Implementation of Alternating Directing Scheme in CDS Computer Simulator for Diblock Copolymers

Sohail Ahmed Memon[†], Nazar Hussain Phulpoto[††], Imtiaz Ali Halepoto[†††], Adnan Manzoor[††††], Muhammad Sulleman Memon[†††††]

[†]Department of Mathematics, SALU Kharipur, Pakistan
[††,††††] Department of Information Technology, QUEST Nawabshah, Pakistan
[†††,†††††] Department of Computer Systems Engineering, QUEST Nawabshah, Pakistan

Summary
The Cell Dynamics Simulation (CDS) technique is considered computationally very efficient and is usually used to investigate large systems, e.g., block copolymers. The CDS method is mainly used for solving the partial differential equations (PDEs). It is recommened by many researchers due to its accuracy and efficiency as compared to the simulators of the same line. This paper provides a detailed study of CDS based on diblock copolymers. It is implemented in Alternating Direction Implicit (ADI) finite difference (FD) method. This FD method is unconditionally stable and second-order accurate compared to conventional Forward Euler's method, which is fast but not very stable.

Key words:
CDS; block copolymers; Lemallar Morphology; Alternating Direction Implicit method; Finite Difference method

1. Introduction

A long chain of molecules caused as a result of reaction is called polymers. These molecules are called monomers and a formation of polymers comprised of two or more different chemical blocks is called block copolymer [1]. Thee chemical formation in melts, blends or solutions are basically polymer based structures in different ranges. The size of these structures varies from nanometer to millimetre scales [2, 3]. There are many applications of block copolymers in variety of fields such as in soft nanotechnology where templates are created for nanoelectronics and further the block copolymers are applicable for catalyst materials, electric fields, mechanical flow fields, nanoparticle synthesis, separation nonporous membranes, temperature gradients, photonic crystals and others [4]-[8].

Moreover, highly ordered and defect-free electronic devices, e.g., fuel cells, batteries and optoelectronics, all require the use of block copolymers in the product development. The block copolymers are also widely used by employing polymer nano-domains in structural materials such as thin films, high density hard drives and patterned magnetic drives [9], [10]. Other than structural materials, the use of block copolymers is also incorporated in commercial products, engineering, artificial organ technology and drug delivery [10].

To develop applications based on block copolymers, a rigorous process is carried out where mathematical models are formulated and the experiments are interpreted with the help of computer technology. Algorithms are developed with various real time parameters such as temperature, volume, etc. [3]. Firstly, these complex systems are experimented through microscopic observation in laboratories and then with the help of aided advantage of computer models, these are presented in a broader view through simulated images for extensive study and analysis [11].

Due to their existing properties, the block copolymers are studied in various aspects, for example, the phase behavior of the mixtures or blends and other identical monomeric units (homopolyme [11], [12]. The phase separation of polymeric alloys, blends and mixtures tend researchers to carry out broad analysis of associated mechanical, chemical and structural properties which are found in various forms of brass as solid phase from a mixture of copper and zinc, steel and carbon or the addition of other elements to iron.

In this article, the studies are presented for block copolymers in computer simulations via CDS. In block copolymers, the polymer blocks bonded into one macromolecule arrange by own to different nanosturectues. These complex structures are lamellae, hexagonal-packed cylinders, spheres, body-centred cubic structures and gyroid [11].

Some of the famous simulation techniques are, Monte Carlo (MC) [2], [13], Molecular Dynamics (MD) [2], Brownian Dynamics [14], Dissipative Particle Dynamics (DPD) [15], the Self-Consistent Field Theory (SCFT) [16], Lattice Boltzman (LM) method [2], [17], [18] and Time-Dependent Ginzburg-Landau (TDGL) method [2], [19] using CDS. Amongst these the CDS based TDGL is commonly applied due its speed and accuracy for simulations. The CDS method yields convenience to study the evolution in microphase separation in binary blends

Manuscript received April 5, 2018
Manuscript revised April 20, 2018

and diffusive structures of both, the polymers and alloys and [20]-[24] block copolymers [25].
In recent research, the implementation of CDS have been reported in several other mathematical modelling and computational work which comprises the study of chemical reactions in reaction-diffusion systems of the Fisher type and popular dynamics and the study of additional factors which exist during the phase separation in block copolymers such as shear, noise, electric fields and confinement [11]. Further, It has been implemented to understand the phase ordering process and the mesoscopic structure in diblock copolymers at a large extent [26], [27]. To study the pahse-ordering dynamics of unstable phases and to develop models of such system, Shinozaki and Oono [20], [23] employed CDS. They found CDS technique to be an optimal numerical approach for spinodal decomposition in comparison of Monte Carlo simulation technique. To study highly non-linear phase separation process, they replaced a time-consuming analytical formulation based on partial differential equations (PDEs) by using efficient CDS method. Similar studies were carried by Oono [28] by incorporating CDS method. A two-dimensional computer simulation based on CDS was also conducted by Kodma and Doi [29] to analyze the structural changes in lamellae under steady shear flow of block copolymers. Other various applications of CDS, described by Ren and Hamley [19] , are microemulations simulations, cross lined polymer blends, simulation of shear orientation of lamellar phases and kinetics of block copolymers and binary blends of hard particles. In another analysis, the order parameter obtained from mesoscopic dynamics (MesoDyn) technique was found similar to CDS for the study of microphase separated structures of block copolymers [30].

Keeping in view the above-mentioned applications of CDS technique in soft matter systems. The CDS method presents a significant importance to simulate, model and efficiently approximate PDEs involved in soft matter systems, e.g., TDGL and Cahn-Hilliard Cook (CHC) equations.

In this piece of work, the CDS is implemented in a finite difference scheme called Alternating Direction Implicit (ADI) method [31]. The ADI method is configured. The similar parameters are also applied to the Euler method and the results are analyzed.

2. The Details of CDS

In this section, an overview of CDS method is presented where CDS is applied to lamellar forming diblock copolymers for one order parameter system. Initially in CDS method, an order parameter $\psi(t,i)$ is evaluated for time variable t at cell i in discrete lattice. The order parameter of an *A–B* diblock copolymer can be taken as [9]:

$$\psi = \phi_A - \phi_B + (1-2f) \tag{1}$$

where ϕ_A and ϕ_B are local volume fractions of A and B monomers and the volume fraction of A monomer is defined as $f = N_A/(N_A + N_B)$. In a single cell, the evolution of the order parameter is calculated as:

$$\psi(t+1,i) = g(\psi(t,i)) \tag{2}$$

where $g(\psi)$ is for map function. The time evolution of an order parameter in non-conserved order parameter considering diffusive dynamics can be given as:

$$\begin{aligned}\psi(t+1,i) &= g\big(\psi(t,i)\big) + D[\langle\langle\psi(t,i)\rangle\rangle - \psi(t,i)] \\ &= \mathcal{T}[\psi(t,i)]\end{aligned} \tag{3}$$

The above equation (3) is given by addition of chemical potential gradients and diffusive dynamics terms where a positive constant *D* is for phenomenological diffusion. The formation $\langle\langle X\rangle\rangle - X$ shows isotropized discrete Laplacian and $\langle\langle X\rangle\rangle$ in two-dimensional square grid is given by:

$$\langle\langle\psi(t,i)\rangle\rangle = W_1 \sum_{NN} \psi(t,i) + W_2 \sum_{NNN} \psi(t,i) \tag{4}$$

where *Ws*, *NN* and *NNN* stand for weights, nearest neighbors and remote nearest neighbors [9],
The CDS model equations are again considered in a conserved case to avoid the anisotropy (artificats) which arise from the inclusion of surrounding cells. It is essential to maintain isotropy for Laplacian operator in a square lattice. Thus, after the net change in cell design, the order parameter is taken as:

$$\mathcal{T}[\psi(t,i)] - \psi(t,i) \tag{5}$$

and the CDS for the evolution of order parameter becomes:

$$\psi(t+1,i) = \mathcal{T}[\psi(t,i)] - \langle\langle\mathcal{T}[\psi(t,i)] - \psi(t,i)\rangle\rangle. \tag{6}$$

The modified equation with additional term $-B\psi(t,i)$, is:

$$\begin{aligned}\psi(t+1,i) &= \mathcal{T}[\psi(t,i)] \\ &-\langle\langle\mathcal{T}[\psi(t,i)] - \psi(t,i)\rangle\rangle - B\psi(t,i).\end{aligned} \tag{7}$$

Equation (6) is basically the finite difference of the Cahn-Hilliard-Cook:

$$\frac{\partial\psi}{\partial t} = \mathrm{K}\nabla^2\left[\frac{\delta F[\psi]}{\delta\psi}\right], \tag{8}$$

where K represents phenomenological mobility constant which is always kept as unity and $F[\psi]$ is showing free energy functional [11]. After algebraic manipulation, Equation (6) and (3) together can be written as:

$$\begin{aligned}\mathcal{T}(t+1,i) &= g\big(\psi(t,i)\big) - B\psi(t,i) \\ &+D[\langle\langle\psi(t,i\rangle\rangle + \psi(t,i)]\end{aligned} \tag{9}$$

where the map function is defined as [11] :

$$g(\psi) = [1 + \tau - A(1-2f)^2]\psi \\ -v(1-2f)\psi^2 - u\psi. \qquad (10)$$

where τ denotes temperature.

3. Implementation of ADI

The implementation of finite difference scheme ADI based on CDS method is given in this section. The partial differential equations in CDS [32]. In first instance, the equation (9) can be written as:

$$\frac{\delta\psi}{\delta t} = -\{\nabla^2(g(\psi) + D\nabla^2\psi) + B\psi\}. \qquad (11)$$

In equation (11), the order parameter ψ is differentiated with respect to time t and ∇^2 is the Laplacian on a function of free energy. It is non–linear and non-homogeneous partial differential equation containing fourth–order *bi*–Laplacian or biharmonic operator ∇^4. After simplifying algebraically, the equation (11) can be written as:

$$\frac{\delta\psi}{\delta t} = -\nabla^2 g(\psi) - \nabla^2(D\nabla^2\psi) - B\psi. \qquad (12)$$

$$\psi_{j,k}^{n+1} = \underbrace{\frac{\psi_{j,k}^n - \Delta t D\nabla^2(\nabla^2)\psi_{j,k}^n - \Delta t B\psi_{j,k}^n}{part\ 1}}\ \underbrace{\frac{-\Delta t\nabla^2 g(\psi_{j,k}^n)}{part2}} \qquad (13)$$

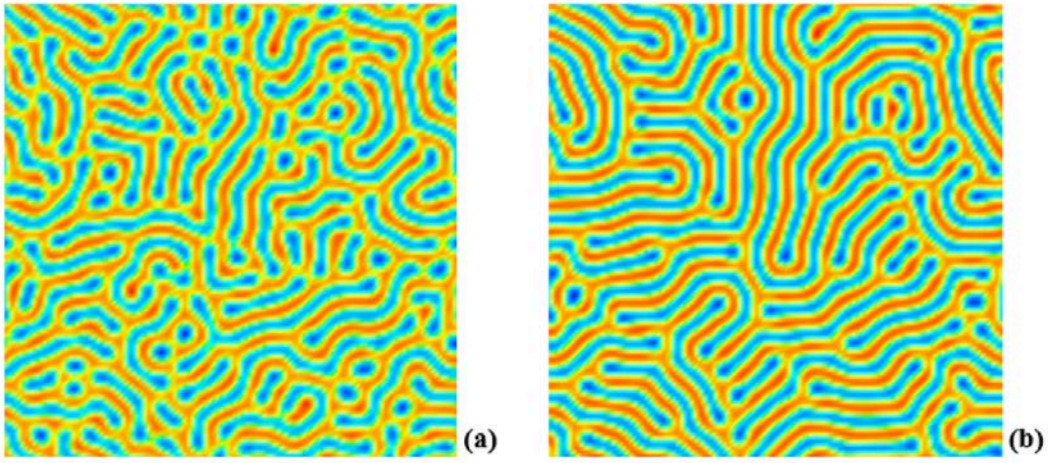

Figure 1: Explicit forward Euler method based on 5–point formula (Laplacian scheme A (D2Q5)) using periodic boundary conditions where images (a) and (b) are at 1000th and 100000th time steps respectively.

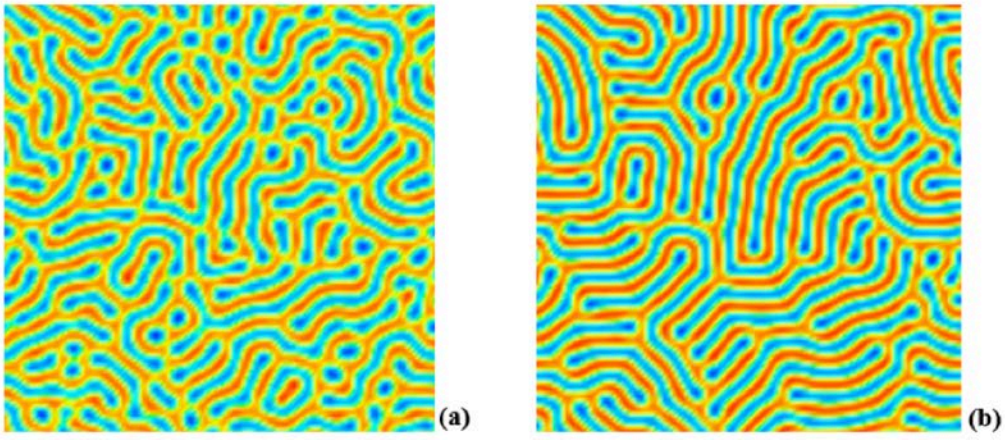

Figure 2: Generalized ADI method based on 5–point formula (Laplacian scheme A (D2Q5)) using periodic boundary conditions where images (a) and (b) are at 1000th and 100000th time steps respectively.

For Laplacian operator ∇^2 in part 2 of the equation (13), the five–point stencil formula is used for approximation of the map function.

The splitting operators are employed for finite differencing of part 1 of the equation (13), the operators $\delta^4/\delta x^4(\psi_{j,k})$ and $\delta^4/\delta y^4(\psi_{j,k})$ in thirteen-point formula are denoted by $\Delta_4^{(x)}$ and $\Delta_4^{(y)}$ respectively. The ADI introduced by Doughlas and Gun [33] for mixed derivatives are applied. The mixed derivatives occur in biharmonic operator.

3.1 Generalized ADI method

In this section, the finite difference approximation for CDS based on ADI method [34] is presented from the method given by Witelski *et al.* [35], it is given below:

$$L_x w = \psi_{j,k}^n - \Delta t D \nabla^4 \psi_{j,k}^n - \Delta t B \psi_{j,k}^n - \Delta t \nabla^2 g\left(\psi_{j,k}^n\right),$$
$$L_y v = w, \qquad \psi_{j,k}^{n+1} = \psi_{j,k}^n + v \tag{14}$$

where:

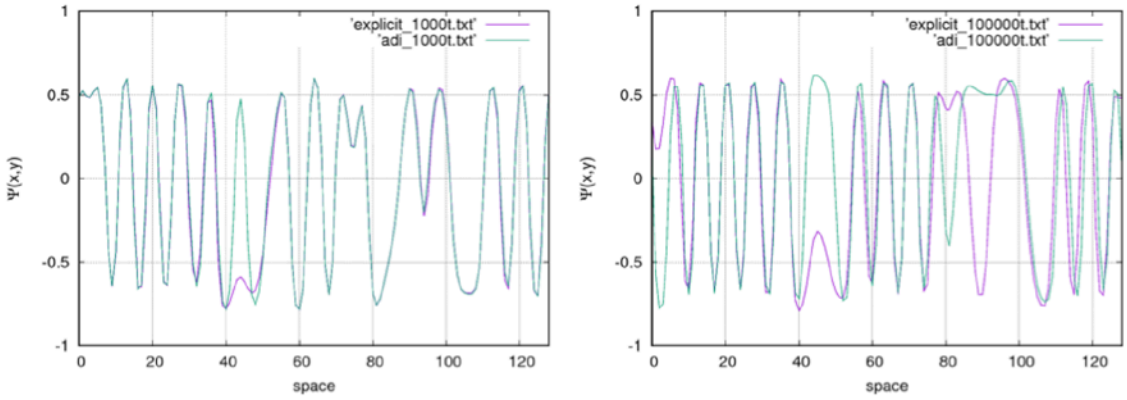

Figure 3: The numerical values of order parameter $\psi(x,y)$ are plotted against the space (0 – 128) for 1000th and 100000th time steps in images (a) and (b) respectively. Numerical values of $\psi(x,y)$ are shown for the forward Euler and generalized ADI methods. The numerical values plotted here were obtained from the simulations shown in Figure 1 and 2.

$$L_x = \left(I + \frac{\Delta tIB}{2} + \frac{\Delta tD}{2}\Delta_4^{(x)}\right)$$
$$L_y = \left(I + \frac{\Delta tIB}{2} + \frac{\Delta tD}{2}\Delta_4^{(y)}\right) \tag{15}$$

The values of the vectors w and v in equation (14) are calculated in a penta-diagonal matrix M by employing periodic boundary conditions. The definition of L_x and L_y in equation (15) in computer algorithm is $L_x = L_y = M$. M is given by:

$$M = \begin{pmatrix} b_1 & c_1 & d_1 & 0 & 0 & f_1 \\ a_1 & b_2 & c_2 & d_2 & 0 & 0 \\ e_1 & a_2 & b_3 & c_3 & d_3 & 0 \\ 0 & e_2 & a_3 & b_4 & c_4 & d_4 \\ 0 & 0 & e_3 & a_4 & b_5 & c_5 \\ f_2 & 0 & 0 & e_4 & a_5 & b_6 \end{pmatrix}$$

Equation (14) is manipulated in three steps. At first step it is approximated for its explicit part on the right hand side where size N vector is evaluated from grid size of $N \times N$. It is clarified that non-homogeneous part of CDS equation (12) is also combined there in the first step and vector w is approximated in x-direction implicitly. At second step, the vector v is approximated in y-direction implicitly from vector w and the last step calculates new values for an order parameter ψ as usual. The LU decomposition technique has been employed to settle down matrix operations for various system of equations.

The results are shown in Figure 1 and Figure 2 for forward Euler's method and ADI method respectively. The images are shown for the simulation images at 1000th and 100000th time steps from both methods.

The details of parameters used in simulations are given in Table 1. For both methods, the simulations were run for 100000 time steps using periodic boundary conditions and the initial values for an order parameter were set as $\psi = \pm 0.3$.

Table 1: Parameters and Value as [9]

Parameter Name	τ	f	u	V	B	D	A
Value	0.36	0.48	0.38	2.3	0.02	0.7	1.5

Different stages of evolution are shown in Figure 1 and Figure 2. The results were successfully obtained from newly implemented generalized ADI method, which are

shown in Figure 2. Figure 3 represents a clear comparison can be observed between two methods. Suitable time steps are chosen and are shown in that figure where Figure 3 (a) depicts curves of for 1000^{th} time step and Figure 3 (b) depicts curves of values for 100000^{th} time step. Two line curves of two different colors in each Figure can be seen. The order parameter values on the vertical axis have been maped against the horizontal axis which shows total grid size. In Figure 3 (a), Only a little difference can be observed between 40 and 50 which is negligible. Otherwise, overall tendency of numerical values seems to be isotropic. In Figure 3 (b), difference of the numerical values exists between 40 - 60 and between 80 - 100 on the horizontal axis and the overall tendency is likewise. In simulations, there can be observed no obvious difference in microphase separation process.

4. Conclusions

The Implementation of ADI method has been carried out for the CDS method for A-B forming system of diblock copolymers. Since long time, the CDS model equations were Euler discretized due to which time step stability of was questionable. The forward Euler method is not adequately stable, however when compared it is faster method. On the other hand, CDS is a powerful method and to make it stronger, a new method of discretization, so called ADI, was implemented and successful results were obtained. The choice of parameters for simulations in both methods were taken same to observe the performance. Different time intervals values were also used to examine the stability of the newly adopted method. The forward Euler method does not allow flexibility for using different time interval values and is first-order accurate. The implementation of ADI for CDS techniques has broken all the limitations and has made the CDS more flexible in terms of time stability, speed and accuracy.

References

[1] A. N. Singh et al, "Block Copolymer Nanostructures and Their Applications: A Review," Polym. Plast. Technol. Eng., vol. 54, (10), pp. 1077-1095, 2015.

[2] S. C. Glotzer and W. Paul, "Molecular and mesoscale simulation methods for polymer materials," Annual Review of Materials Research, vol. 32, (1), pp. 401-436, 2002.

[3] T. P. Lodge, "Block copolymers: past successes and future challenges," Macromolecular Chemistry and Physics, vol. 204, (2), pp. 265-273, 2003.

[4] S. Tallegas et al, "Block copolymer technology applied to nanoelectronics," Physica Status Solidi (C), vol. 10, (9), pp. 1195-1206, 2013.

[5] M. A. Hillmyer, "Nanoporous materials from block copolymer precursors," in Block Copolymers IIAnonymous Springer, 2005, pp. 137-181.

[6] A. Urbas et al, "Tunable block copolymer/homopolymer photonic crystals," Adv Mater, vol. 12, (11), pp. 812-814, 2000.

[7] D. J. Arriola et al, "Catalytic production of olefin block copolymers via chain shuttling polymerization," Science, vol. 312, (5774), pp. 714-719, May 5, 2006.

[8] C. Park, J. Yoon and E. L. Thomas, "Enabling nanotechnology with self assembled block copolymer patterns," Polymer, vol. 44, (22), pp. 6725-6760, 2003.

[9] P. Marco, Mesoscale Modelling of Block Copolymer Systems. Germany: VDM Verlag Dr. Muller Aktiengesellschaft, 2010.

[10] R. A. Segalman, "Patterning with block copolymer thin films," Materials Science and Engineering: R: Reports, vol. 48, (6), pp. 191-226, 2005.

[11] M. Pinna and A. V. Zvelindovsky, "Large scale simulation of block copolymers with cell dynamics," The European Physical Journal B, vol. 85, (6), pp. 1-18, 2012.

[12] F. S. Bates, "Polymer-polymer phase behavior," Science, vol. 251, (4996), pp. 898-905, Feb 22, 1991.

[13] X. He et al, "Self-assembly of the symmetric diblock copolymer in a confined state: Monte Carlo simulation," J. Chem. Phys., vol. 114, (23), pp. 10510-10513, 2001.

[14] S. Lin et al, "Brownian molecular dynamics simulation on self-assembly behavior of rod-coil diblock copolymers," Macromolecules, vol. 40, (5), pp. 1684-1692, 2007.

[15] X. Li et al, "Microphase separation of diblock copolymer poly (styrene-b-isoprene): A dissipative particle dynamics simulation study," J. Chem. Phys., vol. 130, (7), pp. 74908, 2009.

[16] T. L. Chantawansri et al, "Self-consistent field theory simulations of block copolymer assembly on a sphere," Physical Review E, vol. 75, (3), pp. 031802, 2007.

[17] G. Gonnella, E. Orlandini and J. M. Yeomans, "Spinodal decomposition to a lamellar phase: effects of hydrodynamic flow," Phys. Rev. Lett., vol. 78, (9), pp. 1695, 1997.

[18] G. Gonnella, E. Orlandini and J. M. Yeomans, "Lattice Boltzmann simulations of lamellar and droplet phases," Physical Review E, vol. 58, (1), pp. 480, 1998.

[19] S. R. Ren and I. W. Hamley, "Cell dynamics simulations of microphase separation in block copolymers," Macromolecules, vol. 34, (1), pp. 116-126, 2001.

[20] Y. Oono and S. Puri, "Computationally efficient modeling of ordering of quenched phases," Phys. Rev. Lett., vol. 58, (8), pp. 836, 1987.

[21] S. Puri and H. L. Frisch, "Segregation dynamics of binary mixtures with simple chemical reactions," Journal of Physics A: Mathematical and General, vol. 27, (18), pp. 6027, 1994.

[22] S. Puri and Y. Oono, "Study of phase-separation dynamics by use of cell dynamical systems. II. Two-dimensional demonstrations," Physical Review A, vol. 38, (3), pp. 1542, 1988.

[23] A. Shinozaki and Y. Oono, "Spinodal decomposition in 3-space," Physical Review E, vol. 48, (4), pp. 2622, 1993.

[24] Y. Oono and S. Puri, "Study of phase-separation dynamics by use of cell dynamical systems. I. Modeling," Physical Review A, vol. 38, (1), pp. 434, 1988.

[25] I. W. Hamley, "Cell dynamics simulations of block copolymers," Macromolecular Theory and Simulations, vol. 9, (7), pp. 363-380, 2000.

[26] H. Furukawa, "A dynamic scaling assumption for phase separation," Adv. Phys., vol. 34, (6), pp. 703-750, 1985.
[27] M. San Miguel, M. Grant and J. D. Gunton, "Phase separation in two-dimensional binary fluids," Physical Review A, vol. 31, (2), pp. 1001, 1985.
[28] M. Bahiana and Y. Oono, "Cell dynamical system approach to block copolymers," Physical Review A, vol. 41, (12), pp. 6763, 1990.
[29] H. Kodama and M. Doi, "Shear-induced instability of the lamellar phase of a block copolymer," Macromolecules, vol. 29, (7), pp. 2652-2658, 1996.
[30] S. R. Ren et al, "Mesoscopic simulations of lamellar orientation in block copolymers," Macromolecular Theory and Simulations, vol. 11, (2), pp. 123-127, 2002.
[31] S. D. Conte and R. T. Dames, "An alternating direction method for solving the biharmonic equation," Mathematical Tables and Other Aids to Computation, vol. 12, (63), pp. 198-205, 1958.
[32] M. Abramowitz and I. A. Stegun, "Handbook of mathematical functions," Applied Mathematics Series, vol. 55, pp. 62, 1966.
[33] J. Douglas and J. E. Gunn, "A general formulation of alternating direction methods," Numerische Mathematik, vol. 6, (1), pp. 428-453, 1964.
[34] S. D. Conte and R. T. Dames, "On an alternating direction method for solving the plate problem with mixed boundary conditions," Journal of the ACM (JACM), vol. 7, (3), pp. 264-273, 1960.
[35] T. P. Witelski and M. Bowen, "ADI schemes for higher-order nonlinear diffusion equations," Applied Numerical Mathematics, vol. 45, (2), pp. 331-351, 2003.

Sohail Ahmed Memon is working as Assistant Professor in the department of Mathematics Shah Abdul Latif University Khairpur. He has M.Sc in Mathematics from SALU Pakistan, M.Sc in Mathematics from London Metropolitan University UK and PhD degree from the University of Central Lancashire, Preston, United Kingdom. His research expertise includes Data Science, Quantitative Analysis, Mathematical Modelling and Computer simulations.

Nazar Hussain Phulpoto is working as Associate Professor at the Department of Information Technology, QUEST Nawabshah. He has PhD degree in Management Sciences and 15 years of research and teaching experience. His research expertise includes Management Sciences and Information Technology.

Imtiaz Ali Halepoto received Bachelor of Engineering degree in Computer Systems Engineering from QUEST Nawabshah, Pakistan, and both M.Sc and PhD from the Department of Computer Science, the University of Hong Kong in 2010 and 2015. Currently, he is working as Assistant Professor at the Department of Computer Systems Engineering QUEST Nawabshah. His research interests are in communication, network protocols and the heterogeneous networks.

Adnan Manzoor received his bachelor's and master's degree in Computer Science from University of Sindh Jamshoro Pakistan in 2001. He received his Master's in Information Technology from QUEST, Pakistan in 2012. He successfully completed hi PhD in Artificial Intelligence from Vrije University Amsterdam Netherlands in 2017. His research interests include, but are not limited to, computational modeling of cognitive and affective processes and study the role of these processes in the context of a person's social network both for purposes of monitoring and support, for example, via mobile phone apps.

M. Sulleman Memon received the B.E in Computer Engineering and M.E. in Software Engineering from MUET, Jamshoro Pakistan in 1990 and 2004, respectively. He is now a PhD scholar at QUEST Nawabshah. He has submitted thesis. He is working as Assistant Professor in the Department of Computer Engineering. QUEST, Nawabshah. He is author of many International and national papers. He has presented his work at many countries of the word in International Conferences. His field of study is Wireless communications. He is Senior Member of IACSIT and member of Pakistan Engineering Council, ACM, and IEEE.