Modeling of simultaneous nucleation and growth of nanoparticles

A research project with Prof. Charles Y. Cao, Department of Chemistry, UF

A qualifying PDE test for undergraduate students interested to participate

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An overview

Nanopatricles are obtained by growing them in size in a chemical solution. In brief, the objective of this research project is to figure out how to control the size distribution of nanoparticles in the process of their growth by amending physical and chemical parameters of the solution.

For simplicity, all nanoparticles are assumed to be round. Let $f(r,t)$ be the radius distribution of nanoparticles at a time moment t, that is, $f(r,t)dr$ is the number of nanoparticles with radii in a small interval $(r, r+dr)$ at a time t per unit volume so that the total number of nanoparticles with radii in the interval $a < r < b$ at a time t per unit volume reads

$$N_{[a,b]}(t) = \int_a^b f(r,t)\, dr\,.$$

The basic model for evolution of $f(r,t)$ is given by the Lifshitz-Slyozov equation

$$\frac{\partial}{\partial t} f(r,t) + \frac{\partial}{\partial r}\Big(U(r,t) f(r,t)\Big) = 0\,, \quad r > 0\,, \quad t > 0\,.$$

where the function $U(r,t)$ is called the radius growth rate (owing to the method of characteristics for first-order PDEs). You should be able to see the rationale for this name when solving this equation for specific $U(r,t)$ by the method of characteristics (see below). Alternatively, let us integrate the equation with respect to r over an interval $[a,b]$. Assuming that f and U are smooth enough so that the order of differentiation and integration can be interchanged

$$\int_a^b \frac{\partial}{\partial t} f(r,t)\, dr = \frac{d}{dt}\int_a^b f(r,t)\, dr = \frac{d}{dt} N_{[a,b]}(t)$$

it follows from the fundamental theorem of calculus that

$$\frac{d}{dt} N_{[a,b]}(t) = U(a,t) f(a,t) - U(b,t) f(b,t)$$

This shows that the number of nanoparticles with radii $a < r < b$ is increasing because nanoparticles of radius a grow larger at a rate $U(a,t)f(a,t)$ and is decreasing at a rate

$U(b,t)f(b,t)$ because nanopatricles of radius b become bigger and, hence, are no longer in $[a,b]$. So, $U(r,t)$ can be interpreted as the radius growth rate, and the Lifshitz-Slyozov equation is nothing but the conservation of the total number of nanopatricles (if $f(0,t)=0$ which means that there are no nanoparticles of the zero size).

A nanoparticle grows by absorbing "monomers", chemical building blocks that are present in the solution in which nanoparticles grow. Depending on the physical conditions of the solution, nanopatricles can also loose "monomers", thus decreasing in size, by a dissociation process. There are many microscopic models for the rate $U(r,t)$. The simplest and basic model that takes into account the absorption and dissociation processes is

$$U(r,t) = G(r)C(t) - D(r)\,,$$

where $C(t)$ is the concentration of "monomers", and the function $G(r)$ and $D(r)$ are the absorption and dissociation rates for a nanoparticle of radius r, respectively. A nanoparticle of radius r can absorb a "monomer" at a rate of $G(r)$, thus increasing its size. But the rate at which the size is increasing also depends on how many "monomers" are available, that is, it must be proportional to the concentration $C(t)$. A nanoparticle of size r can also loose "monomers" at a rate of $D(r)$, thus decreasing its size. The loss does not depend on how many "momomers" are floating around, it is mostly depends on chemical bonds on the surface of nanoparticle and the temperature. The rates $G(r)$ and $D(r)$ strongly depend on microscopic mechanisms for absorption and dissociation as well as on physical parameters (like temperature) and subject to research. In particular, it is possible to manipulate $U(r,t)$ in a Lab, with a potential possibility to obtain $f(r,t)$ with desired properties.

The basic mathematical problem is the Cauchy problem: find $f(r,t)$ if

$$f(r,t)\Big|_{t=0} = \lim_{t\to 0^+} f(r,t) = f_0(r)$$

where $f_0(r)$ is an initial distribution. It can be solved analytically in some simple cases or numerically in a general case by the method of characteristics for a given $U(r,t)$. This task will comprise a selection test for interested students (see next section below).

The actual project is about modeling of a chemical network that is essential for $U(r,t)$ as well as $f_0(r)$. In real world, $f_0(r)$ is not known and so are $G(r)$, $C(t)$, and $D(r)$. Moreover, the growth of nanopatricles has a back reaction on $U(r,t)$. So, the objective is to develop a system of ordinary differential equations for evolution of concentrations of "monomers" and other solvents participating in chemical reactions producing "monomers", thus describing $U(r,t)$ in terms of these concentrations, as well as a back reaction on this chemical network by evolution of $f(r,t)$. The chemical network should also model the very process of formation of nanoparticles of a "minimal" size, thus naturally generating $f_0(r)$. In other words, the model is expected to be the the Lifshitz-Slyozov equation coupled to a system of ODEs. In the corresponding Cauchy problem the initial distribution of nanoparticles is set to zero, while initial concentrations of building blocks for nanoparticles are given. The modeling will be based on the actual experimental data obtained in the Lab of Prof. Cao (UF, Chemistry).

The main objective is to find out how the chemical network should be controlled in order to obtain a desired distribution of nanoparticles at the end of the growth process.

Funding: There is no funding for this project as of now and there is no money for any research assistant. It has just started and, hence, there are no preliminary results to "sell" to any potential sponsor or funding agency. So, consider your work similar to Research Experience for Undergraduates (REU). Possible benefits include: Honors thesis, potential publications, and my strong support if you want to advance your academic career, e.g., by going to a grad school (not to mention, publications and research experience counts most when selecting grad students).

Expected qualifications: The modeling will include many numerical simulations (e.g., Matlab, or Mathematics, or any numerical tool you are familiar with). So, your knowledge of these tools and some programming skills are important. You should know very well the methods of characteristics. The latter is verified by your recent Test 2 performance and the test problems below.

Expected duties: Learning basic methods of numerical integration of ODE and the use of corresponding libraries in Matlab or any similar tool. Carrying out numerical simulations and reporting the results. Participation in meetings with me and Prof. Cao. Educating yourself about the Lifshitz-Slyozov equation and its modern modifications, that is, reading research literature when necessary (or advised).

Test problems

Problem 1

Let

$$U(r,t) = \frac{C}{r}\,, \quad C = \text{constant} > 0$$

Use the method of characteristics to solve the Cauchy problem for the Lifshitz-Slyozov equation. Express the answer in terms of the initial data $f_0(r)$.

Problem 2

Let $U = U(r) > 0$ be independent of time t. Use the method of characteristics to solve the Cauchy problem for the Lifshitz-Slyozov equation. Express the answer in terms of the initial data $f_0(r)$ and $U(r)$. Explain in detail how $f(r,t)$ is to be computed for a given (r,t) using the functions $f_0(r)$ and $U(r)$, just as you were writing an algorithm for a numerical solution. Remember, a computer does not accept "ideas" and "vague" recommendations. It can multiply and add numbers. It can also use basic subroutines (e.g., solve an algebraic equation, and similar).

Problem 3

The same as in Problem 2 but $U(r,t) = C(t)D(r)$, $D(r) > 0$, $C(t) > 0$.

Problem 4

Use the method of characteristics to convert the Cauchy problem for the Lifshitz-Slyozov equation with a general rate $U(r,t)$ and initial data $f_0(r)$ to initial value problems for ordinary differential equations. To your best knowledge and skills, describe an algorithm for calculating $f(r,t)$ for a given (r,t) from the functions $U(r,t)$ and $f_0(r)$. Make yourself familiar with some basic numerical methods to integrate ODE, like, e.g., Runge-Kutta method. You do not have to use a specific algorithm explicitly (there are libraries for such algorithms, don't invent wheels). However, if you need a solution of ODE, just specify the algorithm you want to use and make sure that you specify the input parameters into this particular algorithm.

Remarks

You can start with Problem 4 and go backward. You already learned enough to do that. However, analytic solutions in Problems 2-3 require a careful use of the implicit function theorem and implicit differentiation especially when you work with general rather then concrete functions for $U(r,t)$ in the method of characteristics. Recall the necessity of finding the inverse of the change of variables obtained from the characteristics. For this reason, solving simple concrete problems, like Problem 1, should be helpful for your understanding. You can always assume that characteristics define a change of variables for some range of t and r and, hence, the solution exists, at least in some interval of time $t > 0$ and $r > 0$. The existence of a global solution for all $t > 0$ is a separate problem that is NOT to be discussed in this test.