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

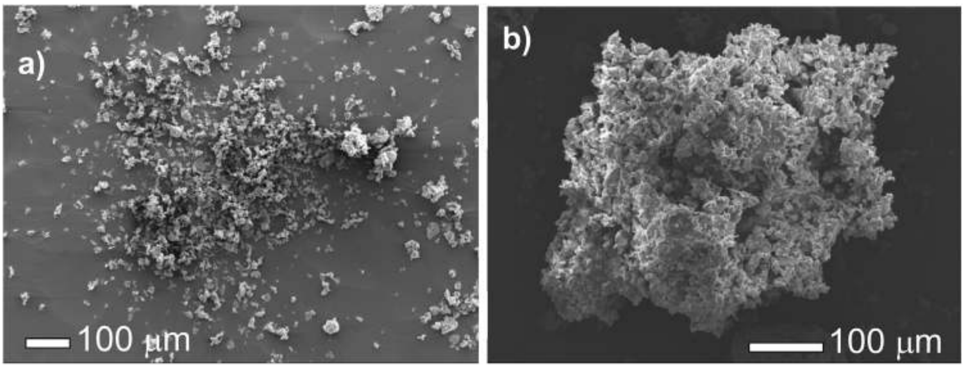

Figure 1.1 SEM images of ash aggregates: (a) a broken ash cluster and (b) an ash cluster. Reprinted from Bonadonna et al. (2011).

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

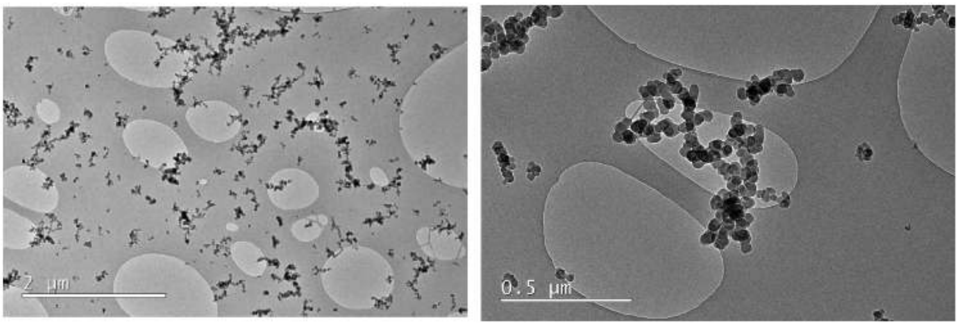

Figure 1.2 Micrographs of soot particles obtained via transmission electron microscopy (TEM); large-scale view (left) and close-up on an aggregate (right). Note that the big 'holes' are from the carbon film. Courtesy of Garcia Gonzalez (2018).

(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

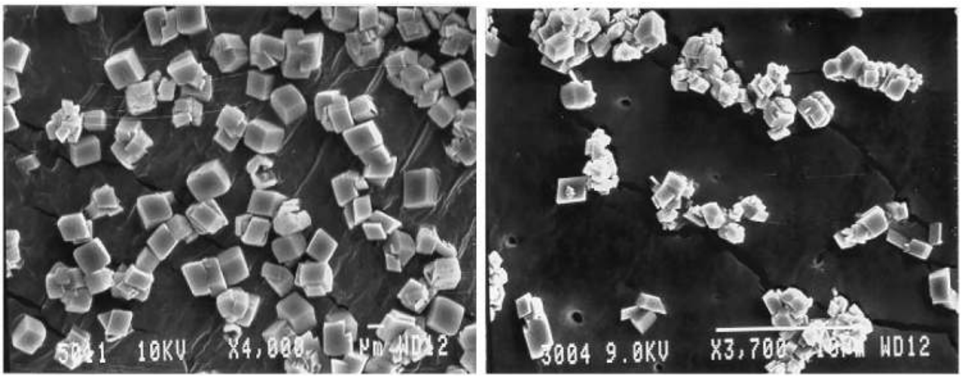

Figure 1.3 Scanning electron microscopy (SEM) images of $CaCO_3$ crystals produced via gas–liquid precipitation at an early (left) and a late (right) stage of the process. Reprinted from Rigopoulos and Jones (2003b) with permission from American Chemical Society.

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).

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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

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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

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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.

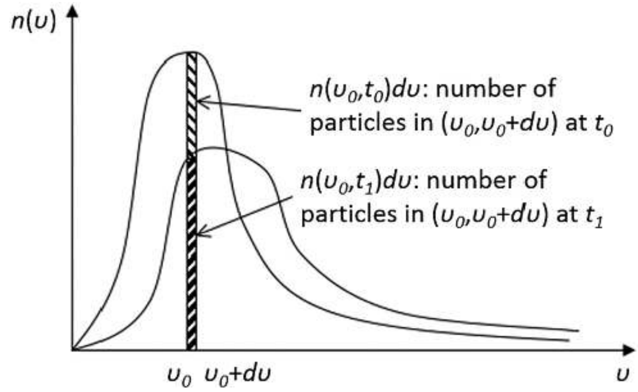

Figure 1.4 The continuous particle size distribution and its time evolution. Reproduced from Rigopoulos (2019) under CC-BY 4.0 license.