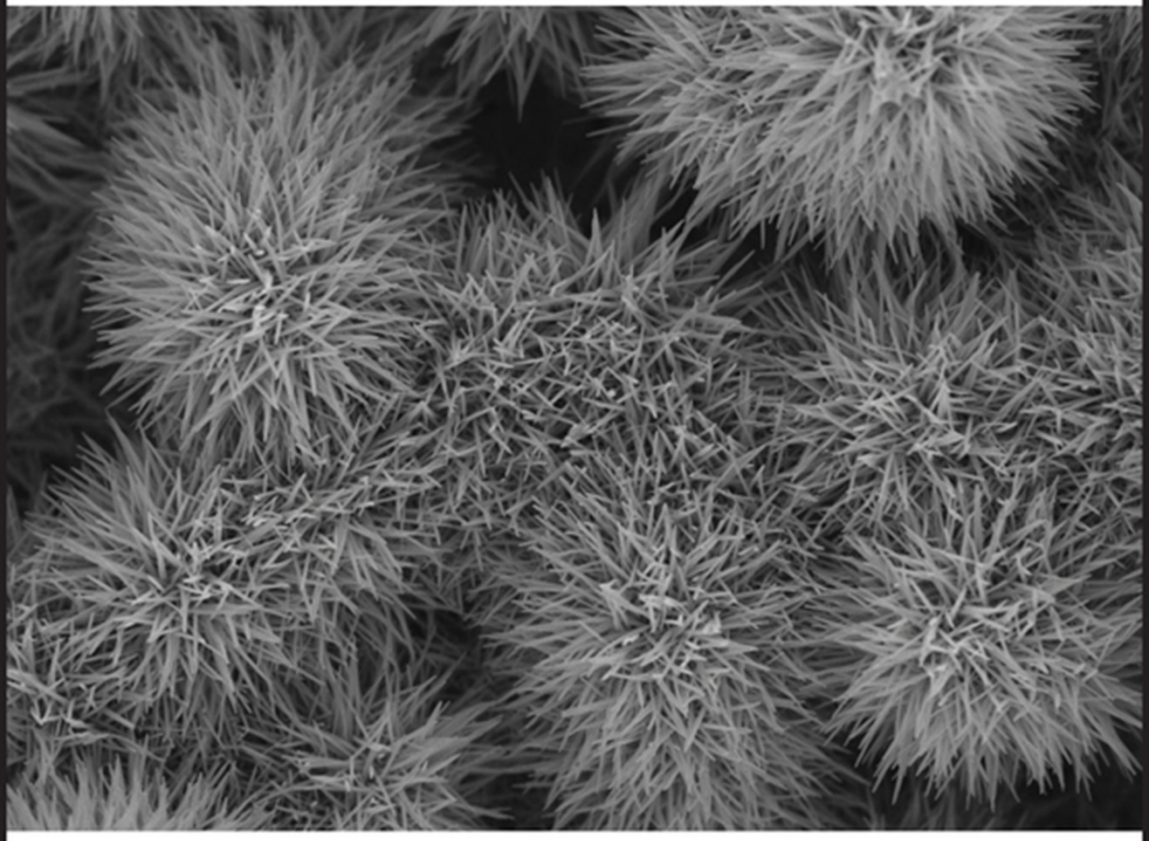
JAYANTA CHAKRABORTY

ENGINEERING OF SUBMICRON PARTICLES

FUNDAMENTAL CONCEPTS AND MODELS



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Fundamental Concepts and Models

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Dedicated to my parents, who had the courage to push us for higher education against many odds.

Contents

Preface

In the process industry, many products and intermediates exist in the form of fine particles. Many next-generation processes, such as colloidal heat transfer fluids for electronic cooling, also involve small particles. However, the ability of the process industry to deal with particulate processes in a quantitative way is limited. The process industry must enhance its capability in the engineering of fine particles.

Many research laboratories also produce and handle submicron particles. In a broader sense, such particulate systems include powders, polymers, colloids or even human populations. While many engineering textbooks and reference books deal with particles of micron scale and above, submicron particles are discussed mostly under very specialized subtopics and a reference book discussing the fundamental concepts of such systems is missing.

Everyday activities in an industrial or academic research laboratory where particulate systems are involved require application of a number of quantitative relations called models. Even experimental facilities use models to relate the raw data with the quantity of interest and often the user is not aware that the outputs are actually from a model. Most models are not straightforward and no single resource is available to provide understanding of frequently used techniques and concepts. New researchers often find themselves at a loss and tend to trust data blindly. This book attempts to resolve this problem by discussing the fundamental theories behind many frequently encountered particulate processes. A large number of diagrams, software, examples, brief experimental demonstrations, and exercises with answers are included and have been carefully planned to provide good learning.

Particulate systems are used by physicists, chemists, mathematicians, and engineers. It is difficult to provide fundamental knowledge to the degree demanded by all. This book is mainly aimed at senior undergraduate or graduate chemical engineering students but provides enough background material in the appendices to be also useful to students from other branches of science and engineering.

Models are used at various levels in particle technology. A set of basic models describe the fundamental process of nucleation, growth, and aggregation of particles. In these models, the rate of nucleation of particles from a medium of given supersaturation, the rate of increase of size of a particle of given size under a set of environmental conditions, and the rate of aggregation of given pairs are provided.

Classical nucleation theory is discussed at length in this text. Other nucleation mechanisms, e.g. the organizer mechanism, are also introduced. For growth, the classical growth models such as diffusion controlled and surface nucleation controlled growth are discussed, along with newer models like connected net analysis. Aggregation models and inter-particle potentials are discussed with a brief but useful prelude on inter-molecular and surface forces.

The basic models alone cannot describe the dynamics of an engineering system containing a large number of particles of varying attributes. For this a number balance equation (population balance) is needed. In this book the emphasis is on formulating the number balance equation (the population balance model) for a given system. Analytical and numerical solutions of population balance models are also discussed briefly. Software with open code is provided for the solution of a population balance model through discretization.

To my knowledge no book serves such a diverse yet unified purpose. This book has been in my mind throughout my career over the past decade, during which I made my journey from an experimental laboratory to two theoretical laboratories and then back to experiments. This book contains useful insights which I acquired over time.

This book is heavily indebted to several books and monographs which helped me in assimilating the content. I kept close to the flow of ideas and concepts of the parent books whenever I felt that was best for the reader. I acknowledge major contributions from the following books and monographs:

- *Foundations of Colloid Science* by R. J. Hunter and *Kinetics of Precipitation* by A. E. Nielsen for the nucleation and growth chapters.
- The chapter on inter-molecular and inter-particle force has ideas and contents from *Intermolecular and Surface Forces* by Jacob Israelachvili.
- The stability chapter is heavily indebted to Paul C. Hiementz (*Principles of Colloid and Surface Chemistry*).
- The particulate system modelling section is indebted to *Population Balances* by D. Ramkrishna and *Theory of Particulate Processes* by A. D. Randolph and M. A. Larson.
- Much of the book is also influenced by the lecture notes circulated during my graduate course on modelling at the Indian Institute of Science, Bangalore by Prof. K. S. Gandhi and Prof. Sanjeev Kumar.

Apart from these major resources there are many other books and monographs that helped me to understand, assimilate, and express the ideas. I also

acknowledge help from students at IIT Kharagpur who took this course (Fundamentals of Particle Technology, CH60026), asked critical questions, and helped me write this book. I hope this book will be useful to the others. Of course there are multiple errors and omissions which I'm eager to hear from the readers and correct in a future edition.

Jayanta Chakraborty
IIT Kharagpur
Autumn 2018

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Nucleation

Nucleation means the creation of new particles, i.e. the creation of a new phase and associated interface. Hence, in order to understand the nucleation process, we need to learn a few key ideas from physical chemistry. The energy of the interface is vital to the nucleation process, which in turn controls the nucleation rate. Hence, our discussion will involve both thermodynamics and kinetics: the thermodynamics of the interface will provide the magnitude of the driving force and the kinetics will provide the rate of nucleation.

1.1 Thermodynamics of Interfaces

An interface is a surface where one phase ends and another starts. It is a narrow region often in the order of a few angstroms where the properties change from that of one phase to another. For a liquid–vapour interface, the density of the medium undergoes an abrupt change. For a liquid–liquid interface, two dissimilar atoms are in contact at the interface.

1.1.1 The Interface is a Surface of High Energy

An interface is known to contain higher energy than the bulk phase. This difference in energy is key to phenomena relating to many important technical problems. The excess energy of the interface, or interfacial energy, is due to the difference between the energies of atoms on surface and in the bulk. The difference may be due to the change in density between the two phases or to the difference in chemical nature.

Let us consider the former as an example. For a liquid–vapour interface the liquid is in contact with its vapour. Hence, although similar atoms/molecules are present on both sides of the interface, the densities are very different. This leads to a different coordination number of atoms in bulk versus atoms on the surface. Next we show how this leads to interfacial energy.

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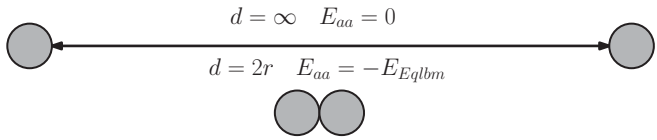

Figure 1.1 Distance-dependant interaction potential. The negative sign indicates energy release.

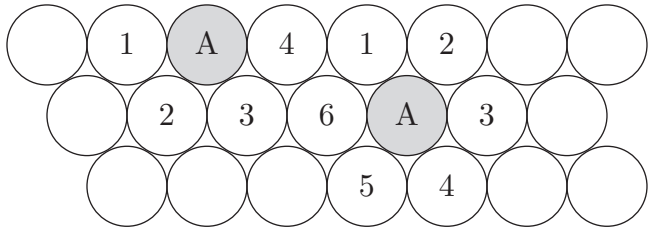

Figure 1.2 Difference in coordination number between surface and bulk atoms. In this case, the surface atom coordinates with only four other atoms while the bulk atom coordinates with six.

The energy of interaction of two isolated atoms at infinite separation is zero. If they are brought closer together, they start to interact. At a specific distance, $2r$, contact between the two atoms, the energy of interaction, becomes a minimum.

Let us denote the amount of energy *released* by bringing a pair of atoms of same chemical species to this distance by E_{AA}. Hence, the energy per atom for constructing a pair is $E_{AA}/2$. What is the energy released per atom where all atoms are jam-packed, as shown in Figure 1.2? A pair of simplifications will be useful in analyzing the case:

- only the nearest neighbours of an atom can impart some force on an atom
- interaction is pairwise additive.

With these assumptions, an atom in the bulk (see Figure 1.2) will release energy corresponding to the pairs A-1, A-2, … A-6 as shown in the figure (the coordination number is 6). If we denote the coordination number in bulk by z_b, the total energy *released* per atom will be

$$-\frac{z_b E_{AA}}{2}.$$

Now, the coordination number is different for the surface. Hence, the energy *released* per atom for the surface will be

$$-\frac{z_s E_{AA}}{2}$$

where the coordination number for the surface is z_s. Because $z_b > z_s$, more energy is *released* for the atoms in the bulk than on the surface. Hence, the

surface atoms *retain* more energy. Hence the system that has more interface, has more energy. In other words, interface contains energy.

1.1.2 The Interface is a Surface Under Tension

Will the surface resist its extension? It should. More surface will require more atoms to join the surface, leaving the bulk, and hence it goes energy uphill. Hence, interfaces normally act like a stretched membrane.

The extra interface will require extra energy, which will be supplied by external work. If we denote the energy needed for the creation of a differential amount of surface δA by δW, the following proportionality can be written:

$$\delta W \propto \delta A.$$

Inserting the constant of proportionality:

$$\delta W = \gamma \delta A.$$

It is clear that the constant γ is the surface energy per unit area and hence is interpreted as the specific surface energy. If work is done by a constant external force F_s to increase the area and the increase in area can be written as $\delta A = l\delta x$, the above equation becomes

$$F_s \delta x = \gamma l \delta x$$

or

$$F_s / l = \gamma,$$

which leads to the popular interpretation of specific surface energy as 'surface tension' with unit force/length.

1.1.3 Pressure Drop Across Curved Interfaces

The higher energy of the interface leads to difference in pressure across a *curved* interface [1]. Let us consider a small area, as shown in the Figure 1.3, and perturb the surface by varying the pressure differentially: the surface expands differentially in response to the differential increase in pressure. The increase in area is

$$(x + dx)(y + dy) - xy = xdy + ydx.$$

This additional area will require additional surface energy, which is

$$\gamma(xdy + ydx).$$

This much energy must be supplied by working against a difference in pressure (ΔP) between the two sides of the curved interface. If the inside pressure during the perturbation changes only differentially, the pressure difference across the

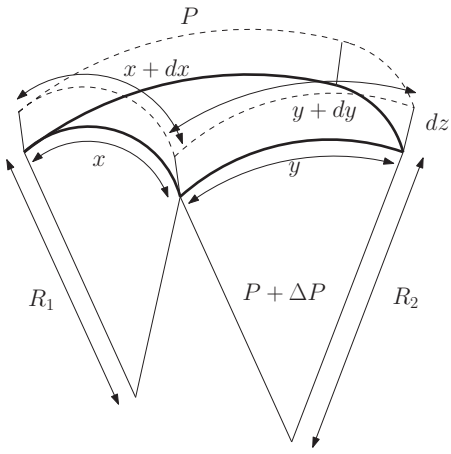

Figure 1.3 The geometry of a curved interface: derivation of the Young–Laplace equation

interface remains ΔP even after the perturbation. Hence the PV work is given by $\Delta P \Delta V$. The increase in volume, ΔV, in this case is given by $xydz$ and hence the energy balance can be written as

$$\gamma(xdy + ydx) = \Delta P xydz$$

or

$$\frac{\Delta P}{\gamma} = \frac{xdy + ydx}{xydz} = \frac{1}{y}\frac{dy}{dz} + \frac{1}{x}\frac{dx}{dz}.$$

Using the property of similar triangles, we can write

$$\frac{x}{R_1} = \frac{x + dx}{R_1 + dz}$$

and

$$\frac{y}{R_2} = \frac{y + dy}{R_2 + dz}.$$

These two expressions lead to

$$\frac{1}{R_1} = \frac{1}{x}\frac{dx}{dz}$$

and

$$\frac{1}{R_2} = \frac{1}{y}\frac{dy}{dz}.$$

Hence, the above equation can be written as

$$\frac{\Delta P}{\gamma} = \frac{1}{R_1} + \frac{1}{R_2}. \tag{1.1}$$

This is known as the Young–Laplace equation and gives the pressure difference across a curved interface as a function of its curvature.

Example 1.1 What is the pressure inside a small water droplet of radius 1 μm and one with radius 1 nm? The surface tension of water is 75 mN/m.

Solution: Because the drop is spherical, both the radii are equal in this case. Hence, the Young–Laplace equation reduces to

$$\frac{\Delta P}{\gamma} = \frac{2}{R}.$$

Hence for a 1 μm drop:

$$\Delta P = \frac{2 \times 75 \times 10^{-3}}{1 \times 10^{-6}} = 0.15 \times 10^{6} \text{ Pa} = 1.5 \text{ atm}.$$

If the drop size is 1 nm,

$$\Delta P = \frac{2 \times 75 \times 10^{-3}}{1 \times 10^{-9}} = 150 \times 10^{6} \text{ Pa} = 1500 \text{ atm}.$$

It can be seen that for the first case the pressure difference is merely 1.5 atm whereas for the later it is huge: 1500 atm. Usually, nuclei are very small, of the order of nanometres, and hence they experience huge pressure due to the curved interface. □

Example 1.2 What is the pressure inside a small soap bubble of radius 1 cm?

Solution: Because the soap bubble has two interfaces, the Young–Laplace equation should be written for both interfaces. Denoting P_i as inside pressure, P_f as film pressure, and P_o as outside pressure, and applying the Young–Laplace equation for both interfaces,

$$P_i - P_f = \frac{2\gamma}{R}$$
$$P_f - P_o = \frac{2\gamma}{R + \delta R}$$
$$\therefore P_i - P_o = \frac{2\gamma}{R} + \frac{2\gamma}{R + \delta R}.$$

Neglecting the film thickness δR:

$$\therefore P_i - P_o = \frac{4\gamma}{R} = 30 \text{ Pa}.$$

Note that we have used the surface tension value of water instead of the surfactant solution in order to obtain an approximate value. The true surface tension of the surfactant solution is dependent on the nature and concentration of the surfactant and should be used for an accurate value. □