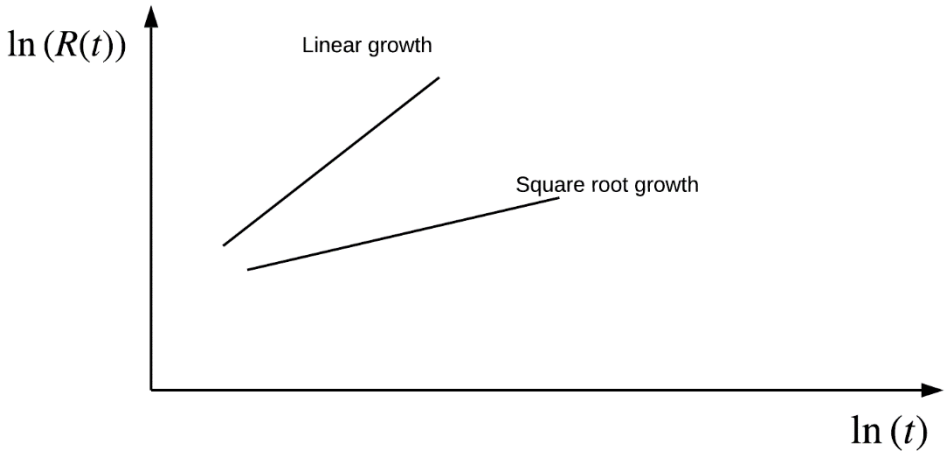
20-02-2020 Meeting Minutes – Nanoparticles Case Study

General Notes:

- Numerical simulations
  - Our simulations compared with the Peng data look promising.
    - For simulations we used inferred parameter values which we found in another paper.
  - We may consider non-dimensionalising everything on the same length-scale as this may make the equations more convenient.
    - There is a bit more book-keeping involved with our approach, however both will produce exactly the same result.
  - Our simulations encounter issues for very large time.
    - We believe that this is because our nanoparticles become arbitrarily small for large time values.
      - There is nothing in the model to stop the radius of the nanoparticles becoming negative.
      - When the radius gets very small the exponential term will dominate.
    - There is a size threshold (when we consider sub-molecular sizes) at which our mathematical model breaks down because the fundamental assumption of the continuum hypothesis is invalid.
    - We were thinking about removing particles from the system when they go below a certain size threshold.
      - This is a very sensible thing to do.
  - Should we use more nanoparticles in our simulation? (we are currently using 50,000).
    - Adding more nanoparticles is unlikely to make a significant difference.
- Is there a chemical reason/intuition why Ostwald ripening occurs?
  - The system wants to minimise its total surface energy.
  - Ostwald ripening is a mechanism by which this minimum may be achieved.
  - Surface energy affects solubility.
  - Surface energy is directly proportional to the total surface area of all the nanoparticles in the system.
    - It may be useful to plot how the total surface area of the nanoparticles in our system evolves with time, in order to better understand the process of Ostwald ripening.
- Asymptotics
  - For certain parameter values, the size of our nanoparticle will grow indefinitely in our model.
  - For other parameter values, our nanoparticle will reach a steady state.
  - We should investigate the necessary conditions for our model parameters, in order for our nanoparticle to reach a steady state.
  - When $D_a \gg 1$ we get the approximate system: $D_a \frac{dR}{dt} \approx \frac{c_\infty(0) - c^* e^{\frac{l_m}{R(0)R(t)}}}{\Delta c}$.
    - By rescaling time, we can absorb the Damköhler number and then by noting that for large values of R we have $\frac{1}{R(t)} \ll 1$, we get asymptotic behaviour of the form: $R(t) = At$, for some constant $A \in \mathbb{R}$.

- When $D_a \ll 1$ we get the approximate system: $\frac{dR}{dt} \approx \frac{c_\infty(0)-c^*}{R(t)\Delta c}$.
    - Therefore, we get asymptotic behaviour $R(t) = \sqrt{2\frac{c_\infty(0)-c^*}{R(t)\Delta c}t + 1}$.
- We can use this asymptotic behaviour to determine whether $D_a \gg 1$ or $D_a \ll 1$ in provided experimental data.
    - This can be done by plotting experimental data on a log-log scale and then looking at the gradient of the best fit line, to determine whether the long-term behaviour has t or $\sqrt{t}$ dependence.

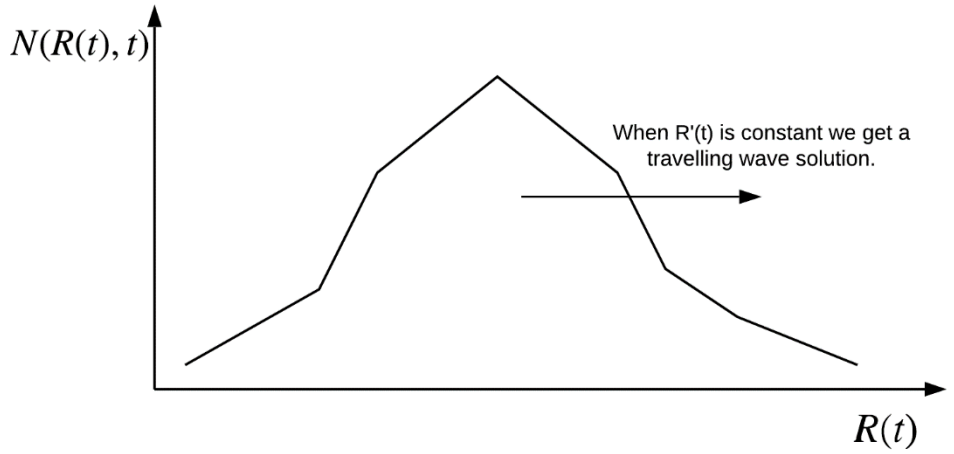


- Note: When comparing to real world data, either we need to dimensionalise our analysis or non-dimensionalise the provided data.
- Depending on the parameter values for our model, our ODE will either approach a steady state or grow indefinitely.
    - When our model approaches a steady state, we can linearise about said fixed point in order to determine how the system approaches this steady state.
        - (This can be done by using a Taylor series expansion).
- We should investigate the asymptotical behaviour of our ODE on short timescales.
    - When $D_a \gg 1$ we don't need to worry about inconsistency with our short timescale and the quasi-steady state.
        - This is because we rescale time in accordance with the Damköhler number, which is large by construction.

<u>Further Directions to Pursue:</u>

- Numerical Simulations
    - We should look at using an optimisation algorithm for model fitting/parameter extraction for more general nanoparticle data sets.
- Derive a PDE model for our population of Nanoparticles.
    - In order to consider the case when there are an arbitrarily large number of nanoparticles in our system, we may wish to derive one overall PDE to describe the evolution of the system (as simulating very large numbers of ODEs concurrently may become intractable).

- We wish to derive a PDE which describes the evolution of the quantity N with time.



  - N is called the population size distribution, which we can find papers for.
  - We want to derive a PDE of the form: $\frac{\partial N}{\partial t} + \dot{R}(t)\frac{\partial N}{\partial R} = ?$
    - We will obtain non-dimensional parameters on the right-hand side of our governing PDE for N.
    - This equation has characteristic curve: $\frac{dr}{dt} = \dot{R}(t)$.
    - When $\dot{R}(t)$ is constant, we have that N is a function of the variable $s := r - \dot{R}(0)t$ and hence our PDE contains a travelling wave solution.
- Isolate the timescale on which Ostwald ripening takes place.
  - This is practically useful because it tells us how long an experiment should be run for before we expect to see any Ostwald ripening taking place.
  - It will be easier to identify the natural Ostwald ripening timescale if we formulate our problem as a single PDE (see above).
    - However, it will be difficult to derive a suitable PDE.
    - This timescale can also be found by using the coupled system of ODEs, but is not obvious to spot, since there are many coupled equations.
- The ultimate goal is to find out how to optimally vary $c_\infty(t)$ in order to ensure that all the nanoparticles are of a very similar size after a fixed amount of time.
  - It is important to note that $c_\infty(t)$ must satisfy the conservation of mass formula, so we are not free to vary $c_\infty(t)$ arbitrarily.
    - We must have that $c_\infty(t) = c_\infty(0) - \frac{4\pi N_0}{3V_m}\sum_{i=1}^{n}(\hat{R}_i(0)R_i(t))^3$ for n nanoparticles.
    - We may vary the parameter $c_\infty(0)$ discontinuously (i.e. it suddenly jumps when we add more solute to the system).
  - Ideally want to get that the model tends to the narrowest distribution possible (all nanoparticles are approximately the same size) in the least amount of time possible.
  - We may look at papers to understand how long these nanoparticle experiments are typically run for in practice.
    - This will give us an idea of how long our simulations should be run for before terminating them and assessing their final size distribution.
- Could investigate how the initial size distribution of the nanoparticles in the solute affects the final distribution (e.g. use starting distributions other than the normal).

- Do different this input distributions affect the time taken for Ostwald ripening to occur?