Chapter 1

Introduction

1.1 General Considerations

Most natural systems are out of equilibrium and are often far-from-equilibrium. Despite many efforts made to formulate laws governing the evolution of these systems, our knowledge regarding nonequilibrium behavior is still rather incomplete. [1, 2, 3].

Systems that are far-from-equilibrium often exhibit some memory effects of their recent history. For example, cold-worked steel maintains an enhanced hardness imparted by its mechanical treatment. But memory eventually fades. In general, systems tend to subside to very simple final states, which are time-independent and are often referred to as equilibrium states. In these states, the properties of systems are determined by intrinsic factors and not by external influences. The rate of evolution towards these final states typically depends on the underlying microscopic interactions between the constituents of the system. In this thesis, we focus on a prototypical far-from-equilibrium situation, viz., the temporal evolution of a multi-component mixture which has been rendered thermodynamically unstable by a rapid quench below the critical temperature. The subsequent evolution is usually referred to as "phase ordering dynamics" or "domain growth".

Experimental interest in the study of phase ordering dynamics comes from metallurgists, who noticed that alloys solidified during casting processes are often inhomogeneous. These alloys possess a complicated microstructure formed of domains of different phases.
An understanding of the dynamics of the solidification front during the fabrication process helps to assess how the processing condition influences the resulting material. In most cases, the microstructures can be considered as fixed after the end of the fabrication process, as diffusion in solids is very slow under normal conditions. However, for alloys with low melting points, or when alloys are kept at high temperatures, the evolution continues to reduce the total surface energy at the domain boundaries. As a result material diffuses through the domains, and the whole structure coarsens. A practical problem related to this process is the stability of solder joints: initially stable joints may become very fragile because of ongoing phase transformation in the solid.

Pedagogically, these systems are interest to physicists because they provide relatively simple examples of pattern-forming processes. It is fascinating to understand how complex structures emerge spontaneously from a homogeneous state and how these structures evolve in time. Much of our present understanding of phase ordering processes has come from numerical studies. The advent of fast computers has made it possible to simulate models on length- and time-scales even beyond those accessible to experiments.

Several types of models have been proposed to study phase ordering dynamics. These can be classified into three categories as macroscopic; mesoscopic; and microscopic [4, 5]. Macroscopic models, also referred to as sharp interface models, are those in which one considers the growth of well-defined domains. The typical size of these domains is much larger than the intrinsic thickness (correlation length) of an interface. If the motion of the interface is very slow in comparison to the time-scale of diffusion, we can assume that their configuration is near local equilibrium. Thermodynamics of the interfaces then gives boundary conditions at the interfaces for the diffusion fields. The solution of the appropriate diffusion equations in the domains then determines the flux through the interfaces and hence their velocity. The result is the free boundary problem: the diffusion equation is linear, however difficulties arise from the boundary conditions to be satisfied on a moving boundary, often of complex shape. These models have been successfully used to describe late stage domain growth during phase separation [6, 7, 8] as well as in many other pattern-forming systems [9].
In mesoscopic models, one assumes that, even if the system as a whole might be in a state far from equilibrium, on a small scale of the order of thickness of the interfaces, the system can be considered to be in local equilibrium and the intensive thermodynamic quantities vary very slightly on this scale. Under this assumption one can write down a free energy functional, which depends on the local fields, and postulate an equation of motion. The first equation of this type was due to Cahn and Hilliard which was put forth to describe the phase separation (spinodal decomposition) in binary alloys [11] and later used in studies of different aspects of spinodal decomposition [7, 12, 13, 14]. The free energy functional contains a double-well free energy density to model two phase-coexistence, and gradient energy term which arises from the interactions between atoms of the diffusing species. The Cahn-Hilliard equation is given by,

$$\frac{\partial \phi(x, t)}{\partial t} = \nabla^2 \left[ \frac{\partial V(\phi)}{\partial \phi} - \nabla^2 \phi \right] + \zeta,$$

(1.1)

where, $V(\phi) = (r/2)\phi^2 + (u/4)(\phi^2)^2$, with $r < 0$ and $u > 0$ is the 'sombrero' potential, $\phi(x, t)$ is a conserved order parameter, and $\zeta$ a white noise satisfying the relation

$$\langle \zeta(x, t)\zeta(x', t') \rangle = -2T\lambda\nabla^2 \delta(x - x')\delta(t, t').$$

(1.2)

Here $T$ is the final temperature of the quench. This equation is a non-linear diffusion equation. It allows for equilibrium interface solutions which have a finite thickness. In contrast to macroscopic models, the local thermodynamics at the interfaces are automatically incorporated, and this makes it convenient for numerical investigation. Another advantage of the Cahn-Hilliard model over the macroscopic model is that it can describe situations where stable interfaces have not yet been formed as is the case, for instance, in the initial stage of phase separation.

Microscopic models are usually based on lattice models of the Ising type, also called lattice gases or more precisely stochastic lattice gases to distinguish them from Boltzmann lattice gases that are used to model hydrodynamic flows. A lattice in this context is then a structure populated by particles. For a single species system characterized by nearest neighbor interactions, this model can be mapped on to the classical Ising model. A configuration is assumed to evolve by jumps of particles from one lattice site
to another. The jumps are determined by the local environment. Usually these models are simulated on computers by dynamic Monte Carlo method and relevant quantities are extracted by averaging over numerous realizations of the stochastic process. Even though these models are only rough pictures of the processes on the microscopic scale they are useful in investigating some of the questions which are inaccessible through other models. For instance, the atomic mobility may show a strong dependence on the local parameters, like the particle density or the local order parameter. This can have macroscopic effects, as for example in the diffusion of atoms in intercalation compounds. In intercalated materials as well as in superionic conductors, ionic species diffuse in host lattice, which makes the lattice a natural setting. Most often the host lattice is strongly coupled to the mobile ions and it can even display structural phase transitions.

In this section we have given a brief account of the general problem in nonequilibrium statistical physics: the evolution of systems far-from-equilibrium. Further more, we have taken as typical example the problem of phase ordering dynamics and summarized extant models used to investigate this phenomenon. As mentioned earlier, this thesis addresses some of the problems of phase ordering dynamics (using a microscopic model which is to be introduced in chapter 2). In the following subsequent sections we give a brief review of extant results on kinetics of phase ordering.

This chapter is organized as follows. In Section 1.2 we review extant results on phase ordering dynamics in systems with: (a) nonconserved dynamics and (b) conserved dynamics. Section 1.3 reviews results on nonlinear relaxation in the context of the autocorrelation function. Section 1.4 presents general objectives and purposes of the thesis and Section 1.5 concludes the chapter with an outline of the thesis.

1.2 Phase Ordering Dynamics: Background

When a system is quenched through a transition from a disordered to an ordered state small domains of the different symmetry manifestations of the ordered phase initially form. These then grow to give larger ordered regions, asymptotically approaching the ideal of very large ordered regions. There has been a great deal of study of this coarsening
process in systems where the different states are equilibrium thermodynamic phases at finite temperature. The nature of evolution in the phase ordering system depends whether or not the evolution conserves the order parameter.

As a typical example consider coarsening in an Ising model when it is quenched from a temperature $T'$ to $T$ such that $T < T_c < T'$ where $T_c$ is the critical temperature. Initially the system is in a homogeneous state where 'spin-up' and 'spin-down' states are equally preferred. However, at the final temperature the preferred state is 'up' or 'down' as a result of which the system starts having a number of domains rich in 'up' or 'down' spins in a short time after the quench. Recall that surface energy is proportional to the number of domains (domain walls to be precise). The stable (preferred) configuration of a system is one that gives minimum interfacial energy. This energy is minimized by reducing the number of domains where by the size of the remaining domains is growing with time. This process of domain growth is a complex process involving shrinking away of smaller domains and straightening of domain boundaries between the walls. In the case of dynamics in nonconserved order parameter (NCOP) there is a possibility that an initial homogeneous mix of species might end up in an ordered state that contains single species. The mechanism of domain growth for systems with conserved order parameter (COP) is different from those with NCOP. In the former case, even though there is local domain growth the dynamics conserves the initial composition globally.

1.2.1 Universality and Scaling in Kinetics of Phase Ordering

Upon close inspection of Fig. 1.1 we see that the domain morphology at later time looks very similar to the one at earlier time except that the later time domains are bigger in size. In fact, if one shrunk the later picture by an appropriate factor it would be practically indistinguishable from the earlier picture. This is the concept of the scaling hypothesis which states that at late times, there exist a single characteristic length $L(t)$, such that when relevant lengths are scaled by $L(t)$ the domain morphology is independent of time.

The two commonly used probes for domain morphology are the real space correlation
Figure 1.1: Typical evolution pictures of an ordering system at various times $t$ following a quench from infinite temperature to temperature $T \sim 0$. The system is spin-1/2 Ising model on a square lattice of size $128 \times 128$ with a single spin-flip dynamics. Time is measured in Monte Carlo step per spin. An up spin is represented by a black square and a down spin by a white square. Note that as time goes on the edges are straightened and small domains that were in the large domains have been 'devoured'.
function $C(\vec{r}, t)$ and its Fourier transform $S(\vec{k}, t)$. According to the scaling hypothesis these take the form:

$$
C(\vec{r}, t) = F(\vec{r}/L(t)),
$$
$$
S(\vec{k}, t) = L^d(t)G(\vec{k}L(t)).
$$

(1.3)

We expect $L(t)$ in the limit $t \to \infty$ to be much greater than other microscopic lengths. In this time limit $L(t)$ has the typical asymptotic forms, which delineates different universality classes. In other words as $t \to \infty$ (or $L(t)$ is much greater than microscopic lengths), neither the details of the Hamiltonian nor the dynamical rules become important in coarsening. The typical forms of $L(t)$ can be classified in two broad categories in which each category defines different universality classes.

(i) Power laws:

The characteristic length in this category of domain growth takes the form

$$
L(t) \sim t^n,
$$

(1.4)

where $n$ can take a few values in the range $0 \leq n \leq 1$ which in turn define the different universality classes we considered in subsections 1.2.2 and 1.2.3.

(ii) Logarithmic laws:

Domain growth in this case is much slower than that of the power law growth and $L(t)$ in this case might be given by

$$
L(t) = (\log t)^\alpha,
$$

(1.5)

where $\alpha$ can take values in the range $0 \leq \alpha \leq 1$. The growth laws for both categories and the universality classes they define are considered in some detail in Chapter 3 in the context of domain growth in systems where the dynamics do not conserve the order parameter.

### 1.2.2 Nonconserved Dynamics: The Lifshitz-Allen-Cahn law

In early studies the value of the exponent $n$ in Eq. (1.4) for systems with nonconserved dynamics was quickly found to be $1/2$. The growth law in this case is referred to as
1.2 Phase Ordering Dynamics: Background

Lifshitz-Allen-Cahn law (LAC) [10, 11]. An example of such a system is provided by an ordering ferromagnet. LAC argued that the motion of boundaries in such systems is driven by their local curvature. This law can be obtained by examining the shrinkage of a spherical droplet of one phase placed in the other phase. The equation of motion of the interface of this droplet is given by \( \frac{dr}{dt} v = -\frac{l}{r} \) where \( r \) is the radius and hence, \( \frac{l}{r} \) is its curvature. Therefore, this simplified version of the LAC gives the rate of change of \( r \) as \( \frac{dr}{dt} = \frac{1}{2} t \).

One can also arrive at the same conclusion by considering the surface tension as a driving force [23]. Consider a spherical droplet of radius \( r \). The work done by a force per unit area \( P \) in shrinking the radius by \( dr \) is \( \delta w = 4\pi Prdr \). The total surface energy is \( E_s = 4\pi r^2\sigma \), where \( \sigma \) is the surface tension. Therefore, the change in surface energy due to change in \( r \) is \( dE_s = 8\pi\sigma rdr \). Equating the two energies we get \( P = 2\sigma/r \). This is the cause for motion of the domain walls with a velocity \( v \) proportional to the local curvature. If \( \eta \) is a friction constant for the motion of a boundary, then we have, \( \eta v = -2\sigma/r \). Finally, \( \eta = \sigma \) gives the same result as in the previous argument.

For this class of systems in the context of spin-1 models with local barriers we have given a random walk interpretation of domain growth which leads to LAC law. This result is given in Chapter 3.

1.2.3 Conserved Dynamics: The Lifshitz-Slyozov Law

A typical example of phase ordering dynamics in systems where the order parameter is conserved is provided by the phase separation in a binary fluid or alloy quenched from its one-phase region (usually this state is taken to be one at infinite temperature) into the two-phase region (a region where the temperature \( T \) is below the critical temperature \( T_c \) that favors a state in which the two species are separated). The classic work of Lifshitz and Slyozov (LS) [6] predicts growth law of the form given in Eq. (1.4) where now \( n = \frac{1}{3} \), in the limit of a dilute amount of one phase. In early studies the value of \( n \) was controversial. For example Mazenko \textit{etal} [15] argued that the spinodal decomposition of the two-dimensional Ising model at 50% concentration has characteristic length \( L(t) \)
that has logarithmic time dependence. However, later on these authors argued in favor of LS law for the late stage growth in spinodal decomposition [16]. Other numerical studies, at the same time, of spinodal decomposition predicted power law growth with the exponent ranging $0.17 - 0.25$ [17]. Huse qualitatively generalized the LS theory to apply to the case of equal fractions of the two phases [18]. Huse's theory assumes that the rate of growth of the average domain can be written at late times, as

$$\frac{dR}{dt} = C_1/R(t) + C_2/R^2(t) + O(R^{-4}),$$

(1.6)

where $C_1$ corresponds to the contribution to growth from diffusion between domains through the bulk and $C_3$ is the first order correction due to the transport of matter along the interface between domains. For large $R$ this yields

$$R(t) = A + Bt^{1/3},$$

(1.7)

where $A$ and $B$ are constants related to $C_1$ and $C_2$. Similar results were obtained by Amar et al for domain growth in the two-dimensional spin-exchange kinetic Ising model [19]. At present the balance seems to swing towards the LS growth law for late stage growth of characteristic length in systems with COP. The three state kinetic Ising model is under investigated in contrast to its spin- $1/2$ counter part. Of course there exist a number of studies on the three state Potts' model [20].

1.3 The Autocorrelation Function

The relaxation behavior of many systems evolving towards equilibrium can be well captured by their memory function, often referred to as the autocorrelation function. The analytical form of this function, for various materials, is still an outstanding issue of debate. However, for a range of materials experimental and numerical data can be well approximated by a non exponential relaxation [21] of the form,

$$\phi(t) = \phi_0(t)e^{-(t/r)\beta}, \quad 0 < \beta < 1$$

(1.8)

which is now commonly referred to as stretched-exponential or Kohlrausch-Williams-Watts relaxation.
To illustrate how non-exponential relaxation occur let us consider the following typical example. Consider a polarizable material with individual dipole moments $\mu(t)$ in an external electric field \[22\]. Suppose one starts measuring time when the field was turned off. The normalized autocorrelation function of the dipole moment is defined by

$$\phi(t, t_0) = \frac{\langle \mu(t)\mu(t_0) \rangle}{\langle \mu^2(t_0) \rangle}.$$  \hspace{1cm} (1.9)

Debye in 1913 treated the relaxation of spherical molecules, of radius $R$, in a fluid of viscosity $\eta$ and derived that

$$\phi_D(t) = e^{-t/\tau_D}$$

with $\tau_D = f(\eta, T)$ which is explicitly given by $\tau_D = \frac{4\pi R^3 \eta}{kT}$. This is often referred to as “Debye relaxation”.

Not surprisingly, the Debye expression does not describe more complicated systems such as polymers and glasses. For these materials it was found that the KWW exponential fits the data exceedingly well. Note that Eq. (1.8) can be written as a continuous distribution of exponents. Shelsinger and Montroll argued that the reason why this equation holds for many materials lies in the fact that the KWW form is the limiting form for the distribution function of a stochastic process governing the relaxation mechanism in many situations.

Bendler and Shelsinger, using the method of continuous random-walk, studied dielectric relaxation and derived Eq. (1.8) for the auto-correlation function defined in Eq. (1.9) \[22\]. In Chapter 3 we used this powerful method to give a stochastic model for the auto-correlation function of systems with NCOP.

In spin models the above outlined relaxation studies correspond to the study of the spin-spin auto-correlation function. Loosely speaking this is a quantity that measures how soon a system forgets its history and it is another quantity proved to be useful in the study of systems evolving towards equilibrium. Review of available materials on the study of this quantity suggests that disagreement remains on the its behavior. For instance, the Ohta-Jasnow-Kawasaki \[23\] theory for spin-1/2 Ising model predicts power law for the long time behavior of the autocorrelation function whereas Graham
and Grant [24] reported ordinary exponential decay and Huse and Fisher [25] argued for stretched exponential decay. On the other hand, hardly any study exists on the nature of the autocorrelation function in spin-1 kinetic Ising models.

1.4 Motivation for our Studies

In Sections 1.2 and 1.3, we reviewed available results for phase ordering dynamics for both the cases of systems with NCOP and COP. An important discovery in these studies was that the domain growth involves a single time-dependent length scale. Most of these earlier studies have focused upon systems with a single order parameter. In this thesis, we investigate n-component mixtures \((n \geq 3)\), which cannot be described by a single order parameter. Typically, this multi-component systems exhibit rather complex phase diagram. Furthermore, the mechanism of domain coarsening is more diverse than in the case of a single order parameter. One of the primary purposes of this thesis is to investigate universality and scaling in spin-1 systems which are characterized by two order parameters.

The other physical quantity of paramount importance is in the study of systems far from equilibrium is the autocorrelation function. As we have seen in the reviews above disagreement remains on the behavior of this quantity and hardly any study exists for it in the context of spin-model.

1.5 Outline of the Thesis

As we have mentioned in the previous section our motivation for this study was 'slow dynamics' in a special class of disordered systems hindered from reaching equilibrium. If we were ambitious we might have found a simple model to investigate the behavior of systems with much slower dynamics. However, we might be too ambitious to pick up a generalized spin-1 model without any randomness in its Hamiltonian nor externally imposed randomness with only nearest neighbor interaction on a square lattice to be such a candidate. Leaving aside the idea of a very slow dynamics, by its own merit
the model has fascinating features. Among other things the scaling of the problem in the case of non-conserved order parameter is outstanding and why the autocorrelation function should follow non-exponential relaxation needs to be explained. Though the scaling in conserved order parameter case is not as outstanding as it is in non-conserved order parameter case the spatial correlation function and its Fourier transform scales very well in late stage growth of the system. This thesis discusses these points in a systematic way.

The thesis is organized as follows. In Chapter 2 we consider phase transitions in spin-1 models. This chapter provides the static properties of the dynamical models considered in latter chapters. Furthermore, in this chapter we discuss how phase transitions can be understood in the context of different ensembles.

Chapter 3 presents domain growth in spin-1 lattice models having non-conserved spin flip kinetics with local barriers. Our primary purpose here is to model the relational behavior of physical systems in which molecular motion is impeded by local kinetic barriers. Furthermore, in this chapter we present numerical results obtained using Monte Carlo simulation for various parameters: domain distribution functions; spatial correlation functions; autocorrelation function etc., in this model.

Chapter 4 presents detailed numerical results from Monte Carlo (MC) simulations of the kinetics of phase separation in ternary mixtures. In particular, we focus on the case of ABV mixtures (where V denotes a vacancy) and investigate segregation kinetics resulting from V-mediated dynamics. We present heuristic arguments for the morphologies arising for different ranges of parameter values. Furthermore, we present comprehensive numerical results for various characteristic features of the domain growth process, e.g., real-space correlation functions, domain-size distribution functions, growth laws, autocorrelation functions, etc.

In Chapter 5 we present macroscopic modeling of phase separation in spin-1 lattice models by deriving mean-field kinetic equations for both non-conserved and conserved dynamic. This chapter examines in what way a choice of external parameters affects the general behavior of the ordering system.