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Revisiting Kinetics of Phase Separation in Binary Mixtures

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ABSTRACT

Binary Mixtures (Binary Alloys or Binary Fluids) exhibit phase separation after a sudden quench below the critical temperature. Domain growth occurs due to the motion of interfaces between deferent phases. The dynamical aspects of phase separation and the domain growth lawshave been studied and explored by the physicists in great deal from several decades. There existvarioustheoretical, experimental or computational methods to dig into the underlying physics. We focus to shed light on this phenomenon and review the framework ofmean field theoreticalstudy, phase-field modelling and simulation techniques. We further discuss about the recent advancements in this field particularly on the use of Cahn-Hilliard equation with activity parameter to describe the active phase separation dynamics.

Keywords: Binary Mixtures, Liquid Crystal, Phase transition

INTRODUCTION

Kinetics of phase ordering has been a topic of great importance among scientists from many decades [1][2][3]. It has been a key research interest of not only physicists but also people from mathematical, chemical and biological fields as well. Till date, there exists a great deal of research by means of experimental, theoretical and computational methods. As a result of it, numerous excellent articles, reviews, and books [1-6][15] have been produced so far. In

this chapter, we do not attempt to cover the entire area of phase transitions or explain the micro details of the various advancements and results found till date, which is beyond the scope of this chapter. Rather, we focus on a part of this vast area i.e., *dynamics of phase separation in binary mixtures* and we further constrain ourselves to the study of it using phase field models (Cahn-Hilliard equation [16]). We aim to provide a summary of the theoretical method, computational modelling andthe recent developments in past few years.

Binary Mixtures (BMs)

A binary mixture comprises of two pure substances (AB), each with its own set of properties. Though the constituent components in the mixture are being mingled together but have not been chemically combined. Thus, the resulting system is a physical mixture of substances that, despite being mixed together retain their identities. The example of these mixtures includes alloys, liquids, suspensions, solutions, colloids and polymers to name a few [6]. Binary mixtures which are made up of two components as fluids or liquids are known as *binary fluid mixtures*or *binary fluids.* Binary mixtures may be both *homogeneous* and *heterogeneous* defined as:

(a) *Homogeneous Binary Mixture*

If both the components of a mixture are in the same amounts and phase, it is said to be homogenous. It may be a solid, liquid, or gaseous mixture [3].

(b) *Heterogeneous Binary Mixture*

When a mixture contains two or more different phases of its elements, it is called a heterogeneous mixture e.g., a mixture of oil and water that is impermeable at room temperature [3].

The above described BMsfall into the category of *passive* BMs. We define theother type i.e., the *active* BMs as below:

The Active Binary Mixture

This is defined as an assembly of self-propelled particles (SPPs) which is of great current research interest. Active BMs differ from the passive one in such a way that SPP use their internal energy by converting it into a systematic movement which results inviolation of

time-reversal-symmetry (TRS) [14]. The constituent components of the active BMs may be in few micrometers such as actin and tubulin filaments, molecular motors, unicellular organisms (amoeba and bacteria) or may be in several meters for example schools of fish, bird flocks and human crowds etc.

Domain Growth in Binary Mixtures

It has been observed both in experiments and simulations that BMs when quenched below the critical temperature T_c,from a high temperature mixed homogeneous state, A-rich and B-rich domains form and grow spontaneously and immediately. If the mixture contains equal number of A and B molecules the domain growth pattern looks like a maze (symmetric or critical case) as shown in Fig. 1 (left panel) whereas if the proportion of type of species are different(asymmetric or off critical case) the droplets of the minority component form and grow (called nucleation and growth) as shown in Fig. 1 (right panel). Here, the total number of molecules (A+B) remains same and it is referred as conserved dynamics unlike the non-conserved case found in para to ferromagnet phase transitions.

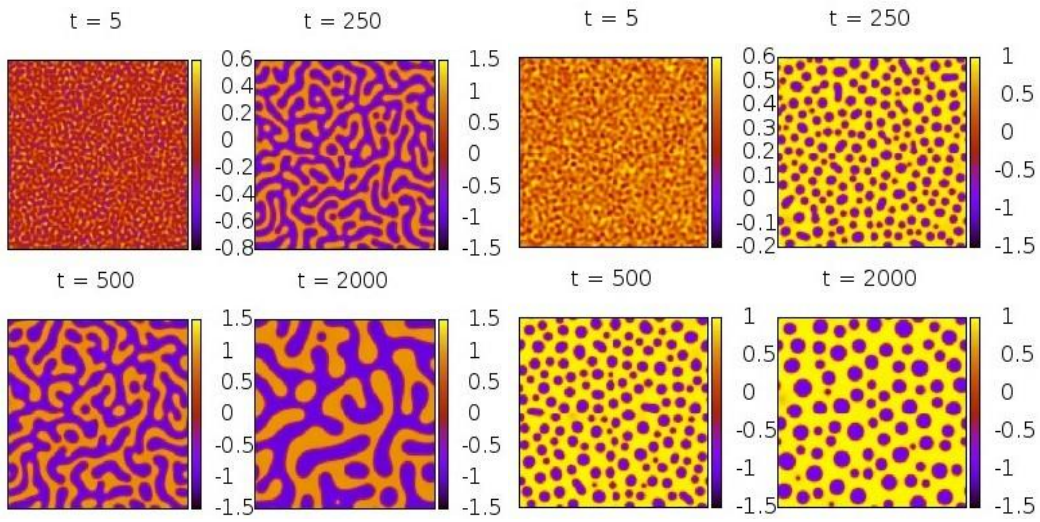


Fig. 1 Evolution snapshots of A-rich and B-rich domains after a temperature quench below a critical temperature T_c. The left panel of images are obtained for a symmetric case (50-50 mixture of A and B molecules) whereas the right panel of images are obtained for a asymmetric case.

Theory

We consider a binary mixture having A and B molecules as its constituent components.The molecules interact in such a way one type of substances are more attractive with each other and would like to sit together Let us assume that the local densities of A and B type of molecules are $n^A(\boldsymbol{r},t)$and $n^B(\boldsymbol{r},t)$ respectively. with local density field $\rho(\boldsymbol{r},t)$ which is the order parameter defined as

$$\rho(\boldsymbol{r},t) = n^A(\boldsymbol{r},t) - n^B(\boldsymbol{r},t) \qquad \text{……(1)}$$

The evolution of order parameter is by the continuity equation

$$\frac{\partial \psi}{\partial t} = -\nabla.\mathbf{J}(\mathbf{r}, t) \qquad \text{……..(2)}$$

where, **J**(**r**,t) is the current density vector given as

$$\mathbf{J}(\mathbf{r},t) = -D\nabla\mu(\mathbf{r}, t) \qquad \text{……...(3)}$$

where $\mu(\mathbf{r}, t)$ is the chemical potential which is given by the derivative of the free energy functional F:

$$\mu(\mathbf{r}, t) = \frac{\delta F[\psi]}{\delta \psi} \qquad \text{…….(4)}$$

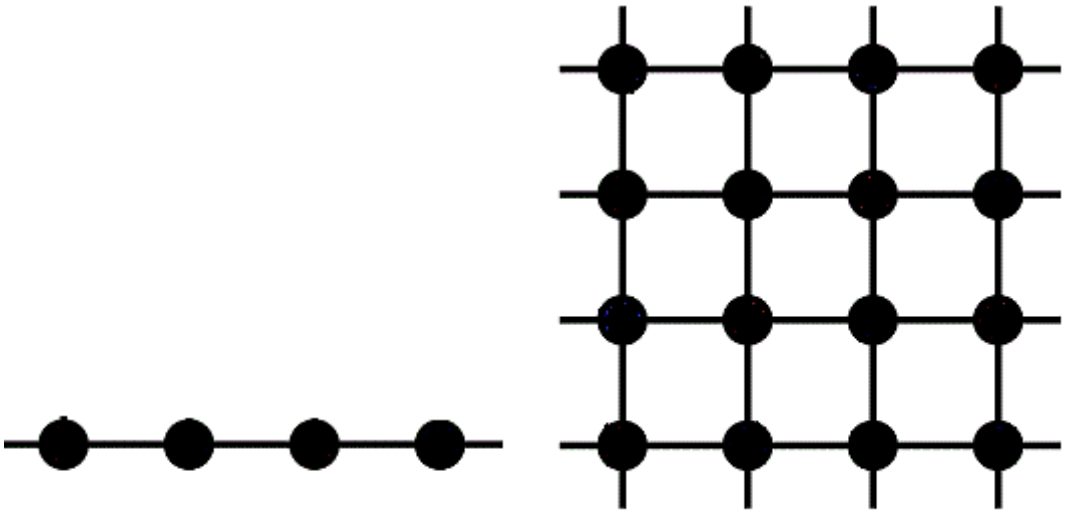
Combining equations (2), (3) and (4) we get

$$\frac{\partial \psi}{\partial t} = D\nabla^2\left(\frac{\delta F[\psi]}{\delta \psi}\right) \qquad \text{…….(5)}$$

Equation (5) is known as Cahn-Hilliard equation [1-4] which we consider here for our numerical discretization and simulation purpose. D is the diffusion coefficient here. Cahn-Hilliard (CH) equation with noise term is known as Cahn-Hilliard-Cook equation. The solution of CH equation gives the time evolution of domain growth of conserved system such as binary mixtures. The typical computational method used to solve it by Euler discretization and using periodic boundary conditions. We discuss the concept of cellular Automata and periodic boundary conditions in detail below.

Cellular Automaton

In software engineering, arithmetic, material science, complexity science, physics, theoretical biology, microstructure modelling, and many-sided quality research, a *Cellular Automaton* is a discrete model [4-8]. Cell spaces, tessellation automata, homogeneous structures, cellular structures, tessellation structures, and iterative arrays are some of the other names for it.



1-D CELLULAR AUTOMATA

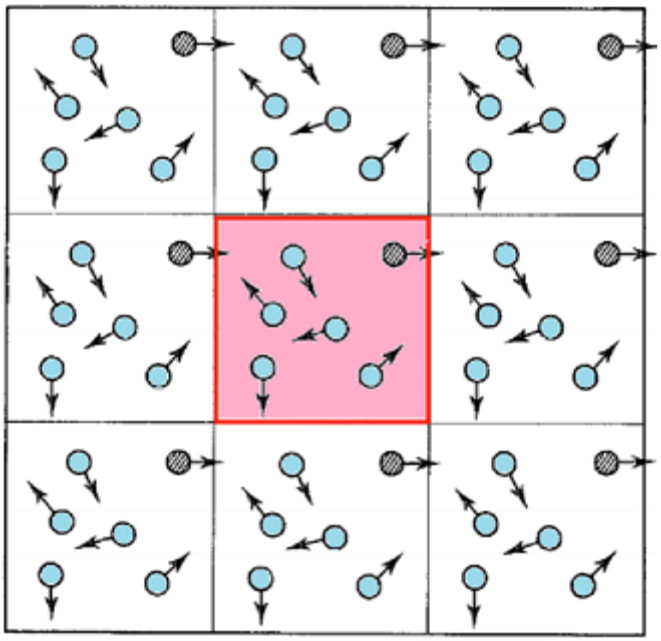
2-D CELLULAR AUTUMATA

A cellular automation system consists of a regular grid/lattice of cells, each of which is in one of a limited number of states, such as on or off. The grid can have any number of dimensions that you specify. A neighbourhood is a collection of cells in each cell that is defined in relation to a preset cell. Specifics a state for each cell and chooses an initial state (time t = 0). On the basis of a fixed rule (most commonly, a mathematical function), a new generation is formed (growing by 1), which determines the new state of each cell in terms of the current state of the cell and the states of the cells around itin its immediate vicinity. In general, the same rule is used to advance the state of each cell, which does not change after a certain amount of time, and it is applied in the entire grid at the same time, but there are exceptions, such as the stochastic cellular automata and the asynchronous cellular automaton. We use the same as discussed above to solve Cahn-Hilliard equations numerically with periodic boundary conditions.

Periodic Boundary Condition

Periodic boundary conditions (PBCs) are a collection of boundary conditions used to approximate a vast (infinite) system using a small component termed a unit cell [8-10]. Periodic boundary conditions are used in computer simulations and mathematical models. In our example, we utilize a computer to solve the big system which cannot be solved directly, thus we employ computer simulations. The core idea is to simulate a small (limited) system in order to forecast the properties of a bulk material. This procedure is obtained in the following manner.

Let us assume that, infinite number of such small system which exist everywhere. All the molecules are identical copies in each of the boxes. It can be depicted as following



Now, we'll use a central box with a size range of 0 to L to display the particle arrangement. According to PBC, the identical layout is present in all boxes near the centre box. Because molecules are identical duplicates, any change in this central box will have the same effect on all the boxes. So, we're actually mimicking a large-scale system. If a molecule departs the box in the +x direction (as illustrated in the diagram above), an exact replica of that molecule will enter the box in the opposite direction (x), and the number of molecules in this box will remain constant.

CONCLUSION

The study of phase separation kinetics is critical from both a scientific and an industrial standpoint. Understanding the diverse physical phenomena displayed by phase transitions is one of the most classic challenges in statistical physics. We havediscussed this problem in the context of binary(AB) mixes.As a consequence, we investigated the temporal dynamics of coarsening of A-rich and B-rich domains aftera quench below the critical temperature. The density difference between A and B is seen here which serve as an order parameter. The order parameter is zero above Tc and has both positive and negative values.

In order to understand the dynamical properties of this model we use computational methods in the light of mean filed approach, particularly Landau theory involving a double well potential. We undertake both the critical and off-critical initial conditions. The coarsening phenomena is observed in both the cases. In critical case we observe mazelike pattern whereas in off-critical case we find nucleation and growth of the minority component in the sea of majority one.

The understanding of phase-separation dynamics allows us to explore many physical phenomena related to the general issues of phase transitions. There are various aspects of ongoing research such as active systems [14], wetting and dewetting (phase separation in the presence of attractive or repulsive surfaces), phase separation in the presence of gravity (the problem of dew drops on lotus leaves) etc.

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