

1 Introduction

Nucleation is the birth of a new phase of matter from an old phase. This occurs when molecules, in sufficient number, configure themselves so as to constitute a “nucleus” of the new phase. The *Oxford English Dictionary* defines “nucleation” as “the formation of nuclei, esp. by the aggregation of molecules into a new phase within a medium.” The Latin word “nucleus” means “kernel” and is related to the English word “nut” (in Latin “nucula” or “nux”) (Simpson and Weiner 1989).

1.1 Significance of Topic

This text is concerned with the nucleation of condensed-phase particles, either solid or liquid, from the gas phase. This process is important for a wide variety of natural and technological phenomena. For example, obtaining a better understanding of the nucleation of particles in the atmosphere is necessary for increasing the accuracy of models for predicting global climate change. Soot formation during combustion is of central importance for fields such as air pollution, design of power plants and combustion engines, and fire science. The nucleation of interstellar dust is thought to play a crucial role in the evolution of the universe. In nuclear fusion reactors, dust formation in the edge plasma adjacent to reactor walls poses a critical challenge to the successful development of fusion as a global energy technology. As characteristic feature sizes in microelectronics shrink to smaller and smaller dimensions, particles that can form by nucleation in the chemically reactive plasmas used for semiconductor processing pose a serious contamination threat that can lead to “killer defects” in integrated circuits. Conversely, deliberate nucleation from the gas phase is one of the main routes to generating nanoparticles for use in a broad range of advanced technologies, including, for example, advanced ceramics, superhard coatings, catalysts, improved solar cells, xerography, ultraviolet-blocking cosmetics, medical diagnostics and therapies, magnetic materials, and electronic devices. Nucleation of particles from the gas phase creates an “aerosol” – a population of particles that are dispersed in a gas – and aerosol science is itself an important discipline with many applications.

An understanding of particle nucleation from the gas phase is thus of practical interest to scientists and engineers in a wide variety of disciplines.

It is also of fundamental interest, as nucleation represents one of the major unsolved problems of science. Despite attracting the interest of many scientists, who over the past century have produced a large body of literature on the subject, it is still not

possible to predict, with reasonable quantitative accuracy, some of the most basic features of nucleation, such as the *nucleation rate* (the rate of formation of new nuclei per unit volume) and the dependence of the nucleation rate on temperature and vapor concentrations. This statement applies even for the simplest nucleation scenario – homogeneous nucleation of a single chemical substance – for the vast majority of chemical substances. That this is so has much to do with the fact that the science of atomic and molecular *clusters* – including the “aggregation of molecules” comprising a nucleus – now the focus of great interest, is still in its infancy.

1.2 Types and Regimes of Nucleation

1.2.1 Nucleation in General

We know from everyday experience that matter can exist in various phases – solid, liquid, or gas – and that the phase of a given substance depends on its temperature and pressure. Thermodynamics teaches us that the phases of a given chemical substance at equilibrium can in general be represented on a diagram such as Figure 1.1. One of the great achievements of thermodynamics is the ability to predict the equilibrium state of a system. A system that is out of equilibrium at a given absolute temperature T and pressure p seeks the state (phase and/or chemical composition) that minimizes its total Gibbs free energy,

$$G \equiv H - TS, \quad (1.1)$$

where H is enthalpy and S is entropy. Enthalpy is defined by

$$H \equiv E + pV, \quad (1.2)$$

where E is energy and V is volume.

Thus the driving force for phase change is the departure of G from its minimum value at the given values of pressure, temperature, and total size (volume or mass). The curves separating the phases in Figure 1.1, known as “saturation curves,” represent regions of pressure–temperature space in which multiple phases can coexist at equilibrium. When the pressure or temperature changes so as to cross a saturation curve, the system seeks a new equilibrium by undergoing a phase change. However, this process is not instantaneous, because it must be initiated by the formation of nuclei of the new phase, a process that occurs at a finite rate.

Nucleation refers to the initiation of phase change between any two phases. Examples include crystallization from a melt or from an amorphous solid, transition from one crystalline phase to another, bubble formation in a liquid, and condensation of particles from a gas. Traditionally nucleation processes are divided into *homogeneous* nucleation and *heterogeneous* nucleation. Homogeneous nucleation refers to nucleation in the absence of any foreign nuclei or free surfaces. Heterogeneous nucleation occurs when the new phase forms on preexisting foreign nuclei or free surfaces. For example, the formation of solid crystals within the interior of a melt, assuming that the melt is free of void spaces and of preexisting solid particles, is a homogeneous nucleation process, whereas the initial stage

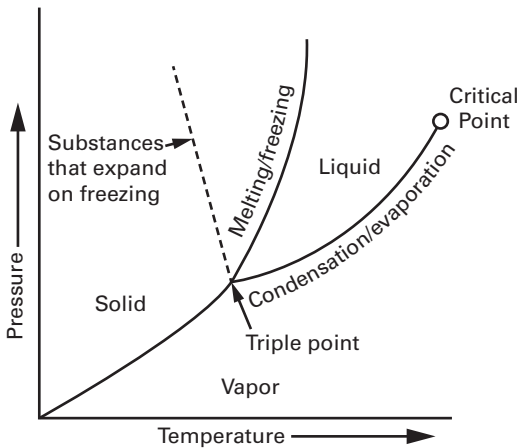


Figure 1.1 Equilibrium phase diagram of a pure substance. For simplicity, the fact that multiple solid phases can coexist for many substances is neglected.

of thin film growth by physical or chemical vapor deposition on a solid surface involves a heterogeneous nucleation process. Both homogeneous and heterogeneous nucleation may be either single-component (homomolecular), involving a single chemical species, or multicomponent (heteromolecular), involving two or more species.

1.2.2 What Is a “Particle”?

Homogeneous nucleation from a vapor leads to the appearance of discrete particles of a condensed phase.

How large must a cluster be before it can be considered a particle? There is no universally agreed definition.

Intuitively, one would want a cluster to be of some minimum size, or to contain some minimum number of atoms or molecules, before it could reasonably be termed a particle.¹ Figure 1.2 shows the relation between the diameter and number n of water molecules in a water cluster, $(\text{H}_2\text{O})_n$, assuming that the cluster is spherical and has the same mass density as liquid water at 298 K and 1 atm. These assumptions are obviously simplistic for small values of n , for which an H_2O cluster has a complicated, nonspherical geometry, with an electron cloud whose structure is described by quantum mechanics, and whose volume is thus not well defined. Nevertheless this exercise is instructive.

The calculation is straightforward. An effective molecular volume can be defined by

$$v_1 = \frac{m_1}{\rho} = \frac{\widehat{M}}{\rho N_A}, \quad (1.3)$$

¹ Throughout this text, our usage of the term “particle” refers to discrete entities of a condensed phase, an altogether different usage than the elementary “particles” (e.g., atoms, electrons, and other subatomic particles) of physics.

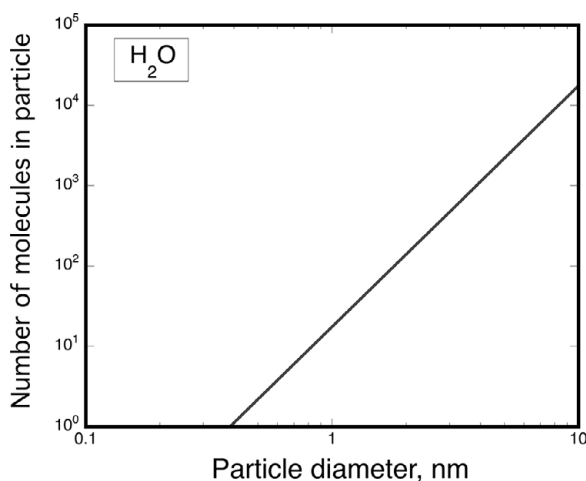


Figure 1.2 Relation between the diameter and number of water molecules in a spherical liquid water cluster.

where m_1 is the mass of one molecule, ρ is the mass density of the bulk condensed phase, \hat{M} is the molar mass (molecular weight) of the substance, and N_A is the Avogadro constant, $6.022 \times 10^{23} \text{ mol}^{-1}$. Thus v_1 represents the volume occupied per water molecule, in bulk liquid water.

Treating a water molecule as a sphere, the corresponding effective molecular diameter is

$$d_1 = \left(\frac{6v_1}{\pi} \right)^{1/3}. \quad (1.4)$$

For water, we find $d_1 = 0.385 \text{ nm}$. The number n of molecules contained in a cluster of diameter d_n is then simply

$$n = \left(\frac{d_n}{d_1} \right)^3. \quad (1.5)$$

Based on this analysis, a 1-nm-diameter water “droplet” contains about 17 molecules, but a 4-nm-diameter water droplet contains more than a thousand molecules. At 17 molecules, the assumption of sphericity is dubious, but at a thousand molecules it is probably reasonable, assuming that the droplet is liquid as opposed to an ice crystal.

Let us consider some possible criteria for how large a cluster should be to be called a particle:

- (1) In nucleation theory, the nucleation rate is usually defined as the rate of formation of clusters whose size is just above a so-called “critical size.” However, as we shall see, these critical-size clusters may be as small as just a few atoms or molecules or even just a dimer. It seems contrary to common sense to refer to such a small entity as a “particle” of the condensed phase. Indeed, the cluster of

critical size is often termed an “embryo,” suggesting that it is not yet a condensed-phase particle but is likely to grow to become one.

- (2) One might identify a cluster as a particle when it is large enough so that some of its properties – for example, density, binding energy per atom, or melting point – are similar to those of the bulk condensed phase of the same substance. However, here one encounters the problem that many properties of nanoparticles, even up to sizes of several tens of nanometers, may be quite different than those of the bulk. For example, for many substances, the melting temperature of particles smaller than about 5 nm in diameter is depressed by several hundred °C compared to the bulk (Goldstein et al. 1992). Many properties of particles smaller than about 10 nm in diameter are strongly affected by the fact that a large fraction of the atoms comprising them lie on or within a monolayer of their surfaces, and for some substances, quantum confinement effects at these sizes can drastically alter their electronic and magnetic properties. Yet it is common to call clusters larger than about one nanometer in diameter “particles,” so this test seems inadequate.
- (3) Some researchers involved in computational simulations of chemical nucleation have chosen to define a cluster containing more than an arbitrary number of atoms or molecules – for example, more than 10 or 12 silicon atoms in a silicon hydride (De Bleecker et al. 2004a; Giunta et al. 1990; Swihart and Girshick 1999) – as a “particle,” where this definition is made purely for computational convenience.
- (4) It might be argued that a cluster is a “particle” when its structure is that of a solid or a liquid. However, all molecules containing at least two atoms would seem to qualify under this definition, so it makes little sense. A cluster may be “solid-like” or “liquid-like,” according to whether it has a well-defined structure and relatively rigid bonds or is instead structureless with its constituent atoms or molecules having considerable mobility. Thus a cluster may experience a melting or freezing transition, and it is meaningful to distinguish between whether it is above or below critical size (and thus whether or not it is stable for growth), but, if it is a constituent of an aerosol, what is meant by saying that it represents a “condensed” phase as opposed to a molecule (even a large one) in the gas phase? The particles in an aerosol, after all, have complete translational freedom, and in most cases, the distances between them are much larger than their individual diameters, similarly as for molecules in a gas.
- (5) An important characteristic of clusters, as noted above, is that a large fraction of their atoms or molecules lie on the surface. One might argue that one should not use the term “particle” until some minimum fraction, for example, 90% or 50%, of the atoms or molecules were located in the “interior” of the cluster as opposed to the surface. To estimate how large the cluster would have to be to satisfy this criterion, suppose for simplicity that the atoms in an atomic cluster were all evenly spaced and arranged in a cube, as in Figure 1.3. Let N denote the width of the cube in number of atoms. The number of atoms in the cluster equals N^3 . The fraction f_{int} of atoms located in the interior of the cube is then given by

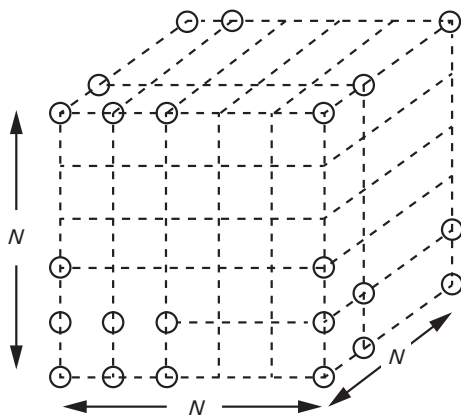


Figure 1.3 Model for the relation between cluster size and the fraction of atoms on the surface. The cube consists of $N \times N \times N$ evenly spaced atoms.

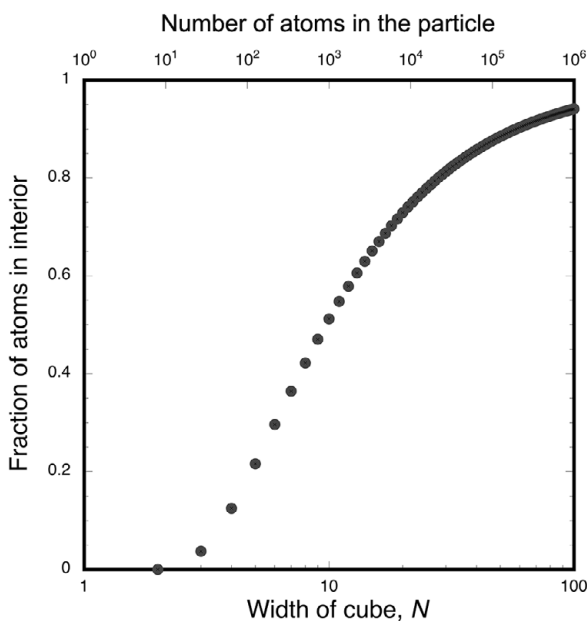


Figure 1.4 Fraction of atoms in the interior (i.e., not on the surface) of a cubic particle vs. number of atoms comprising the width of the cube.

$$f_{\text{int}} = \frac{(N - 2)^3}{N^3}. \quad (1.6)$$

Figure 1.4 graphs the result. One finds that the 50% criterion is not satisfied until $N = 10$, corresponding to a cluster of 1,000 atoms, and the 90% criterion is not satisfied until $N = 58$, corresponding to a cluster of almost 2×10^5 atoms. The corresponding width of the cube in nanometers would depend on the size

of the atoms and the spacing between them. If one assumed, for example, that each atom, accounting for the spacing, occupied a lateral dimension of 0.3 nm, then over 50% of the atoms would lie on the surface for cube widths smaller than 3.0 nm, and over 10% of the atoms would lie on the surface for cube widths smaller than 17.4 nm. As most current usage would accept the term “particle” for sizes somewhat smaller than 3 nm, it is evident that one must recognize that “particle” is used to denote entities for which a very large fraction of atoms lie on the surface and which therefore may have properties that are quite different from those of the bulk condensed phase. Indeed, this is a major reason for the strong interest in nanoparticles for a variety of technological applications.

- (6) Taking account of the problems with (4) and (5), one could reserve the term “particle” for a cluster for which the structure of the interior atoms was identical to that of a bulk crystalline phase of that substance. It does seem reasonable to call such a cluster a “particle” and even to acknowledge that in this case a phase transition appears to have occurred. However, this definition would be too restrictive, as one also wants to use the term “particle” to describe liquid droplets and amorphous solids.
- (7) Experimentalists studying nucleation rates may for practical reasons define the minimum size of a “particle” as the smallest cluster in an aerosol that can be detected by methods such as laser light scattering or instruments such as differential mobility analyzers. In this case, the minimum size of a “particle” depends on the detection limit of the method and/or instrument. For example, at present the lower detection limit for differential mobility analyzers equals about 1 nm, suggesting a practical experimental demarcation between “clusters” and “particles.”
- (8) Given the above, a reasonable choice for the minimum diameter of a “particle” might be taken as 1 nm.² This choice emphasizes the approximate nature of the division between clusters and particles and is clearly the order of magnitude in the SI unit system that best corresponds to the lower limit of particle size. Nevertheless, one must keep in mind that a 1-nm “particle” contains very few atoms or molecules and may be highly nonspherical, with an ill-defined volume. Indeed, in many cases large organic molecules are themselves larger than 1 nm.

In summary, what constitutes a particle of a condensed phase is not well defined. However, this does not present a problem for gas-phase nucleation theory, because it focuses not on the formation of “particles” but on the formation of nuclei – the entities that are likely to grow to the size of particles. And, as shall be seen, “nuclei” *are* rigorously defined.

For a further discussion of length scales that are pertinent to the transition from “molecules” to “particles,” the reader is referred to an interesting paper by Preining (1998).

² We use the term “diameter” in the generic sense to denote a characteristic linear dimension of a particle that is not necessarily spherical.

1.2.3 Single-Component Homogeneous Nucleation from the Gas Phase

Phase-change processes between any pair of phases have enough in common to be considered within a general theory of nucleation. A comprehensive text on the general theory of nucleation is *Nucleation*, by Kashchiev (2000). However, each type of nucleation also presents a number of issues that are unique to the phases involved. In this text, we are concerned with the nucleation of condensed-phase particles from gases. An earlier textbook focused on this subject is *Homogeneous Nucleation Theory: The Pretransition Theory of Vapor Condensation*, by Abraham (1974).

The simplest case involves homogeneous nucleation of a single-component supersaturated vapor, which can occur when the saturation curve in Figure 1.1 is crossed from the region marked “vapor” to either of the regions marked “solid” or “liquid.”³ This process is often termed “self-nucleation,” meaning that the vapor condenses on itself, and the term “homomolecular” is sometimes used to indicate that only one molecular species condenses.

Consider, for example, water vapor at equilibrium at a pressure of 1 atm and a temperature of 101°C that is cooled at constant pressure to a temperature of 99°C, as illustrated in Figure 1.5. By definition of the Celsius scale, the equilibrium vapor pressure of water equals 1 atm (101.325 kPa) at 100.0°C. At 101°C, the equilibrium vapor pressure of water equals 105.0 kPa; at 99°C, it equals 97.76 kPa (Haar et al. 1984).

The saturation ratio, S , of a vapor is defined by

$$S = \frac{p}{p_s(T)}, \quad (1.7)$$

where p is the actual partial pressure of the vapor and p_s is the equilibrium (or “saturation”) vapor pressure.⁴

At the state marked “1” in Figure 1.5, $S = 101.3/105.0 = 0.965$; at State 2, $S = 1$; and at State 3, $S = 101.3/97.76 = 1.04$. If the system at each of these states were given sufficient time to reach equilibrium, State 1 would be vapor, State 2 would be a mixture of vapor and liquid – the proportion of each depending on the specific volume – and State 3 would be all liquid. However, if this experiment were conducted in such a way that effectively no walls or preexisting particles existed, one would find that one could substantially overshoot the saturation curve before any condensation was observed. Upon crossing the saturation curve from the vapor side to the liquid side, S becomes greater than unity, and the vapor is said to be “supersaturated.” In this case, the system is out of equilibrium, and thermodynamics tells us that a driving force for phase change exists. However, nucleation is a kinetic process, and the time required for observable condensation depends on various conditions. In many cases, it is possible for vapors to

³ While the words “vapor” and “gas” can be used interchangeably, the use of “vapor” emphasizes that the gas in question is condensible under the conditions of interest.

⁴ The literature is inconsistent on terminology here. We will usually use “saturation ratio,” as in standard textbooks on aerosol science (Friedlander 2000; Hinds 1999; Seinfeld and Pandis 1998), although one often finds S referred to as the “supersaturation,” which strictly speaking should refer to the quantity $(S - 1)$. One also finds the terms “supersaturation ratio” and the “degree of supersaturation.”

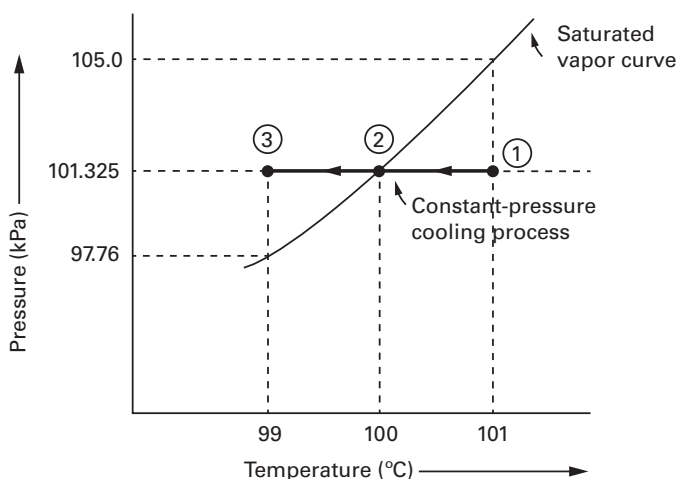


Figure 1.5 Constant pressure cooling of water, causing it to cross the liquid–vapor saturation curve.

be highly supersaturated (e.g., saturation ratios of several hundred or greater) without observable condensation over laboratory time scales. C. T. R. Wilson, who conducted cloud chamber experiments for which he won the 1927 Nobel Prize in Physics, observed no nucleation in water vapor free of ions at room temperature until the saturation ratio reached a value of about eight (Wilson 1897). Indeed, the classical theory of single-component homogeneous nucleation, discussed in Chapter 3, predicts for water vapor at 20°C and at a relative humidity of 200% (i.e., $S = 2$) that the steady-state nucleation rate equals about $10^{-54} \text{ cm}^{-3} \text{ s}^{-1}$, which works out to equal about one water droplet per cm^3 per 10^{47} years. The estimated life of the universe being only about 10^{10} years, one is not likely to have observed that droplet.⁵

The physical nature of the self-nucleation process is that molecules of the vapor collide with each other and stick together to form larger and larger clusters. In general, these clustering collisions are reversible, that is, a molecule can “evaporate” from a cluster and return to the vapor phase. In fact, until a cluster grows to a certain critical size, the value of which depends on the properties of the substance and on conditions, it is more likely to shrink than to grow. But should it succeed in growing past the critical size, further growth becomes effectively irreversible. The existence of a critical size larger than a monomer thus poses a barrier to nucleation, and clusters of critical size represent the “nuclei” for phase change.⁶

⁵ The steady-state assumption would obviously not be valid here, and even if it were, the classical theory can be in error by many orders of magnitude, but even so this calculation gives a qualitative sense of how rare homogeneous nucleation of water would be under these conditions.

⁶ In organic chemistry, the term “monomer” is used to mean a simple organic molecule that can join in long chains with other molecules to make a polymer. Here we use the term “monomer” more generally to mean the smallest entity, not necessarily organic, having the same chemical composition as the nucleating substance. In most cases, a “monomer” is simply a single molecule (or atom, if the molecule is monatomic) of the condensable vapor.

Nucleation is the process of forming these nuclei. Note that the nuclei themselves are not necessarily entities of the new phase. They are simply molecular or atomic clusters, often just large (or even not so large) molecules. Per the preceding discussion, entities large enough to be considered particles of the condensed phase may be much larger than the nuclei. However, as the nuclei are by definition the entities that are stable for growth, the rate of particle formation can be closely related to the rate of nuclei formation – the nucleation rate.

According to the value of the critical size, one may distinguish between two different regimes. Most of the literature on the theory of homogeneous nucleation is concerned with the scenario discussed above, in which the critical size is larger than a monomer and growth to the critical size requires passage through a sequence of reversible clustering reactions, each of which has a higher rate in the direction of decay than in the direction of growth. This scenario describes what is known as the “condensation/evaporation” regime.

However, in cases of extremely high supersaturation, the critical size may be as small as the monomer itself. This could occur, for example, when a substance with very low equilibrium vapor pressure is generated at high rates by chemical reactions. In that case, the saturation ratio could shoot to an extremely high value in a time shorter than is required for significant clustering to occur. For example, powders of ceramic materials can be synthesized by generating the monomer vapor in a flame or plasma. In some cases, the chemical generation of the vapor occurs at a temperature where the equilibrium vapor pressure is extremely low. In this case, there might effectively be no barrier to nucleation, and the nucleation rate is limited only by the rate of monomer–monomer collisions that form dimers. This situation is sometimes termed the “collision-controlled regime” (McMurry and Friedlander 1979; Rao and McMurry 1989) or “collisional limit” (Dingilian et al. 2021).

1.2.4 Other Types of Nucleation from the Gas Phase

As noted above, in general the driving force for phase change is the departure of the total free energy of a system from its minimum value at given temperature and pressure. Homomolecular homogeneous nucleation is a special case of this, in which the clustering involves a single chemical species.⁷

It is also observed that multiple vapors can nucleate together, with the nuclei being composed of a mixture of two or more substances, and that this can occur under conditions where neither substance would nucleate by itself. In general, this is termed “heteromolecular” or “multicomponent” nucleation, with specific scenarios being denoted “binary nucleation,” “ternary nucleation,” etc., depending on how many species of condensing vapors are involved. Examples that are important for atmospheric aerosols include the binary nucleation of sulfuric acid and water and the ternary nucleation of sulfuric acid, ammonia, and water.

⁷ We will always use “free energy” to mean “Gibbs free energy,” defined by equation (1.1), not to be confused with the Helmholtz free energy, $F \equiv E - TS$, where E is internal energy.

The presence of ions can lower the degree of vapor supersaturation required for observable nucleation to occur. Thus ions are said to “induce nucleation.” Ion-induced nucleation is conventionally classified in the literature as a heterogeneous nucleation process, in the sense that ions are viewed as constituting preexisting seeds onto which a vapor condenses. Note, however, that this usage of the term “heterogeneous” is peculiar to nucleation, as ion-molecule reactions occurring in the gas phase are considered homogeneous processes from the viewpoint of chemical kinetics. Indeed, ion-induced nucleation is a special case of gas-phase nucleation and thus fits within this book on the nucleation of particles from the gas phase.

On the other hand, in the growth of thin films by physical or chemical vapor deposition on solid surfaces, the initial stage of film growth involves the nucleation of small islands on the surface, which ultimately may grow to comprise a continuous film. Nucleation here is inherently a heterogeneous process, involving reactions of gas molecules on a solid surface. A similar situation pertains to nucleation that occurs as the initial phase of vapor condensation on preexisting condensed-phase particulates, for example, raindrop formation on cloud condensation nuclei. Thus these processes would not be considered “gas-phase nucleation” and do not fall within the scope of this book.

Most of the literature on homogeneous nucleation assumes implicitly that nucleation is a “physical” condensation process, that is, involving physisorption not chemisorption, and that the molecules comprising the critical nucleus are held together by relatively weak van der Waals forces, as opposed to chemical bonds. However, the increasing appreciation and understanding of chemically bound clusters, and of systems in which clusters grow by chemical reactions, has made “chemical nucleation” a fertile area of research. An important example is the nucleation of soot during hydrocarbon combustion. It should be noted that the term “chemical nucleation” has sometimes been applied to processes in which a supersaturated vapor is generated by chemical reactions and then nucleates via cluster growth that does not itself involve chemical reactions (e.g., Katz and Donohue 1982). Indeed, if the rate of chemical generation of the vapor is high enough, then the subsequent nucleation may be in the collision-controlled regime described above, in which case the rate-limiting process may be the rate of vapor generation by chemical reactions itself. In this text, we reserve the term “chemical nucleation” for processes in which clusters are chemically bound entities that grow by chemical reactions.

Another type of gas-phase nucleation discussed in this text is nucleation in plasmas, which can involve aspects of both ion-induced nucleation and chemical nucleation, as well as a wealth of phenomena that are not typically considered in nucleation theory. Plasmas that contain condensed-phase particles, termed “dusty plasmas,” are the subject of a considerable body of literature. Much of the universe is in a plasma state, and nucleation of dust in space under plasma conditions may play a key role in the birth of stars and other astrophysical bodies. Plasmas are widely used in semiconductor processing for microelectronics fabrication. As the characteristic feature sizes of integrated circuits shrink to nanometer dimensions, avoidance of particle nucleation in processing plasmas presents an important technological challenge, because deposition of particles on processing wafers can cause unacceptable defects. On the other hand, plasmas are increasingly used for the deliberate synthesis of nanoparticles for various applications.

1.3 Scope and Level of This Text

This text is concerned with the transition of a system that is completely in the gas phase to one that includes condensed-phase particles, dispersed in the gas phase – an “aerosol.” Thus, although much of the material presented here may be more broadly applicable, this text does not consider other phase transitions, such as crystallization of a melt, bubble formation in liquids, and so forth.

This text adopts the viewpoint that nucleation can and should be considered within the general framework of thermochemistry and chemical kinetics, regardless of whether cluster growth actually involves the making and breaking of chemical bonds. Classical theories of nucleation, which model clusters as having the same properties as the bulk condensed phase, are often presented using rather different concepts and terminology than would be natural from the viewpoint of thermochemistry and kinetics. However, classical theories are seen to fit perfectly well within the broader context of thermochemistry and kinetics and indeed are based on reasonable approximations for those cases where necessary data on cluster properties are unavailable. At the time of this writing, that is still most often the case, and classical models are still widely used for estimating nucleation rates for many kinds of systems. Therefore, both for completeness and because they are still in widespread use, this text presents detailed discussions of the classical theories of single-component, multicomponent, and ion-induced nucleation.

One can confidently predict, however, that atomistic approaches will increasingly be used, as more data become available on the properties and kinetics of clusters. This text does not attempt to describe in detail the methods of computational or experimental chemistry that are used to generate these data. It does, however, provide a framework for how these data can be used within models for various types of particle nucleation from the gas phase, and considers ways in which atomistic approaches might predict qualitative differences in our picture and understanding of nucleation.

We hope that this text will be of interest to specialists in the field of nucleation, but we intend for it to be comprehensible to senior undergraduates and beginning graduate students in physical sciences and engineering, and to researchers in broader fields such as aerosol science and materials synthesis for whom nucleation is an important topic. Thus we do not assume any prior knowledge of nucleation, only that the reader has a good basic undergraduate education in some area of the physical sciences or engineering.

Homework Problems

In these and other homework problems throughout the text, it is assumed that you can find any necessary property data in suitable reference sources, including widely accessible online sources such as Wikipedia. Always state the source of your data.

1.1 Based on the model presented in Section 1.2.2, what is the diameter of one molecule of ethanol at 20 °C?

1.2 Figure 1.2 plots the number of water molecules in a spherical liquid water cluster or nanoparticle as a function of particle diameter. Prepare a similar graph for silicon,

assuming the same mass density as for bulk silicon at room temperature, $2.33 \text{ g}\cdot\text{cm}^{-3}$. Based on your calculations, what is the number of silicon atoms in spherical silicon particles having diameters of 1, 10, and 100 nm?

1.3 Assuming the same mass density for silicon as in the previous example, consider a silicon cube measuring 2 nm on a side. What fraction of the Si atoms are located on the surface? Note that 2 nm may not be an exact multiple of the interatomic spacing, so make a suitable approximation.

1.4 Consider water vapor at a pressure of 10 kPa. How does the saturation ratio change as the temperature changes from $50 \text{ }^\circ\text{C}$ to $10 \text{ }^\circ\text{C}$, keeping the pressure constant?