

STABILITY OF EQUILIBRIA IN ONE DIMENSION FOR DIBLOCK COPOLYMER EQUATION

Olga Stulov

Department of Mathematics, Department of Electrical and Computer Engineering
State University of New York at New Paltz

Project Mentor(s): Dr. Evelyn Sander and Dr. Thomas Wanner

Abstract

This paper demonstrates the use of the mathematical model for diblock-copolymer equilibria to obtain the solutions of the homogeneous and inhomogeneous equilibria. In order to determine the stability of the system in the time varying solution, the eigenvalues and eigenfunctions were found. The positive eigenvalues represented the unstable directions, thus allowing to study the behavior of the diblock copolymers near the equilibria. While the homogeneous equilibrium solution was found analytically, the solution of the inhomogeneous equilibrium had to be solved for numerically. The various sets of the solutions of the linearized model were found by means of software AUTO. These sets were then embedded in MATLAB to solve for the eigenvalues and eigenfunctions of the system. In addition, the latter were plotted for the interpretation of the results. For simplicity the model was studied in one dimension.

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1 Introduction

Block copolymers is the class of soft materials produced by combining two or more chemically distinct polymer blocks (a linear series of identical monomers), which may be thermodynamically incompatible. The structure developed by segregation of these blocks can allot block copolymers many useful and desirable properties. These unique properties, and as a result the applications, of block copolymer materials depend on their mesoscopic self-assembly in the solid and molten states.

The material of our interest is the AB diblock copolymer that consists of a long sequence of type A monomers covalently bonded to a chain of type B monomers. Variations in the molecular topology formed during different chemical coupling strategies lead to distinct changes in morphology and thus material properties, as it was mentioned above. This implies that the material with special properties can be designed for, which is of great technological importance [1].

There are three experimentally controllable factors that govern the phase behavior of copolymer melts: χ , the A-B segment-segment (Flory-Huggins) interaction parameter measuring the incompatibility of the two monomers; $N = N_A + N_B$, the index of polymerization measuring the number of monomers per macromolecule; and $f = N_A/N$, the composition, i.e. overall volume fraction of the A component [4, 5, 6].

In order to avoid practical difficulties in copolymer synthesis, the patterns of diblock copolymers can be studied through the equilibrium equation for the diblock-copolymer model, which is known as

$$-(u_{xx} + \lambda(u - u^3))_{xx} + \sigma(u - \mu) = 0, \quad (1)$$

where u represents the macroscopic relative monomer density, or in other words the difference between relative density of the A monomer and that of the B. Studied on $\Omega = (0, 1)$, the above equation is subject to Neumann boundary conditions

$$u_x(0) = u_{xxx}(0) = u_x(1) = u_{xxx}(1) = 0 \quad (2)$$

and the integral constraint

$$\int_0^1 u(x) dx = \mu. \quad (3)$$

Since the time was removed from (1), the matter concerns the integral constraint and not the conservation of mass. In addition, due to the time limit the model was contemplated in one dimension, rather than 2 or 3D. However, once one has a thorough comprehension of the process occurring in 1D, he/she can move to the higher dimensions.

Now let us take a closer look at the diblock-copolymer equation. It is a fourth-order nonlinear partial differential equation. All three parameters in the equation (1) (λ , σ , and μ) correlate to the fundamental material parameters (χ , N , and f). Before providing these relationships that connect the physical factors to the parameters used in the mathematical model, the definition of λ , σ , and μ should be presented:

- μ - mass average
- σ - constant mobility
- $\lambda = \frac{1}{\varepsilon^2}$, where ε is the interfacial thickness at the A and B monomer intersections.

The above quantities are related to the dimensionless parameters χ , N , and f through the following expressions:

$$\lambda \sim \frac{f(1-f)\chi}{l^2}, \quad \sigma \sim \frac{1}{f^2(1-f)^2 l^2 \chi N^2}, \quad \mu = 2f - 1,$$

where l is the Kuhn statistical length (in this case, the average monomer space size) [5, 6].

Using (1) homogeneous and inhomogeneous equilibria solutions of the diblock-copolymer equilibria were explored, thus providing us with an understanding to a certain extent of the phase behavior of the diblock copolymers in one dimension at the equilibrium as well near the equilibrium of the system. The description of thereof is listed below in more details.

2 Background and Research Methods

2.1 Homogeneous Equilibrium Solution

Physically homogeneous equilibrium is the moment in which the substances involved are in the same phase of matter. Meanwhile, inhomogeneous equilibrium is a mixture between several phases, which are demonstrated in Figure 1. The depicted structures are formed by block copolymers, where the B blocks are in blue and the A blocks are in red, respectively.

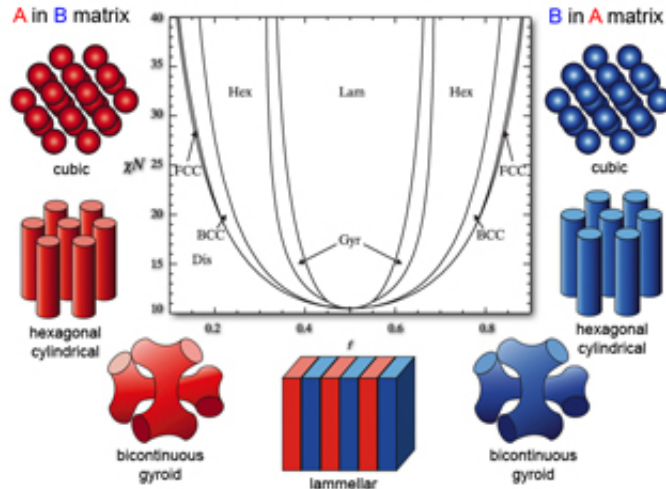


Figure 1: Phase Diagram for AB Diblock Copolymers [2].

Since there is a homogeneous equilibrium corresponding to each integral constraint, (3) allows location of those phases. Mathematically homogeneous equilibrium implies no variation in space, which occurs when $u(x) \equiv \mu$ for (1). In other words u solves the diblock-copolymer equation and is independent of x . Once the location of the homogeneous equilibrium was found, it was desirable to solve for the eigenvalues and eigenfunctions of the system, which determine the stability in the time varying solution. Thus, the eigenvalues were necessary in order to study the behavior of the diblock copolymers near the point of equilibrium [3]. However, since (1) is a nonlinear differential equation, it had to be linearized in the direction of u first, so that the local stability of an equilibrium point of a system could be assessed.

The only nonlinear term in (1) is $f(u) = (u^3)_{xx}$. In order to linearize it recall the definition of the directional derivative:

$$\nabla f_u(v) = \lim_{h \rightarrow 0} \frac{f(u + hv) - f(u)}{h} \quad (4)$$

Substituting (4) into the nonlinearity of the diblock-copolymer equation gives the following:

$$\begin{aligned} \nabla f_u(v) &= \lim_{h \rightarrow 0} \frac{((u + hv)^3)_{xx} - (u^3)_{xx}}{h} \\ &= \lim_{h \rightarrow 0} (3u^2v + 3uhv^2 + h^2v^3)_{xx} \\ &= (3u^2v)_{xx} \end{aligned} \quad (5)$$

Using the result from (5), the linearization of the right hand side at the equilibrium value u of the diblock-copolymer equation can be written in the form of

$$-v_{xxxx} - \lambda v_{xx} + \lambda(3u^2v)_{xx} + \sigma v.$$

Thus, solving for stability results in the following eigenvalue problem

$$-v_{xxxx} - \lambda v_{xx} + \lambda(3u^2v)_{xx} + \sigma v = \Lambda v, \quad (6)$$

where Λ represents the eigenvalues and v is the eigenfunction of the system. The above system has the homogeneous Neumann boundary conditions given as

$$v_x(0) = v_{xxx}(0) = v_x(1) = v_{xxx}(1) = 0$$

and the mass constraint of

$$\int_0^1 v(x) dx = 0.^1$$

Rearranging some of the terms in (6) evaluated at the homogeneous equilibrium ($u \equiv \mu$) results in the following equation:

$$-\Delta(\Delta v) - \lambda \Delta v(1 - 3\mu^2) + (\sigma - \Lambda)v = 0 \quad (7)$$

Next one can solve for the eigenvalues and eigenfunctions of the Laplacian subject to homogeneous Neumann boundary conditions for $\Omega = (0, L) \subset \mathbb{R}$:

$$\varphi_k(x) = \cos \frac{(k-1)\pi x}{L} \quad \text{and} \quad \kappa_k = \frac{(k-1)^2\pi^2}{L^2}, \quad \text{for } k \in \mathbb{N} \quad (8)$$

Applying (8) to (7) furnishes

$$\begin{aligned} v_k(x) &= \cos((k-1)\pi x), \quad \lambda = (k-1)^2\pi^2 \quad \text{for } k \in \mathbb{N} \\ -\frac{d^4}{dx^4}(\cos((k-1)\pi x)) - \lambda \frac{d^2}{dx^2}(\cos((k-1)\pi x)(1 - 3\mu^2)) + (\sigma - \Lambda) \cos((k-1)\pi x) &= 0 \end{aligned} \quad (9)$$

Taking the corresponding derivatives of certain terms in the above equation has the following outcome:

$$-\pi^4(k-1)^4 \cos((k-1)\pi x) + \lambda\pi^2(k-1)^2 \cos((k-1)\pi x)(1 - 3\mu^2) + (\sigma - \Lambda) \cos((k-1)\pi x) = 0$$

¹The only way to keep the mass same as before (3) is by making it zero.

$$\cos((k-1)\pi x)(-\pi^4(k-1)^4 + \lambda\pi^2(k-1)^2(1-3\mu^2) + \sigma - \Lambda) = 0 \quad (10)$$

The latter gives the relationship for Λ such as

$$\Lambda = -\pi^4(k-1)^4 + \lambda\pi^2(k-1)^2(1-3\mu^2) + \sigma \quad (11)$$

The zeros of this equation is the set of the solutions in the form of the smooth curves that may intersect each other. These points of intersections are known as bifurcation points. (11) can be recognized as a quadratic equation, the roots of which can be found by the following:

$$k = \sqrt{\frac{\lambda(1-3\mu^2) \pm \sqrt{[\lambda(1-3\mu^2)]^2 + 4\sigma}}{2\pi^2}} + 1 \quad (12)$$

where k indexes the mode numbers (eigenvalues). One should notice that there is only one (positive) set of solutions for k provided in (12). It is reasonable in this case, since the eigenvalues and eigenfunctions of the homogeneous equilibrium solution are symmetrical. As a result there is no need to show the negative set of the solutions for k .

When plotting indexes (k) versus eigenvalues (Λ), the obtained graph will intersect the k -axis at the two points determined by (12). The positive eigenvalues represent the unstable directions, i.e. the behavior of the diblock copolymers near the homogeneous equilibrium.

Consider the case when both $\mu = 0$ and $\sigma = 0$. Then (12) reduces to:

$$k = \sqrt{\frac{\lambda \pm \lambda}{2\pi^2}} + 1$$

which result in the following bifurcation points:

$$k = 1, k = \frac{\sqrt{\lambda}}{\pi} + 1 \quad \text{such that} \quad \lambda = (k-1)^2\pi^2$$

The plots of the eigenvalues for the homogeneous equilibrium solution for two different λ values, 500 and 1000, generated in MATLAB are displayed in Figures 2 and 3, respectively. One should notice that as the value of λ increases, the number of unstable eigenvalues grows as well. That is, homogeneous state becomes unstable as λ increases.

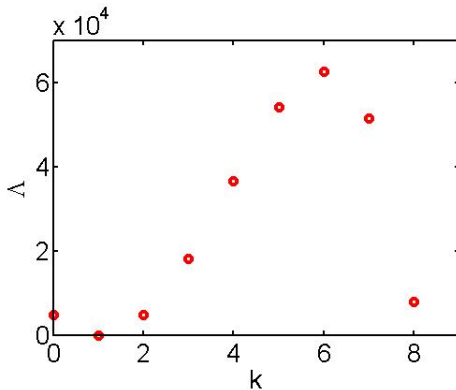


Figure 2: $\lambda = 500$, $\mu = 0$, $\sigma = 0$.

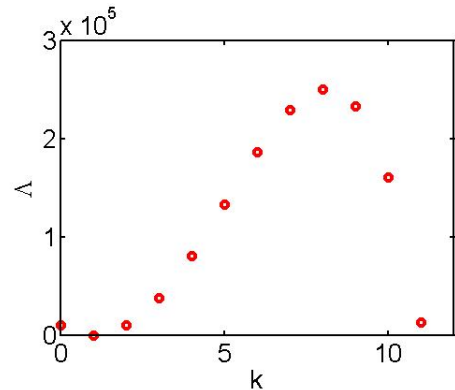


Figure 3: $\lambda = 1000$, $\mu = 0$, $\sigma = 0$.

Once the homogeneous equilibrium solution of the diblock-copolymer equation was obtained, the next goal was to find the solution of the inhomogeneous equilibrium of the system.

2.2 Numerical Scheme

As it was previously shown in (6), the linearized Diblock-Copolymer equation is of the following form:

$$-v_{xxxx} - \lambda v_{xx} + \lambda(3u^2v)_{xx} + \sigma v = \Lambda v \quad (13)$$

with the homogeneous Neumann boundary conditions

$$v_x(0) = v_{xxx}(0) = v_x(1) = v_{xxx}(1) = 0 \quad (14)$$

and the integral constraint

$$\int_0^1 v(x) dx = 0. \quad (15)$$

The only difference now is that u is no longer constant as it was for the homogeneous equilibrium solution, but varies with respect to x . This means that the solution has to be solved for numerically rather than analytically.

The use of numerical methods implies the necessity to express all of the terms in the equation (13) in a matrix form. For a start, v can be rewritten as a series with respect to the eigenfunctions φ_k such that there exist numbers $a_k \in \mathbb{R}$ satisfying the expression listed below

$$v_N(x) = 0 + \sum_{k=1}^N a_k \varphi_{k+1}(x), \quad (16)$$

where the first term of zero indicates the mass constraint. Recall that a solution approximation of a nonlinear elliptic problem

$$\Delta u + f(u) = 0 \quad \text{in } \Omega \subset \mathbb{R}^d \quad (17)$$

can be found by letting κ_k and φ_k denote the eigenvalues and eigenfunctions of the Laplacian subject to the corresponding boundary conditions

$$\Delta \varphi_k + \kappa_k \varphi_k = 0 \quad \text{in } \Omega, \quad \text{for all } \kappa \in \mathbb{N}. \quad (18)$$

The only term in (13) that cannot be expressed by applying (16) and (18) alone is $(3u^2v)_{xx}$. However, from linear algebra one knows that any linear map $f : \mathbf{z} \rightarrow \mathbf{w}$ between finite-dimensional vector spaces can be described by a matrix $\mathbf{A} = (a_{ij})$ such that

$$f(\mathbf{z}_j) = \sum_{i=1}^M a_{i,j} \mathbf{w}_i \quad j = 1, \dots, N \quad (19)$$

where $\mathbf{z} = (z_1, z_2, \dots, z_N)$ and $\mathbf{w} = (w_1, w_2, \dots, w_M)$. That is, the column j of \mathbf{A} expresses the image of \mathbf{z}_j in terms of the basis vectors \mathbf{w}_i . Applying (19) to the term of our interest gives the following

$$F(\hat{v}) = \mathbf{A}\hat{v}, \quad F : \mathbb{R}^N \rightarrow \mathbb{R}^N, \quad (20)$$

where

$$\mathbf{A}\hat{v} = \widehat{3u^2v}, \quad (21)$$

and $F(e_k) = \mathbf{A}e_k$ is the k^{th} column of the matrix \mathbf{A} . The latter can be found using the Discrete Cosine Transform, following the below procedure:

$$\hat{u}, \hat{v} \xrightarrow{\sqrt{N}idct} u, v \rightarrow 3u^2v \xrightarrow{\frac{dct}{\sqrt{N}}} \widehat{3u^2v}, \quad (22)$$

where N is the number of discretization points, which plays the role of the scaling factor in (22), when converting from a frequency domain to a time domain and vice versa.

Recall from (8) the eigenfunctions and eigenvalues of the Laplacian subject to homogeneous Neumann boundary conditions

$$\varphi_{k+1}(x) = \cos(k\pi x), \quad \kappa_{k+1} = k^2\pi^2 \quad \text{for } k \in \mathbb{N}, \quad (23)$$

which furnishes $\mathbf{v} = (1, 0, \dots, 0)^t$. The method for finding a solution to the function $u(x)$ will be shown further down in the paper. For now assume that it is already given, thus enabling us to solve for the matrix \mathbf{A} employing (22):

$$\mathbf{A} = 3Ndct\{(idct(u))^2 \cdot (idct(v))\},^2 \quad (24)$$

where dct stands for Discrete Cosine Transform and $idct$ implies Inverse Discrete Cosine Transform, respectively. As a result, (13) can be rewritten as

$$-v_{xxxx} - \lambda v_{xx} + \lambda(\mathbf{A}v)_{xx} + \sigma v = \Lambda v \quad (25)$$

Finally applying (16) and (18) to the above equation produces the following eigenvalue problem:

$$\Lambda v = (-\kappa_{k+1}^2 + \lambda\kappa_{k+1} - \lambda\mathbf{A}\kappa_{k+1} + \sigma)v \quad (26)$$

where v is the eigenfunction that governs the solution of the inhomogeneous solution for the Diblock-Copolymer equation, and Λ represents the eigenvalues.

This numerical scheme for the inhomogeneous equilibrium can be verified using MATLAB by defining u in (13) as a constant (determined by a mass constraint), thus testing it on the homogeneous equilibrium solution, which was already found in the previous subsection. Figure 4 demonstrates the plot of the eigenfunction v for the homogeneous equilibrium solution.

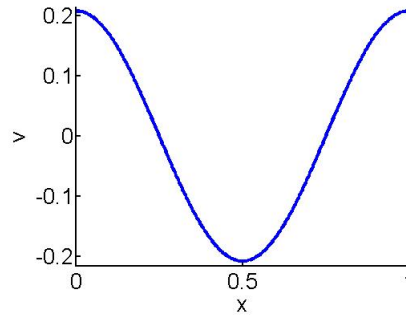


Figure 4: Eigenfunction of Linearization at Homogeneous Equilibrium Solution Obtained Numerically.

From (23) the reader knows that the eigenfunction $v_{k+1}(x) = \cos(k\pi x)$. Clearly the above graph is the cosine function, thus assuring that the developed numerical scheme is correct.

² $(idct(u))^2 \cdot (idct(v))$ implies a component wise product of the entries and not a dot product

3 Results and Discussion

3.1 Inhomogeneous Equilibrium Solution

As it was mentioned in Section 2.2 in case of the inhomogeneous equilibrium the function u varies with respect to x . One way to find solutions to $u(x)$ is by applying the arclength continuation method, which computes a single continuation curve within the zero set of a function. However, all continuation curves that are connected by bifurcation points, which occur at $\lambda = k^2\pi^2$ for $k \in \mathbb{N}$ according to (23), can be computed by a software package AUTO.

Figure 5 depicts the inhomogeneous equilibrium solution with λ varying, where each curve corresponds to a fixed λ value, obtained in AUTO with the following parameter settings:

- $\sigma = 1000$,
- $\mu = -0.5$,
- $\lambda = 2000$.

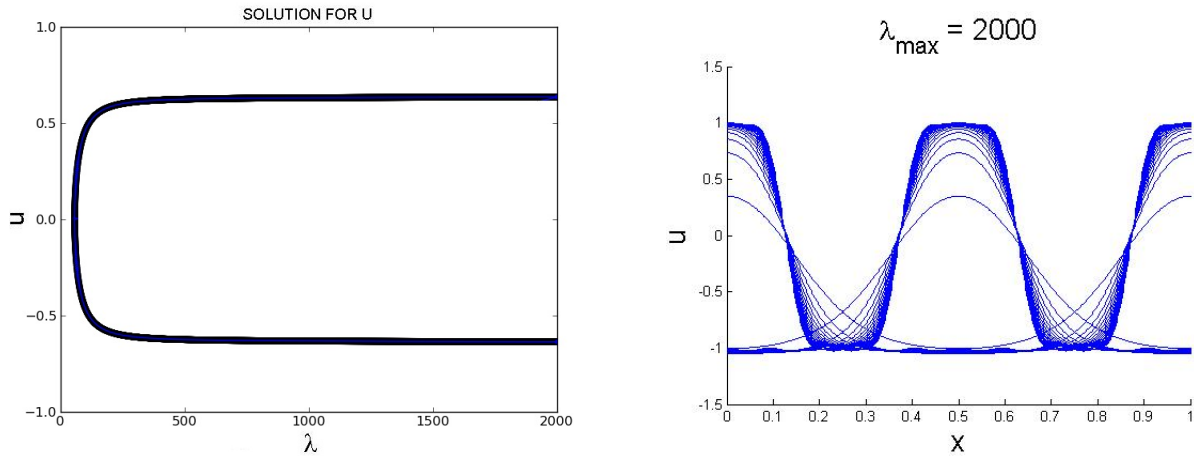


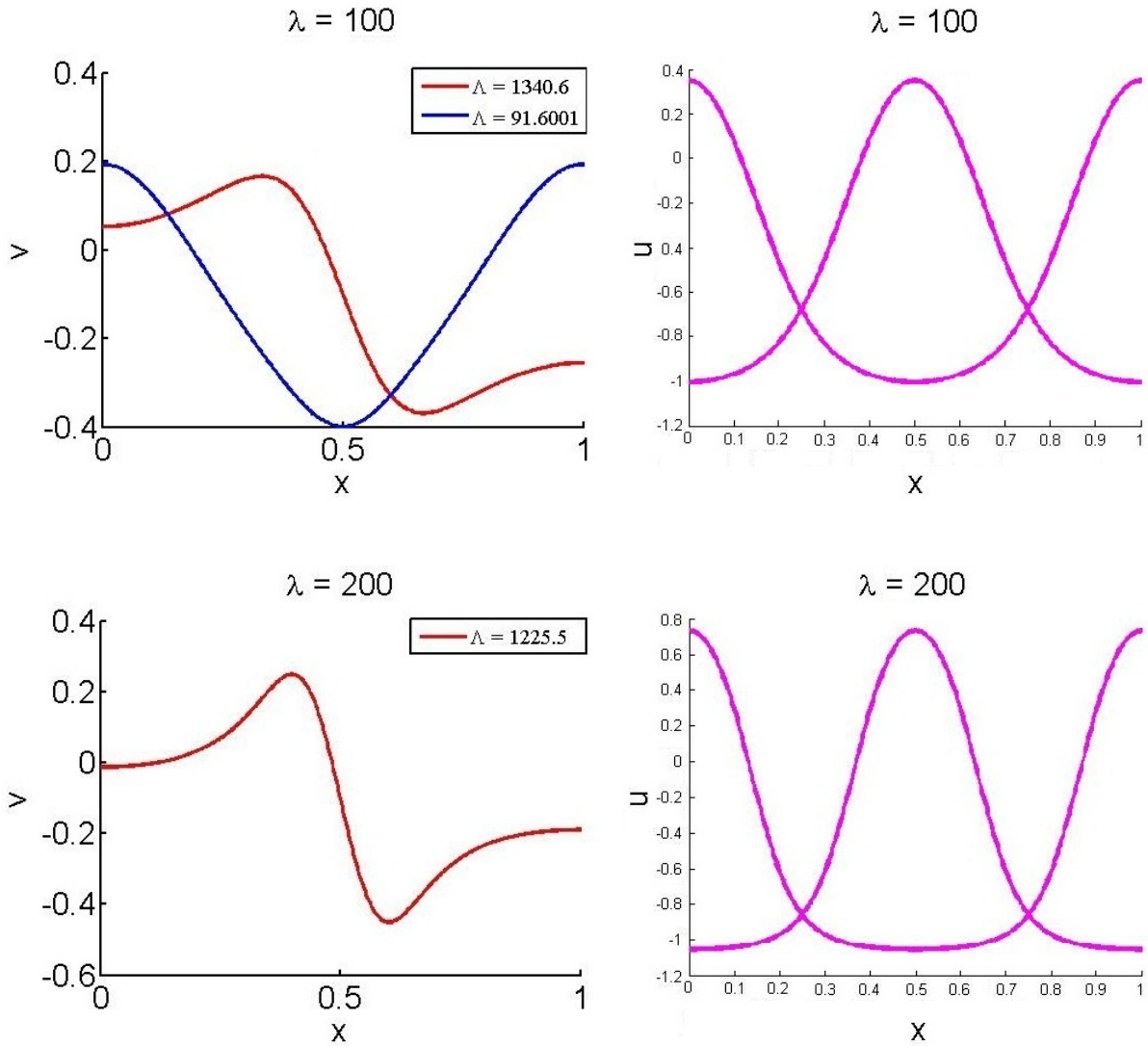
Figure 5: Bifurcation Diagram for Inhomogeneous Equilibrium (on the left). Set of solutions for $u(x)$ (on the right).

Using the Fourier coefficients for $u(x)$ generated in software AUTO, the eigenvalues (Λ) and eigenfunctions (v) can be found by MATLAB solver as the parameter λ varies. The latter is necessary in order to follow the change in the number of positive eigenvalues. As it was discussed earlier in Section 2.1, the positive eigenvalues correspond to the unstable directions. Thus, slicing the solution of $u(x)$ computed by AUTO at different λ values and solving for the eigenvalues and eigenfunctions enables us to analyze the behavior of the diblock copolymers near the inhomogeneous equilibrium.

For the solution provided in Figure 5 the first λ value was chosen to be 100 with the equivalent step size. Table 1 shows the number of unstable directions with the variation in λ . A change in the number of unstable directions implies that a bifurcation point occurred on the continuation curve (refer to the left side of Figure 5). Thus from the data provided in Table 1, it is clear that the bifurcation points appear somewhere between $\lambda = 100$ and $\lambda = 200$, between $\lambda = 400$ and $\lambda = 500$, between $\lambda = 600$ and $\lambda = 700$, and lastly between $\lambda = 1800$ and $\lambda = 1900$. The graphs of positive eigenfunctions with the corresponding eigenvalues at those λ values where the number of unstable directions is different from the previous time can be found in Figure 6.

λ	# of $\Lambda > 0$
100	2
200	1
\vdots	\vdots
400	1
500	2
600	2
700	3
\vdots	\vdots
1800	3
1900	4
2000	4

Table 1: Relationship between variation in λ and the number of unstable directions.



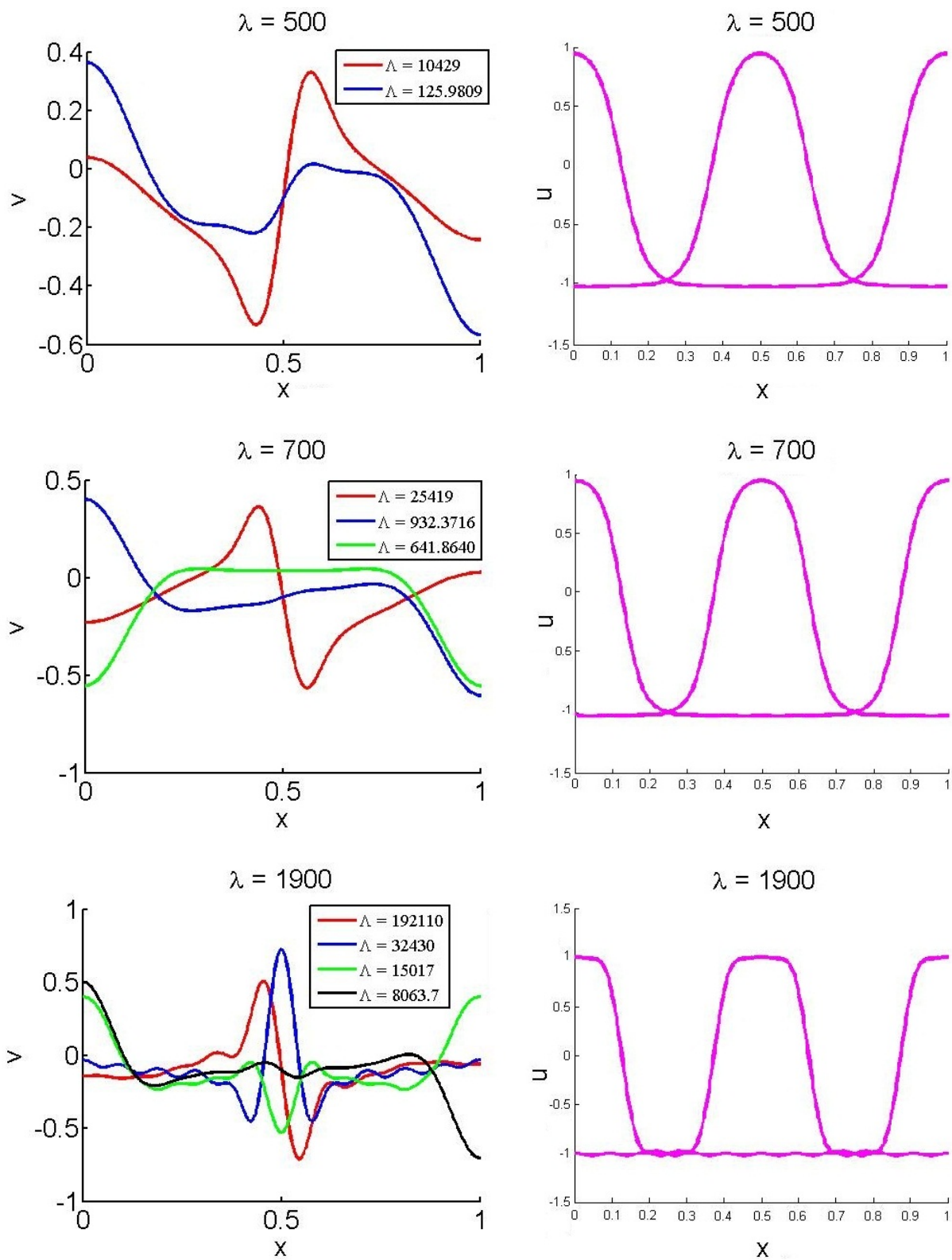


Figure 6: Positive Eigenfunctions of Linearized Diblock-Copolymer Equation at Inhomogeneous Equilibrium Solution for Different λ Values (on the left). Corresponding Solutions for $u(x)$ (on the right).

The right side plots of Figure 6 demonstrates the solutions for $u(x)$ at the specific λ values. Clearly there are two solutions for each value of λ parameter coinciding with the solutions of the upper and lower parts of the bifurcation diagram (refer to Figure 5 on the left). It should also be noticed that these two curves are not symmetrical. However, they are symmetrical to each other once we get close enough to the homogeneous equilibrium. In addition, the reader should observe the shape of the curves. One of the solutions is definitely flatter than the other. This is caused by the mass constraint. Recall that μ was set to -0.5 . The mass pushes down meaning that when the solution is a little below -1 , the curve falls into the flat state. At the same time, the other solution is not near 1 and as a result is not flat.

As for the plots of positive eigenfunctions, they are symmetrical about zero because of the mass constraint (15). The largest changes in eigenfunctions happen at the interfaces of the solutions. Based on the data provided in Table 1 it can be concluded that in general as the value of λ parameter increased, the number of unstable directions went up as well. However, for the solution shown above the number of positive eigenvalues diminished from at $\lambda = 200$ to $\lambda = 500$, which probably implies that there is a bifurcation going in the other direction. Thus, the solution for $\lambda = 200$ is more stable than the one for $\lambda = 100$. Meanwhile, the solution for $\lambda = 1900$ is highly unstable. Moreover, the latter has high frequency of squiggles, which is a clear indication that we are not using enough dimensions.³ Obviously, increasing the number of modes will fix this issue.

The reader has probably already noticed that the graphs of the eigenfunctions in the region with the same number of unstable directions are not shown in Figure 6. The reason for it is because the shapes of those plots are similar to each other. For instance, Figure 7 displays the graphs of positive eigenfunctions for the λ values between 200 and 400 including, where according to Table 1 there is only one unstable direction.

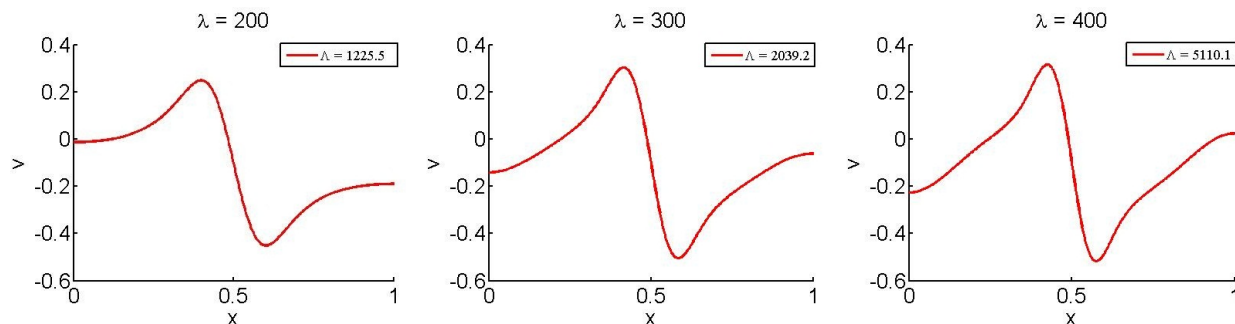


Figure 7: Positive Eigenfunctions for $\lambda = 200, \dots, 400$

It is obvious from the above plots that the direction varies smoothly as a function of the parameter. This effect can be explained by the unstable manifold theorem. The latter states that for the equilibria with smooth variation of the parameter the unstable manifold is going to change smoothly as well. As expected same occurs for the graphs of eigenfunctions when λ values extend from 700 to 1800.

4 Conclusion and Future Work

In this paper thoroughly demonstrates the solution for stability of the diblock-copolymer equilibria. However, the system was analyzed time independently, which means that eventually it would be

³For this problem we chose 20 dimensions.

useful to find the time varying solution. Coming up with nice parameter values that yet have to be determined a set of equilibria can be found using the method provided here. This will allow to do time variation between equilibria, which will help understanding how they match up.

In addition to solving for the time varying solution, the system can be studied in a higher dimensions putting it on a larger scale and thus making it applicable in real life. The latter is definitely the ultimate goal of this research. As it was already discussed in the beginning of this paper, the ability to predict the properties of the diblock copolymers in certain proportions determined by the parameter values without going through the process of complicated synthesis will not just save time and processing issues during the chemical reactions, but also save money and more important will most likely be more eco friendly. Thus, the significance of capability to simulate the inhomogeneous equilibria (structures of phases) in three dimensions is obvious.

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