Chapter 2

Control of Structure Formation in Phase-Separating Systems

2.1 Introduction

In Chapter 1, we considered a binary mixture \((AB)\), which is homogeneous (or disordered) at high temperatures and phase-separated (or ordered) at low temperatures. If the homogeneous mixture is rapidly quenched below the critical temperature \(T_c\), it becomes thermodynamically unstable. Then, the mixture undergoes phase separation via the formation and growth of domains of \(A\)-rich and \(B\)-rich phases. Much research interest has focused on this far-from-equilibrium evolution [1, 2]. There now exists a good understanding of segregation dynamics for binary mixtures [3, 4, 5, 6, 7]. In cases where phase separation is driven by diffusion, these coarsening processes may be modeled using kinetic Ising models with locally conserved magnetization, e.g., the spin-exchange Kawasaki-Ising model [1, 8, 9] (for details see Sec. 1.3.2). The possible spin values \((s = \pm 1)\) represent the two species of particles that are demixing. The coarse-grained order parameter (magnetization) of such models is described by the Cahn-Hilliard-Cook (CHC) equation [10, 11] or Model B [12]. In the dilute limit, where droplets of the minority phase grow in a homogeneous background, Lifshitz and Slyozov (LS) have shown that the average domain size increases as \(L(t) \sim t^\phi\), where \(t\) is the time after the quench and \(\phi = 1/3\) [13]. Huse [14] has shown that the LS growth
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law also applies to the case where there are approximately equal fractions of the two phases.

Apart from the domain growth laws, experimentalists are also interested in quantitative features of the phase-separating morphologies. An important experimental quantity is the time-dependent structure factor \( S(\vec{k}, t) \) (\( \vec{k} \) being the wave vector) or its Fourier transform, the correlation function \( C(\vec{r}, t) \). Our understanding of \( S(\vec{k}, t) \) for a phase-separating system is relatively limited. The structure factor exhibits dynamical scaling, \( S(\vec{k}, t) \approx L^d f(kL) \), where \( d \) is the dimensionality. It has a single peak at the inverse of the characteristic length scale, \( k_m \sim L(t)^{-1} \). With the passage of time, \( k_m \to 0 \) as \( k_m \sim t^{-\theta} \). We also know the behavior of \( S(\vec{k}, t) \) in the limits \( k \to 0 \) [i.e., \( S(\vec{k}, t) \sim k^4 \)] [15, 16] and \( k \to \infty \) [i.e., \( S(\vec{k}, t) \sim k^{-(d+1)} \)] (see Sec. 1.6.2). The latter result is known as Porod’s law, and is a result of scattering from sharp interfaces [17]. However, there is still no theory which describes the complete functional form of \( S(\vec{k}, t) \).

In this chapter, we study the phase-separation dynamics of a binary mixture with a specific interest in the structure factor. In particular, we study the effect of a time-dependent variation of temperature on \( S(\vec{k}, t) \). There have been several studies of phase separation with a time-dependent temperature [18, 19, 20]. The general question which motivates our study is whether it is possible to create a domain morphology with a predefined structure factor by temporal variation of external parameters. This issue is of great technological importance, especially in the context of tailoring micro-structures and nano-structures. The present study is a first step in this direction.

In this context, we study phase separation via computer simulations of (a) the conserved Kawasaki-Ising model; and (b) the CHC model. In contrast to most earlier studies of this problem, we change external parameters (e.g., temperature) during the simulation to influence the shape of the structure factor. We consider a simple protocol for variation of the temperature, viz., the temperature is cycled between high and low values. Depending on the frequency and amplitude of the cycling, we obtain structure factors with multiple peaks, instead of the usual single peak.

This chapter is organized as follows. In Sec. 2.2, we present comprehensive Monte Carlo (MC) results for the Kawasaki-Ising model (for detail discussion on
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Kawasaki Ising model, see Sec. 1.3.2) subjected to a cyclical variation of the temperature. We also present analytical arguments to understand the evolution of the structure factor and correlation function during the heating part of the cycle. In Sec. 2.3, we present analogous results for the CHC model, which is the coarse-grained counterpart of the Kawasaki-Ising model. Finally, Sec. 2.4 concludes this chapter with a summary and discussion.

2.2 Phase Separation in the Kawasaki-Ising Model with A Time-Dependent Temperature

A binary mixture (AB) is usually described by the Ising model, with Hamiltonian

\[ H = -J \sum_{\langle ij \rangle} s_i s_j, \quad s_i = \pm 1. \]  

(2.1)

Here, \( s_i \) denotes the spin variable at site \( i \). We consider two-state spins: \( s_i = +1 \) denotes an A-atom and \( s_i = -1 \) denotes a B-atom. If the exchange interaction \( J \) is positive, the system segregates into A-rich and B-rich regions below the miscibility gap. In Eq. (2.1), the subscript \( \langle ij \rangle \) denotes a summation over nearest-neighbor pairs \( i \) and \( j \). The total magnetization \( M = \sum_{i=1}^{N} s_i \) (\( = N_A - N_B \), where \( N_A \) and \( N_B \) are total numbers of A and B, respectively) is a conserved quantity. We associate stochastic dynamics with the Ising model by placing it in contact with a heat bath (cf. Sec. 1.3). The appropriate dynamics for the phase-separation problem is spin-exchange kinetics or Kawasaki kinetics [8, 9].

It is straightforward to implement a MC simulation of the Ising model with spin-exchange kinetics. In a single step of MC dynamics, we choose at random a pair of adjacent spins on the lattice. The change in energy \( \delta H \) that would occur if the spins were exchanged is computed. The step is then accepted or rejected with Metropolis acceptance probability [21, 22]:

\[ P = \begin{cases} 
  e^{-\beta \delta H} & \text{if } \delta H > 0, \\
  1 & \text{if } \delta H < 0.
\end{cases} \]  

(2.2)

Here, \( \beta = (k_B T)^{-1} \) denotes the inverse temperature (for more detail see Sec. 1.3.1). In the simulations reported here, the temperature has a time-dependent
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form $T(t)$. This stochastic move is repeated many times. One Monte Carlo step (MCS) is completed when this algorithm is performed $N$ times (where $N$ is the total number of spins), regardless of whether the move is accepted or rejected.

All our simulations have been performed on a 2-dimensional Kawasaki-Ising model, defined on a square lattice of size $L^2$ ($L = 512$) with periodic boundary conditions. The simulation starts with a randomly-mixed state with equal numbers of up and down spins ($\rho = 0.5$ is the density of up or down spins, which corresponds to a mean magnetization $m = 0$). At time $t = 0$, the system is quenched to a temperature $T = 1.5$, measured in units of $J$ ($T_c \approx 2.269$ for the 2-d Ising model on a square lattice). After the system has evolved for time $t_1$, we heat the system to $T = \infty$ (first heating), and allow it to evolve till time $t_2$. Therefore, the duration of the first heating period is $t_2 - t_1$. The system is then quenched again to $T = 1.5$ (second quench till time $t_3$), and then heated again (second heating till time $t_4$), etc. The precise temperature protocol followed in different simulations will be specified at the appropriate place.

2.2.1 First Quench

In Fig. 2.1, we show the evolution of the system after a quench to $T = 1.5$ at $t = 0$. The frames in this figure correspond to $t = 5 \times 10^4, 2 \times 10^5, 6 \times 10^5$ and $10^6$ MCS. Regions with $s_i = +1$ ($A$-rich) and $s_i = -1$ ($B$-rich) are marked in black and white, respectively. In Fig. 1.4, the system is quenched to a lower temperature $T = 1.0$; it has lesser thermal fluctuations and faster growth than Fig. 2.1. The structure of the evolving system is characterized by the correlation function:

$$C(\vec{r}_i, \vec{r}_j; t) \equiv \langle s_i s_j \rangle - \langle s_i \rangle \langle s_j \rangle = \langle s_i s_j \rangle - m^2. \quad (2.3)$$

Here, the angular brackets denote an averaging over the initial ensemble and different noise realizations. As the system is translationally invariant, the correlation function depends only on $\vec{r} = \vec{r}_j - \vec{r}_i$:

$$C(\vec{r}_i, \vec{r}_j; t) = C(\vec{r}_i, \vec{r}_i + \vec{r}_j; t) = C(\vec{r}_i, t). \quad (2.4)$$
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Figure 2.1: Evolution snapshots from a simulation of the Kawasaki-Ising model. The details of the simulation are provided in the text. The system size is $512^2$ and periodic boundary conditions are applied in both directions. The system was quenched from $T = \infty$ to $T = 1.5$ at time $t = 0$. The up spins (A-atoms) are marked in black, whereas the down spins (B-atoms) are unmarked. The snapshots correspond to different times, measured in Monte Carlo steps or MCS.

Actually, most experiments study the structure factor, which is the Fourier transform of the correlation function:

$$S\left(\vec{k}, t\right) = \sum_{\vec{r}} e^{i\vec{k} \cdot \vec{r}} C\left(\vec{r}, t\right).$$

(2.5)

Since the system is isotropic, we can improve statistics by spherically averaging the correlation function and the structure factor. The corresponding quantities are denoted as $C\left(r, t\right)$ and $S\left(k, t\right)$, respectively. The numerical results presented here are obtained as averages over 10 independent runs on systems of size $512^2$. In Fig. 2.2, we show the correlation function $[C\left(r, t\right)$ vs. $r]$ and the structure factor $[S\left(k, t\right)$ vs. $k]$ for three different times. Notice that we do not present here the usual scaling plot as in Fig. 1.14, where data sets at different times collapse onto a
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master function [23, 24]. The structure factor in Fig. 2.2(b) contains information about the presence of sharp interfaces (defects) in the phase ordering system. The tail of the structure factor decays as $S(k,t) \sim k^{-3}$, which is Porod's law in $d=2$ (cf. Sec. 1.6.2). The Porod tail only persists up to values of $k$ corresponding to the typical width of the wall, $k < \xi^{-1}$. Figures 2.1 and 2.2 will serve as a reference point for later results, obtained for a variety of cooling-heating cycles.

Finally, let us examine the time-dependence of the characteristic domain size $L(t)$. There are many equivalent definitions for measuring the domain size. For example, $L(t)$ can be defined as the point where the correlation function in Fig. 2.1 first crosses zero. Alternatively, we can define the length scale as the inverse of the location of the structure-factor peak [$L(t) \sim k_m^{-1}$], or the inverse of the first moment of the structure factor [$L(t) \sim \langle k \rangle^{-1}$]. All these definitions are equivalent in the scaling regime. In this chapter, we use the definition $L \sim k_m^{-1}$. In Fig. 2.3, we show the time-dependence of the length scale on a log-log plot. We see that the domain growth depicted in Fig. 2.1 is consistent with the LS growth law, $L(t) \sim t^{1/3}$ (cf. Sec. 1.6.1).

### 2.2.2 First Heating

After the system shown in Fig. 2.1 has evolved for time $t_1 = 10^6$ MCS, we suddenly heat the system to $T = \infty (\beta = 0)$. The preferred equilibrium structure is now the homogeneous state, and the domain structure will start melting. At $T = \infty$, all proposed spin exchanges will be accepted. On the average, each spin pair is exchanged once during 1 MCS. This means that every particle will make two steps, either along the x-axis or the y-axis. Therefore, within a few MCS, the domain walls get fuzzier and domains becomes less distinctive. Inside a domain, the concentration of particles with opposite spin increases.

We start the first heating with the final configuration (at $t_1 = 10^6$ MCS) in Fig. 2.1. We evolve the system for 700 MCS at temperature $T = \infty$. The snapshots of the resultant disordering dynamics are shown in Fig. 2.4. In Fig. 2.5, we show the evolution of the structure factor during the heating process in Fig. 2.4. We see that the structure factor retains a peak at small values of $k$ after heating for 700 MCS. The peak amplitude becomes lower as heating
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Figure 2.2: (a) Correlation function data \([C(r, t) \text{ vs. } r]\) at three different times after the first quench shown in Fig. 2.1. (b) Structure factor data \([S(k, t) \text{ vs. } k]\) for the same times as in (a). The line of slope \(-3\) denotes the Porod tail in \(d=2\), \(S(k, t) \sim k^{-3}\) as \(k \to \infty\).

The large values of \(k\) correspond to small-scale structure, which is seen to become disordered as the corresponding \(S(k, t)\) is flat. A homogeneous system of spins with magnetization \(m = 0\) (i.e., the initial state for the first quench) has \(S(k, 0) = 1\) in our units—the corresponding data set is denoted by a solid line in Fig. 2.5. The corresponding correlation function is \(C(r, 0) = \delta_{r,0}\). The solid lines...
superposed on the data sets for \( t = t_1 + 100, t_1 + 300, t_1 + 700 \) (during heating) will be explained shortly. The time-dependence of the length scale during the first heating is shown in Fig. 2.6.

We would like to know how the heating process influences the structure factor of the system. In other words, if \( S(\vec{k}, t_1) \) is the structure factor when heating starts, is it possible to predict \( S(\vec{k}, t) \) for \( t > t_1 \)? Recall that the particles are performing random walks in \( d=2 \). After \( t \) MCS of heating, the average displacement of a particle is \( \sqrt{2t} \). The corresponding probability distribution for a particle to be displaced \((x, y)\) from its initial position is

\[
g_{\vec{a}}(x, y) = g_{\vec{a}}(x) g_{\vec{a}}(y) = \frac{1}{\sqrt{2\pi \tilde{\sigma}^2}} e^{-x^2/(2\tilde{\sigma}^2)} \cdot \frac{1}{\sqrt{2\pi \tilde{\sigma}^2}} e^{-y^2/(2\tilde{\sigma}^2)},
\]

where \( \tilde{\sigma} = \sqrt{2t} \). The correlation function changes over time by convolution with the Gaussian distribution. The predicted correlation function after \((t-t_1)\) MCS of heating is

\[
C(x, y, t) = C(x, y, t_1) * g_{\vec{a}}(x) * g_{\vec{a}}(y)
= \frac{1}{2\pi \tilde{\sigma}^2} \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' C(x', y', t_1) \exp \left[ -\frac{(x-x')^2 + (y-y')^2}{2\sigma^2} \right],
\]

(2.7)

Figure 2.3: Time-dependence of domain size \([L(t)\) vs. \(t\)] for the evolution depicted in Fig. 2.1. The line of slope 1/3 denotes the Lifshitz-Slyozov (LS) growth law, \( L(t) \sim t^{1/3} \).
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Figure 2.4: Evolution snapshots from the Kawasaki-Ising model during the first heating period. The system was heated to $T = \infty$ at time $t_1 = 10^6$ MCS, corresponding to the final snapshot in Fig. 2.1. From top left, the frames show the system at $t = t_1 + 50$, $t_1 + 100$, $t_1 + 300$ and $t_1 + 700$ MCS.

where $\sigma^2 = 2(t - t_1)$. The above expression only applies for $r = \sqrt{x^2 + y^2} > 0$. In polar coordinates,

$$C(r, t) = \frac{e^{-r^2/(2\sigma^2)}}{2\pi\sigma^2} \int_0^\infty dr' r' C(r', t_1) \frac{e^{-r^2/(2\sigma^2)}}{2\pi} \int_0^{2\pi} d\theta' \exp \left( \frac{rr' \cos \theta'}{\sigma^2} \right)$$

$$= \frac{e^{-r^2/(2\sigma^2)}}{\sigma^2} \int_0^\infty dr' \frac{r'}{2\pi} \int_0^{2\pi} d\theta' \exp \left( \frac{rr' \cos \theta'}{\sigma^2} \right) I_0 \left( \frac{rr'}{\sigma^2} \right), \quad r > 0, \quad \text{(2.8)}$$

where $I_0(z)$ is the zeroth-order modified Bessel function [25].

For $r = 0$, we always have $C(r = 0, t) = 1$. This is clear from the definition in Eq. (2.3) as $s^2 = 1$, and $m = 0$ for a critical quench. In Fig. 2.7, we show simulation data for the correlation function at three different times in the first heating period. The solid lines denote the expression in Eq. (2.8), where $C(r, t_1)$
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Figure 2.5: Structure factor data for three different times during the first heating period shown in Fig. 2.4: $t = t_1 + 100$, $t_1 + 300$ and $t_1 + 700$ MCS. For comparison, we also plot the structure factor of the initial disordered state ($t = 0$); and the structure factor at the end of the first quench, $t_1 = 10^6$ MCS.

Figure 2.6: Time-dependence of domain size $[L(t) \text{ vs. } t - t_1]$ during the first heating period at temperature $T = \infty$. The duration of the first heating period is 700 MCS.
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Figure 2.7: Correlation function data \[C(r, t)\text{ vs. } r\] at three different times during the first heating period shown in Fig. 2.4. The solid lines denote the functional form in Eq. (2.8) with \(C(r, t_1)\) (correlation function at the end of the first quench) obtained numerically.

is obtained numerically. There is an excellent agreement between the simulation data and Eq. (2.8).

Next, we consider the structure factor, which is the Fourier transform of the correlation function. On the discrete lattice, we have for the correlation function [analogous to Eq. (2.7)]

\[
C(\vec{r}, t) = \sum_{\vec{r}'} C(\vec{r}', t_1) \exp \left[ -\frac{(\vec{r} - \vec{r}')^2}{2\sigma^2} \right] + [1 - a(t)] \delta_{\vec{r}, 0},
\]

where we have explicitly included the case \(\vec{r} = 0\). Here,

\[
a(t) = \sum_{\vec{r}'} C(\vec{r}', t_1) \exp \left( -\frac{\vec{r}'^2}{2\sigma^2} \right).
\]

The decay of \(a(t)\) with \(t\) is shown in Fig. 2.8. The corresponding expression for
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![Graph showing decay of \( a(t) \) with \( t - t_1 \) during the first heating. The solid line denotes \( C(0, t) \) from Eq. (2.8). The asymptotic behavior is described by \( a(t) \sim (t - t_1)^{-2} \).

In Fig. 2.9, we plot \( S(k, t) \) vs. \( k \) for three times in the first heating period. The solid lines denote the expression in Eq. (2.11), with \( S(k, t) \) obtained numerically. They are seen to be in excellent agreement with the numerical data. Notice that the Porod tail immediately disappears as we start heating. This is because the interfaces become fuzzy as particles at the interfaces start performing random walks. The flat portion of the structure factor has the value \( S(k, t) \sim 1 - a(t) \), which corresponds to the difference between \( C(\vec{r} = 0, t) = 1 \) and \( \lim_{r \to 0} C(r, t) = a(t) \) in Fig. 2.7. As \( t \to \infty \), \( a(t) \to 0 \) and \( S(k, t) \approx 1 \), which corresponds to the initial homogeneous state in Fig. 2.5.

\[
S(\vec{k}, t) = \sum_{\vec{r}} e^{i\vec{k} \cdot \vec{r}} \sum_{\vec{r'}} C(\vec{r'}, t_1) \exp \left[ -\frac{(\vec{r} - \vec{r'})^2}{2\sigma^2} \right] + 1 - a(t)
\]

\[
\leq S(\vec{k}, t_1) e^{-k^2\sigma^2/2} + 1 - a(t).
\] (2.11)
2.2 Phase Separation in the Kawasaki-Ising Model with A Time-Dependent Temperature

2.2.3 Second Quench

In a single-quench experiment, the small-distance structure corresponds to the large-\(k\) part of the structure factor. This is the region where domain formation begins, with a peak emerging at large \(k\) and moving to smaller values of \(k\) as time progresses. As we have seen earlier, the large-\(k\) region after heating (see Fig. 2.5) resembles the homogeneous initial condition of a single-quench experiment. The heating process breaks up the domain structure, starting from the smallest length scales, and progressing to larger length scales. We expect that we can grow a second peak by continuing the evolution of the heated system in the previous subsection at a lower temperature. Therefore, we undertake a second quench at time \(t_2\). Again, the system is cooled to the temperature \(T = 1.5\).

Recall that we started our simulation with a homogeneous system having \(m = 0\). This system was evolved at \(T = 1.5\) for \(t_1 = 10^6\) MCS. Subsequently, it was heated for 700 MCS \((t_2 = t_1 + 700)\) at \(T = \infty\). Now, the temperature has been quenched again to \(T = 1.5\). The evolution snapshots for this second quench are shown in Fig. 2.10. The snapshots at \(t = t_2 + 200\) MCS and \(t = t_2 + 2000\) MCS clearly show the existence of structure on two length-scales. As we will see

![Figure 2.9](image)

Figure 2.9: Structure factor data \([S(k,t) \text{ vs. } k]\) at three times during the first heating period. The solid lines denote the expression in Eq. (2.11), with \(S(k,t_1)\) obtained numerically.
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![Figure 2.10: Evolution snapshots during the second quench period. The quench occurs at \( t_2 = t_1 + 700 \) MCS—the initial state is shown in the last snapshot of Fig. 2.4. The snapshots shown here correspond to \( t = t_2 + 200, t_2 + 2000, t_2 + 8000, t_2 + 20000 \) MCS.](image)

shortly, this two-scale morphology is characterized by a structure factor with two peaks.

The structure factor of a homogeneous system with equal number of up and down spins \((m = 0)\) is \( S(k, 0) \simeq 1 \). It is clear from Fig. 2.9 that it requires some amount of heating before the large-\(k\) part of \( S(k, t) \) reaches the value 1. We perform the second quench before \( S(k, t) \to 1 \) due to heating. The evolution of the corresponding two-peak structure factor is shown in Fig. 2.11. Notice that one of the peaks at \( k_1 \) (corresponding to the large-scale structure) is almost static, whereas the other peak at \( k_2 \) (corresponding to the small-scale structure) moves with time. The time-dependence of the relevant length scales, defined as \( L_1 = k_1^{-1} \) and \( L_2 = k_2^{-1} \), are shown in Fig. 2.12.

The flat region of the structure factor during first-heating, \( S(k, t) < 1 \), charac-
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Recall from Eq. (2.11) that the flat portion of the structure factor is

$$ S(k, t) \sim 1 - a(t), \quad (2.12) $$

where $a(t) \rightarrow 0$ as the heating continues. Therefore, the effective magnetization characterizes a homogeneous system with mean magnetization different from 0.
of the corresponding homogeneous system is

\[ m_{\text{eff}}(t) = \sqrt{\alpha(t)}, \quad (2.13) \]

and the effective density is

\[ \rho_{\text{eff}} = \frac{1 + \sqrt{\alpha(t)}}{2}. \quad (2.14) \]

We can now obtain a better understanding of the growth of the second peak during the second quench. The heating period during first-heating was 700 MCS. At the end of this time period, we estimate the flat portion of the structure factor as \( S(\vec{k}, t) \approx 0.98 \) from Fig. 2.5. This corresponds to \( m_{\text{eff}} \approx 0.14 \). For purposes of comparison, we undertake a conventional first-quench simulation of phase separation at \( T = 1.5 \). The initial condition consists of a homogeneous off-critical mixture with \( m_{\text{eff}} \approx 0.14 \). In Fig. 2.13, we compare the two-peak structure factor from our second-quench simulation with the usual one-peak structure factor from the off-critical (\( m_{\text{eff}} \approx 0.14 \)) simulation. Other than the first peak, the structure factors are in excellent agreement.

![Figure 2.13: Structure factors at \( t = t_2 + 2000, t_2 + 20000 \) MCS from Fig. 2.11. The solid lines denote the structure factors obtained from a single-quench simulation at \( t = 2000, 20000 \) MCS. The initial condition for this simulation was slightly off-critical with \( m_{\text{eff}} \approx 0.14 \).](image-url)
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The above results clarify the general scenario. The first quench leads to
typical phase-separation dynamics. When the system is heated, the do-
main domains homogenize (melt at small length-scales), but an imprint of the larger
domain scale survives. The second quench leads to the re-emergence of domains
from the homogeneous state. This is characterized by the usual LS growth law,
$L_2(t) \sim (t - t_2)^{1/3}$. This growing length scale coexists with the larger length scale
$L_1$, which is approximately static. If the second quench lasts sufficiently long,
$L_2$ becomes comparable to $L_1$—subsequently, the system segregates in the usual
manner.

2.2.4 Further Heating and Quenching

Now that the scenario is clear, we can generalize it to the case of multiple quench-
ing and heating. For example, we have performed a second-heating simulation at
$T = \infty$, by starting with the system at $t_3 = t_2 + 20000$ MCS (last snapshot in
Fig. 2.10). We heat the system up to $t_3 + 25$ MCS, and the resultant evolution
snapshots are shown in Fig. 2.14. In Fig. 2.15, we show the evolution of the
structure factor during the second heating period. As expected, the structure
starts melting at the smallest length scales, and this propagates to larger and
larger length scales. The solid lines denote the expression in Eq. (2.11) with the
appropriate functional form of $S(k, t_3)$.

Figure 2.14: Evolution snapshots during the second heating period, which starts at $t_3 = t_2 + 20000$
MCS—the initial state is shown in the final snapshot of Fig. 2.10.
2.3 Cahn-Hilliard-Cook Model with A Time Dependent Temperature

The third quench is performed at \( t_4 = t_3 + 25 \) MCS. The resultant evolution morphology in Fig. 2.16 has three length scales. The plot of \( S(k, t) \) vs. \( k \) in Fig. 2.17 shows that two of these are static and the third one increases with time. The time-dependence of these length scales is shown in Fig. 2.18. In general, \( n \) quenches give rise to a morphology with \( n \) length scales. However, we must be careful that the heating period is not so long that it washes out the structure existing at the end of the previous quench.

2.3 Cahn-Hilliard-Cook Model with A Time Dependent Temperature

In Sec. 2.2, we have described a method to generate a multi-scale structure for the Kawasaki-Ising model. Let us now approach this problem via the CHC model, which is the appropriate coarse-grained model for phase-separation dynamics (cf. Sec. 1.4.3). In this model, the system is described by an order parameter \( \psi(\vec{r}, t) = \rho_A(\vec{r}, t) - \rho_B(\vec{r}, t) \), where \( \rho_A \) and \( \rho_B \) denote the local densities of species A and
2.3 Cahn-Hilliard-Cook Model with A Time Dependent Temperature

$$t = t_4 + 80 \quad \quad t = t_4 + 400$$

Figure 2.16: Evolution snapshots during the third quench period. The quench occurs at $t_4 = t_3 + 25$ MCS—the initial state is shown in the final snapshot of Fig. 2.14.

Figure 2.17: Structure factors at three times during the third quench period.

B. The CHC equation for phase separation has following form:

$$\frac{\partial \psi (\vec{r}, t)}{\partial t} = \vec{\nabla} \cdot \left\{ D \vec{\nabla} \left[ -a(T_c - T) \psi + b\psi^3 - K \nabla^2 \psi \right] + \bar{b} (\vec{r}, t) \right\}. \quad (2.15)$$
2.3 Cahn-Hilliard-Cook Model with A Time Dependent Temperature

We will use the dimensionless version of the CHC equation [see Eq. (1.81)], which is obtained by a suitable rescaling of space, time and order parameter [26]:

\[
\frac{\partial}{\partial t} \psi (\vec{r}, t) = \vec{\nabla} \cdot \left\{ \vec{\nabla} \left[ \pm \psi + \psi^3 - \nabla^2 \psi \right] + \vec{\theta}(\vec{r}, t) \right\}, \tag{2.16}
\]

where

\[
\left\langle \vec{\theta}(\vec{r}, t) \right\rangle = 0,
\]

\[
\left\langle \vec{\theta}_i(\vec{r}', t') \vec{\theta}_j(\vec{r}'', t'') \right\rangle = 2\epsilon \delta_{ij} \delta(\vec{r}' - \vec{r}'') \delta(t' - t''). \tag{2.17}
\]

In Eq. (2.16), the + sign corresponds to \( T > T_c \) and the - sign corresponds to \( T < T_c \). For \( T > T_c \), which corresponds to the heating period, the nonlinear term is not relevant.

We implemented an Euler-discretized version of Eq. (2.16) with an isotropic Laplacian on a square lattice of size \( L \times L \) (\( L = 512 \)). Periodic boundary conditions were imposed in both directions. The discretization mesh sizes in space and time were \( \Delta x = 1.0 \) and \( \Delta t = 0.02 \), respectively. The initial condition consisted of small fluctuations about \( \psi_0 = 0 \), i.e., a critical quench. Finally, the thermal noise of strength \( \epsilon \) is mimicked by uniformly-distributed random numbers between \( [-A_n, A_n] \). (We obtain similar results if a Gaussian-distributed noise is
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used.) The appropriate noise amplitude in our Langevin simulation is

\[ A_n = \sqrt{\frac{3\epsilon}{(\Delta x)^6 \Delta t}}. \]  \hfill (2.18)

The results reported here correspond to \( \epsilon = 0.00042 \), i.e., \( A_n = 0.25 \) for \( \Delta x = 1.0 \) and \( \Delta t = 0.02 \).

In Fig. 2.19, we show evolution snapshots for the CHC system subjected to alternating cycles of cooling and heating, i.e., switching between the \(-\) and \(+\) signs in Eq. (2.16). The system is evolved (a) at \( T < T_c \) upto \( t_1 = 20000 \); (b) at \( T > T_c \) upto \( t_2 = t_1 + 500 \); (c) at \( T < T_c \) upto \( t_3 = t_2 + 800 \); (d) at \( T > T_c \) upto \( t_4 = t_3 + 40 \). The emergence of a two-scale structure is evident in the snapshot at \( t_3 = t_2 + 800 \), corresponding to the end of the second quench. As in the Kawasaki-Ising model, the cooling-heating cycles produce multiple length scales (see snapshots in Fig. 2.20 for the evolution after the third quench). The corresponding correlation functions and structure factors no longer show dynamical scaling. In Fig. 2.21, we show the structure factors at different stages of the evolution in Fig. 2.19. We show two data sets in the cooling periods \( [t = 20000 \ and \ t = t_2 + 800 \ in \ Fig. \ 2.21(a)] \), and two data sets in the heating periods \( [t = t_1 + 100 \ and \ t = t_3 + 10 \ in \ Fig. \ 2.21(b)] \). As expected, \( S(k, t) \) vs. \( k \) in the cooling periods shows a Porod tail. The data set for \( t = t_2 + 800 \) corresponds to the second quench, and shows a two-peak structure (cf. Fig. 2.11).

The data sets for \( S(k, t) \) vs. \( k \) in the heating periods show a characteristic flat behavior at large values of \( k \). Their functional form can be obtained from the CHC equation for \( T > T_c \):

\[ \frac{\partial}{\partial t} \psi(\vec{r}, t) = \vec{\nabla} \cdot \left[ \vec{\nabla} \psi + \tilde{\theta} (\vec{r}, t) \right]. \]  \hfill (2.19)

Equation (2.19) is obtained by neglecting the cubic and the fourth-derivative terms in Eq. (2.16). These terms are not relevant in the dynamics for \( T > T_c \). Consider the case when the system is heated at \( t = t_1 \). We can solve Eq. (2.19) in momentum space as follows:

\[ \psi\left(\vec{k}, t\right) = \psi\left(\vec{k}, t_1\right) e^{-k^2(t-t_1)} - i \int_{0}^{t-t_1} dt' \ e^{-k^2(t-t_1-t')} \left[ \vec{k} \cdot \tilde{\theta} \left(\vec{k}, t'\right) \right]. \]  \hfill (2.20)
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Figure 2.19: Evolution snapshots for the CHC system subjected to alternate cycles of cooling and heating. The switching times are as follows: $t_1 = 20000$ (end of first quench); $t_2 = t_1 + 500$ (end of first heating); $t_3 = t_2 + 800$ (end of second quench); $t_4 = t_3 + 40$ (end of second heating). The simulation details are provided in the text. Regions with $\psi > 0$ (A-rich) and $\psi < 0$ (B-rich) are marked in black and white, respectively. To the right of each snapshot, we show the variation of the order parameter along a cross-section at $y = L/2$, where $L$ is the lateral system size.
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This yields the structure factor as

\[
S(\vec{k}, t) = \langle \psi(\vec{k}, t) \psi(-\vec{k}, t) \rangle
= S(\vec{k}, t_1) e^{-2k^2(t-t_1)} + e^{-2k^2(t-t_1)} \times \\
\int_0^{t-t_1} dt' \int_0^{t-t_1} dt'' e^{k^2(t'+t'')} \left\langle \left[ \vec{k} \cdot \vec{\theta}(\vec{k}, t') \right] \left[ \vec{k} \cdot \vec{\theta}(-\vec{k}, t'') \right] \right\rangle.
\]

(2.21)

Thus, \( S(\vec{k}, t) \) is obtained in terms of \( S(\vec{k}, t_1) \) as

\[
S(\vec{k}, t) = S(\vec{k}, t_1) e^{-2k^2(t-t_1)} + \epsilon \left[ 1 - e^{-2k^2(t-t_1)} \right].
\]

(2.22)

The solid lines in Fig. 2.21(b) denote the functional form in Eq. (2.22), and are in reasonable agreement with the numerical data.

Figure 2.20: Evolution snapshots for the CHC system after the third quench at \( t_4 = 21340_7 \).
2.4 Summary and Discussion

Let us conclude this chapter with a summary and discussion of the results presented here. We consider the effect of a time-dependent variation of temperature on the morphology of a phase-separating binary mixture \((AB)\). We find that alternate cycles of cooling and heating give rise to a multiple-length-scale morphology. During a quench period, the resultant pattern contains imprints of (static) length scales from previous quenches, as well as a growing length scale from the most recent quench. On the other hand, during a heating period, there is a melting of the domain structure as the \(A, B\) particles perform random walks. We can use this picture to analytically obtain the structure factor \(S(k, t)\) during a heating period \([t_i, t_{i+1}]\) as a function of \(S(\vec{k}, t_i)\).

To confirm the above scenario, we have presented results from (a) Monte Carlo (MC) simulations of the Kawasaki-Ising model, and (b) Langevin simulations of the Cahn-Hilliard-Cook (CHC) model. The numerical results are in excellent agreement with our analytical results. The fabrication of multi-scale morphologies offers intriguing possibilities for technological applications. It also suggests the possibility that we can formulate temperature-variation protocols for the manufacture of materials with predesignated morphologies. Our work in this chapter is a modest first step in this direction.
2.4 Summary and Discussion

In future work, we intend to combine the work presented here with earlier work on the phase separation of mixtures of immiscible polymers [27]. This will allow us to study the interplay of temperature variations and polydispersity.
References


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