1

Introductory Concepts

1.1 Overview of the Population Balance Methodology

1.1.1 Introduction

A number of physical problems are described by a population of entities with a distribution of one or more properties. Some examples are the distributions of sizes and shapes in crystals, molecular weights in polymers and ages in microbial cells. The evolution of these properties may be shaped by processes such as particle formation and aggregation, as well as by transport within a flow field.

There are several reasons why we may be interested in this distribution. It may determine the properties of a product, as in the case of the size distribution of purpose-made nanoparticles. By controlling it, we can tailor the product to particular applications. In other cases, it may determine the impact of the entities on the environment or human health, as in the case of the size distribution of soot and other aerosols, where the smaller particles can penetrate deeper into the body when inhaled. Finally, it may be an important process variable and thus essential for developing a model of the process; for instance, the surface area distribution of crystals in a reaction crystallisation process determines the rate of a surface reaction.

The population balance is a general methodology for describing systems with distributed properties. We will often use the term 'particle' in the present book with the understanding that it may refer to a solid particle, droplet or bubble. The objective of a population balance model is to predict the distribution of the properties of interest by linking it to the physical and chemical processes that shape it. These processes include interaction of particles between themselves, such as aggregation into larger particles or fragmentation into smaller ones, interaction of particles with their environment, such as particle formation from a precursor or disintegration into it, and transport of particles by processes such as convection by a carrier fluid and Brownian motion.

In problems involving transport in physical space, the population balance is intricately connected with fluid dynamics. This is because fluid dynamics, apart from controlling the transport of particles, also 'set the stage' for the physical and chemical processes that appear in the population balance by, for example, determining the local concentration of a chemical species that acts as a precursor for particle formation.

The main purpose of this introductory chapter is to define the scope of the population balance methodology and to introduce certain basic concepts and terminology that will be used in the rest of the book. Before commencing, we first take a brief look at some of the problems to which the population balance can be applied.

1.1.2 Applications of the Population Balance

The processes involved in the population balance, such as the merging of two units into one or the breaking of a unit into fragments, appear in many different (and sometimes seemingly unrelated) problems. While the laws governing these processes may be problem specific, they share enough common features to allow a unified description under the population balance framework. For example, depending on their size range, the aggregation of small aerosol particles may be governed by a collision model based on the kinetic theory of gases, while the coalescence of larger droplets may be due to a mechanism determined by the flow field. As we will see in Chapter 3, both phenomena can be described with the same population balance equation, with the different mechanistic models entering as constitutive equations. A number of representative applications are briefly described below. While only a few of these will feature in the present book, each of them has an extensive literature of its own, and selected references are mentioned to provide an entry point to that literature.

Atmospheric Aerosols

Aerosols are small solid particles or droplets suspended in a gas, with diameters typically in the range of 1 nm–100 μm (although this is not strict). Atmospheric aerosols arise from both natural sources and human activities. They can exhibit a variety of sizes, morphologies and chemical compositions which determine their physical and chemical properties and, consequently, their environmental impact, which includes effects on both human health and climate change. Kreyling et al. (2006) discuss the effect of particle size on particle–lung interactions, while Stettler et al. (2013a,b) and Zhang et al. (2019) focus on aviation black carbon emissions and the importance of particle size.

A number of significant questions about aerosols can be answered by the population balance – for example, how do the distributions of their properties evolve, how are they dispersed in the atmosphere and what is their state when they reach the ground and affect populated areas. The size distribution plays also a role on their action in activating cloud condensation (Calderón et al., 2022). Population balance models of aerosols constitute a major part of atmospheric dispersion simulations, where they are coupled with models for atmospheric flow. Reviews of aerosol science with emphasis on distributions and their modelling can be found in Hidy and Brock (1970), Williams and Loyalka (1991), Friedlander (2000) and Seinfeld and Pandis (2016).

Cloud and Rain Formation

Cloud and rain formation occurs via collision, coalescence and break-up of droplets. The evolution of the drop size distribution in the atmosphere was thus one of the first applications of population balance modelling, as exemplified by early works such as Warshaw (1967). An account of research in this area can be found in Chapter 15 of Pruppacher and Klett (1996). The interaction of aerosols and clouds is also important, as mentioned in the previous paragraph.

Volcanic Ash

The ash resulting from volcanic eruptions poses a major hazard for aeroplanes, and therefore the prediction of the evolution of ash clouds is a major task for meteorologists. Apart from the transport and dispersion of the ash plume in the atmosphere, models have to account for aggregation, which gives rise to bigger particles with different transport properties. The combination of aggregation with transport of volcanic ash is a typical problem that involves coupled population balance and fluid dynamics. Reviews of models for volcanic ash dispersion and aggregation can be found in Brown et al. (2012) and Beckett et al. (2020), while Suman et al. (2019) deal with the impact of ash (alongside that of other particles) on aircraft engines. Fig. 1.1 shows images of volcanic ash particles, where the effect of aggregation is evident.

Soot and Carbonaceous Nanoparticles

Soot is particulate material consisting mainly of carbon (with a small amount of H and other compounds present in the fuel). It is formed in combustion processes such as engines, gas turbines and furnaces. Soot is a special case of aerosol particles and has severe impacts on human health that depend to a large extent on particle size. Smaller particles penetrate into the lungs with potentially adverse effects (Kreyling et al., 2006). For this reason, the minimisation of soot formation is a major objective of designers of internal combustion engines and gas turbines. At the same time, carbon black (another form of particulate carbon) is manufactured for use in tires, inks, batteries and solar cells, while new purpose-made

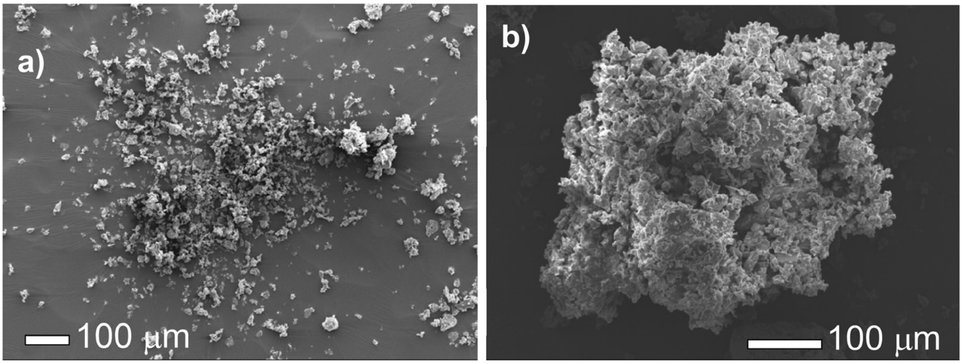

Figure 1.1 SEM images of ash aggregates: (a) a broken ash cluster and (b) an ash cluster. Reprinted from Bonadonna et al. (2011).

carbonaceous nanoparticles can have exceptionally high value; these include carbon quantum dots and carbon-coated nanoparticles for use as magnetic biofluids (Kelesidis et al., 2017). The size and morphology of such particles determine their suitability for particular applications.

The formation of soot and carbonaceous nanoparticles is very complex and its prediction requires a combination of fluid dynamics, chemistry and population balance modelling. Earlier work relied on simplified models and has been reviewed by Kennedy (1997). More recently, detailed population balance models have started to be incorporated into turbulent combustion models and reviews can be found in Raman and Fox (2016) and Rigopoulos (2019).

Fig. 1.2 shows images of soot particles obtained from a laminar flame. It is evident that the particles exhibit a range of size and morphologies. The picture on the right shows a close-up of an aggregate with a fractal structure, a feature that will be discussed in Section 3.2.3. The simulation of sooting flames is the objective of the case study in Section 6.2.

Nanoparticle Synthesis

Engineered nanoparticles such as silica and titania have multiple applications such as in pigments and optical fibers, while carbonaceous nanoparticles were discussed in the previous paragraph. The value of such products depends on particle size and morphology, and therefore the ability to control these properties yields the potential for manufacturing tailor-made nanoparticles for specialised uses. Population balance modelling can provide a predictive approach of the outcome of aerosol synthesis based on the process and equipment design. Reviews of nanoparticle synthesis can be found in Pratsinis (1998), Kruis et al. (1998), Kodas and Hampden-Smith (1999) and Pratsinis (2010), while Raman and Fox

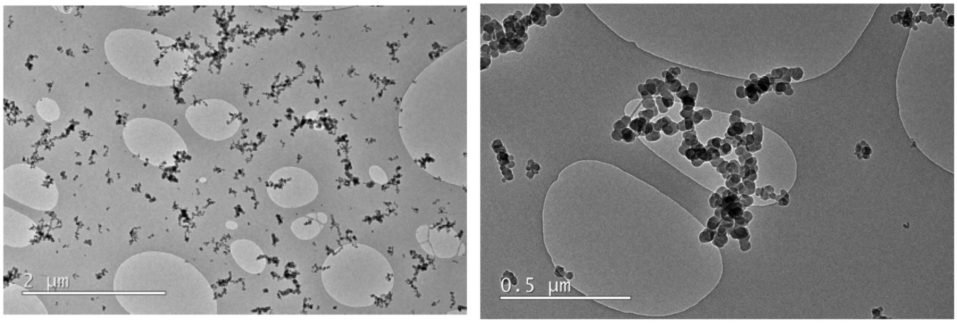

Figure 1.2 Micrographs of soot particles obtained via transmission electron microscopy (TEM); large-scale view (left) and close-up on an aggregate (right). Note that the big 'holes' are from the carbon film. Courtesy of Garcia Gonzalez (2018).

(2016) discuss the modelling of the process based on population balance and fluid dynamics.

The formation of silica particles via flame synthesis is the objective of the case study in Section 6.1.

Metal Particles as Energy Carriers

Metal particles such as aluminium have many applications, including their use as recyclable energy carriers and thus carbon-free alternatives to fossil fuels (Bergthorson, 2018). The size distribution of the oxide smoke is of primary importance, both as a process variable and for its role in the design of the subsequent separation processes. A comprehensive population balance model of this process can be found in Finke and Sewerin (2023).

Crystallisation

Crystallisation and precipitation processes are widely employed in the chemical and pharmaceutical industries for the formation of crystalline products from solutions. The size distribution and morphology of the crystals produced determine their properties and suitability for particular applications, as well as their behaviour during separation processes. Fig. 1.3 shows images of $CaCO_3$ crystals obtained from a precipitation process; the presence of both single crystals and agglomerates can be noted.

The modelling of crystallisation is one of the oldest applications of population balance modelling, having received its first detailed exposition in Randolph and Larson (1971) (see Randolph and Larson, 1988 for the latest edition). More recent reviews can be found in Mersmann (2001), Mullin (2001), Lewis et al. (2015) and Myerson et al. (2019). While the aforementioned literature refers to crystallisation

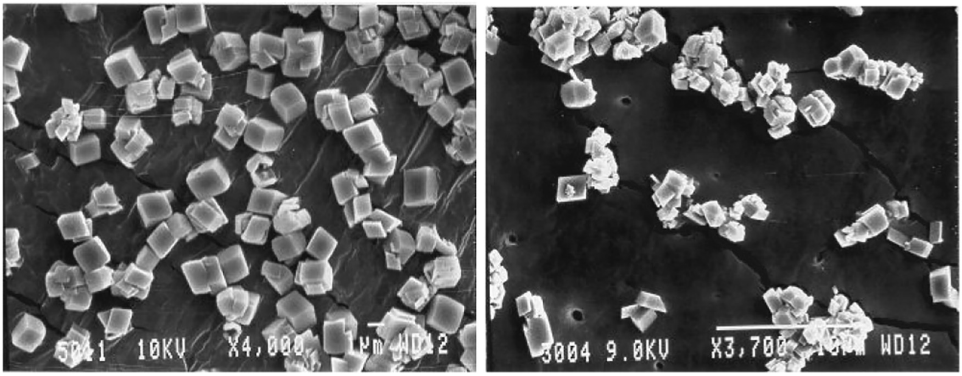

Figure 1.3 Scanning electron microscopy (SEM) images of $CaCO_3$ crystals produced via gas–liquid precipitation at an early (left) and a late (right) stage of the process. Reprinted from Rigopoulos and Jones (2003b) with permission from American Chemical Society.

and precipitation from solution, there are also processes involving precipitation of grains from supersaturated solutions, as discussed in the classic work of Lifshitz and Slyozov (1961).

The application of population balance to crystallisation will be shown in detail in the context of the case study in Section 6.3.

Spray Dynamics

Sprays are encountered in applications such as fuel injection and inhalation of medicines. In combustion, the size of the droplets determines the surface area and, therefore, the rate of evaporation, on which combustion depends. In medicinal sprays, the droplet size distribution determines whether the spray will penetrate and reach the targeted deposition sites in the lungs. The prediction of this distribution requires population balance models of spray break-up and evaporation, coupled with fluid dynamics that describe droplet dispersion. A comprehensive discussion of sprays can be found in Sirignano (2010).

Disease Transmission via Aerosol Droplets

The cloud of droplets resulting from a cough or sneeze is akin to a spray and can be analysed with similar experimental and modelling tools. The droplet size distribution determines their transport properties and therefore how far they reach, which is very important in the transmission of diseases such as COVID-19 (Bourouiba, 2020). For a modelling perspective on the link between droplet physics and disease transmission, one may consult Stilianakis and Drossinos (2010), Robinson et al. (2012), Drossinos and Stilianakis (2020), De Oliveira et al. (2021) and Drossinos et al. (2022).

Colloid Dynamics and Flocculation

The flocculation of suspended matter in waterways and in water treatment plants is of great importance for the destabilisation and treatment of particulate matter. Flocculation is induced by particle collisions and the ensuing size distribution determines the settling properties of the flocs. As such, it is a classical application of population balance modelling and its coupling with hydrodynamics. Reviews can be found in Thomas et al. (1999) and Partheniades (2009).

Asphaltene Fouling

Asphaltenes are carbonaceous compounds of moderately high molecular weight that are present in crude oil. As these compounds aggregate into colloidal particles, they form deposits that result in fouling of oil pipelines and result in heavy costs to the oil industry. An analysis of the formation of asphaltenes with population balance modelling can be found in Vilas Bôas Fávero et al. (2017).

Bubble Flows

In bubble flows, the population of bubble sizes determines the rates of interfacial processes such as mass transfer, as well as the momentum exchange. Reviews of population balance modelling of bubble column reactors can be found in Jakobsen et al. (2005) and in Chapter 8 of Jakobsen (2014).

Nuclear Engineering

Nuclear accidents result in the emission of aerosols with significant amounts of radioactivity. The prediction of such emissions and their impact is required for assessing nuclear safety. Models for such predictions combine population balance modelling with nuclear reactor thermal hydraulics. For an account of such models, the reader may consult Chapter 8 of Williams and Loyalka (1991).

Granulation

Granulation is the process of producing a granular material with desired properties, which depend on the distribution of size and possibly other variables, such as porosity or composition. Reviews of population balance modelling of granulation can be found in Reynolds et al. (2005) and Abberger (2007).

Biology and Biochemical Engineering

Many biological and biochemical problems are described by a population balance. Cell populations have distributed properties such as mass and age that determine various important process parameters. The application of population balance modelling to biology and biochemical engineering has a long history, and one may consult Ramkrishna (2000), Hjortsø (2004) or Ramkrishna and Singh (2014) for more details.

Polymerisation

Polymerisation can be described as a population balance of molecules with a distribution of molecular weights, starting from the monomers. Accounts of the application of population balance modelling to polymerisation can be found in Ziff (1980) and Wulkow (1996).

Another important problem is the design of polymerisation processes. Heterogeneous processes, in particular, such as emulsion polymerisation (Rawlings and Ray, 1988), involve a dispersed phase with a distribution of one or more properties that are important for the process, and their prediction can be approached with population balance modelling. For more information, one may consult the review of Kiparissides (2006).

Astrophysics

Certain astrophysical problems, such as clustering of planets, stars and galaxies have been described with a population balance equation that accounts for the dynamics of coagulation and fragmentation. Examples of such works can be found in Lee (2000) and Lombart and Laibe (2021).

1.1.3 Scope and Methodology of Population Balance

Owing to its generality and wide range of applications, the population balance has appeared in the literature under different guises, and one of the objectives of this book is to present a unifying framework for them. In the context of aerosol science, the population balance has more often been called the General Dynamic Equation (GDE). In dispersed multiphase flow, multi-fluid models (cf. Section 2.7) are forms of population balance for dispersed entities with a distribution of size and velocity. In many fields, ad hoc models have been proposed for integral properties of distributions, such as total number and volume of particles, and these are also forms of population balance.

The population balance approach is built around the formulation of a population balance equation (PBE), which links the dynamics of the distribution of the property or properties under investigation to the physical and chemical models that determine it. The PBE is a conservation equation akin to the equations of conservation of mass, momentum and energy. It includes source terms that account for processes such as growth and aggregation, arising from interaction of particles with their environment or with other particles, as well as terms that depict transport in physical space, such as convection by a fluid flow.

The PBE must be complemented by expressions for the rates of the physical and chemical processes considered, which play the role of constitutive relations. For some processes and problems, these expressions are well established. In other cases, considerable uncertainty may be present and experiments or simulations at the microscopic level (where the dynamics of individual particles are simulated, as opposed to the statistics of their population) may need to be combined with a population balance study. The combination of microscopic methods, population balance modelling and fluid dynamics yields a truly multiscale modelling approach.

The application of the population balance methodology can be summarised in the following four steps:

Step 1: Formulation of the population balance model. This step involves the choice of the appropriate form of the PBE and the identification of the physical and chemical processes to be included.

Step 2: Selection of kinetic models. Once the processes involved have been identified, models and kinetic data for them must be selected. If such data are not available in the literature, their determination may require further experiments or microscopic simulations.

Step 3: Coupling with flow, species and energy transport. In some cases, this coupling can take the form of an ideal reactor model, while in others, the equations of fluid dynamics and transport phenomena have to be coupled with the PBE. Turbulence, if present, may require additional modelling elements.

Step 4: Application of a solution method. In most cases, this will be a numerical method, as analytical solutions are available only for a few special cases. If the population balance is coupled with fluid dynamics, the solution will involve combining the PBE solution method with computational fluid dynamics (CFD).

The execution of these steps will be explained in Chapters 2–5. In Chapter 6, a number of case studies are presented where the procedure above is demonstrated.

1.2 Distributions and Their Properties

1.2.1 Discrete and Continuous Distributions

In the present section, we briefly review the basic features of distributions, with focus on the issues relevant to the material in the present book. For more details, one may consult a book on probability such as Papoulis (1991) or Grimmett and Stirzaker (2001).

Both discrete and continuous distributions are used in the population balance framework, the choice depending on the nature of the problem. Discrete distributions are suited to populations of particles comprising an integer number of units, such as a population arising from the coagulation of a monodisperse colloid. Continuous distributions are required for problems where a smallest building block cannot be defined (e.g. a population of droplets or bubbles whose size can change continuously via evaporation or dissolution respectively). Populations described by discrete distributions can also be described by continuous distribution functions, and this is often preferable for reasons that will be further explained in Section 2.2.4.

A discrete distribution of a single property is defined by a set of variables as $(n_1, \ldots, n_n)$, where n_i is the number of particles comprising i units of that property. A typical example is a population arising from coagulation of monodisperse particles, where n_1 is the number of particles of volume v_0 (the volume of the smallest particle), n_2 is the number of particles of volume $2v_0$ and so on.

For a distribution of a continuous variable, such as particle volume, v, we define the number density function, $n(v)$ (we will refer to it as simply *number density*), as a continuous function such that the number of particles with volume within an infinitesimally small range between v and $v + dv$ is $n(v)dv$, as shown in Fig. 1.4. The unit of the number density, therefore, is the inverse of particle volume (or whichever independent variable is employed). If the distribution is evolving with time, such as the one shown in Fig. 1.4, then the number density is time dependent.

A continuous distribution can be *discretised* to yield a set of particle numbers $(n_1, \ldots, n_n)$, each denoting the number of particles within intervals $(dv_1, \ldots, dv_n)$, not necessarily uniform. Such a discretisation is often employed in the measurement of distributions and in numerical methods for solution of the PBE.

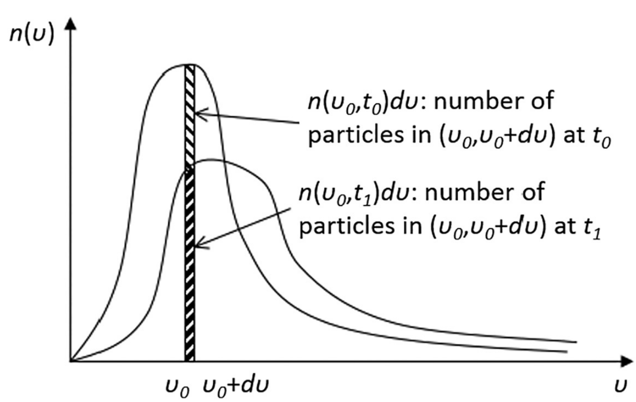

Figure 1.4 The continuous particle size distribution and its time evolution. Reproduced from Rigopoulos (2019) under CC-BY 4.0 license.

Both discrete and continuous distributions can be extended to distributions of several variables (multivariate distributions) in a straightforward manner. For example, if α is the surface area of a particle, then $n(v, \alpha)$ is the number of particles with volume between v and $v + dv$ and surface area between α and $\alpha + d\alpha$.

1.2.2 Number Density and Probability Density Function

An associated concept is the probability density function (PDF). The PDF describing a distribution over particle volume, for example, is defined so that $f(v)dv$ is the probability of finding a particle with volume between v and $v + dv$. The number density function and PDF are closely related, the only difference being that the integral of the number density is the total number of particles (also called the zeroth moment of the distribution, m_0):

$$\int_0^\infty n(v)dv = m_0. \tag{1.1}$$

By contrast, the PDF depicts a probability and therefore has the normalisation property:

$$\int_0^\infty f(v)dv = 1. \tag{1.2}$$

Equations for the evolution of a probability distribution are used in numerous areas of science. The *Boltzmann equation* is an equation for the PDF of velocities and momenta of gas molecules. The *Fokker–Planck equation* is an equation for the PDF of a random variable undergoing drift and diffusion processes. *PDF transport equations* are used in turbulent flow and particularly in reacting flow as closure models for the unclosed correlations involving velocities and scalars (cf. Section 5.5). The number density function and the probability density function are related as follows:

$$n(v) = m_0 f(v). \tag{1.3}$$

In this book, an equation is termed a PBE if formulated in terms of a number density and a PDF transport equation if written in terms of a probability density function. It follows that a PBE can be converted to a PDF transport equation via normalisation with the zeroth moment of the number density function. PDF transport equations are employed when the number of particles is not relevant or has no meaning. For example, in the description of turbulence, we may consider the PDF of velocity as the probability of finding a fluid element with velocity within a range $(\mathbf{u}, \mathbf{u} + d\mathbf{u})$ at a certain location and time. However, no meaning can be ascribed to the number of fluid elements. An approach consisting of a combination of PDF and PBE will be described in Section 5.5.2 for population balance modelling in turbulent flow.

1.2.3 Properties of Distributions

We will now summarise some important properties of distributions, with emphasis on quantities relevant to population balance modelling.

The moments of a distribution are defined as follows. For a discrete distribution of one variable, the k-th moment is:

$$m_k = \sum_{i=1}^{\infty} i^k n_i. \tag{1.4}$$

For the distribution of a continuous variable, such as the particle volume, moments are defined via an integral over the whole range of values of this variable, which is $(0,\infty)$ in this case:

$$m_k = \int_0^{\infty} v^k n(v) dv. \tag{1.5}$$

The moments are defined in the same way for number and probability density functions, while the zeroth moment of the latter is equal to one. Note also that the moments, as defined above, are about the value zero. They may also be defined about an arbitrary value; for example, the moments of the aforementioned distribution about a value v_0 are:

$$m_k = \int_0^{\infty} (v - v_0)^k n(v) dv. \tag{1.6}$$

However, only moments about zero will be used in the present book, and the term ‘moment’ will be always interpreted in this sense.

Physical meaning can be ascribed to certain low order moments of number density functions. As mentioned in Section 1.2.2, the zeroth moment represents the total number of particles. Other moments may have a physical meaning that depends on the choice of independent variable. In the case of a distribution of particle volume, for example, the first moment represents the total volume of the particles, as can be seen from its definition:

$$m_1 = \int_0^{\infty} v n(v) dv. \tag{1.7}$$

Moments of fractional order can also be defined. For example, the fractional moment of order 2/3 of the volume distribution is proportional to the total surface area (the constant of proportionality being a shape factor):

$$m_{2/3} = \int_0^{\infty} v^{2/3} n(v) dv. \tag{1.8}$$

For a distribution in terms of measure of particle length, ℓ, such as particle diameter or radius, the second moment is proportional to total surface area:

$$m_2 = \int_0^\infty \ell^2 n(\ell) d\ell, \tag{1.9}$$

while the third moment is proportional to total volume:

$$m_3 = \int_0^\infty \ell^3 n(\ell) d\ell. \tag{1.10}$$

Shape factors will also have to be introduced in Eqs. 1.9 and 1.10 in order to obtain the surface area and volume.

Joint moments of various orders can be defined for a multivariate discrete or continuous distribution. Again, certain moments have a physical meaning; for example, in the case of a bivariate continuous distribution in terms of particle volume and surface area, α, the first moment with respect to volume will be the total volume of the particles:

$$m_{1,0} = \int_0^\infty \int_0^\infty v n(v, \alpha) d\alpha dv. \tag{1.11}$$

Certain important properties of distributions are defined in terms of moments. It is instructive to define them first in context of probability density functions. The *mean* (or *expectation*) of a PDF, μ, is defined as the first moment – for example, for the PDF of particle volume, $f(v)$, we have:

$$\mu = \int_0^\infty v f(v) dv = m_1. \tag{1.12}$$

The *variance* of a PDF, σ^2, is the second central moment (i.e. the second moment about the mean):

$$\sigma^2 = \int_0^\infty (v - \mu)^2 f(v) dv. \tag{1.13}$$

It can be shown[1] that:

$$\sigma^2 = m_2 - m_1^2. \tag{1.14}$$

The *standard deviation*, σ, is the square root of the variance and a measure of the spread of a distribution. Similar definitions hold for discrete distributions.

For a number density function, the mean and variance have the same values as those of the corresponding PDF and can be obtained by normalising the above equations with the zeroth moment:

[1] $\int_0^\infty (v-\mu)^2 f(v) dv = \int_0^\infty v^2 f(v) dv - 2\mu \int_0^\infty v f(v) dv + \mu^2 \int_0^\infty f(v) dv = m_2 - m_1^2$.

$$\mu = \frac{1}{m_0} \int_0^\infty v n(v) dv = \frac{m_1}{m_0}, \tag{1.15}$$

$$\sigma^2 = \frac{1}{m_0} \int_0^\infty (v - \mu)^2 n(v) dv = \frac{m_2 - m_1^2}{m_0}. \tag{1.16}$$

1.3 Choice of Distributed Variables

The choice of the variables whose distribution is sought is very important for the formulation of the population balance. Some common choices, along with the considerations involved, are listed below.

- *Number of discrete units.* This choice is appropriate for problems described by the discrete PBE, such as coagulation of initially monodispersed particles or polymerisation. The smallest unit present in the system is called a *monomer*.
- *A measure of particle length.* This could be, for example, the diameter or radius of spherical particles. This choice is particularly suitable for problems involving a surface growth rate independent of length (cf. Section 2.3.2), although it makes the description of aggregation and fragmentation more complicated. Furthermore, experimental measurements often report length distributions. Some problems, such as crystal growth, may involve different faces growing with different rates, and in that case multiple length variables can be employed, thus enabling the prediction of particle morphology.
- *Particle volume or mass.* This choice is particularly suitable for aggregation or fragmentation problems, where the particle volume and mass are conserved. It is also easy to accommodate surface growth with this description, so it will be the default formulation for most of the examples in the present book. The final results may be converted to a length distribution for the purpose of comparison, as that is often reported in experiments. If the particle density is constant, the formulations in terms of volume and mass are equivalent.
- *Particle surface area.* This variable can be used to described the morphology of particles with irregular shapes, in addition with a variable describing particle size (such as length or volume). In that case, particles with the same size may have different surface areas.
- *Number of primary particles.* This is an alternative option for describing particle morphology, where one distinguishes between primary particles and aggregates. It is a special case of the first option, that is, a number of discrete units.
- *Particle velocity.* A population of particles with considerable inertia features a distribution of particle velocities, as the particles deviate from the fluid streamlines to a varying extent depending on their inertia.
- *Temperature.* This is needed for problems such spray combustion, which features a population of droplets with different properties. The droplet temperature is

important for several purposes, such as the determination of the evaporation and combustion rates.

- *Concentration of chemical species.* This is important, for example, in the case of atmospheric aerosols that comprise various chemical species and the distribution of their composition is important.
- *Cell age.* This is a variable relevant for biochemical problems, because important processes such as growth or the probability of a division may depend on it.

In many population balance problems, the distributed property is a measure of particle size (such as diameter or volume). In these cases, we speak of a particle size distribution (PSD). In the case of crystals, this is often referred to as a crystal size distribution (CSD). In polymers, the quantity of interest is the molecular weight distribution (MWD).

1.4 Kinetic and Transport Processes

Having reviewed the basic features of distributions, we now turn to the physical, chemical or biological processes that may be acting to bring changes into a population of particles. The very purpose of a population balance model is to predict how the distribution is shaped by the action of these processes. It is instructive to classify them into two groups: *kinetic processes*, which bring changes to the distribution due to interactions of particles with their environment or between themselves, and *transport processes*, which result in changes of the distribution due to transport of particles in physical space.

Kinetic processes include:

- *Nucleation*. This is the formation of new particles, or nuclei, from precursors in the carrier fluid. The term *inception* is also used in the case of soot.
- *Surface processes*. This includes all processes taking place at the surface of the particles and resulting in a continuous change of their size. Examples of such processes are surface growth of crystals and aerosols, oxidation of soot particles, evaporation of droplets and dissolution of bubbles.
- *Aggregation*. This is the formation of a particle from two other particles that collide. Several other terms such as *coagulation*, *coalescence*, *agglomeration* and *flocculation* are used in the literature for such processes, based on the nature of the particular process (such as whether the resulting particle is spherical or not) or on the field of application, although the definitions of these terms are not universal and varies with subject. In the present book, the term ‘aggregation’ will be used as a generic term, while other terms will also be used in more specific contexts; more details on this are provided in Section 3.2.1.
- *Fragmentation* (or *breakage*). This is the process where particles break into smaller ones. There are various special cases, such as *binary fragmentation* (breaking into two fragments) or *erosion* (removal of a small fragment).

Transport processes may be described in a simplified way in problems where spatial dependence is not considered. If the PBE is to be coupled with fluid dynamics, however, a detailed account of them is needed. They include the following:

- *Convection.* This is the transport of particles by the carrier fluid.
- *Hydrodynamic forces.* This includes forces such as drag and lift.
- *Body forces.* This includes forces due to external fields, such as the weight and the Coulomb force, and forces due to non-inertial frames of reference, such as the centrifugal and Coriolis forces. Other forces that may be included are particle migration due to temperature gradients (*thermophoresis*) or concentration gradients (*diffusiophoresis*).
- *Thermal motion.* This is a mechanism relevant for small particles and may resemble molecular motion or be induced by collisions with fluid molecules (Brownian motion).
- Momentum exchange between particles or between particles and walls, and momentum transfer from particles to flow.

The mechanisms and models for these processes will be considered in more detail in Chapter 3.

1.5 Population Balance and Fluid Dynamics

Many of the processes that can be described by the population balance take place within fluid flows. In these cases, the distribution is spatially non-uniform and the independent variables include both distributed properties and spatial coordinates. For example, a distribution of particle volume that is space and timedependent would be represented by the number density $n(v, \mathbf{x}, t)$, such that the concentration of particles with volume between v and $v + dv$ contained in a fluid element located at $\mathbf{x}$ at time instant t is ndv. Apart from the distribution, other important variables that affect it, such as temperature or concentration of precursors, may also be spatially variable. An example of a spatially non-uniform population balance problem is the crystallisation process in a T-mixer shown in Fig. 1.5, where the spatial variation of supersaturation results in different nucleation and growth rates and different crystal size distributions throughout the reactor.

In a spatially non-uniform formulation, the number density must be considered in the sense of a concentration, that is, number density of particles per unit volume of fluid. Since this is a continuous function of space, the implicit assumption is that the scale at which the flow is varying is considerably larger than the particles. This requirement is easily satisfied for many problems that involve small particles such as aerosols, soot and crystallisation. For larger particles, the population

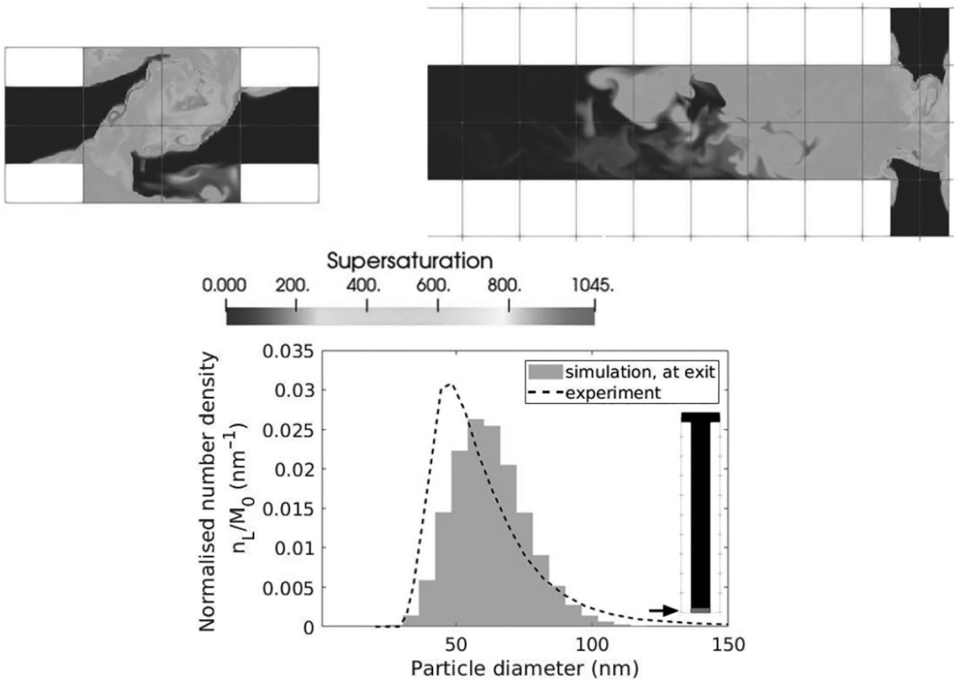

Figure 1.5 Precipitation of $BaSO_4$ in a T-mixer (cf. Section 6.3). Top row: spatial distribution of supersaturation (top left: a cross-section around the inlets, top right: a top view). Bottom: prediction of CSD with coupled CFD-population balance modelling (Tang et al., 2022) and comparison with the experiments of Schwarzer et al. (2006). Reproduced from Tang et al. (2022) under CC-BY 4.0 license.

balance must be applied to a sufficiently bigger volume. This may still be adequate if the flow varies on an even larger scale, such as in the case of atmospheric flows. Otherwise, either the PBE must be applied to a sufficiently large region that can be considered as well mixed (via an ideal reactor or reactor network model as opposed to a coupling with fluid dynamics) or a different approach must be pursued (such as a multiphase flow or discrete element model).

In the case of probability density functions, we will denote spatial dependence by $f(v;\mathbf{x},t)$ (the symbol ';' is used to indicate that the PDF is normalised with respect to v but not with respect to $\mathbf{x}$ or t). On the other hand, a number density is not normalised with respect to any of its arguments, hence the integration of $n(v;\mathbf{x},t)$ with respect to v yields the local value of the zeroth moment (which is also spatially dependent):

$$\int_0^\infty n(v,\mathbf{x},t)dv = m_0(\mathbf{x},t). \tag{1.17}$$

1.6 Two Examples of Population Balance in Flows

We will now show two examples of population balance models, in order to provide a 'first taste' of the issues to be discussed in the present book. Both cases demonstrate also the role played by fluid dynamics, which will be a major features throughout the book. For now, no equations will be shown, as the mathematical framework and physical models have not been presented yet; this is only a first look at these problems focussing on what the population balance approach can do for each of these cases. Both problems will be discussed in detail in Chapter 6.

1.6.1 Precipitation of Crystals

Crystallisation is a process of producing a crystalline material from a solution. The crystal size distribution (CSD) of the product is of great importance for its properties and its suitability to particular applications. Here, we are considering the case of reaction crystallisation, or precipitation, which is driven by a chemical reaction between species that are fed separately and mix into a reactor. For fast reactions, the mixing is the controlling factor for the outcome of the process, thus presenting a problem featuring strong coupling between population balance and fluid dynamics.

The case shown here involves two reactants are fed from two opposing streams into a T-mixer. As the reactants are brought into contact, a supersaturated solution is formed. Supersaturation is the driving force for crystallisation, and the processes of nucleation and growth depend on it in a nonlinear manner, with nucleation featuring a stronger dependence. Aggregation may also be present under certain conditions. The balance between these two processes determines the CSD; a high nucleation rate results in a large number of crystals and rapid consumption of the reactants, thus yielding small crystals at the end, while a low nucleation rate is followed by longer growth into bigger crystals. The population balance describes the delicate balance between these processes, while the equations of fluid dynamics and mass transfer describe the mixing of reactants. Fig. 1.5 shows the spatial distribution of supersaturation and the CSD at the exit as measured by experiments and predicted by population balance modelling. It is evident that the supersaturation is highly non-uniform and strong gradients are present; thin zones of high supersaturation can also be identified, which give rise to nucleation bursts. This problem will be revisited in Section 6.3, where the methods developed in the book will be employed to analyse the interaction between the processes of nucleation and growth, as well as their interaction with turbulence.

1.6.2 Formation of Soot and Carbonaceous Nanoparticles

The simulation of soot formation is needed to assist in the design of combustion devices. The soot particle size distribution is of increasing importance, as new regulations require control of the number of particles (particularly the smaller ones, which have far more harmful effects) as opposed to the mass of it, as was the case in the past. Similarly, the production of carbonaceous nanoparticles can be aided by modelling and simulation that permits tailoring of the product to applications. The dynamics of carbonaceous nanoparticles is a complex problem that involves fluid mechanics, turbulence, transport phenomena, chemical kinetics and population balance modelling.

Soot precursors are polyaromatic hydrocarbons (PAHs), which are themselves formed from smaller compounds found in flames via complex chemical mechanisms. Soot nucleation, or inception, involves heavy PAH molecules and is poorly understood, partly due to the experimental difficulties in observing these molecules or the soot nuclei. The evolution of soot particles involves surface growth by acetylene and consumption by oxidation, and the detailed description of these processes is also complex as it involves surface chemistry. Aggregation and fusing of soot aggregates also play a role in determining the distribution. Since chemistry is involved in most of these processes, the soot particle size distribution is spatially dependent and heavily influenced by the local concentrations of precursors and by temperature. In flames, concentrations and temperature exhibit large gradients and many species are present in thin zones, due to the interaction of fast chemical reactions with turbulence. The prediction of soot in a turbulent flame is thus one of the most complex challenges for population balance modelling, requiring coupling of a CFD code with chemical kinetics, a turbulence–chemistry interaction model and a population balance model.

Most practical combustion processes involve turbulent flows, which introduces several further implications that will be studied further in Chapter 5. Fig. 1.6 shows results from a CFDPBE simulation of a turbulent sooting flame that will be studied in the case study of Section 6.2. The figure shows contour plots of temperature and of two particle formation processes, nucleation and growth (more processes will be shown in Fig. 6.20). A full discussion of these results will be undertaken in Chapter 6 but, for now, we note this as an example of complex spatial distribution of the physical and chemical processes that are involved in the population balance and shape the particle size distribution.

1.7 A Brief Historical Survey

The concept of describing physical systems with a probability density function and linking the evolution of the latter to physical processes originates in Boltzmann and his famous equation. However, in the present book we employ the term ‘population balance’ in the more specific context of number density functions, for systems where the concentration of the particles is important as well as their probability

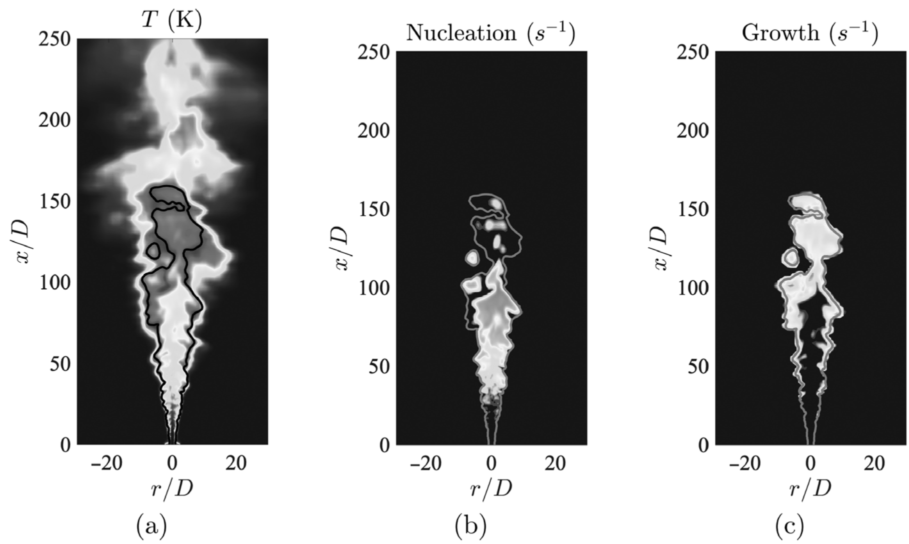

Figure 1.6 Simulation of a turbulent sooting flame with a coupled fluid dynamics – population balance formulation (cf. Section 6.2). Contour plots of the instantaneous (a) temperature, (b) nucleation rate and (c) growth rate. The iso-contour of stoichiometric mixture fraction (cf. Section 5.4) is shown as a solid line in the instantaneous plots. Reproduced from Sun and Rigopoulos (2022) under CC-BY 4.0 license.

distribution. In this sense, the origins of the subject can be traced to Smoluchowski (1917), who formulated a discrete PBE for the coagulation of colloidal particles. Smoluchowski was also able to derive the first solution for his equation, which will be shown in Chapter 4.

Other notable works in the early twentieth century include those of Müller (1928) and Schumann (1940), who derived the continuous PBE for coagulation, although the term 'population balance' was not used at that time. Schumann's work was motivated by atmospheric science and the need to predict the size distribution of cloud and fog droplets. This was the case also for several of the works that followed, including those of Scott (1968), who derived analytical solutions for coagulation equations, and of Bleck (1970), who derived an early numerical method. Melzak (1957a,b) extended the equation to include fragmentation; these two works are not concerned with any particular application but rather with the mathematical properties of the equation. Friedlander and Wang (1966) extended the coagulation equation to include condensation, evaporation and homogeneous nucleation; his work was motivated by the problem of the formation of aerosols. Friedlander and his co-workers are also responsible for the early developments of similarity solutions (Swift and Friedlander, 1964; Friedlander and Wang, 1966). The early works in the colloid, atmospheric and aerosol science communities have been reviewed by Hidy and Brock (1970) and Drake (1972).

Another important stream of research originates in the pioneering works of Randolph and Larson (1962) and Hulburt and Katz (1964), which were motivated by chemical engineering problems. The first of these works was concerned with the problem of crystallisation and formulated an equation for a continuous reactor with inlet and outlet; the term 'population balance' appeared, possibly for the first time, in that paper. The second work emphasised the importance of spatial dependence of the distribution and formulated a continuous PBE (termed a form of Liouville equation) that included spatial transport as well as nucleation, growth and agglomeration; that paper was also responsible for some of the earliest developments in the method of moments for the solution of the PBE. The introduction of the population balance as a general transport equation that includes spatial transport was also brought forward in a short note by Randolph (1964). Several works followed, and this line of research was summarised in the book by Randolph and Larson (1971) (see also Randolph and Larson, 1988, for the latest edition).

The application of the population balance to biochemical engineering commenced at about the same period with works such as Fredrickson and Tsuchiya (1963) and Fredrickson et al. (1967). Early work is summarised in the review of Tsuchiya et al. (1966), while Fredrickson et al. (1967) mention the term 'population balance' and the link of their work in this field with those of Randolph (1964) and Hulburt and Katz (1964). Later reviews of this literature can be found in Ramkrishna (1985, 2000).

With the fundamentals of the subject established, research in the following decades focussed on expanding the range of applications and developing methods of solution. Apart from the work in the communities of aerosol science and crystallisation, which largely fostered the subject's initial growth, a wide range of applications appeared in fields such as multiphase flow, fluidisation, granulation, comminution and biochemical engineering; a comprehensive list of applications up to 1985 can be found in the review by Ramkrishna (1985).

The seminal book of Ramkrishna (2000) was the first one to focus on the population balance as a methodology, while at the same time showcasing many of its applications. Several other books include an account of the population balance (in one of its many guises) in the context of a particular field of application. Williams and Loyalka (1991) is a treatise on aerosol science but includes an extensive treatment of the PBE (or GDE, in the context of that book) and a detailed account of analytical solutions. The books by Friedlander (2000) and Seinfeld and Pandis (2016) on aerosol science also include extensive discussions of the PBE (GDE). Treatises focussing on dispersed multiphase flows from the population balance point of view include Marchisio and Fox (2013) and Yeoh et al. (2014); the former, furthermore, includes valuable material on kinetic theory and moment methods. Hjortsø (2004) deals with biochemical problems. Jakobsen (2014) is a comprehensive treatise on chemical reactors that includes also an extensive section on the population balance. Litster and Ennis (2004) is focussed on granulation and includes a discussion of the PBE, while Litster (2016) deals with design and processing of particulate products and includes a treatment of the PBE with focus is on its application to particulate processes. Several review papers of a more general nature are also available, including Hounslow (1998), Ramkrishna and Mahoney (2002), Sporleder et al. (2012), Ramkrishna and Singh (2014) and Solsvik and Jakobsen (2015).

While the link between population balance and fluid dynamics had been established as early as in the work of Hulburt and Katz (1964), the computational power at the time did not allow the application of numerical methods to the coupled fluid dynamics-PBE problem. Therefore, applications prior to the nineties were based on simplified flow models such as ideal reactors. CFD was developed in the seventies and eighties and enabled the numerical solution of fluid dynamics and scalar transport equations. The development of coupled CFD–PBE methods commenced in the mid-nineties, initially with moment methods in order to minimise the storage and computation time requirements and later with discretisation methods; more information on these methods will be provided in Chapter 4. Methods for dealing with the coupling of population balance and turbulent flow are among the most recent developments at the time of writing. The focus on the coupling of fluid dynamics and population balance is reflected in several recent books and reviews, such as Rigopoulos (2010), Marchisio and Fox (2013), Yeoh et al. (2014), Jakobsen (2014), Raman and Fox (2016) and Rigopoulos (2019).

1.8 Summary

In the present chapter, the population balance has been introduced as an approach for modelling problems involving a population of particles with a distribution of one or more properties. The distribution is determined by a number of processes that can be classified into two groups: kinetic processes, which change the distribution due to interactions of particles with their environment or between themselves, and transport processes, which involve motion of particles in physical space. A number of problems to which the population balance approach can be applied have been identified, as well as possible choices of distributed variables. In many problems, the population balance must be coupled with fluid dynamics in order to determine the spatially varying distribution.

Approaching a problem with the population balance framework involves formulating the PBE for the distribution of the properties of interest, selecting models for the kinetic and transport processes involved, coupling the PBE with a flow model (either a simplified one or a detailed solution of the equations of fluid dynamics), and applying a solution method. The details of how these steps are to be carried out will be the subject of the following chapters. In particular, the formulation of the PBE and coupling with fluid dynamics will be addressed in Chapter 2, with the case of turbulent flow receiving a more extensive treatment in Chapter 5. Models for kinetic and transport processes will be discussed in Chapter 3, while solution methods will be treated in Chapter 4. Finally, Chapter 6 will demonstrate the overall population balance – fluid dynamics approach via three extensive case studies.