence modelling or LES cannot provide closure of these terms, especially when the timescales associated with the particle formation are fast, and a model for the interaction of turbulence with particle formation processes is needed. Overall, modelling approaches for particle formation in turbulent flows can therefore be classified according to three criteria: the model employed for obtaining the flow field (RANS or LES), the model used for turbulence-particle formation coupling (e.g. turbulent mixer, flamelet, transported probability density function (PDF) - to be defined later in this section) and the modelling of the PBE itself (method of moments, approximate closure such as QMOM, discretised PBE). In the following sections, we will classify the models from this perspective (fig. 6).

The starting point will be the population balance equation for particle nucleation and growth in a flow field. It is assumed here that the particles are non-inertial and that only one characteristic dimension is required in the distribution, the particle volume (v). The particle nucleation ($\dot{N}$) and growth (G) functions are functions of the local environment, i.e. the concentrations of the chemical species that react or condense to form the particles. This type of equation would

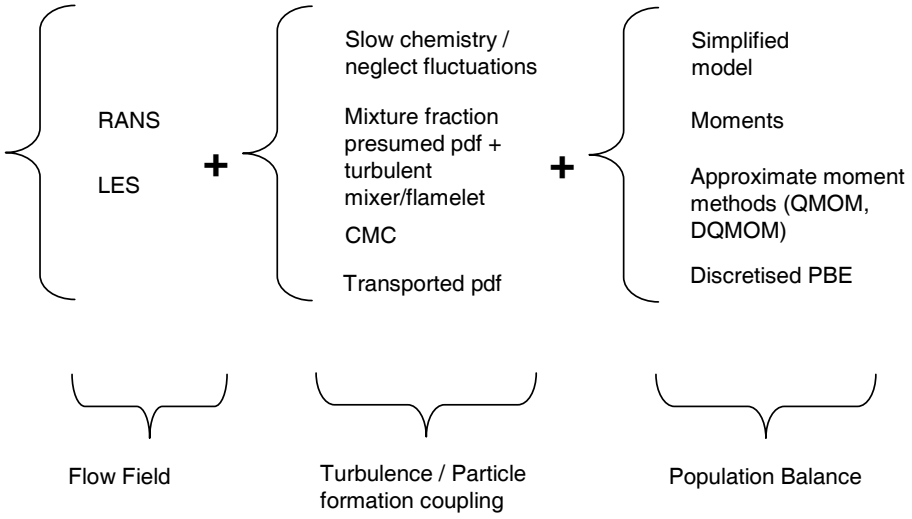


Figure 6: Hierarchy of models for the turbulent PBE

be appropriate to describe e.g. soot formation, nanoparticle growth or crystal precipitation from solution, as long as no additional variables are required to describe e.g. the morphology of the particles. The focus on this section will be on the interactions between the scalar field and the particle processes. The PBE is:

$$\frac{\partial N(\upsilon;x,t)}{\partial t}+\frac{\partial}{\partial x_i}\left(u_i(x,t)N(\upsilon;x,t)\right)+\frac{\partial}{\partial \upsilon}\left(G(\upsilon,Y_a)N(\upsilon;x,t)\right) = \frac{\partial}{\partial x_i}\left(D_N\frac{\partial N(\upsilon;x,t)}{\partial x_i}\right)+\dot{N}(Y_a)\delta(\upsilon-\upsilon_0) \quad (53)$$

The majority of works on PBE with flow have been based on a moment transformation of the PBE. The moment-transformed equation is (omitting the space/time dependence of the moments):

$$\frac{\partial m_k}{\partial t}+\frac{\partial u_i m_k}{\partial x_i}+G(\upsilon,Y_\alpha,t)m_k-k\int_0^\infty \upsilon^{k-1}G(\upsilon,Y_\alpha,t)n(\upsilon,t)d\upsilon = \frac{\partial}{\partial x_i}\left(D_N\frac{\partial m_k}{\partial x_i}\right)+\upsilon_0^k\dot{N}(Y_\alpha) \quad (54)$$

As discussed in sec. 3.2, this set of equations is already unclosed for a finite set of moments due to the presence of the integral term, unless the growth term should assume a very simple form. This equation would have to be coupled with the Navier-Stokes/continuity and species transport equations to formulate a complete description of the problem. The flow being turbulent, however, these equations would be valid only for the instantaneous flow, concentration and number density/moment fields, which could be computed only via direct numerical simulation (DNS). Here we are interested in developing a modelling approach to the turbulent PBE. Applying the Reynolds decomposition to the moment transport equation, we obtain:

$$\frac{\partial\langle m_k\rangle}{\partial t}+\frac{\partial\langle u_i\rangle\langle m_k\rangle}{\partial x_i}+\frac{\partial\langle u_i'm_k'\rangle}{\partial x_i}+\langle G(\upsilon,Y_\alpha,t)m_k\rangle - \left\langle k\int_0^\infty \upsilon^{k-1}G(\upsilon,Y_\alpha,t)n(\upsilon,t)d\upsilon\right\rangle = \frac{\partial}{\partial x_i}\left(D_N\frac{\partial\langle m_k\rangle}{\partial x_i}\right)+\upsilon_0^k\left\langle\dot{N}(Y_\alpha)\right\rangle \quad (55)$$

There are several unclosed terms in this equation. The accumulation, convection by the mean velocity and diffusion of the moments are all closed. The transport due to the fluctuating component of the velocity is unclosed, but it can be closed using a gradient diffusion assumption, along the same lines as that employed for the transport of scalars in turbulence models. The term involving the product of the growth rate and the moment, however, is unclosed, due to the non-linear dependence of the growth function on the reactive scalars - similar to the problem of closure of the reaction source term in combustion. The nucleation term results in a closure problem of the same sort. The integral, finally, is already unclosed as it cannot be expressed in terms of a finite set of moments. We conclude that a RANS treatment of the moment transport equation presents us with closure problems at two levels: the transition from the number density distribution to a truncated set of moments and the fluctuations of the non-linear terms involving moments and reactive scalars. Both of these problems must be treated with suitable closure models.

The most straightforward approach of modelling particle formation in turbulent flows is to couple the moment equations with CFD while neglecting fluctuations. If size-independent growth is assumed, the need for closing the growth integral disappears as well. This approach was adopted in early works [254],[255] and is employed in many straightforward implementations of the PBE in commercial CFD codes. Neglecting fluctuations, however, would be valid only if the particle formation reactions were very slow compared to mixing. In most problems of soot and nanoparticle formation, an overlap of time scales for diffusive transport and reaction is likely to occur. In addition, many problems of crystal and soot growth involve size-dependent growth kinetics. In that case, the integral must be approximated by methods such as Laguerre quadrature and QMOM.

To obtain a closed form for the average of a non-linear term, in general one must know the probability density function (PDF) of the random variable appearing in that term. E.g. if $G(U)$ is a nonlinear function of a random variable U, then the decomposition in terms of average and fluctuation $\langle G(U)\rangle = \langle G(\langle U\rangle + U')\rangle$ cannot be further elaborated without assumptions, while if the pdf $f(u)$ of U is known we have

$$\langle G(U)\rangle = \int G(u)f(u)du \tag{56}$$

which is closed. Presumed-shape PDF methods transport the moments of the random variable (typically the mean and variance) and subsequently reconstruct the pdf by assuming a fixed shape for it to close the non-linear terms, therefore transforming the problem from a functional equation into a set of equations for the moments. Applications of presumed PDF methods typically reduce the problem into a description featuring a small number of variables - usually just one or two, such as the mixture fraction and its variance (for non-premixed reactive flows) or a progress variable (for premixed ones). A further model is then required for obtaining the mean reaction or particle formation rates from the pdf of that variable.

In a series of articles, Baldyga et al. [14], [13], [12] treated the closure problem for particle formation and growth in a liquid phase using presumed-shape pdf methods. Since the problem considered by Baldyga et al. involved mixing and reaction between two inlet streams, it could be described in terms of a mixture fraction, for which a β-pdf was assumed. Subsequently an approximate model, the turbulent mixer model [10], was employed to obtain the species' concentrations from the mixture fraction pdf, thus closing the turbulent PBE. The assumption of size-independent growth allowed reducing the PBE into a closed set of four moments (the number density being defined in terms of particle size). Results showed qualitative agreement with experiments in terms of mean sizes, although the distribution (as retrieved from the moments) showed a deviation in shape.

The presumed-shape PDF method for the mixture fraction has also been used in conjunction

with the flamelet approach to simulate soot formation by Moss et al. [164], [165], [237] and Fairweather et al. [65]. A sample of predictions from the work of Fairweather et al. is shown in in fig. 7. More information on the flamelet approach can be found in the reviews by Peters [174], [175]. The PBE employed in soot studies ranges from simplified forms for the prediction of soot number density and mass fraction to comprehensive formulations, usually casted in discrete form, incorporating nucleation, growth/oxidation and, in some cases, coagulation . The latter are usually solved with the method of moments (Frenklach and Wang, [72]). Kronenburg et al. [122] applied the Conditional Moment Closure (CMC) method [115] to soot formation. CMC is not based on a presumed pdf for the mixture fraction, but rather uses it as an independent dimension and solves for the conditional (on the mixture fraction) means of the remaining scalars. The assumption there is that conditional fluctuations are much smaller than conditional means (as compared to unconditional fluctuations), which is reasonable because reactive scalars are usually correlated to mixture fraction. The study of Kronenburg et al. concluded that differential diffusion is crucial, as without it soot mass fraction was underpredicted by at least 40%, and predictions of soot mass fraction from that study are shown in fig. 8. CMC was also employed in a recent study of soot formation by Yunardi et al. [264]. To summarise, the approximations involved in this class of methods involve: the presumed shape of the mixture fraction pdf, the model employed for correlating the particle formation to the mixture fraction and the assumptions used to retrieve the shape of the PSD from the moments. As discussed in sec. 3.2, the limitations of moment-based methods become more apparent when considering problems involving both particle formation/growth and coagulation.

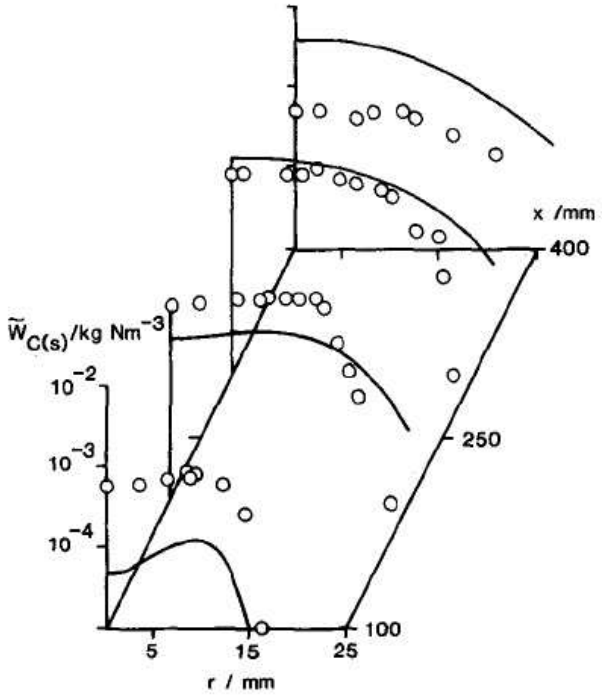


Figure 7: Soot mass fraction - comparison of predictions from the flamelet model of Fairweather et al. with experimental results, reprinted with permission from [65].

Transported PDF methods are a powerful and general class of methods that, in contrast with the presumed-shape PDF ones, do not impose any assumption on the shape of the distribution. In these methods, a transport equation is derived for the joint pdf of all random variables appearing in the non-linear terms - i.e. $f(u_1, u_2, ..., u_n)$. As a result, these terms appear in

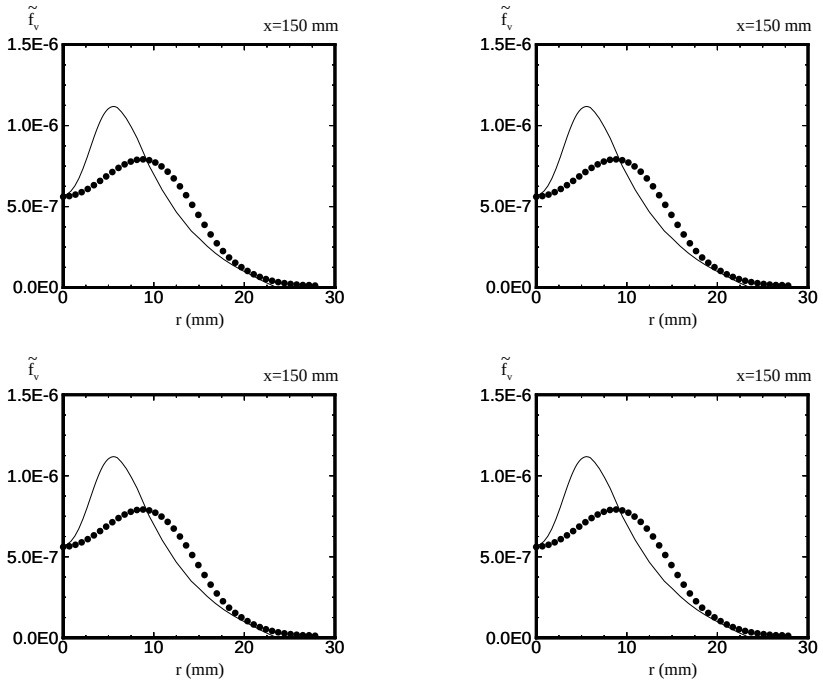


Figure 8: Comparison between predicted (lines) and measured (symbols) radial soot volume fraction profiles at different downstream locations using CMC - reprinted with permission from Kronenburg et al. (2000) [122].

closed form:

$$\langle G(U_1, U_2, ..., U_n)\rangle = \int\int ... \int G(u_1, u_2, ..., u_n) f(u_1, u_2, ..., u_n) du_1 du_2 ... du_n \qquad (57)$$

The transported PDF approach originates in the early works of Lundgren [141] on the velocity PDF. It gained significant interest when applied to scalar mixing and reaction problems, especially in combustion; see O'Brien [170] for a review of early work). Not all terms in the pdf transport equation are closed, however; a full closure would require the joint pdf of the values in all spatial and temporal positions, resulting in an infinite-dimensional functional equation, and while such an equation has been considered ([94], [51], [161] - see chap. 10), no solutions of practical problems have been obtained. Therefore the majority of research so far has focussed on transport equations for the one-point joint pdf of scalar variables or for the joint velocity-scalar pdf. Models have been developed to obtain closure of the terms arising from the two-point correlations (mostly those arising from diffusion terms). Apart from the closure problem, the main feature of pdf methods is the increase in dimensionality, as each dependent variable in the domain of the pdf becomes an independent one (see eq. 57). This feature rules out traditional discretisation methods (as they scale exponentially with dimensionality) and necessitates a stochastic approach for its numerical solution. Pope [181],[182], [185] showed how Monte-Carlo methods could be combined with CFD simulations to model scalar and velocity correlations. Recent reviews of this approach have been contributed by Dopazo [50], Kollmann [118], Jones [106] and Fox [67], with the latter two focussing on scalar pdfs. Their application to particle formation problems, however, has started to be investigated relatively recently.

The derivation of the one-point pdf transport equation can be accomplished in several ways [141], [118], [182]. Here we will outline briefly the method of Lundgren, which is most commonly employed. The joint pdf of several random variables $y_1, y_2, ..., y_n$ is represented as the ensemble average of the fine-grained density function, which is composed of dirac delta functions and

can be perceived to represent the pdf of a single realisation of the turbulent flow in which each random variable assumes a certain value:

$$f(y_1, y_2, ..., y_n) = \langle F \rangle = \left\langle \prod_{\alpha=1}^{M} \delta(Y_\alpha - y_\alpha) \right\rangle \tag{58}$$

The pdf evolution equation is thus obtained by taking the time derivative of eq. 58:

$$\frac{\partial f}{\partial t} = \left\langle \frac{\partial F}{\partial t} \right\rangle = \left\langle -\sum_{\alpha=1}^{M} \frac{\partial F}{\partial y_\alpha} \frac{\partial Y_\alpha}{\partial t} \right\rangle \tag{59}$$

But since the fine-grained density represents a single realisation, its evolution must obey the instantaneous transport equations. Therefore one proceeds by substituting the instantaneous equations for the the random variables in eq. 59 and manipulating the resulting expression. As expected, some terms will remained unclosed, in particular those associated with two-point correlations (since this is an one-point pdf). In addition, if velocity is not included in the pdf sample space, an unclosed term will appear expressing transport by fluctuating (or subgrid) velocity components. This term is usually modelled via a gradient transport hypothesis.

Transported PDF methods were first applied to particle formation problems in conjunction with the method of moments. Kollmann et al. [120] presented a simulation employing a transport equation for the soot moments, while the chemistry was assumed to be in equilibrium constrained by the local enthalpy and mixture fraction. The formulation of Lindstedt and Louloudi [137] included the joint pdf of all reactive scalars in the mechanism (15) together with the soot moments. In these works, the PDF transport equation was solved using the method of stochastic particles in a Lagrangian framework [182], [184]. These methods are based on the following concept: an ensemble of stochastic entities ('particles') is created, each particle featuring sample values of the reactive scalars and PSD moments. The particles then move according to a Langevin equation with drift and diffusion, so that the statistics of the particles in each computational cell approximate the local value of the PDF. The equivalence of this stochastic simulation - solution of the Langevin equation - and of the transport equation for the pdf - essentially a Fokker Planck equation - is well established by the Feynman-Kac theorem (see e.g. [77], [110], [230]). The implementation involves transporting the particles by the flow field (usually computed externally via a finite-volume CFD code) and superimposing a random motion to them. Mixing is also simulated according to one of several mixing models ([49], [36], [234], [183] - see also the review by Kollmann [119]).

An alternative approach to the numerical solution of the pdf transport equation has been suggested by Valino [246] and Sabelnikov and Soulard [215]. This approach resolves the Eulerian PDF transport equation by resorting to an equivalent stochastic partial differential equation for an ensemble of fields that evolve in a stochastic manner. The pdf is then represented by the ensemble of local field values, rather than particles. Mastorakos and Garmory [78] have applied the field approach to a particle formation problem (aerosol nucleation and growth in a turbulent jet). A PBE transformed via the method of moments was employed. The stochastic field method is more limited in the range of mixing models that can be employed, but it provides smooth density fields and is therefore convenient for combustion problems, while its LES implementation is straightforward.

We finally consider the possibility of working with the PBE directly (rather than with the moment transformation). To see clearly the need for closure, we apply the Reynolds decomposition to the number density function:

$$N(v, x, t) = \langle N(v, x, t) \rangle + N'(v, x, t) \tag{60}$$

Applying the Reynolds decomposition to the PBE, eq. 53, we obtain the following:

$$\left\langle \frac{\partial N(\upsilon)}{\partial t} \right\rangle + \left\langle \frac{\partial}{\partial x_i}(u \cdot N(\upsilon)) \right\rangle + \left\langle \frac{\partial}{\partial \upsilon}(G(Y_\alpha, \upsilon) \cdot N(\upsilon)) \right\rangle = \left\langle \frac{\partial}{\partial x_i}\left(D_p \frac{\partial N(\upsilon)}{\partial x_i} \right) \right\rangle + \langle B(Y_\alpha, \upsilon) \cdot \delta(\upsilon - \upsilon_0) \rangle \quad (61)$$

For brevity, we have dropped the explicit dependence of N on x, t. From the resulting terms, only the accumulation and diffusion are closed. All of the remaining terms require closure of some sort. As before, the convection in physical space gives rise to an unclosed term of the form $\nabla \langle u' \cdot N' \rangle$ which can be modelled along the same lines as passive scalar diffusion, i.e. with the introduction of an eddy diffusivity. The nucleation and growth terms, however, present a closure problem of a different kind, due to their non-linear dependence on the species mass fractions. The nucleation is similar to a non-linear reaction source term for which - as in the case of the reaction source term in combustion - a Taylor expansion that neglects of higher-order terms is unlikely to suffice. The growth term, also a non-linear function, yields [205]:

$$\left\langle \frac{\partial}{\partial \upsilon}(G(\upsilon, Y_\alpha) \cdot N(\upsilon)) \right\rangle = \langle N(\upsilon) \rangle \cdot \left\langle \frac{\partial G(\upsilon, Y)}{\partial \upsilon} \right\rangle + \left\langle \frac{\partial G(\upsilon, Y_\alpha)}{\partial \upsilon} \cdot N'(\upsilon) \right\rangle + \frac{\partial \langle N(\upsilon) \rangle}{\partial \upsilon} \cdot \langle G(\upsilon, Y_\alpha) \rangle + \left\langle \frac{\partial N'(\upsilon)}{\partial \upsilon} \cdot G(\upsilon, Y_\alpha) \right\rangle \quad (62)$$

Therefore the growth term presents a closure problem akin to the nucleation term, i.e. due to its non-linear dependence on the species' mass fractions; in addition, however, it is correlated with the particle number density. Again, there is no comprehensive way to model these, and therefore the PBE remains unclosed under Reynolds averaging.

Recently, Rigopoulos [205] proposed the transported PBE-PDF approach to overcome the closure problem. This approach proceeds as follows: at first, the number density is discretised in the size domain. The details of the discretisation approach are immaterial here, and indeed any of the methods cited in Section 1 above can be employed. The transported PBE-PDF approach then proceeds by defining the joint PDF of the reactive scalars and discretised number densities, $f(y_\alpha, n_i; x, t)$. This is the probability that a certain particle size distribution (in addition to the values of reactive scalars) will exist at a certain point in space and time. The derivation of the transport equation for the joint PDF is shown in [205], and the final equation is:

$$\frac{\partial f}{\partial t} + \langle u_j \rangle \frac{\partial f}{\partial x_j} = -\frac{\partial}{\partial x_j}\left[\langle u_j' | \mathbf{y}, \mathbf{n} \rangle \cdot f \right] - \frac{\partial}{\partial y_\alpha}\left[\left\langle D \frac{\partial^2 y_\alpha}{\partial x_j^2} \middle| \mathbf{y}, \mathbf{n} \right\rangle \cdot f \right] - \frac{\partial}{\partial y_\alpha}\left[w_\alpha(\mathbf{y}, \mathbf{n}) \cdot f \right] - \frac{\partial}{\partial n_i}\left[\left\langle D_p \frac{\partial^2 n_i}{\partial x_j^2} \middle| \mathbf{y}, \mathbf{n} \right\rangle \cdot f \right] - \frac{\partial}{\partial n_i}\left[W_i(\mathbf{y}, \mathbf{n}) \cdot f \right] \quad (63)$$

where W_i is the source term including all particulate mechanisms. The main advantages of the transported PBE-PDF method are that: a) it resolves the closure problem of precipitation and, more generally, of turbulent reactive flows with particles formation, b) it allows for kinetics of arbitrary complexity (such as size-dependent growth and aggregation) to be incorporated without the need for approximations, and c) it directly computes the entire particle size distribution. On the other hand the approach involves the transport of a larger number of scalars, but application to turbulent precipitation [45] has reported reasonable times in multi-core desktop PCs. The approach would be prove useful in cases where the timescales associated with transport, mixing, and particle formation are of similar orders of magnitude, thereby not permitting simplifications

of the problem based on timescale separation (such as the neglect of fluctuations or conserved scalar approaches).

An investigation based on a stirred-reactor model [205] demonstrated the effect of correlations by comparing the transported PBE-PDF equation with two simplified models. In the first one, the means of all non-linear terms were approximated with the mean values of the variables involved; thus all correlations were neglected, an assumption equivalent to assuming that each CFD cell is fully micromixed or that the reactions are very slow compared to mixing, which is often employed in early models (e.g. [254]). The second approach employs the joint-scalar pdf of species, which allows closure of the terms involving the dependence of nucleation and growth on supersaturation, but not of the correlation between growth and number density (see e.g. the terms in eq. 62). An investigation over a range of micromixing and residence times showed that significant deviations occur when the simplified methods are employed, even in the mean size predictions, when these timescales are of the same order. What is more striking is that, in that case, the first simplified method appeared to be closer than the second one, in spite of including less physics. The reason is that an even number of mistakes is made, i.e. it neglects two kinds of correlations that cancel each other to some extent. That, however, may not always occur, and further investigations into these phenomena are warranted; this case does serve, however, to illustrate the errors that may be hidden in the assumptions implicit in neglecting these correlations.

Recently, di Veroli and Rigopoulos [45], [44] have simulated the experiment of Baldyga and Orciuch [14] on barium sulfate precipitation in a turbulent pipe flow using the transported PBE-PDF method. A comparison of the simulation with the measurements, as well as with the presumed-shape pdf approach of Baldyga and Orciuch is shown in fig. 9. It can be seen that transported PBE-PDF method provides very good predictions, not only of the mean size but also of the shape of the distribution. The full benefits of the method are yet to be explored, however, as the case study of Baldyga and Orciuch featured size-independent growth and no aggregation; in cases where these assumptions do not hold, the correlations neglected by simplified methods would be more pronounced and the advantage of the transported PBE-PDF approach would be more evident. Even in this case, however, a recent study by the same authors [44] has shown that the neglect of correlations can result in up to 50% errors in the mean particle size, at certain points in the reactor. Furthermore, a comparison with the simplified models similar to that in [205] was performed, together with a timescale analysis along the whole body of the reactor. Results showed that there are areas (mainly close to the injection) where the mixing and nucleation/growth timescales were within the same order of magnitude, and in these areas significant deviations occur. Simplified models also showed a tendency similar to the PMSR studied in [205]: neglecting both kinds of correlations resulted in better results than neglecting just the growth-number density correlation. This effect was explained by looking at the spatial distribution of the growth rate fluctuations, which can be computed by the transported PBE-PDF method; an examination of these profiles revealed distinct zones where the effect on the precipitate production was positive or negative.

5.3 The closure problem for coagulation

The coagulation of particles in turbulent flows is a very complex problem, many aspects of which are only partially understood. As before, problems involving turbulent coagulation can be studied either from the Lagrangian viewpoint or via the PBE approach. The former involves tracking the motion of individual particles and accounting for all potential collisions between them and is used mainly for DNS studies (e.g. [200], [235], [253], [252], [266], [251]. The PBE approach can be applied for modelling large-scale systems, while the link between the two approaches is provided by the fact that the PBE relies on constitutive equations for the kernel,

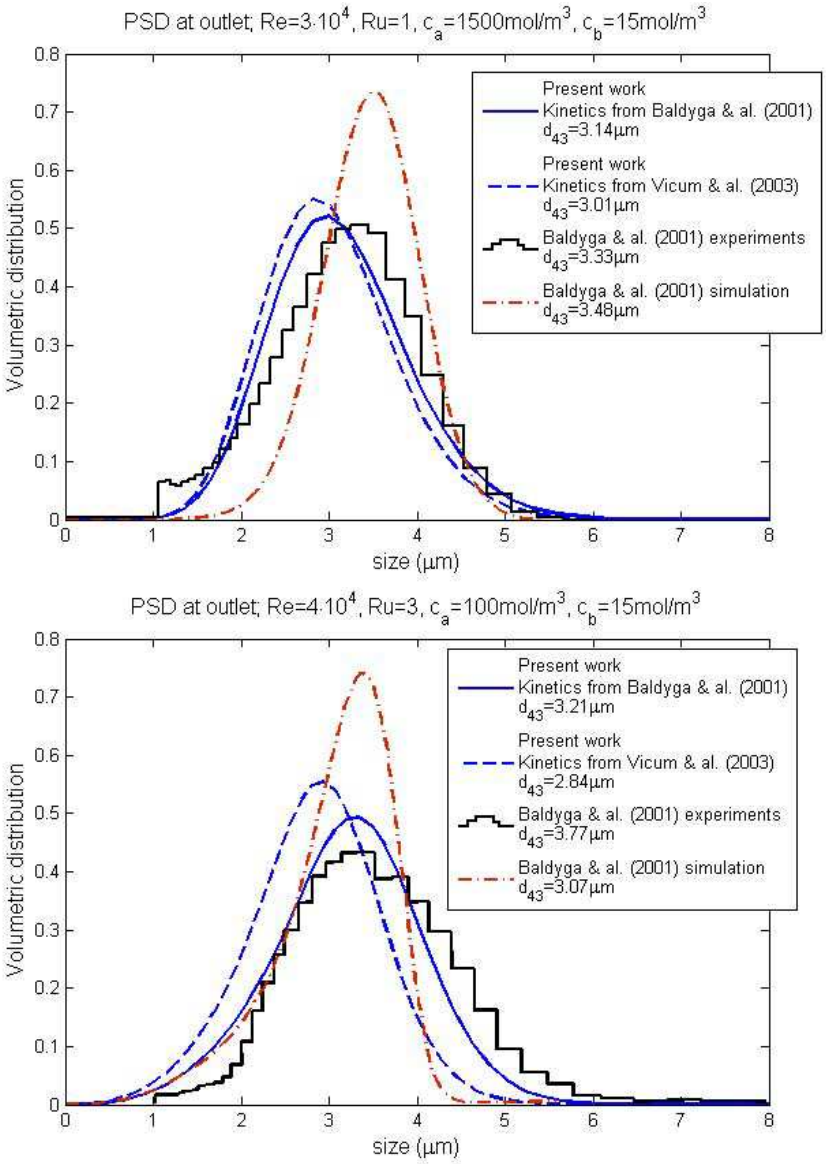


Figure 9: Comparison of Particle Size Distribution computed by the transported PBE-PDF approach with the presumed PDF and the experiments of Baldyga and Orciuch - from di Veroli and Rigopoulos [45], reprinted with permission.

which can be derived with the aid of DNS studies.

We now consider the PBE of a coagulating system. For simplicity, we will consider an equation involving only convective transport, Brownian diffusion and coagulation, since the remaining terms (particle formation etc.) have already been discussed:

$$\frac{\partial N(v,x_i,t)}{\partial t}+\frac{\partial}{\partial x_i}(u_i N(v,x_i,t))=\frac{\partial}{\partial x_i}\left(D\frac{\partial N(v,x_i,t)}{\partial x_i}\right)$$
$$+\frac{1}{2}\int_0^v \beta(v-v',v')N(v-v',x_i,t)N(v',x_i,t)dv'-\int_0^\infty \beta(v,v')N(v,x_i,t)N(v',x_i,t)dv' \quad (64)$$

The effect of turbulence on coagulation is being manifested in two ways. The first one is through the kernel, $\beta(v,v')$, which encompasses all the microscopic hydrodynamic information about the coagulation phenomenon. In sec. 2.3 we saw that, for particles larger than the mean free path, the main coagulation mechanisms are Brownian motion (for smaller particles) and coagulation due to laminar shear. Naturally turbulence plays an important role in the micromechanics of coagulation, and different coagulation mechanisms have been proposed for laminar and turbulent flows. The second way is related to the averaging of the population balance equation, which is valid in the instantaneous sense. An averaging results in correlations between particle concentrations and hydrodynamic properties, on which the coagulation rate depends in a non-linear fashion. Here we will concentrate on this issue, as it is directly related to the PBE approach.

The derivation of hydrodynamic kernels for turbulent coagulation has been the subject of extensive research combining experiments (e.g. Delichatsios and Probstein, [41]), theoretical analyses (e.g. Levich [134], Saffman and Turner [216], Kruis and Kusters [123], Brunk et al. [28]), Wang, Wexler and Zhou [252], and DNS (e.g. Reade and Collins [200], [199], Sundaram and Collins [235] and Wang, Wexler and Zhou [253], [252], [266], [251]). A detailed account is out of the scope of this review; only a brief outline will be given. Again, the size of the particles is the dominant parameter and different mechanisms become prominent for particles of different sizes. For very small particles, a comparison with the mean free path of the carrier gas molecules determines whether they coagulate according to kinetic theory or Brownian motion (see sec. 2.3). Mechanisms of turbulent coagulation operate on somewhat larger particles, and the appropriate comparison there is with the size of the Kolmogorov eddies, i.e. whether the particles are fully entrained in them. According to Friedlander [73], this mechanism can be expected to be prominent for particles larger than a few microns but may be important for sub-micron particles for very intense turbulence. Assuming that the particles are large enough to aggregate due to shear, but not too large for inertial effects to be important, Levich [134] argued that the particles are entrained by the turbulent eddies. In that case, the local velocity gradient can be related to the turbulence timescale. The expression commonly employed for this type of mechanism is: (Saffman and Turner, [216]):

$$\beta(v,v')=1.3\left(\frac{\epsilon}{\nu}\right)^{1/2}(v^{1/3}+v'^{1/3})^3 \quad (65)$$

A comparison of kernels is shown in fig. 10. Considerable research has been carried out to determine the appropriate forms for the collision kernels for larger particles whose collisions are dominated by inertial mechanisms; for this, the reader may refer to [134], [216], [73], [123], [266], [199], [235], [28].

We now turn our attention to the averaging of the PBE for turbulent coagulation and the

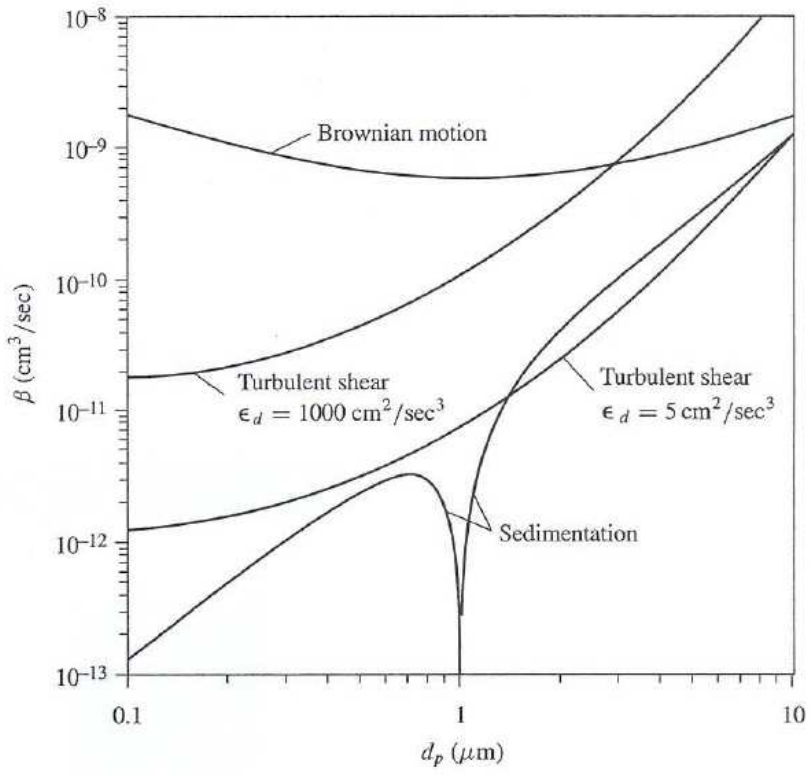


Figure 10: Comparison of coagulation kernels for 1 μm particles interacting with 0.1-10 μm particles. Reprinted from Friedlander (2000) [73] with permission.

fluctuations that arise. An averaging of eq. 64 results in:

$$\frac{\partial \langle N(v,x_i,t)\rangle}{\partial t} + \frac{\partial}{\partial x_i}\langle u_i\rangle \langle N(v,x_i,t)\rangle + \frac{\partial}{\partial x_i}\left\langle u_i' N'(v,x_i,t)\right\rangle = \frac{\partial}{\partial x_i}\left(D\frac{\partial \langle N(v,x_i,t)\rangle}{\partial x_i}\right)$$
$$+\frac{1}{2}\int_0^v \beta(v-v',v')\left\langle N(v-v',x_i,t)\right\rangle \left\langle N(v',x_i,t)\right\rangle dv'$$
$$+\frac{1}{2}\int_0^v \beta(v-v',v')\left\langle N'(v-v',x_i,t)N'(v',x_i,t)\right\rangle dv'$$
$$-\int_0^\infty \beta(v,v')\langle N(v,x_i,t)\rangle \left\langle N(v',x_i,t)\right\rangle dv' - \int_0^\infty \beta(v,v')\left\langle N'(v,x_i,t)N'(v',x_i,t)\right\rangle dv' \quad (66)$$

This equation involves the unknown correlations between products of number densities of different sizes, i.e. $\langle N'(v)N'(v')\rangle$. Correlations of this sort were first identified in the context of cloud droplet coalescence [220]; see also Drake [53] and references therein. The simplest form of closure is to neglect these correlations, i.e. to assume that

$$\left\langle N'(v-v',x_i,t)N'(v',x_i,t)\right\rangle = \langle N(v,x_i,t)\rangle \left\langle N(v',x_i,t)\right\rangle \quad (67)$$

Scott [220] argued that, in the context of cloud droplet coalescence, such correlations are small and decrease in time; he also derived equations for the second-order correlations and closed it by neglecting the third-order correlations that appear there. In general, however, it is not clear under what conditions correlations of various orders could be neglected. The issue is also discussed by Friedlander [73], who also states that the effect of such correlations has not been studied.

Rigopoulos [205] revisited the problem of correlations in turbulent coagulation via the transported PBE-PDF method described in sec. 5.2. In that approach, the joint pdf of number densities of different sizes being available, it is possible to include the effect of such correlations without invoking simplifying assumptions. Neglecting Brownian diffusion, the transported PBE-PDF equation for turbulent coagulation would be:

$$\frac{\partial f}{\partial t} + \langle u_j \rangle \cdot \frac{\partial f}{\partial x_j} + \frac{\partial}{\partial x_j}\left[\langle u_j' | \mathbf{n} \rangle f\right] = -\sum_{i=1}^{n} \frac{\partial}{\partial n_i}\left[\left(\frac{1}{2}\sum_{j=1}^{i-1} a_{ij} n_j n_{i-j}\right) f\right] + \sum_{i=1}^{n} \frac{\partial}{\partial n_i}\left[\left(n_i \sum_{i=1}^{n} a_{ij} n_j\right) f\right] \quad (68)$$

where a_{ij} is the matrix of coefficients that result from the discretisation of the number density. A study of a partially stirred reactor in [205] showed that the importance of these correlations depends on the ratio of a mixing time to a residence time and that it can lead to a significant spreading of the distribution.

Koch and Pope [116] studied the effect of fluctuations in the dissipation rate, which appears in the kernel for the turbulent shear mechanism (eq. 65). They argued that such fluctuations will become more pronounced in concentrated suspensions, as the shear rate and number density are negatively correlated due to preferential depletion of single particles in regions characterised by large turbulent shear rates. They performed a stochastic simulation where the shear rate was modelled by Ornstein-Uhlenbeck processes. Results showed variations in the coagulation rate and a broadening in the resulting PSD. An idealised problem of aggregation in a turbulent pipe flow was also studied by Nere and Ramkrishna [167]; in that work, the 1-D PBE for aggregation was transformed into a PBE for batch aggregation, which enabled the use of discretisation methods for the homogeneous PBE.

Several studies on soot formation processes that included coagulation have employed the method of moments. The resulting formulations present a closure problem at two stages: the derivation of a closed set of equations in terms of the moments, and the closure of the terms involving moment fluctuations. The former issue has been discussed in sec. 3.2. As we saw, in the case of the size-independent kernel (which is an approximation to Brownian kernel), a closed set of moment equations can be derived. Otherwise, a method such as QMOM or DQMOM is usually employed - these have also been discussed in sec. 3.2. The resulting approximate equations, after the application of Reynolds averaging, include terms involving moment fluctuations which are unclosed. As the importance of these fluctuations is again unknown, the most comprehensive way of obtaining closure is via the transported PDF approach that includes the moments in the sample space of the joint PDF, as has been carried out in the studies of Kollmann et al. [120] and Lindstedt and Louloudi [137].

Finally, a note must be made about turbulent fragmentation (break-up) problems. The terms in the fragmentation equation (eq. 27) are only first order in number density, and therefore the correlations appearing in coagulation due to number density products do not arise there. If, however, the kernel is a function of the shear rate, then the issues discussed in [116] may need to be taken into account.

5.4 The closure problem for dispersion

As discussed in sec. 4.2, the problem of inertial particles in laminar flows can be approached in the following ways: Lagrangian tracking of particles, two-fluid, multi-fluid and population balance methods. The last three of these can be grouped together, as the second and third methods can be derived from the PBE by taking moments. The presence of turbulence results in a random dispersion of particles whose Stokes number is large enough to deviate from the

streamlines. A direct solution of the equations of motion for the particles is possible only in the context of DNS studies (see e.g. Squires and Eaton [228], Elghobashi and Truesdell [60]). For engineering purposes, an averaging of some sort must be applied.

Turbulent transport of inertial particles has a very long history of investigations by the multiphase flow community. The focus of most of this research is the turbulent dispersion of inertial particles, often assumed to be monodispersed. Since this body of research is very extensive and has been covered by several excellent reviews, no detailed account will be attempted here, apart from a short discussion to indicate its link to the framework of this paper and to point the interested reader to the relevant literature. Many of these works are on spray modelling, as sprays are one of the most important classes of inertial, polydispersed reactive flows.

The first question posed here is what should be the starting point for the averaging. There are two possibilities: either to employ the Newtonian equations of motion for the particles (in a Lagrangian framework) or to take the population balance as the starting point. The first point of view leads to pdf methods for the particles' position, while the second one involves two levels of averaging - one inherent in the derivation of the PBE itself and one over the realisations of the turbulent particle-laden flow. The choice between the two is a matter of both numerics and physics: employing the Newtonian equations for individual particles is more appropriate for small populations, as well as providing a more natural framework for modelling dispersion. The population balance approach, by contrast, is more appropriate for large populations and for describing coagulation.

The derivation of pdf transport equations based on the Lagrangian framework proceeds from the same basic steps outlined in eqs. 58 59, the difference here being that the instantaneous equation substituted in eq. 59 is the Newtonian equation of motion for the particle (eq. 2). Since both fluid and particle properties are random variables, the pdf is defined over a phase space comprising the velocity of the particle, the velocity of the fluid 'viewed' by the particle and the remaining particle properties. Derivation of the pdf transport equation is along the same lines outlined in 5.2. The resulting equation is fundamentally unclosed, and closure models have been proposed by Reeks [201] [203]. This area has been reviewed extensively, by Mashayek and Pandya [154] and Minier and Peirano [160], [172] among others and therefore lies out of the scope of the present paper. A similar approach has been adopted by Jones and Sheen [107] and by Bini and Jones [25] but their pdf is formulated in terms of the particle properties alone; appropriate models for the particle acceleration are discussed in [24].

By contrast, population balance formulations implicitly assume a continuously distributed number density, implicitly assuming an averaging over the Newtonian equations of motion. As we saw in sec. 4.2, a direct solution of the inertial PBE is already overwhelming in the context of laminar flows due to its high dimensionality. Taking moments of the PBE results in the two-fluid and multi-fluid models. These models can be extended to turbulent flows if one accounts for the turbulent dispersion of each size class of particles. PDF equations obtained from the Lagrangian equations of motion involve only one level of averaging. By contrast, a PDF or moment (multifluid) method based on the PBE involves averaging at two levels - the continuum level inherent in the PBE and the randomness caused by turbulence. The former class of methods is perhaps more appropriate for dilute sprays, as it does not involve the assumption of a particle continuum; it is more difficult, however, to treat interparticle events such as coagulation. The PBE-based multifluid approach provides a natural framework for modelling such events, albeit at the expense of a greater complexity and a more approximate modelling of dispersion.

Modelling of turbulent flows with polydispersed inertial particles using the multifluid model is a very challenging problem. So far, many studies on spray and bubble coalescence have neglected inertial forces, and dispersion studies have been conducted mainly with the two-fluid model. As mentioned, this model can be regarded as a degenerate case of the PBE for inertial particles, where a moment transformation has been applied with respect to both size and velocity

domain. Two-fluid models are usually derived via volume or ensemble averaging. Since these approaches do not account for polydispersity they will not be further discussed here - they have been reviewed comprehensively e.g. by Crowe et al. [35], Sirignano [224] and Mashayek and Pandya [154]. The multifluid model seems to be the way forward for a population balance formalism of turbulent flows with inertial particles, but its formulation and basic assumptions are still under development even for laminar flows. Progress in that direction has been made in the field of bubble flows, and the reader is referred to the review of Jakobsen et al. [103] for that purpose. Finally, a number of works such as Archambault et al. [8], [9] and Beck and Watkins [18], [20], [19] have attempted to describe sprays using a small number of low-order moments, an approach that can be considered to lie between the two-fluid and multi-fluid approaches. These methods are further discussed in sec. 6.3.

6 Applications

6.1 Reactive Precipitation

The problem of reactive precipitation is a very good example of a polydispersed particulate system in a reactive flow. The process is akin to nanoparticle formation, apart from the fact that it takes place in the liquid phase: a number of chemical species enter the reactor in the liquid phase and react to form a solid, usually crystalline product. Precipitation is employed in a number of industrial manufacturing processes, such as the production of both utility and fine chemicals, as well as pharmaceuticals. The main property of interest in the characterisation of crystalline products is the particle size distribution (PSD), as it determines the physicochemical properties of the final product and therefore its market value. Therefore the ability to predict the product PSD is invaluable to the precipitation process designer and, not surprisingly, a considerable amount of work has been devoted to the application of PBE methods to precipitation. Often particle morphology is also of importance, and multivariate PBEs have been considered for this purpose (e.g. [248]). Industrial precipitation processes occur mostly under highly turbulent conditions within mixing equipment such as stirred tanks, and the reactions involved are usually rapid; as a result, the turbulence and mixing timescales are often within the same order of magnitude and an analysis of the turbulence-chemistry coupling is necessary. The particles generated in precipitation are usually in the sub-micron or nano range, and therefore inertial dispersion effects are not important.

The study of crystallisation and precipitation with PBE methods began with the pioneering works of Hulburt and Katz [97] and Randolph and Larson [198]. The former work set the stage in several aspects, from formulation to numerical solution and application. Both one-dimensional and multi-dimensional population balance equations were formulated for crystal nucleation and growth as well as agglomeration, and the method of moments - both exact and approximate, via Laguerre quadrature - was developed. The paper outlined how the method could be applied to model precipitation in batch and plug flow reactors, but no numerical examples or applications were presented there. The latter work presented an extensive body of applications of population balance theory to the design and control of crystallisation and precipitation reactors. The focus was on nucleation and growth problems; agglomeration was not extensively treated. A common feature of both of these works is that the population balance equation was applied in conjunction with simplified hydrodynamic models, either fully mixed or plug flow. While the coupled PBE-fluid flow equations were known, numerical solution could not be attempted with the resources available at that time, and the assumption of perfect mixing was based on the intense turbulent conditions prevalent in stirred tanks. Several subsequent works focussed on solution of the PBE in perfectly mixed systems (e.g. [146], [69], [39]).

Despite the intense mixing in stirred tanks, the precipitation reactions are usually very fast

and the crystal formation processes (nucleation and growth) very sensitive to the local supersaturation. Therefore micromixing effects play a major role in the process outcome, particularly in the vicinity of the points of injection, resulting in significant deviations from the results of the perfect mixing model. The next logical step was therefore to refine the simplified reaction engineering models by introducing micromixing models. A considerable body of work was devoted to the development of mixing models based on turbulence phenomenology and to their application to continuous and semibatch precipitation - see Baldyga et al. [12], [178], [179], David and Marcant [38], [144], David [37] and others; for a comprehensive review, see Tavare [240].

Even in stirred reactors, the turbulent flow field can exhibit large-scale features and inhomogeneities rendering the task of accurately describing them with a simplified model impossible. Thus it was soon acknowledged that detailed input from fluid dynamics would need to be integrated at some stage, and progress in CFD made this possible in the mid-nineties. Due to the complexity of the problem, some researchers have pursued a hybrid method of attack, where a 'zone' model comprising several fully-mixed compartments is employed and parametrised through CFD [265], [208], [206]. Phenomenological micromixing models can also be incorporated in this framework in order to determine the mass exchange between compartments. This approach offers a practical compromise between the simplified models and the computationally expensive CFD solution.

Ultimately, however, only consideration of the fully coupled fluid dynamics and population balance equations can provide a correct and sufficiently general modelling framework for precipitation in arbitrary flow fields. In several works [254], [255], [247], [104], [171], the majority of them on precipitation of $BaSO_4$ in a tubular reactor, turbulent precipitation has been modelled by implementing method of moments for a nucleation-growth PBE into a commercial CFD code, with turbulence models (usually based the $k - \epsilon$ model) employed for closing the Reynolds stresses and scalar transport correlations. In this approach, however, correlations due to fluctuations in moments, nucleation and growth rates (see eq. 55 are being neglected.

A more rigorous treatment of turbulent precipitation taking account of fluctuations was later presented in a series of articles by Baldyga et al. [14], [13], [12]. The problem was again turbulent precipitation of $BaSO_4$ in a pipe, but a presumed-shape pdf method was employed for the reactants; this allowed proper closure of the nucleation and growth averages. As the problem was still based on size-independent growth and no agglomeration, it was solvable via the method of moments and there was no need to consider fluctuations of number density. Comparison with experimental data showed reasonable prediction of the mean size; the shape of the pdf showed large deviations due to the fact that it had to be reproduced from the moments via an assumed shape. A similar method was also applied by Vicum and Mazzotti [250]. Later work on agglomeration [11] of the same system, could not produce good predictions, indicating that agglomeration presents a severe challenge for modelling.

In a series of articles, Schwarzer, Peukert et al. [219], [218], [217] studied a T-mixer configuration for $BaSO_4$ precipitation. This configuration results in higher mixing intensities, thereby shifting the product particle size distribution to the nanoparticle region (due to the sensitivity of nucleation to local supersaturation). They employed a population balance with nucleation, growth and aggregation, at first in conjunction with a plug flow and phenomenological micromixing model. [218]. In that work, comparison between predicted and experimentally measured PSDs showed a large underestimation of the PSD spread, with only the mean size being reasonably predicted. A recent study by the same authors [86] employed a direct numerical simulation (DNS) of flow and passive scalar dispersion in conjunction with a Lagrangian micromixing model and yielded very good predictions of both size and shape of the PSD. The authors concluded that, in their configuration, hydrodynamics were more prominent in determining the PSD than the precipitation process.

DQMOM (or multi-environment or finite-mode PDF) methods have also been employed by Piton et al. [176], Marchisio et al. [149], [150] and Gavi et al. [147]. In [176] the experimental configuration was that of Baldyga et al., but significant discrepancies were found. As pointed out in [67], that multi-environment methods can exhibit difficulties when dealing with chemical kinetics that are highly sensitive to the shape of the joint PDF for a small number of environments, and precipitation kinetics are usually very sensitive to small variations in concentration. Apart from the pipe flow experiments of Baldyga et al., these studies also extended the investigation of precipitation to different reactor designs, such as a Taylor-Couette reactor [147] and confined impinging jet reactor [79]. In most of these studies, aggregation was neglected in the modelling.

Falk and Schaer [66] presented a transported PDF simulation of aggregation of silica particles. The method of moments was employed for the PBE and the evolution of the joint PDF of moments was carried out using a Monte Carlo method coupled with FLUENT for computation of the flow field, but no comparison with experiments was attempted (except for validation of the scalar transport). Finally, di Veroli and Rigopoulos recently studied the experiments of Marchisio et al. [42], [43] and Baldyga et al. [45], [44] using the transported PBE-PDF method, which overcomes the need for closure and resolves the PSD directly (see sec. 5.2). A Lagrangian Monte Carlo method was developed for the joint species and number density distribution and the IEM model was employed for the micromixing. So far, good results have been obtained for nucleation-growth and simulations for aggregation are under way.

In conclusion, turbulent precipitation still poses a challenge for comprehensive models integrating fluid dynamics and PBE modelling. The main issues arise from the coupling of turbulence, chemistry and particle formation and from turbulent aggregation. The former have relatively recently started to be investigated with methods that take fluctuations into account, while the latter are much less explored and validation with experiments is still very limited. Difficulties in obtaining distributed and instantaneous measurements of the PSD and uncertainties in precipitation kinetics are also hampering the progress in linking experiments and models. The majority of validation cases are for turbulent pipe flow and $BaSO_4$ precipitation, although other configurations have started to be explored recently; progress in both experiments and modelling approaches for quantifying fluctuations is needed in the future.

6.2 Soot formation and Nanoparticle synthesis

Soot is particulate material formed during combustion of hydrocarbons, particularly under fuel-lean conditions. Its hazardous impact on human health means that its formation must be mitigated, and strict legislation is imposed on manufacturers of combustion devices [114]. Nanoparticle synthesis refers to the manufacturing of advanced materials comprised of ultrafine particles such as silica, titania and nanocomposite ceramic powders, via gas phase reactions. Both are examples of particulate formation in a reacting flow.

Soot and nanoparticle synthesis are akin to reactive precipitation, with typically nano-sized particles being formed as the result of a reaction or condensation process; as with precipitation, inertial effects are usually negligible due to the small size of the particles. The main difference is that the carrier phase is a gas rather than a liquid. In addition, the reaction is usually a combustion reaction that releases heat, thus requiring the solution of an energy equation and resulting in two-way coupling between the chemical and particle formation phenomena and fluid dynamics. Naturally, methods developed for combusting flows have provided the starting point for the analysis of this class of problems. Prediction of the PSD is of importance for various reasons; in the case of soot, engine designers are interested in mitigating its formation (although it can be desirable in furnaces for enhancing radiation), and the PSD controls the surface growth and reaction rates. Nevertheless, since soot is not a final product in these cases, simplified

models have been developed to predict integral properties such as soot volume fraction, as often only these are of importance. The lack of accuracy of these models is the driving force for the development of comprehensive models. On the contrary, in the formation of nanoparticles (which has been attracting increasing attention lately) one is interested in manufacturing a product with desired properties, and therefore obtaining a narrow PSD is of primary importance.

Soot formation and mitigation is a multi-faceted problem and the research conducted ranges from fundamental studies on soot chemistry, experimental and modelling flame studies and technological aspects. Early studies on soot were reviewed by Haynes and Wagner [92]. Soot formation models range from the purely empirical or semi-empirical to comprehensive models that employ detailed chemistry to predict key species involved in soot formation (such as C_2H_2) and mechanistic models of the soot nucleation and growth phenomena. A comprehensive review of these models has been provided by Kennedy [111]. Advanced chemical models of soot pathways have been reviewed by Richter and Howard [204]. For technological aspects such as soot emissions from engines and environmental concerns one may refer to Kittelson [114], while Tree and Svensson [244] have recently contributed a comprehensive review of soot formation in compression ignition engines. Here we will only look at applications of the population balance approach to soot formation processes.

Many studies on soot describe its formation in terms of a simplified model that correlates the soot number density and mass fraction in terms of key variables such as mixture fraction and temperature - see e.g. Moss [164], Beji et al. [22]. These models have a similar form to the nucleation-growth PBE, with the competition between surface growth and oxidation appearing in the equation. These models can then be implemented within a laminar flame simulation by Kennedy et al. [113], [112]. More elaborate PBEs can also be solved in the context of ideal reactors or laminar flames; Balthasar and Kraft [15] employed a stochastic method to solve the PBE for soot formation in a laminar flame. The presence of turbulence, however, requires treatment of the turbulence-chemistry-particle formation interaction. Soot models for turbulent flames initially proceed in the same direction as turbulent combustion models, employing models such as eddy dissipation (Magnussen and Hjertager, [143]) or flamelet (Peters, [174], [175]). In the latter a presumed pdf is assumed for the mixture fraction and the reaction source term is closed using the flamelet model. This approach has been adopted for a number of authors and in early studies [164], [165] soot is often computed as a post-processor, which involves an additional assumption on the correlations between species and soot concentrations - indeed, Syed et al. [237] employed a correction factor to account for soot oxidation. The flamelet model was also used by Fairweather et al. [65] to model turbulent, non-premixed propane flames (see fig. 7).

More sophisticated models of soot formation involve nucleation and growth rates based on the concentration of certain key species, usually acetylene (C_2H_2), as in the models of Lindstedt et al. [133] (see fig. 11, and Frenklach and Wang [72]. In that case a discrete PBE involving nucleation, growth/oxidation and, in some cases, coagulation is derived and modelled using the method of moments. Pitsch et al. [177] employed the unsteady flamelet model (see Peters [174], [175] for a detailed account of flamelet models) that included the moments of the soot PSD. Differential diffusion effects were included and predictions of soot mass fraction were reasonable, except close to the nozzle. The study of Kronenburg et al. [122] also focussed on differential diffusion effects, and applied the Conditional Moment Closure (CMC) method [115]. CMC was also employed in a recent study by Yunardi et al. [264] to model soot formation in turbulent, nonpremixed ethylene flames. Differential diffusion was accounted for, and very good predictions of soot mass fractions were obtained (fig. 12). More recently, El-Asrag et al. [58] and El-Asrag and Menon [59] have presented an LES simulation of sooting premixed and non-premixed flames. The soot model was again moment-based, and the MOMIC method [70] was employed to close the equations at the subrgrid level.

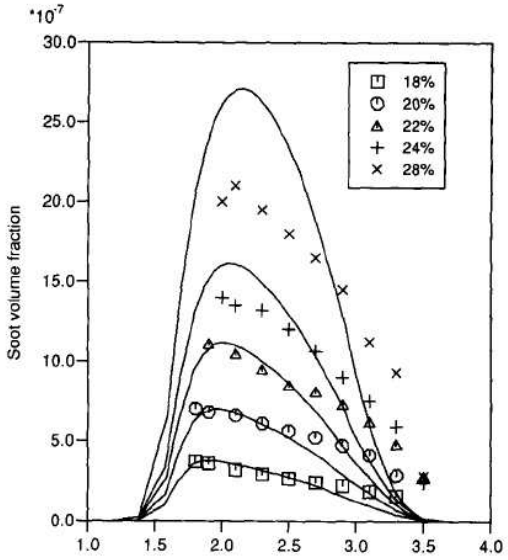


Figure 11: Soot predictions in a laminar flame from the model of Lindstedt et al. - reprinted with permission from [133].

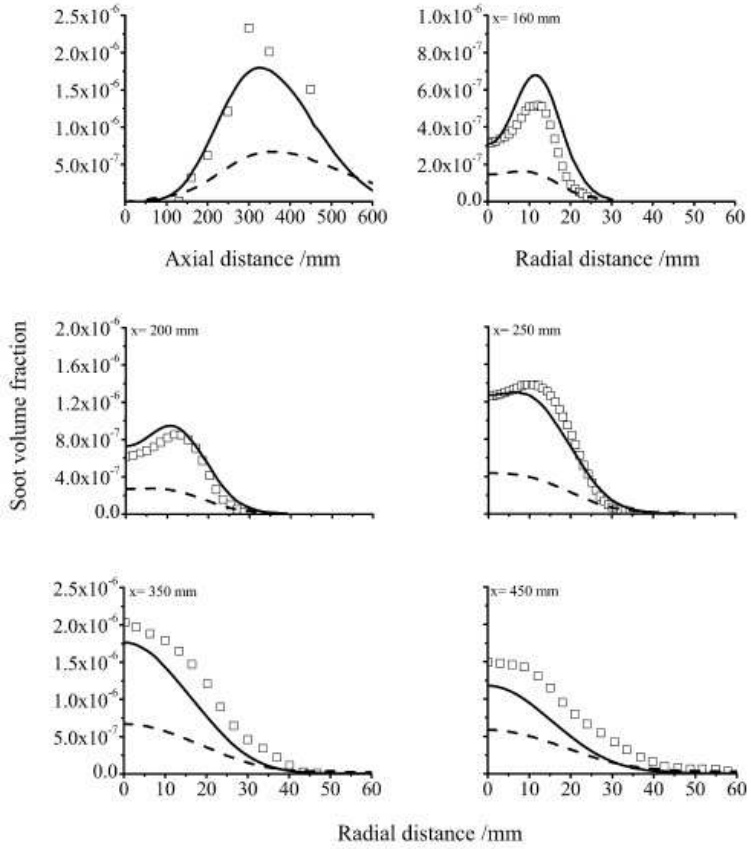


Figure 12: Soot mass fraction - comparison of predictions from the CMC model of Yunardi et al. with experimental results, reprinted with permission from [264]. Solid line - predictions with differential diffusion, dashed line - differential diffusion has been neglected.

Transported PDF methods were first applied to particle formation problems in conjunction with the method of moments. Kollmann et al. [120] performed a simulation employing a transport equation for the soot moments, while the chemistry was assumed to be in equilibrium constrained by the local enthalpy and mixture fraction. The formulation of Lindstedt and Louloudi [137] included the joint pdf of all reactive scalars in the mechanism (15) together with the soot moments. In these works, the PDF transport equation was solved using the method of stochastic particles in a Lagrangian framework [182], [184].

Early reviews on the various physical, chemical and technological aspects of gas phase synthesis of particulate products have been contributed by Kodas and Hampden-Smith [117], Pratsinis [187], Wooldridge [263] and Pratsinis and Vemury [189]. The subject has been attracting increasing attention in the last decade due to the increasing need for manufacturing nanoparticles with tailor-made properties, a problem for which flame synthesis provides a viable solution. As in the case of soot, early works on modelling nanoparticle synthesis with CFD relied on a moment approach to predict integral properties such as volume fraction and surface area. Pratsinis et al. [188] simulated ideal reactors with moment methods and Johannessen et al. [105] modelled the combustion synthesis of alumina particles by coupling a moment method with FLUENT. Muhlenweg et al. [158] compared the moment approach with a discretised PBE and a two-dimensional PBE that predicted a distribution in both particle size and surface area, and implemented them into a FLUENT with the objective of comparing the CPU time requirements in a simple plug flow. It was concluded that, among the PBE models, the one-dimensional PBE was feasible for coupling with CFD though still somewhat expensive. The study was conducted on a single processor, however, and advances in computer processing power since then as well as the availability of moderate-size clusters at a reasonable price means that such simulations are now well within the capacity of modern computing systems. Morgan et al. [163] applied a stochastic PBE to simulate the formation of silica, titania and iron oxide particles in a 1-D laminar premixed flame environment. Rosner and Pyykonen [212] coupled a two-dimensional PBE resolved by a QMOM approach with CFD to model the formation of alumina in a counterflow diffusion flame reactor.

Transported PDF methods have recently been employed to simulate nanoparticle formation under turbulent conditions: Mastorakos and Garmory [78] applied the stochastic field approach to a particle formation problem, nucleation and growth of liquid dibutyl phthalate (DBP) particles in a turbulent jet, based on experimental data of Lesniewski and Friedlander [132]. A moment formulation was employed, while growth was via condensation and therefore thermodynamically driven; the discrepancies were attributed mainly to the number of moments employed and the assumption of a log-normal distribution. Recent reviews by Roth [213] and Rosner [210] summarise the state of the art in this rapidly evolving field.

6.3 Sprays and bubbles

The subject of sprays and spray combustion is very broad, involving aspects such as atomization, single droplet burning, droplet coalescence and break-up, combustion etc., each of which could be studied as a subject of its own. In the present section we will concentrate on a single aspect of relevance to the subject of this paper: the prediction of size polydispersity in sprays using population balance approaches. For other aspects of sprays and spray combustion such as droplet behaviour, experimental approaches and technological aspects, or for a comprehensive review, the reader may consult the excellent reviews of Chigier [31], [32], Faeth [64], [63], Sirignano [223], [222], Bellan [23], Chiu [33], Aggarwal [2], Crowe et al. [35], A. Williams [258]. Bubble flows share many of the same issues, with bubble coalescence and break-up being of primary importance in the modelling of bubble column reactors, hence similar methods have been applied; again, our review will not be comprehensive, for which the reader is referred to Jakobsen et al.

[102], [103]; here we will view the subject from the population balance perspective only.

Sprays and bubbles are polydispersed multiphase flows involving a dispersed phase with a distribution of sizes. They differ from precipitation and nanoparticle formation in some important ways, however, and therefore the population dynamics approach has not been employed there as much as in those problems. While, with nanoparticles, the particle size distribution is a property that characterises the final product and therefore its prediction is a number one priority, the droplet or bubble size distribution is not a product property but rather an intermediate process variable. Therefore, in early studies monodispersed droplets or bubbles were being assumed as a first-order approximation. Still, the size distribution and consequently the interfacial area determines the rates of mass transfer and subsequent combustion or other reactions taking place in the carrier phase. As such, it plays a prominent role in the process outcome and it must be accounted for in comprehensive models. Droplets have generally larger sizes than nanoparticles ($1 - 100\mu m$) and are usually injected with an initial momentum that differs from that of the carrier phase, so their inertia must often be considered. This is a fact that further complicates the use of population balance models, as a distribution over droplet velocities may have to be considered and, in the case of spray combustion, over their temperatures as well. In dilute sprays, the number of droplets may be small enough to enable direct tracking of individual droplets. In denser sprays, an assumption of droplet "parcels" is often employed to reduce the number of particles to be tracked in Lagrangian approaches. Overall, works based on the Lagrangian are much more numerous than those based on population balance, which is an essentially Eulerian approach.

The population dynamics approach to spray modelling was pioneered in an early work by Williams [259], [260], [262], [261]. He postulated what is, essentially, a population balance equation for the spray in a phase space of droplet radius, velocity, space and time. His equation, generally referred to as the Williams spray equation, was discussed in sec. 4.2; the right-hand side of this equation constituted of a collision integral that redistributed the number density in terms of both size and velocity. Williams obtained solution only for some idealised cases using asymptotic methods. These were: steady-state impinging jet atomisation, neglecting inertia and evaporation and assuming that the flow field is known (i.e. considering only collisions), and steady-state combustion neglecting collisions, again on a known flow field. The lack of computational resources at that time did not permit a numerical solution for more complicated cases.

Westbrook [256] attempted a direct numerical treatment of Williams' spray equation by discretising the domain of all four independent variables. This was a formidable approach, and naturally severe constraints had to be placed on the refinement of the mesh employed for each coordinate. Westbrook employed 10 intervals along each spatial coordinate, 5 for each velocity coordinate, and 14 for the size (droplet radius). Naturally, explicit integration was rejected due to the inability to refine the grid in order to meet stability criteria and an implicit integration of the finite difference expressions was adopted. Boundary conditions included Gaussian distributions for the velocity components and the Nukiyama-Tanasawa distribution for the droplet size out of the atomizer. The ambient velocity field was assumed known (swirling flow with constant angular velocity, zero axial and radial components). The work of Westbrook demonstrated the feasibility of spray prediction via a population balance equation in terms of both velocity and droplet size, but the high-dimensional space (8 dimensions including time) place severe limitations on the approach. No coagulation/break-up or source terms were considered, and in addition, it is difficult to prescribe accurate boundary conditions for the velocity pdf. Similar works on the numerical treatment of the Williams equation were presented by Gany et al. [76] and Sutton et al. [236].

Gupta and Bracco [90] followed on the work on the solution of the Williams equation without sources. Two approaches were presented and compared, the first one being similar to that of

Westbrook, i.e. discretising the entire domain of the equation. The second approach, also present in an earlier publication of the same group [27], was based on the following concept: the (continuously injected) spray was regarded as an ensemble of a discrete number of sprays, each one injected at a different time with a certain initial distribution. The authors called this approach an initial value problem, because it converts the boundary value problem posed by the original equation into an ensemble of initial value problems. This approach requires the prescription of an initial distribution throughout the whole volume, which was prescribed in that work so as to be consistent with the Nukiyama-Tanasawa distribution for droplet size and the Gaussian distribution for velocity (as in the work of Westbrook) with the parameters determined from experiments. The advantage of the initial value problem was that an analytical solution for the individual members of the ensemble could be derived, and subsequently the solution to the spray could be constructed by a convolution of the individual sprays at time intervals $\Delta\tau$. The two approaches yielded similar results.

Tambour [238] revisited the problem of polydispersity in sprays and formulated a population balance equation for a spray polydispersed in size only. He assumed that the droplets follow the fluid streamlines, an assumption valid for smaller droplets ($< 50\mu m$) and possibly for bigger ($< 130\mu m$) for the downstream section of the spray where most droplets have accelerated to the gas velocity. Furthermore, he considered droplet evaporation as the only mechanism affecting the distribution. His equation therefore amounted to a population balance for non-inertial particles with size and physical space being the independent dimensions. Tambour coupled this equation with the equations of fluid dynamics for a boundary layer flow. His method of solving the PBE, called a 'sectional approach', is similar to the discretised population balance methods discussed in chap. 3.3. As in the case of Williams, strong assumptions and simplifications had to be applied in order to obtain solution via asymptotic methods. Greenberg et al. [87], [7] extended the method of Tambour into a multi-fluid model by integrating the (inertial) spray equation with respect to the velocity coordinate and subsequently discretising into a number of size classes. In addition, they considered coagulation via a sum over the discretised classes. No solutions or applications were presented; however, their formulation demonstrated the link between population balance and multi-fluid methods and also accounted for both inertial forces and coagulation. The method of Greenberg et al. was also used to model combustion in a laminar spray [88]. The work on multi-fluid models for laminar sprays was carried on by Laurent and Massot [128] who derived the sectional equations from the fundamental kinetic equation of Williams thus establishing the link between multi-fluid models and the PBE. Subsequently Laurent et al. [129] extended the apprcoach to coalescing sprays, while Laurent et al. [130] provided validation of the multi-fluid model with experiments. More recently, Fox et al. [68] applied both DQMOM and the multi-fluid model to a laminar spray and compared results to a Lagrangian solver, indicating that both are viable alternatives to it. The theoretical relationships between the various approaches were also investigated by Subramaniam [232], [233].

The PBE for inertial particles, either in the form of the discretised Williams Spray equation or in the form of the multi-fluid model, has found applications mainly in laminar sprays. The vast majority of turbulent spray simulations have been conducted via Lagrangian approaches complemented by stochastic terms to account for turbulent dispersion, via two-fluid models or via pdf equations derived from the Lagrangian framework. The two-fluid model, which amounts to transporting the moments of the PBE, was derived initially via volume or ensemble averaging [101], [54]. For these approaches, the reader may consult the excellent reviews of Drew and Passman [55], Mashayek and Pandya [154], Crowe et al. [35] and Sirignano [223], [224].

The development of Lagrangian stochastic approaches has its origins in the early works of Dukowicz [56] and Gosman and Ioannides [85], [84]. In this approach, the spray is modelled by an ensemble of 'parcels', each one containing droplets of the same size, whose motion comprises of a deterministic as well as a stochastic part. The Lagrangian approach formed the basis of the

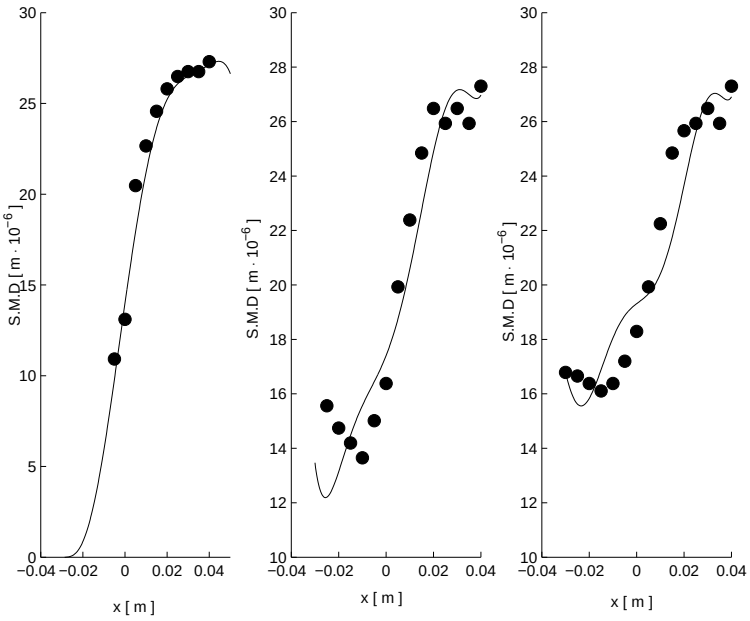


Figure 13: Comparison of predicted mean droplet diameters and experimentally measured ones - reprinted with permission from Bini and Jones (2008) [25].

well established KIVA code [6] and has been the basis of a number of works on sprays. Recently it was employed by Utyuzhnikov [245] to model the combustion of fuel-droplet-vapour releases in the atmosphere.

Jones and Sheen [107] modelled a turbulent spray via a PDF transport equation for the pdf of size, position, temperature and number of droplets. The equation was solved via a Lagrangian method tracking a number of stochastic particles carrying the above properties. This approach was later coupled with LES by Bini and Jones [25]; in that work, the transport equation was derived for the filtered pdf and stochastic models were employed for the subgrid contribution. The models employed for particle acceleration were discussed in [24]. Fig. 6.3 shows a comparison of predicted mean droplet diameters and experimentally measured ones in [25]. Subramaniam [233] provides an in-depth discussion of this viewpoint, its link with the PBE and its implicit assumptions; he stresses the fact that the computational particles are not to be confused with the physical droplets.

Other researchers have postulated different stochastic models, where the random variable comprises of the properties of both particle and fluid element 'viewed' by the particle; this enables the use of stochastic Langevin models, and for these the reader is referred to the reviews of Minier and Peirano, [160], [172]. The works of Reeks [201] and Hyland et al. [98] are also concerned with the derivation and closure of kinetic equations for particle dispersion; these have been comprehensively reviewed in Mashayek and Pandya [154].

The approach to modelling turbulent flows with inertial polydispersed particles that is most close to the class of methods reviewed in this study is the multifluid method. As discussed in sec. 4.2, it can be considered as a PBE where a moment transformation has been applied in the velocity domain and a discretisation into classes has been applied in the size domain. This results in a number of PDEs for the droplets in each size class, and the size-dependent drag force means that momentum equations must be solved for each size class. Mostafa and Mongia [166] presented a study implementing such a model for turbulent sprays and compared it with the Lagrangian stochastic approach, concluding that the Lagrangian approach was more costly than the Eulerian, even for multi-size droplets.

A further simplification can be attained by employing moments of the PBE in both size and velocity. If only one moment (corresponding to volume fraction) is retained, the approach collapses into the two-fluid model. An intermediate solution, however, is to employ a small number of low-order moments. This direction was adopted by Beck and Watkins [18], [20], [19] and by Archambault et al. [8], [9]; the latter, in particular, employed a maximum entropy assumption to obtain closure.

Significant work on the PBE has also been conducted by the bubble flow community, where the prediction of bubble coalescence and break-up and of their effect on interfacial area distribution is of primary importance. The two-fluid and multi-fluid models are prominent there. Carrica [29] presented a model for bubble flow around a surface ship where bubbles were divided into groups according to size. A link was also made between this multifluid method and the PBE, or Boltzmann transport equation for bubble size distribution in the terminology of that paper. Much of the research has been conducted with the objective of predicting the multiphase flow in vertical bubble flows [180] such as bubble column reactors, where the bubble size distribution can have a profound effect on the physicochemical phenomena. Since this research has been comprehensively reviewed by Jakobsen et al. [103], the interested reader is referred to that work.

A related problem is the burning of coal particles in pulverised coal burners and circulating fluidised beds. Particle size undoubtedly plays an important role there, as it determines the rates of burning, and since the particles can have substantial sizes and density mich higher than that of the gas phase, the problem is treated as a two-phase flow problem similar to sprays and bubbles. The Shadow Method of Spalding [227] is most frequently employed in that area; in that method, an extra equation is being solved for the fraction of the particulate phase, ignoring the effect of combustion. This allows for a leading order estimation of the mean particle size. Markatos and Kirkcaldy [153] and Markatos [152] studied the combustion of granular propellants with a two-phase flow model that included the effect of average particle size. Fueyo et al. [74], [75] applied the shadow method to an Eulerian-Eulerian model of coal combustion and tested the model with an analytical solution for a simple problem. Abbas et al. [1] investigated the effect of particle size on NO formation in pulverised coal furnaces and found that small and large particles generated more NO emissions than mediun-sized particles. Liakos et al. [135] employed the same approach for modelling pulverised coal combustion and found that particle size can aid in controlling the temperature inside the furnace. The effect of feed droplet size in fluidised catalytic cracking (FCC) reactors has been investigated by Theologos et al [242]. It can be concluded that, while detail PBE methods have not yet been applied in this area due to the complexity of the combined phenomena, particle size definitely exerts a profound influence in the processes and their outcome and there is potential for more detailed PBE-CFD methods to be explored in the future.

7 Perspective and Conclusions

The subject of polydispersed particle formation and transport is very wide and a meeting point for several disciplines and academic communities such as combustion, aerosol science and multiphase flow. Problems studied in these disciplines have common features and universal themes have emerged in the methodologies employed. In this paper we have presented a review of the population balance framework for polydispersed particles in flows and demonstrated that many of the methods employed for dealing with such problems can be presented under this common viewpoint. It is an essentially statistical approach, along the lines of the kinetic theories of gases and plasmas. Mathematically it is expressed via the population balance or general dynamic equation (PBE/GDE). Originally formulated for systems that are spatially homogeneous, the PBE framework can be extended to systems with flows assuming that a local distribution of

particle sizes (or shapes, temperatures etc.) exists at any point in the flow field. The result is a transport equation for a distribution over a phase space consisting of both physical dimensions and a number of variables characterising the particle state. The equation can then be made more specific to describe a large variety of phenomena, such as particle formation and growth, coagulation, sprays etc..

This statistical viewpoint is not the only way to approach the problem of polydispersed particles. The alternative approaches are generally derived from the Lagrangian viewpoint, where one works directly with the Newtonian equations of motion or, in the case of turbulence, derives probabilistic equations from them. While this approach was not reviewed here, it is worthwhile to examine the relatiohship between the two of them. The Newtonian approach is certainly the most fundamental one while the PBE is derived from it via a statistical averaging process [195], [196], [197], [232], [128]. For the simulation of the dynamical behaviour of a small system of particles, the Newtonian approach is to be preferred as it is simpler and direct while the statistical approach would have to account for fluctuations [195], [196]. For large populations, on the other hand, the Newtonian formulation is not feasible except for academic DNS studies and the statistical approach is necessitated. Soot formation, nanoparticle production, crystallisation and precipitation have invariably been studied with the statistical approach.

One potential drawback of the statistical approach, however, is that the number of independent variables is increased. This is an important complication in the case of inertial particles, as in that case the velocity has to be included in the probability phase space. This issue can be treated via discretising or averaging over the velocity space, thus resulting in the multifluid and two-fluid approaches. The cost is a loss of information regarding the response of particles to inertial forces. The statistical approach, on the other hand, provides a more appropriate framework for studying problems with interacting particles, such as aggregation and agglomeration. Such problems are more naturally formulated using population dynamics and the discrete or continuous aggregation equation. By contrast, a direct simulation of aggregation in a Newtonian framework requires a search for all possible aggregation events and calculation of the appropriate collision cross-sections, which is a formidable task, usually reserved for the framework of DNS studies only.

The choice of an appropriate framework, therefore, depends on the problem to be studied. In soot and precipitation, for example, inertia is negligible, while coagulation is a dominant mechanism of evolution of the particle spectrum. On the other hand, studies of inertial particle dispersion and deposition are naturally carried out in the Newtonian framework. More complex is the class of problems that fall between these two extremes. In sprays, for instance, some studies have neglected inertia and applied the multifluid approach, while others have focussed mainly on dispersion. A solution of the complete problem without simplifications is possible with both approaches. The complete statistical formulation, as exemplified e.g. in the equation of Williams, operates over the entire droplet size-velocity space and its numerical solution (as carried out e.g. by Westbrook) involves no assumptions. On the other hand, a Newtonian formulation would have to track individual droplets as well as collision events. Both approaches would be formidable in this context, and therefore the choice of a simplified approach would depend on which aspects of the problem are to be highlighted.

While the coupling of population balance models with fluid dynamics in laminar flows is relatively straightforward, the extension to turbulent flows presents us with severe theoretical and computational issues. An averaging of some sort is required, as fluctuations of the distribution are going to occur due to turbulence. The first issue here is which equation should be the starting point for this averaging. Two options are possible. The first one is to regard the Newtonian equations of motion as the instantaneous equations and derive equations for the mean and fluctuating motion of individual particles, or for the pdf of the individual particle' position. The second one is to start from the population balance as the instantaneous equation

and derive averaged equations for the mean and fluctuations of the particle size distribution as a whole, thus involving two levels of averaging. As before, the first option is more appropriate for smaller populations at the expense of formulation complexity, while the second one is more appropriate for large populations.

A modelling framework for polydispersed particles in turbulent flows can therefore be broken into the following following elements:

- Turbulence modelling/simulation.
- Models for the turbulence-particle interaction.
- Models for the PBE itself.

With respect to the first, the choice lies between RANS modelling and LES. The vast majority of applications so far have been based on RANS. The extension to LES may not pose major problems from the theoretical point of view, but is computationally very expensive for the coupled CFD-PBE problem. The number of LES studies is likely to increase in the future, however. As in the case of combustion, the benefits from LES are going to be better simulation of turbulence structures and hence of the distribution of the reactants' supersaturation, especially in unsteady problems, although the particle formation and interaction phenomena are likely to occur in the sub-grid scales and a further model for the sub-grid scale chemical and particulate phenomena will be necessary.

The interaction of turbulence with particles can be divided into three parts: momentum exchange, chemical exchange and turbulent coagulation. The first is an issue only for inertial particles, and so far the only feasible approach seems to be the multi-fluid method, based on moments with respect to the velocity domain. Chemical interactions are related to particle formation and growth processes, which depend on the local composition of the reacting or condensing species in a non-linear way, and methods similar to those applied for the closure of the reaction source term have been employed. Several studies for soot have extended the flamelet approach, while CMC has also been employed in that context, and in precipitation the mixing models of Baldyga have been applied. Further generality can be accomplished by transported pdf methods, at the expense of the cost of computational solution, which has to resort to stochastic methods. The stochastic particle method has been employed in several studies of soot formation, both moment and PBE-based, while the field methods have started to be employed only recently. The presence of the PBE increases the number of scalars and thus the memory requirements of such methods, but recent studies have demonstrated proof of concept. The application of mixing models should be further investigated, as the diffusion coefficient for particle transport is smaller than that of chemical species. Finally, the effect of turbulence on coagulation is manifested in two ways: the coagulation kernel and the number density correlations. The former must receive timescale information from the turbulence model, while the effect of the latter must be either modelled in the context of a moment method or simulated via a transported pdf approach.

In terms of the numerical solution of the PBE itself, the classes of methods that have seen widespread application to flow problems are the methods of moments and discretised PBEs, though other methods such as stochastic and perturbation methods have also been employed. Moment methods are fundamentally unclosed and require closure models, and an extensive body of literature exists on this topic. For discrete PBE formulations, the method of moments with interpolative closure (MOMIC) has seen widespread application, while for continuous PBES the Laguerre quadrature, the quadrature method of moments (QMOM) and its extension (DQMOM) have all been employed, mainly in the context of precipitation. Discretised PBEs have started to be explored recently; they exhibit greater memory requirements due to the larger number of variables to be stored, but overcome the closure problems encountered by moment methods,

and as CPU power and memory/storage capacity increases, more applications are expected to be seen.

With respect to applications, so far precipitation has provided the majority of cases for development, application and testing of detailed population balance methods. The majority of this body of research was done on homogeneous systems, however, and the coupling of the PBE with fluid dynamics has started to be explored relatively recently. As the flow is usually incompressible and the particles in the nano-range, the modelling of the flow field and the particle formation can usually be treated sequentially. While in the laminar flow no fundamental problems are being posed, the effect of turbulence on the size of precipitated particles is almost unexplored, with such effects being often implicitly ignored in simulations with commercial codes. Recent stuidies have identified the issue; what remains is to systematically study these effects and the range of conditions where they can be important.

In soot and nanoparticle formation in flames, fluid dynamics are of primary importance and therefore most approaches are based on a detailed solution of the flow field coupled with a simplified chemistry and particle formation model that concentrates on predicting the soot volume fraction. Prediction of particle sizes and particle size distribution are far less common and mainly encountered in simulations of laminar flames. The complex chemistry of soot formation, together with the coupling of chemistry and fluid dynamics via heat release, render the coupled problem much more complex and computationally demanding. Particles are still in the nano-range, so their hydrodynamic effect on the flow is negligible. A crucial question to be answered is whether more resources should be allocated to the flow modelling (e.g. via LES/DNS) or to the chemistry and particle formation processes. We can expect more detailed PBE formulations to appear in soot problems in the future. The effect of particle size in soot is undeniably important, as it affects formation and oxidation rates, but it is even more pronounced in the case of nanoparticle synthesis, where the particles are a commercial product whose value depends on their size and size distribution (ideally narrow). In view of increasing interest in this field, we can expect to see more applications of the PBE in it.

Finally, regarding sprays, bubbles and coal burning, the particles there are often of significant dimensions and/or exhibit different densities to the carrier flow phase, so that one often has to use two-phase flow modelling approaches. In addition, the particle populations are more dilute than in the case of soot and nanoparticles. For this reason, research in these areas has begun with two-phase flow models, where often the effect of particle size appears in the form of a mean diameter. However, particle size distributions are undoubtedly important, and population balance methods have started to appear in the literature. The coupling of multiphase flow modelling and variable particle sizes is the main issue to be addressed in the future.

What is evident is that particulate processes in flows, especially turbulent, constitute a multi-faceted problem. Several aspects of it, such as turbulent dispersion, have a long history of investigations, while others, such as coagulation, have started to be explored relatively recently. The population balance is a statistical approach, which can be seen as complementary to the Newtonian/Lagrangian viewpoint, and which has relatively recently started to be extended from statistically homogeneous systems to spatially distributed ones. Formulation-wise, further work is needed in exploring the PBE-turbulence interaction, while numerically the coupled formulation is expensive but feasible.

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