Modeling the Phase Separation of Polymers

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Abstract

The phase separation of polymers is an important process in chemical engineering involving the diffusion and attraction/repulsion of two kinds of polymers. We begin by deriving the diffusion equation using Fick's law and then solving it using Fourier Series and the finite-difference method. This is followed by an analysis of the Allen-Cahn equation, a phase field model illustrating the phase separation process.

Contents

1 Introduction

This REU project is motivated by the study of phase separation of polymers through analysis, computations, and experiments. The project examines and solves several partial differential equations which are pertinent to modeling phase separation experiments.

1.1 What is phase separation?

A mixture of two kinds of molecules can undergo a process called phase separation in which the molecules separate into distinct spatial regions comprising a single kind of molecule. Phase separation arises due to molecular diffusion and the electrostatic attraction or repulsion among the molecules.

This video shows the phase separation occurring in a mixture of oil and water. Water molecules are polar and each moelcules has an electric dipole due to the charge gradient between the oxygen atom and hydrogen atoms; on the other hand, an oil molecule is a hydrocarbon chain with oxygen atoms at the ends, hence oil is nonpolar and hydrophobic. The video shows that the oil floats on top of the water; this is because oil has fewer oxygen atoms than water and hence has lower density.

1.2 What is a polymer?

Polymers are an important type of molecule in chemistry, chemical engineering, and macromolecular science. A polymer is a chain of repeating monomers each of which is a simple chemical unit. Figure 1 shows an example of a polymer chain with carbon atoms as black, oxygen atoms as red, hydrogen atoms as white. A polymer generally has a three-dimensional structure.

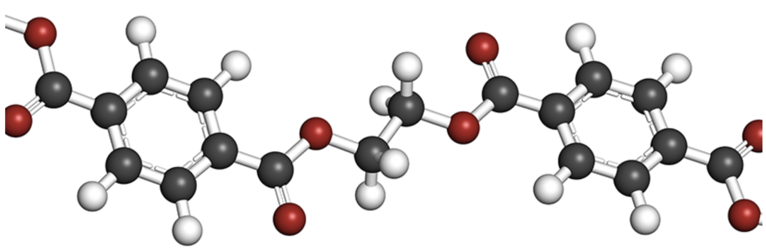

Figure 1: The chain of repeating monomers which form a polymer.

1.3 Polyelectrolyte experiments

The Larson Group in the Department of Chemical Engineering is researching the phase separation of polyelectrolytes. A polyelectrolyte is a macromolecule with charged groups and they can be classified according to their charge as either polycations (positive) or polyanions (negative) [2]. Figure 2 illustrates the phase separation of polyelectrolytes induced by various salts.

Box 1 shows a diagram of polycations and polyanions in a sample tube along with a picture of the phase separation of polymers.

Box 2 shows the liquid to solid transition observed by rheology, which examines the viscosity of non-Newtonian matter.

Box 3 shows salt cations and anions bonding to polyelectrolytes. Naturally, the polycations are attracted to salt anions and polyanions are attracted to salt cations.

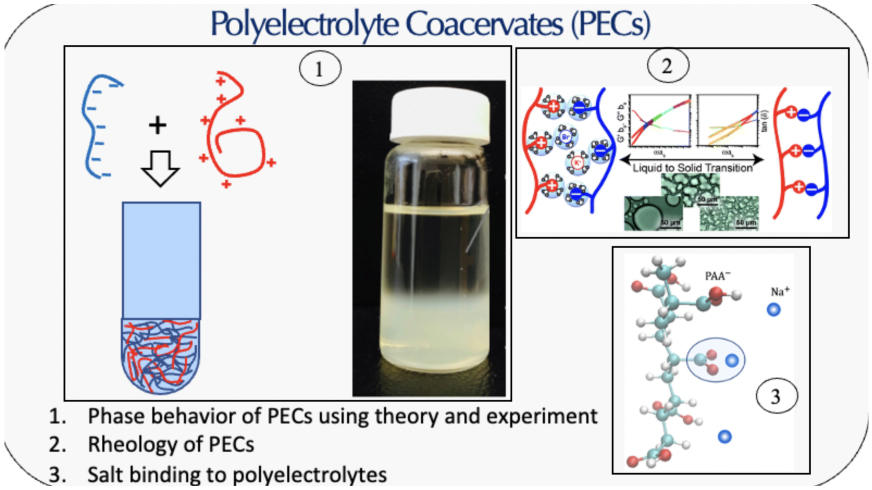

Figure 2: Larson Group, Department of Chemical Engineering, University of Michigan, larsonlab.engin.umich.edu, accessed 28 May, 2024.

2 Diffusion Equation

Diffusion is an important factor in the phase separation of polymer mixtures. This section presents the derivation of the diffusion equation by Fick's law, then the solution by Fourier series, and then the solution by the finite-difference method.

2.1 Derivation of diffusion equation by Fick's law

We will present the derivation of the diffusion equation in one space dimension. The derivation depends on Fick's 1st law and 2nd law. Fick's 1st law is

$$J = -D\frac{\partial \phi}{\partial x}, \tag{1}$$

where J is the diffusion flux, D is the diffusion coefficient, ϕ is the concentration, and x is the spatial variable. In words, the diffusion flux is proportional to the concentration gradient. In the absence of any chemical reactions, the law of mass conservation states

$$\frac{\partial \phi}{\partial t} + \frac{\partial J}{\partial x} = 0, \tag{2}$$

which relates the rate of change of concentration with respect to time and the rate of change of diffusion flux with respect to space. The next step is to replace the diffusion flux, J, using Fick's 1st law,

$$\frac{\partial \phi}{\partial t} - \frac{\partial}{\partial x}\left(D\frac{\partial \phi}{\partial x}\right) = 0. \tag{3}$$

This yields Fick's 2nd law,

$$\frac{\partial \phi}{\partial t} = D\frac{\partial^2 \phi}{\partial x^2}, \tag{4}$$

which is the diffusion equation for the concentration. This is a partial differential equation in space and time, which requires an initial condition and boundary conditions. We will consider the space domain to be the unit interval $0 \leq x \leq 1$ with Dirichlet boundary conditions $\phi(0,t) = \phi(1,t) = 0$. The initial condition is denoted $\phi(x,0) = f(x)$. Next, we present the solution of the diffusion equation by Fourier Series.

2.2 Solution by Fourier series

2.2.1 Introduction to Fourier series

Let $f(x)$ be a given function defined on the unit interval $0 \leq x \leq 1$ and consider the Fourier Sine series,

$$f(x) = \sum_{n=1}^{\infty} a_n \sin(n\pi x), \tag{5}$$

where a_n are the Fourier Sine coefficients and they are determined as follows. Note that each term in the series vanishes for $x = 0$ and $x = 1$. Multiply Eq. (5) by $\sin(j\pi x)$, where j ranges over the same values as n (namely $j = 1, 2, 3, \ldots$),

$$f(x)\sin(j\pi x) = \sum_{n=1}^{\infty} a_n \sin(n\pi x)\sin(j\pi x). \tag{6}$$

The next step is to integrate from $x = 0$ to $x = 1$,

$$\int_0^1 f(x)\sin(j\pi x)dx = \int_0^1 \sum_{n=1}^{\infty} a_n \sin(n\pi x)\sin(j\pi x)dx \tag{7a}$$

$$= \sum_{n=1}^{\infty} a_n \int_0^1 \sin(n\pi x)\sin(j\pi x)dx, \tag{7b}$$

where we have interchanged the order of integration and summation. Now we need to compute the following integral, where $n, j = 1, 2, \ldots$,

$$\int_0^1 \sin(n\pi x)\sin(j\pi x)dx, \tag{8}$$

which is done by using the trigonometric identities.

$$\cos(a+b) = \cos(a)\cos(b) - \sin(a)\sin(b), \tag{9a}$$

$$\cos(a-b) = \cos(a)\cos(b) + \sin(a)\sin(b). \tag{9b}$$

Now set $a = n\pi x$ and $b = j\pi x$.

$$\cos((n+j)\pi x) = \cos(n\pi x)\cos(j\pi x) - \sin(n\pi x)\sin(j\pi x), \tag{10a}$$

$$\cos((n-j)\pi x) = \cos(n\pi x)\cos(j\pi x) + \sin(n\pi x)\sin(j\pi x). \tag{10b}$$

Now take Equation (10b) and subtract Equation (10a) to obtain,

$$\sin(n\pi x)\sin(j\pi x) = \frac{1}{2}(\cos((n-j)\pi x) - \cos((n+j)\pi x)), \tag{11}$$

and then substitute into Equation (8),

$$\int_0^1 \sin(n\pi x)\sin(j\pi x)dx = \frac{1}{2}\int_0^1 \big[\cos((n-j)\pi x) - \cos((n+j)\pi x)\big]dx \tag{12a}$$

$$= \frac{1}{2}\left[\frac{\sin(n-j)\pi x}{(n-j)\pi} - \frac{\sin(n+j)\pi x}{(n+j)\pi}\right]_0^1 = \begin{cases} 0, & n \neq j, \\ 1/2, & n = j. \end{cases} \tag{12b}$$

Figure 3 plots the integrand in Eq. (12a), where by symmetry one can see that when $n \neq j$, the area under the curve is zero, which is consistent with Eq. (12b).

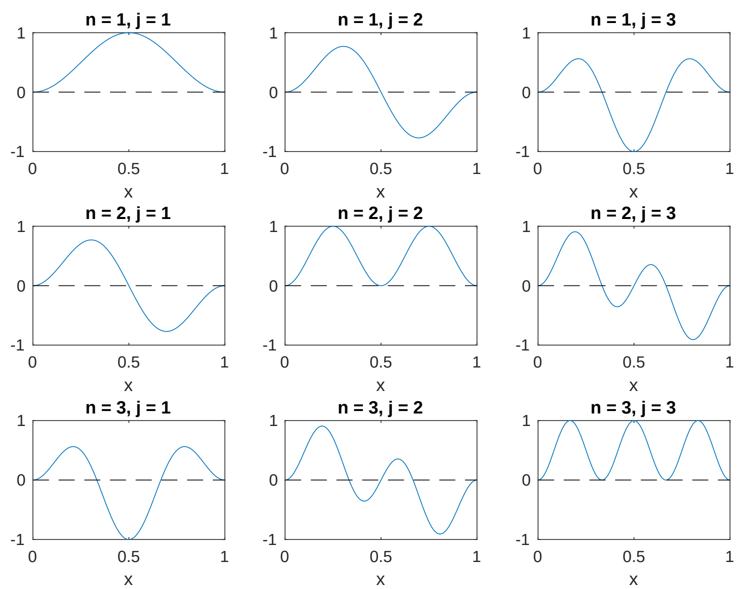

Figure 3: Plot of $\sin(n\pi x)\sin(j\pi x)$ for $n = 1, 2, 3$ and $j = 1, 2, 3$.

Substituting the result from Eq. (12) into Eq. (7) yields

$$\int_0^1 f(x)\sin(j\pi x)dx = \sum_{n=1}^{\infty} a_n \int_0^1 \sin(n\pi x)\sin(j\pi x)dx = a_j/2, \tag{13}$$

This yields the Fourier Sine series

$$f(x) = \sum_{n=1}^{\infty} a_n \sin(n\pi x), \quad a_n = 2\int_0^1 f(x)\sin(n\pi x)dx. \tag{14}$$

2.2.2 Square wave example

Next we are going to illustrate the Fourier Sine Series expansion with an important example, the square wave defined by

$$f(x) = \begin{cases} 1, & 0 \leq x < 1/2 \\ 0, & x = 1/2 \\ -1, & 1/2 < x \leq 1. \end{cases} \tag{15}$$

Equation (14) gives the Fourier Sine coefficients,

$$a_n = 2\int_0^1 f(x)\sin(n\pi x)dx = 2\left[\int_0^{1/2} f(x)\sin(n\pi x)dx + \int_{1/2}^1 f(x)\sin(n\pi x)dx\right] \tag{16a}$$

$$= 2\left[\int_0^{1/2} \sin(n\pi x)dx - \int_{1/2}^1 \sin(n\pi x)dx\right] = 2\left[\frac{-\cos(n\pi x)}{n\pi}\bigg|_0^{1/2} + \frac{\cos(n\pi x)}{n\pi}\bigg|_{1/2}^1\right] \tag{16b}$$

$$= \frac{2}{n\pi}\big[-\cos(n\pi/2) + \cos(0) + \cos(n\pi) - \cos(n\pi/2)\big]. \tag{16c}$$

At this point, we note that

$$\cos(0) = 1, \quad \cos(n\pi) = (-1)^n, \quad \cos(n\pi/2) = \begin{cases} 1, & n = 0, 4, 8, 12, \ldots \\ 0, & n = 1, 3, 5, 7, \ldots \\ -1, & n = 2, 6, 10, 14, \ldots \end{cases} \tag{17a}$$

$$-\cos(n\pi/2) + \cos(0) + \cos(n\pi) - \cos(n\pi/2) = \begin{cases} 0, & n = 0, 4, 8, 12 \ldots \\ 0, & n = 1, 3, 5, 7, \ldots \\ 4, & n = 2, 6, 10, 14, \ldots \end{cases} \tag{17b}$$

Substituting this into Eq. (16c) yields the Fourier Sine coefficients of the square wave,

$$a_n = \begin{cases} 0, & n = 0, 4, 8, 12, \ldots \\ 0, & n = 1, 3, 5, 7, \ldots \\ 8/(n\pi), & n = 2, 6, 10, 14, \ldots \end{cases} \tag{18}$$

The Fourier Series approximation of the square wave is

$$f_N(x) = \sum_{n=1}^{N} a_n \sin(n\pi x). \tag{19}$$

Figure 4 shows the Fourier Series approximation of the square wave for $N = 2, 6, 10, 14$. As the value of N increases, we see that the approximation becomes more accurate.

2.2.3 Separation of Variables

This subsection derives the Fourier Sine series solution of the diffusion equation in Eq. (4) with $D = 1$ by separation of variables. Let $\phi(x,t) = X(x)T(t)$, a function of x multiplied by a function of t. Then substitute into the diffusion equation in Eq. (4) to obtain $X(x)T'(t) = X''(x)T(t)$. Then divide both sides by $X(x)T(t)$ to obtain

$$\frac{T'(t)}{T(t)} = \frac{X''(x)}{X(x)} = c, \tag{20}$$

where c is a constant; this follows because t and x are independent variables. We then have two ordinary differential equations,

$$X''(x) = cX(x), \quad T'(t) = cT(t). \tag{21}$$

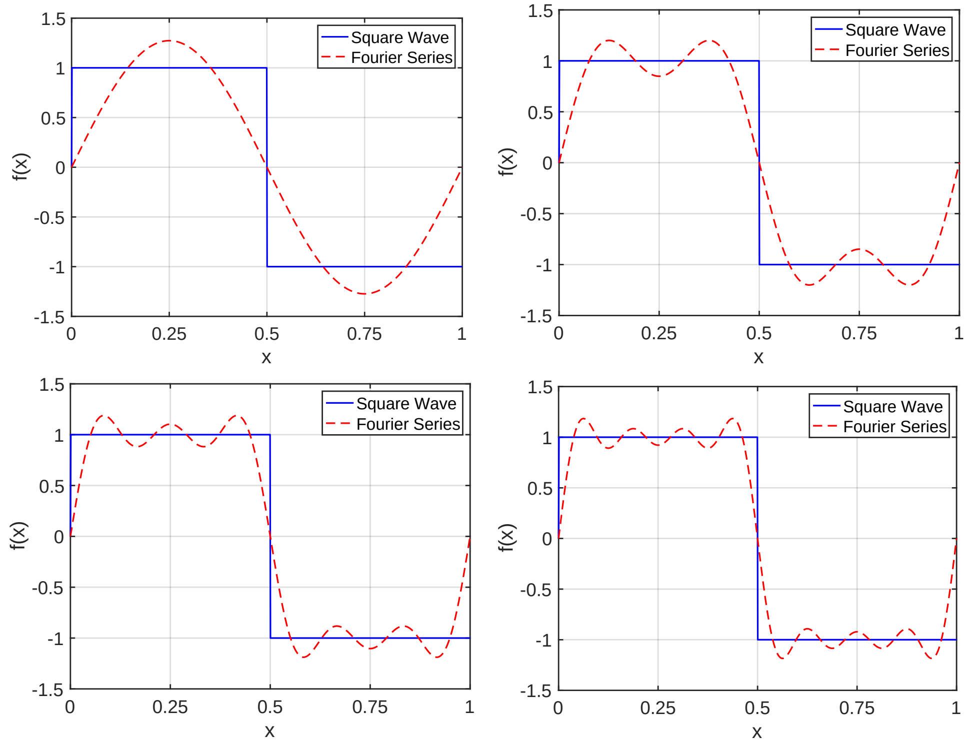

Figure 4: The square wave curve and its Fourier Series approximation for $N = 2, 6, 10, 14$

The first equation. The general solution of the first equation is $X(x) = Ae^{\sqrt{c}x} + Be^{-\sqrt{c}x}$, where the constants A, B are determined by satisfying the Dirichlet boundary conditions, $X(0) = A+B = 0$ and $X(1) = Ae^{\sqrt{c}}+Be^{-\sqrt{c}} = 0$. This gives $B = -A$ and $Ae^{\sqrt{c}}-Ae^{-\sqrt{c}} = 0$, which can be rewritten as $A(e^{\sqrt{c}} - e^{-\sqrt{c}}) = 0$. To obtain a non-zero solution $X(x)$ we must have $A \neq 0$, so therefore $e^{\sqrt{c}} - e^{-\sqrt{c}} = 0$, which implies $e^{\sqrt{c}} = e^{-\sqrt{c}} = 1/e^{\sqrt{c}}$, which implies $e^{\sqrt{c}} \cdot e^{\sqrt{c}} = 1$, or equivalently, $e^{2\sqrt{c}} = 1$. To solve for c we apply Euler's formula, $e^{ix} = \cos(x) + i\sin(x)$, which implies that $2\sqrt{c} = 2n\pi i$, where $n = 0, \pm1, \pm2, \ldots$, and this gives infinitely many constants $c = c_n = -n^2\pi^2$.

The second equation. Substituting this into the second equation in Eq. (21) gives the differential equation $T'(t) = -n^2\pi^2T(t)$, and the solution is $T(t) = T(0)e^{-n^2\pi^2 t}$, where $T(0)$ is a constant. Recall that $X(x) = Ae^{\sqrt{c}x} + Be^{-\sqrt{c}x}$, which yields

$$X(x) = Ae^{n\pi ix} - Ae^{-n\pi ix} = A(e^{n\pi ix} - e^{-n\pi ix}) \tag{22a}$$
$$= A(\cos(n\pi x) + i\sin(n\pi x) - \cos(-n\pi x) - i\sin(-n\pi x)). \tag{22b}$$

Since cosine is an even function, we have $\cos(-n\pi x) = \cos(n\pi x)$, and since sine is an odd function, we have $\sin(-n\pi x) = -\sin(n\pi x)$, and therefore $X(x) = 2Ai\sin(n\pi x)$.

This shows that separation of variables gives solutions of the diffusion equation satisfying the Dirichlet boundary conditions of the form

$$T(t) \cdot X(x) = T(0)e^{-n^2\pi^2 t} \cdot 2Ai\sin(n\pi x) = a_n e^{-n^2\pi^2 t}\sin(n\pi x), \tag{23}$$

where a_n is an arbitrary constant.

2.2.4 Fourier Series Solution

The solutions of the diffusion equation in Eq. (23) can be added together giving the Fourier Sine series solution of the diffusion equation in Eq. (4) with $D = 1$,

$$\phi(x,t) = \sum_{n=1}^{\infty} a_n e^{-n^2\pi^2 t} \sin(n\pi x), \quad a_n = 2\int_0^1 f(x)\sin(n\pi x)dx, \tag{24}$$

where the coefficients a_n have been chosen in accordance with Eq. (14) to satisfy the initial condition $\phi(x,0) = f(x)$.

2.3 Solution by Finite-Difference Method

This section presents the solution of the diffusion equation by the finite-difference method.

2.3.1 Finite-difference approximations of derivatives

Given a function $f(x)$, we can consider finite-difference approximations to the first and second derivatives. The forward difference approximation of the first derivative is defined by

$$f'(x) \approx \frac{f(x+h) - f(x)}{h} = D_+ f(x), \tag{25}$$

where h is the step size. The exact value of the derivative is obtained in the limit $h \to 0$ and for any finite value $h > 0$ we have an approximation. To analyze the error we consider the Taylor expansion,

$$f(x+h) = f(x) + f'(x)h + \frac{1}{2}f''(x)h^2 + \cdots, \tag{26}$$

which can be rearranged in the form

$$\underset{\substack{\uparrow \\ \text{approximation}}}{D_+ f(x) = \frac{f(x+h) - f(x)}{h}} = \underset{\substack{\uparrow \\ \text{exact value}}}{f'(x)} + \underset{\substack{\uparrow \\ \text{error}}}{\underbrace{\frac{1}{2}f''(x)h + \cdots}}. \tag{27}$$

Equation (27) shows that the error is proportional to h, and we write this as

$$D_+ f(x) = f'(x) + O(h). \tag{28}$$

For example if $f(x) = e^x, x = 1$, then $f'(x) = e = 2.71828\ldots$ is the exact value. In the Table below, column 1 is the step size h, column 2 is the approximation $D_+ f(1)$, column 3 is the truncation error $|D_+ f(1) - f'(1)|$, and column 4 is the ratio of column 3 to column 1. The final column shows that the error is proportional to the step size, h.

We shall also need the backward difference approximation of the first derivative defined by

$$D_- f(x) = \frac{f(x) - f(x-h)}{h} = f'(x) + O(h), \tag{29}$$

and the central difference approximation of the second derivative defined by

$$D_+ D_- f(x) = \frac{f(x+h) - 2f(x) + f(x-h)}{h^2} = f''(x) + O(h^2). \tag{30}$$

h	$D_+f(1)$	$\lvert D_+f(1) - f'(1)\rvert$	$\lvert D_+f'(1) - f'(1)\rvert/h$
0.1	2.8588	0.1406	1.4056
0.05	2.7874	0.0691	1.3821
0.025	2.7525	0.0343	1.3705
$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$
0	e	0	$\frac{0}{0} = \frac{1}{2}f''(1) = \frac{e}{2}$

Table 1: Forward Difference Approximation

2.3.2 Finite-difference solution of diffusion equation

The finite-difference method replaces the derivatives by finite-difference approximations defined on a grid in space and time. Let $h = \Delta x = 1/N$ be the space step and let $k = \Delta t$ be the time step. Then define the spatial grid points $x_j = jh, j = 0, 1, \ldots, N$, and the temporal grid points $t_n = nk, n = 0, 1, 2, \ldots$, as shown in Fig. 5. The approximation values are denoted by $u_j^n \approx \phi(x_j, t_n)$ and the derivatives in the diffusion equation are approximated by finite differences,

$$\phi_t = \phi_{xx} \to \frac{u_j^{n+1} - u_j^n}{k} = D_+D_-u_j^n = \frac{u_{j+1}^n - 2u_j^n + u_{j-1}^n}{h^2}. \tag{31}$$

Let $\lambda = k/h^2$. Then the finite-difference equation can be rewritten as

$$u_j^{n+1} = u_j^n + \lambda(u_{j+1}^n - 2u_j^n + u_{j-1}^n) = \lambda u_{j+1}^n + (1 - 2\lambda)u_j^n + \lambda u_{j-1}^n. \tag{32}$$

Hence, the numerical solution at time step $n + 1$ is given by a linear combination of the numerical solution values at time step n as indicated by the stencil in Fig. 5.

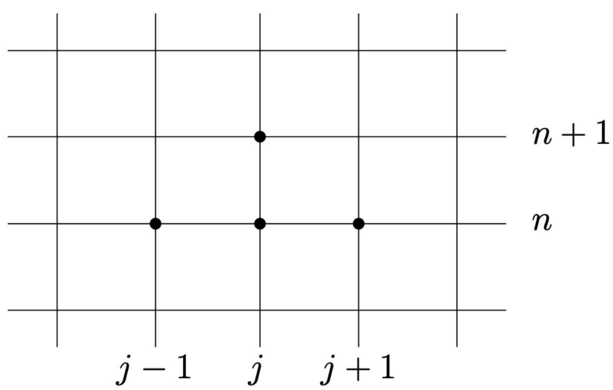

Figure 5: Stencil for finite-difference approximation of the diffusion equation.

It can be shown that the finite-difference method in Eq. (32) is stable only if the coefficients are positive, which requires that $\lambda \leq 1/2$.

3 Allen-Cahn Equation

Consider a mixture of two kinds of polymers labeled A and B. The phase separation of the polymers can be modeled by the Allen-Cahn equation [1], which adds a reaction term to the

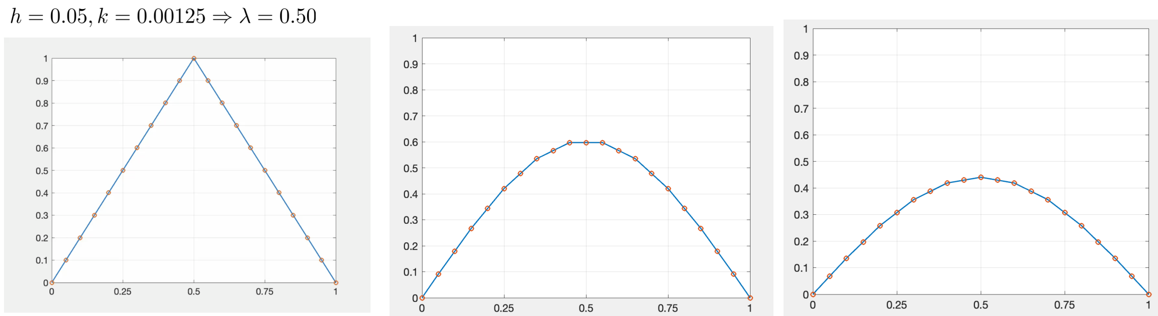

Figure 6: Stable figure for finite-difference approximation of the diffusion equation. The first figure shows the initial condition, the second is at 25 time steps, and the final figure is at 50 time steps.

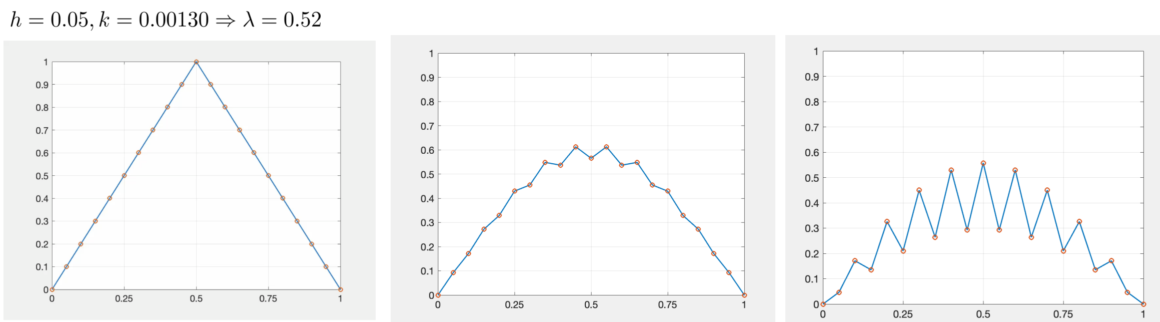

Figure 7: Unstable figure for finite-difference approximation of the diffusion equation.The first figure shows the initial condition, the second is at 25 time steps, and the final figure is at 50 time steps.

diffusion equation,

$$\frac{\partial \phi}{\partial t} = \frac{\partial^2 \phi}{\partial x^2} + \phi - \phi^3. \tag{33}$$

The function $\phi(x, t)$ is called the phase function and it measures the amount of polymer A compared to the amount of polymer B at any spatial point x and time t. The phase function lies in the range $-1 \leq \phi(x, t) \leq 1$ in such a way that $\phi(x, t) \approx 1$ corresponds to polymer A, $\phi(x, t) \approx -1$ corresponds to polymer B, and intermediate values indicate a mixture. Given an initial distribution of polymers $\phi(x, 0)$, we want to determine the distribution $\phi(x, t)$ at later times $t > 0$.

3.1 Without diffusion

First we consider the Allen-Cahn equation without diffusion. This yields an ordinary differential equation, which for convenience is written in the form

$$\frac{dy}{dt} = y - y^3. \tag{34}$$

The equation has three constant solutions $c = -1, 0, 1$. Figure 8 shows the phase plane which plots dy/dt versus y, where the arrows denote whether the solution $y(t)$ is increasing or decreasing in time, which depends on the sign of dy/dt. Hence, from the direction of the arrows, we see that the constant solution $c = 0$ is unstable, while the constant solutions $c = -1, 1$ are both stable.

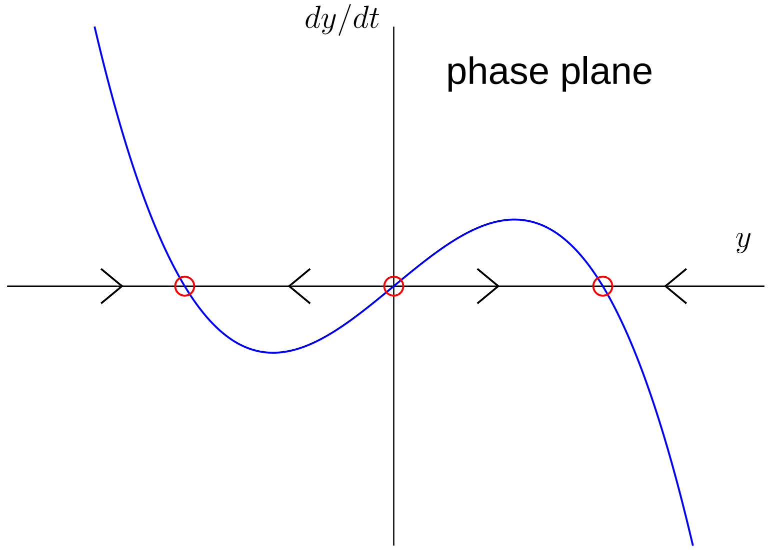

Figure 8: Phase plane of Allen-Cahn equation without diffusion.

3.1.1 ODE Solution by Separation of Variables

3.2 With diffusion

$$\frac{\partial\phi}{\partial t} = \frac{\partial^2\phi}{\partial x^2} + \gamma(\phi - \phi^3)$$

$$\begin{aligned}
\frac{u_j^{n+1} - u_j^n}{k} &= D_+D_-u_j^n + \gamma(u_j^n - (u_j^n)^3) \\
&= \frac{u_{j+1}^n - 2u_j^n + u_{j-1}^n}{h^2} + \gamma(u_j^n - (u_j^n)^3) \\
u_j^{n+1} &= \lambda u_{j+1}^n + (1-2\lambda)u_j^n + \lambda u_{j-1}^n + k\gamma(u_j^n - (u_j^n)^3)
\end{aligned}$$

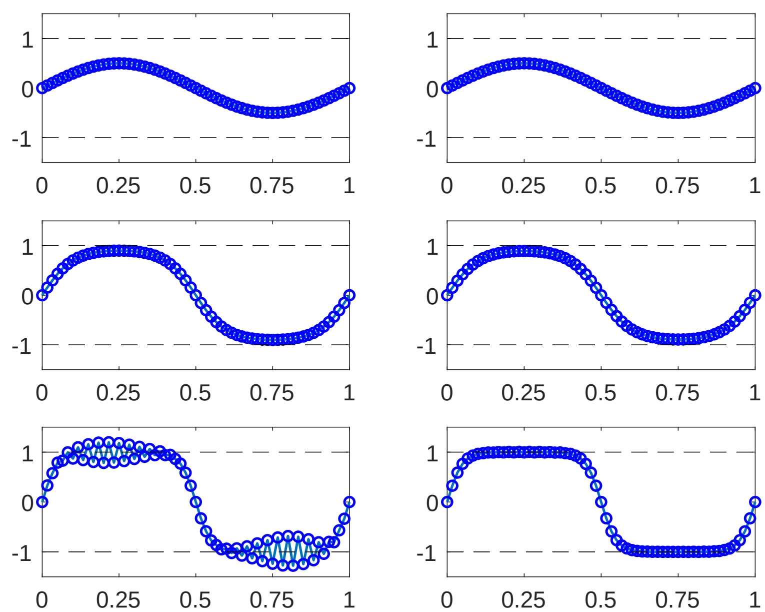

Figure 9: Allen-Cahn Equation with Diffusion, left side time step $k = 0.000165$ is unstable, while right side $k = 0.00016$ is stable. Time steps $0, 10, 80$ are shown.

4 Future Work

4.1 Solution of Diffusion Equation by the Heat Kernel

There is another way to solve the diffusion equation with the heat kernel, defined by

$$f(x,t) = \frac{1}{\sqrt{4\pi t}}\, e^{-(x-\mu)^2/4t}, \tag{35}$$

where $f(x,t)$ is the temperature induced by a point heat source at location x and time $t > 0$, but this is left to future work. Note however that $f(x,t)$ is the pdf of a normally distributed random variable with mean μ and variance $2t$.

4.2 Cahn-Hilliard Equation

The Cahn-Hilliard equation [3] is closely related to the Allen-Cahn equation, but that is left for future work.

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