M.Sc. Numerical Solution of Differential Equations

Numerical Modelling of Island Ripening

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Abstract

The Tarr and Mulheran growth rate equation for island ripening on a material substrate has been studied here with the continuity equation that contains the growth rate equation which describes the evolution of an island and the distribution function representing the spread of islands on the material surface. We have numerically solved the resulting conservation equation for the absolute distribution function using a non-standard L-W like central difference numerical method with three different initial conditions. Previous work on growth rate equations, including the Tarr and Mulheran growth rate equation, have only been concerned with a scaling solution calculated from scaled variables in the quasi-steady state since an analytic solution can be found which has always yielded an asymptotic solution. Here, we look at the early stages of evolution and to see if an asymptotic state is reached by the absolute distribution function using both the numerical scheme and the characteristic equations giving a part numerical and part analytic solution. A scaling solution is also looked at with a different growth rate equation but using the same arguments used by Tarr and Mulheran to calculate the scaled distribution function.

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I confirm that this is my own work and the use of all material from other sources has been properly and fully acknowledged.

Contents

List of Figures

Chapter 1

Introduction

Nanoscale devices are an upcoming advancement in the field of technology which has been a large topic of research over the past decade within academia. Nanotechnology is the study of material properties on small scales of $10^{-9}m$ and at this scale the properties of materials change due to the small scale size with possible quantum effects becoming dominant rather than the classical mean field approximations. Since we are dealing with scales which are considerably smaller than we are able to manipulate at this present time the applications appeal to a wide range of industries. These include quantum computing and manufacture of quantum devices which can be used in computers to increase storage capacity. There are also medical applications in which smaller robotic devices can be made to help diagnose illnesses such as cancer.

A nanoparticle is the object of interest here which is a grouping together of atoms, or can possibly be just a single atom depending on the substance being used, the properties of which we wish to explore. For example, when a group of nanoparticles form how do they interact with other groups of nanoparticles. This is an integral part of the research area since the knowledge of these interacting properties would allow us to manipulate them and so use them in our various fields of technology. The example given here is what we go on to look at in this project.

There are various ways in which this can be studied and here we look at island evolution on a material substrate. Figure 1 shows the basic procedure that takes place in the evolution process.

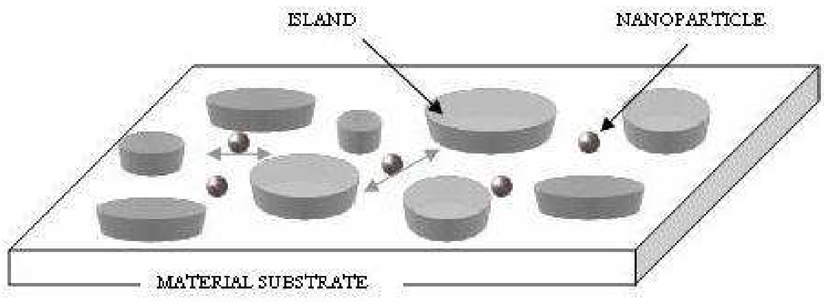

Figure 1.1: *Island evolution on a material substrate*

An island is a group of nanoparticles, Figure 1, considered as one entity and varying in size. Once these islands have formed and with no addition of nanoparticles added to the system, i.e a set amount of material on the surface, we look to see how the islands evolve over time. The evolution process involves particles moving about from different islands where the number of islands starts to decrease and at some point will slow down enough that we can say that it is reached a quasi-steady state. Note that the ripening process does not stop and islands will continue to disappear where all depends on the temperature of the system although we will not consider this variable in our calculations. The movement is due to different types of interactions [3] that can be driving the evolution, of which part of the research in this area is trying to study.

In this project we look at two properties of island evolution, the growth rate equation for an island and the distribution function. The growth rate equation describes how an island can possibly evolve and the distribution function is a measure of islands over the whole surface. Firstly, we look at the origin of the growth rate equation.

1.1 Origin of the Growth Rate Equation

1.1.1 Lifshitz and Slyozov

The equations that we look at have their origin in a paper written by Lifshitz and Slyozov [1] in 1961. They look at the diffusion effects of the precipitate formed in a supersaturated solid solution. These diffusion effects bring about the formation of grains of a new phase in the solution. The grains arise due to the supersaturated part of the solution and then grow due to the coalescence effects brought about by molecules attaching themselves onto larger grains making them bigger. The smaller than average grains shrink and disappear back into the solution and so larger grains grow at the expense of smaller grains. Lifshitz and Slyozov used a set of fundamental equations starting with

$$C_R = C_\infty + \frac{\alpha}{R}, \tag{1.1}$$

in which C_R, the equilibrium concentration at the grain boundary, is related to C_∞, the concentration of the saturated solution, the grain radius R and a parameter α that contains atomic volume and surface tension of the solute. They also assume that the degree of supersaturation is small so that

$$C - C_\infty = \Delta \ll 1, \tag{1.2}$$

where C is the total concentration of the solution. The formation of the grains brings about a concentration gradient in the solution that drives the grain flow since the diffusion flux of solute toward the grain boundary must equal the rate, j, at which solute is incorporated into the grain per unit area. This is given by

$$j = D\frac{\partial C}{\partial r}\bigg|_{r=R} = \frac{D}{R}(C - C_R) = \frac{D}{R}\left(\Delta - \frac{\alpha}{R}\right). \tag{1.3}$$

There is a grain boundary at which the concentration gradient is zero and it follows that there is a small initial supersaturation, Δ. The concentration gradient can now be approximated by $(C - C_R)/R$ shown by the second term in 1.3 and then using 1.1 and 1.2 we obtain the final term on the right hand side of 1.3.

The rate at which solute is incorporated into the grain boundary, j, is simply the rate of change of radius of the grain, so that equation 1.3 can be written as

$$\frac{dR}{dt} = \frac{D}{R}\left(\Delta - \frac{\alpha}{R}\right). \tag{1.4}$$

Depending on the amount of supersaturation, Δ, there will exist a critical radius R_c when $\Delta = \alpha/R$ from equation 1.4. Therefore, if $R > R_c$ then the grain will grow and if $R < R_c$ then the grain dissolves. Writing $R_{c0} = \alpha/\Delta_0$ as the initial critical radius and with $T = R_{c0}^3/\alpha D$ and using the dimensionless variables

$$\rho = \frac{R}{R_{c0}} \qquad \text{and} \qquad t' = \frac{t}{T},$$

Lifshitz and Slyozov change 1.4 to a dimensionless form

$$\frac{d\rho}{dt'} = \frac{1}{\rho^2}\left(\frac{\Delta}{\Delta_0}\rho - 1\right). \tag{1.5}$$

Substituting in $x(t) = \Delta_0/\Delta = R_c/R_{c0}$ which is a dimensionless critical radius such that $x(0) = 1$ and using the relation

$$\frac{d\rho^3}{dt'} = 3\rho^2\frac{d\rho}{dt'},$$

Lifshitz and Slyozov end up with the volume growth rate for a grain

$$\dot{V} = \frac{d\rho^3}{dt'} = 3\rho^2\left(\frac{\rho}{x} - 1\right). \tag{1.6}$$

Note here that the above growth rate equation describes the volume growth of a grain; however, it can be easily adapted for a two-dimensional growth equation [2]. Next they introduce a volume distribution function $f(\rho^3, t)$ that tells us the volume distribution of grains in the solution. The volume distribution function is an unknown quantity that we wish to find and is related to the growth law via the continuity equation,

$$\frac{\partial f(\rho^3, t)}{\partial t} + \frac{\partial}{\partial \rho^3}(\dot{V} f(\rho^3, t)) = 0. \tag{1.7}$$

The first term is the time rate at which the distribution increases and the second term tells us the accumulation of material due to the grain growing or dissolving in the solution. Note that the equation is essentially one-dimensional although the quantities considered are three-dimensional in nature.

Conservation

A conservation property must hold for this system. As a grain grows the amount of supersaturation must reduce to compensate for the growth. The grain grows due to the over saturation of the solution. The total initial supersaturation of the solution is

$$Q_0 = \Delta_0 + q_0, \tag{1.8}$$

where the initial supersaturation Δ_0 is as before and also a term q_0 which allows for the initial volume of material already in the grains. This term is quantified through

$$q_0 = \frac{4}{3}\pi R_{c0}^3 \int_0^\infty f \rho^3 d\rho^3 \tag{1.9}$$

which is the volume of a grain multiplied by the first moment of the volume distribution function. Also as we already know, the number density, n, of grains (number of grains per unit volume) is represented by the area under the curve which is the normalised zeroth moment

$$n = \int_0^\infty f d\rho^3. \tag{1.10}$$

Lifshitz and Slyozov then use the normalisation to unit volume to relate a one-dimensional distribution function $F(\rho, t)$ to the three-dimensional volume distribution function via

$$F(\rho, t)d\rho = f(\rho^3, t)d\rho^3. \tag{1.11}$$

This can be simplified further to

$$F(\rho, t) = 3\rho^2 f(\rho^3, t). \tag{1.12}$$

From here on Lifshitz and Slyozov go on to solve the continuity equation by changing the growth law to more appropriate units and using the type of scaling used above to relate the volume distribution function to the absolute distribution function. Their approach is to substitute a scaled distribution function which is equal to the absolute distribution function, via a scaling relation like the one above, into the continuity equation and solve for this, rather than the absolute distribution function which relates the absolute dimensions of the grain.

The main conclusion reached in Lifshitz and Slyozov that is of relevance to this dissertation is the asymptotic behaviour shown by the distribution function as the coalescence process reaches a steady state. Here the critical radius (or size/volume depending the dimension that is being used) of the grain is equal to the average radius of the grain which has a linear relationship with time,

$$R_c = \overline{R} = \gamma t, \tag{1.13}$$

where γ is the proportionality constant. Their conclusions will later be compared when we look at the distribution function of the absolute size.

1.1.2 Hillert

Further to Lifshitz and Slyozov [1], Hillert [2] approached the problem of grain growth from a different view point but ultimately ending up with a similar growth equation. This was done deliberately so that the method of Lifshitz and Slyozov could be implemented when coming to solve the continuity equation. The grain growth equation was

$$\frac{dR^2}{dt} = 2\alpha M\sigma\left(\frac{R}{R_c} - 1\right), \tag{1.14}$$

where M, α and σ are parameters controlling how and when grains come together. Note here that the growth equation describes the rate of change of grain size rather than grain volume, as Hillert found this to be easier to study theoretically. The scaled distribution function, $P(u)$, then comes out to be

$$P(u) = (2e)^2 \frac{2u}{(2-u)^4} \exp\left\{\frac{-4}{2-u}\right\}, \tag{1.15}$$

where $u = R/R_c$ the relative grain size. Note here the exponential (asymptotic) nature of the solution as discussed in [1].

1.2 Tarr and Mulheran

Having discussed the origin of growth rate equations above we now move to its relevance in this dissertation. The growth rate equations describe the basic process of coalescence between particles and grains, therefore with a change of parameters the growth equations above can be adapted to problems of a similar nature. Tarr and Mulheran [3] used growth rate equations to describe island growth. As described in the introduction above, islands grow and shrink until the process slows down enough so that a quasi-steady state is reached. Tarr and Mulheran compare distribution functions calculated from two different growth rate equations to Monte Carlo simulation data describing island evolution.

The Monte Carlo data look at two types of evolution; the pedophagous effect (PE) and the non-pedophagous effect (NPE). The PE effect is when a particle escapes from an island but the same island is then able to capture it back, thus enabling it to absorb its own offspring, while the NPE is when this is not allowed to happen. The results found were that the Hillert growth law in the 2-D form

$$\dot{s} = \frac{ds}{dt} = \frac{r}{\overline{r}(t)} - 1, \tag{1.16}$$

where $s = \pi r^2$ the island size, r the island radius and $\overline{r}(t)$ the average radial island growth, showed good correlation with the NPE simulation (with no spatial order of islands) when the scaled distribution function

$$f(u) = \begin{cases} \frac{u}{2}\left(\frac{2}{2-u}\right)^4 \exp\left(\frac{-2u}{2-u}\right), & u < 2 \\ 0, & u \geq 2 \end{cases} \tag{1.17}$$

is that of Hillert [2]. Note that equation 1.17 has a cut-off point at $u = 2$ and if $u > 2$ the scaled distribution function is zero. Spatial ordering is when islands in the quasi-steady state exhibit ordering between neighbouring islands [3] which can be calculated.

However, the PE effect which allows for particle recapture and gives rise to spatial order of islands found good correlation with the growth equation

$$\dot{s} = \frac{ds}{dt} = k\left(\frac{s}{\overline{s}} - 1\right), \tag{1.18}$$

where k is a parameter allowing for particle recapture and the radius r has been replaced by the size $s = \pi r^2$ of an island. In this case, using this growth law along with the continuity equation the scaled distribution function found was

$$g(u) = \frac{\pi}{2} u \exp\left(-\frac{\pi}{4}u^2\right), \tag{1.19}$$

where $u = s/\overline{s}$ in this case. Again the quasi-steady state solution that is found here is as found by Lifshitz and Slyozov where the exponential part represents the asymptotic nature of the solution. The conclusion reached is that a spatial order of islands arise due to the PE but not in the NPE case. The growth rate equations of Hillert and Tarr and Mulheran are the ones we go on to study.

Chapter 2

Asymptotic Analysis

2.1 Tarr and Mulheran

The quasi-steady state solution as $t \to \infty$, i.e the scaled distribution function, has been the preferred choice for solving the continuity equation since an analytical solution has been shown to be available [1, 2, 3, 4]. We also take a look at a scaling solution following the working from Tarr's Law [4]. Tarr's Law uses the growth equation

$$\frac{ds}{dt} = k\left(\frac{s}{\overline{s}} - 1\right) = k(v - 1) \tag{2.1}$$

as used by Tarr and Mulheran [3] where k is a parameter allowing for particle recapture considered to be constant. Here, $v = s/\overline{s}$, is the scaled island size with $s = \pi r^2$, the island size. The average island size $\overline{s}$ is equal to

$$\overline{s} = \frac{\int_0^\infty sF(s,t)ds}{\int_0^\infty F(s,t)ds} = \frac{\Omega}{N(t)}, \tag{2.2}$$

in the early stages of evolution, where $F(s,t)$ is the island distribution function. The integrals represent the volume of material making up the islands, Ω and the number density of islands, $N(t)$. Note that the volume of material, Ω should remain constant throughout the evolution.

2.1.1 Scaling Solution

In the quasi-steady state limit Tarr's Law makes the assumption $\overline{s} = ct$ with c a constant of proportionality and made on the grounds of dimensionality. The following quantities can then be calculated,

$$v = \frac{s}{ct}, \qquad \frac{\partial v}{\partial s} = \frac{1}{ct}, \qquad \frac{\partial v}{\partial t} = -\frac{s}{ct^2} = -\frac{v}{t}, \qquad N(t) = \frac{\Omega}{\overline{s}} = \frac{\Omega}{ct},$$

The island distribution function, $F(s,t)$, is now related to the scaled island distribution function, $f(v)$, and $N(t)$ via the scaling relation

$$F(s,t)ds = N(t)f(v)dv \tag{2.3}$$

which can be written as

$$F(s,t)ds = \frac{\Omega}{c^2t^2}f(v), \tag{2.4}$$

from the definitions defined above. The continuity equation for this growth law then becomes (cf. 1.7)

$$\frac{\partial F(s,t)}{\partial t} + \frac{\partial}{\partial s}\Big[k(v-1)F(s,t)\Big] = 0, \tag{2.5}$$

where the derivatives can now be calculated using the scaling relation 2.4 to replace $F(s,t)$ by $f(v)$. Working through this Tarr's Law end up with the ODE

$$\left(\frac{k}{c} - 2\right)f(v) + \left[\left(\frac{k}{c} - 1\right)v - \frac{k}{c}\right]f'(v) = 0. \tag{2.6}$$

Tarr's Law then takes a special case and chose $f(0) = f_0 = c/k = 1$ where $f(0)$ comes from

$$\dot{N} = -k\frac{\Omega}{ct^2} = \lim_{s\to 0}\left(\frac{ds}{dt}F(s,t)\right) = -k\frac{\Omega}{c^2t^2}f(0) \tag{2.7}$$

which describes how islands are able to disappear as $s \to 0$ with a rearrangement giving the required special case. Thus, the ODE reduces to

$$-f - f' = 0 \tag{2.8}$$

which has the solution

$$f(v) = \exp(-v). \tag{2.9}$$

However, other solutions may exist by solving the original ODE 2.6 with a general $c/k = f_0$. This yields

$$(1 - 2f_0)f(v) = [1 - (1 - f_0)v]f'(v) \tag{2.10}$$

which gives

$$\int \frac{df}{f} = \int \frac{1 - 2f_0}{1 - (1 - f_0)v}\, dv \tag{2.11}$$

in the integral form. Thus, the scaling solution to the continuity equation is found as

$$f(v) = A[1 - (1 - f_0)v]^{\frac{1-2f_0}{f_0-1}}, \tag{2.12}$$

with A an integration constant. Tarr's Law then uses the fact that v has a finite range $v \in [0, 1/(1 - f_0)]$ for a solution to exist and then normalising $f(v)$ finds the constant $A = f_0$ to give another solution

$$f(v) = f_0[1 - (1 - f_0)v]^{\frac{1-2f_0}{f_0-1}}. \tag{2.13}$$

So Tarr's Law [4] finds two solutions to the continuity equation of which the special case seems to be the solution of choice experimentally and the one that also should be found numerically.

2.2 Hillert Growth Rate Equation

Using the above procedure we now try to find a scaling solution like the one above using the Hillert growth rate equation in the form

$$\frac{ds}{dt} = v^{1/2} - 1, \tag{2.14}$$

where $v^{1/2}$ represents the Hillert form,

$$v^{1/2} = \left(\frac{s}{\overline{s}}\right)^{1/2} = \left(\frac{\pi r^2}{\pi \overline{r}^2}\right)^{1/2} = \frac{r}{\overline{r}}, \tag{2.15}$$

and the constant k has for simplification been incorporated into the time derivative. Note that this will be the case throughout the rest of the dissertation. The continuity equation for this growth equation is then

$$\frac{\partial F(s,t)}{\partial t} + \frac{\partial}{\partial s}\Big[(v^{1/2} - 1)F(s,t)\Big] = 0 \tag{2.16}$$

and with the substitution of the scaling $\overline{s} = ct$ we can calculate the derivatives. The time derivative becomes

$$\frac{\partial F(s,t)}{\partial t} = \frac{\Omega}{c^2 t^3}(-2f(v) - vf'(v)) \tag{2.17}$$

and the size derivative becomes

$$\frac{\partial F(s,t)}{\partial s} = \frac{\Omega}{c^3t^3} f'(v), \tag{2.18}$$

from equation 2.4. Now, using equation 2.18 the complete size derivative in the continuity equation we find

$$\frac{\partial}{\partial s}\Big[(v^{1/2}-1)F(s,t)\Big] = \frac{\Omega}{c^3t^2}\Big[(v^{1/2}-1)f'(v) + \frac{f(v)}{2v^{1/2}}\Big]. \tag{2.19}$$

Substituting equations 2.17 and 2.19 into the continuity equation 2.16 we find the ODE

$$f[1-4cv^{1/2}] + f'[2(v-v^{1/2}) - 2cv^{3/2}] = 0, \tag{2.20}$$

where separation of variables gives

$$\int \frac{df}{f} = \int \frac{1-4cv^{1/2}}{[2(v-v^{1/2})-2cv^{3/2}]}\, dv. \tag{2.21}$$

The left hand integral is trivial but the right hand side requires some calculation. First we make the substitution $v = w^2$ to give

$$\ln f = \int \frac{1-4cw}{cw^2-w+1}\, dw \tag{2.22}$$

and expand to

$$\ln f = \int \frac{-2(2cw-1)}{cw^2-w+1}\, dw - \int \frac{1}{cw^2-w+1}\, dw, \tag{2.23}$$

enabling us to integrate. The solution to the above continuity equation using the growth rate equation 2.14 depends on the value of c, so for $4c < 1$ we find

$$f(v) = A(cv - v^{1/2}+1)^{-2}\left(\frac{2cv^{1/2}-1-\sqrt{1-4c}}{2cv^{1/2}-1+\sqrt{1-4c}}\right)^{-\frac{1}{\sqrt{1-4c}}} \tag{2.24}$$

and if $4c > 1$

$$f(v) = A(cv - v^{1/2} + 1)^{-2} \exp\left\{ \frac{-2}{\sqrt{4c-1}} \arctan\left[\frac{2cv^{1/2} + 1}{\sqrt{4c-1}} \right] \right\} \tag{2.25}$$

where in both cases we have converted back to the scaled island size, v, with A integration constant is dependent on the allowed values for v. We can also find a solution when $4c = 1$ by going back to equation 2.22 to give

$$\ln f = \int \frac{1-w}{\frac{1}{4}w^2 - w + 1} \, dw \tag{2.26}$$

which is equal to

$$\ln f = \int \frac{1-w}{\frac{1}{4}(w-2)^2} \, dw \tag{2.27}$$

We can now integrate this by parts giving

$$\ln f = 4\left[\frac{-(1-w)}{w-2} - \ln(w-2) \right] + \text{constant} \tag{2.28}$$

which gives the solution

$$f(v) = A \exp\left\{ \frac{4(v^{1/2} - 1)}{(v^{1/2} - 2)} \right\} (v^{1/2} - 2)^{-4} \tag{2.29}$$

for the $4c = 1$ case and where A is again an integration constant dependent on the allowed values for v. Note that $v^{1/2} = r/\overline{r} = u$ from section 1.1.2. Since we are using a growth rate equation similar to Hillert the solutions found should also be similar to the Hillert scaled distribution function. We can see that when $4c = 1$ we do obtain a similar equation to that of hillert but not exactly.

2.3 Characteristics for the Tarr and Mulheran Scaling Solution

The equation that we wish to solve has the form (cf. 1.7)

$$u_t + g(u, s, t)_s = 0 \tag{2.30}$$

which represents a one-dimensional conservation law [5]. Note here that $F(s,t)$ has been replaced by $u(s,t)$ for convenience (more standard notation in mathematics) for the remaining part of this dissertation and $g(u,s,t)$ represents the flux function so that we have

$$u_t + (\dot{s}u)_s = 0 \tag{2.31}$$

as our continuity equation. Before using a type of numerical scheme we first take a look at the characteristics of our problem. The characteristics are calculated from the total derivative of $u(s,t)$

$$\frac{du}{dt} = \frac{\partial u}{\partial t} + \frac{ds}{dt}\frac{\partial u}{\partial s} \tag{2.32}$$

which is equal to

$$\begin{aligned} \frac{du}{dt} &= -(\dot{s}u)_s + \dot{s}u_s \\ &= -\left(\frac{s}{\bar{s}} - 1\right)u_s - \frac{u}{\bar{s}} + \dot{s}u_s, \end{aligned} \tag{2.33}$$

from the conservation law 2.30. Rearranging we find

$$\frac{du}{dt} = \left[\dot{s} - \left(\frac{s}{\bar{s}} - 1\right)\right]u_s - \frac{u}{\bar{s}}. \tag{2.34}$$

By setting the term in the square brackets to zero the characteristics are given by the growth rate equation 2.1 where the constant k has been scaled into the time derivative. The function u is not constant on the characteristics due to the total derivative of $u(s,t)$ being non zero

$$\frac{du}{dt} = -\frac{u}{\overline{s}}. \tag{2.35}$$

The characteristic equation is analytically solvable for the quasi-steady state of the system when we replace $\overline{s}$ with t, in this case taking $c = 1$ for simplicity. The growth rate equation becomes

$$\frac{ds}{dt} = \frac{s}{t} - 1 \tag{2.36}$$

which can be solved using the integrating factor t^{-1} to give

$$\frac{d}{dt}(t^{-1}s) = -t^{-1}. \tag{2.37}$$

Integrating we find

$$s = -t \ln t + Bt, \tag{2.38}$$

where B is a constant of integration.

However, since u is not constant on the characteristics, i.e $\dot{u} \neq 0$, we can solve equation 2.35 as well, again with $\overline{s} = t$, which tells us what happens on the characteristics. This is trivial coming out to be

$$u = At^{-1}, \tag{2.39}$$

where A is a constant of integration.

Now that we have the full characteristic story we can plot them. Using values of $t \in [1, 5]$ and with different values of $B \in [0, 10]$ for each characteristic, they can be plotted as shown in Figure 2.1.

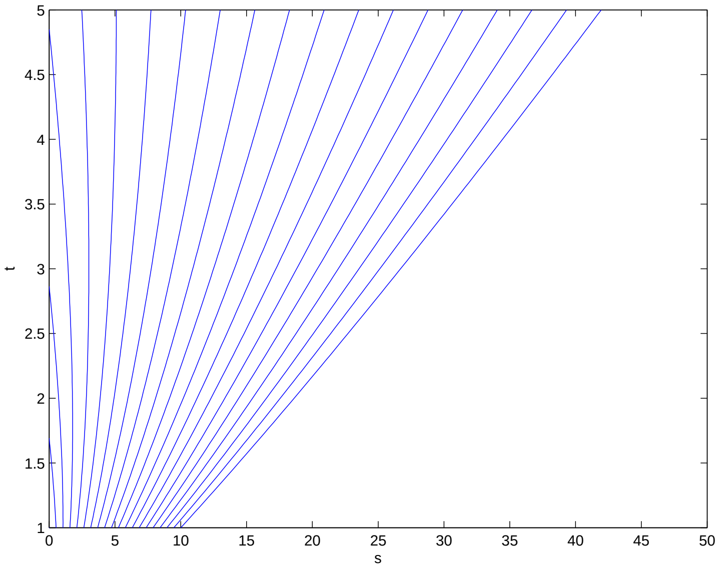

Figure 2.1: *Characteristics for the continuity equation when* $\overline{s} = t$

The characteristics are curved as we expected and the curves indicate the movement of material partly out the left hand boundary in the quasi-steady state. This movement represents smaller islands disappearing which is still expected in the quasi-steady since we know that ripening process does not stop.

Hence, an analytic solution is available if and when the system reaches a state where $\overline{s} \propto t$ using the characteristic equations. In chapter 4 we compute a numerical method which can tell us if the relation $\overline{s} \propto t$ is reached, and if so then we can move to the characteristic solution.

Chapter 3

Numerical Schemes

Let us now look at some numerical schemes that we could implement to solve the continuity equation.

3.1 First Order Upwind (FOU) Scheme

Let us start with the first order upwind scheme. Using an upwind discretisation of 2.30 gives

$$\frac{u_j^{n+1} - u_j^n}{\Delta t} + \frac{g_j^n - g_{j-1}^n}{\Delta s} = 0 \qquad (\dot{s} > 0) \tag{3.1}$$

$$\frac{u_j^{n+1} - u_j^n}{\Delta t} + \frac{g_{j+1}^n - g_j^n}{\Delta s} = 0 \qquad (\dot{s} < 0), \tag{3.2}$$

where $\dot{s}$ is the wave speed indicating the direction to take the discretisation. A simple rearrangement of the above gives us

$$u_j^{n+1} = u_j^n - \frac{\Delta t}{\Delta s}(g_j^n - g_{j-1}^n) \qquad (\dot{s} > 0) \tag{3.3}$$

$$u_j^{n+1} = u_j^n - \frac{\Delta t}{\Delta s}(g_{j+1}^n - g_j^n) \qquad (\dot{s} < 0), \tag{3.4}$$

in computable form.

3.2 A Second Order L-W like Scheme

We now construct a Lax-Wendroff (L-W) like central difference scheme based on the Taylor expansion of $u(s, t + \Delta t)$ to second order,

$$u(s, t + \Delta t) = u(s, t) + \Delta t u_t(s, t) + \frac{(\Delta t)^2}{2} u_{tt}(s, t). \tag{3.5}$$

As in the L-W derivation the next step is to replace the first and second time derivatives of $u(s, t)$ with space derivative terms using 2.30,

$$\begin{aligned} u_{tt} &= -((\dot{s}u)_s)_t \\ &= -((\dot{s}u)_t)_s \\ &= -[\ddot{s}u + \dot{s}u_t]_s. \end{aligned} \tag{3.6}$$

Expanding out and replacing u_t from 2.30 we find

$$u_{tt} = -(\ddot{s})_s u - \ddot{s}u_s + (\dot{s})_s(\dot{s}u)_s + \dot{s}[(\ddot{s})_{ss}u + \dot{s}u_{ss} + 2(\dot{s})_s u_s]. \tag{3.7}$$

Next we replace some of the terms with the computable terms below

$$\ddot{s} = -\frac{\dot{\overline{s}}}{(\overline{s})^2} s \tag{3.8}$$

$$(\ddot{s})_s = -\frac{\dot{\overline{s}}}{(\overline{s})^2} \tag{3.9}$$

$$(\dot{s})_s = \frac{1}{\overline{s}} \tag{3.10}$$

$$(\dot{s})_{ss} = 0 \tag{3.11}$$

to give

$$u_{tt} = \frac{\dot{\overline{s}}}{(\overline{s})^2}u + \frac{\dot{\overline{s}}}{(\overline{s})^2}su + \frac{1}{\overline{s}}((\dot{s}u)_s) + \dot{s}(\dot{s}u_{ss} + \frac{2\dot{s}}{\overline{s}}u_s). \tag{3.12}$$

Finally substituting the above into 3.5 we obtain

$$\begin{aligned} u(s,t+\Delta t) &= u(s,t) - \Delta t(\dot{s}u)_s \\ &+ \frac{(\Delta t)^2}{2}\Big[\frac{\dot{\overline{s}}}{(\overline{s})^2}u + \frac{\dot{\overline{s}}}{(\overline{s})^2}su_s + \frac{1}{\overline{s}}((\dot{s}u)_s) + \dot{s}(\dot{s}u_{ss} + \frac{2\dot{s}}{\overline{s}}u_s)\Big]. \end{aligned} \tag{3.13}$$

However $\dot{\overline{s}}$ is non trivial and is calculated from the initial $\overline{s}$ value given by equation 2.2, using the product rule to give

$$\dot{\overline{s}} = \frac{\int_0^\infty suds}{(\int_0^\infty uds)^2}\int_0^\infty (\dot{s}u)_s ds - \frac{\int_0^\infty s(\dot{s}u)_s ds}{\int_0^\infty uds}. \tag{3.14}$$

Calculating the integrals, $\dot{\overline{s}}$ becomes in computable form

$$\dot{\overline{s}} = \frac{\int_0^N suds}{(\int_0^N uds)^2}[\dot{s}u]_0^N - \frac{1}{\int_0^N uds}\Big([\dot{s}su]_0^N - \int_0^N (\dot{s}u)ds\Big), \tag{3.15}$$

where the integration limits are now on the finite region [0,N] so as to be computable. The scheme is thus achieved, as in the L-W schemes, by discretising 3.13 using central differences, giving

$$\begin{aligned} u_j^{n+1} &= u_j^n - \Delta t\Big[\frac{(\dot{s}u)_{j+1}^n - (\dot{s}u)_{j-1}^n}{2\Delta s}\Big] \\ &+ \frac{(\Delta t)^2}{2}\Bigg\{\frac{\dot{\overline{s}}}{(\overline{s})^2}\Big[u_j^n + s_j^n\Big(\frac{u_{j+1}^n - u_{j-1}^n}{2\Delta s}\Big)\Big] \\ &\quad + \frac{1}{\overline{s}}\Big[\frac{(\dot{s}u)_{j+1}^n - (\dot{s}u)_{j-1}^n}{2\Delta s}\Big] \\ &\quad + \frac{2\dot{s}_j}{\overline{s}}\Big(\frac{u_{j+1}^n - u_{j-1}^n}{2\Delta s}\Big) \\ &\quad + \dot{s}_j^2\Big(\frac{u_{j+1}^n - 2u_j^n + u_{j-1}^n}{(\Delta s)^2}\Big)\Bigg\}. \end{aligned} \tag{3.16}$$

This is longer than the standard L-W scheme but is still computable.

3.2.1 The CFL Stability Condition

We cannot perform the usual fourier stability analysis for this scheme so we look to the CFL stability condition which is a necessary condition for stability for numerical schemes of this sort [5, 6]. The stability condition we require is

$$\left|\dot{s}\frac{\Delta t}{\Delta s}\right| \leq 1, \tag{3.17}$$

where

$$\dot{s} = \frac{s}{\overline{s}} - 1. \tag{3.18}$$

Initially when s is large, depending on what domain size is taken, the value of $\dot{s}$ can be very large. Therefore, if the ratio $\Delta t/\Delta s$ is not small enough the stability condition can be violated. By choosing a smaller time step, Δt, we can avoid this problem in the case of large s but at small s the condition is always satisfied. Note that initially $\overline{s}$ is 1 but increases as time evolves which keeps the stability condition satisfied from the initial time step.

3.3 Conservation

Numerically we can lose conservation of material if the correct boundary conditions are not implemented but for this system we can always check the property

$$\int_0^\infty su(s,t)ds = 1 \tag{3.19}$$

which tells us that the volume of material is constant. Notice that the integral is equal to 1, here, but can be just a known fixed value depending on the initial volume of islands, as shown in Appendix A. So, we can check if our numerical scheme conserves material by approximating the integral above using the trapezium rule on the finite interval $s \in [0, N]$ representing the numerical boundary.

Chapter 4

Numerical Results

4.1 Tarr and Mulheran Growth Law: Gaussian

We now have a second order L-W like numerical scheme that we can use to solve the continuity equation 2.30. The conditions we start with are a Gaussian initial condition with peak centered at $\overline{s} = 1$ as a starting initial average island size and we take $\Delta t = 2.5\text{x}10^{-5}$ and $\Delta s = 0.01$ where the domain size is $s \in [0, 100]$. Ideally we would like to increase the domain size since this becomes important toward the later stages of evolution. This means that the time step would have to be very small and so increasing the execution time for the numerical scheme but the domain size used is sufficient for the initial Gaussian condition. Also, initially, the Δt used satisfies the CFL condition at large s when $s = 100$

$$\left|\left(\frac{s}{\overline{s}} - 1\right)\frac{\Delta t}{\Delta s}\right| = \left|(100 - 1)\frac{\Delta t}{\Delta s}\right| = |0.2475| \leq 1. \tag{4.1}$$

Since we are using a second order L-W like scheme there is a need for boundary conditions. We use extrapolating boundary conditions since these would be the most natural to use as we have a cut-off point at one of the boundaries. Beyond this we still have part of the solution although it does not have much effect in this case.

Figure 4.1 shows what happens as we evolve to $t = 1$ where the initial Gaussian condition is also shown for comparison.

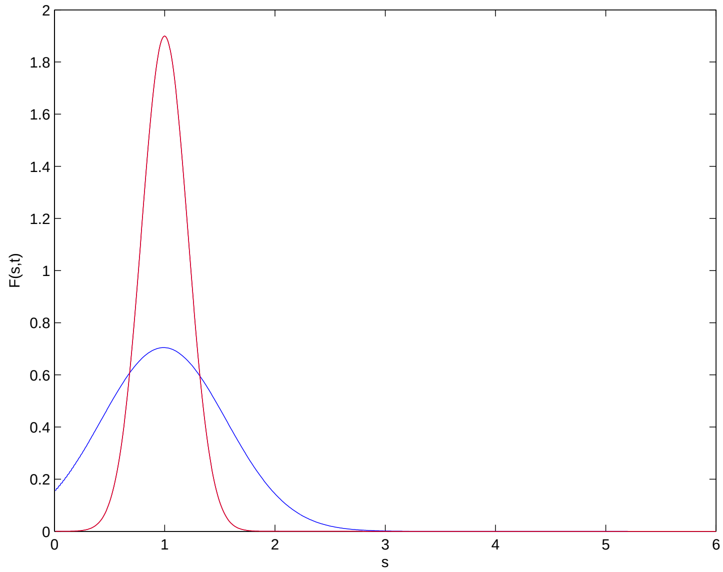

Figure 4.1: *Solution to continuity equation evolving to* $t = 1$ *along with the initial Gaussian curve in red*

There are two main features to Figure 4.1; First the left hand boundary has risen indicating that the solution may be evolving to an exponential solution as we expect. We are expecting the asymptotic exponential solution because the scaled distribution function, $f(v)$, found in the quasi-steady state in section 2.1.1, was an exponential solution for scaled variables when $\overline{s} = ct$ and $c/k = 1$ so this may also be the case for the absolute distribution function, $u(s,t)$, apart from some scaling factor and if $\overline{s} \propto t$ is reached. Second, the number density of islands, $N(t)$, represented by the area under the distribution curve and given by the definite integral

$$N(t) = \int_0^N u(s,t)ds \tag{4.2}$$

has reduced as can be seen from Table 4.1. as can be seen from Table 4.1.

This is what we expected since the number of islands initially on the material

Time	*N(t)*	Ω	$\overline{s}$
0.0000000	0.99999902	1.0000000	1.0000010
0.9999750	0.95987905	1.0000000	1.0417979
1.9999500	0.72008166	0.9999999	1.3887313
2.9999249	0.51032327	1.0000000	1.9595422
3.9998999	0.38058150	1.0000000	2.6275580
4.9998749	0.29884216	1.0000000	3.3462480

Table 4.1: *Table of Moments, $\overline{s}$ and evolution times*

surface reduces as the system reaches a quasi-steady state where smaller islands disappear [3]. The conservation property represented by

$$\Omega = \int_0^N su(s,t)ds \tag{4.3}$$

has remained constant, equal to 1 as shown in Table 4.1, as required. Note that both integrals have been approximated using the whole domain as stated above and not just the size shown in the figures. The figures are shown in this way so that a clear picture of the solution can be shown.

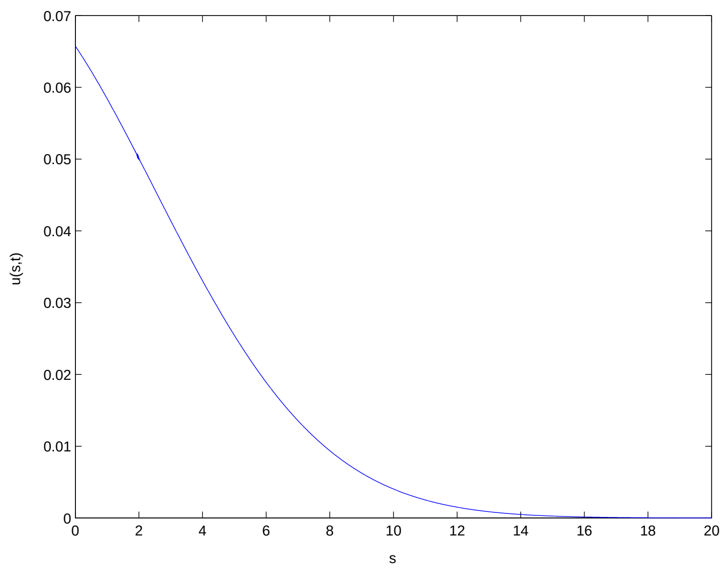

Figure 4.2: *Solution to the continuity equation evolving to $t = 5$*

Figure 4.2 shows the solution obtained at $t = 5$. Note that the initial condition has been omitted so that the solution can be seen more clearly. Here the solution has started to look more like an exponential solution, as we expect, and $N(t)$ has also reduced in size from Table 4.1. There is a slight problem with the scheme though. In Figure 4.2 there are very small oscillations that are just about visible at about $s = 2$ which is because of the central difference nature of the numerical scheme [5] where we know the L-W scheme generates oscillations.

However, they do not cause any problems since the linear relationship of $\overline{s} \propto t$ has been achieved in Figure 4.3 so now we can change to the solution from the characteristic equations.

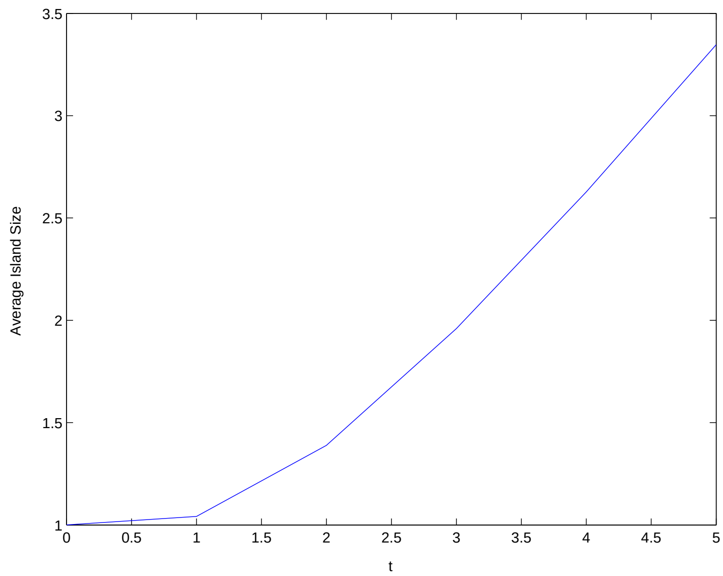

Figure 4.3: *This graph shows the linear relationship* $\overline{s} \propto t$ *has been attained by evolving to a time of* $t = 5$

Before we calculate this we can make another comparison to check our numerical results by converting to the scaled variables, $f(v)$ and v. This is done through the transformations

$$f(v) = \frac{\Omega}{N^2(t)} u(s,t) \tag{4.4}$$

and

$$v = \frac{N(t)}{\Omega} s, \tag{4.5}$$

where $N(t)$ and Ω represent the integrals defined above. Figure 4.4 shows the scaled distribution function at $t = 5$ and also at $t = 10$ and $t = 20$ to show that the exponential solution found by the scaling solution is slowing being achieved by the numerical solution.

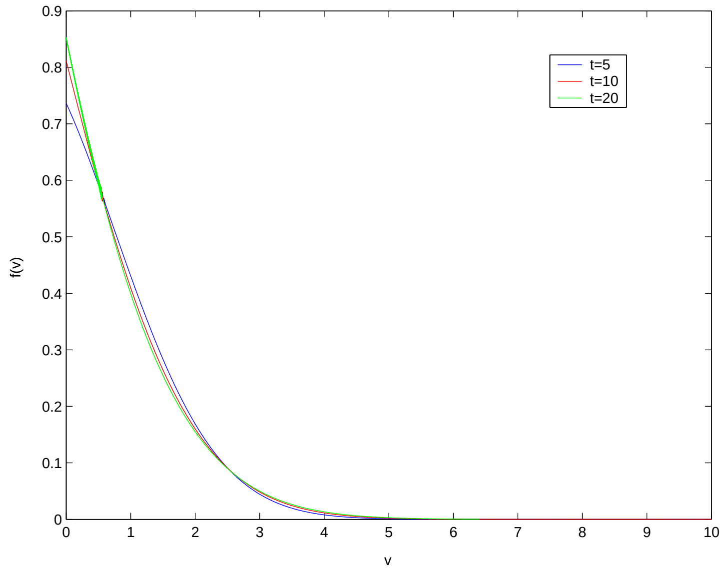

Figure 4.4: *Scaled distribution function calculated from the absolute distribution function at* $t = 5$*,* $t = 10$ *and* $t = 20$

However, since we have already observed the relation $\overline{s} \propto t$ by $t = 5$ this is where we calculate the characteristic solution from since the oscillations observed above will start to grow as time evolves.

4.1.1 Characteristic Solution

The characteristic solution is calculated from the numerical solution at $t = 5$, in this case. Using the numerical solution we can calculate the constants A and B

by rearranging the characteristic equations

$$u = At^{-1} \tag{4.6}$$

and

$$s = -t \ln t + Bt, \tag{4.7}$$

where we use $u(s,t)$ and s from the numerical scheme at $t = 5$ to calculate the constants above. These constants now enable us to calculate the solution from the above equations for any value of t we choose, thus enabling us to evolve the system further.

Therefore, evolving the system to $t = 10$ the solution as expected is similar to the solution in Figure 4.2 from the numerical scheme, shown in Figure 4.5.

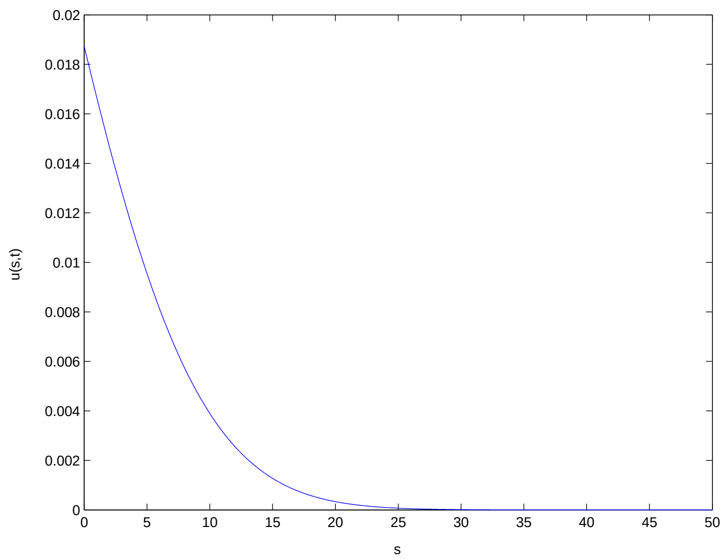

Figure 4.5: *Characteristic Solution calculated at* $t = 10$

The difference between the numerical scheme solution at $t = 5$, Figure 4.2, and the characteristic solution at $t = 10$, Figure 4.5, is the area under the distribution curve which has reduced and the shape of the curve which looks more like an exponential solution at $t = 10$.

Evolving further in time to $t = 40$, Figure 4.1.1, we find the same shape to the distribution curve except with a reduced number island density, $N(t)$ but becoming

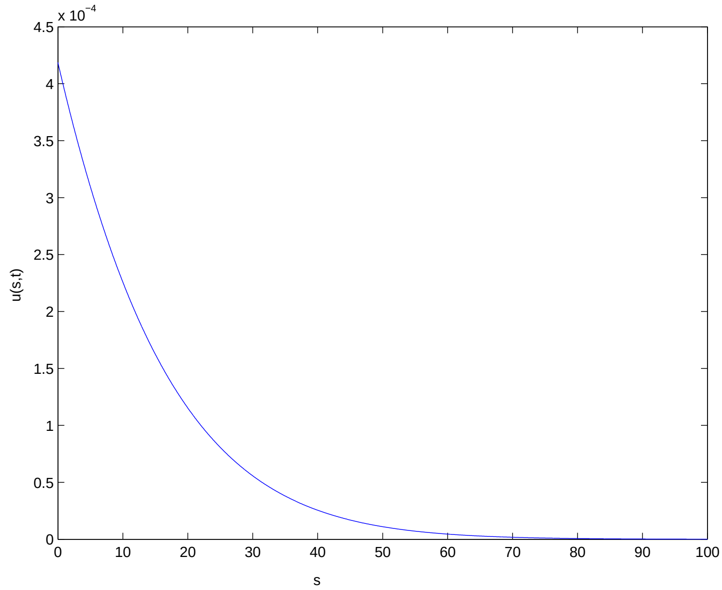

Figure 4.6: *Characteristic Solution calculated at* $t = 40$

more asymptotic like as it reaches a quasi-steady state.

4.2 Tarr and Mulheran Growth Law: Exponential

Let us now look at a different initial condition, an exponential. For the scaled distribution function, $f(v)$, this is the analytical solution obtained making it interesting to look at to see what happens. Ideally it should hold its shape and then when it comes to changing to the scaled variables it should be exactly the exponential solution found in section 2.1.1. The same domain has been used along with the same values for Δt and Δs to ensure the CFL condition has been satisfied.

Evolving to $t = 1$, shown in Figure 4.7, we see that the value of $N(t)$ has decreased as we already know it should, from Table 4.2.

The conservation property, Ω, which should remain equal to 1 for the exponential case as with the Gaussian initial condition remains the same, as it should.

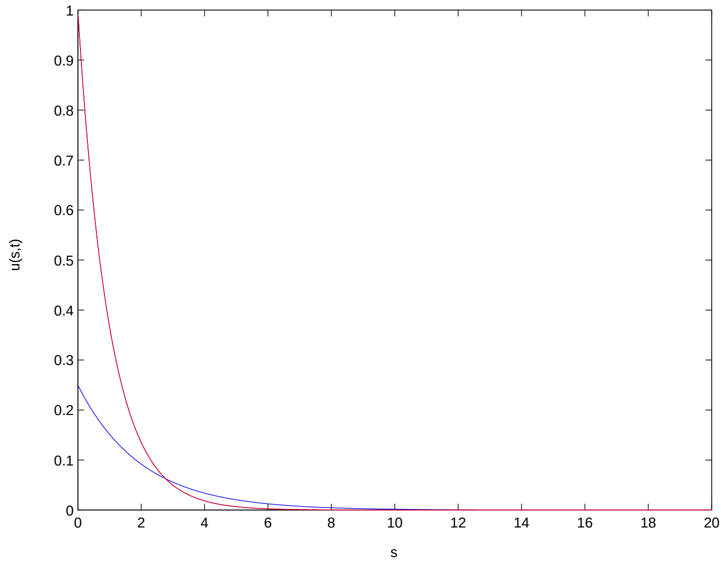

Figure 4.7: *Solution to continuity equation evolving to* $t = 1$ *along with the initial exponential curve in red*

Time	*N(t)*	Ω	$\overline{s}$
0.0000000	0.99995858	0.99999166	1.0000330
0.9999750	0.50000001	0.99999163	1.9999832
1.9999500	0.33333426	0.99999165	2.9999665
2.9999250	0.25000130	0.99999165	3.9999458
3.9998999	0.20000140	0.99999162	4.9999229
4.9998749	0.16666803	0.99999070	5.9998948

Table 4.2: *Table of Moments,* $\overline{s}$ *and evolution times*

Figure 4.8 shows the numerical solution at $t = 5$ where again the value of $N(t)$ has reduced, Table 4.2, but the shape of the curve remains similar to an exponential solution.

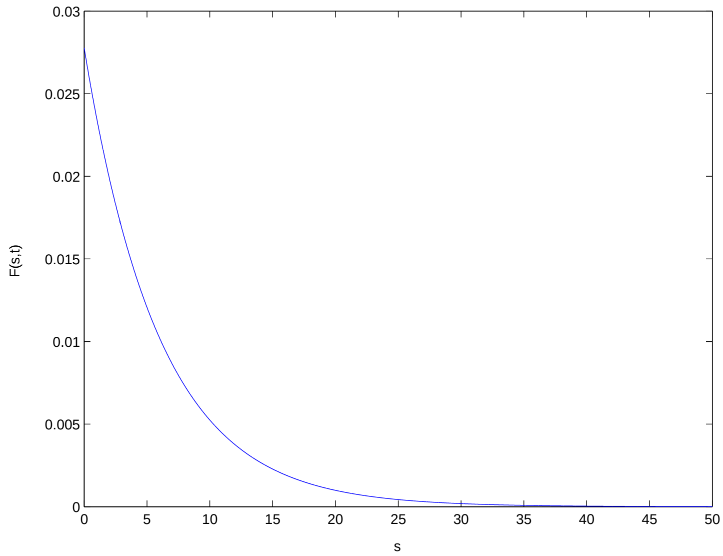

Figure 4.8: *Solution to the continuity equation evolving to* $t = 5$

Again at this time of $t = 5$ we observe the linear relationship of $\overline{s} \propto t$, Figure 4.9, although in this case it seems that the relationship held from the beginning.

We can now move to the characteristic solution.

4.2.1 Characteristic Solution

Again, we start by finding the values of the constant A and B by rearranging equations 4.6 and 4.7 and then using these values find the characteristic solution at various times. The characteristic solution at $t = 10$ and $t = 40$ are given by Figures 4.10 and 4.11.

Both figures show the asymptotic nature the solution is moving toward. We can also convert the characteristic solutions to the scaled variables using

$$f(v) = \frac{1}{t^2} u(s,t) \tag{4.8}$$

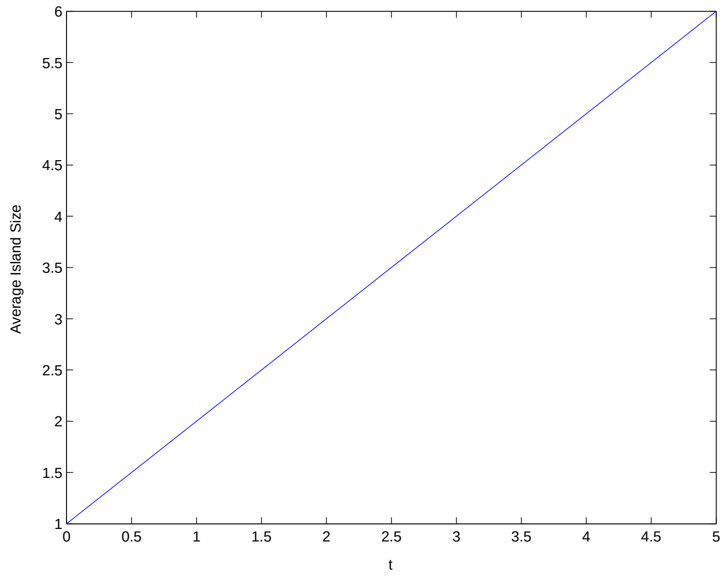

Figure 4.9: *This graph shows the linear relationship* $\overline{s} \propto t$ *has been attained by evolving to a time of* $t = 5$

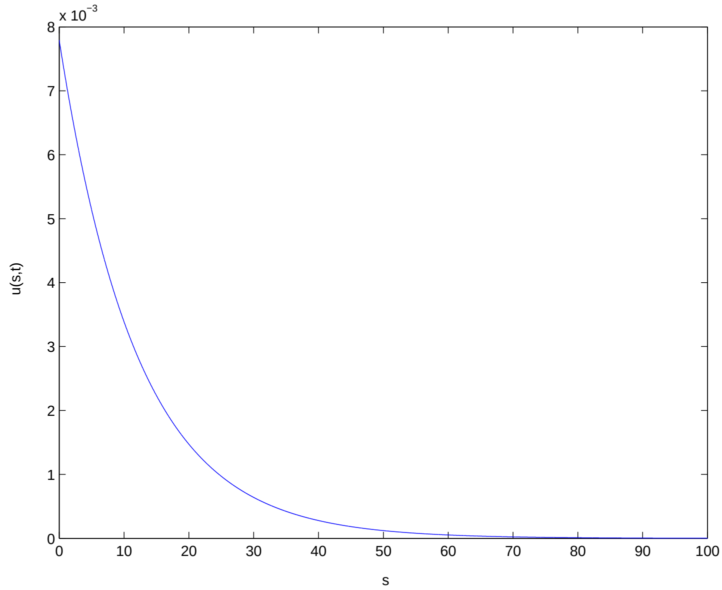

Figure 4.10: *Characteristic Solution calculated at* $t = 10$

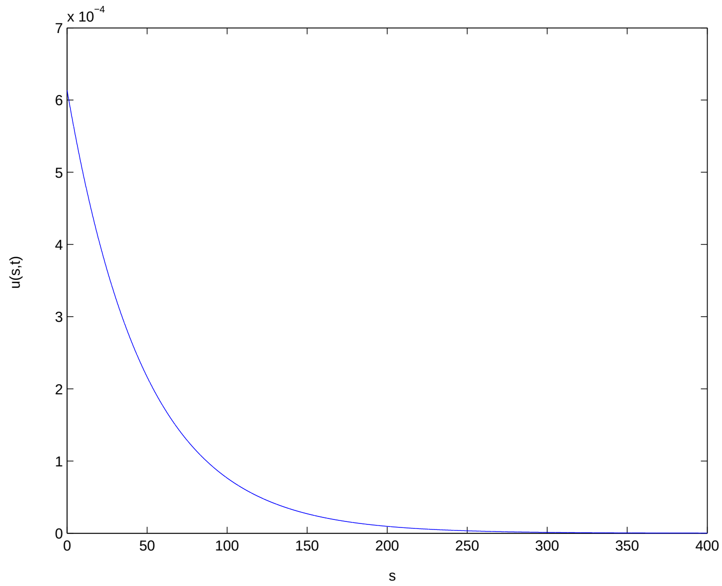

Figure 4.11: *Characteristic Solution calculated at* $t = 40$

and

$$v = ts, \tag{4.9}$$

where we have taken $\overline{s} = t$ and $\Omega = 1$ which ensures conservation of material shown in Figure 4.12.

At $t = 10$ the solution is moving toward 1 on the left hand boundary and we know this since at a later time $t = 40$ it reaches this and turns out to be exactly an exponential. An exponential solution can be plotted with the scaled distribution function in Figure 4.12 but it turns out that at $t = 40$ the exponential solution is found.

4.3 Tarr and Mulheran Growth Law: Power law

Next we look at a power law, as an initial distribution function but this time we choose a smaller time step, $\Delta t = 2.5\text{x}10^{-6}$ and a domain size $s \in [0, 500]$ where Δs has remained the same. The time step is very small so that the CFL condition can be satisfied for this large domain size s

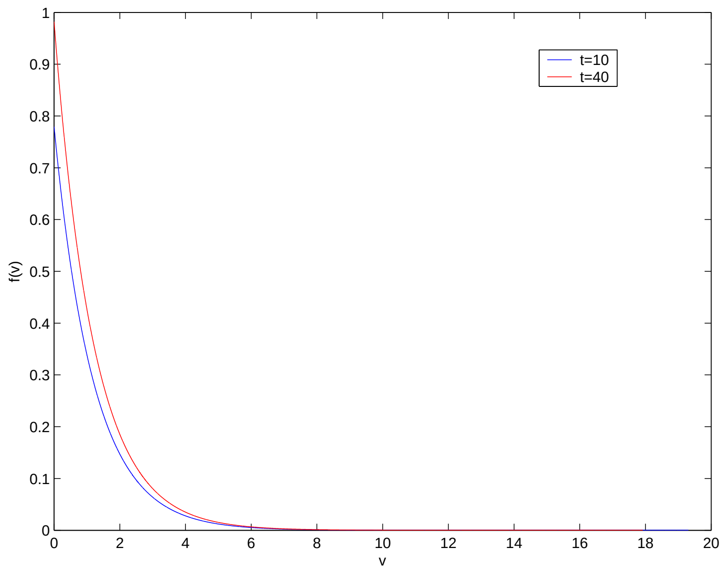

Figure 4.12: *Scaled distribution function calculated from the characteristic solution at $t = 10$ and $t = 40$*

$$\left|(500-1)\frac{\Delta t}{\Delta s}\right| = |0.12475| \leq 1. \tag{4.10}$$

The domain size has been changed because the value of $u(s,t)$ at large s is significant, for the power law, when calculating the conservation property so that we can conserve material through the calculation of Ω shown by Table 4.3. However, even with a large domain, it has not done so compared to the other initial conditions for the same time period. Note that neither $N(t)$ or Ω are initially equal to one, here, compared to the Gaussian and the exponential starting conditions. This is not a necessary requirement because their values depend on how much material has been used at the starting point where for the Gaussian and exponential starting conditions it happened to be the case.

Figures 4.13 and 4.14 shows the case at $t = 1$ and $t = 5$ where as expected we find a reduction in the value of $N(t)$, Table 4.3, as we evolve from the initial state to $t = 1$ and then to $t = 5$.

Again we find very small oscillations in Figure 4.14 as with Figure 4.8 for the exponential case at the same time $t = 5$.

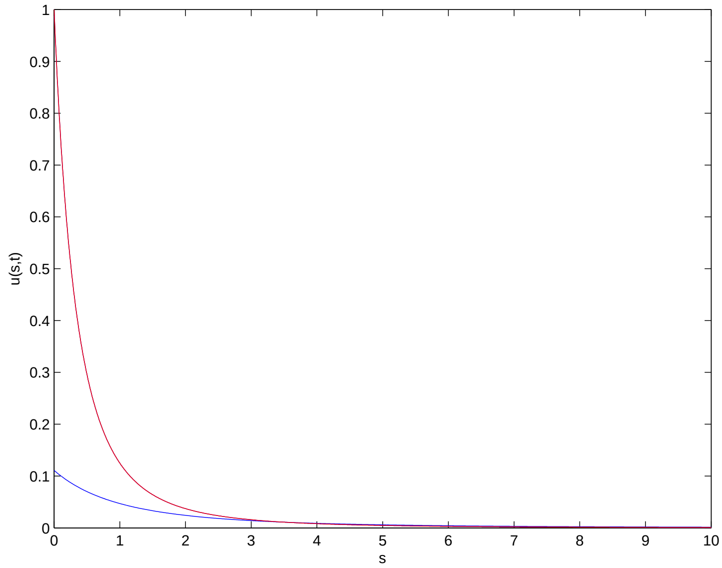

Figure 4.13: *Solution to continuity equation evolving to $t = 1$ along with the initial power law curve in red*

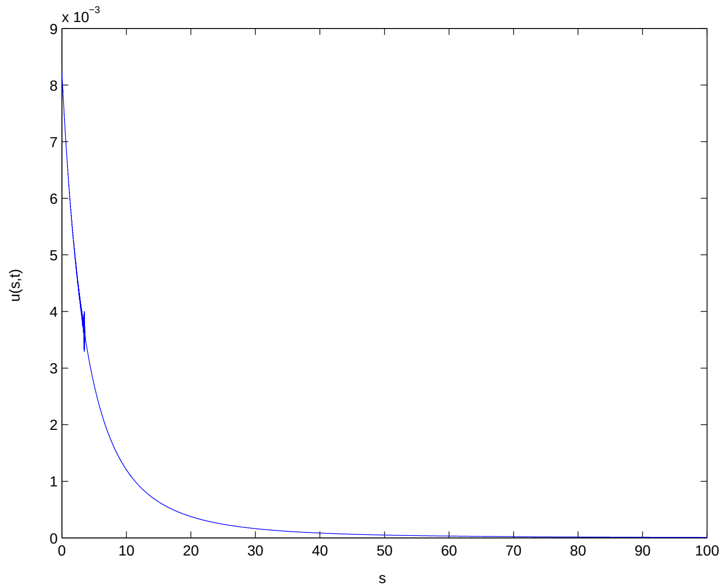

Figure 4.14: *Solution to continuity equation evolving to $t = 5$*

Time	*N(t)*	Ω	$\overline{s}$
0.0000000	0.50002300	0.49799765	0.99594947
0.9999975	0.16687689	0.49600964	2.97230861
1.9999949	0.10030785	0.49402960	4.92513360
2.9999924	7.1781E-02	0.49205745	6.85496147
3.9999899	5.5932E-02	0.49009317	8.76219618
4.9999874	4.5846E-02	0.48813672	10.6472200

Table 4.3: *Table of Moments,* $\overline{s}$ *and evolution times*

However, the value of Ω has not held even when evolving to small times, t. This is, as stated above, due to the domain size. The only way to get round this is to increase the size of the domain but due to the small time steps taken this would mean it would take much longer for the numerical scheme to execute.

This does not help us evolve the system further either by using the characteristics or numerically because the system will not reach the the quasi-steady state where $\overline{s} \propto t$ and so moving to the characteristic solution would not be an option and numerically we would not conserve material. Figure 4.15 shows us exactly that where there is a slight bend in the line even though it is not very clear form the figure.

However, if we assume that the line in Figure 4.15 is a straight line since there is only a slight error, then we can move to the characteristic solution. Here, we find much the same as the previous initial conditions as seen in Figures 4.16 and 4.17 at times of $t = 10$ and $t = 40$, respectively.

The area under the distribution curve reduces as time evolves and we also see the asymptotic tail, which is due to the initial power law distribution function.

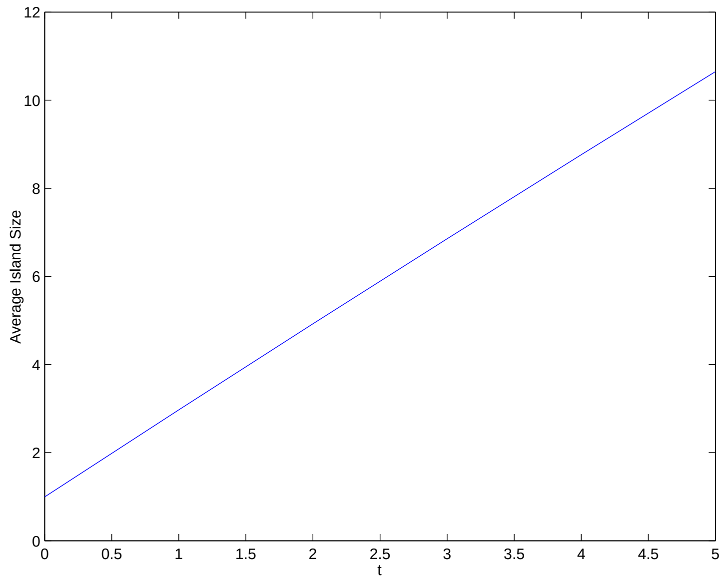

Figure 4.15: *This graph shows the linear relationship $\overline{s} \propto t$ has not been attained by evolving to a time of $t = 5$*

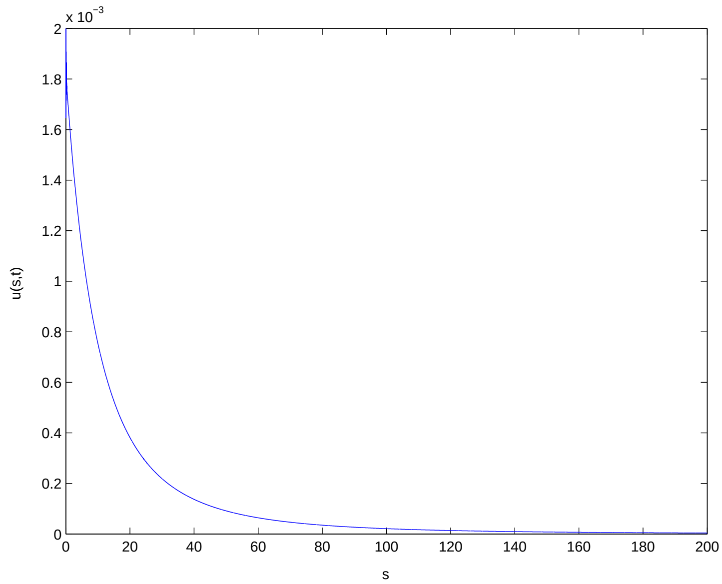

Figure 4.16: *Characteristic Solution calculated at $t = 10$*

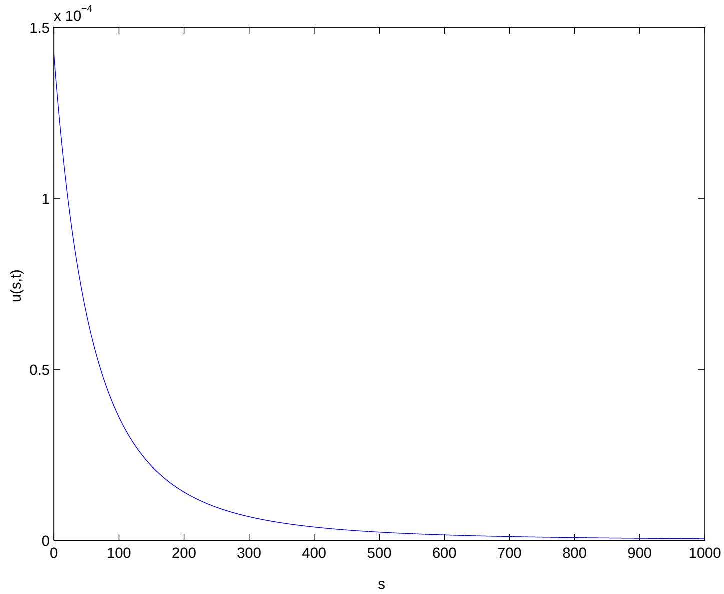

Figure 4.17: *Characteristic Solution calculated at* $t = 40$

Chapter 5

Conclusions and Further Work

Taking the Tarr and Mulheran growth rate equation we found that the assumption where the average island size grows linearly with time in the quasi-steady state is correct for the three different initial conditions tested in this dissertation. When this happens we were able to solve the characteristic equations to yield a method for solving the continuity equation using the numerical solution with the characteristic solution. This proved to be very efficient because of the long execution time needed when small time steps were taken. We also found that in the long time limit as the quasi-steady state is approached the solution did tend toward the asymptotic solution as shown first by Lifshitz and Slyozov.

The starting conditions used in this dissertation were all continuous functions which was deliberate because of the type of numerical scheme used. Using a discontinuous solution is something that does need to be looked at so as to check that in the long time limit an asymptotic solution is found. To do this a better and more efficient numerical method must be found where it is able to cope with discontinuities.

Also work on other growth rate equations is recommended since the Tarr and Mulheran growth rate equation is not the one that describes island evolution on an experimental level [7]. In section 2.2 the Hillert growth rate equation was used to calculate a scaling solution where a power half was used in conjunction with the Tarr and Mulheran growth rate equation. A general power could be used here along with a numerical scheme that can sufficiently deal with the continuity equation produced.

Appendix A

Conservation Property

There is a conservation property we can check to ensure that we have conservation of material. This is

$$\int_0^\infty sF(s,t)ds = \text{constant}. \tag{A.1}$$

We can check this property is valid from the continuity equation

$$\frac{\partial F(s,t)}{\partial t} + \frac{\partial}{\partial s}\Big[\dot{s}F(s,t)\Big] = 0. \tag{A.2}$$

Multiplying through by s and integrating with respect to s the continuity equation becomes

$$\int_0^\infty \Big[\frac{\partial}{\partial t}\Big(sF(s,t)\Big) + s\frac{\partial}{\partial s}\Big(\dot{s}F(s,t)\Big)\Big]ds = 0. \tag{A.3}$$

Separating the two terms we find

$$\int_0^\infty \frac{\partial}{\partial t}\Big(sF(s,t)\Big)ds + \int_0^\infty s\frac{\partial}{\partial s}\Big(\dot{s}F(s,t)\Big)ds = 0, \tag{A.4}$$

where we can take out the time derivative to yield the conserving property A.1 in the first term

$$\frac{d}{dt}\int_0^\infty \Big(sF(s,t)\Big)ds + \int_0^\infty s\frac{\partial}{\partial s}\Big(\dot{s}F(s,t)\Big)ds = 0. \tag{A.5}$$

The first integral on the left is the conservation property which we have said should be constant. Therefore, the conservation property holds if

$$\int_0^\infty s\frac{\partial}{\partial s}\Big(\dot{s}F(s,t)\Big)ds = 0. \tag{A.6}$$

We can integrate by parts to give

$$\Big[s\dot{s}F(s,t)\Big]_0^\infty - \int_0^\infty \dot{s}F(s,t)ds \tag{A.7}$$

and substituting $\dot{s}$ with the growth rate equation 2.1 we get

$$\Big[s\dot{s}F\Big]_0^\infty - \int_0^\infty \left(\frac{sF}{\overline{s}} - F\right)ds \tag{A.8}$$

which can be written as

$$\Big[s\dot{s}F\Big]_0^\infty - \frac{1}{\overline{s}}\int_0^\infty sFds - \int_0^\infty Fds, \tag{A.9}$$

since $\overline{s}(t)$ is only a function of time. Substituting the integral form of $\overline{s}(t)$ 2.2 we find that the integrals all cancel out leaving

$$\Big[s\dot{s}F\Big]_0^\infty = s\dot{s}F\Big|_{s=\infty} - s\dot{s}F\Big|_{s=0}. \tag{A.10}$$

At $s = 0$ the term is zero so that we are left with

$$s\dot{s}F\Big|_{s=\infty}. \tag{A.11}$$

This term is zero since we know that $F(\infty, t)$ tends to zero quicker than any other term. Hence from A.5

$$\frac{d}{dt}\int_0^\infty \Big(sF(s,t)\Big)ds = 0 \tag{A.12}$$

and this conservation property is valid.

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