Aerosol Formation in High Temperature Vapour-Gas Mixtures

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By

Thomas James BALDWIN

Department of Chemistry
University of Surrey

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Understanding the formation and growth of aerosols is important to a better understanding of a diverse range of problems. The identification of key parameters affecting aerosol behaviour is discussed, and a number of approaches for predicting this behaviour are developed in this thesis.

Models appropriate to a wide range of industrial processes are used. Turbulent and laminar flow scenarios are considered, and an assessment is made of the likely differences in system behaviour according to whether nucleation occurs by a predominantly homogeneous, binary or ion-induced mechanism.

A number of techniques for predicting aerosol behaviour are compared, ranging from the rigorous to more elementary approaches. It is shown that the simpler techniques are able to demonstrate many of the most important features of aerosol behaviour, whilst allowing the isolation of the parameters which influence this behaviour.

This thesis presents methods which are capable of rapidly characterising the growth and formation behaviour of an aerosol system, and in doing so has identified many of the parameters which control this behaviour.
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Chapter 1

Introduction
1.1 Introduction

Suspensions of microscopic particles, known as aerosols, play an important role in many everyday processes. Formed from either liquid (e.g. spray paint) or solid (e.g. asbestos dust) material, these particles, which range in size from tens of nanometres to hundreds of microns, are often of fundamental importance in determining system behaviour. Specifically, practitioners in such diverse fields as meteorology, pollution control, nuclear safety, occupational health, medicine and climate control are interested in a better understanding of the way in which aerosols interact with their environment. Within these various industrial and environmental applications, many different processes combine to control the size and the temporal and spatial distributions of aerosols. Although computer models exist to describe many situations of interest to workers in these fields, they are frequently rudimentary in nature. Often this is due to the high computational cost of modelling processes precisely over large data grids (e.g. meteorology). A further obstacle to high accuracy modelling is the uncertainty surrounding nucleation theory.

A number of different processes are responsible for the formation of aerosol particles from bulk phases, whether solid, liquid or gas. In addition to processes such as mechanical abrasion, which is responsible for the formation of, for example, dust particles, nucleation is responsible for the formation of a wide range of aerosols in some of the contexts mentioned above. Nucleation is a stochastic process whereby random collisions between molecules lead occasionally to the formation of clusters of molecules which are large enough to sustain subsequent growth to sizes characteristic of aerosols. When water is frozen, the seemingly random patterns formed in the resultant ice are a result of the stochastic nature of the nucleation process which caused this phase change. In the field of cryopreservation of biological tissue there is therefore an interest in inhibiting the nucleation of ice crystals in order to prevent damage to the sample.

Vapour phase nucleation is of great importance in a number of areas, particularly meteorology and nuclear safety. Our theoretical understanding of nucleation is still plagued by a number of uncertainties, among them the use of macroscopic properties to describe the microscopic cluster nuclei; in particular it is suspected that surface tension changes with surface curvature. Assumptions have also been made about the rate at which embryonic nuclei lose molecules. Although a
number of approaches have been tried (for example statistical mechanics) none has yet proved itself. The original theoretical work, known as classical nucleation theory (CNT), has a number of weaknesses. However no theory has since been developed which offers fundamental improvements. Classical theory assumes that the free energy of formation of a cluster comprises only terms for the free energy change of condensation and the work involved in creating the droplet surface (which is assumed to be proportional to the macroscopic surface tension and radius of the droplet). Other workers have proposed additional terms, but their work has not met with widespread acceptance. It is also known that classical nucleation theory fails to adequately reproduce the variation of nucleation rates with temperature.

In the field of nuclear safety, the large number of other processes which must be modelled when dealing with complete accident scenarios mean aerosol formation is often handled using simple approximations. For example, the main code used in the UK nuclear industry, VICTORIA, assumes that supersaturated vapours automatically and immediately equilibrate to saturated vapour, with any excess material forming aerosol. The mechanics of the nucleation process are not treated at all.

This work develops a number of methods to enable predictions of the likely aerosol behaviours in various cooled tube flow scenarios to be made. It is not intended to address the uncertainties in nucleation theory, but rather to develop ideas in such a way that dependencies upon system parameters may be identified without regard to the specific form of nucleation theory chosen. In this way an improved understanding of aerosol behaviour can be obtained without this understanding being compromised by uncertainties in nucleation theory.
1.2 Introduction to Nuclear Power Generation

Since the original aim of this project is related to the Naval Pressurised Water Reactor (PWR), a brief overview of nuclear power is given here.

1.2.1 Safety Justification

Licences to operate civilian nuclear facilities in the UK are granted by the Nuclear Installations Inspectorate (NII). Part of the licensing procedure involves demonstrating that the plant will present a tolerable risk to both the public and on-site workers by means of a Probabilistic Safety Assessment (PSA). Such an assessment involves identifying all the fault sequences capable of leading to core damage. For each identified sequence, routes by which fission products may be released from the system must be considered, and finally the radiological consequences of such releases evaluated. Naval nuclear plant operation is regulated by the Chairman of the Naval Nuclear Regulatory Panel (CNNRP), who ensures compliance with MoD-internal standards which are at least as good as those required by the NII.

Various computer codes are used to model the processes considered in a PSA: in the UK VICTORIA is the primary code for aerosol and vapour behaviour modelling in the reactor circuit. VICTORIA does not, however, model the kinetics of the aerosol formation process, instead it assumes that the vapour and aerosol produced by core melt are in equilibrium. It is considered possible that in some loss of coolant accidents (LOCA) significant quantities of fission product may be retained in the primary circuit pipework between the degrading core and the leak site. By considering in more detail the processes affecting aerosol formation, this project aims to improve the MoD's modelling capability. Since current studies assume that no fission products are retained in the primary circuit, a better understanding of aerosol formation has the potential to reduce the pessimism inherent in present studies, and present a more realistic assessment of the risk presented by the use of nuclear power generation.
1.2.2 The Pressurised Water Reactor

The pressurised water reactor (PWR) is one of the most popular types of ‘nuclear reactor’ in use around the world today. The principles of its operation are outlined below.

The basis of all fission reactors is the splitting of a fissile fuel material (usually uranium-235) by thermal neutrons. This produces fission products (which are usually prone to radioactive decay), energy and two or three fast neutrons. These neutrons are not capable of directly causing further fission as their high energy would cause them to be scattered by the next uranium atom. A moderator such as water is used, which by removing some of the energy from the fast neutrons, turns them into thermal neutrons capable of being absorbed by the uranium atom, thus causing further fission. Since each fission typically produces between two and three neutrons, each of which is capable of causing a further fission event, it is clear that if some of these neutrons are not absorbed by control rods the rate of fission will increase exponentially, leading to catastrophic system failure.

![Figure 1.1]

*The fission of uranium-235 by thermal neutrons*

Coolant flow in the primary circuit removes heat from the core, transferring it to steam in the secondary circuit, where useful work such as turning the blades of a turbine takes place. Control rods, made of strongly neutron absorbing material, regulate the neutron flux within the core.

In a PWR water acts as both coolant and moderator. In order to prevent boiling within the core, the water must be held at high pressure. This has safety implications, in that were a leak to develop in a primary pipe, a large volume of coolant would be lost rapidly. In a PWR this also implies loss of the moderator, which would rapidly terminate fission. The fission products produced will however continue to decay e.g. $^{134}\text{I} \rightarrow ^{134}\text{Xe} + \beta^- + \gamma$, producing *decay heat*. Significant quantities of heat are produced, and in normal use it is necessary to ensure continued coolant flow.
after a reactor has been shutdown in order to prevent core melt. In accident scenarios, cooling must quickly be reapplied in order to prevent damage to the core. This class of accident is referred to as a Loss Of Coolant Accident (LOCA).

![Diagram of a pressurised water reactor](image)

**Figure 1.2**

*Simplified schematic of key elements of a pressurised water reactor*

### 1.2.3 Description of Aerosol Behaviour

In the event that core melt occurs, volatile fission products will be released from the damaged fuel modules. These vapours may then be transported around the reactor’s primary circuit and containment, both of which will be significantly cooler than the melting core. They may remain in the vapour phase, condense to form aerosol, or may deposit on reactor structural surfaces. Figure 1.3 illustrates the mass transfer pathways between these three possibilities.

Hot vapour will condense upon the cool surfaces without ever becoming an aerosol. It is likely to remain there unless the heat released by the radioactive decay of the fission products is sufficient to revaporise it. Fission products may also be deposited upon the walls in the form of aerosol by processes such as gravitational sedimentation and thermophoresis. Both decay heating and mechanical resuspension (due to turbulent eddies in the gas flow) can transfer this material back into the bulk flow. Although nucleation is a vital step in forming fresh aerosol, the amount of mass transferred in this step is minuscule compared to the amount involved in growing the
aerosol to its final size. It is also possible for fission products to be entrained as aerosol by condensing upon existing aerosol particles, formed perhaps from finely divided structural materials (e.g. concrete dust). Aerosol may potentially evaporate to rejoin the vapour phase, although this is likely to occur only in localised areas.

Figure 1.3
Overview of aerosol pathways considered
1.3 Aims and Objectives

The aim of this work is to develop models and methods which can be applied to the formation of aerosol during transport of fission product vapours through the primary circuit pipework of a degraded PWR. The methods developed should provide ready analytical solutions which are not inherently dependent upon classical nucleation theory. Simplifications should be sought in order to identify the essential parameters which characterise systems.

In order to allow the process of aerosol formation and transport through the primary circuit pipework to be better understood, the following objectives will be addressed:

- develop numerically soluble models describing aerosol formation and growth during turbulent and laminar tube flow
- develop analytically soluble approximations to these models
- check the analytically soluble approximations against the numerical models
- use these analytical solutions in the development of rules to determine
  i) maximum saturation
  ii) conditions for significant nucleation
  iii) cases when vapour consumption by aerosol growth is sufficient to significantly affect nucleation
- assess the effect of conditions on the distribution of fission products between vapour phase, aerosol and walls
- compare predictions with experimental results, identifying strengths and weaknesses in the selected approaches

Although the above work is conducted with reference to homogeneous nucleation, Chapter 7 addresses the potential effects of other nucleation mechanisms.
Chapter 2

Literature Survey
2.1 Introduction to Aerosols

The term aerosol, used to describe a dispersion of fine solid particles or liquid droplets in a gas, first appeared in the literature as an analogue to hydrosol, a similar suspension of solid particles in a liquid. Depending upon the means by which they were formed, aerosol particles can have sizes in the range 1 nm to 100 µm. The discussion which follows will restrict itself to phenomena of relevance to liquid aerosols, since in the Naval PWR these are expected to be the only type of interest.

2.1.1 Formation of Aerosols

The formation of liquid aerosols from a bulk (supersaturated) condensible vapour can occur by a number of different mechanisms. This nucleation process may be split broadly into two categories. The first is homogeneous nucleation, where clusters form from the vapour by spontaneous fluctuations, leading to an embryonic aerosol (critical cluster) composed purely of the condensing species. In the event that an existing aerosol particle (liquid or solid) acts as a substrate for the nucleation process, the resulting mechanism is said to be heterogeneous. In either case, the nucleation event may occur with one or more condensible vapour species (single- or multi-component). Multicomponent nucleation often leads to nucleation occurring more readily than in the single component case. This is exemplified by the strong increase in the nucleation rate of water in the atmosphere in the presence of tiny concentrations of sulphuric acid. It is worth noting that homogeneous single component nucleation will not occur at any perceptible rate as soon as the saturation of the condensing vapour exceeds unity. Rather, a critical saturation exists, which is commonly taken to be the saturation necessary to cause a nucleation rate of $10^6 \text{ m}^{-3}\text{s}^{-1}$ ($1 \text{ cm}^{-3}\text{s}^{-1}$) at a specified temperature. The critical saturation varies widely between different vapours and with temperature. For caesium iodide it is typically in the range 1.2 – 1.5, whilst for dibutyl phthalate (DBP) it is usually several thousand.

2.1.1.1 Homogeneous Nucleation

A number of theories have been proposed to describe homogeneous nucleation. Of these, Classical Nucleation Theory (CNT), as developed by Becker and Döring (1935), has been the most successful, despite characterising microscopic droplets using the properties of the bulk liquid. CNT treats nucleation using
thermodynamics and kinetics, describing the emerging nucleus as a tiny liquid drop in unstable equilibrium with the bulk vapour. Through random collisions the droplet gains molecules of condensible vapour, which then evaporate and leave the droplet again. In a supersaturated environment, it is possible that the rate at which a droplet gains molecules will exceed the rate at which it loses them; in this case the droplet will continue growing, and a nucleation event may be said to have occurred.

If the rates at which monomer attaches to a cluster and at which it leaves a cluster are combined, the rate at which that cluster grows can be expressed. Classical theory considers only the addition of monomer to a droplet. Clement and Ford (1996) have investigated the effect of treating also the addition of dimers to the cluster. They find that the difference in nucleation rate is of the order of a few percent. Given the low concentration of dimers expected (relative to the monomer concentration) this is an unsurprising result.

The number of clusters containing \( i \) molecules will vary with time. At time \( t \), the rate at which the number of clusters of size \( i \) (written \( n(i,t) \)) is varying is given by

\[
\frac{\partial n(i,t)}{\partial t} = \beta(i-1)n(i-1,t) - \gamma(i)n(i,t) + \gamma(i+1)n(i+1,t) - \beta(i)n(i,t)
\]

(2.1)

where \( \beta(i) \) is the rate at which a cluster of \( i \) molecules gains a monomer molecule, and \( \gamma(i) \) is the reverse rate at which a cluster of size \( i \) loses a monomer molecule. This may be summarised in words as:

\[
\text{variation in number of clusters of size } i \text{ with time} = \text{rate of growth of clusters of size } i-1 - \text{rate of shrinkage of clusters of size } i + \text{rate of shrinkage of clusters of size } i+1 - \text{rate of growth of clusters of size } i
\]

where \( J(i+\frac{1}{2},t) \) is the net rate at which clusters of size \( i \) become clusters of size \( i + 1 \).

\[
J(i+\frac{1}{2},t) = \beta(i)n(i,t) - \gamma(i+1)n(i+1,t)
\]

(2.2)

Note that anything else which happens to the cluster of size \( i+1 \) is not relevant to this process as it is not part of the net flux from \( i \leftrightarrow i+1 \).

When considering a steady state scenario, then the net rate of formation of any one cluster size will be equal to the net rate of formation of any other cluster size, i.e.:

\[
J(i,t) = J(\text{anything},\text{anything})
\]

(2.3)
The derivation of classical theory is made easier by the use of a function $f(i)$, defined by the recurrence relation:

$$f(i + 1) = \left[ \frac{\beta(i)}{\gamma(i + 1)} \right] f(i) \quad \text{with} \quad f(1) = 1 \quad (2.4)$$

Note that $f(i)$ cancels out at a later stage. Using (2.4) to divide (2.2) by $\beta(i)f(i)$ gives:

$$\frac{J(i + \frac{1}{2},t)}{\beta(i)f(i)} = \frac{\beta(i)n(i,t) - \gamma(i + 1)n(i + 1,t)}{\gamma(i + 1)f(i + 1)} \quad (2.5)$$

which rearranges to:

$$\frac{J(i + \frac{1}{2},t)}{\beta(i)f(i)} = \frac{n(i,t)}{f(i)} - \frac{n(i + 1,t)}{f(i + 1)} \quad (2.6)$$

In a steady state situation there is no time dependence in any of the terms. The sum of all the fluxes, up to the cluster size $i_{max}$, can be represented as (where for convenience $J(i,t)$ is simply written as $J$):

$$J \sum_{i=1}^{i_{max}} \frac{1}{\beta(i)f(i)} = \sum_{i=1}^{i_{max}} \frac{n(i)}{f(i)} - \sum_{i=1}^{i_{max}} \frac{n(i+1)}{f(i+1)} \quad (2.7)$$

Since most terms in the two sums on the right hand side cancel with each other, this simplifies to:

$$J \sum_{i=1}^{i_{max}} \frac{1}{\beta(i)f(i)} = n(1) - \frac{n(i_{max})}{f(i_{max})} \quad (2.8)$$

Reconsidering briefly the definition given in (2.4), which may be expressed as

$$f(i) = \prod_{j=1}^{i-1} \frac{\beta(j)}{\gamma(j + 1)} f(1) \quad (2.9)$$

i.e. it is the cumulative product of all the ratios of forward and reverse rates. $\beta(i)$ is a smooth function, which increases with $i$ for large $i$. Since $f(i)$ falls off exponentially, the summation on the left hand side of (2.8) may be extended to infinity, and expression (2.8) rewritten thus:

$$J = n(1) \left[ \sum_{i=1}^{\infty} \frac{1}{\beta(i)f(i)} \right]^{-1} \quad (2.10)$$
This is the nucleation rate expression in terms of forward and reverse rate expressions. It remains only to determine these rates. Unfortunately this is not a trivial task, although progress can be made by considering $f(i)$.

If, as assumed, the forward rate constant is proportional to the partial pressure of the condensable vapour, whilst the reverse rate is independent of this quantity, then:

$$f(i) = S^{i-1} \prod_{j=1}^{i-1} \frac{\beta_{e}(j)}{\gamma_{e}(j+1)} f(1) \quad (2.11)$$

where it is assumed that $\beta(i) = S\beta_{e}(i)$, where $S$ is the saturation ratio, the ratio of the actual partial pressure of a component to the equilibrium partial pressure for that component, and $\beta_{e}(i)$ is the forward rate at equilibrium. The ratio of the forward and reverse rates for a reaction is defined as the equilibrium constant for that reaction, so the cumulative product in (2.11) may be seen as the equilibrium constant for the transformation of $i$ molecules of monomer to a cluster of size $i$, i.e.

$$f(i) = S^{i-1} \mathcal{K} \quad (2.12)$$

Since

$$k_{B}T \ln \mathcal{K} = -\Delta G \quad (2.13)$$

$$f(i) = S^{i-1} \exp \left( \frac{-\Delta G}{k_{B}T} \right) \quad (2.14)$$

i.e. $\Delta G$ is the free energy change involved in going from $i$ molecules of monomer to a cluster of size $i$.

The problem remains of how to calculate this change. Classical theory proceeds as follows: $i$ molecules are transferred from the vapour phase to the liquid. Since the phases are at coexistence there is no free energy change associated with this step. Then the $i$ molecules are carved out of the liquid, creating a gas-liquid interface. This step is assumed to have the free energy change:

$$\Delta G_{i} = \sigma A(i) \quad (2.15)$$
where \( A(i) \) is the surface area of the droplet created. For a sphere, where \( v_1 \) is the volume of one molecule of monomer:

\[
V = \frac{4}{3} \pi r^3 = iv_1 \quad (2.16)
\]

\[
\sqrt[3]{\frac{3V}{4\pi}} = r \quad (2.17)
\]

\[
A = 4\pi r^2 = 4\pi \left( \frac{3iv_1}{4\pi} \right)^{\frac{2}{3}} \quad (2.18)
\]

which rearranges to:

\[
A = (36\pi)^{\frac{1}{3}} i^{\frac{2}{3}} v_1^{\frac{2}{3}} \quad (2.19)
\]

A ‘reduced surface tension’, \( \theta \), can be defined viz.:

\[
\theta = \frac{A \sigma}{k_B T} = \frac{(36\pi)^{\frac{1}{3}} v_1^{\frac{2}{3}} \sigma}{k_B T} = \frac{\Delta G}{k_B T} \quad (2.20)
\]

Using (2.14), (2.15) and (2.20) in (2.10) gives:

\[
J = n(1) \left[ \sum_{i=1}^{\infty} \frac{1}{\beta_c(i) S_i \exp(-\theta i X)} \right]^{-1} \quad (2.21)
\]

noting that \( \beta(i) = S_S(i) \). The next stage proceeds via a series of mathematical approximations. Considering the terms in the denominator of (2.21) reveals that \( S_i \) will increase exponentially with \( i \), whilst \( \exp(-\theta i X) \) will fall off exponentially with \( i X \). \( \beta(i) \) is a slowly increasing function of \( i X \). These three terms combine to give a denominator which decreases rapidly initially, reaches a minimum, and then starts to rise again as the \( S_i \) term dominates. The value of \( i \) at which this minimum is found is known as \( i^* \). This minimum will be found when the derivative of the denominator (w.r.t. \( i \)) is zero, i.e.:

\[
\frac{d}{di} \left( \beta_c(i) S_i \exp(-\theta i X) \right) = 0 \quad (2.22)
\]

It is usually assumed that \( \beta_c(i) \) is a slowly varying function of \( i \), and can be replaced by \( \beta_c(i^*) \). Defining a new function, \( g(i) \), as follows allows the expression for \( J \) to be rewritten:

\[
g(i) = \theta i X - i \ln S \quad (2.23)
\]
\[ J = n(i) \left( \sum_{i=1}^{\infty} \frac{\exp[g(i)]}{\beta_e(i)} \right)^{-1} = n(i) \left( \sum_{i} \frac{\exp[g(i)_{\text{around } i}]}{\beta_e(i)^{*}} \right)^{-1} \quad (2.24) \]

\( i^* \) will be found where the derivative of \( g(i) \) is zero:

\[ i^* = \left( \frac{2\theta}{3\ln S} \right)^{3} = \frac{32\pi}{3} \frac{v_i^2 \sigma^3}{(k_B T)^3 (\ln S)^3} \quad (2.25) \]

Having identified the size at which the forward rate must be evaluated, it remains to determine the value of the summation in (2.24). In the method of steepest descents, \( g(i) \) can be approximated near its maximum by a Taylor series expansion

\[ g(i) = g(i^*) + \frac{dg}{di} \bigg|_{i=i^*} (i - i^*) + \frac{1}{2} \frac{d^2g}{di^2} \bigg|_{i=i^*} (i - i^*)^2 + \ldots \quad (2.26) \]

Since when \( i=i^* \) the differential of \( g(i) \) w.r.t. \( i \) is zero, the second term in the right hand side of (2.26) above disappears. Equation (2.24) can then be expressed as:

\[ J = n(i) \beta_e(i^*) \left( \sum_{\text{around } i^*} \exp[g(i^*) \exp(-\frac{1}{2} g''(i^*)(i - i^*)^2)] \right)^{-1} \]

\[ = n(i) \beta_e(i^*) \exp(-g(i^*) \left( \sum_{\text{around } i^*} \exp(-\frac{1}{2} g''(i^*)(i - i^*)^2) \right)^{-1} \quad (2.27) \]

and the summation can be replaced by an integral from \(-\infty\) to \(+\infty\). Note that \( g''(i^*) \) is negative. Using the substitution

\[ y = \sqrt{\frac{g''(i^*)}{2}} (x - i^*) \quad (2.28) \]

allows the summation to be written as

\[ = \int_{-\infty}^{\infty} \exp(-\frac{1}{2} g''(i^*) (x - i^*)^2) dx \quad (2.29) \]

\[ = \int_{-\infty}^{\infty} \frac{2}{\sqrt{g''(i^*)}} \exp(-y^2) dy \quad (2.30) \]

Using the standard result

\[ \int_{-\infty}^{\infty} \exp(-x^2) dx = \sqrt{\pi} \quad (2.31) \]

gives the summation as:
\[
J = n(t) \beta_e \left( \theta \right)^{\frac{1}{3}} \left( i^* \right)^{\frac{1}{3}} \exp \left( -\frac{1}{3} \beta \right) \exp \left( \frac{-\frac{1}{6} \beta}{\ln^2 S} \right) \quad (2.35)
\]

This leaves only the forward rate expression at the for a cluster of size \( i^* \). For a spherical nucleus with which monomer molecules collide at the gas kinetic rate, it follows that the forward rate is given by:

\[
\beta_e (i) = \left( \frac{k_B T}{2 \pi m_1} \right)^{\frac{1}{6}} \frac{A(i)n(1)}{S} \quad (2.36)
\]

The surface area of a cluster, \( A(i) \), is given by (2.19). Account is taken of the fact that the monomer concentration \( n(1) \) is increased with respect to its equilibrium value at pressure \( P_e \) by a factor \( S \). Combining (2.36), (2.19) and (2.35), the final result is the classical nucleation theory:

\[
J = \left( \frac{2 \sigma}{\pi m_1} \right)^{\frac{1}{2}} \nu_i n(1)^{\frac{1}{2}} \exp \left( -\frac{16 \pi}{3} \frac{\nu_i^2 \sigma^3}{(k_B T)^3 \ln^2 S} \right) \quad (2.37)
\]

Equation (2.37) includes a \( S^{-1} \) term, omitted in derivations of classical theory until Oxtoby (1992) pointed out this deficiency. Equation (2.2) can be seen as consisting of two parts; the pre-exponential term, which is a kinetic growth factor, and the exponential term, which describes the probability of forming a critical nucleus.

### 2.1.1.2 Heterogeneous Nucleation

The process of heterogeneous nucleation is of great importance in atmospheric and industrial work, and may be a dominant mechanism in some accident sequences affecting civil reactors.
A complete treatment of heterogeneous nucleation is complicated by the fact that the substrate onto which nucleation occurs may take any, possibly irregular, geometry. Classical theory can be extended by considering not only the surface tension of the condensible vapour – air interface, but also of the substrate – air and substrate – vapour interfaces in defining the free energy change of nucleation. Because of this highly simplified approach, which is itself based upon the greatest weakness in classical homogeneous nucleation theory, the success of heterogeneous nucleation theory has been mixed.

For the purposes of this work, to provide first estimates of the effect of seed aerosol particles, heterogeneous nucleation has been modelled by the growth rate mechanism described in Section 2.1.3.

2.1.1.3 Ion-Induced Nucleation

A special sub-case of heterogeneous nucleation, ion-induced nucleation (IIN) is better characterised in that the geometry of the ion is not expected to take the irregular forms possible for solid substrates.

Again, classical theory is extended by considering the free energy change associated with clustering (nucleating) about an ion. In addition to the terms discussed previously, an extra term is added to the free energy expression to account for the attraction between an ion and the condensible vapour. This leads to the expression given in Equation (2.38):

\[ \Delta G_0 = 4\pi \sigma \left( r_k^2 - r_a^2 \right) - \frac{4\pi}{3V_m} \left( r_k^3 - r_a^3 \right) kT \ln S + \left( 1 - \frac{1}{\varepsilon} \right) \frac{e^2}{8\pi \varepsilon_0} \left( \frac{1}{r_h} - \frac{1}{r_a} \right) \]

(2.38)

In contrast to previous expressions, there are two radii in Equation (2.38); \( r_a \) the radius of a stable ion, and \( r_h \) the radius of the critical cluster. Plotting the free energy as a function of radius (see Figure 2.1) reveals a minimum, corresponding to \( r_a \) and a maximum, representing the energetic barrier to nucleation. These turning points can be found by equating the differential of Equation (2.38) with respect to radius to zero and solving the resultant equation.
The final nucleation rate expression for classical IIN theory (CIINT) is of a similar form to CNT, with the prefactor modified to take account of ion–vapour interactions.

2.1.4 Multicomponent Nucleation

As noted earlier, the nucleation of water in the presence of minute quantities of sulphuric acid has been shown to occur in the atmosphere (Covert et al., 1992). Jaecker-Voiriot et al. (1987, 1988) extended the original work on binary nucleation performed by Reiss (1950) and Heist (1974) to account for the formation of stable clusters of water molecules about a single acid molecule. Laaksonen (1991) reviewed this work and used it in a series of calculations. Hydrated clusters were found to be important in atmospheric situations. Kulmala (1991a, 1991b) extended this work to the case of hydrogen iodide and steam in a nuclear reactor scenario, where the concentrations of the two species are much more similar.

Extension of previous results to systems containing more than two condensing vapours has only recently been attempted. Oxtoby (1994) proved a general result giving the work of formation in terms of size and composition of the critical nucleus. Difficulties arise in the application of this work to the nuclear safety arena in that activity and surface tension data (as functions of composition) are not available for the high temperature “cocktails” of fission products which are likely to form in postulated accident sequences. Gorbunov (1999) considers heterogeneous multicomponent nucleation, and reports an approximation to the work of formation based upon the assumption that a non-volatile insoluble spherical core is at the heart of any droplets formed. Whilst this methodology has application in the fields of
pollution (e.g. particulates from diesel engines acting as the "core"), it is of no use in the high temperature nuclear reactor scenarios of interest.

2.1.2 Scaled Nucleation Theorems

Hale (1988) has presented a scaled model for nucleation, which allows the critical saturation, that is the saturation required for a specified nucleation rate, to be predicted. Whilst this is possible with all nucleation theories, by the use of a number of scaling theorems and approximations, she has managed to produce a form which is applicable to a wide range of materials, usually without the need to take account of what the material is.

The model is derived initially from classical nucleation theory. Hale scales key parameters \((T, P, n)\) by their values at the critical point (e.g. \(T / T_c\)); however in contrast to previous attempts at a scaled nucleation model (e.g. Binder, 1980), she claims applicability far from the critical point. By rederiving classical nucleation theory in terms of scaled parameters (from the literature), Hale has created a new theory which is found to give better agreement between experimental data and theoretical predictions than classical theory. However, to date, nobody (including Hale herself) has been able to explain the reason for the success of a method which was originally intended as an approximate form for the identification of key dependencies in nucleation theory.

For a nucleation rate of \(1 \text{ cm}^{-3} \text{ s}^{-1}\) Hale derives the following expression for the critical saturation (the saturation required to cause this nucleation rate):

\[
\ln S_{cr} \approx 0.53 \left( \frac{T_c}{T} - 1 \right)^{1/3} \quad (2.39)
\]

This comes from considering classical nucleation theory, with the application of a number of scaling laws. This result is rederived below.

Classical nucleation theory (as given by Equation (2.35)) gives the rate of nucleation of droplets. This may be rewritten as:

\[
J = J_0 \exp \left( -\left( \frac{x_e}{x} \right)^2 \right) \quad (2.40)
\]

where
and a scaled supersaturation

\[ x = \frac{\ln S}{\theta^\frac{3}{2}} \]  

(2.42)

Introducing the scaled form for surface tension:

\[ \sigma = \sigma_0 (T_c - T) \]  

(2.43)

allows \( \theta \) (Equation (2.20)) to be written:

\[ \theta = \left( \frac{36\pi}{n^2} \right)^\frac{3}{2} \frac{\sigma_0 (T_c - T)}{k_B T} = \left( \frac{36\pi}{n^2 k_B} \right)^\frac{3}{2} \frac{\sigma_0}{n^2 k_B} \left( \frac{T_c - 1}{T} \right) \]  

(2.44)

where

\[ \Omega = \left( \frac{\sigma_0}{n^2 k_B} \right) \]  

(2.45)

Hale notes that the parameter \( \Omega \) is nearly constant \((\approx 2)\) for most liquids, falling to approximately 1.5 for associated liquids. Other definitions come from either approximation to the Eötvös constant (Equation (2.46)) or from the derivative of the surface tension with respect to temperature (Equation (2.47)):

\[ K_s \approx \Omega k_B N_A^\frac{3}{2} \quad \therefore \quad \Omega = \frac{\eta^\frac{3}{2} \sigma}{(T_c - T) k_B N_A^\frac{3}{2}} \]  

(2.46)

\[ \Omega = -\left[ \frac{\partial \sigma}{\partial T} \right] \frac{1}{k_B \rho^\frac{3}{2}} \]  

(2.47)

Considering next the pre-exponential term, \( J_0 \), Hale defines this as:

\[ J_0 = J_c \left( \frac{P_v}{P_f} \right)^\alpha \left( \frac{T_v}{T} \right)^\alpha = J_c \omega \]  

(2.48)

where for the standard classical model, \( \alpha = 2 \), and \( \omega \) is a variable defined solely for convenience of manipulation. Combining equations (2.40) and (2.48) and rearranging gives:

\[ \frac{J}{J_c} = \omega \exp \left( -\left( \frac{x_0}{x} \right)^2 \right) \]  

(2.49)

Taking the natural logarithm of both sides and rearranging gives:
\[
\frac{x_0^2}{x^2} = \ln \omega + \ln \left( \frac{J_c}{J} \right) \tag{2.50}
\]

Rearranging to make \( x \) the subject gives:
\[
x = \frac{x_0}{\left( \ln \omega + \ln \left( \frac{J_c}{J} \right) \right)^{\frac{1}{3}}} \tag{2.51}
\]

which may be factorised to:
\[
x = \frac{x_0}{\sqrt[3]{\ln \left( \frac{J_c}{J} \right) \left( 1 + \frac{\ln \omega}{\ln \left( \frac{J_c}{J} \right)} \right)}} \tag{2.52}
\]

and defining \( \delta_0 \) as
\[
\delta_0 = \left[ 1 + \frac{\omega}{\ln \left( \frac{J_c}{J} \right)} \right]^{-\frac{1}{3}} \tag{2.53}
\]

allows equation (2.52) to be written
\[
x = \frac{x_0 \delta_0}{\sqrt[3]{\ln \left( \frac{J_c}{J} \right)}} \tag{2.54}
\]

which, in light of equation (2.42) is the same as equation (II.13) in Hale’s (1988) paper.

Since the saturation ratio of a system \( (S) \) is defined as the ratio of the actual partial pressure of a component to the equilibrium partial pressure for that component (at a given temperature), it follows that to a good approximation:
\[
P_r = SP_w \tag{2.55}
\]

Equation (2.53) can therefore be expanded and rewritten as:
\[
\delta_0 = \left[ 1 + \frac{-\alpha \ln \left( \frac{P_c}{P_{we}} \right) + \alpha \ln S + \ln l + \alpha \ln \left( \frac{T_c}{T} \right)}{\ln \left( \frac{J_c}{J} \right)} \right]^{-\frac{1}{3}} \tag{2.56}
\]
which apart from a typographical error in Hale’s work regarding the temperature term, is identical to equation (11.14). Hale reports that the contribution of the terms \( \ln I + \alpha \ln(T_e/T) \) to the value of \( \delta^0 \) is less than 1.5%, allowing them to be ignored.

From the Clausius-Clapeyron equation, the vapour pressure is approximated thus:

\[
P_v = A \exp\left(-\frac{M_vL}{kT}\right) \quad (2.57)
\]

where \( A \) is atmospheric pressure, \( L \) the latent heat (enthalpy) of vaporisation and \( M_v \) the molar mass of the substance.

The natural logarithm of the ratio of equilibrium vapour pressure to critical vapour pressure is therefore given by:

\[
\ln\left(\frac{P_v}{P_{vc}}\right) = \ln A - \frac{m_vL}{k_BT} - \ln A - \frac{m_vL}{k_BT}
\]

\[= \frac{m_vL}{k_BT} \left(\frac{1}{T-T_c}\right)
\]

\[= \frac{m_vL}{k_BT} \left(\frac{T_c}{T}-1\right)
\]

\[= W_0 \left(\frac{T_c}{T}-1\right) \quad (2.58)
\]

where \( L \) in Hale’s work is the latent heat of vaporisation per molecule. According to Hale most substances can be represented by \( W_0 \equiv 7 \).

Combining equations (2.56) and (2.58) whilst neglecting the terms responsible for less that 1.5% of the final value as described above gives:

\[
\alpha W_0 \left(\frac{T_c}{T}-1\right) + \alpha \ln S
\]

\[= 1 - \frac{\ln\left(\frac{J}{J_c}\right)}{\ln\left(\frac{J_c}{J}\right)} \quad (2.59)
\]

Hale reports that \( \ln J_c = 72 \), and considers in her derivation the condition for a nucleation rate of \( J = 1 \) cm\(^{-3}\) s\(^{-1}\) (the paper is presented in non-SI units); therefore \( \ln J = 0 \). Assuming that \( \delta^0 = 1 \), and substituting typical values for other parameters into equation (2.54) gives:

\[
\ln S = \frac{2}{3} \cdot \frac{1}{3} \cdot \frac{(36\pi)^{\frac{1}{2}} \left(\frac{T_c}{T} - 1\right)^{\frac{3}{2}}}{\sqrt{72}} = 1.5 \left(\frac{T_c}{T} - 1\right)^{\frac{3}{2}} \quad (2.60)
\]
In practice, the value of $\delta_0$ is actually slightly greater than 1.0 and the derivation presented below is therefore approximate. It would of course be possible to iteratively progress through the next steps to refine the value of $\delta_0$. Since Hale restricts her range of applicability to:

$$0.3 < \frac{T_e}{T} < 0.5 \quad \therefore \quad 2 < \frac{T_e}{T} < 3 \quad (2.61)$$

it follows that:

$$1.5 \left( \frac{T_e}{T} - 1 \right) < \ln S < 2.5 \left( \frac{T_e}{T} - 1 \right) \quad (2.62)$$

If, for simplicity’s sake, $\ln S$ is considered to take the midpoint value of this expression, it may be re-expressed, in light of equation (2.58) and the value of $W_0$ as:

$$\ln S = 2 \left( \frac{T_e}{T} - 1 \right) \approx 0.3 W_0 \left( \frac{T_e}{T} - 1 \right) \quad (2.63)$$

Using this result in equation (2.59) and utilising the first term only of a Taylor series expansion yields her result (II.15a):

$$\delta_0 = 1 + 0.7 \alpha \frac{W_0 \left( \frac{T_e}{T} - 1 \right)}{2 \ln \left( \frac{J_c}{J} \right)} \quad (2.64)$$

For the range of values of $T_e/T$ to which Hale restricts herself, the range of $\delta_0$ is 1.13 to 1.17. Linearly interpolating between these values gives (roughly) equation (2.65), which is equation (II.15b) in Hale’s work.

$$\delta = 1.13 \pm 0.04 \left[ \frac{T_e}{T} - 1 \right] \quad (2.65)$$

Combining equations (2.54), (2.44), (2.41), (2.65) and (2.42) gives:

$$\ln S = \frac{2}{3^\frac{1}{4}} \sqrt{\frac{3}{72}} \left[ \frac{1}{(36\pi)^\frac{1}{2}} W_0 \left( \frac{T_e}{T} - 1 \right) \right]^{\frac{3}{2}} \quad (2.66)$$

which evaluates to the result presented in equation (2.39).

In the event that a critical saturation other than $J = 1$ cm$^3$ s$^{-1}$ is required, Hale gives equation (2.67), which allows equation (2.39) to be adapted:

$$\ln S = \ln S_c \left[ 1 + \frac{\ln J}{2 \ln J_c} \right] \quad (2.67)$$
The only adjustable parameter in Hale’s scaled nucleation theorem is $\Omega$, which she describes as the excess surface entropy per molecule. Two theoretical methods exist for determining a precise value for $\Omega$, both based upon the surface tension. Both (in effect) apply a linear extrapolation to the variation of the surface tension with temperature. This is, in fact, the largest single approximation made in Hale’s work.

A number of papers (Hale and Kelly, 1992; Kane and El-Shall, 1996; Wright and El-Shall, 1992; Wright et al., 1993) have looked at the influence of this parameter on the predictions of Hale’s theorem and concluded that it has a significant influence in determining the accuracy of her method. Additionally, Kane & El-Shall and Wright extract an experimental value of $\Omega$ from their data. By reference to their results it can be seen that neither method of calculating $\Omega$ achieves reliable agreement with values of $\Omega$ extracted from the experimental data. There is also no consistency regarding which of the two methods most accurately predicts the theoretical value of $\Omega$ as the compound under study changes. Experimental reports in the literature have found values ranging from slightly less than unity to 2.5 (Kane and El-Shall, 1996; Wright et al., 1993; Hale et al., 1989; Wright and El-Shall, 1992; Hale and Kelly, 1992). It is worth noting that values at the lower end of this range refer to highly polar molecules for which Hale (1988) expects a lower value of $\Omega$.

2.1.3 Growth of Aerosols

The nucleation event is defined as creating a cluster of molecules, taken from the condensible vapour, which is more likely to grow due to random fluctuations than to shrink. These clusters are referred to as critical clusters, and contain typically $10^1 - 10^2$ molecules. The growth of these clusters to radii up to $10^{-4}$ m can occur by two basic routes. More vapour from the bulk may condense upon the cluster, or collisions between clusters may lead to coagulation. Except in the case of liquid droplets, aerosols which have coagulated are unlikely to remain spherical. In some circumstances (particularly aerosols formed from combustion products) this can lead to large “fluffy” aerosols which have a fractal structure.

2.1.3.1 Condensative growth

Barrett and Clement (1988) derive an expression for the growth rate of a drop in a supersaturated vapour. Two regimes of condensative growth are identified and results proposed for both. For larger molecules supersaturated vapour will diffuse
towards the droplet surface (which is just saturated) in much the same way steam will diffuse towards and condense upon the mirror in a bathroom. Smaller molecules will not perturb the system in this way, and instead will grow only by the random collision of vapour molecules with the surface of the droplet. The growth rate expression in this case contains a "sticking probability", which describes the likelihood that a vapour molecule which collides in this way will remain. Clement et al. (1996) reviewed experimental and theoretical work considering the value of this parameter, for which reported values ranged from 0.02 to 1.0, and found that it should be very close to unity.

For the continuum regime (where vapour diffusion dominates) the growth rate is given by:

\[ I_c = 4\pi R \frac{\mu_V p}{R_g T} D \left[ \ln(p - p_{\infty}) - \ln(p - p_{\infty}(T_d)) \right] \] (2.68)

and for the free molecular regime, where gas phase kinetics is important the growth rate is given by:

\[ I_k = 4\pi R^2 S_A \left( \frac{\mu_v}{2\pi R_g} \right)^{\frac{1}{3}} \left[ \frac{p_{\infty}(T_d)}{T_d^{\frac{1}{3}}} - \frac{S p_{\infty}(T_{\infty})}{T_{\infty}^{\frac{1}{3}}} \right] \] (2.69)

There is a range of droplet sizes where neither diffusion-controlled nor kinetic (random collision) growth occur. To describe this regime, Barrett and Clement (1988) propose an interpolation formula which tends to the correct limits for large and small droplets, and varies smoothly over the interpolation regime. Whilst there is no theoretical basis for the nature of this interpolation, it is a reasonable approximation which is used here in the absence of a form offering demonstrable improvement.

2.1.3.2 Coagulative growth

A number of different mechanisms are responsible for the collision of particles leading to coagulation. Aerosol particles are in constant movement due to Brownian motion of the gas in which they are suspended. This leads to a number of collisions between slow moving large particles and fast moving small particles. It is the ratio of the sizes of the colliding particles which ultimately affects the coagulation rate.

A second mechanism is caused by particles settling out under gravity. Large particles falling under the influence of gravity will "sweep out" a path through other (smaller) particles, leading to growth of the large particles.
Gases which are turbulent will cause additional collisions between aerosol particles. This can be due either to differing moments of inertia for different sized particles or to particles following turbulent eddies.

Although it is an approximation (Williams, 1988), the sum of the coagulation rates from all these mechanisms is usually taken to be the overall coagulation rate. This depends upon the number of particles present. For many cases, coagulation will be a much slower process than nucleation or condensative growth, in which case it may be treated separately after the aerosol size distribution has been established. Colbeck (1998) gives estimates of the timescales for coagulation to halve the number of particles present which range from 20 μs to 231 days, corresponding to $10^{14}$ to $10^2$ particles per cubic centimetre respectively. Barrett (2000) describes a method of estimating the timescale over which nucleation and condensative growth takes place, allowing the validity of treating aerosol “formation” separately from coagulation to be tested.

2.1.4 Aerosol Removal

Once formed into a system, there are certain circumstances in which material contained in an aerosol may no longer be airborne, and will consequently no longer contribute to the total mass of suspended material. This can occur when particles settle out under the force of gravity. Large particles will settle more quickly than small ones, which may remain suspended for some time. Near the walls of a container, Brownian motion may deflect some particles onto a collision course with the walls. Although the Brownian displacement is on average zero, fluctuations about this mean can lead to impacts. This is, however, a slow process for large particles, and so is most applicable to small particles. Two further processes are closely related to each other. Thermophoresis occurs when the walls are cooler than the bulk. In this case, heat flowing from the bulk to the walls will carry aerosol with it. Diffusiophoresis occurs when vapour in the hotter bulk diffuses towards the cooler walls, carrying aerosol with it.

2.1.5 Experimental Aerosol Studies

Heist and He (1994) offer an excellent review of experimental studies of nucleation to which the reader is referred. The experiments reported upon in their paper are summarised here.
A wide range of experimental techniques are described. These can be broadly classified into two main groups: those where the expansion of a condensible vapour leads to nucleation, and those where the exchange of heat, promoted by mixing, contrives to form aerosol. Of this second group, a subset may be identified where counter to common practice the mixing is promoted not by forced flow but by natural diffusion currents.

Most notable amongst the first group are the expansion cloud chamber studies of Wagner and Strey (1981, 1984) who introduced a hitherto unseen level of accuracy into this type of measurement. Perhaps foremost amongst the second group are thermal diffusion cloud chamber experiments. Leading researchers in this field include El-Shall, Katz, Smolik, Vitovec, Mirabel, Rabeony and Heist himself.

Perhaps the most famous aerosol nucleation experiments are the cloud chamber studies of Wilson, in which the track of ions through a supersaturated vapour was revealed by the aerosol nucleation they caused.

For many years after this point it was only possible to experimentally measure the conditions required for the onset of nucleation. When compared with experiments, these theories predicted reasonably well the critical nucleation point. From these results it was therefore inferred that aerosol behaviour was well characterised by these theories.

However, in recent years more advanced techniques have been developed, which are capable of revealing the dependence of nucleation rates upon temperature and vapour saturation. Experiments based on these techniques have shown that in fact all current aerosol formation theories are not capable of accurately describing real nucleation scenarios.

2.2 Tube Flow Studies

A number of authors have looked at aerosol behaviour in tube flow, either theoretically or in experimental studies. Much work has been done to describe analytically the thermal hydraulics of flows in tubes. The work to apply this to situations where aerosol behaviour is important is due to Clement (1985), who presented general equations for all flow regimes and applied them to the laminar flow regime. Clement and Ford (1988) then derived from this work the equations for turbulent flow.

For turbulent flow the equations for heat and mass transport respectively are:
while the general flow equations, expressed in three dimensions terms of concentration and temperature are more complicated:

\[ \frac{dT}{dz} = \frac{4}{d} \frac{q}{\rho c_p} + \frac{L m}{\rho c_p} \]  \hspace{1cm} (2.70)

\[ \frac{dp_c}{dz} = \frac{4}{d} j_s - \dot{m}_c \]  \hspace{1cm} (2.71)

For a true three-dimensional description of the problem, it is necessary to use the Navier-Stokes equation to determine the flow velocity. Often this velocity is approximated by assuming a parabolic variation with radius.

These equations (in their fullest form) are only soluble numerically. Whilst making some simplifications to the turbulent equations allows them to readily be solved analytically in the neglect of the vapour flux to the aerosol, this is not the case for laminar flow. Nusselt (1910) derived an infinite series solution to the thermal hydraulic equations for laminar flow. Ingham (1975) corrected these results to give a form which is soluble analytically.

Peshty et al. (1981, 1983) have presented a detailed summary of the processes involved in the nucleation and growth of aerosol in a laminar flow tube. They consider a polydisperse aerosol population, formed from dibutyl phthalate vapour, flowing along each streamline. Heat and mass balance equations are solved over a grid of points, and from this data a nucleation rate calculated at each point. The authors suggest that immediately adjacent to a nucleated droplet the vapour concentration will fall to its equilibrium value. This will lead to a lower nucleation rate near the droplet, and (according to them) a higher nucleation rate (than the mean) at some distance away from the droplet. They conclude that the errors due to using the bulk nucleation rate will be small in a dilute system. Peshty et al. apply classical nucleation theory and a theory due to Lothe and Pound in their work, and conclude that the theory of Lothe and Pound predicts fundamentally different outcomes compared to classical theory. It is worth noting that the method of Lothe and Pound (which attempted to include energetic contributions from the rotation and translation of the droplet) demonstrates poor agreement with experiment (Heist and He, 1994), and has fallen from use. Peshty et al. conclude that, although under the conditions...
they studied little nucleation would be seen, that occurring would occur in the centre of the tube. They note that the effects of growth on the vapour concentration are sufficient that aerosol formation and growth must be considered concurrently.

Workers at the University of Helsinki (Hämeri et al., 1996; Hämeri and Kulmala, 1996) have studied DBP nucleation in a laminar flow diffusion chamber to test various nucleation theories, to establish critical cluster sizes and to quantify the effect of carrier gas on nucleation rates. Although particles formed in such apparatus will also grow, the authors rely upon the fact that this growth will take place at a location away from that of nucleation (due to the continual flow of carrier gas sweeping particles along the tube) to uncouple the formation and growth processes. They acknowledge that high nucleation rates may lead to growth being significant near the nucleation sites, and therefore attempt to operate at sufficiently low rates to prevent difficulty. The authors used an ultrafine condensation particle counter to determine the extent of aerosol formation. They note that more nucleation is expected in the centre of the tube than near the walls, therefore requiring mixing of the tube outflow prior to measurement. For experiments performed with water they note that nucleation will occur mainly near the tube walls, leading to experimental difficulties (due to aerosol retention on the tube walls). In common with many previous authors, the Finnish workers find that classical theory does not correctly predict the nucleation rates seen under given conditions, nor does it predict the saturation necessary for a specified nucleation rate correctly (the so-called critical saturation). Although they find no evidence for an effect of carrier gas on the rate of nucleation, they are unable to conclusively prove no such effect exists, and recommend further investigation in light of the results of another paper (Volra and Heist, 1996) which suggests an effect. It appears from their data, however that any effect is small, and may be neglected given current uncertainties in nucleation theory.

Wilck and Stratmann (1997) discuss an aerosol model which they apply to the results of the Finnish team (Wilck et al., 1998) as well as to the results of Peshty et al. (1983). Their model treats the aerosol population as comprising a number of modes (sizes of particle) whose interaction is described by differential equations which must be solved. Thermal hydraulic information is provided by a separate code. The authors overcome the apparent inability of current nucleation theories to predict aerosol formation accurately by the use of correction factors to match the predicted rates to those experimentally observed. By use of this technique they are able to assess the
ability of different nucleation theories to predict the temperature dependence of nucleation. A good knowledge of the wall temperature along the laminar tube is noted to be essential for accurate prediction of experimental results.

Mikheev has performed laminar flow tube reactor studies of aerosol nucleation. Using an interesting combination of condensation particle counters and diffusional aerosol spectrometers he has made comparisons of nucleation theories. To date, little of his work has been published in the Western literature, although information presented at a conference (Mikheev, 1998) suggests that he observes nucleation maxima near the centre of the tube for most compounds, with the exception of water.

Other studies, more geared to nuclear safety studies include the FALCON series of thermal gradient tests, carried out at AEA Technology Winfrith. The tests were modelled by the code VICTORIA (see below for an explanation of this code). The tests aimed to study the interaction of a wide range of reactor materials (Ag, Ca, In, Ba, Cs, I, Mo, Sn, Sr, Te, Ur, Zr, B, Si), in helium carrier gas, with steam and hydrogen. Representing the product of reactor structural materials degrading, boric acid was present in some tests. Comparisons were made with VICTORIA to assess its ability to model the interaction of these species. Shepherd et al. (1995) drew the conclusion that VICTORIA tends to predict aerosol formation where none is seen experimentally. In such a complex "soup" of compounds, despite its large database of material thermodynamics VICTORIA is still unable to accurately predict speciation, which is believed to be key to understanding the processes occurring in such a complex situation.

Simpler tube flow studies, performed in respect of the nuclear safety issue, were carried out by workers at the Japan Atomic Energy Research Institute (Hidaka et al., 1995). The authors studied the deposition of caesium iodide aerosol onto tube walls, using a laminar flow CsI/ N2 system with isothermal walls. The experiments were then modelled using the three-dimensional thermal hydraulics code ART, which predicted that the radial variation of temperature in the tube would not be symmetric after a short distance into the tube. Based on this information, the authors conclude that their experimental observation of significant deposition on the tube floor near the inlet to be due to diffusion and condensation of vapour upon the walls, aided by this non-symmetric temperature gradient. They attribute the increasing amount of ceiling deposition at longer lengths to the thermophoretic deposition of aerosol nucleated in
the tube. These results are predicted by their code, and are claimed to be in agreement with the results of the FALCON experiments. This is in itself interesting, as the WAVE experiments were performed in an isothermal tube, while the FALCON ones used a thermal gradient tube. This agreement can only be considered as “broad”, as the extent of this differentiation between early and late deposition is far more pronounced in the WAVE experiments than in the FALCON tests.

Okuyama et al. (1991) and Adachi et al. (1992) are unique among the authors discussed here in that they elected to study nucleation upon ions in tube flow rather than homogeneous nucleation. The authors established conditions in the tube leading to a nucleation rate “fewer than \(1 \text{ cm}^{-3} \text{ s}^{-1} \text{ particles}\)” (a value which is commonly considered to represent the onset of nucleation). They find an immediate increase in aerosol formation upon introducing ions into the flow reactor. They note that only a small percentage of the ions in the tube are implicated in nucleation, and that increases in the ion concentration do not lead to a directly comparable increase in aerosol formation. Doubling the ion concentration is seen to increase the aerosol concentration by a factor 1.5; as the ion concentration increases further so the extent of its effect diminishes. The authors also report increased aerosol formation in the presence of positive ions compared to negative ions under the same conditions. The tendency of compounds to nucleate better in the presence of ions of a particular charge (different compounds prefer different charges) has been noted before in a number of other works, summarised well in the 1986 paper of Rabeony and Mirabel. Katz et al. (1994) note that some disagreement exists between experimenters as to the charge required for enhanced nucleation by specific compounds. Rabeony and Mirabel (1986, 1987) suggest that the magnitude of the sign effect is dependent upon the strength of the electric field present. Katz et al. (1994) refute this, suggesting that while the nucleation rate is not dependent upon the electric field, the number of nucleation events is influenced by the field strength due to the length of time that the ions are in the nucleation zone. Neither set of authors are able to offer an explanation for the presence of this sign effect, although some of the data of Katz et al. shows no difference between positive and negative ions. Classical theory does not predict a sign effect in ion-induced nucleation. In an attempt to address this issue, Chan and Mohnen (1980) proposed a semi-molecular model of ion-induced nucleation which was able to take the charge of the ion into account. This is achieved by considering the different orientations in which polar molecules will align themselves to an ion. A
preferred surface orientation will lead to a different arrangement of molecules in the
droplet with a different configuration energy.

2.3 Nuclear Safety Work

Much work has been done studying the potential consequences of nuclear reactor accidents, to allow improvements to plant designs to be made, as well as enabling plans for the mitigation of any accident to be developed. Due to the high cost of experimental studies performed at the high temperatures expected in a reactor accident, only a very limited number of researches have been carried out. A number of models exist to describe an accident sequence, with varying degrees of empiricism. Some of these are now being tested against data from the PHEBUS-FP project as it becomes available.

2.3.1 Experimental

Experimental studies may be divided into two main categories: single-effect and integral. In the former, one solitary aspect of reactor accident phenomenology is investigated in isolation, in an experimental set-up which is designed to display the appropriate characteristics of part of a reactor plant.

One ongoing integral study is the $\frac{1}{5000}$-th-scale PHEBUS-FP project (Krischer and Rubinstein, 1992), which is a series of six "in pile" (i.e. carried out using fuel in the core of a working reactor) tests designed to capture key processes and phenomena associated with particular accident sequences, with the aim of assessing the validity of existing analytical models. Only by comparing these models (which are developed by combining theoretical understanding of a variety of processes) with experiment can their completeness and correctness be checked. It is not intended to demonstrate single effects which would be of use in developing models.

The project is being carried out at CEA Cadarache in France as part of an international collaboration. A test reactor (light water) of 20-40 MW capacity is used; one fuel bundle attached to pipework simulating the primary circuit and a tank to simulate the primary containment will be used in the tests. On-line instrumentation is provided to measure some parameters during the tests, other data (such as deposition profiles) will be determined by destructive post-test analysis. The key objective of the project is to assess the validity of existing analytical models in predicting accident consequences.
The programme of tests was originally scheduled to finish prior to the completion of this PhD project. However, the PHEBUS-FP project is now running seriously behind schedule, with final reports for the first test still not yet available.

A series of single-effects experiments performed in the Falcon facility at AEA Winfrith treat the problem of fission product vapour transport in cooled tube flow (Shepherd et al., 1995; also unpublished AEA technical reports). These experiments transport a volatilised sample (either CsI, CsOH or a mixture) through a heated pipe in an inert carrier gas stream. A variety of temperatures and flow rates were studied using this setup. Deposition of aerosol and vapour onto the walls of the tube were measured, and impaction studies of the aerosol formed carried out.

Similar studies to the Falcon tests have been carried out at the Japan Atomic Energy Research Institute. Hidaka et al. (1995 and 1997) investigated the spatial variation of fission product deposition and also the effect of carrier gas on aerosol formation. They report enhanced aerosol growth in the presence of steam which could not be explained by their existing model. Limited numerical data is presented in their papers.

2.3.2 Modelling

A wide range of codes exist to model various aspects of a reactor accident sequence. They can be broadly divided into three categories. Codes such as TRAPMELT2 assume a fixed speciation of fission products, based upon previous thermodynamic predictions. The commonest assumption is that all iodine will exist as caesium iodide, with excess caesium forming caesium hydroxide. Examples have been presented of cases where this assumption would seem to be invalid, for example, in the presence of boric acid, caesium borate forms from caesium hydroxide (Bowsher and Nichols, 1985; Hontaño et al., 1996). Kissane (1998) reports that in the presence of molybdenum most of the caesium is contained in caesium molybdenate, with the majority of the iodine consequently in the form of a telluride. For the purposes of this thesis it is assumed that speciation into CsI/ CsOH is applicable, and these two substances considered.

A second family of codes, represented by RAFT (Im et al., 1985) models the chemical interaction between a range of species in tube flow. Another code provides input to RAFT regarding the fission product inventory of fuel bundles. The release of these fission products then proceeds at rates given by the United States' nuclear
regulatory authority. Transport of this release is then modelled by RAFT. Localised chemical equilibrium is assumed, although non-equilibrium with condensed species is allowed. Aerosol formation occurs by either homogeneous or heterogeneous nucleation. Coagulation of the aerosol particles due to Brownian motion, turbulent eddies and gravitation is modelled, as is deposition to the tube walls by thermophoresis, Brownian deposition and gravitational sedimentation. By including these processes as well as nucleation, RAFT is able to characterise the aerosol particles formed, and quantify the competition between these mechanisms, to identify which is of primary importance in a given situation. The transport properties of compounds modelled in the system are based upon the kinetic theory of gases, rather than experimental data, an understandable decision given the lack of experimental data available for many of the compounds thought to be involved in reactor accidents.

The final approach is used in the code VICTORIA, which is the most widely used in the UK. Capable of modelling the release of fission products from the fuel, their transport and interaction, and possible conversion to aerosol, VICTORIA has the largest database of chemical species of all the modelling codes. It is known (Nichols, 1991) that the large number of species potentially present in an accident can lead to chemical interactions which significantly alter the nature of the compounds present. In particular, boric acid (Dickinson et al., 1988; Hontañón et al., 1996) and molybdenum (Kissane et al., 1998) are considered “key” in determining which species are present. Thus the completeness of VICTORIA can be pivotal in civil reactor accidents. However it is believed that such effects do not exist in the different conditions prevalent in Naval nuclear reactors.

VICTORIA is reliant on external models to determine the variation of the fuel temperature and fission product inventory with time. From this information it is then able to calculate release rates of fission products, either through breaches in the fuel cladding or by diffusion through the fuel-clad gap. It is also able to calculate rates of reaction with the clad (typically leading to zirconium oxide and hydrogen production) and thus the rate of release of these reaction products. The transport through the reactor pipework of all the species predicted by these calculations is modelled; chemical interactions are allowed to occur. VICTORIA treats chemistry from an equilibrium standpoint; thermodynamic considerations do not limit the rates of reaction; rather reactions are assumed to go to equilibrium at a rate governed only by
the rate at which they can diffuse. An interesting omission from the range of compounds which VICTORIA models is water, meaning that the effects of steam condensation cannot be modelled. The modelling of the behaviour of aerosols is very comprehensive in VICTORIA, encompassing many agglomeration and removal phenomena, including gravitational, turbulent effects, the effects of bends, thermophoresis and sedimentation. Unfortunately, the formation of aerosols is treated in the same way as chemical interactions; i.e. a pure equilibrium approach is taken where supersaturation is prevented by the immediate conversion of excess vapour material to aerosol. This has the limitation that the aerosol may be poorly characterised in terms of size and time of formation, both parameters which can affect the extent and likelihood of retention. Resuspension is also not modelled currently. Finally, VICTORIA models the release of decay heat from fission products, a process which is likely to have an impact on the aerosol formation process.
Chapter 3

Turbulent Tube Flow
3.1 Introduction

Models are developed for turbulent tube flow, with and without aerosol processes. Two approaches, based on simple analytical solutions and more complete numerical modelling (simple versus computationally expensive) are compared, and a basic model developed which allows predictions to be made on the likelihood of nucleation occurring. The aerosol behaviour dependencies on key parameters are identified to allow heuristic predictions of likely outcomes.
3.2 Basic Thermal Hydraulics of Turbulent Tube Flow

The results of Clement and Ford (1988) presented in Chapter 2 give a description of aerosol processes in turbulent tube flow, provided plug flow is assumed. Their differential equations can only be solved numerically, however. In order to gain an appreciation of some of the processes at play, simplifications were made to enable a preliminary study to be conducted using an analytical form of the solution. The first (and most drastic) approximation is to set the term which describes the flux of mass from the bulk to the aerosol, $\dot{m}$, equal to zero; that is aerosol growth does not release latent heat nor consume vapour. The second approximation centres on the fact that most of the material properties are not in reality constant, but actually vary with temperature. Allowing properties in the vapour density equation to vary with temperature would create a pair of non-linear coupled differential equations, which are very rarely soluble analytically. Given these approximations, the temperature and vapour density in a tube of diameter $d$ are described by:

$$T = T_v + \Delta T \exp(-\alpha z) \quad (3.1)$$

$$\rho_v = \rho_v(T_w) + \Delta \rho_v \exp(-\beta z) \quad (3.2)$$

where $\alpha = \frac{4kNu}{c_p \rho vd^2}$ and $\beta = \frac{4DSh}{vd^2}$. The Nusselt and Sherwood numbers, Nu and Sh characterise the enhancement to heat and mass transport respectively due to turbulent mixing. They are defined in terms of three other numbers, the Prandtl and Schmidt numbers, Pr and Sc, which define the susceptibility of heat and mass transfer respectively to enhancement by turbulence, and the Reynolds number (Re) which quantifies the amount of turbulence in a system. $\Delta T$ and $\Delta \rho_v$ are, for temperature and vapour density respectively, the difference between the inlet and wall values. The temperature of the walls is specified by $T_w$.

From

$$Z = \exp(-\alpha z) \quad (3.3)$$

it follows that:

$$Z^{\%} = \exp\left((-\alpha z)\frac{\rho_v}{\rho_v'}\right) = \exp(-\beta z) \quad (3.4)$$

and Equations (3.1) and (3.2) can be written as:
These Equations were encoded as the code PROFSI (temperature and vapour density PROFiles, Simple version) Figure 3.1 shows a sample run for the flow of water vapour along a tube.

\[
T = T_w + \Delta T Z \quad (3.5)
\]
\[
\rho = \rho_{v_0}(T_w) + \Delta \rho_{v_0} Z^\theta \quad (3.6)
\]

Also shown is the saturation ratio, strictly defined by Equation (3.7),

\[
S = \frac{p_v}{p_{v_0}(T)} \quad (3.7)
\]

but equivalent, under the assumption of ideal gas behaviour, to Equation (3.8)

\[
S = \frac{\rho_v}{\rho_{v_0}(T)} \quad (3.8)
\]

The effects of varying parameters such as flow rates and temperature differentials were examined: observations are tabulated below.
It can be seen that both temperature and vapour density experience exponential decay, as predicted by Equations (3.1) and (3.2). Since the equilibrium vapour density, $\rho_v$, is an exponential function of temperature it will fall much faster than either the temperature or vapour density, leading to the peaked form of saturation ratio seen. Because the nucleation rate is a function of saturation, it may be expected that the maximum nucleation rate will be seen near this point. In fact, since the temperature also affects the nucleation rate, the actual nucleation peak will be slightly before the saturation peak where the temperature is higher.
3.3 Prediction of Conditions for "Significant" Nucleation

The scaled nucleation theorems of Hale (1988) allow predictions of the critical saturation (i.e. the saturation required for a specified nucleation rate) to be made based on far fewer parameters than using the full form of classical nucleation theory. By combining her work with an analytical expression for the maximum saturation ratio seen (derived below from the combination of Equations (3.5), (3.6) and (3.8)) it should be possible to produce a simple tool for determining whether specified conditions will result in "significant" nucleation (the definition of "significant" will be deferred until later).

3.3.1 Theory

The saturation maximum is a turning point on the plot of $S$ vs $z$, which can be identified by solving $dS/dz = 0$. Only one turning point is expected, therefore this approach will yield the maximum saturation. In practice it turns out to be easier to look at the natural log of $S$. Equation (3.9) shows that since $S^{-1}$ is non zero (for the range of interest) the solution to $d\ln S/dz = 0$ will be the same as that to $dS/dz = 0$:

$$\frac{d\ln S}{dz} = \frac{1}{S} \frac{dS}{dz} \quad (3.9)$$

Using the form

$$\rho_v(T_v) = A \exp(-B/T) \quad (3.10)$$

for the equilibrium vapour density allows the saturation as a function of distance to be written:

$$S = \frac{\rho_v(T_v) + \Delta \rho_v Z^\gamma}{A} \exp\left(\frac{B}{T_v + \Delta T Z}\right) \quad (3.11)$$

Assuming $\rho_v(T_v)$ is negligible compared to $\Delta \rho_v Z^\gamma$ leads to:

$$\ln S = \ln\left(\Delta \rho_v Z^\gamma\right) - \ln A + \left(\frac{B}{T_v + \Delta T Z}\right) \quad (3.12)$$

thus

$$\frac{d\ln S}{dZ} = 0 = \frac{\beta Z^{\gamma - 1}}{\alpha Z^{\gamma}} - \frac{B \Delta T}{(T_v + \Delta T Z)^2} = \frac{\beta}{\alpha} - \frac{B \Delta T}{(T_v + \Delta T Z)^2} \quad (3.13)$$

which may be rewritten:

$$0 = \beta(T_v^2 + 2\Delta T + \Delta T^2 Z^2) - \alpha Z B \Delta T \quad (3.14)$$
which is a quadratic in $Z$. It is assumed that the term in $Z^2$ is small, and may be ignored, which gives:

$$Z\Delta T = \delta T = \frac{T_w^2 \beta}{B \alpha - 2T_w \beta} \quad (3.15)$$

where $\delta T$ may be interpreted as the temperature difference between the wall and the point of maximum saturation. Combining Equations (3.15) and (3.11) and assuming that the inlet to the tube is saturated gives the following expression for the maximum saturation seen in the tube:

$$S_{\text{max}} = \left[ \frac{T_w^2 \beta}{\Delta T (B \alpha - 2T_w \beta)} \right] \exp \left( \frac{B}{T_w + \frac{T_w^2 \beta}{B \alpha - 2T_w \beta} - \frac{B}{T_w + \Delta T}} \right) \quad (3.16)$$

The condition given by Hale (1988) for the saturation necessary to achieve a nucleation rate $J$ (in m$^3$ s$^{-1}$) is given by combining Equations (2.39) and (2.67) to yield:

$$\ln S_\varphi = 0.53 \Omega \chi \left( \frac{T_c}{T} - 1 \right)^{\chi} \left( 1 + \frac{\ln 10^6 \cdot J}{2 \ln (10^6)} \right) \quad (3.17)$$

When the natural logarithm of Equation (3.16) equals Equation (3.17), the maximum nucleation rate seen in the tube will be $J$. This equivalence takes the form of Equation (3.18):

$$f(\Omega, T_c, J, T_w, \Delta T, \alpha, \beta, B) = 0 \quad (3.18)$$

Solving this equality analytically for all of the parameters listed is not possible and so some iterative search routine must be employed to investigate the parameters which affect whether nucleation is seen.

In the experimental literature a nucleation rate of $10^6$ m$^3$ s$^{-1}$ is commonly taken as the onset of nucleation. The use of this value would be ill-advised in the present application since $J$ is the maximum rate ever seen in the tube. $J$ should instead be specified as the peak rate desired.

### 3.3.2 Calculations

In order to reduce the number of parameters which need to be investigated from the 8 presented in Equation (3.18), the problem is instead considered by scaling
temperatures and the parameter $B$ by the wall temperature. It is also possible to combine $\alpha$ and $\beta$ into a parameter related to the Lewis number. Given that:

$$\frac{4kNu}{\beta} = \frac{c_p \rho v d^2}{4DSh} = \frac{4kNu}{c_p \rho v d^2} \frac{vd^2}{4DSh}$$

(3.19)

it follows that

$$\frac{\alpha}{\beta} = \left( \frac{k}{c_p \rho D} \right) \left( \frac{Nu}{Sh} \right)$$

(3.20)

where the first term on the right hand side is equal to the Lewis number, which is always represented as $Le$. The Lewis number describes the relationship between the rate at which heat conducts through a system and the rate at which mass diffuses through that same system. Lewis numbers less than unity indicate that mass is more mobile than heat, while for Lewis numbers greater than unity the converse is true.

Substituting definitions for the Nusselt and Sherwood numbers into Equation (3.20) gives:

$$\frac{Nu}{Sh} = 0.023 \Re^{0.8} \Pr^{0.33} = \left( \frac{Pr}{Sc} \right)^{0.33}$$

(3.21)

which can be shown to be equal to $Le^{-0.33}$ thus:

$$\frac{Nu}{Sh} = \left( \frac{v c_p \rho D}{k v} \right)^{0.33} = \left( \frac{1}{Le} \right)^{0.33}$$

(3.22)

Thus Equation (3.19) becomes

$$\frac{\alpha}{\beta} = Le \cdot Le^{-0.33} = Le^{0.67}$$

(3.23)

Using this result allows the natural logarithm of Equation (3.16) to be written:

$$\ln S_{max} = \frac{1}{Le^{0.67}} \ln \left( \frac{T_w^2}{\Delta T B Le^{0.67} - 2 \Delta T T_w} \right) + \frac{B}{T_w + \Delta T} - \frac{B}{T_w + \Delta T}$$

(3.24)

Considering first the term in brackets, multiplying through by $T_w^{-2}$ gives:

$$\frac{T_w}{B} \frac{\Delta T Le^{0.67} - 2 \Delta T T_w}{T_w} = \frac{1}{B \Delta T Le^{0.67} - 2 \Delta T T_w}$$

(3.25)
Multiplying each element of the second term in Equation (3.24) by \( T_w^{-2} \left( BL e^{0.67} - 2 T_e \right) \) gives:

\[
\frac{B^2 T_w^2}{T_w^2} \left( \frac{B T_e}{T_w} \right)^2 L e^{0.67} - 2 \frac{B T_e}{T_w} T_w = \left( \frac{B}{T_w} \right)^2 L e^{0.67} - 2 \frac{B}{T_w} T_w
\]

and finally for the third term of Equation (3.24) division of each term by \( T_w \) leads to:

\[
\frac{B}{T_w + \Delta T} = \frac{B}{1 + \Delta T} T_w \tag{3.27}
\]

Combining Equations (3.25), (3.26), (3.27) and (3.24) gives:

\[
\ln S_{\text{max}} = -\frac{1}{L e^{0.67}} \ln \left( \frac{B \Delta T}{T_w} \right) \left( \frac{L e^{0.67}}{T_w} - 2 \frac{B}{T_w} \Delta T \right) + \left( \frac{B}{T_w} \right)^2 L e^{0.67} - 2 \frac{B}{T_w} T_w \frac{B}{T_w + \Delta T} T_w \tag{3.28}
\]

which is written in terms of three quantities: \( L e^{0.67}, \frac{B}{T_w} \) and \( \Delta T \) only.

Applying similar arguments used in Equations (3.28) to (3.26) to the temperature term of Equation (3.17) leads to

\[
\ln S_{\text{up}} = 0.53 \Omega \left( \frac{T_e}{T_w} \right)^2 \left( \frac{B \Delta T}{T_w} L e^{0.67} - 2 \frac{T_e}{T_w} T_w \right) + 2 \left[ \ln \left( \frac{10^5}{T_e} \right) \right] \left( 1 + \frac{1}{2 \ln T_e} \right) \tag{3.29}
\]

Using a combined Newton Raphson / bisection routine (Press, 1992) allows the conditions to be found when Equations (3.28) and (3.29) are equal for a range of Lewis numbers at specified nucleation rates. The parameter \( T_e / T_w \) was fixed at 2.0, which is similar to the ratio found in most systems.

Figure 3.2 (on page 45) shows the results of these calculations.

Any combination of conditions which plot a point above the appropriate line in Figure 3.2 will result in nucleation occurring. It can be seen that the Lewis number has a much greater effect on the conditions required for significant nucleation than the precise definition of "significant". As the value of \( B / T_w \) increases, (corresponding to a stronger temperature dependence of the equilibrium vapour pressure expression) so
the differentiation between different nucleation rate conditions is removed. This acts as a reminder of the sensitivity of nucleation calculations to conditions.
Figure 3.2

Conditions in turbulent pipe flow necessary to achieve specified nucleation rates. Lines for $Le = 10$ are dashed for clarity.
The graph also illustrates well the observation that dibutyl phthalate (Le \equiv 5) is seen to nucleate more readily than water (Le \equiv 0.8) for given conditions. This is not only because of the different Lewis numbers, but also the fact that the value of the parameter B is 5300 for water and 11500 for DBP. The increased value of B for DBP explains the higher saturations seen (the stronger temperature dependence leads to a more rapid fall-off of equilibrium vapour pressure, ergo a higher increase in saturation). However, this does not explain why the nucleation rates seen for water and DBP are comparable (within a few orders of magnitude of each other for similar conditions) when the saturation is so much higher.
3.4 Mass Transfer to Aerosol

The use of Hale’s theorem above allows us to determine when the simple analytical solution given by PROFSI is inadequate due to nucleation being significant. In such cases a more complete solution is required, taking account of vapour depletion by aerosol formation and growth as well as latent heat. These effects are encapsulated in the mass flux expression term in Equations (2-70) and (2-71), \( \bar{m}_v \), which consists of two terms, one of which relates to aerosol growth, whilst the second describes vapour depletion due to aerosol formation (nucleation). It will be shown later that aerosol nucleation consumes a negligible amount of vapour compared with that consumed by condensative growth. As described in Chapter 2, current theory treats aerosol growth in two separate size regimes. In order to produce a unified growth rate, some form of interpolation is required.

3.4.1 Interpolation Between Growth Regimes

In the case that the droplet is either very small or very large the growth rate is defined solely by Equation (2.68) or (2.69) respectively. In the transition regime, generally considered to lie between 100 nm and 1 \( \mu \)m, this is not true. Whilst accurate solutions for this regime have been proposed, they are very complex, and in practice some form of interpolation is needed. Barrett and Clement (1988) propose the following interpolation scheme with an error "far outweighed at present by the uncertainties in \( S_A \):"

\[
I(R) = \frac{I_c \cdot I_k}{I_c + I_k} \quad (3.30)
\]

3.4.2 Evaluation of Bulk and Droplet Temperatures

Equations (2.68) and (2.69) above require the bulk and droplet temperatures to be known explicitly. Whilst the bulk temperature is known from Equation (3.1), the droplet temperature cannot be found explicitly. If, however, an approximate mass transfer rate which does not require knowledge of the droplet temperature, \( T_d \), is calculated, this can then be used to infer the droplet temperature as detailed below.
This value can then act as a seed value in the iterative refinement of estimates of the droplet temperature and hence droplet growth rate.

From Barrett and Clement the approximate growth rate is given by:

$$\dot{R} = \frac{1}{\rho_i} \frac{S - 1}{[\text{MASS}] + [\text{HEAT}]} \quad (3.31)$$

which may be related to the mass flux to give:

$$I_{\text{approx}} = \frac{-4\pi R^2 (S - 1)}{[\text{MASS}] + [\text{HEAT}]} \quad (3.32)$$

They then define the heat flux away from the droplet and use energy conservation to relate this to \(I\) and hence \(T_d\). Heat fluxes are defined viz.:

$$\hat{Q}_c = -4\pi k R (T_d - T_\infty) = I I_c \quad (3.33)$$

$$\hat{Q}_k = -4\pi H R^2 (T_d - T_\infty) = I_n I_K \quad (3.34)$$

Rewriting these Equations in terms of \(I_c\) and \(I_k\), then substituting into Equation (3.30) gives (after cancelling):

$$I = \frac{4\pi R^2 H k (T_d - T_\infty)}{L_n k + H R L} \quad (3.35)$$

Since \(L_m\), the modified latent heat is a function of \(T_d\) which is not known at this stage, to a first approximation the latent heat, \(L\), is used instead. Using the approximate growth mass flux in this Equation and rearranging gives the droplet temperature:

$$T_d = T_\infty - \frac{IL(k + HR)}{4\pi R^2 H R} \quad (3.36)$$

This droplet temperature can now be used in Equations (2.68) and (2.69) to give first estimates of the mass fluxes in continuum and kinetic regimes. Combination of Equations (2.68) and (3.33) gives a function \(f_c(T_d)\) which should converge towards zero as the droplet temperature is found with increasing accuracy:

$$f_c(T_d) = 4\pi R k (T_d - T_\infty) + I I_c \quad (3.37)$$

and similarly for the kinetic regime:

$$f_k(T_d) = 4\pi R^2 H (T_d - T_\infty) + L_n I_K \quad (3.38)$$

Using Newton-Raphson root finding allows the droplet temperature for both continuum and kinetic regimes to be refined independently, giving final solutions for \(I_c\) and \(I_k\) which may then be combined using Equation (3.27) to give the final result.
3.4.3 Conversion of Droplet Growth Rates to Mass Transfer Rates

In order to convert the droplet mass flux, \( I(R) \), into a total mass flux it is necessary to know the size distribution of the droplets present.

If Figure 3.3 represents a size distribution, then the number of droplets in the range \( R \) to \( R + \delta R \) at time \( t \) is given by:

\[
n(R, t) \delta R \quad (3.39)
\]

For a given nucleation rate, \( J \), the number of particles produced between times \( t' \) and \( t' + \delta t' \) is equal to

\[
J(t') \delta t' \quad (3.40)
\]

thus:

\[
n(R) \delta R = J \delta t' \quad (3.41)
\]

where \( R \) is the radius at time \( t \) of a droplet nucleated at time \( t' \).

Given a droplet growth rate \( \dot{R}(t) \) it is possible to write an expression for the radius of a droplet at any time, viz.:

\[
R = R_0 + \int_{t'}^{t} \dot{R}(t'') dt'' \quad (3.42)
\]

The mass transfer rate at a given radius can thus be expressed as the condensative growth rate at that radius, multiplied by the number of particles of this size, i.e.

\[
\delta m_v = I(R) n(R) dR \quad (3.43)
\]

The total condensative growth rate (for all radii) is thus given by:

\[
m_v = - \int I(R) n(R) dR \quad (3.44)
\]

which is equivalent to:
\[ \dot{m}_v = \int_0^t I(R) J(t') dt' \quad (3.45) \]

### 3.4.4 Monodisperse Aerosol

In practice Equation (3.45) is too complicated, and the procedure of Warren and Seinfeld (1984a, 1984b) is followed by assuming that the aerosol may reasonably be characterised as monodisperse. In this case the radius of the aerosol is given by:

\[ R = \frac{3M_{\text{vap}}}{4\pi\rho_t N_A} \quad (3.46) \]

The integral expressed in Equation (3.45) is no longer needed and the mass flux due to growth is then given by:

\[ \dot{m}_v = -I(R) N \quad (3.47) \]

### 3.4.5 Relative Importance of Mass Transfer Terms

It was mentioned earlier that by far the dominant cause of vapour to aerosol mass transfer is condensative droplet growth, and that nucleation depletes the vapour only negligibly. Using the results of a PROFSI calculation the nucleation rate along the tube was calculated, and from this the amount of vapour consumed by nucleation (= nucleation rate \times mass of particle nucleated) calculated. The amount of vapour present in the tube was given by the PROFSI calculation; comparison of these two quantities reveals that nucleation consumes approximately no more than 0.00001% of the vapour present. Within the limitations of the model, this can be ignored.
3.5 Summary of Equations Solved for Turbulent Case

Prior to presenting the results of investigations into turbulent flow, the equations solved to produce the results are stated below.

There are four main (differential) equations for temperature, vapour density, aerosol number and aerosol mass:

\[
\frac{dT}{dz} = -\alpha (T - T_w) + \frac{Lm_v}{v} \quad (3.48)
\]

\[
\frac{d\rho_v}{dz} = -\beta (\rho_v - \rho_v(T_w)) - \frac{\dot{m}_v}{v} \quad (3.49)
\]

\[
\frac{dN}{dz} = \frac{J}{v} \quad (3.50)
\]

\[
\frac{dM}{dz} = -\frac{IN}{v} \quad (3.51)
\]

where if the removal of vapour due to the actual nucleation of droplets (of radius \(R_0\)) is included the mass flux is given by:

\[
\dot{m}_v = \frac{4\pi R_0^3 \rho_v J - IN}{3} \quad (3.52)
\]

Note the first term refers to vapour depletion by the nucleation process itself: \(R_0\) is an arbitrary small radius defined as the radius at which droplets nucleate. It is held to a fixed value, although it could in theory be found from the critical cluster size.

The growth rate is calculated at a radius given by:

\[
R = \frac{3M}{4\pi \rho_i} \quad (3.53)
\]

which simply divides the total aerosol mass present over all droplets to find a mean radius.

Classical nucleation theory, as stated in equation (2.37) (with the \(S'\) correction term due to Oxtoby (1992)) is used to give the nucleation rate, although again any theory could potentially be substituted.
3.6 Turbulent Flow Results

A series of calculations were performed to demonstrate features of the full turbulent model, incorporating mass transfer to aerosol. Thermophysical properties of the systems were allowed to exhibit temperature dependencies. Conditions, for both water and caesium iodide vapours, were chosen to be representative of the problem under consideration. Temperatures were chosen to reflect (in part) the vapour under investigation.

3.6.1 Water Vapour

3.6.1.1 Comparison with Analytical Solution.

The numerical solution described in Section 3.5 was coded, subject to the same simplifications used in the analytical solution, and compared with results from PROFSI. Agreement was excellent, limited only by computational considerations (accuracy of input data to PROFSI, accuracy of requested solution in the numerical solution code's ODE solver). However, a number of approximations are used in PROFSI, which should ideally be removed in the numerical case. These limitations are as follows:

- material properties do not vary with temperature
- the contribution of aerosol and vapour terms to the expression \( \rho c_p \), the sum of the products of heat capacity and density for each component (aerosol, vapour, carrier gas), is assumed to be zero
- droplet growth is not modelled

3.6.1.2 Variation of Properties with Temperature

Figure 3.4 compares results from calculations made with the simplifications used in the analytical model against the improved numerical solution which corrects the first two limitations described above. Although the vapour density profile is higher than before the corrections, the saturation ratio is significantly lower. This is due to the strong temperature dependence of the equilibrium vapour density. As the temperature increases, so \( \rho_v \) increases faster, causing the ratio \( \rho_v / \rho_{ve} \), i.e. saturation, to fall. Where significant nucleation rates were seen previously, the reduced saturation...
prevents particle formation. Examining the mass balance shows that vapour deposition to the tube walls is reduced by around 5½ percentage points.

<table>
<thead>
<tr>
<th>model</th>
<th>$\rho_v$ in</th>
<th>$\rho_v$ out</th>
<th>$\rho_v$ deposited to walls</th>
<th>% retention</th>
</tr>
</thead>
<tbody>
<tr>
<td>improved</td>
<td>0.632</td>
<td>0.293</td>
<td>0.339</td>
<td>53.6</td>
</tr>
<tr>
<td>simple</td>
<td>0.632</td>
<td>0.327</td>
<td>0.304</td>
<td>48.2</td>
</tr>
</tbody>
</table>

Table 3.2

*The effect on mass balances of varying thermophysical properties with temperature*

![Graph showing temperature, saturation ratio, and vapour density profiles for simple and improved modelling of turbulent flow case.]

Figure 3.4

*Temperature, saturation and vapour density profiles for simple and improved modelling of the turbulent flow case*

3.6.1.3 Nucleation and Growth

Finding conditions conducive to nucleation and growth was not easy. For the investigation of the model, conditions were chosen which assume that somehow the saturation starts at 1.2 or 1.5. In reality, saturations this high are unlikely to spontaneously arise.

As discussed previously, there is no need to take account of the vapour consumed directly by nucleation, this being expected to be negligible compared to vapour consumption by condensative droplet growth.
Modelling droplet growth causes a marked change in the results. This is due to the release of latent heat and depletion of vapour as it condenses onto the droplets, causing them to grow. Figure 3.5 shows the results of two calculations for the same conditions, with growth modelled only in the second case. It can be seen that at approximately 14 m the saturation starts to fall. This is due in part to latent heat release slowing the rate at which the temperature falls, which in turn impacts upon the equilibrium vapour density. The depletion of vapour by growing particles is also responsible for the fall in saturation.

Figure 3.5
The effect of modelling vapour consumption by aerosol growth

Figure 3.6 shows the effect this had on the number of particles nucleated. With no growth the saturation was free to rise higher, leading to the formation of roughly 200 times as many droplets. Note that several tens of thousands of droplets must nucleate before any effect is seen in Figure 3.5. The low individual mass of a droplet requires many to be present to exert an influence on the bulk material. Figure 3.6 also shows a calculation addressing the question of the relative importance of vapour depletion vs. latent heat release as a mechanism for lowering the saturation. Growth was modelled, but the latent heat release was assumed to be zero, although vapour depletion still occurred. It can be seen that the number of particles nucleated is roughly seven times greater than when latent heat release occurs. However, when fewer particles nucleate, those which are formed grow to a larger size.
If latent heat release is ignored, the total mass of aerosol formed is roughly five times greater, showing the importance of latent heat release not only on the amount of aerosol formed, but also on the nature of that formed.

![Diagram](image-url)

**Figure 3.6**

*The reduction in aerosol number density attributable to condensative growth (and associated latent heat release) on nucleated aerosol*

The mass balance for the results shown in Figures 3.5 and 3.6 indicate that the formation of aerosol does not have a significant effect on the amount of vapour being retained in the tube:

<table>
<thead>
<tr>
<th>no growth</th>
<th>vapour in</th>
<th>vapour out</th>
<th>aerosol out</th>
<th>vapour to walls</th>
</tr>
</thead>
<tbody>
<tr>
<td>no growth</td>
<td>5.6748e-1</td>
<td>8.1521e-2</td>
<td>0</td>
<td>4.8596e-1</td>
</tr>
<tr>
<td>with growth</td>
<td>5.6748e-1</td>
<td>7.6891e-2</td>
<td>5.8812e-3</td>
<td>4.8470e-1</td>
</tr>
</tbody>
</table>

**Table 3.3**

*The effect of condensative growth on mass balances*

Reducing the tube diameter reduces the mass of aerosol produced. Two calculations (T\text{inlet}=360 \text{ K}, T\text{wall}=275 \text{ K}, S\text{inlet}=1.2, v=25 \text{ m/s}, length=100 \text{ m}) for tube diameters of 0.1 m and 0.3 m showed that the smaller tube produced 10 times fewer particles, although the droplet radii were similar. Since the cross sectional area of the smaller tube is about \(\frac{1}{10}\)th that of the larger, this is not unexpected.

From a cursory examination of Equations (3.1) and (3.2) it might be expected that doubling the flow rate would double the distance at which nucleation is
first seen, or at which any other feature may be identified, but this is not the case. Comparing two runs with different flow rates reveals that the maximum saturation reached is different in each case, as is the size and number density of aerosol produced. Since increasing the flow rate increases the degree of turbulence in the tube, the increased mixing promotes better heat and mass transfer, resulting in profiles which do not have an identical form to those at other flow rates. Faster flow rates equilibrate over greater distances than slower ones, although this cannot be described simply by the ratio of the flow rates. It appears that slower flow rates beget fewer particles, although these then grow to larger sizes than those created in fast flows. The total mass of aerosol produced is therefore dependent upon flow rate.

Reducing the temperature differential between bulk flow and wall dramatically cuts the amount of nucleation seen.

3.6.2 Caesium Iodide

A similar parametric study was performed, using data for caesium iodide vapour. Because CsI is liquid over a wider range of temperatures than water, a wider range of “experimental” conditions can be considered. For example, nucleation and growth may be considered for a 450 K wall-inlet temperature differential in the ranges 650 K - 1100 K and 1050 K - 1500 K. This explains partly why more nucleation was seen for CsI than water (with plausible saturation ratios).

In all cases, the temperature difference studied was greater for CsI than for water vapour. Calculations performed for a 200 K difference (T_{inlet}=850 K, T_{wall}=650 K with S_{in}=1.01, v=20m/s and diameter=0.3m) saw no nucleation: this was only observed when the inlet temperature was raised to give a 350 K difference. In contrast to water vapour, latent heat release was not seen to be important as a mechanism for terminating nucleation. At higher initial temperatures latent heat accounted for a 10% deviation in values, whilst at lower temperatures no effect was seen whatsoever. The general form of the temperature and vapour density profiles (ergo saturation) was the same as for water vapour, although the unimportance of latent heat release is reflected in the temperature profile (its fall is not checked).
3.6.2.1 Nucleation Rates

Nucleation rates for caesium iodide were seen to be much higher, leading to sudden, sharp drops in the vapour density as the large number of particles nucleated in a short time start to grow. Figure 3.7 shows a typical example, contrasting conditions when only nucleation was modelled with those prevailing when aerosol growth was also modelled.

3.6.2.2 Tube Diameter and Flow Rate

These parameters exhibited the same influence as for water vapour.

3.6.2.3 Nature of Droplet Growth

Figure 3.8 illustrates one consequence of using a characteristic radius to describe all the droplets nucleated. Figure 3.7 shows the saturation and temperature profile for these conditions. Initially not many droplets are nucleated, and so those present are able to grow quickly. At the height of the nucleation peak, many droplets are being born at a small radius, so the average radius grows more slowly than the true radii of the individual particles. Once nucleation ceases, all the particles present...
are growing, no new, small ones are being added, and the characteristic droplet radius proceeds as though only one droplet size were in fact present.

\[ T_{\text{in}} = 1500\text{K} \quad T_{\text{out}} = 650\text{K} \quad S_{\text{str}} = 1.01 \quad \text{veloc} = 25\text{m/s} \quad \text{diameter} = 0.3\text{m} \]

![Graph showing droplet radius evolution](image)

**Figure 3.8**
*The evolution of mean droplet radius along the length of a tube*

### 3.6.2.4 Mass Balance

The higher nucleation rates seen for caesium iodide manifest themselves in a greatly reduced wall deposition, with much of the vapour being diverted to form aerosol. The mass balance below for the conditions charted in Figures 3.7 and 3.8 indicates the extent to which this occurs:

<table>
<thead>
<tr>
<th></th>
<th>vapour in</th>
<th>vapour out</th>
<th>aerosol out</th>
<th>vapour to walls</th>
</tr>
</thead>
<tbody>
<tr>
<td>no growth</td>
<td>1.4496</td>
<td>0.40653</td>
<td>0</td>
<td>1.0401</td>
</tr>
<tr>
<td>with growth</td>
<td>1.4496</td>
<td>0.20699</td>
<td>1.0164</td>
<td>0.22621</td>
</tr>
</tbody>
</table>

**Table 3.4**
*The effect of condensative growth on mass balances*
3.7 Conclusions

Depending upon the accident sequence being modelled, either laminar or turbulent flows may be experienced. Due to the relative simplicity of the turbulent models these were approached first, and codes developed to model in both simple and more complete fashions the processes which may be occurring.

These studies have demonstrated that the nucleation and growth of caesium iodide aerosol during realistic accident conditions is possible in turbulent flows. The nature of the aerosol formed (number of particles and size of droplet) is determined by the flow conditions and the temperature gradients. Conditions which lead to large numbers of droplets forming produce smaller droplets than those cases with fewer droplets.

The application of Hale’s scaled nucleation theorems allow predictions to be made about the conditions required for “significant” nucleation to be seen. A free choice of the definition of “significant” is possible.

Materials with more strongly temperature dependent vapour pressure fitting functions are seen to nucleate more readily than those with a weaker temperature dependence, due to the greater maximum saturations shown.

Larger temperature differentials are seen to increase the amount of aerosol formed, particularly for lower Lewis numbers. This raises the question of nucleation in the boundary layer. Although not currently modelled, the steep temperature and vapour density gradients anticipated there have led to the suggestion (Clement et al., 1997) that nucleation may be more likely to occur under these conditions.
Laminar Flow without Vapour Depletion
4.1 Introduction

Initial calculations have been based around the assumption that the flow rate through the primary circuit would be sufficient to cause turbulence. Whilst this enabled calculations to be performed more simply, an examination of the Reynolds number suggest that for some cases of interest (Clough, 1997) the flow may be better characterised as laminar. In this case the well mixed approximation used to describe turbulent flow no longer holds and a new approach is needed.

Laminar flow is an extreme case of the boundary layer problem outlined in chapter 2; the turbulent core does not exist, and the velocity varies across all radial positions within a tube. Figure 4.1 shows how the velocity reaches a maximum at the axis of the tube, and falls off to zero at the tube wall. If it is assumed that there is no variation in the thermal properties of the gas with radius in the tube (caused by temperature variations within the tube), then the velocity profile is parabolic, viz.:

\[ v(r) = v_{\text{max}} \frac{(r_0^2 - r^2)}{r_0^2} \]  (4.1)

Models are developed which describe the heat and mass transport processes in laminar tube flow, soluble both analytically and numerically. Key parameters controlling these processes identified, and a condition for the validity of ignoring mass transport from the vapour to aerosol presented. A condition, similar to that used in the turbulent flow case, is presented to estimate the onset of nucleation.
4.2 Formulation of Equations for Laminar Tube Flow

4.2.1 Origin of Equations

The equations presented by Clement (1985) describe in some detail the spatial variation of temperature and vapour density during laminar tube flow. They are repeated here for convenience:

\[ \rho c_p \nu_0 \nabla T - (c_p' - c_p) D \rho \nabla c \cdot \nabla T + \nabla \cdot (-k \nabla T) = L \dot{m}_v \] \hspace{1cm} (4.2)

\[ \rho \nu_b \cdot \nabla c + \nabla \cdot (- D \rho \nabla c) = (1 - c) \dot{m}_v \] \hspace{1cm} (4.3)

In order to obtain simple relationships which reveal fundamental information about aerosol processes in laminar tube flow, a simpler form of Equations (4.2) and (4.3) which can be solved analytically would be beneficial.

4.2.2 Analytical Solution

Nusselt (1910) gives an infinite series solution of Equations (4.2) and (4.3) when re-expressed in terms of dimensionless temperatures and concentrations, provided the mass transfer term \( \dot{m}_v \) is ignored. Ingham (1975) corrected the results of Nusselt to give equations for temperature and concentration throughout a laminar flow tube:

\[ T(r,z) = T_w + \vartheta(r,z) \Delta T \] \hspace{1cm} (4.4)

\[ c(r,z) = c_w + \vartheta \left( r \frac{z}{L_e} \right) \Delta c \] \hspace{1cm} (4.5)

where \( \vartheta(r,z) \) is given by the infinite series:

\[ \vartheta(r,z) = \sum_{i=1}^{\infty} a_i \chi_i(r) \exp \left( - \beta_i^2 z \right) \] \hspace{1cm} (4.6)

and \( a_i \) and \( \beta_i \) are known constants. A polynomial can be used to approximate \( \chi_i(r) \). It is worth noting that the quantities \( r \) and \( z \) are dimensionless in this treatment, and may be related to “real” quantities by:

\[ r = \frac{r'}{r_0} \] \hspace{1cm} (4.7)

\[ z = \frac{z' \alpha'}{r_0^2 V_w} \] \hspace{1cm} (4.8)
4.2.2.1 Method of maximum saturations

Given an explicit analytical solution for the variation of temperature and vapour concentration over the tube allows the saturation to be expressed as a combination of Equations (4.4) and (4.5) viz.:

\[ S(r, z) = \frac{c_w + \Delta c \cdot \theta(r, z)}{A} \cdot \exp \left( \frac{B}{T_w + \Delta T \cdot \theta(r, z)} \right) \]  \hspace{1cm} (4.9)

where the saturation is given by \( S = c / c_r(T) \) and the equilibrium concentration fitted by \( c_e = A \exp(-B/T) \).

Since the nucleation rate depends primarily upon the saturation and temperature, finding the maximum saturation will allow the maximum nucleation rate to be approximated. In all situations where cooled laminar flow occurs, the saturation will rise to a maximum at some point in the tube and then fall again. It is expected that only one maximum and no minima will be found in the tube, allowing it to be uniquely identified by the fact that the gradient at this point is zero. In order to simplify the method which follows, the maximum saturation is identified only for a specified streamline:

\[ \frac{\partial S}{\partial z} = 0 \]  \hspace{1cm} (4.10)

From Equation (4.9) it can be seen that the saturation is actually a function of \( \theta(r, z) \) and \( \theta(r, z/L_e) \). From the first term in the series expansion of \( \theta \) (Equation (4.6)) it is possible to write:

\[ \theta(r, z) = a_1 X_1(r) Z \]  \hspace{1cm} (4.11)

where

\[ Z(z) = \exp(-\beta \frac{z}{L_e}) \]  \hspace{1cm} (4.12)

therefore

\[ \theta(r, \frac{z}{L_e}) = a_1 X_1(r) e^{-\beta \frac{z}{L_e}} \]  \hspace{1cm} (4.13)

which can be more neatly expressed as:

\[ \theta(r, \frac{z}{L_e}) = a_1 X_1(r) Z e^{-\beta} \]  \hspace{1cm} (4.14)

This allows the condition for the saturation maximum to be written:
\[ \frac{dS}{dZ} = 0 \quad (4.15) \]

although in practice it is easier to work in terms of \( \ln S \). Equation (4.16) shows that whenever \( d\ln S/dZ \) is zero, so is \( dS/dZ \) since \( S \) is merely some finite (non-zero) quantity:

\[ \frac{d\ln S}{dZ} = \frac{1}{S} \frac{dS}{dZ} \quad (4.16) \]

Using the result of Equation (4.14) in Equation (4.9) gives:

\[ S(r,z) = \left[ \frac{c_w + \Delta c \cdot a_1 \chi_1 Z^{1e^{-1}}}{A} \right] \exp \left( \frac{B}{T_w + \Delta T \cdot a_1 \chi_1 Z(z)} \right) \quad (4.17) \]

taking natural logarithms:

\[ \ln S = \ln \left( \frac{c_w + \Delta c \cdot a_1 \chi_1 Z^{1e^{-1}}}{A} \right) - \ln A + \left( \frac{B}{T_w + \Delta T \cdot a_1 \chi_1 Z(z)} \right) \quad (4.18) \]

which when differentiated yields:

\[ \frac{\partial \ln S}{\partial Z} = \frac{Z^{1e^{-1}}}{\text{Le} (c_w + \Delta c \cdot a_1 \chi_1 Z^{1e^{-1}})} - \frac{B\Delta T \cdot a_1 \chi_1}{(T_w + \Delta T \cdot a_1 \chi_1 Z(z))^2} \quad (4.19) \]

Since the condition for maximum saturation is that \( \partial \ln S/\partial Z \) is zero:

\[ \frac{B\Delta T a_1 \chi_1}{(T_w + T\Delta a_1 \chi_1 Z)^2} = \frac{\Delta c a_1 \chi_1 Z^{1e^{-1}}}{\text{Le} \cdot c_w + \Delta \text{Le} c_1 \chi_1 Z^{1e^{-1}}} \quad (4.20) \]

It is assumed that \( c_w << \Delta c \) and therefore the first term in the denominator on the right hand side may be ignored:

\[ B\text{Le}\Delta T a_1 \chi_1 \Delta c a_1 \chi_1 Z^{1e^{-1}} = \Delta c a_1 \chi_1 Z^{1e^{-1}} \left( T_w + \Delta T a_1 \chi_1 Z \right)^2 \quad (4.21) \]

which cancels and expands to:

\[ B\Delta T a_1 \chi_1 \text{Le} Z^{1e^{-1}} = Z^{1e^{-1}} \left( T_w^2 + 2T_w \Delta T a_1 \chi_1 Z + \Delta T^2 a_1^2 \chi_1^2 Z^2 \right) \quad (4.22) \]

\[ 0 = T_w^2 Z^{1e^{-1}} + 2T_w \Delta T a_1 \chi_1 Z^{1e^{-1}} + \Delta T^2 a_1^2 \chi_1^2 Z^{1e^{-1}} - B\Delta T a_1 \chi_1 \text{Le} Z \quad (4.23) \]

which when multiplied by \( Z^{1-e^{-1}} \) becomes:

\[ 0 = T_w^2 + 2T_w \Delta T a_1 \chi_1 Z + \Delta T^2 a_1^2 \chi_1^2 Z^2 - B\Delta T a_1 \chi_1 \text{Le} Z \quad (4.24) \]

which is a quadratic in \( Z \). Whilst this could be solved by the quadratic formula, in cases where the \( Z^2 \) term is small compared to the other two terms, it may be neglected, giving a linear equation which is readily solved. Whilst the value of \( Z \) is not yet known in this case, proceeding on the assumption that the approximation is correct.
allows the derived value of $Z$ to be used to test the approximation. If, as in this case, the $Z^2$ term is small then the approximation holds. This allows

$$0 = T_w^2 - Z(B\Delta T a_1, \chi_1, Le - 2T_w\Delta T a_1, \chi_1)$$

(4.25)
to be written. Therefore:

$$0 = T_w^2 - Z\Delta T a_1, \chi_1 (BLe - 2T_w)$$

(4.26)

$$\delta T(Le) = \Delta T a_1, \chi_1 Z = \frac{T_w^2}{BLe - 2T_w}$$

(4.27)

Equation (4.27) gives $\delta T$, the temperature difference between the wall and the point of maximum saturation, referred to as the distance $z_p$, along a given streamline.

Since it is assumed that $c_w$ is negligible compared to $\Delta c$ it follows that for a saturated system $\Delta c$ is equal to $c_v(T_{inlet})$:

$$\Delta c = A \exp\left(\frac{-B}{T_w + \Delta T}\right)$$

(4.28)

therefore

$$S_{max} = a_1 \chi_1 Z^{Le^{-1}} A \exp\left(\frac{-B}{T_w + \Delta T}\right) \exp\left(\frac{B}{T_w + \Delta T \delta T / \Delta T}\right)$$

(4.29)

which cancels to:

$$S_{max} = a_1 \chi_1 Z^{Le^{-1}} \exp\left(\frac{B}{T_w + \delta T} - \frac{B}{T_w + \Delta T}\right)$$

(4.30)

noting that

$$\frac{\delta T}{\Delta T} Z^{Le^{-1}} = \frac{\Delta T a_1 \chi_1 Z}{\Delta T} Z^{Le^{-1}} = a_1 \chi_1 Z^{Le^{-1}}$$

(4.31)

then

$$S_{max} = \frac{\delta T}{\Delta T} Z^{Le^{-1}} \exp\left(\frac{B}{T_w + \delta T} - \frac{B}{T_w + \Delta T}\right)$$

(4.32)

The value of $Z^{Le^{-1}}$ is given by rearranging Equation (4.27):

$$Z = \left(\frac{T_w^2}{BLe - 2T_w}\right) \left(\frac{1}{\Delta T a_1 \chi_1}\right) = \frac{\delta T}{\Delta T} \frac{1}{a_1 \chi_1}$$

(4.33)

thus the final solution is:
\[ S_{\text{max}} = \frac{\delta T}{\Delta T} \exp\left( \frac{B}{T_w + \delta T} - \frac{B}{T_w + \Delta T} \right) \cdot \left( \frac{T_w^2}{(B\text{Le} - 2T_w)(\Delta T a_i \chi_i)} \right)^{1.0} \] (4.34)

It is worth noting that this solution is expressed in terms only of five adjustable parameters: the wall temperature \( T_w \), the inlet temperature differential \( \Delta T \), the Lewis number \( \text{Le} \), the parameter \( B \) from the equilibrium concentration expression and the radius, \( r \), of the streamline under consideration. \( \delta T \) is given in terms of these quantities by Equation (4.27) and \( a_i \) is a constant. The polynomial:

\[ \chi_1(r) = 0.65r^4 - 1.63r^2 + 1 \] (4.35)

approximates \( \chi_1(r) \) to within 3% provided \( r < 0.9 \), and is of course constant for a specified streamline.

### 4.2.2.2 Key parameters affecting saturation

Equation (4.27) reveals something fundamental about the relationship between the radial position, \( r \), of the streamline under consideration and the axial distance, \( z \), at which the maximum saturation is seen. Since:

\[ Z(z) \chi_1(r) = \text{constant} \] (4.36)

then it follows that:

\[ Z = \frac{\text{constant}}{\chi_1(r)} \] (4.37)

When \( r = 1 \) then \( \chi_1(r) = 0 \), and when \( r = 0 \) then \( \chi_1(r) = 1 \). The function is continuous over this range and has no turning points. It can therefore be seen that when \( r = 1 \), \( Z = \infty \), which implies \( z = 0 \). Conversely, when \( r = 0 \), \( Z = \text{constant} \), which implies \( z \) is equal to some finite value. In plain English, for a streamline near the wall \( (r \rightarrow r_0) \) the saturation maximum will be near the inlet \( (z \rightarrow 0) \). As the streamline under consideration moves closer to the tube axis, so the position of maximum saturation for that streamline will move away from the tube inlet. This result holds for every scenario, regardless of the substances or temperatures in use.

A second universal result which can be derived from this treatment allows the parametric dependence of the global saturation maximum to be determined. This can be isolated by rewriting Equation (4.32) as:

\[ S_{\text{max}} \propto Z^{1.0} \] (4.38)

which if the function \( Z(z) \) is expanded becomes:
When the Lewis number is greater than unity, the term in round brackets will be positive and the largest value of $S_{\text{max}}(r)$ seen in the tube will occur where $z$ is large. Conversely, values of the Lewis number less than unity dictate that $S_{\text{max}}(r)$ will have its largest value when $z$ is small. Combining this result with the relationship between $r$ and $z$ already shown, the following it becomes possible to produce Table 4.1:

<table>
<thead>
<tr>
<th>Le</th>
<th>$r$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&lt; 1$</td>
<td>large</td>
<td>small</td>
</tr>
<tr>
<td>$&gt; 1$</td>
<td>small</td>
<td>large</td>
</tr>
</tbody>
</table>

Table 4.1
Dependence of the position of saturation maxima upon the Lewis number

The only parameter which controls where nucleation is seen is the Lewis number. Table 4.2 shows a number of Lewis numbers for water and dibutyl phthalate (commonly used in the experimental aerosol science literature) and caesium iodide and caesium hydroxide (expected to be important in reactor accident scenarios). Because the pressure dependencies of the vapour diffusivity and bulk density cancel out the Lewis number is virtually independent of pressure. A small sensitivity remains due to small variations in thermal conductivity and heat capacity.

<table>
<thead>
<tr>
<th>vapour</th>
<th>carrier gas</th>
<th>temperature</th>
<th>Le</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>air</td>
<td>313 K</td>
<td>0.9</td>
</tr>
<tr>
<td>dibutyl phthalate</td>
<td>air</td>
<td>313 K</td>
<td>5.0</td>
</tr>
<tr>
<td>caesium iodide</td>
<td>hydrogen</td>
<td>900 K</td>
<td>3.6</td>
</tr>
<tr>
<td>caesium iodide</td>
<td>hydrogen</td>
<td>1400 K</td>
<td>3.4</td>
</tr>
<tr>
<td>caesium iodide</td>
<td>steam</td>
<td>900 K</td>
<td>1.9</td>
</tr>
<tr>
<td>caesium iodide</td>
<td>steam</td>
<td>1400 K</td>
<td>2.2</td>
</tr>
<tr>
<td>caesium iodide</td>
<td>85:15 steam / H$_2$</td>
<td>900 K</td>
<td>2.3</td>
</tr>
<tr>
<td>caesium iodide</td>
<td>85:15 steam / H$_2$</td>
<td>1400 K</td>
<td>2.5</td>
</tr>
<tr>
<td>caesium hydroxide</td>
<td>hydrogen</td>
<td>900 K</td>
<td>5.5</td>
</tr>
<tr>
<td>caesium hydroxide</td>
<td>hydrogen</td>
<td>1400 K</td>
<td>5.4</td>
</tr>
</tbody>
</table>

Table 4.2
Typical Lewis numbers for experimental and reactor accident materials

It is worth noting two limitations to the method outlined above. Firstly, when the series solution for $\theta$ is truncated to the first term it is only applicable to
dimensionless axial distances greater than about 0.1. Although a modification to the above method has been proposed which allows nucleation near the walls to be treated (Barrett and Baldwin, 2000) this is not considered here because of the Lewis numbers of the substances found in reactor accidents. Since in every case the Lewis number is greater than unity, the global maximum saturation will occur at the centre of the tube, with \( z > 0.1 \). Consequently, the method outlined above may confidently be used for the assessment of reactor accident scenarios. The second limitation relates to the fact that the maximum saturation has been used to identify the location at which the nucleation rate will be greatest. Although the nucleation rate is a strong function of saturation, it also has a strong temperature dependence. Figure 4.2 shows the variation of temperature, saturation and nucleation rate along a streamline:

![Graph showing theoretical nucleation rate, saturation, and temperature profiles for a single streamline.](image)

**Figure 4.2**

*Temperature, saturation and nucleation rate profiles for a single streamline*

It can be seen that at a small distance prior to the saturation peak the temperature is significantly higher, although the saturation has fallen only slightly. In practice the maximum nucleation rate will always be seen at a slightly smaller axial displacement that the saturation maximum. Again, a modification of the method outlined above has been developed to address this issue (Barrett and Baldwin, 2000). However, it was found that within the scope of a first order correction the improvement in the results did not justify the added complexity, and the method of this work is used.
4.2.2.3 Number as a function of radius

To determine the number of particles flowing in the tube at a specified radius \( r \) requires the integration of the nucleation rate along the length of the tube. Although this is possible in theory, it is in fact simpler to use the approximation presented below to obtain the number of particles flowing. From the treatment above the temperature at \( z_p \) is known, as is the saturation at this point. This allows a quantity \( J_p \) to be calculated, the nucleation rate at the point of maximum saturation. The variation of the nucleation rate about \( z_p \) can be approximated by a Gaussian about this point, having the form:

\[
J(r, z) = J_p(r) \exp\left(-\frac{(z - z_p)^2}{2\sigma_z^2}\right) \quad (4.40)
\]

where \( \sigma_z \) represents the width of the peak. It may be found setting the second derivative with respect to \( z \) of the natural log of Equation (4.40) equal to that of the classical nucleation rate expression. This may be written:

\[
J(S, T) = K \exp\left(-\frac{f(T)}{\ln^2 S}\right) \quad (4.41)
\]

where

\[
K = \frac{2\sigma \nu T}{\sqrt{\pi m_1}} \left(\frac{\varepsilon \rho}{m_1}\right)^2 \quad (4.42)
\]

and

\[
f(T) = -\frac{16\pi \nu^2 \sigma^2}{3 (k_B T)^3} \quad (4.43)
\]

The second derivative of the natural logarithm of Equation (4.41) is:

\[
\frac{d^2 \ln J}{dz^2} = \frac{dZ}{dz} \left(\frac{dZ}{dZ} \frac{d \ln J}{dz} + \frac{dZ}{dz} \frac{d^2 \ln J}{dz^2}\right) \quad (4.44)
\]

which expands to:

\[
\frac{d^2 \ln J}{dz^2} = \frac{dZ}{dz} \left(\frac{dZ}{dz} \frac{d \ln J}{dz} + \frac{dZ}{dz} \frac{d^2 \ln J}{dz^2}\right) \quad (4.45)
\]

In order to find the derivatives of \( \ln J \) w.r.t. \( Z \)

\[
\frac{d \ln J}{dZ} = \frac{d \ln J}{d \ln S} \frac{d \ln S}{dZ} \quad (4.46)
\]

and
\[ \frac{d^2 \ln J}{dz^2} = \frac{d}{dz} \left( \frac{d \ln J}{d \ln S} \right) \left( \frac{d \ln J}{d \ln S} \right) \]  

(4.47)

are used.

Since by definition the maximum saturation is a turning point, \( d \ln S/dZ = 0 \) and thus Equation (4.46) evaluates to 0 also. Evaluating Equation (4.47) further yields:

\[ \frac{d^2 \ln J}{dz^2} = \frac{d^2 \ln S}{dz^2} \frac{d \ln J}{d \ln S} + \frac{d \ln S}{dz} \frac{d \ln J}{d \ln S} + \frac{d \ln S}{dz} \frac{d \ln J}{d \ln S} \]  

(4.48)

where the second term is equal to zero for the same reasons outlined above for Equation (4.46), allowing Equation (4.49) to be written:

\[ \frac{d^2 \ln J}{dz^2} = \left( \frac{d}{dz} \right)^2 \frac{d \ln J}{d \ln S} \left( \frac{d \ln J}{d \ln S} \right) \]  

(4.49)

the second derivative of \( \ln S \) w.r.t. \( Z \) is still required:

\[ \frac{d \ln S}{dz} = \frac{L e^{-1}}{Z} - \frac{B \Delta T a}{(T_w + \Delta T a Z)^2} \]  

(4.50)

and again:

\[ \frac{d^2 \ln S}{dz^2} = -\frac{1}{LeZ^2} + \frac{2Ba^2 \Delta T^2}{(T_w + \Delta T a Z)^3} \]  

(4.51)

where if \( \delta T (= \Delta T a) \ll \Delta T \) the second term can be ignored. The final version of Equation (4.49) also requires that \( d \ln J/d \ln S \) be known:

\[ \frac{d \ln J}{d \ln S} = \frac{d}{d \ln S} \left( \ln K - \frac{f(T)}{\ln^2 S} \right) \]  

(4.52)

\[ \frac{d \ln J}{d \ln S} = \frac{2f(T)}{\ln^3 S} \]  

(4.53)

combining all the above into Equation (4.49) gives:

\[ \frac{d^2 \ln J}{dz^2} = \left( \beta^2 Z \right)^2 \left( \frac{-1}{LeZ^2} \right) \frac{2f(T)}{\ln^3 S} \]  

(4.54)

This is to be set equal to the second derivative of the natural logarithm of Equation (4.40) w.r.t. \( z \), which is found thus:

\[ \frac{d \ln J}{dz} = \frac{d}{dz} \left( \ln J - \frac{(z - z_p)^2}{2\sigma_z^2} \right) \]  

(4.55)

\[ \frac{d \ln J}{dz} = \frac{z - z_p}{\sigma_z^2} \]  

(4.56)
setting Equations (4.54) and (4.57) equal gives:

\[- \frac{1}{\sigma_z^2} = \left( \beta_i^2 Z \right)^2 \left( \frac{-1}{LeZ^2} \right) \frac{2f(T)}{\ln^3 S} \]  

(4.58)

hence

\[ \sigma_z = \left( \frac{Le \ln^3 S}{2f(T)} \right)^{\frac{1}{2}} \left( \frac{1}{\beta_i^2} \right) \]  

(4.59)

The number of particles flowing in the tube a specified radius comes from the integral of Equation (4.40), however this is expressed in dimensionless terms. Multiplying by the ratio of dimensioned to dimensionless variables (from Equation (4.8)) gives:

\[ N(r) = \frac{r_0^2 V_m}{\alpha} \int_{-\infty}^{\infty} J(r, z) \, dz = \frac{r_0^2 V_m}{\alpha} J_p(r) \sqrt{2\pi \sigma_z} \]  

(4.60)

where the standard integral

\[ \int_{-\infty}^{\infty} J_p \exp \left( - \frac{(z - z_p)^2}{2\sigma_z^2} \right) \, dz = J_p \sqrt{2\pi \sigma_z} \]  

(4.61)

is used.
4.2.3 Numerical solution

The equations presented by Clement (1985) (Equations (4.2) and (4.3)) describe in some detail the spatial variation of temperature and vapour density during laminar tube flow. There are a number of obstacles to solving these equations numerically, however, many of which may be overcome by the simplifications to the problem outlined below.

4.2.3.1 Derivation of simplifications

Both Equations (4.2) and (4.3) contain the velocity vector, $\mathbf{v}_0$. Due to the temperature variations expected in all directions in the tube, it is probable that there will be significant variations in the density of the carrier gas. These variations will introduce non-axial flows, i.e. $\mathbf{v}_0$ will have non-zero components in the $x$ and $y$ directions. Determining $\mathbf{v}_0$ in this case would usually require that a momentum equation be solved, making the problem far more complicated. If it is assumed that the only bulk flow is along the tube axis, that is, the only non-zero component of $\mathbf{v}_0$ is in the $z$ direction, then $\mathbf{v}_0$ may be expressed more simply as the parabolic form given in Equation (4.1)

Because of the characteristics of the systems of interest (temperature differences, physical dimension) it is a reasonable approximation to assume that the gradients of temperature and vapour concentration in the axial direction are negligible compared to those in the radial direction (with the exception of the flow term, the first element in each equation). Combining this simplification with the new expression for the velocity, Equation (4.67), allows Equations (4.2) and (4.3) to be written:

\[
\rho(r,z)\bar{c}_p v(r,z) \frac{\partial T}{\partial z} - (c_{pV} - c_p) \frac{\partial c}{\partial r} - \frac{1}{r} \frac{\partial}{\partial r} \left( kr \frac{\partial T}{\partial r} \right) = \hat{L} \hat{m}_v \quad (4.62)
\]

\[
\rho(r,z)\bar{v}_0 v(r,z) \frac{\partial }{\partial r} - \frac{1}{r} \frac{\partial}{\partial r} \left( D \rho \frac{\partial v}{\partial r} \right) = - (1 - v_0) \hat{m}_v \quad (4.63)
\]

Expanding Equation (4.63) reveals the need to know the value of $\partial(D\rho)/\partial r$. The exact expression is

\[
\frac{\partial}{\partial r} (D\rho) = \frac{\partial}{\partial r} \left\{ \frac{D}{T} \left( \frac{M_g P}{R_g} + \left[ 1 - \frac{M_g}{M_v} \right] \frac{M_v M_g P c}{R_g (M_v - (M_r - M_g)c)} \right) \right\} \quad (4.64)
\]
unless the vapour concentration is very large, the term in square brackets may reasonably be ignored, simplifying Equation (4.64) to:

\[ \frac{\partial}{\partial r} D_{\rho} \approx \frac{\partial}{\partial r} \left( D \frac{M_{g}P}{R_{g}T} \right) = \frac{M_{g}P}{R_{g}} \frac{d}{dT} \left( \frac{D}{T} \right) \frac{\partial T}{\partial r} \]  

(4.65)

It is worth noting at this point that the equations for nucleation and growth of aerosol droplets are the same as used in the turbulent case.

A further series of approximations simplify the problem, whilst not compromising significantly the accuracy of the results.

Eliminating the temperature dependence of all thermophysical properties (except \( \rho_{ve} \) and \( P_{ve} \)) by setting them equal to constant (characteristic) values impacts directly upon the differential equations being solved, in that the differential of \( k \), the thermal conductivity, with respect to temperature is used in equation (4.62), and similarly the differential of \( D_{\rho} \) with respect to temperature is used in equation (4.63). Setting these derivatives to zero gives:

\[ \rho_{v} c_{p} \frac{\partial T}{\partial z} = \left( c_{p,v} - c_{p,g} \right) D_{\rho} \frac{\partial T}{\partial r} + k \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + L \dot{m}_{v} \]  

(4.66)

\[ \rho_{v} \frac{\partial \rho}{\partial z} = \frac{\partial}{\partial r} \left( \rho \frac{\partial r}{\partial r} \right) - \left( 1 - \rho \right) m_{v} \]  

(4.67)

Further, if the concentration is small, i.e. \( c << 1 \), then the radial vapour concentration gradient term will be close to zero, while the term \( (1-c) \) will be approximately equal to unity, giving:

\[ \rho_{v} c_{p} \frac{\partial T}{\partial z} = k \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + L \dot{m}_{v} \]  

(4.68)

\[ \rho_{v} \frac{\partial \rho}{\partial z} = \frac{\partial}{\partial r} \left( \rho \frac{\partial r}{\partial r} \right) - \dot{m}_{v} \]  

(4.69)

Finally, for a fairer comparison with the analytical solution (which can take no account of vapour mass depletion by condensation upon aerosol), the mass transfer term, \( \dot{m}_{v} \), is assumed to be zero.
The partial differential Equations (4.68) and (4.69) are turned into a set of ordinary differential equations by the use of orthogonal collocation (see Appendix A for a description), becoming:

\[ \frac{d}{dz} \left( r_i \right) = k \sum_{j=1}^{N_{cell}} b_{ij} T(r_j, z) + Lin_i(r_j, z) \]  

(4.70)

\[ \rho \nu(r_i) \frac{dc}{dr} = D \rho \sum_{j=1}^{N_{cell}} b_{ij} c(r_j, z) - \dot{m}_r \]  

(4.71)

The resulting equations (which are usually stiff) are solved by a predictor – corrector method, described in section A1.2.1.
4.3 Comparison of analytical and numerical forms

Comparing the numerical solution in the case where vapour depletion by aerosol processes is not treated to the analytical solution allows the accuracy of the analytical manipulations presented previously to be assessed.

A comparison of a number of cases reveals that the agreement between the two methods is excellent, and is in fact so good that a comparative graph would not show anything because of overlap between the series. To demonstrate qualitatively the nature of the results, a number of surfaces are plotted below.

The concentration surface is very similar to the temperature surface, differing only in that it is shifted left or right by the value of the Lewis number for the substance under consideration. Lewis numbers greater than unity shift the concentration surface to the right, less than unity to the left.

Figure 4.3
*The variation in temperature over a radially symmetric laminar flow tube*

Figure 4.4
*The effect of differing Lewis numbers on the spatial detail of saturation maxima in laminar tube flow*
Reference to Figure 4.4 confirms the conclusions of Table 4.1 demonstrating the
dependence of the position of maximum saturation (and hence nucleation rates) on the
Lewis number. They also confirm the inverse relationship between $r$ and $z$: when
looking at low values of $z$ (near the tube inlet), the saturation is seen to be highest near
the wall ($r$ is near 1). Conversely, further along the tube the highest saturation is
always seen near the middle, regardless of Lewis number.

Figures 4.5 – 4.7 compare the maximum saturation method with the maximum
saturation found by numerical calculations for water, dibutyl phthalate and caesium
iodide. Each graph shows the highest saturation found as a function of radius, the
corresponding axial position varies with radius as discussed above.

![Figure 4.5](image)

**Figure 4.5**

*Maximum saturation as a function of radius for water vapour in air. $T_w=260K$, $\Delta T=65K$*

It can be seen that agreement between the two methods is good in the centre of the
tube, but increasingly poor near the wall. This is unsurprising, given the expected
inability of the analytical method to deal well with short distances. For substances
with a Lewis number greater than 1 (CsI, DBP) this is unimportant as the saturations
seen near the wall will lead to negligible aerosol production compared to the amount
produced nearer the centre of the tube. The analytical method is seen to slightly over-
predict the saturation near the global saturation maximum (near the wall for water,
near the axis for DBP and CsI). This has the happy effect of improving the accuracy
of estimates of the maximum nucleation rate based upon maximum saturation, and
explains in part why the first order correction discussed earlier provides no great
improvement. Looking at the numerical results near the wall, it can be seen that the results tend to a constant value as the radius increases. Baldwin and Barrett (2000) rederived the results shown here using a solution of \( \phi(r,z) \) due to Ingham (1975) which is valid in the region near the inlet and near the wall. Results from this analytical method exhibit this tendency towards a fixed value near the wall. In light of the Lewis numbers of materials of interest to the reactor accident problem, this solution will not be developed further.

![Graph showing maximum saturation as a function of radius for dibutyl phthalate vapour in air.](image1)

**Figure 4.6**

*Maximum saturation as a function of radius for dibutyl phthalate vapour in air. \( T_w=260K, \Delta T=80K \)*

![Graph showing maximum saturation as a function of radius for caesium iodide vapour in hydrogen.](image2)

**Figure 4.7**

*Maximum saturation as a function of radius for caesium iodide vapour in hydrogen. \( T_w=800K, \Delta T=150K \)*
4.4 Prediction of Conditions for "Significant" Nucleation

Using the same idea used in section 3.3 to determine the conditions for the "significant" nucleation in turbulent flow, the result of section 4.2.2.1 (Equation (4.34)) can be combined with Hale's scaled nucleation theorem to determine when nucleation will occur in laminar flow. Substituting Equation (4.27) into Equation (4.34) and taking natural logarithms gives:

\[
\ln S_{\text{max}} = \ln \left( \frac{T_w^2}{\Delta T(B\text{Le} - 2T_w)} \right) + \frac{B}{T_w} \frac{T_w^2}{\text{Le} - 2T_w} - \frac{B}{T_w + \Delta T} + \left( \frac{1}{\text{Le} - 1} \right) \ln \left[ \frac{T_w^2}{B\text{Le} - 2T_w} \frac{1}{\Delta T a_i \chi_i(r)} \right]
\]

(4.72)

By the same arguments used to produce Equations (3.24), (3.26) and (3.27), the variables \( \Delta T \) and \( B \) in Equation (4.72) can be scaled by \( T_w \) to give Equation (4.73):

\[
\ln S_{\text{max}} = -\ln \left( \frac{\Delta T \left( \frac{B}{T_w} \text{Le} - 2 \right)}{T_w} \right) + \frac{\left( \frac{B}{T_w} \right)^2 \text{Le} - 2 \frac{B}{T_w}}{\text{Le} - 1} - \frac{B}{T_w + \Delta T} + \left( \frac{1}{\text{Le} - 1} \right) \ln \left( a_i \chi_i(r) \frac{\Delta T}{T_w} \left( \frac{B}{T_w} \text{Le} - 2 \right) \right)
\]

(4.73)

The critical saturation is scaled in a near identical fashion to that used in the turbulent case to give:

\[
\ln S_{c_r} = 0.53 \Omega^1 \left\{ \frac{T_e - B}{T_w T_e - 2} \frac{T_e T_w}{T_w - 1} \right\}^{\frac{1}{2}} \left( 1 + \frac{\ln(10^6 J)}{2\ln J_e} \right)
\]

(4.74)

Setting Equations (4.73) and (4.74) equal gives an equality which is solved using the same routine from Press et al. (1992) as used in the turbulent case:

\[
f\left( \frac{B}{T_w}, \text{Le}, \frac{\Delta T}{T_w}, \frac{T_e}{T_w}, \Omega, \chi_i, J \right) = 0
\]

(4.75)

Note the addition of the radial position to the list of parameters.

Hale's recommended value for \( \Omega \) of 2.1 is used, and the ratio \( T_e / T_w \) again held equal to 2.0.
Figure 4.7
*Conditions in laminar tube flow necessary to achieve specified nucleation rates. Calculated at dimensionless radius \( r = 0.8 \)*

Figure 4.7 shows that as in the turbulent case, the Lewis number is a more important condition for the occurrence of “significant” nucleation than is the actual definition of “significant”. Since, in laminar flow, the radius at which the global maximum saturation is seen varies with the Lewis number, it may be expected that calculations performed at different radii will give different conditions. Figure 4.8 confirms this, and shows the effect of using the “wrong” radius. Since for \( Le = 0.8 \) the maximum saturation is seen near the wall, it follows that calculating the condition away from the wall (e.g. \( r = 0.8 \)) will require more vigorous conditions for the same peak saturation (ergo peak nucleation rate) to be achieved. Conversely, Lewis numbers greater than 1 lead to saturation maxima at the centre of the tube: calculating the condition near the wall will again require more vigorous conditions to achieve the requisite saturation away from the maximum.

As a practical footnote, it is important to choose the conditions over which the algorithm is required to search carefully, as it is possible to devise combinations of conditions in which the temperature differential between wall and the point of maximum saturation is greater than the temperature differential at the inlet. This is true equally for turbulent and laminar flow.
4.5 Condition for vapour condensation to be important

The removal of vapour due to the growth of nucleated particles has so far been assumed not to consume sufficient vapour to perturb the nucleation rate. This assumption will not be valid in all cases, and a means of determining when condensation on to particles is significant is now derived. The first step is to produce an estimate of the change in saturation caused by particle growth. This change can then be related to the change in saturation required to reduce the nucleation rate by a factor e.

The derivation which follows is for the laminar flow scenario; further it is assumed that \( Le > 1 \) and \( Cn \gg 1 \). In light of this Lewis number, consideration is restricted to flow at the axis (\( r=0 \)).

4.5.1 Condensation upon new aerosol

Previous work gives analytical forms for the distance \( z_p \) at which the highest saturation \( S_{max} \) is seen along a specified streamline. The temperature at this point is known to be \( T_p \), and the nucleation rate at this point \( J_p \). It is assumed that this is the maximum nucleation rate seen. The evolution of the nucleation rate in the axial direction is approximated by a Gaussian, centred about \( z_p \), given by Equations (4.40) and (4.59).

Integration of Equation (4.40) will yield the number of particles formed over a specified axial distance. Equation (4.40) can only be integrated analytically over the range \(-\infty \) to \( +\infty \). Although distances less than \( z = 0 \) are meaningless in this context, in most cases the analytical integral can be used satisfactorily due to the rapid fall-off of a Gaussian with distance. From tables (Spiegel, 1968), only 16% of the area under a Gaussian occurs prior to a point \( \sigma_z \) away from the peak. When this point is \( 3\sigma_z \) away from the peak, less than 0.2% of the area occurs prior to it. Therefore, provided a distance of at least \( 3\sigma_z \) separates the peak of the Gaussian and the inlet to the tube, the use of this method involves a very small loss of accuracy. The integral is given by Equation (4.60) which is the total number of particles nucleated per unit area per second at a given radius. The number per second is obtained by multiplying this quantity by an area \( \pi x^2 \), where \( x \) is some small, arbitrary distance in the radial direction.
From the form of Equation (4.40) it follows that at a distance $\sigma_z/\sqrt{2}$ prior to $z_p$, the nucleation rate will be reduced by a factor $e^{-\lambda}$ (compared to that at the point $z_p$). Since (in the Gaussian approximation) exactly half the particles to be nucleated have formed by distance $z_p$, it is assumed that at this earlier distance (named $z_A$) approximately one quarter of the total nucleation has occurred, i.e. $N(0)/4$. By considering the growth of all particles nucleated up to $z_A$ during their passage from $z_A$ to $z_p$ the effect of this condensation can be assessed. From Barrett and Clement (1988) the growth rate in the continuum regime can be stated as:

$$\dot{R} = \frac{dR}{dt} = \frac{A(S-1)}{R}$$

(4.76)

If the effects of radiation are not considered, and $C_n >> 1$, their terms [RAD] and [HEAT] may be neglected, and $A$ is defined:

$$A = \frac{D\rho_w(T_p)}{\rho_l}$$

(4.77)

It is assumed that the saturation near the peak remains constant, allowing the use of $S_{max}$ in Equation (4.76). Integration of this expression with respect to time is now simpler, and yields the radius of the particles at $z_p$:

$$\int_0^R R' dR' = A(S_{max} - 1)\int_0^{t_g} dt$$

(4.78)

$$\frac{1}{2} R^2 = A(S_{max} - 1)t_g$$

(4.79)

$$R = \sqrt{2A(S_{max} - 1)t_g}$$

(4.80)

where $t_g$ is the time for the particles nucleated at $z_A$ to travel to $z_p$. This is found viz.:

$$t_g = \frac{\text{distance}}{\text{velocity}} = \frac{\sigma_z}{\sqrt{2} V_m \alpha'}$$

(4.81)

Note the second term is required to give dimension to the distance $\sigma_z/\sqrt{2}$.

The mass consumed by the growth of these particles is then found from their volume and density:

$$M = \frac{4\pi}{3} \rho_l R^3 \left( \frac{N(r)}{4} \right) \pi x^2$$

(4.82)

Since the mass required to change a vapour density is given by

$$V_m \pi x^2 [\rho_v(\text{before}) - \rho_v(\text{after})]$$

(4.83)
it follows that the saturation change by the growth of particles nucleated up to \( z_d \) as they travel from \( z_d \) to \( z_p \) is:

\[
\Delta S = \frac{M}{\pi x^2 V_m \rho_m(T_p)} \tag{4.84}
\]

Barrett and Clement (1990) state the saturation change required to reduce a nucleation rate by a factor \( e \) as (where \( A \) in their work is equivalent to \( f(T) \) in this work):

\[
\Delta S = S_0 \left(\frac{\ln S_0}{2f(T)}\right)^3 \tag{4.85}
\]

which is derived as follows:

A nucleation rate, \( J' \), which is equal to \( J_p/e \) is sought. Therefore:

\[
\frac{J'}{J_p} = \frac{1}{e} \tag{4.86}
\]

and:

\[
\ln\left(\frac{J_p}{e}\right) - \ln(J_p) = -1 \tag{4.87}
\]

which is the change in \( J \) with respect to \( S \) for a given change, i.e.

\[
1 = \frac{d(\ln J)}{dS} \Delta S \tag{4.88}
\]

Classical nucleation theory can be written in the following form:

\[
\ln J = \ln K - \frac{f(T)}{(\ln S)^2} \tag{4.89}
\]

which when differentiated with respect to \( S \) and substituted into Equation (4.88) above gives Equation (4.85), the result of Barrett and Clement.

Equation (4.84) can be combined with (4.82) to give

\[
\Delta S = \frac{4\pi \rho_p R^3}{3V_m \rho_m(T_p)} \left(\frac{N(r)}{4}\right) \tag{4.90}
\]

using the definition of \( R \) in Equation (4.80) gives Equation (4.90) as:

\[
\Delta S = \frac{4\pi \rho_p \left(2A(S_{\text{max}} - 1) t_g \right)^{1/3}}{3V_m \rho_m(T_p)} \left(\frac{N(r)}{4}\right) \tag{4.91}
\]

Incorporating the definitions of \( A \) and \( t_g \) from Equations (4.81) and (4.77) gives:
\[
\Delta S = \frac{4\pi \rho \left( \frac{2D\rho w (T_p)}{\rho_{eq}} \left( S_{\text{max}} - 1 \right) \sigma_{\text{p}}^2 \right)^{\frac{3}{2}}}{3V_n \rho_{w} (T_p)} \left( \frac{N(r)}{4} \right) \tag{4.92}
\]

Further incorporation of the definition of the number, \(N\), from Equation (4.60) gives
\[
\Delta S = \frac{4\pi \rho \left( \frac{2D\rho w (T_p)}{\rho_{eq}} \left( S_{\text{max}} - 1 \right) \sigma_{\text{p}}^2 \right)^{\frac{3}{2}}}{3V_n \rho_{w} (T_p)} \left( \frac{r_s^2 \rho_{w} J_p (r) \sqrt{2\pi\sigma_z}}{4\alpha'} \right) \tag{4.93}
\]

which simplifies to:
\[
\Delta S = \frac{\sigma_{\text{p}}^2 \rho_{w} J_p \rho_{eq}^\frac{1}{4} \pi^\frac{3}{2} 2^\frac{3}{2} D^\frac{3}{2} (S_{\text{max}} - 1)^\frac{3}{2}}{3\alpha'\rho_{eq}^\frac{1}{3}} \tag{4.94}
\]

Cancelling, and using the definition of \(\sigma_{\text{p}}\) from Equation (4.59) gives Equation (4.94) as:
\[
\Delta S = \frac{r_s^2 J_p \rho_{eq}^\frac{1}{4} \pi^\frac{3}{2} 2^\frac{3}{2} D^\frac{3}{2} (S_{\text{max}} - 1)^\frac{3}{2}}{3\alpha'\rho_{eq}^\frac{1}{3}} \left[ \frac{Le \ln^3(S)}{2f(T)} \right] \tag{4.95}
\]

When the change in saturation due to growth is less than that required to change the nucleation rate by a factor \(e\), this condensation may be assumed to be unimportant. This condition can be written by combining Equations (4.95) and (4.85) into an inequality viz.:
\[
\frac{r_s^2 J_p \rho_{eq}^\frac{1}{4} \pi^\frac{3}{2} 2^\frac{3}{2} D^\frac{3}{2} (S_{\text{max}} - 1)^\frac{3}{2}}{3\alpha'\rho_{eq}^\frac{1}{3}} \left[ \frac{Le \ln^3(S)}{2f(T)} \right] << \frac{S_{\text{max}} \ln^3(S_{\text{max}})}{2f(T)} \tag{4.96}
\]

Provided \(S_{\text{max}} \gg 1\) then
\[
\frac{1}{r_s^2} \frac{3\beta_i^\frac{1}{3}}{2\sqrt{\rho_{w} \pi^3 S_{\text{max}}}} \frac{\rho_{eq}^\frac{1}{4}}{D^\frac{3}{2}} \left[ \frac{f(T)}{Le \ln^3 S} \right] \gg J_p \tag{4.97}
\]

and since
\[
\alpha' = \frac{k}{c_p \rho} \quad \text{and} \quad Le = \frac{k}{c_p \rho D} \quad \therefore \quad Le = \alpha' \quad \frac{D}{4} \tag{4.98}
\]

Equation (4.97) becomes:
\[
\frac{1}{r_s^2} \frac{3\alpha' \beta_i^\frac{1}{3}}{2\sqrt{\rho_{w} \pi^3 S_{\text{max}}}} \left[ \frac{Le \cdot f(T)}{\ln^3 S} \right] \gg J_p \tag{4.99}
\]

which is the condition for the growth of previously nucleated aerosol to have a negligible impact on subsequent nucleation.
4.5.2 Condensation upon seed aerosol particles

When seed particles enter the tube, condensation upon these particles also has the potential to affect the saturation and hence nucleation rate in the tube significantly. Although in principle the approach described above can be adopted to assess the effect of such aerosols, because of the large variations in saturation from z=0 to z_p it is no longer satisfactory to consider the saturation in the growth rate expression (4.76) as constant. Instead the growth rate is given by:

$$\dot{R} = \frac{dR}{dt} = \frac{A(S(z)-1)}{R}$$  (4.100)

Integration of Equation (4.100) now requires integration of the saturation with time (or distance). Although combination of the analytical solutions for temperature, Equation (2.70), and concentration, Equation (2.71), gives an Equation for the spatial variation of the saturation, analytical integration of this expression is not possible. However, it is possible to integrate Equation (4.100) if S(z) is approximated by a Gaussian, i.e.:

$$S(z) = (S_{max} - 1) \exp\left(-\frac{(z - z_p)^2}{2\sigma_r^2}\right)$$  (4.101)

where \(\sigma_r\) is found by taking logarithms and equating the second derivative with respect to \(z\) of Equation (4.101) with the second derivative of the analytical form for \(S(r,z)\). Firstly, for Equation (4.101), this gives:

$$\ln S = \ln(S_{max} - 1) - \frac{(z - z_p)^2}{2\sigma_r^2}$$  (4.102)

$$\frac{d\ln S}{dz} = -\frac{2(z - z_p)^2}{2\sigma_r^2}$$  (4.103)

$$\frac{d^2\ln S}{dz^2} = -\frac{2}{2\sigma_r^2} = -\frac{1}{\sigma_r^2}$$  (4.104)

Differentiation of the analytical expression for ln(S) is more involved.

$$\ln(S) = \ln\left(c_e + \Delta c \theta\left(r, \frac{z}{L_e}\right)\right) - \ln(A) + \frac{B}{T_w + \Delta T\theta(r,z)}$$  (4.105)

Since in the truncated form

$$\theta(r,z) = a_1 x_1(r)Z(z) \quad \text{where} \quad Z(z) = \exp(-\beta_l^2 z)$$  (4.106)

then when \(r = 0\)
\[ \theta(z) = a_1 Z(z) \quad \text{(4.107)} \]

and Equation (4.105) can be written (assuming that \( c_w >> \Delta c \))

\[ \ln(S) = \ln\left(\Delta c a_1 Z(z)^{T_e} \right) - \ln A + \left( \frac{B}{T_w + \Delta T a_1 Z(z)} \right) \quad \text{(4.108)} \]

The differential of \( S \) with respect to \( z \) is given by:

\[ \frac{d \ln S}{dz} = \frac{d \ln S}{dz} \frac{dZ}{dz} \quad \text{(4.109)} \]

where

\[ \frac{dZ}{dz} = \frac{d}{dz} \left( \exp(-\beta^2 z) \right) = -\beta^2 Z \quad \text{(4.110)} \]

However, it is the second differential w.r.t. \( z \) which is required, which is of course the derivative of Equation (4.109) w.r.t. \( z \):

\[ \frac{d^2 \ln S}{dz^2} = \frac{dZ}{dz} \left( \frac{dZ}{dz} \right) \frac{d\ln S}{dz} + \frac{dZ}{dz} \frac{d^2 \ln S}{dz^2} \quad \text{(4.111)} \]

where the first and second differentials of \( S \) w.r.t. \( Z \) are given by Equations (4.50) and (4.51) respectively. Again, it is assumed that \( \delta T = \Delta T a_1 Z \ll \Delta T \) and the second term is ignored.

Since at the peak (which is the point at which gradients are being equated) the first derivative of \( S \) w.r.t. \( z \) (and hence \( Z \)) is, by definition, zero. Equation (4.112) then becomes:

\[ \frac{d^2 \ln S}{dz^2} = \left( \frac{dZ}{dz} \right)^2 \frac{d^2 \ln S}{dz^2} = -\beta^2 \frac{-1}{Le Z^2} = -\beta^4 \frac{1}{Le} \quad \text{(4.113)} \]

which when set equal to Equation (4.104) gives

\[ \frac{-1}{\sigma_s^2} = -\beta^4 \frac{1}{Le} \quad \text{(4.114)} \]

and thus

\[ \sigma_s = \sqrt{\frac{Le}{\beta^4}} \quad \text{(4.115)} \]

Equation (4.101) can then be integrated using the standard integral of a Gaussian thus:

\[ \int_{-\infty}^{\infty} (S-1)dz' = \frac{r_s^2 V_m}{\alpha} \int_{-\infty}^{\infty} (S-1)dz \quad \text{(4.116)} \]
\[
\frac{r^2 V_n}{\kappa'} \int_{-\infty}^{z} (S-1) \, dz = \frac{r^2 V_n}{\kappa'} (S_{\text{max}} - 1) \sqrt{\frac{\pi}{2}} \sigma_x \quad (4.117)
\]

Note the term to give the expression dimension, and also that the same assumption as applied to the integration of Equation (4.40) holds here too.

This result allows the radii reached by seed aerosol at point \( z_p \) to be calculated by solving the growth rate Equation from \( z = 0 \) to \( z = z_p \):

\[
\frac{dR}{dt} = \frac{V(r)}{dR} \frac{dR}{dz} = \frac{A(S(z)-1)}{R} \quad (4.118)
\]

which is solved:

\[
V(r) \int_{R_0}^{R} dR' = A \int_{-\infty}^{z_p} (S(z)-1) \, dz' \quad (4.119)
\]

where Equation (4.117) gives the solution to the integral on the right hand side, hence:

\[
\frac{1}{2} V(r) \left[ R^2 - R_0^2 \right] = A \frac{r^2 V_n}{\kappa'} (S_{\text{max}} - 1) \sigma_x \sqrt{\frac{\pi}{2}} \quad (4.120)
\]

thus

\[
R = \left( \frac{2A r^2}{\kappa'} (S_{\text{max}} - 1) \sigma_x \sqrt{\frac{\pi}{2}} + R_0^2 \right)^{1/2} \quad (4.121)
\]

which can be written

\[
R = \left( \varphi (S_{\text{max}} - 1) + R_0^2 \right)^{1/2} \quad (4.122)
\]

if

\[
\varphi = \frac{2A r^2}{\kappa'} \sigma_x \sqrt{\frac{\pi}{2}} = \frac{2A r^2}{\kappa'} \sqrt{\frac{Le}{\beta_i^2}} \sqrt{\frac{\pi}{2}} \quad (4.123)
\]

In principle, Equation (4.121) could be substituted into Equation (4.90), and the derivation of the condition for condensation upon seed aerosol to significantly affect nucleation would proceed largely as before. However, the final result is now far more complicated. This is simplified by identifying two limiting cases. When the seed aerosol particles are small (compared to the amount by which they grow) then \( R_0^2 \ll \varphi (S_{\text{max}} - 1) \) and the \( R_0^2 \) term can be ignored. The radius is then defined as for the nucleation case. When the seed aerosol particles are large compared to their growth, \( R_0^2 \gg \varphi (S_{\text{max}} - 1) \), and it becomes necessary to consider this expression in more detail. Rearrangement of Equation (4.123) followed by a Taylor series expansion gives:
\[(\phi(S_{\text{max}} - 1) + R_0^2) = R_0 \left(1 + \frac{\phi(S_{\text{max}} - 1)}{R_0^2}\right)^{\frac{1}{2}} \] (4.124)

The volume change associated with the growth of an aerosol from a radius \(R_0\) to a radius \(R\) is given by:

\[
\Delta V = \frac{4}{3} \pi \left[ R^3 - R_0^3 \right] \quad (4.125)
\]

or

\[
\Delta V = \frac{4}{3} \pi \left[ R_0^3 \left(1 + \frac{\phi(S_{\text{max}} - 1)}{2R_0^2}\right) - R_0^3 \right] \quad (4.126)
\]

again, using the first term only of a Taylor series expansion gives:

\[
\Delta V = \frac{4}{3} \pi \left[ R_0^3 \left(1 + \frac{3\phi(S_{\text{max}} - 1)}{2R_0^2}\right) - R_0^3 \right] \quad (4.127)
\]

which cancels to:

\[
\Delta V = 2\pi R_0 \phi(S_{\text{max}} - 1) \quad (4.128)
\]

Strictly in Equation (4.90) it is the change in volume due to aerosol growth which is required anyway, allowing Equation (4.128) to be substituted straight in.

Following first the case when the seed aerosol is small compared to the amount by which it grows (where \(N_s\) is the number density of seed aerosol particles):

\[
\Delta S = \frac{4\pi\rho_l}{3\rho_w} (\phi(S_{\text{max}} - 1))^3 N_s \quad (4.129)
\]

Incorporation of Equations (4.77) and (4.122) for \(A\) and \(c_p\) respectively gives:

\[
\Delta S = \frac{4\pi\rho_l}{3\rho_w} \left[ \frac{2Le^{-\frac{1}{2}} \rho_w r_0^2}{\rho_l \beta_l^2} \sqrt{\frac{\pi}{2}} (S_{\text{max}} - 1) \right] N_s \quad (4.130)
\]

which may be tidied to

\[
\Delta S = \frac{4}{3} \frac{\pi \rho_l}{\beta_l^2 \rho_w^2} Le^{-\frac{1}{2}} r_0^3 (S_{\text{max}} - 1)^{\frac{3}{2}} N_s \quad (4.131)
\]

Combining Equations (4.131) and (4.85) give the inequality:

\[
\frac{2\pi \rho_l^2 Le^2 r_0^3}{3\beta_l^3 \rho_w} (S_{\text{max}} - 1)^{\frac{3}{2}} N_s \ll S_{\text{max}}^3 \left(\frac{\ln S_{\text{max}}}{2f(T)}\right) \quad (4.132)
\]

which rearranges to:

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In the alternative case where the seed aerosol is large compared to the amount by which it grows, from the expression below relating a change in aerosol volume to a change in saturation:

\[
\Delta S = N_s \frac{\Delta V \rho_f}{\rho_{ve}} \quad (4.134)
\]

From Equation (4.128) which gives the volume change associated with the growth of a particle from radius \(R\) to \(R_0\) as a function of saturation it is possible to write:

\[
\Delta S = N_s \frac{2 \rho_f \pi R_0 \varphi (S_{max} - 1)}{\rho_{ve}} \quad (4.135)
\]

therefore, combination with the result of Barrett and Clement (1990), Equation (4.85) gives:

\[
N_s \frac{2 \rho_f \pi R_0 \varphi (S_{max} - 1)}{\rho_{ve}} < N_s < \frac{\ln S_{max}}{2 f(T)} \quad (4.136)
\]

which when expanded using the definitions of \(\varphi\) and \(A\) (4.123) and (4.77) respectively gives:

\[
N_s \frac{4 \rho_f \pi R_0 D \rho_{ve} r_0^2 (S_{max} - 1) \sqrt{Le}}{\rho_f \rho_{ve} \alpha \beta_i^2} \sqrt{\frac{\pi}{2}} < \frac{\ln S_{max}}{2 f(T)} \quad (4.137)
\]

cancelling and rearranging gives:

\[
N_s < \frac{\beta_i^2 Le^\frac{1}{3}}{2^\frac{1}{3} \pi^\frac{2}{3} R_0 r_0^2} \frac{\ln S_{max}}{f(T)} \quad (4.138)
\]
4.5.3 Results and Conclusions

Figure 4.9 shows both the peak nucleation rate for DBP as a function of inlet temperature differential, and the condition for condensation upon aerosol nucleated to be important under these (peak) conditions.

**Figure 4.9**
*Comparison of peak nucleation rates and the condition for condensation to be important for DBP as a function of ΔT*

**Figure 4.10**
*Peak saturations as a function of inlet temperature differentials*
As well as the expected result that increasing temperature differentials cause rapidly increasing nucleation rates, it can be seen that the number of particles which must be nucleated to perturb subsequent nucleation falls slightly with increasing temperature. This can be explained by the dependence of the maximum saturation on the inlet temperature differential (shown in Figure 4.10). Any particles nucleated in more highly saturated environments will grow more rapidly, causing a bigger drop in the saturation. Given a large per droplet fall in saturation, it is clear that fewer droplets are required to cause a given change.

Figure 4.11 shows a similar comparison for the case of seed aerosol. The nucleation rate plotted in Figure 4.9 has been converted to a total number of particles nucleated, using the methods of Barrett and Baldwin (2000). Since the condition for seed which does not grow significantly compared for its initial size is a function seed aerosol radius, it is plotted in generic form as $NR_0$ rather than $N$; to make comparisons for a specific radius the results shown are simply divided by this radius.

![Figure 4.11](image)

**Figure 4.11**

Comparison of the total number of aerosol particles nucleated with the number of seed particles required to cause a significant change in nucleation. Note the condition for “large” seed particles is plotted as $NR_0$

Considering first the case of “small” aerosols ($R_0$ is negligible) a similar situation is seen to the nucleation only case: a small decrease in the number of seed
particles required to affect nucleation significantly is seen as the inlet temperature rises. This is again due to the concomitant higher saturations which increase the per droplet saturation decrease, thus reducing the total number required. When considering larger seed aerosols, which do not grow much, the effect of the increased saturation at higher inlet temperature differentials is nowhere near as pronounced. A simple increase in number density is all that is required to counter the effect of more particles being nucleated.
4.6 Conclusions

Using the results of previous workers it has been possible to develop a number of new analytical methods for determining the nature of aerosol behaviour in laminar tube flow. Some key parameters control this behaviour have also been identified through this work.

A comparison of the analytical equations used to describe basic laminar tube flow with more complex numerically soluble forms shows good agreement in the case where vapour depletion by mass transfer to aerosol is ignored. These analytical approximations have been used to determine an expression for the maximum saturation seen along a specified streamline. Comparison with the numerical results shows this method gives good agreement near the centre of the tube. This is as expected given a limitation of the analytical solution used. Although a modified analytical solution has been applied to the problem for this case it is not used here for reasons outlined below. The Lewis number has been shown to be instrumental in determining the location of the global maximum saturation. All materials considered of interest in nuclear reactor accidents have Lewis numbers greater than unity, implying the maximum saturations at the tube axis. This information confirms the applicability of the maximum saturation method developed here to reactor accident scenarios. Further, this method has revealed a universal inverse relationship between the radius at which maximum saturation is seen and the axial displacement of this point.

In an extension of the work presented in Chapter 3, the maximum saturation solution is combined with the work of Hale to allow the rapid prediction of conditions liable to cause “significant” nucleation. Again, the definition of “significant” may be freely chosen, and the conclusions drawn are largely the same. In addition, the radial dependencies inherent in laminar flow problems confer a radial aspect to the problem. Unsurprisingly it is found that the choice of radius is crucial to the accuracy of the method.

From previous work by Barrett and Clement conditions for the effect of vapour depletion to be important have been developed. They allow the estimation of the peak nucleation rate or quantity of seed aerosol particles required to cause a significant fall in nucleation. In each case, the primary dependency is found to be the radius of the tube.
Chapter 5

Laminar Flow with Vapour Depletion
5.1 Introduction

So far, all work has assumed that the consumption of vapour and concomitant release of latent heat due to the growth of aerosol (either seed or freshly nucleated) can be ignored. Whilst this allows simple analytical forms to be developed which give some insight into the possible extent and location of nucleation, it does not directly allow the quantitative effects of aerosol processes to be accounted for. It is expected that the effects of vapour depletion will be significant in reducing the peak nucleation rate as well as reducing the amount of vapour leaving the system or being deposited upon the walls in several cases. It is therefore important to quantify these effects, particularly as these cases will probably involve the highest aerosol densities.

This chapter will evaluate some of the methods developed in previous chapters for assessing the significance of vapour depletion processes and develop a semi-analytical approach for estimating the extent of aerosol formation when vapour depletion is significant. In this way it will be possible to determine when vapour depletion may be expected to be important in controlling aerosol processes in the tube, and to allow (semi-) analytical predictions of aerosol formation and growth processes to be made in the event that depletion is important.

Comparisons are made with the numerical method of solution presented in Section 4.2.3 to assess the accuracy of the new method. The numerical method of solution is implemented in the full form of Equations (4.70) and (4.71), taking account of vapour depletion and latent heat release. The mass flux term \( \dot{m}_v \) is calculated for each collocation radius as shown in Equation (5.1). This comprises two terms, the first related to the consumption of vapour by aerosol nucleation, and the second due to the growth of this aerosol. It is worth recalling that this form assumes a monodisperse aerosol, as was discussed in Section 3.4.4.

\[
\dot{m}_v = \frac{4\pi I_n dR_0^3}{3} + I_n N \quad (5.1)
\]

This form is also used to assess the mass balance of vapour flowing into the tube, to enable qualitative predictions of the distribution of fission product vapours between the tube walls, aerosol and the vapour phase to be made.
5.2 Comparison of Growth Rate Forms

The linearised form used to provide a first estimate of the droplet growth rate and thus droplet temperature (Section 3.4.2) is only expected to be valid when the supersaturation is low, an issue previously addressed by Williams (1995). In the turbulent flow case the droplet temperature was always found iteratively using the full droplet growth expressions. The issue of whether this is necessary for the materials of interest is now addressed.

Calculations were made of the droplet growth rate as predicted by both the linearised and iteratively determined growth rates for water, dibutyl phthalate and caesium iodide at two temperatures. Growth rates were found for a range of saturations. A different range was used for each compound, and was selected to extend from unity to slightly beyond the highest saturation which might reasonably be expected when growth consumes sufficient vapour to adversely affect nucleation (nucleation is said to be "quenched"). Table 5.1 shows the ranges of saturations investigated.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Minimum saturation</th>
<th>Maximum saturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>1.1</td>
<td>4</td>
</tr>
<tr>
<td>dibutyl phthalate</td>
<td>1.1</td>
<td>6000</td>
</tr>
<tr>
<td>caesium iodide</td>
<td>1.1</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 5.1
The ranges of saturations considered in investigating the accuracy of the linearised approximation to droplet growth rates

It was found that water showed the greatest difference between the two methods, with the linearised form over-predicting growth rates by up to 83% at the highest saturations (see Figure 5.1, overleaf). By contrast, for caesium iodide the two forms were within 0.4% of each other. In writing the linearised form, the approximation was made that $S_P\text{_{sw}}$ is much less than the total pressure. Table 5.1 shows that for both caesium iodide and water this approximation is invalid in similar measure. The question which must then be answered is why two compounds show such markedly different sensitivities to this approximation at comparable saturations. The answer can be found by considering the condensation number.
Clement (1985) defines the condensation number as the ratio of the conductive heat current to the latent heat carried by the mass current. It is defined in Equation (5.2):

\[ Cn = \frac{k}{LD\rho_e'(T)} \quad (5.2) \]

Values of the condensation number for the substances studied are given in Table 5.2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>‘low’ temperature</th>
<th>‘high’ temperature</th>
<th>Condensation Number</th>
<th>Condensation Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>300 K</td>
<td>350 K</td>
<td>0.24</td>
<td>0.03</td>
</tr>
<tr>
<td>dibutyl phthalate</td>
<td>300 K</td>
<td>350 K</td>
<td>16250</td>
<td>474</td>
</tr>
<tr>
<td>caesium iodide</td>
<td>700 K</td>
<td>1100 K</td>
<td>15611</td>
<td>5.3</td>
</tr>
</tbody>
</table>

Table 5.2
Condensation numbers as a function of temperature for substances considered in growth rates comparison.

Barrett and Clement (1988) note that when the condensation number is much less than unity heat conduction limits growth. Given the low condensation numbers associated with water, it is reasonable to expect latent heat release to be significant, leading to
the temperature of the droplet rising. This is confirmed by the droplet temperature data. By contrast, the high condensation numbers of caesium iodide and dibutyl phthalate suggest that latent heat release will be negligible, leading to the linearised form predicting droplet temperatures accurately. As noted above, both growth rate methods yield extremely similar results for caesium iodide, in line with expectations. At low temperatures, calculations for dibutyl phthalate show both methods in agreement to within 0.1%, however at higher temperatures, the error rises to a 25% over-prediction. Although the condensation number for dibutyl phthalate is still significantly greater than unity, the high saturations lead to the assumption that $SP_{\text{e}}$ is much less than the total pressure being violated.

It can be seen that for compounds with a condensation number significantly greater than unity the linearised growth rate form gives good agreement with the more accurate iteratively calculated results, provided the maximum saturation of interest is not too great. Since the compounds of interest to the reactor accident scenario have condensation numbers significantly greater than unity, and are expected to achieve significant nucleation rates at saturations well below 10, it may safely be concluded that the use of the linearised approximation is valid in the circumstances of interest.
5.3 Approximate Solutions

In order to make quick predictions of the likely extent of aerosol formation, when considering the vapour-depleting effects of the growth process, it would be useful to have an analytical form which approximates the amount of aerosol produced. The development of such a method is dealt with in this section.

5.3.1 Development

Barrett (2000) has presented a method based upon projected rates of change in the nucleation rate due to vapour diffusion and (expected) growth rates. The method is developed here for laminar tube flow, and a means outlined of expressing this methodology in a closed form.

Figure 5.2 shows how the nucleation rate might vary along a streamline, both with and without consideration of vapour depletion due to the growth of the nucleated aerosol.

Two mechanisms combine to reduce the supersaturation in a system. Once the peak saturation has been reached, the flow of vapour to the tube walls will cause $S$ to fall. Also, the growth of any particles nucleated will consume vapour, thus reducing the saturation. If the first mechanism is ignored, then only condensation upon growing particles will cause the saturation to fall. Barrett assumes an aerosol size distribution, based upon a nucleation rate which varies as a Gaussian. Knowing this size distribution allows the mass flux attributable to aerosol growth to be calculated. This
can then be related to the rate at which this growth is causing the saturation (and hence nucleation rate) to fall.

In contrast, the saturation in a system rises initially, due to the flow of heat from the bulk to walls (causing a rapid falloff in the equilibrium concentration). If the temperature and concentration are known, then the rate at which this effect causes the saturation (and hence projected nucleation rate) to rise may be calculated.

Barrett proceeds by considering the rate of nucleation rate rise due to both heat and vapour flux and the rate of nucleation rate decline due to aerosol growth at various points along the tube. Initially there will be no aerosol, and so the nucleation rate will rise. As the number of particles nucleated increases, so the vapour flux to them due to growth will increase, and their potential effect upon the nucleation rate will also increase. When the rate at which heat flux is increasing the nucleation rate is equal to the rate at which the growth of particles would decrease the nucleation rate, the nucleation peak is deemed to have been found.

These rates are expressed as times for the nucleation rate to change by a factor $e$ in Barrett’s paper. The effects of heat flux and droplet growth are characterised by the rise and cut-off times $t_R$ and $t_c$, respectively.

$$t_R = \left[ \frac{\ln^2 S}{f(T)} \left( \frac{f'(T) dT}{f(T) dt} - \frac{2}{S} \ln S \left[ \frac{1}{c_e(T)} \frac{dc}{dt} - \frac{c}{c_e(T)} \frac{c'(T) dT}{c_e(T) dt} \right] \right) \right]^{-1} \tag{5.3}$$

$$t_c = \left[ \frac{f(T) L}{\ln^2 S \rho c_p} + \frac{2}{S} \ln S \left[ \frac{1}{\rho c_e(T)} - \frac{c}{c_e(T)} \frac{c'(T) L}{c_e(T) \rho c_p} \right] \right]^{-1} \tag{5.4}$$

If closed analytical forms are available for $T$ and $c$, then these can be differentiated w.r.t. time for use in Equations (5.3) and (5.4). Since the laminar flow solution (Equations (4.4) and (4.5)) is given in terms of an infinite series, it is more convenient to use finite differencing to determine the derivative, instead of differentiating a number of terms in the truncated series solution. Equation (5.5) allows Equations (4.4) and (4.5) to be expressed in terms of time rather than distance:

$$z = \frac{\alpha'(1-r^2)}{r_0^2} t \tag{5.5}$$

The code used to give the results presented below steps through time, calculating the temperature, concentration and saturation using the infinite series solution, truncated to one or six terms at the time in question and also at a time $\delta t$ later.
(to allow finite differencing to occur). From this data the nucleation rate and droplet growth mass flux can be calculated, which allows $t_R$ and $t_C$ to be calculated. At each time step, these values are compared, and the nucleation peak defined as the point at which $t_C$ equals $t_R$.

5.3.2 Results

Comparison of the results for a number of different scenarios showed that the timescales method outlined above is able to reproduce the results of numerical calculations reasonably well. Table 5.3 shows the total amount of aerosol produced in the tube for a number of conditions and for each calculation method. It can be seen that in all cases the agreement between the timescales method using six terms in the infinite series solution and the numerical results is within an order of magnitude. Interestingly, the timescales solution based upon only one term appears to give better agreement with the numerical results than the more accurate six term solution in most cases. This is explained by the fact that in most cases the timescales solution overpredicts the amount of aerosol formed. Because the one term solution cannot return valid results for radial positions near the wall, only results near the centre of the tube are available. These missing values lead to the result of the integration being too low, and so a less dramatic over-prediction results.

<table>
<thead>
<tr>
<th>Compound and conditions</th>
<th>Numerical</th>
<th>6 term</th>
<th>1 term</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBF; $\Delta T = 90$ K</td>
<td>$7.622 \times 10^6$</td>
<td>$1.286 \times 10^6$</td>
<td>$1.261 \times 10^6$</td>
</tr>
<tr>
<td>DBF; $\Delta T = 110$ K</td>
<td>$2.678 \times 10^6$</td>
<td>$6.360 \times 10^6$</td>
<td>$5.097 \times 10^6$</td>
</tr>
<tr>
<td>CsI; $\Delta T = 300$ K</td>
<td>$1.057 \times 10^8$</td>
<td>$1.457 \times 10^7$</td>
<td>$4.681 \times 10^7$</td>
</tr>
<tr>
<td>CsI; $\Delta T = 500$ K</td>
<td>$9.398 \times 10^7$</td>
<td>$1.724 \times 10^7$</td>
<td>$2.409 \times 10^6$</td>
</tr>
</tbody>
</table>

Table 5.3
Comparison of total aerosol number densities (per m$^3$s$^{-1}$) for a range of conditions and calculation methods

The results also show that in many cases the timescales method predicts peak nucleation rates which are much higher than those found by numerical solution. If the growth of aerosol is reducing the vapour concentration significantly prior to the peak then the timescales method (which does not include the effects of this prior to the peak) will over-predict the saturation and hence the nucleation rate. This phenomenon is not observed for CsI with a large temperature differential; these conditions are in
far greater excess of the condition for nucleation to be self-quenching than in any other case. In this case it may therefore be expected that the point of peak nucleation occurs so soon after the commencement of nucleation that no significant vapour is consumed by growth, thereby allowing the timescales method to give its best performance.

Considering the data as a function of radius, the qualitative agreement was also excellent, with quantitative agreement (particularly for the number of particles formed) usually within a factor of two or three of the numerical modelling solution. By far the most important factor in determining the accuracy of the timescales method was the number of terms used in the infinite series solution. When only one term was used in the solution the results near the wall were often very poorly reproduced. Using six terms improved the agreement significantly, although it is still necessary that an expression for the temperature and vapour concentration which is accurate near the wall be used at larger radii in order to give results which reflect most accurately the numerical calculations. The results of a typical calculation are shown in Figure 5.3 below.

![Graph](image)

**Figure 5.3**
The radial variation of the number density of aerosol, calculated by a number of methods for DBP with $T_w = 260$ K and $\Delta T = 110$K.
The results of the one term solution near the wall are not shown due to the inaccuracy of the solution at such short axial displacements. It can be seen that the six term solution follows the trend in the numerical solution very well up to a radius of about 0.9, when the corresponding axial distances become too small for the results to be accurate. An interesting trend which can be observed in this graph is that the highest number densities are not seen near the centre of the tube where previous analyses have indicated the maximum saturation (and hence nucleation rate) might be expected, but near the wall. Figure 5.4 shows the variation of the saturation and nucleation rate with radius at two temperatures. It can be seen that this unexpected behaviour is even more pronounced when the saturation is considered.

![Graph showing the radial variation of the maximum saturation of DBP found by numerical calculation, as a function of inlet temperature differential.](image)

**Figure 5.4**
The radial variation of the maximum saturation of DBP found by numerical calculation, as a function of inlet temperature differential.

An explanation for this behaviour can be found by considering the radial variation of the maximum nucleation rate (in the absence of vapour depletion) and the condition for nucleation to be self-quenching (Figure 5.5). Figure 5.4 is for dibutyl phthalate; consideration will be given first to the result for an inlet temperature differential of 110 K. For most radial positions, the conditions are such that nucleation is strongly self-quenching, however near the wall the condition is only just exceeded, suggesting that the effect of quenching will be much less than at radii away from the
Near the wall, the consumption of vapour by the growth of freshly nucleated particles is not especially significant, allowing saturations (and hence nucleation rates) to remain near the values expected from the non-vapour depletion case analysis. Near the centre of the tube, however, the effect of freshly nucleated aerosol growth consuming vapour is so great that the saturation is markedly reduced from the no-vapour depletion case values. For the lower inlet temperature differential of 90 K, reference to Figure 5.5 shows that the condition for nucleation to be self-quenching is only exceeded for radial distances less than about 0.6. Above this radius the expected trend, a fall in saturation with increasing radius, can still be seen in Figure 5.4. At radii prior to this point, the expected rise with decreasing radius is not seen. The saturation actually falls as the radius decreases. As the radius decreases from 0.65, so the extent to which the condition for nucleation to be self-quenching is exceeded increases. The depletion of vapour by growth on new aerosol particles will therefore have an increasingly strong effect on the saturation as the radius falls, leading to the unusual peaked shape seen here.

![Figure 5.5](image)

Figure 5.5

The radial variation of the peak nucleation rate and the condition for nucleation to be self-quenching as a function of inlet temperature differential, for dibutyl phthalate.
5.3.3 Fully Analytical Form

A fully analytical version of the above procedure, soluble without recourse to the time-stepping techniques used above is only possible when both the function describing the variation of temperature and vapour concentration can be readily rearranged and the derivatives with respect to time of the temperature and concentration expressions can be found. For the infinite series solution for the laminar flow case this can be achieved only when the series is truncated to one term. Although the radial agreement presented by the single term solution is poor, the data for total number produced agree reasonably with more accurate numerical calculations. If one is prepared to accept this limited accuracy, and the possibility that in some cases the one-term solution may fail to produce results which mimic the numerical solution to any appreciable extent, then such a derivation may prove of use in providing basic scoping calculations. In cases where nucleation is quenched heavily, and is expected to occur at very short distances into the tube, the use of this approximation would be ill-advised.
5.4 Prediction of Condition for Nucleation to be Affected

Section 4.5 derived expressions which allow an estimate to be made of the maximum nucleation rate (or seed aerosol concentration) which can be present in a system before the vapour consumed by the growth of these particles significantly affects subsequent nucleation. The accuracy of these estimates may be tested by comparing them with the numerical solution of the laminar tube flow equations, when these equations include the mass transfer term to aerosol.

5.4.1 Freshly Nucleated Aerosol

Figure 5.6 shows, in addition to the information contained in Figure 4.9, the peak nucleation rate at the centre of the tube, as found by numerical solution, both with and without the mass transfer to aerosol term.

![Graph showing nucleation rate vs temperature difference](image)

**Figure 5.6**

*Comparison of the condition for aerosol growth to significantly affect subsequent nucleation with numerical results (with and without vapour to aerosol mass transfer)*

It can be seen that the numerical results with and without vapour depletion are overlay each other when $\Delta T = 85$ K, and have diverged significantly when $\Delta T = 90$ K. As the analytically found nucleation rate for a specified inlet temperature differential exceeds the condition for condensation to be important somewhere in this interval, it
can be seen that the condition is able to identify quite well situations when condensation is important. Closer examination shows that at the point where the theoretical nucleation rate and the condition are equal, the numerically found peak nucleation rate with vapour depletion is half that found in the absence of vapour depletion. Recalling that the original definition of a “significant” effect was that the peak nucleation rate change by a factor $e$ ($=2.7$), it can be seen that the described method is actually very good indeed in this case, although it is possible the extent of the agreement in this case is fortuitous.

5.4.2 Seed Aerosol

The work of Section 4.5 also derived conditions for the presence of seed aerosol particles to have a significant effect on the nucleation of fresh aerosol. Reference to Figure 4.11 shows that as was the case for the effect of freshly nucleated aerosol, the condition does not vary greatly with temperature. However, the number density of seed particles (and in some cases their initial radius) does have a significant effect.

Consideration is given first to the case where the seed aerosol is sufficiently small that only a number density is specified by the condition. Figure 4.11 shows that approximately $5 \times 10^6$ particles per m$^3$ are needed for an effect to be seen. A comparison was therefore made between the number of particles nucleated at the centre of the tube in the presence of varying concentrations of seed aerosol particles. Figure 5.7 shows the results of this comparison.

It can be seen that at all temperatures a large change in the amount of aerosol nucleated is seen when the amount of seed aerosol increases above $10^6$ m$^{-3}$. Interestingly, when the inlet temperature differential exceeds 90 K, this change becomes much smaller. This can be explained by reference to Figure 4.9, which shows that the vapour consumed by the growth of freshly nucleated aerosol is effective in reducing nucleation above $\Delta T = 87$ K. At $\Delta T = 90$ K, the point representing a seed aerosol concentration of $10^6$ m$^{-3}$ no longer represents the number nucleated in the absence of any significant quenching effects, since the growth of freshly nucleated particles is now significant in reducing the total number nucleated. This trend continues with increasing temperature. The points representing $10^6$ m$^{-3}$ seed aerosol particles are increasing “too low” due to the effect of freshly nucleated
aerosol reducing the nucleation rate. This also accounts for the convergence of the points for seed aerosol densities of $10^4 \text{ m}^{-3}$ and $10^6 \text{ m}^{-3}$.

It appears that when growth on new aerosol is not significant the condition presented in Section 4.5 is well able to predict the conditions for seed aerosol to affect nucleation. At higher inlet temperature differentials this methodology still gives good agreement with numerical calculations, particularly when the effects of the new aerosol are taken into account. Warren and Seinfeld (1985) discussed a similar problem and concluded that:

"to minimize the number and maximize the size of particles formed from a condensable vapour, one should begin with a seed aerosol number concentration approximately an order of magnitude less than the number concentration which would have resulted from the absence of initial aerosol under the same conditions."

Reference to Figure 5.7 suggests their postulate is approximately correct, although a better form might recommend a seed aerosol concentration equal to that nucleated in the absence of seed at the temperature at which the condition for growth on new aerosol is expected to become important.
As a footnote to this section, the calculations presented in Figure 5.7 also included a seed aerosol concentration of \(10^9\) m\(^{-3}\); this totally suppressed all nucleation, however.

Considering next the case where “large” seed aerosol particles grow by a smaller amount, it is necessary to specify both their size and concentration. Figure 4.11 is plotted in terms of the product of these two values; the condition (expressed as this product) is in the range \(10\) m\(^2\) – \(15\) m\(^2\) for temperatures likely to achieve interesting nucleation rates. Figure 5.8 shows the number of new aerosol particles nucleated for different combinations of seed aerosol size and concentration. The colour of the floor in the graph indicates whether the product of size and concentration is: less than the condition (green); roughly equal to the condition (yellow); or greater than the condition (red). These calculations were performed with an inlet temperature differential of 90 K, at which temperature growth on freshly nucleated aerosol may be expected to play a significant role.

![Figure 5.8](image)

*Figure 5.8*

The variation in number of new aerosol particles nucleated with seed aerosol size and concentration, for DBP with \(\Delta T = 90\) K. Seed aerosol size is shown on the x-axis, seed concentration on the y-axis.

It can be seen that the method is reasonably successful, with the yellow floor region indicating the conditions where a reduction in new aerosol formation is seen. Very sharp decreases in new aerosol production are again seen when the condition is
exceeded by an order of magnitude. It is likely that there is some sort of “capping” effect, due to new aerosol, as seen in Figure 5.7.

Four basic scenarios can be identified when considering condensative growth (see Figure 5.9). In the first and simplest case, neither new nor seed aerosol grows sufficiently that it affects subsequent nucleation. In the second two cases, one of new or seed aerosol affects the production of new aerosol. The methods tested above were originally conceived to identify whether Case 1 or Case 2 or 3 applies. They have also been of utility in predicting results in Case 4, when both seed and new aerosol affect the rate at which further aerosol is formed.

![Figure 5.9](image)

*Figure 5.9*

*The four possible scenarios which arise when considering the effects of condensative growth*
5.5 Mass Balances

Vapour flowing into a cooled tube may remain in the vapour phase, be deposited onto the walls or be consumed by aerosol formation. A parametric study was performed in order to determine the effects of physical parameters (tube size, flow rate, inlet temperature differential) on the distribution between these three destinations. A fixed length tube (30 m) was used. The evolution of this distribution along the length of the tube was also examined. Calculations are for caesium iodide in hydrogen; specific conditions are detailed in the legends accompanying the graphs.

The first parameter considered was the radius of the tube itself. Reference to Figure 5.10 shows that when the tube radius decreases so the amount of vapour deposited to the walls within a specified distance increases. This is in line with the expectation that the increased proximity of the walls would result in faster vapour transfer from the bulk. This is explained by the fact that in the dimensionless representation the rate at which vapour flows to the walls does not vary with tube radius. However, when the problem is expressed in dimensional form the “real” distance at which a certain percentage of the in-flowing vapour has transferred to the walls is decreases as smaller tube radii are considered.

![Figure 5.10](image1.png)

**Figure 5.10**
The variation in vapour distribution with tube radius
\((\Delta T = 100 \, K; \, v_m = 1 \, m \, s^{-1})\)

![Figure 5.11](image2.png)

**Figure 5.11**
The variation in vapour distribution with inlet temperature differential
\((r_0 = 0.1 \, m; \, v_m = 1 \, m \, s^{-1})\)
The next parameter considered was the inlet temperature differential. Figure 5.11 illustrates the increased fraction of in-flowing vapour which is transferred to aerosol as the temperature rises. Reference to the temperature dependence of the condition for the growth of aerosol to be important suggests that once this condition is significantly exceeded the majority of the in-flowing vapour will leave the tube as aerosol.

The final parameter considered was the flow rate. Given an infinitely long tube, it may reasonably be expected that the vast majority of the vapour would either deposit upon the tube walls or have been converted. That remaining in the vapour phase would be due to the equilibrium vapour concentration not being zero at the wall temperature (which is equal to the final temperature of the bulk). Since slower flow rates imply longer residence times for the vapour in the tube, it is unsurprising to observe in Figure 5.12 that the slower the flow rate, the closer the results are to this final result. The non-zero vapour phase components for the lower flow rates are, in fact, the equilibrium vapour concentrations at the wall temperature.

![Figure 5.12](image)

*Figure 5.12*

The variation in vapour distribution with carrier gas flow rate ($r = 0.1 \, m; \Delta T = 100 \, K$)

As discussed previously, vapour flowing into the tube will partition itself between the tube walls, the vapour phase and aerosol material. Figure 5.13 illustrates the total percentage of in-flowing vapour remaining in the vapour phase and
converted to aerosol as a function of axial position in the tube. It can be seen that initially the amount of material flowing as vapour is reduced solely due to condensation upon the cold tube walls. Only beyond about 2½ m does the formation of aerosol commence, shown by the rise in the amount of material contained within this phase. From this point on both aerosol growth and wall condensation combine to remove further material from the vapour phase. Beyond 15 m it appears that the conditions in the tube are very near their final values due to the very small rate at which any further material is removed from the vapour phase.

![Graph showing the variation in vapour distribution with axial distance for CsI; $\Delta T = 100 \, K$, $v = 1 \, m \, s^{-1}$, $d = 0.2 \, m$](image)

**Figure 5.13**
The variation in vapour distribution with axial distance for CsI; $\Delta T = 100 \, K$, $v = 1 \, m \, s^{-1}$, $d = 0.2 \, m$
5.6 Conclusions

A number of issues relating to vapour depletion due to the growth of aerosol, whether new or pre-existing have been examined to determine the nature of their influence on aerosol production.

In Chapter 3 the rate at which aerosol particles grow was always found using an iterative method. Examination of data for a range of compounds reveals that in fact, for compounds of interest in reactor accident scenarios, a simpler linearised form has equal value. In general terms, provided the vapour pressure of the condensing species is low compared to the system pressure, and the condensation number of this species is larger than unity, the linearised form will perform as well as the more time-consuming iterative solution.

Continuing the theme of previous chapters, an approximate method for predicting the likely extent of nucleation was developed. Comparison with fuller numerical calculations show the total amount of aerosol formed is reasonably well characterised by this method. During the course of these comparisons (which were only for substances with a Lewis number greater than unity) it was observed that in many cases the maximum aerosol formation was not at the centre of the tube as expected, but near the walls. Comparison of the radial nucleation rate profile (ignoring vapour depletion) with the condition for nucleation to be self-quenching (developed in Section 4.5) allows the inlet temperature differential at which nucleation becomes self-quenching to be identified. The results presented in this Chapter suggested that when the inlet temperature differential for nucleation to be self quenching was just exceeded (up to ~10%) then quenching would occur only at the centre of the tube. Only in more extreme cases (inlet temperature differential exceeded by more than 25%) would nucleation be likely to be quenched across the entire tube radius. Thus in most cases the nucleation rate at the centre of the tube is suppressed to the extent that the maximum is seen near the walls. The corollary of this is that in many cases it is imperative that the nucleation rate near the wall be known accurately in order to correctly predict the amount of nucleation expected. It was found that using the infinite series solution truncated to 6 terms gave good results in most cases, while the single term solution was unreliable. Since a fully analytical version of this method requires rearrangement of the functions describing the temperature and vapour concentration it is likely that only the single term solution
could be used as the basis of such a method. However, given the unreliability of this truncated solution noted above, it appears that a fully analytical form of this method is not currently possible.

The conditions for growth to affect subsequent nucleation, developed in Section 4.5 were tested in this Chapter. Agreement for freshly nucleated aerosol was excellent, suggesting that this method allows the onset of quenching to be accurately identified. Similar success was experienced by the condition for the growth of small seed particles to inhibit fresh nucleation. When considering large aerosol particles (> 1 μm) the condition succeeded in predicting approximate combinations of size and concentration necessary to cause an effect, although the agreement was less striking than in other cases. The conditions for seed to have an effect were tested under conditions when the nucleation of fresh aerosol would also be expected to have an effect in reducing further nucleation. Although the agreement achieved was (unsurprisingly) not as good, the method still performed reasonably well.

The distribution of in-flowing condensible vapour between the tube walls, aerosol particles and the vapour phase was also considered using a parametric study in this chapter. All systems considered had a fixed length of 30 m. The general trend seen in all cases was for the condensible vapour to partition itself between walls and aerosol; when condensible material did remain as vapour the “equilibration” of the system was less complete. Unsurprisingly, slower flow rates were seen to give more equilibrated systems, with correspondingly less vapour phase material leaving the tube. Higher inlet temperatures lead to more nucleation and consequently less material both in the vapour phase and on the walls. Conversely, small tubes allowed for quicker diffusion of vapour to the walls, and a concomitant reduction in aerosol formation and vapour phase transport.
Chapter 6

Experimental Comparison
6.1 Introduction

In order to validate some of the conclusions drawn during the course of this work, comparisons with experimental results would be beneficial. Unfortunately, few studies of aerosol formation and behaviour in tube flow exist. Of those that do, few are sufficiently well characterised to allow comparison with theoretical calculations. The experiments of Hämmeri and Kulmala (1996) have been compared with the no-vapour depletion work of Chapter 4 (Barrett and Baldwin, 2000). These experiments dealt with DBP at low temperatures. To increase confidence in the models developed it is desirable to test them against experimental results for compounds which would be found in a postulated severe accident. It is also desirable to test methods developed for the case where vapour depletion is important against experiment.

A number of experiments were performed by the UKAEA (now AEA Technology plc) at Winfrith to investigate the formation and transport of aerosol particles in cooled tube flow. The behaviour of simulant fission products (caesium iodide and caesium hydroxide containing non-radioactive isotopes) was studied in a thermal gradient tube under a range of conditions. Experiments were performed using the simulant fission products both in combination and in isolation. The parameters varied were flow rate, carrier gas, source concentration and the rate of temperature variation within the thermal gradient section. Mass balances and basic particle sizing measurements were carried out.

Calculations have been carried out for this thesis, using techniques described in previous chapters, in an attempt to validate these techniques. In addition to attempting to reproduce the experimental results of the workers at Winfrith, the ability of the models to reproduce trends found in their data was also examined.
6.2 Experimental Set-Up

In order to perform a meaningful comparison with any calculations, it is important to understand how the experiments were performed at Winfrith. Figure 6.1 illustrates the experimental set-up used. A glass tube, lined with nickel foil to allow wall deposition to be measured, was heated using a number of heaters. In this way the temperature profile over the length of the tube could readily be varied. One or two crucibles containing caesium iodide and/or caesium hydroxide were heated to 1073 K near the inlet of the tube. A stream of pure argon carrier gas was passed over the crucible(s). Volatilised simulant fission product vapours then flowed through a "superheated" region, at 1273 K. It was intended that this region would ensure that all vapours were subsaturated. The thermal gradient section follows this region; over a distance of either 0.23 m, 0.4 m or 1.6 m the wall temperature falls to 473 K, corresponding to thermal gradients of 35 °C cm⁻¹, 20 °C cm⁻¹ and 5 °C cm⁻¹ respectively. No further heating is applied beyond the end of the thermal gradient section. Vapours and aerosol flow through a Nucleopore filter which is at ambient temperature (293 K). This creates, in effect, a second thermal gradient section, with a wall temperature drop of 180 K over a short distance. The occurrence of aerosol growth in this section is noted in the report; however insufficient data are given about the nature of this section to allow it to be modelled accurately.

![Figure 6.1](attachment:image)

*Figure 6.1 Schematic of the experimental set-up used in the Winfrith experiments*
6.3 Comparison with Experiment

The experiments performed at Winfrith span a wide range of conditions, in both laminar and turbulent flow regimes. Many of the ideas presented previously in this thesis have been most fully developed for the laminar flow regime, and comparison with the results from Winfrith were therefore restricted to experiments with slower gas flows. For those scenarios where both simulant fission products were present, separate theoretical calculations were performed, as the models currently do not allow for multi-component systems. It was hoped that nucleation of the two species (as studied independently) would occur at distinct distances, allowing simplifying assumptions to be made. One obstacle to performing the comparison arose from a lack of knowledge about the equilibrium vapour pressure of caesium hydroxide. Bowsher et al. (1990) report the inlet concentration of simulant fission product in terms of a partial pressure. It is worth noting that this figure was derived by weighing the crucible before and after the experiment, and relating the weight loss to a uniform vaporisation rate. In order to calculate nucleation rates this partial pressure must be converted into a saturation ratio, which requires the equilibrium vapour pressure be known. Data from Cordfunke and Konings (1990) was initially used, however this led to saturations at the tube inlet of up to 2.25. Recalling that the experimental apparatus was designed to preclude supersaturated inlet vapour pressures, it seems likely that the data of Cordfunke and Konings are not applicable. Caesium hydroxide calculations were performed again, using a fitting function, based upon the data of Jordan and Leonard (1986). Their data show that the equilibrium vapour pressure of caesium hydroxide is roughly 2 – 3 times less than that of caesium iodide at a given temperature. A new fitting function was therefore created for caesium hydroxide which reflected this relationship to caesium iodide.

6.3.1 Quantitative Agreement

Validation efforts concentrated initially on calculations which mimicked exactly the experimental conditions for a number of runs. Whilst exact agreement was not expected for several reasons, it was hoped that patterns seen in the experiments would also be reproduced by the calculations. Aerosol sampling is a difficult procedure even under ideal conditions, and so it is expected that some inaccuracies
arose in the Winfrith work. In particular, it is likely that measuring apparatus disturbed the conditions in the system. Examples of this include the use of 'coupons' to measure the amount of aerosol flowing at a given point (which were of comparable dimension to the tube itself) and the use of thermocouples to measure the gas temperature. Because of the size of these items relative to the tube diameter it is likely that these devices disturbed the laminar flow established in the tube. A theoretical difficulty which was expected to hinder agreement between calculations and experiment is the uncertainty surrounding nucleation theory. Calculations were performed using classical nucleation theory with the $S^{-1}$ correction attributable to Oxtoby (1991). This theory is known not to reproduce experimental temperature dependencies.

6.3.1.1 Does Nucleation Occur?

In several of the experiments performed at Winfrith, no aerosol formation was seen. A simple test of the calculations, therefore, would be to check that the models used are capable of identifying the conditions under which nucleation would occur. Seventeen of the Winfrith experiments were modelled. In twelve cases, the calculations successfully predicted whether nucleation would occur or not. In the remaining cases, nucleation was predicted when none was seen in the experiments. Considering the twelve successful comparisons, nine involved aerosol nucleation. The extent of this was over-predicted by the calculations in all but one case. In summary, it seems that whilst generally able to establish whether nucleation will occur or not, the calculations tend predict the occurrence of nucleation too readily. Not only the number of aerosol particles produced, but also the size of these particles is important in determining the consequences of a postulated accident. Comparison between the experimentally determined radii and the calculated values showed that the calculations did not produce values which matched well the experimental results. Unlike the comparison of percentage conversion of vapour to aerosol, which showed a definite tendency to over-predict, the particle sizes predicted were over- and under-predictions in approximately equal measure.

This lack of agreement between the calculated and experimentally determined results, whilst not unexpected, does not lend credibility to the models used in the code. However, given the nature of the expected problems outlined above, it should be possible to perform some validation, by demonstrating trends in the results.
Bowsher et al. identify a number of trends in their results, which might be expected to be present in the calculated results as well. Unfortunately, the lack of turbulent calculations mean that most calculations were performed only at two flow rates, which is an insufficient number of points for a good analysis of trends. The results of this attempt at comparisons must therefore be deemed inconclusive.

### 6.3.2 Qualitative Agreement

Since it appears that the failure of classical nucleation theory prevents exact numerical agreement with the results from Winfrith, calculations were performed with the intention of eliciting trends in the behaviour of systems as input parameters vary. The original Winfrith report draws a number of conclusions about the effects of varying various input parameters; the calculations performed were selected to allow these trends to be demonstrated by the model. Bowsher et al. found similar trends in the behaviour of caesium iodide and caesium hydroxide when each was considered separately. They also drew conclusions about the interaction of these simulant fission products when a multicomponent system was used.

A total of eighteen calculations, nine each for caesium iodide and for caesium hydroxide were carried out to allow the effects of the thermal gradient and flow rate to be assessed. The calculation matrix is shown in Table 6.1 below. In all cases the partial pressure of the vapour was 100 Pa.

<table>
<thead>
<tr>
<th>Run</th>
<th>Thermal Gradient (°C m⁻¹)</th>
<th>Length (m)</th>
<th>Reynolds Number (-)</th>
<th>Velocity (m s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>35</td>
<td>0.23</td>
<td>200</td>
<td>0.20</td>
</tr>
<tr>
<td>B</td>
<td>35</td>
<td>0.23</td>
<td>1000</td>
<td>1.02</td>
</tr>
<tr>
<td>C</td>
<td>35</td>
<td>0.23</td>
<td>2000</td>
<td>2.04</td>
</tr>
<tr>
<td>D</td>
<td>20</td>
<td>0.40</td>
<td>200</td>
<td>0.20</td>
</tr>
<tr>
<td>E</td>
<td>20</td>
<td>0.40</td>
<td>1000</td>
<td>1.02</td>
</tr>
<tr>
<td>F</td>
<td>20</td>
<td>0.40</td>
<td>2000</td>
<td>2.04</td>
</tr>
<tr>
<td>G</td>
<td>5</td>
<td>1.60</td>
<td>200</td>
<td>0.20</td>
</tr>
<tr>
<td>H</td>
<td>5</td>
<td>1.60</td>
<td>1000</td>
<td>1.02</td>
</tr>
<tr>
<td>I</td>
<td>5</td>
<td>1.60</td>
<td>2000</td>
<td>2.04</td>
</tr>
</tbody>
</table>

Table 6.1

*The conditions used to examine trends in the behaviour of a tube flow system*
6.3.2.1 Particle Size as a Function of Temperature Gradient

Bowsher et al. found that the mean radius of particles formed increased as the thermal gradient decreased. Table 6.2 shows the results of a number of calculations.

<table>
<thead>
<tr>
<th>Run</th>
<th>Thermal Gradient (°C m⁻¹)</th>
<th>CsI radius (μm)</th>
<th>CsOH radius (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>35</td>
<td>0.53</td>
<td>0.302</td>
</tr>
<tr>
<td>D</td>
<td>20</td>
<td>0.56</td>
<td>0.347</td>
</tr>
<tr>
<td>G</td>
<td>5</td>
<td>0.09</td>
<td>1.340</td>
</tr>
<tr>
<td>B</td>
<td>35</td>
<td>0.22</td>
<td>0.031</td>
</tr>
<tr>
<td>E</td>
<td>20</td>
<td>0.25</td>
<td>0.074</td>
</tr>
<tr>
<td>H</td>
<td>5</td>
<td>0.53</td>
<td>0.202</td>
</tr>
<tr>
<td>C</td>
<td>35</td>
<td>0.17</td>
<td>0.027</td>
</tr>
<tr>
<td>F</td>
<td>20</td>
<td>0.22</td>
<td>0.029</td>
</tr>
<tr>
<td>I</td>
<td>5</td>
<td>0.46</td>
<td>0.112</td>
</tr>
</tbody>
</table>

Table 6.2
Predicted particle radius as a function of wall temperature gradient

It can be seen that in all cases (bar one) this trend is reproduced well for both caesium iodide and caesium hydroxide. Relatively small amounts of material are involved in this case, and it seems likely that these results are anomalous due to limitations in the accuracy of the calculation method.

6.3.2.2 Particle Size as a Function of Flow Velocity

A second trend observed by Bowsher et al. is the increase in particle radius with increasing Reynolds number. Table 6.3 shows the variation of calculated droplet sizes with Reynolds number.

<table>
<thead>
<tr>
<th>Run</th>
<th>Reynolds number</th>
<th>CsI radius (μm)</th>
<th>CsOH radius (μm)</th>
<th>R_{CsI} ± R_{CsOH}</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>200</td>
<td>0.53</td>
<td>0.302</td>
<td>1.8</td>
</tr>
<tr>
<td>B</td>
<td>1000</td>
<td>0.22</td>
<td>0.031</td>
<td>7.1</td>
</tr>
<tr>
<td>C</td>
<td>2000</td>
<td>0.17</td>
<td>0.027</td>
<td>6.4</td>
</tr>
<tr>
<td>D</td>
<td>200</td>
<td>0.56</td>
<td>0.347</td>
<td>1.6</td>
</tr>
<tr>
<td>E</td>
<td>1000</td>
<td>0.25</td>
<td>0.074</td>
<td>3.3</td>
</tr>
<tr>
<td>F</td>
<td>2000</td>
<td>0.22</td>
<td>0.029</td>
<td>7.7</td>
</tr>
<tr>
<td>G</td>
<td>200</td>
<td>0.10</td>
<td>1.340</td>
<td>0.1</td>
</tr>
<tr>
<td>H</td>
<td>1000</td>
<td>0.53</td>
<td>0.202</td>
<td>2.6</td>
</tr>
<tr>
<td>I</td>
<td>2000</td>
<td>0.46</td>
<td>0.112</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Table 6.3
The variation in droplet radius with Reynolds number
It appears that the calculations show the opposite trend to that found in the experiments. However, it is important to remember exactly what is being modelled in the calculations. As noted previously, the experimental set-up at Winfrith actually includes two thermal gradient regions; the formal region which is considered by Bowsher et al., and a second, equally important zone, where the wall temperature walls sharply to the ambient temperature. The results presented above are from modelling the first region only. Table 6.4 shows the distribution of in-flowing mass at the end of the first section for some of the caesium iodide calculations.

<table>
<thead>
<tr>
<th>Run</th>
<th>Reynolds Number</th>
<th>% Walls</th>
<th>% Vapour</th>
<th>% Aerosol</th>
<th>% Lost</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>200</td>
<td>54.0</td>
<td>0.0</td>
<td>46.6</td>
<td>-0.6</td>
</tr>
<tr>
<td>B</td>
<td>1000</td>
<td>26.4</td>
<td>48.4</td>
<td>27.2</td>
<td>-1.9</td>
</tr>
<tr>
<td>C</td>
<td>2000</td>
<td>15.7</td>
<td>67.8</td>
<td>15.7</td>
<td>0.9</td>
</tr>
<tr>
<td>D</td>
<td>200</td>
<td>66.8</td>
<td>0.0</td>
<td>32.5</td>
<td>0.7</td>
</tr>
<tr>
<td>E</td>
<td>1000</td>
<td>33.0</td>
<td>18.6</td>
<td>48.6</td>
<td>-0.2</td>
</tr>
<tr>
<td>F</td>
<td>2000</td>
<td>23.9</td>
<td>52.1</td>
<td>25.2</td>
<td>-1.2</td>
</tr>
</tbody>
</table>

Table 6.4
The mass distribution in caesium iodide calculations, at the end of the formal thermal gradient section

It can be seen that the amount of vapour deposited upon the walls decreases with increasing Reynolds number. Since the effect of the region of changing wall temperature will be to produce a second peak in the saturation, it may be expected that this will lead to further growth of the particles in the tube. As discussed in Chapter 5, and illustrated by cases A and D here, the final mass distribution of any tube flow system will be between the walls and the aerosol phase only, with negligible amounts of material flowing as vapour. Although a peak in the saturation may potentially lead to more nucleation, it is felt unlikely that at the (relatively) low temperatures under consideration that nucleation will occur. Taking all these factors into account, it seems probable that the effect of this final wall temperature change will be to transfer the majority of the vaporised material from the vapour phase to the aerosol phase without creating any new aerosol particles. Reference to Table 6.4 suggests that when total conversion of vapour to aerosol takes place, the final size of particles in case C is greater than those in case B, which in turn are larger than those in case A. It is expected that this pattern of behaviour will occur in all cases. It therefore seems that the calculated results are in agreement with experiment. Confirmation of this point
could be achieved by performing calculations taking this second wall temperature change into account, provided data about this change were available.

6.3.2.3 Aerosol Formation as a Function of Temperature Gradient

Bowsher et al. report that increased aerosol formation is seen with increasing wall temperature gradient. Table 6.5 shows the percentage of in-flowing vapour which does not deposit upon the walls. Assuming total conversion of vapour as described above makes this quantity equal to the total amount of material exiting as aerosol.

<table>
<thead>
<tr>
<th>Run</th>
<th>Thermal Gradient (°C cm⁻¹)</th>
<th>Caesium Iodide % non-wall</th>
<th>Caesium Hydroxide % non-wall</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>35</td>
<td>46.0</td>
<td>52.7</td>
</tr>
<tr>
<td>D</td>
<td>20</td>
<td>33.2</td>
<td>46.0</td>
</tr>
<tr>
<td>G</td>
<td>5</td>
<td>1.0</td>
<td>6.5</td>
</tr>
<tr>
<td>B</td>
<td>35</td>
<td>73.6</td>
<td>80.3</td>
</tr>
<tr>
<td>E</td>
<td>20</td>
<td>67.0</td>
<td>71.8</td>
</tr>
<tr>
<td>H</td>
<td>5</td>
<td>38.8</td>
<td>50.3</td>
</tr>
<tr>
<td>C</td>
<td>35</td>
<td>84.3</td>
<td>85.2</td>
</tr>
<tr>
<td>F</td>
<td>20</td>
<td>76.1</td>
<td>80.9</td>
</tr>
<tr>
<td>I</td>
<td>5</td>
<td>54.6</td>
<td>65.9</td>
</tr>
</tbody>
</table>

Table 6.5

The variation in aerosol formation with wall temperature gradient

It can be seen that in all cases the calculations reproduce the trend found in experiments. The experimental methods used do not allow the number of aerosol particles nucleated to be calculated directly. It is therefore interesting to note from calculations that an increase in the number of particles formed is responsible for the trend shown above. This can be explained as follows. The maximum saturation seen in the tube if vapour depletion is ignored will not change with varying wall thermal gradients. However, steeper thermal gradients along the wall will cause the saturation to rise more rapidly, with the result (in the vapour depletion case) that more particles are nucleated before the consumption of vapour due to their growth acts to quench nucleation. The experiments also find that increasing Reynolds numbers lead to increased aerosol mass; reference to the calculations show that this is also due to increasing numbers nucleated which then grow consuming vapour. The faster flow rates associated with larger Reynolds numbers sweep any particles which have been
formed through the system more quickly, allowing them less opportunity to growth. This reduced vapour consumption therefore allows greater nucleation.

6.3.2.4 Relative Behaviour of Caesium Iodide and Caesium Hydroxide

Although the thermophysical properties of caesium iodide and caesium hydroxide are thought to be very similar, some differences remain which could lead to differences in behaviour. Due to a paucity of data for caesium hydroxide, data for caesium iodide has been used to characterise CsOH, with the exception of the vapour diffusivity and the equilibrium vapour pressure (as noted above in Section 6.3). This is expected to give results which are reasonably realistic; of the remaining parameters only a change in the surface tension is likely to be significant in affecting the behaviour of caesium hydroxide.

Caesium hydroxide particles were reported to be formed with radii four to five times smaller than those of caesium iodide particles under identical conditions by workers at Winfrith. Table 6.3 compares the mean radii of particles for the nine pairs of calculations. It can be seen that in all cases (bar one) caesium hydroxide particles are found to be smaller than caesium iodide particles. The ratio varies from 1.6 times to 7.7 times, which given the limitations in the characterisation of the experiments may be considered very good agreement. Bowsher et al. suggest that this difference in size

"may reflect the fact that CsI and CsOH aerosol particles exhibit different physicochemical behaviour and transport characteristics."

Whilst this statement is not incorrect, it does not identify the specific parameter and mechanism by which this difference is effected. Since the equilibrium vapour pressure of caesium hydroxide is lower than that of caesium iodide, for the same input conditions a caesium iodide system will achieve higher saturations. This will lead to increased aerosol nucleation compared to caesium hydroxide. Given that more particles are formed, there will be less vapour available for each particle to grow, leading to smaller particles. This explanation is supported by the observation that the number of particles nucleated in caesium hydroxide calculations is usually an order of magnitude greater than the corresponding caesium iodide calculation.

The experimental results also show that more caesium hydroxide is retained in the tube than is caesium iodide for given conditions. The same explanation is given as before, but in this case it offers even less value. Although differences in the materials
are in all probability responsible, it seems likely that the answer is more involved than in the previous case.

The observation that caesium hydroxide is retained more than caesium iodide is not supported by the results of calculations. Reference to Table 6.5 shows that in every case the calculated data follows the opposite trend. Since caesium hydroxide is expected to nucleate more rapidly, it might be expected that particles will be formed sooner in the tube. This would lead to less vapour being deposited upon the tube walls, which is the result obtained by the calculations. It should be noted that the vapour diffusivity of caesium hydroxide is approximately 25% greater than that of caesium iodide; however this will affect both diffusion to walls and diffusion to aerosol. It is therefore not possible to say from this information whether it is responsible for the effect or not. It seems most likely that this discrepancy between calculation and experiment is due to a process which is not modelled in the calculations. Bowsher et al. claim that the wall temperatures were significantly lower than the gas temperatures in all experiments, leading to a situation where thermophoresis could occur. Whilst workers at Winfrith claim that the smaller particles produced from caesium hydroxide favours thermophoretic deposition, it seems unlikely that the difference in size is sufficient to produce the differences found in the experiments (which were up to 50%). Ahluwalia and Im (1985) report that modelling particle transport to the walls increases the total wall deposition in laminar flow. This process is not currently modelled, aerosols being assumed to continue flowing along the streamline in which they were formed until they exit the tube. Other authors (Allen et al., 1987) have discussed the adsorption of caesium hydroxide onto container walls. Although this work has concentrated upon stainless steel because of its relevance to nuclear plants, it is possible that a similar effect is seen with the nickel foil used to line the experimental apparatus. If aerosol particles are deposited to the walls and then resuspended by turbulence at the walls, the adsorption of caesium hydroxide would serve to increase its retention over caesium iodide, potentially leading to the result found in the experiments. It should be noted, however, that these explanations are speculative, and requires verification by further calculations and experiments.
6.3.2.5 Two-Component System Behaviour

Samples were analysed using Electron Diffraction Spectrometry (EDS), a technique which allows materials to be identified by their response to an electron beam. By varying the accelerating potential applied to this beam, analyses can be carried out at varying depths into the sample. The results of this analysis of the particles formed when both caesium iodide and caesium hydroxide were present in the same system indicate a decreasing iodide concentration with increasing depth into the droplet. Bowsher et al. conclude that this is due to the heterogeneous nucleation of caesium iodide onto caesium hydroxide clusters. The corollary of this conclusion is that caesium hydroxide nucleates before caesium iodide. Whilst calculations for a multicomponent system were not carried out, it is possible to determine whether caesium iodide or caesium hydroxide nucleated first for a given set of experimental conditions. The comparison is complicated by the fact that the time at which nucleation occurs varies across the tube. Comparisons were therefore made at each collocation radius for each set of conditions. Table 6.6 shows the result of this comparison.

<table>
<thead>
<tr>
<th>Run</th>
<th>near axis</th>
<th>Collocation Radius</th>
<th>near wall</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>CsOH</td>
<td>CsOH</td>
<td>CsOH</td>
</tr>
<tr>
<td>B</td>
<td>-</td>
<td>CsOH</td>
<td>CsOH</td>
</tr>
<tr>
<td>C</td>
<td>-</td>
<td>-</td>
<td>CsI</td>
</tr>
<tr>
<td>D</td>
<td>CsOH</td>
<td>CsOH</td>
<td>CsOH</td>
</tr>
<tr>
<td>E</td>
<td>CsOH</td>
<td>CsOH</td>
<td>CsOH</td>
</tr>
<tr>
<td>F</td>
<td>-</td>
<td>CsI</td>
<td>CsI</td>
</tr>
<tr>
<td>G</td>
<td>CsOH</td>
<td>CsOH</td>
<td>CsOH</td>
</tr>
<tr>
<td>H</td>
<td>CsOH</td>
<td>CsOH</td>
<td>CsOH</td>
</tr>
<tr>
<td>I</td>
<td>CsOH</td>
<td>CsOH</td>
<td>CsOH</td>
</tr>
</tbody>
</table>

Table 6.6
Comparison of whether caesium iodide or caesium hydroxide particles nucleate first for specific conditions at various radial positions. Failure to nucleate by both compounds is indicated by a dash (-).

It can be seen that in many cases the calculations confirm the experimental result that caesium hydroxide nucleates before caesium iodide. In fact, the comparison is more favourable than may appear from Table 6.6 due to a number of factors. The number of particles nucleated at the collocation radius near the wall is in most cases negligible; it is therefore irrelevant which compound nucleates first. Secondly, the Winfrith
multicomponent experiments were performed with a CsI:CsOH partial pressure ratio of 1:22. Combined with the fact that the equilibrium partial pressure of caesium hydroxide is lower anyway, the caesium hydroxide would therefore be much more saturated than the caesium iodide (all other thermochemical properties being nearly equal) leading to the critical saturation being achieved sooner. It is therefore unsurprising that caesium hydroxide nucleates before caesium iodide, even in the comparison above, where the inlet partial pressures were equal.
6.4 Conclusions

The results of experimental workers at AEA Winfrith have been used to investigate the validity of the numerically soluble model in conditions appropriate to possible nuclear reactor accidents.

The theoretical prediction of nucleation processes requires a good nucleation model in order to accurately determine the number of particles formed. Classical nucleation theory, as employed in the model used is known to suffer from problems in predicting the temperature dependence of nucleation. For this reason, the calculations were unable to reproduce the results of the Winfrith experiments. This failure is also expected to be due, in part, to poor characterisation of the experiments in the reported data, for example the determination of the partial pressure of fission product simulant by the time-averaged mass depletion method.

Whilst specific results cannot be reproduced by the computational methods employed, trends reported by Bowsher et al. can be reproduced well. In nearly every case, calculations reveal exactly the same trend as found in the experimental studies. The comparison draws attention to the importance of the sharp fall in temperature between the thermal gradient region of the experiment and the filter used for sampling. Significant growth of the aerosol was seen to occur in this region, highlighting the importance of thermal gradients in aerosol formation and growth. Only one experimental trend could not be reproduced; the increased retention of caesium hydroxide compared to caesium iodide. It seems that processes which were not modelled in the code differentiate the two materials. Suggestions include thermophoretic deposition (with differentiation on grounds of particle diameter), adsorption of caesium hydroxide onto the tube walls, and a failure to model aerosol deposition onto the tube walls. Further calculations and experiments will be required to satisfactorily resolve this question.

Overall, the results of this exercise give confidence to the application of the methods developed in this thesis to the determination of trends in aerosol behaviour in primary circuit tubing.
Chapter 7

Ion-Induced and Binary Nucleation
7.1 Introduction

In all the situations considered so far, nucleation has been assumed to occur by a single component homogeneous mechanism. However, other mechanisms exist by which nucleation may occur. This chapter will deal with improvements to one of these methods (ion-induced nucleation), and will consider the influence of these methods on aerosol behaviour in a reactor accident scenario.

Heterogeneous nucleation, whereby a “seed” particle lowers the energy barrier to nucleation by providing a site for condensation, is in direct contrast to homogeneous nucleation, where nucleation is spontaneous and involves no foreign materials. Examples of such “seed” particles include finely divided structural materials formed by violent degradation of components of the reactor (e.g. concrete dust) as well as ions. Because of the special conditions in a Naval PWR the formation of seed particles from structural materials may reasonably be precluded. Instead, ion-induced nucleation (IIN), a special subclass of heterogeneous nucleation is considered in some depth. Large amounts of ionising radiation are expected to be released during an accident sequence; consequently the effect of IIN must be assessed. As with homogeneous nucleation, classical IIN theory (CIINT) is based upon the application of macroscopic approximations to microscopic droplets. An assessment of the validity of this approach is attempted. Clustering of subsaturated water vapour about ions is also expected to occur, potentially producing larger seed nuclei than might be formed in a single component system. Since this will also act to reduce the energy barrier to nucleation, a method is proposed to take this into account.

Both homogeneous and heterogeneous nucleation can occur in the presence of one or more condensible species. So far only the single component case has been addressed in this work. Multicomponent nucleation may be expected to increase the nucleation rate, again by providing a lower energy pathway to cluster formation. The significance of this effect will be demonstrated.
7.2 Ion Induced Nucleation

Since the number of ions present in a system will impact directly on the extent of their effect in promoting nucleation, it is first necessary to determine their number concentration.

7.2.1 Estimate of Ion Concentrations

Clement et al. (1993) have calculated the maximum ionisation rate (ion production rate) from releases into the containment of a civil PWR in the event of an accident. They derive a Figure of $2.738 \times 10^{18} \text{ m}^{-3}\text{s}^{-1}$ from data which pertain to the Sizewell PWR (Kelly and Clarke, 1982). No data detailing expected releases from Naval PWRs are available in the public domain. The data of Clement et al. is therefore scaled with approximate reactor power to give a production rate in the Naval PWR of one-thirtieth of their value, i.e. $9 \times 10^{16} \text{ m}^{-3}\text{s}^{-1}$.

7.2.1.1 Method of Estimation

The procedure of Harrison (1992) is followed to determine the ion concentration from the above production rate. Due to ion–ion recombination the ion concentration rises to a limiting value very rapidly – typical timescales are less than 0.1s for cases considered. The method used to calculate the ion concentration is briefly outlined here.

The variation in number $n$ of ions with time can be written as follows:

$$\frac{dn}{dt} = q - \alpha n^2 \quad (7.1)$$

where $q$ is the production rate of ions, and $\alpha$ the recombination coefficient. Equation (7.1) could of course be modified to take account of other ion-removal processes. Integration of equation (7.1) gives the number of ions as a function of time:

$$n = \left( \frac{q}{\alpha} \right)^{\frac{1}{2}} \frac{1 - \exp(-2\sqrt{\alpha q t})}{1 + \exp(-2\sqrt{\alpha q t})} \quad (7.2)$$

McDaniel (1964) identifies three theories for ion-ion recombination. That of Thomson (1924) is adopted here, although it’s experimental agreement is recognised to be poorer at higher pressures. This has the form:

$$\alpha = \frac{\pi a^2 \sqrt{c_+^2 + c_-^2}}{2s} \left[ 2 - \frac{\lambda_+}{2s} \left( 1 - e^{2\lambda t} \right) - \frac{\lambda_-}{2s} \left( 1 - e^{2\lambda t} \right) \right] \quad (7.3)$$
where \( c \) is the root-mean square speed of positive or negative ions, and \( \lambda \) their mean free path. These are given by equations (7.4) and (7.5) respectively:

\[
c_+ = \sqrt{\frac{8kT}{\pi m_+}} \quad (7.4)
\]

\[
\lambda_+ = \left( \frac{8\mu_+}{3e} \right) \left[ \frac{kTm_+M}{(M+m_+)} \right]^{\frac{1}{2}} \quad (7.5)
\]

The ion mobility, \( \mu \), is given by the Langevin theory:

\[
\mu_+ = 0.5105 \sqrt{\varepsilon_0 \left( 1 + \frac{M m_+}{m_+} \right)} \quad (7.6)
\]

The parameters \( a \) and \( s \) in equation (8.3) are in fact equivalent, and given by:

\[
a = s = \frac{e^2}{6\pi \varepsilon_0 kT} \quad (7.7)
\]

\( a \) is defined as the recombination distance: it is assumed that two ions passing within this distance of each other will recombine. It is defined by comparing their kinetic energy with the potential energy of interaction; these energies are equal at an ionic separation \( a \).

### 7.2.1.2 Dependencies of Ion Concentration

Due to the large number of equations involved in the calculation of ion recombination rates, the variation of ion concentration with parameters such as temperature, pressure and ion production rate is not obvious. A number of calculations were performed in order to determine the effect of such changes, and identify the key intermediate values which were affected.

Ion density increases roughly linearly with temperature. Although the mean free speed increases with the square root of temperature, this increase is countered by the \( 1/T \) dependence in the recombination radius. Increasing the system pressure decreases both the mobility and mean free path, both linearly with the pressure variation. The final number concentration decreases roughly as \( \sqrt{P} \). The dependence of the final number concentration upon the production rate is obvious from equation (7.2): the final number varies with \( \sqrt{q} \).

As noted above, the timescale for equilibration is extremely short (< 0.1s for conditions of interest). The ion concentration can therefore be treated as constant.
7.2.2 Clustering

Molecules from the vapour will tend to condense upon ions present in the system. The clusters thus formed may assist the nucleation process, by providing stable sites, of a size larger than would otherwise be formed, which can act as seed particles for aerosol nucleation. By reducing the free energy change of formation of critical clusters, ion-clusters can enhance the rate of nucleation.

7.2.2.1 Equilibrium Clusters

In their 1967 paper Kebarle et al. published equilibrium constants for the clustering of water molecules about a proton. From these, it is possible to determine the concentration of any size cluster (for which data is available).

If \( c_n \) is the concentration of the cluster \( H^+ (H_2O)_n \), then it follows from the definition of an equilibrium constant that:

\[
c_2 = c_1 p_v K_{1,2}
\]

and therefore

\[
c_3 = c_2 p_v K_{2,3} = c_1 p_v^2 K_{1,2} K_{2,3}
\]

where \( p_v \) is the water vapour pressure (= \( S p_{v_0}(T) \)).

Equation (7.9) may be extended in general to

\[
c_n = c_1 p_v^{n-1} \exp[\ln K_{1,2} + \ln K_{2,3} + ... + \ln K_{n-1,n}]
\]

(7.10)

In their paper, Kebarle et al. also present an expression for \( K_{n-1,n} \) in terms of two parameters \( A \) and \( B \). The expression is as follows:

\[
\log K_{n-1,n} = \frac{A}{T} 10^3 - B
\]

(7.11)

To express this using natural logarithms, with conversion from Torr (used by Kebarle for pressure) to Pascals requires \( A \) and \( B \) to be converted thus:

\[
A' = A \ln 10 = 2.3026 A
\]

(7.12)

\[
B' = -2.3026 B - 4.893
\]

(7.13)

This allows the concentration of any cluster to be written:

\[
c_n = c_1 \exp \left[ (n-1) \ln S + \sum_{i=2}^{n} \left( \frac{1000 A_{i-1,i}'}{T} + B_{i-1,i}' + \ln p_v (T') \right) \right]
\]

(7.14)

Comparison with the thermodynamic relation

\[
c_n = c_1 \exp \left( \frac{-\Delta G}{kT} \right)
\]

(7.15)
allows the identification of the term in square brackets as being the free energy change of cluster formation (divided by $-kT$).

In order to calculate $c_n$ it is necessary to know $c_i$, the concentration of monohydrates. If the ion concentration, $N_i$, is assumed to be equal to the sum of the concentrations of all the hydrates then:

$$N_i = c_1 + c_2 + c_3 + \cdots + c_{n-1} + c_n \quad (7.16)$$

Defining a new quantity (for convenience), $\hat{c}_n$, and expanding in terms of (7.14) gives

$$\hat{c}_n = \frac{c_n}{c_1} = \exp \left[ (n-1) \ln S + \sum_{i=2}^{n} \left( \frac{1000}{A_i'} + B_i + \ln p_i(T) \right) \right] \quad (7.17)$$

Combining and rearranging (7.16) and (7.17) gives:

$$N_i = c_1 \left( 1 + \hat{c}_2 + \hat{c}_3 + \cdots + \hat{c}_{n-1} + \hat{c}_n \right) \quad (7.18)$$

hence

$$c_1 = \frac{N_i}{1 + \sum_{i=2}^{n} \hat{c}_i} \quad (7.19)$$

Equation (7.14) can then be used to calculate the exact concentration of any cluster, provided that the sum includes all clusters with a significant population.

Harrison (1992) presents calculations based upon this methodology in his thesis. However, there is an error in his work which has quantitative significance. In his equation [3.22] for the concentration of a cluster of $n$ water molecules, the factor for saturation (expressed as $r$, the relative humidity in his work) is used as a multiplier for the logarithm of the water concentration rather than as a multiplier to the concentration itself. Correcting this error shows that the equilibrium cluster size for water is significantly higher than supposed by Harrison. Figure 7.1 shows the corrected results. Since Kebarle’s data extends only as far as clusters of 8 molecules, the corrected results beyond a relative humidity of about 0.4 cannot be taken as reliable. This is due to the condition attached to equation (7.19) that all clusters with significant population be accounted for. It seems almost certain that at higher relative humidities the equilibrium cluster will be larger than $n = 8$. The effect at higher temperatures is even more striking. It is not possible to predict from Kebarle’s data what the equilibrium cluster size will be, other than to say it exceeds $n = 8$ for all but the lowest relative humidity. Shi et al. (1993) report data for clusters of up to 28 water molecules. Their work was carried out at low temperature (130 K) and pressure and
has therefore not been used to extrapolate data at higher temperatures. For all other situations (larger water clusters or any other cluster, e.g. CsI), it remains necessary to use CIINT due to a lack of appropriate experimental data. A comparison was therefore made between CIINT and the experimental results of Kebarle et al.

![Graph showing populations of water clusters about H+ ions at 300K as a function of saturation.](image)

**Figure 7.1**
*Populations of water clusters about $H^+$ ions at 300K as a function of saturation*

### 7.2.2.2 Comparison of CIINT cluster sizes with experiment

From the distribution of clusters, the mode size can be identified as the equilibrium size and compared with the predictions of CIINT which predicts two turning points in the free energy surface as it varies with droplet radius. The turning point at the higher radius is a free energy maximum which marks the critical size, which is the radius beyond which the probability of the droplet growing is greater than that of it shrinking. The other turning point is a free energy minimum, and represents the point at which the stabilisation of the ion due to clustering is balanced by the tendency of small droplets to evaporate. This size can be identified as the equilibrium cluster radius, and the prediction of CIINT compared with Kebarle’s experimental data. Table 7.1 compares the number of water molecules clustered around a proton, as predicted by CIINT with Kebarle’s results.
Table 7.1  
<table>
<thead>
<tr>
<th>Saturation</th>
<th>n (experiment)</th>
<th>n (CIINT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>0.05</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>0.1</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>0.15</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>0.2</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>0.3</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>0.5</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>1.0</td>
<td>?8?</td>
<td>9</td>
</tr>
</tbody>
</table>

Comparison of experimental data with theory for equilibrium cluster size at 300K

The experimental value for a saturation of 1.0 is flanked by question marks to indicate that the lack of data for $n > 8$ makes it probable that this result is too low.

7.2.2.3 Free energy changes of cluster formation

As noted above, it is possible to use Kebarle’s experimental data to predict the free energy change of cluster formation. This value is of great importance in determining nucleation rates, and so a comparison of theory with experiment will provide a stringent test of CIINT.

Figure 7.2

Free energy changes for the addition of a water molecule to a cluster, calculated from the experimental data of Kebarle et al. (1967) and CIINT for saturation equal to unity.
Figure 7.2 compares the free energy change for the addition of a single molecule to a cluster at unity saturation. Summing the values presented here will give the free energy change for the formation of a cluster of size \( n \). It can be seen that the size dependence of the two methods (illustrated by the slope of the lines) is different, leading to different estimates of the critical cluster. Although for larger clusters the results of experiment and theory are very similar, because of the summation just mentioned, even for large clusters the free energy change of formation will still be significantly offset from the correct value.

7.2.2.4 Evaluation of CIINT compared with experimental data

The comparisons presented above should allow a basic picture of the quality of CIINT to be built up. The lack of experimental data for larger clusters, thus restricting comparisons to subsaturated situations and other materials limits the amount of detail in this picture. It can be seen that although CIINT does not exactly reproduce the size \((n)\) dependence shown in experiments, the predictions of the minimum stable cluster, \( r_m \), are quite good. In the light of this and the fact that the gradient \( \frac{\partial \Delta G}{\partial n} \) of CIINT appears to be converging towards the experimental gradient, it seems likely that CIINT will predict the size of the critical cluster reasonably accurately. In conclusion, the limited comparisons made above appear to suggest that despite the macroscopic approximations underlying CIINT, it is capable of predicting sizes and free energy changes with respectable accuracy. In the following sections, modifications to the theory will be proposed in an attempt to increase the accuracy with which it describes the mechanics of cluster formation.

7.2.3 Ion-Induced Nucleation about Water Clusters

In accident scenarios under consideration the release of both steam and condensible fission product vapours is likely. Under any specified conditions, it is likely that the equilibrium cluster radii for water and caesium iodide will be different. If the clustering of water about ions produces larger clusters than the ion stabilisation radius for caesium iodide, we may expect that the free energy change for nucleation will be reduced compared to that predicted by CIINT. This will have the effect of increasing the rate of nucleation, and is illustrated in Figure 7.3. Note that in the event
that the equilibrium size of water clusters is smaller than that of CsI clusters, the postulated pathway will become irrelevant.

**Figure 7.3**

*The effect of cluster size on free energy change in classical and extended classical ion-induced nucleation theories for caesium iodide*

The rate of nucleation both with and without water clusters is compared below. An enhancement is only possible for temperatures below the critical temperature of water (647.3 K) since above this temperature condensation to the liquid phase will not occur. In principle vapour – solid nucleation could occur, however examination of the phase diagram for water reveals that this need only be considered at very high pressures (tens of thousands of atmospheres) which will never be seen in a PWR. From the solution to:

\[
\frac{\partial [\Delta G(r)]}{\partial r} = 0 \quad (7.20)
\]

the equilibrium cluster radius for both water (\(r_{\text{water}}\)) and caesium iodide (\(r_{\text{CsI}}\)) can be found. When \(r_{\text{water}} > r_{\text{CsI}}\) the value of \(r_{\text{water}}\) is used in equation (\(\Delta G\) for CIINT).

Tables 7.2 and 7.3 (overleaf) show cluster radii for a number of water and CsI saturations.
\[ S \quad r_{\text{water}} \]
\begin{array}{cc}
0.01 & 3.27 \times 10^{-10} \\
0.03 & 3.50 \times 10^{-10} \\
0.05 & 3.63 \times 10^{-10} \\
0.1 & 3.87 \times 10^{-10} \\
0.15 & 4.05 \times 10^{-10} \\
0.2 & 4.22 \times 10^{-10} \\
0.3 & 4.51 \times 10^{-10} \\
0.5 & 5.13 \times 10^{-10} \\
1.0 & 1.04 \times 10^{-9} \\
\end{array}

Table 7.2
equilibrium cluster radii for water at 600 K

\[ S \quad r_{\text{CsI}} \]
\begin{array}{cc}
1.1 & 3.61 \times 10^{-10} \\
1.2 & 3.63 \times 10^{-10} \\
1.5 & 3.66 \times 10^{-10} \\
2 & 3.71 \times 10^{-10} \\
3 & 3.79 \times 10^{-10} \\
4 & 3.86 \times 10^{-10} \\
5 & 3.91 \times 10^{-10} \\
6 & 3.96 \times 10^{-10} \\
7 & 4.00 \times 10^{-10} \\
8 & 4.04 \times 10^{-10} \\
9 & 4.08 \times 10^{-10} \\
10 & 4.12 \times 10^{-10} \\
\end{array}

Table 7.3
equilibrium cluster radii for caesium iodide at 600 K

Data from Rolls Royce suggest that the pressure in differing accident scenarios spans the range 1 to 50 atmospheres. Given that the equilibrium vapour pressure of water at 600 K is approximately 240 atmospheres, the saturation ratio of water in a total steam environment can be expected to lie in the range 0.004 to 0.2. For scenarios in which hydrogen is present in significant quantities, these saturations will of course reduce. From Tables 7.2 and 7.3 it can be seen that only at higher pressures will the condition for enhancement be true. In cases where the pressure is around 50 atmospheres, enhancement can be expected even for high caesium iodide
saturations, although as the caesium iodide saturation rises, so the enhancement becomes less.

The variation in the rate of nucleation with saturation was investigated for both CIINT and the water cluster enhanced mechanism (eCIINT) at 600 K. The results are shown in Figure 7.4. The enhancement is extremely small when the steam pressure is 50 atmospheres: the lines for CIINT and eCIINT overlay each other except at the lowest saturations, when the rate is insignificant anyway. The enhancement is seen, however, to be very sensitive to the size of the water cluster. A steam pressure of 175 atmospheres corresponds to a water cluster radius of $6.10 \times 10^{-10}$ m, only slightly larger than for 50 atmospheres. The nucleation rate is enhanced by a factor which ranges from 30000 to 20 as the saturation increases. At 250 atmospheres, the enhancement is over 9 orders of magnitude when the saturation is below about 14. Beyond this point, the water cluster is larger than the critical cluster, and nucleation becomes barrierless. Given that comparisons with the data of Kebarle et al. have suggested that CIINT underestimates the size of the equilibrium cluster, it may be supposed that the effect of water cluster formation upon the nucleation of caesium iodide is greater than demonstrated here.

Figure 7.4
The pressure dependent enhancement of caesium iodide nucleation by water molecule clusters
7.2.4 Comparison of CNT with CIINT for CsI

Nucleation in the presence of ions is expected to occur at a greater rate than without ions, due to the increased stability of small clusters afforded by the ion. A simple comparison of the rates of nucleation, modelled by CNT and CIINT is demonstrated here.

An important point concerning ion-induced nucleation is the proportionality of the rate to the ion concentration. If the number of ions present in the system decreases, so will the rate of nucleation. The work detailed in section 7.2.1 accounts for a reduction in the concentration of ions present due to recombination, but ignores the fact that nucleation itself reduces the number of ions available for nucleation to occur upon. If the effect of ions which have been nucleated upon recombining is ignored, the following reformulation of equation (7.1) will allow a more accurate assessment of ion density:

\[ \frac{dn}{dt} = q - \alpha n^2 - J \quad (7.21) \]

Since the expression for the ion induced nucleation rate is linearly proportional to the ion concentration, equation (7.21) may be rewritten

\[ \frac{dn}{dt} = q - \alpha n^2 - nx \quad (7.22) \]

where

\[ J = nx \quad (7.23) \]

Equation (7.22) may then be expressed as:

\[ \frac{dn}{dt} = q - \alpha \left( n + \frac{\kappa}{2\alpha} \right)^2 + \frac{\kappa^2}{4\alpha} \quad (7.24) \]

Defining

\[ N = n + \frac{\kappa}{2\alpha} \quad (7.25) \]

\[ Q = q + \frac{\kappa^2}{4\alpha} \quad (7.26) \]

then the combination of the previous three equations allows

\[ \frac{dN}{dt} = Q - \alpha N^2 \quad (7.27) \]

to be written. Provided \( \alpha \) and \( \kappa \) are independent of time, \( t \), then the steady state solution to the integration of equation (7.27) is:
which reduces to the steady-state solution of equation (7.1) if ion-induced nucleation is ignored. From the solution of the differential equation (7.27) the timescale for the steady state condition to be reached can be found:

\[
\tau = \frac{1}{2\sqrt{\alpha \left( q + \frac{\kappa^2}{4\alpha} \right)}}
\]  

Figure 7.5 (on page 144) compares homogeneous nucleation rates with ion induced nucleation rates for caesium iodide, both based on a constant ion density and also allowing for the non-availability of ions due to prior use as nucleation sites. The value of \( \kappa \) as a function of temperature and saturation was calculated. Multiplying by the ion densities given in Equations (7.2) and (7.28) results in ion-induced nucleation rates for constant and varying ion densities respectively. For the range of temperatures considered, the “constant” ion densities lie in the range \( 8 \times 10^{14} \text{ m}^{-3} \) to \( 5 \times 10^{15} \text{ m}^{-3} \). When account is taken of nucleation making ions unavailable for subsequent nucleation, ion densities fall to values as low as \( 6 \times 10^6 \text{ m}^{-3} \).

Considering first the case of IIN where ion removal is not treated, it can be seen that a similar (but slightly stronger) saturation dependence is seen compared to that exhibited by CNT. The temperature dependence of CIINT is however weaker. Under conditions where the nucleation rate is of comparable magnitude to the ion density CIINT can no longer be used successfully because of the removal of ions by nucleation. With an ion density of \( 5 \times 10^{15} \text{ m}^{-3} \) a nucleation rate of \( 1 \times 10^{16} \text{ m}^{-3} \) might be expected to consume all of the ions with 0.5 s, thus shutting off nucleation almost immediately. In practice, the self-recombination rate of ions will fall, but since ions are being produced at a constant rate they will be replenished. A quantitative treatment of this situation requires the use of Equation (7.28). At low nucleation rates, the results of Equations (7.2) and (7.28) are equal and the effect of ion removal by nucleation need not be considered. As \( \kappa \) increases, so the density of ions available for fresh nucleation to occur upon falls, and the nucleation rate will tend to a limiting
value. It can be seen that this value is constant for all temperatures, and is in fact equal to the production rate considered here.

For both IIN models, the point at which the lines stop represent the point at which nucleation becomes barrierless, i.e. the equilibrium cluster size is actually smaller than the critical cluster. Since in this case there is no longer a free energy barrier to nucleation, the nucleation “rate” becomes simply the collision rate (which is proportional to the saturation) multiplied by the ion density.

It can be seen that for the conditions considered, the onset of IIN occurs at lower saturations than the onset of homogeneous nucleation. Since the ion density is simply a multiplicative factor in the ion-induced nucleation rate expression, this situation could of course be reversed in cases with low ion densities. As noted above, IIN is limited to a rate equal to the production rate of ions, while homogeneous nucleation in theory has no upper rate limit. In practice, growth upon the nucleated particles will serve to reduce the saturation so that nucleation rates as high as some of those plotted will never be seen in reality.
Figure 7.5
The dependence of nucleation rate upon saturation and temperature, modelled for homogeneous and ion-induced nucleation (with and without ion depletion)
### 7.3 Binary Nucleation

Nucleation of water in the atmosphere has been observed to occur more readily (at lower saturations) in the presence of sulphuric acid vapour. The phenomenon of binary nucleation, where the presence of small quantities of a second component causes enhancement of the nucleation rate has already been applied to one system of potential interest in the nuclear safety field. Kulmala et al. (1991) studied the enhancement of hydrogen iodide vapour to aerosol conversion in the presence of steam molecules. The unique nature of the Naval PWR makes the presence of hydrogen iodide unlikely; however the same enhancement might be expected for caesium iodide and water.

As a preliminary test of the relevance of binary nucleation to the overall vapour – aerosol conversion process, the equilibrium cluster distribution was investigated. The form of Wilemski and Wyslouzil (1995) is used to describe the concentration of clusters of a given composition:

\[ c(i,j) = \left( \frac{P_{rel}}{kT} \right)^x \left( \frac{P_{rel}}{kT} \right)^{(n-1)} \exp \left( x \sigma_1 + (1-x) \sigma_2 - \theta(i,j) \right) \]

(7.30)

where \( x \) is the mole fraction of caesium iodide (component 1), \( P_{rel} \) and \( P_{rel} \) are the saturation pressures of water (component 2) and caesium iodide respectively. \( \theta \) is defined as follows:

\[ \theta_n = \frac{\sigma_n A_n}{kT} \]

(7.31)

where \( \sigma_n \) is the surface tension either of a pure component or a mixture of specified composition, and similarly \( A_n \) is the surface area of one molecule (if \( n = 1 \) or \( n = 2 \)) or the surface area of the cluster in question if \( n = i/j \), where \( i \) represents the number of molecules of caesium iodide and \( j \) the number of water molecules. Since no experimental data for the surface tension of caesium iodide/water mixtures was available, some form of interpolation is required. For the purposes of this simple calculation a linear interpolation form, given in Equation (7.32), was used between the two pure substance values.

\[ \sigma_{ij} = \sigma_i + (1-x)(\sigma_j - \sigma_i) \]

(7.32)

The high temperature water value comes from data adopted by the International Association for the Properties of Steam (Sengers and Watson, 1986).
A sample calculation at 600 K, with water saturation = 0.2 and caesium iodide saturation = 15.0 shows a saddle point in the equilibrium cluster population surface (Figure 7.6). The significance of this region is due to the correlation between higher equilibrium populations and lower free energy changes. The most energetically favourable pathway from single molecule to viable cluster is the one with the smallest free energy change; this corresponds to the highest concentrations. In the single component case, the caesium iodide critical cluster would comprise 40 molecules. Adding 13 water molecules to this cluster increases the equilibrium population by three orders of magnitude, significantly increasing the rate of nucleation. Although more detailed calculations are required to quantify exactly the influence of binary nucleation upon the overall picture, these results confirm that water can significantly affect the nucleation rate of caesium iodide by a binary mechanism.

Figure 7.6
Equilibrium concentration of a binary caesium iodide – water cluster as a function of composition at 600K
7.4 Conclusions

The importance of ions to nucleation processes in reactor accidents has been demonstrated. An examination of the processes governing ion densities (upon which ion-induced nucleation rates are dependent) reveals that temperature, pressure and the ion production rate are the key parameters, with temperature the most important. The timescale for ion densities to equilibrate is seen to be very short, allowing these to be treated as constant.

From considerations of experimental data relating to the clustering of water molecules about a proton it has been possible to assess CIINT. A lack of data precludes a full investigation, particularly for supersaturated systems, but it appears that, despite some discrepancies, CIINT overcomes many of the limitations apparently posed by its macroscopic origins to provide respectable results.

The co-operative nucleation of water vapour and caesium iodide has been investigated via two routes. A new possibility, that of equilibrium clusters of subsaturated steam acting as condensation nuclei for caesium iodide has been described, and shown to be significant only at high pressures (when the water vapour approaches saturation). Binary nucleation of mixed caesium iodide/ water clusters has been demonstrated to be a feasible mechanism for reducing the free energy barrier to nucleation (ergo increasing the rate). Because of the relatively low critical point of water (647.3 K) this route will not occur at high temperatures, where nucleation rates are normally low.

A modification to the expressions used to calculate ion densities has been proposed which takes into account the fact the once nucleation has started on an ion that ion is no longer available for nucleation. The effect of this reduction in nucleation sites with increasing nucleation rate is to cap the effects of ion-induced nucleation to a limiting value. However, this effect is only seen at relatively high nucleation rates which may not be reached in practice due to condensative aerosol growth. For the conditions expected to be prevalent in the Naval PWR it is likely that ion induced nucleation will occur more readily and at greater rates than homogeneous nucleation. This situation could be reversed with a significant change in the ion density (to which the ion induced nucleation rate is proportional)
Conclusions
8.1 Introduction

This thesis has addressed a number of issues related to the behaviour of aerosols in theoretical accidents in pressurised water reactors. A better understanding of such processes is essential in improving the hitherto pessimistic estimates of probable radionuclide release.

8.2 Key Areas

The formation and growth of aerosol has been studied under both turbulent and laminar flow conditions. Nucleation has been seen to be possible in both regimes for conditions which are considered probable in a theoretical reactor accident. Regardless of flow rate, nucleation is seen to occur more readily for compounds whose equilibrium vapour pressure is a strong function of temperature. Large temperature gradients are also seen to enhance nucleation. It is suggested that in turbulent flow the boundary layer may well experience the greatest nucleation because of the sharp temperature differentials seen there. Calculations using both simplistic models which aim to encapsulate theoretical understanding in a small group of readily understandable parameters, as well as more complicated calculations, intended to check the accuracy of the simpler methods have been used.

Simple, analytically soluble forms have been developed for the maximum saturation and thus nucleation rate. These forms have been shown to reproduce more complex, numerically soluble, results well for cases when vapour depletion is not important. These forms have allowed the identification of the Lewis number as a key parameter in determining the location of maximum nucleation. It has also been possible to use these forms to provide a method for estimating the conditions necessary for the onset of significant nucleation (where the definition of significant can be chosen at will) and to determine when vapour depletion due to the growth of aerosol will be important. Comparisons with more detailed calculations have shown that particularly good agreement when small seed particles or new aerosol are considered.

The effects of aerosol growth leading to vapour depletion have also been considered. It has been shown that significant changes in the extent of nucleation and the position at which the maximum rates are seen occur when nucleation is quenching. The condition described above has been used in identifying cases where
the simpler forms above cannot be directly applied. These simpler forms have, however, been used as a starting point for a new semi-analytical form which allows estimates of the extent of nucleation expected to be made. A surprising result, revealed by this method, and confirmed by more detailed calculations is that in many situations where the growth of aerosol leads to quenching the maximum nucleation is seen near the walls, regardless of the Lewis number of the compound involved. Investigation revealed that quenching begins at the centre of the tube, and gradually extends towards the walls as the conditions become increasingly conducive to nucleation. For many cases where quenching occurred, the extent of the quenching was such that nucleation near the centre of the tube was suppressed sufficiently that the nucleation rate near the wall was in fact higher.

The methods developed during the course of this work were tested against experimental results from AEA Winfrith. Due to the current lack of a high quality nucleation theory, it was not possible to reproduce precise numerical results from these experiments. However, by considering the trends found in the experimental results, it was possible to demonstrate good qualitative agreement between calculation and experiment. It is expected that, given a sufficiently accurate nucleation theory, it will be possible to reproduce these results. It is felt that the qualitative agreement seen in this comparison gives weight to the general trends predicted in this work.

An assessment of alternative methods of aerosol formation has been carried out. Other nucleation mechanisms (such as ion-induced and binary) are shown to be of potentially great importance in determining the amount of aerosol formed in a reactor accident situation. It would be possible to determine the primary nucleation mechanism for any given situation and use the relevant formalism in the methods outlined above, in order to give the best estimate of aerosol formation.

In addition to providing a number of insights with wider applicability this thesis also provides information about nucleation specific to nuclear reactor accidents. Nucleation has been shown to be more likely when the vapour pressure of the species under consideration has a strong temperature dependence. Higher temperature differentials between the bulk and cooling surfaces have also been shown to promote nucleation. The consequences of clustering by water molecules about caesium iodide molecules for nucleation have been investigated and found to offer a route by which the nucleation rate may be enhanced, particularly at lower temperatures when the nucleation rate would otherwise be low.
8.3 Conclusion

This project has established some of the key parameters on which the nature of aerosol formation and growth depend, and provided analytical means to assess the likely extent of aerosol processes. It has been shown that it is not necessary to model situations with a high resolution grid of points in order to obtain qualitative agreement with experiment. Failings in nucleation theory remain the single largest obstacle to obtaining accurate agreement with experiment. It is believed that when this issue has been resolved the methods presented in this work will be well able to rapidly and accurately characterise aerosol behaviour in tube flow scenarios.
Bibliography
Adachi, M., Okuyama, K., Seinfeld, J.H., Experimental studies of ion-induced

Ahluwalia, R.K., Im, K.H., Mass transfer of trace species from a superheated stream

Surface studies of the interaction of cesium hydroxide vapour with 304 stainless

Ball, R.G.J., Bowsher, B.R., Cordfunke, E.H.P., Dickinson, S., Konings, R.J.M.,
Thermochemistry of selected fission product compounds, *J. Nuclear Materials*,
201, 81-91, (1993)


Barrett, J.C., Timescales for nucleation and growth in supersaturated vapour – gas

Barrett, J.C., Baldwin, T.J., Aerosol nucleation and growth during laminar tube flow:

223-242, (1988)

Barrett, J.C., Clement, C.F., Aerosol concentrations from a burst of nucleation, *J.

Barrett, J.C., Fissan, H., Wall and aerosol condensation during cooled laminar tube

Barua, A.K., Afzal, M., Flynn, G.P., Ross, J., Viscosity of hydrogen, deuterium,
methane and carbon monoxide from -50°C to 150°C below 200 atmospheres,

Becker, R., Döring, W., Kinetische Behandlung der Keimbildung in übersättigten

Binder, K., Nucleation theory and dynamics of first-order phase transitions near a

Bowsher, B.R., Nichols, A.L., *High temperature studies of simulant fission products: Part IV Interaction of caesium iodide with boric acid over the temperature range 400 to 1000°C*, United Kingdom Atomic Energy
Authority, July 1985. (AEEW-R1973)

Brown, D. P., private communications, October 1998

(2), 135-147, (1991)

Chan, L.Y., Mohnen, V.A., Ion nucleation theory, *J. Atmos. Sci.*, 37, 2323 – 2331,
(1980)


Clement, C.F., Aerosol formation from heat and mass transfer in vapour – gas


Clough, P.N., Bryant, R., Ash, L., Barrett, J.C., Baldwin, T.J., Meeting at Rolls Royce, Derby, 18th June 1997


Kissane, M.P., private communication, October 1998


Mikheev, V.B., Pervukhin, V.V., Laulainen, N.S., Advanced nucleation studies using a laminar flow tube reactor and a mass spectrometer with atmospheric pressure ionization. At the 72\textsuperscript{nd} ACS Colloid and surface science symposium, sponsored by the American Chemical Society, and held in State College, Pennsylvania, 21 June – 24 June 1998.


Thomson, J.J., Recombination of gaseous ions, the chemical combination of gases and mono-molecular reactions, Phil. Mag., 47 (278), 337 - 378, (1924)


Appendix A

Numerical Methods
A.1 Solution of Ordinary Differential Equations

Analytical solution of sets of differential equations is rarely possible, except in simple cases. However, several techniques exist to numerically solve a set of ordinary differential equations (ODE). Whilst some situations are more intractable than others (see Section A2 on stiff equations) most yield to numerical solution, for example by the Runge-Kutta method which has been used in this work (Press et al., 1992).

A.1.1 Runge-Kutta Methods

Consider the problem:

$$\frac{dy}{dx} = f(x,y) \quad (A.1)$$

For an initial value problem the value of the function underlying the differential equation is known at the lower limit of integration. When a solution for $a<x<b$ is sought, $y$ at $x=a$ must be known. Naturally the form of the function $f$ must also be known. In this case, the value of the derivative at $a$ can be calculated. A series of "mesh points", with interval $h$ are placed in the range $a$ to $b$. Since the value of both the underlying function and its derivative are known at the first mesh point, an estimate for the value of the underlying function at the second mesh point can be made.

Continuing in this manner results in an approximation to the underlying function being generated. This is known as the Euler method, and is neither especially accurate nor stable. The error in this method is of the order $h^2$ per step, and of order $h$ overall. A simple modification, using the value of the derivatives at points intermediate to the mesh leads to the midpoint method, also known as second order Runge-Kutta, with error of order $h^3$. Extending this principle yields the fourth-order Runge-Kutta method, with usually greater accuracy than second-order. Whilst the above example showed a fixed stepsize $h$, the algorithm implemented in ALBERT (the turbulent tube flow code) adjusts the stepsize during its progress across the interval $a \rightarrow b$ to achieve a specified accuracy. Feedback on this comes from a technique known as step doubling, where the solution is compared with one found using stepsizes equal to $\frac{1}{2}h$. 

A-1
A.1.2 “Stiff” Systems

Sets of differential equations whose components have widely differing timescales are known as “stiff” systems. A typical example is:

\[ y'_1 = 998y_1 + 1998y_2 \quad \text{and} \quad y'_2 = -999y_1 - 1999y_2 \]  

(A.2)

which can be solved analytically to reveal

\[ y_1 = 2e^{-x} - e^{-1000x} \quad \text{and} \quad y_2 = -e^{-x} + e^{-1000x} \]  

(A.3)

The problem is that although for any significant value of \( x \) the \( e^{-1000x} \) term makes a negligible contribution to the numerical value of the solution, its presence forces the use of a much smaller stepsize than would otherwise be required. The degree to which a problem is stiff varies according to the nature of the problem. Whilst tests have been proposed to determine the stiffness of a problem (Kreiss, 1978), it is often not immediately apparent whether a problem will be stiff. The first indication may well be the failure of ‘ordinary’ methods such as the Runge Kutta method detailed above to solve the problem.

A number of schemes have been developed to deal with the problem of stiff equations. Largely these are modifications of schemes which exist, using information about the point under investigation as well as the previous point(s) to proceed the solution. For example, the Euler scheme described above may be written as:

\[ y_{n+1} = y_n + hy'_n \]  

(A.4)

The implicit version of this, suitable for stiff systems is:

\[ y_{n+1} = y_n + hy'_{n+1} \]  

(A.5)

In general, implicit schemes offer better stability than explicit ones, although some systems may be too stiff to yield a solution. In this work a predictor-corrector scheme is used. The operation of this method is described below.

A.1.2.1 Predictor-Corrector Methods

As the name suggests, a prediction of the value of \( y_{n+1} \) is made, followed by some correction to this. The comparison of predicted and corrected values allows the deduction of information about accuracy and required stepsize. The prediction is made by approximating \( f(x,y) \) with a polynomial which passes through a number of previous points and the current point. Newton-Raphson iteration is used to find the roots of the resulting polynomial giving a prediction of the value of the next point. The Newton-Raphson
iteration is seeded by a guess for the value of \( y_{n+1} \), derived from an explicit method, like the Runge-Kutta outlined above. The prediction is used to calculate an updated value of \( y'_{n+1} \), which is then used in the corrector term. This is a polynomial of similar form to the predictor step, but it includes the value of \( y'_{n+1} \). In this fashion the solution can be advanced to the required limit. This method is implemented in the code EPISODE, written by Byrne and Hindmarsh, which is used to solve differential equations in this thesis.
### A.2 Solution of Partial Differential Equations

Sets of partial differential equations (PDE) cannot be solved by the standard methods used to solve ODE due to their multidimensional nature. Whilst methods exist to solve sets of PDE their application can be problematic due to the difficulties of working in two or more dimensions (Press et al., 1992). Consequently, approximations have been developed to ease the solution of such equations. The finite difference method (Ortega and Poole, 1981) divides the multidimensional space in which a solution is sought into a gridded mesh. The path from point to point is traced using the gradient at points intermediate to the mesh points. Projection methods (Wait and Mitchell, 1985) (including the well-known finite element method) approximate the solution by a finite linear combination of known functions, which are usually relatively simple. Another variant of projection methods - orthogonal collocation (Finlayson, 1972) - was used in this work and is described below.

#### A.2.1 Orthogonal Collocation

Let us consider $T(r, z)$. For a value of $r$, this can be approximated by a power series in $r$. Since (in all systems studied in this work) the solution is symmetric about $r=0$ and contained within the normalised domain $0 \leq r \leq 1$, the power series will contain only even powers of $r$, viz.:

$$T(r, z) = a_0(z) + a_1(z)r^2 + a_2(z)r^4 \quad \text{(A.6)}$$

and by considering only one radius, e.g. $r_1$ we can derive an expression for $T(r_1, z)$

$$T(r_1, z) = a_0(z) + a_1(z)r_1^2 + a_2(z)r_1^4 \quad \text{(A.7)}$$

which for a set of three radii can be represented in matrix form as

$$T = Q \cdot a, \quad \text{where} \quad Q = \begin{pmatrix} 1 & r_1^2 & r_1^4 \\ 1 & r_2^2 & r_2^4 \\ 1 & r_3^2 & r_3^4 \end{pmatrix} \quad \text{(A.8)}$$

and

$$a = \begin{pmatrix} a_0(z) \\ a_1(z) \\ a_2(z) \end{pmatrix} \quad \text{(A.9)}$$

Since $T$ and $Q$ are known, the vector $a$ is readily found from $Q^{-1}T = a$. 

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A-4
We now have an expression for $T$ at any value of $z$, provided the value of $r$ is one of the three chosen to calculate $a$. Extending the number of values of $r$ (collocation points) treated is simply a matter of reformulating equation (A.8). Obtaining the value of $T(r, z)$ at some intermediate value of $r$ is discussed later.

Given (A.8), this enables the calculation of the partial derivative of $T$ with respect to $r$, $T_r$:

$$T_r = C \cdot a = C \cdot Q^{-1} \cdot T$$

where:

$$C = \begin{pmatrix}
0 & 2r_1 & 4r_1^3 \\
0 & 2r_2 & 4r_2^3 \\
0 & 2r_3 & 4r_3^3
\end{pmatrix} \quad (A.10)$$

which gives a set of three ordinary differential equations for the variation of $T$ with displacement $z$. Application of this method to the radial part of the Laplacian $\nabla^2$, given (in cylindrical co-ordinates) by:

$$\begin{bmatrix}
\frac{1}{r} \partial \left( r \frac{\partial}{\partial r} \right)
\end{bmatrix} \quad (A.11)$$

allows it to be written:

$$D \cdot a = B \cdot T$$

where $B = D \cdot Q^{-1}$ and $D = \begin{pmatrix}
0 & 4 & 16r_1^2 \\
0 & 4 & 16r_2^2 \\
0 & 4 & 16r_3^2
\end{pmatrix} \quad (A.12)$

The number of collocation points may be readily changed from 3, but the issue of the values of $r$ at which an exact solution is found remains unresolved. Since it is desired to perform integrations in the $r$ direction it makes sense to choose radial displacements which are directly suitable for use in some quadrature scheme.

### A.2.1.1 Quadrature Schemes

The crudest way of numerically integrating any function over a specified range is to use the trapezoidal rule. The function is divided into a number of trapezoids with bases of equal width, whose area is summed. More refined is Simpson’s Rule, which uses the weighted sum of three equally spaced abscissae. With increasing numbers of points the accuracy of these formulae increases. If we have the freedom to choose not only the
weights, but also the location of the points at which the function is evaluated we can achieve still greater accuracy. The form of the integration is thus:

\[ \int_{a}^{b} f(x) \, dx = \sum_{i} w_i f(x_i) \quad (A.13) \]

The collocation points will therefore be chosen to facilitate an accurate integration by of this form. In the orthogonal collocation method the points are taken to be the roots of orthogonal polynomials. The polynomials themselves are specified by the range of values over which integration is to take place, and the weighting function used. For reasons which will become apparent, it is expedient to choose the weighting function to be

\[ w(x) = x(1 - x^3) \quad (A.14) \]

Since a set of \( m \) orthogonal polynomials can represent any polynomial of order \( (m-1) \), including the power series described in (A.6), a set of polynomials \( p_j(x) \) can be found which represent (A.6) and are orthogonal, taking account of the weighting function. Each pair of polynomials will conform to the condition

\[ \int_{a}^{b} x(1 - x^3) \cdot p_i(x) \cdot p_j(x) \, dx = 0 \quad \text{for all } i \neq j \quad (A.15) \]

Evaluating this condition for each pair will result in a set of definitions which can then be used in the solution of the roots of these polynomials, giving the collocation points.

In the program the collocation points are found using a subroutine from the Numerical Recipes book (Press et al, 1992), which determines the roots of the polynomials from coefficients \( a_j \) and \( b_j \), which derive from recurrence relations used in actually determining the polynomials in the first place, given below:

\[ a_j = \frac{2j^2 + 4j + 1}{(2j+1)(2j+3)} \quad (A.16) \]
\[ b_j = \frac{j(j+1)}{4(2j+1)^2} \quad (A.17) \]

and the polynomials are given by:

\[ p_{-1}(x) = 0 \]
\[ p_0(x) = 1 \]
\[ p_{j+1}(x) = (x-a_j)p_j(x) - b_j p_{j-1}(x) \quad (A.18) \]
A.2.1.2 Interpolation of Results

The orthogonal collocation method produces solutions at values of $r$ which cannot be chosen by the user. Comparing the results of the same calculation, performed with differing numbers of collocation points, is not possible since the results will be returned for points at different values of $r$ in each case. Interpolating the results allows answers to be returned for any value of $r$. The method is as follows:

The variation of $T$ is approximated by equation (A.6) which may be written:

$$ T = Q \cdot a \quad \text{(A.19)} $$

Thus for a given set of $T$, at known $r$, we can find $a$.

The value of $T$ at some other (specified) value of $r$ is given by inserting that new value into the polynomial listed above, and using the values of $a$ determined previously.

If we define a column vector $r^*$ containing powers of the unknown radius $r^*$ viz.:

$$ r^* = \begin{pmatrix} 1 \\ r_1^* \\ r_2^* \\ r_3^* \end{pmatrix} \quad \text{(A.20)} $$

then

$$ T(r^*) = r^* T = r^* T \cdot Q^{-1} \cdot T \quad \text{(A.21)} $$

and we may find $T$ as a function of $r$. Note that since by (A.6) $a$ is a function of $z$, $a$ must be evaluated at each value of $z$ for which an interpolation in $r$ is desired.