

Chapter 2

Linear Theory of Evolution to an Unstable State

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2.1 Introduction

The simple theory of nucleation that we introduced in Chapter 1 makes use of the idea that the metastable state is similar to an equilibrium state. If a quench brings the system into the unstable region, equilibrium ideas no longer apply, and we need to consider the laws governing the dynamical evolution. In this chapter we will discuss two models. The first model allows all extensive variables to fluctuate; that is, no extensive variables are conserved. In particular, the order parameter will be allowed to fluctuate. The system will be connected to a heat bath so that the temperature is fixed, and hence the energy will also fluctuate. The second model will have one conserved extensive quantity, the order parameter.

To investigate dynamical models we will use the same coarse grained approach employed in Chapter 1. We begin by considering the evolution of the order parameter. For a one-component fluid the global order parameter is the time-dependent density with $\int \psi(\vec{x}, t) d\vec{x} = \rho(t)$. From thermodynamics we know that

$$\frac{\partial \rho(t)}{\partial t} = -M\mu(t). \quad (2.1)$$

where the proportionality constant M is the mobility, and $\mu(t)$ is the time dependent

chemical potential. We also have

$$\mu(t) = \frac{\partial F(\rho)}{\partial \rho(t)}. \quad (2.2)$$

For the coarse grained model we will assume that these relations also hold so that

$$\frac{\partial \psi(\vec{x}, t)}{\partial t} = -M\mu(\vec{x}, t) \quad (2.3)$$

and

$$\mu(\vec{x}) = \frac{\delta F(\psi(\vec{x}, t))}{\delta \psi(\vec{x}, t)}, \quad (2.4)$$

where the derivative in Eq. (2.4) is the functional derivative and $F(\psi)$ is a functional of $\psi(\vec{x}, t)$. Recall that in the coarse grained model $\psi(\vec{x}, t) = b^{-d} \sum s_i$, where b is the coarse grained block size, and the sum is over all the spins (in magnetic language) in the block. Fluctuations of length scales less than b are ignored so we have to choose $b \gg a$, where a is a microscopic length scale such as the lattice constant or molecular size of a particle. We also have to choose b to be much less than any important length scale such as the correlation length or the droplet size if we are considering nucleation.

We assume that the form of $F(\psi)$ is given by Eq. (1.9), the Landau-Ginzburg model. From Eq. (1.9), Eqs. (2.3) and (2.4) we obtain

$$\frac{\partial \psi(\vec{x}, t)}{\partial t} = -M \left[-R^2 \nabla^2 \psi(\vec{x}, t) + 2\epsilon \psi(\vec{x}, t) + 4\psi^3(\vec{x}, t) - h \right]. \quad (2.5)$$

This dynamical model is usually referred to as model *A* in the Hohenberg-Halperin classification [Hohenberg and Halperin 1977] or the Langevin equation for the non-conserved order parameter [Gunton et al. 1983].

For the conserved order parameter we have

$$\frac{\partial \psi(\vec{x}, t)}{\partial t} = M \vec{\nabla} \cdot J(\psi), \quad (2.6)$$

where $J(\psi)$ is the current and

$$J(\psi) = \vec{\nabla} \mu(\vec{x}). \quad (2.7)$$

We use Eqs. (1.9), (2.4), (2.6), and (2.7) to obtain

$$\frac{\partial \psi(\vec{x}, t)}{\partial t} = M \nabla^2 \left[-R^2 \nabla^2 \psi(\vec{x}, t) + 2\epsilon \psi(\vec{x}, t) + 4\psi^3(\vec{x}, t) \right]. \quad (2.8)$$

Equation (2.8) is model *B* in the Hohenberg-Halperin classification.

Several comments are in order. First Eq. (2.6), the continuity equation, imposes a local conservation condition on the order parameter. Secondly, Eqs. (2.5) and (2.8) are mean-field for the same reason that Eq. (1.11) is mean-field. Finally, these equations of motion are nonlinear so that complicated behavior may result. We are interested in the evolution of two quantities: the order parameter $\psi(\vec{x}, t)$ which can be measured directly only in simulations and the correlation function

$$\langle \psi(\vec{x}, t) \psi(\vec{x}', t) \rangle - \langle \psi(\vec{x}, t) \rangle \langle \psi(\vec{x}', t) \rangle, \quad (2.9)$$

which can be related to scattering measurements. The notation $\langle \dots \rangle$ refers to an ensemble average.

The quantity actually related to experimental measurements is the structure factor $S(\vec{k}, t)$, which is the Fourier transform of the correlation function. If the system is isotropic and the potential spherically symmetric, then (see the Supplementary Notes)

$$S(\vec{k}, t) \propto \langle \hat{\psi}(\vec{k}, t) \hat{\psi}(-\vec{k}, t) \rangle. \quad (2.10)$$

2.2 Continuous ordering

We first consider continuous ordering for a critical quench. A critical quench is a quench at the critical concentration ($m = 0$ in an Ising model) if the order parameter conserved, or at $h = 0$ if it is not. All quenches will be instantaneous and in this chapter we will only consider the linear theory. We begin at $h = 0$ with $T > T_c$ and instantaneously lower the temperature to $T < T_c$ with $h = 0$. The spatially averaged order parameter is $\psi = 0$ before the quench and is zero immediately after the quench. Note also from Eq. (1.11) that $\partial^2 f(\psi) / \partial \psi^2 < 0$ at $\psi = 0$ for $\epsilon < 0$ so that the system is unstable. We will investigate the initial evolution away from $\psi = 0$ described by $\psi(\vec{x}, t) = \psi(\vec{x}, 0) + u(\vec{x}, t) = u(\vec{x}, t)$, which is assumed to be small during the time we are studying. With this assumption we can linearize Eq. (2.5) as

$$\frac{\partial u(\vec{x}, t)}{\partial t} = -M \left[-R^2 \nabla^2 u(\vec{x}, t) - 2|\epsilon| u(\vec{x}, t) \right], \quad (2.11)$$

where $T < T_c$ or $\epsilon < 0$.

We now assume

$$u_\lambda(\vec{x}, t) = e^{\lambda t} \phi(\vec{x}), \quad (2.12)$$

and substitute Eq. (2.12) into Eq. (2.11). The result is

$$\lambda \phi(\vec{x}) = M \left[R^2 \nabla^2 \phi(\vec{x}) + 2|\epsilon| \phi(\vec{x}) \right]. \quad (2.13)$$

The Fourier transform of Eq. (2.13) is

$$\lambda = M[-R^2k^2 + 2|\epsilon|], \quad (2.14)$$

where

$$\phi(\vec{x}) \propto e^{i\vec{k}\cdot\vec{x}}, \quad (2.15)$$

and $k = |\vec{k}|$.

The general solution of Eq. (2.11) is

$$u(\vec{x}, t) = \int c(\vec{k}) e^{i\vec{k}\cdot\vec{x}} e^{M(-R^2k^2+2|\epsilon|)t} d\vec{k}, \quad (2.16)$$

where the coefficients $c(\vec{k})$ are determined by the initial conditions. Modes with $R^2k^2 > 2|\epsilon|$ decay with time, and modes with $R^2k^2 < 2|\epsilon|$ grow exponentially with time. This instability is the one we have been seeking and is the reason that equilibrium methods do not work in the unstable region. For t very large, the $k = 0$ mode dominates the growth. We have assumed implicitly that the linear theory is valid for such large times.

What is the time dependence of the structure factor? From the previous discussion we have

$$\hat{u}(\vec{k}, t) = c(\vec{k}) e^{(-R^2k^2+2|\epsilon|)t}. \quad (2.17)$$

In the linear approximation for a critical quench

$$S(\vec{k}, t) \propto \hat{u}(\vec{k}, t) \hat{u}(-\vec{k}, t) \quad (2.18)$$

or

$$S(\vec{k}, t) \propto \langle c(\vec{k}) c(-\vec{k}) \rangle e^{2(-R^2k^2+2|\epsilon|)t}. \quad (2.19)$$

Note that there is a factor of the form $e^{D(k)t}$, which we will call the amplification factor, which appears in the evolution of both the order parameter in Eq. (2.16) and the structure factor in Eq. (2.19), where $D(k)$ is given by

$$D(k) = -R^2k^2 + 2|\epsilon|. \quad (2.20)$$

Because the quench is instantaneous, the structure at $t = 0$ is the structure of the equilibrium state before the quench. Therefore $\langle c(\vec{k}) c(-\vec{k}) \rangle$ is the equilibrium structure factor at the start of the quench. If we quench from $T = \infty$, the equilibrium structure factor is zero because there are no correlations at $T = \infty$. This result implies from Eq. (2.19) that the structure factor would remain zero for all t after the quench, a prediction that is clearly not correct. The problem is that we have neglected fluctuations. To see why, we need to take a closer look at mean-field theories.

2.3 Mean-field theory and fluctuations

There are many ways to derive mean-field theories. The one that we will use was first proposed by Kac, Uhlenbeck, and Hemmer and refined by Lebowitz and Penrose [1983]. We will consider the Ising model in the lattice gas representation, so that conservation of particles is natural. In the language of spins this conditions means we consider over all configurations consistent with a fixed magnetization. We will use fluid language so that the partition function in the canonical ensemble is given by

$$Z = \frac{1}{N!} \int d\{\vec{x}_i\} e^{\sum_{ij} K(x_{ij})}. \quad (2.21)$$

We assume

$$K(x_{ij}) = -\beta \gamma^d v(\gamma x_{ij}), \quad (2.22)$$

where $\gamma = R^{-1}$ and there are no restrictions on $v(\gamma x_{ij})$ except that

$$\int \gamma^d v(\gamma x) d\vec{x} = 1. \quad (2.23)$$

We will also assume that $v(\gamma x_{ij}) \geq 0$ for all i, j .

If we make a change of variables $\vec{y} = \gamma \vec{x}$, we obtain

$$\int v(y) d\vec{y} = 1. \quad (2.24)$$

We see that doing an integral removes a factor of γ^d . More precisely, the length scale of the lattice spacing is no longer the fundamental physical length scale. Instead the scale is now $\gamma^{-1} = R$. All lengths must be scaled with the interaction range.

We define the Mayer function [Hill 1956, Gould and Tobochnik 2010] as

$$f(x_{ij}) = e^{K(x_{ij})} - 1. \quad (2.25)$$

With this definition the partition function can be written as

$$Z = \frac{1}{N!} \int d\{\vec{x}_i\} \prod_{i \neq j} \left(f(x_{ij}) + 1 \right). \quad (2.26)$$

We can now expand the product in Eq. (2.26) and write the partition function as a sum of products of Mayer functions. We can then group the terms in the expanded product into classes. For example, there is a term in the partition function that has the form

$$\int d\{\vec{x}_i\} \sum_{\text{pairs}} f(x_{ij}), \quad (2.27)$$

which equals

$$\frac{V^N}{2} \rho \int f(x) d\vec{x}. \tag{2.28}$$

for $N \gg 1$. In Eq. (2.28) V is the volume and ρ is the number density.

In this way the partition function can be written as a sum of products of Mayer functions which are generic. That is, the terms do not refer to specific particles but can be grouped into two particle graphs, three particle graphs, etc. However this classification is not quite good enough. To see this we need to introduce Mayer graphs. In a Mayer graph each vertex corresponds to a particle and each line to a factor of $f(x)$ which we will refer to as a Mayer bond as well as a Mayer function. For example, the term $f(x_{12})$ is represented by the graph in Fig. 2.1. Within the classes of for example, three particle graphs, there are two distinct subclasses which are topologically different. One three particle graph corresponding to $f(x_{12})f(x_{23})$ is shown in Fig. 2.3(a) and the other corresponding to $f(x_{12})f(x_{13})f(x_{23})$ is given in Fig. 2.3(b). Note that the number of lines is equal to the number of Mayer functions or bonds in the expansion of the partition function and the number of vertices minus one is equal to the number of restricted integrals left to perform. One integral always gives a factor of V due to the homogeneity of space. A restricted integral is one which does not range over the entire volume but is restricted by the range of the potential through the Mayer function.

We now choose for $K(x_{ij})$ the Kac potential in Eq. (2.22). The Mayer function is now expanded in a power series in γ^d .

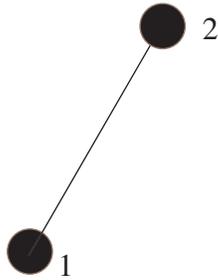


Figure 2.1: Mayer diagram corresponding to $f(x_{12})$.

To first order in γ^d , $f(x) = \gamma^d v(\gamma x)$. Consequently each line in a graph carries a weight proportional to γ^d . In our expression for the partition function all particles, and hence all vertices imply a corresponding integration. As discussed after Eq. (2.23), each restricted integral removes a factor of γ^d . Or more precisely, each restricted integral when rescaled absorbs a factor of γ^d in the rescaling. In the limit $\gamma \rightarrow 0$, the only graphs that contribute are not proportional to γ^d and are thus the tree graphs, that is, graphs with

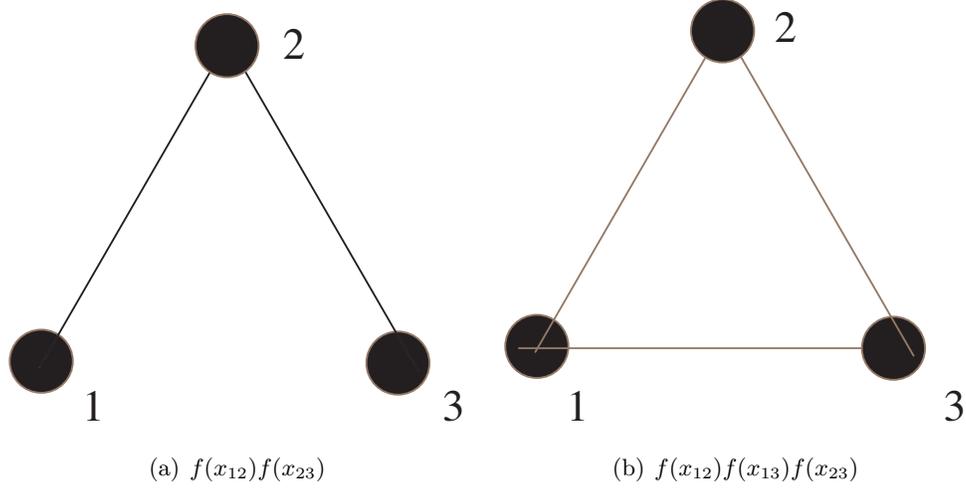


Figure 2.2: Mayer diagrams for three vertices.

no loops. Each loop implies one more Mayer bond than an integration and hence a factor of γ^d remains. Hence for mean-field thermodynamics the only contribution in the limit $\gamma \rightarrow 0$ comes from tree graphs.

What about fluctuations? Fluctuations imply correlations. We can see this relation from the correlation function in Eq. (2.9). If there are no fluctuations, then $\langle \psi(\vec{x}) \rangle = \psi(\vec{x})$ because there is only one state. Moreover, $\langle \psi(\vec{x})\psi(\vec{x}') \rangle = \psi(\vec{x})\psi(\vec{x}')$ for the same reason. From Eq. (2.9) the correlation function is zero. Hence, no fluctuations implies no correlations.

What is the correlation function in the lattice gas model with a Kac potential? The correlation function in fluid language is the probability that there is a particle at \vec{x}_1 given that there is a particle at \vec{x}_2 [$\rho_2(\vec{x}_1, \vec{x}_2)$] minus the probability that there is a particle at \vec{x}_1 [$\rho_1(\vec{x}_1)$] times the probability that there is a particle at \vec{x}_2 . We write

$$\rho_2(\vec{x}_1, \vec{x}_2) = \frac{1}{N!} \frac{1}{Z} \int d\vec{x}_3 \cdots d\vec{x}_N e^{\sum_{ij} K(x_{ij})}, \quad (2.29)$$

and

$$\rho_1(\vec{x}_1) = \frac{1}{N!} \frac{1}{Z} \int d\vec{x}_2 \cdots d\vec{x}_N e^{\sum_{ij} K(x_{ij})}, \quad (2.30)$$

where Z is given by Eq. (2.21). There is a similar expression for $\rho_1(\vec{x}_2)$ with the obvious changes of notation.

Graphical expansions can be developed for $\rho_2(\vec{x}_1, \vec{x}_2)$ and $\rho_1(\vec{x}_1)$ in the analogous way as we did for the partition function with two significant differences. These graphs will

contain root points, that is, vertices that are not integrated. This difference follows from the absence of integration over particles 1 and 2 in Eq. (2.29) and particle 1 in Eq. (2.30). The second important difference is that the only graphs that give a nonzero contribution to the correlation function are graphs that connect particles 1 and 2. Although this result can be proven [Stell 1964] it is easy to see that it must be so. If the distance $|\vec{x}_1 - \vec{x}_2|$ is taken to infinity, then there will be no correlation between particles 1 and 2, which implies that

$$\lim_{|\vec{x}_1 - \vec{x}_2| \rightarrow \infty} \rho_2(\vec{x}_1, \vec{x}_2) - \rho_1(\vec{x}_1)\rho_1(\vec{x}_2) = 0. \quad (2.31)$$

However, the only graphs that are affected by the separation of particles 1 and 2 are those that connect these two particles via Mayer bonds. Because all graphs give a zero contribution when $|\vec{x}_1 - \vec{x}_2| = x_{12} \rightarrow \infty$, the graphs that are independent of x_{12} must give zero contribution for all values of x_{12} .

From this discussion we see that all graphs associated with the pair correlation function in Eq. (2.9) have at least one factor of γ^d . Consider, for example, the graph in Fig. 2.4 which appears in the expansion of the pair correlation function. The root points are designated by open circles and stand for particles 1 and 2. These points are not integrated. The filled circle is called a field point and all field points indicate an integral. As before all represent a Mayer function and hence in the case of the Kac potential contribute a factor of γ^d . The graph in Fig. 2.4 has two Mayer bonds but only one field point or integration and hence is of order γ^d . Then to zeroth order correlation functions are zero and hence there are no fluctuations.

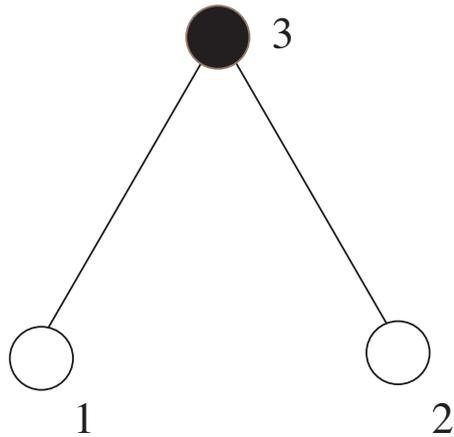


Figure 2.3: Term in the graphical expansion of the pair correlation function. Open circles are root points and filled circles are field points.

However, this conclusion is not the whole story. The *static* structure factor $S(\vec{k})$,

which is the time independent, equilibrium version of Eq. (2.10) is related to the isothermal compressibility κ_T as

$$\lim_{\vec{k} \rightarrow 0} S(\vec{k}) \propto \kappa_T. \quad (2.32)$$

The integral in the Fourier transform used to obtain the structure factor from the correlation function removes a factor of γ^d so that the isothermal compressibility in Eq. (2.32) is of zeroth order. In other words the correlation function to order γ^d leads to the isothermal compressibility and structure factor to order zero in γ^d . Hence if we wish to describe experimental measurements of the structure factor, even in a mean-field context, we must include fluctuations in our description of the correlation function.

The simplest way to do include fluctuations is to add a term to the Landau-Ginzburg free energy of the form

$$\int \eta(\vec{x}, t) \psi(\vec{x}, t) d\vec{x}, \quad (2.33)$$

where $\eta(\vec{x}, t)$ is a Gaussian random noise. The only restrictions on $\eta(\vec{x}, t)$ are that

$$\langle \eta(\vec{x}, t) \rangle = 0 \quad (2.34)$$

and

$$\langle \eta(\vec{x}, t) \eta(\vec{x}', t') \rangle = k_B T \delta(\vec{x} - \vec{x}') \delta(t - t'). \quad (2.35)$$

2.4 Return to continuous ordering

To obtain $u(\vec{x}, t)$ we need to solve

$$\frac{\partial u(\vec{x}, t)}{\partial t} = -M \left[-R^2 \nabla^2 u(\vec{x}, t) - 2|\epsilon| u(\vec{x}, t) \right] + \eta(\vec{x}, t). \quad (2.36)$$

instead of Eq. (2.11). The solution, of course, is the sum of two terms. One is the solution to the homogeneous equation and is given by Eq. (2.16). The second is the solution to the inhomogeneous equation and can best be obtained by transforming Eq. (2.36) into Fourier space. That is, we wish to solve

$$\frac{\partial \hat{u}(\vec{k}, t)}{\partial t} = M \left[-R^2 k^2 \hat{u}(\vec{k}, t) + 2|\epsilon| \hat{u}(\vec{k}, t) \right] + \hat{\eta}(\vec{k}, t). \quad (2.37)$$

The homogeneous solution to Eq. (2.37) is given by Eq. (2.17). To obtain the inhomogeneous solution we solve for the Green's function

$$\frac{\partial G(t, t')}{\partial t} + M \left[R^2 k^2 - 2|\epsilon| \right] G(t, t') = \delta(t - t'). \quad (2.38)$$

We take the Fourier transform with respect to time and find

$$\hat{G}(\omega) = \frac{e^{-i\omega t'}}{i\omega + M[R^2 k^2 - 2|\epsilon|]}. \quad (2.39)$$

If we invert the Fourier transform, we obtain

$$G(t, t') = \frac{-i}{2\pi} \int \frac{e^{i\omega(t-t')}}{\omega - iM[R^2 k^2 - 2|\epsilon|]} d\omega. \quad (2.40)$$

We can do the inversion as a contour integral. We impose the causality condition (retarded Green's function) so that $t > t'$, close the contour in the upper half plane for $R^2 k^2 > 2|\epsilon|$, and analytically continue to values of k for which $R^2 k^2 < 2|\epsilon|$. The result is

$$G(t, t') = G(t - t') = e^{-(t-t')M(R^2 k^2 - 2|\epsilon|)}. \quad (2.41)$$

Hence the solution to Eq. (2.37) is

$$\hat{u}(\vec{k}, t) = \hat{c}(\vec{k})e^{M(-R^2 k^2 + 2|\epsilon|)t} + \int_0^t \eta(\vec{k}, t')G(t - t')dt'. \quad (2.42)$$

To obtain the structure factor we again form the product $\langle \hat{u}(\vec{k}, t)\hat{u}(\vec{k}', t) \rangle / V$, where we have made the V^{-1} term explicit (see Supplementary Notes). From Eq. (2.42) we find

$$\begin{aligned} \frac{1}{V} \langle \hat{u}(\vec{k}, t)\hat{u}(\vec{k}', t) \rangle &= \frac{1}{V} \langle \hat{c}(\vec{k})\hat{c}(-\vec{k}) \rangle e^{2D(k)t} \\ &+ \frac{1}{V} \int_0^t \int_0^t \langle \eta(\vec{k}, t')\eta(-\vec{k}, t'') \rangle G(t - t')G(t - t'')dt'dt'', \end{aligned} \quad (2.43)$$

where we have used Eq. (2.34) to eliminate the cross terms. From Eq. (2.35) and the discussion in the Supplementary Notes we have

$$\frac{1}{V} \langle \eta(\vec{k}, t')\eta(-\vec{k}, t'') \rangle = k_B T \delta(t' - t''). \quad (2.44)$$

We then use Eq. (2.44) and Eq. (2.41) to rewrite Eq. (2.43) as

$$S(k, t) = S_0(k)e^{2D(k)t} + \frac{1}{2D(k)} [e^{2D(k)t} - 1], \quad (2.45)$$

where we have set $S_0(k) = \langle \hat{c}(\vec{k})\hat{c}(-\vec{k}) \rangle / V$ to make explicit that for instantaneous quenches this term is the equilibrium structure factor at the temperature at which the quench initiated.

Now we have a result that makes sense. The first term in Eq. (2.45) is the Cahn-Hilliard term [Gunton et al. 1983, Cahn and Hilliard 1959, Cahn 1961, Cook 1970], which describes the evolution of modes present in the system at the quench. The second term in Eq. (2.45) is the Cook [Gunton et al. 1983, Cook 1970] term which describes us how the modes associated with the fluctuations present at the quench temperature evolve.

Two final points. The time scale for the evolution described by Eq. (2.45) is set by $D(k)$ and hence by $|\epsilon|$. As $\epsilon \rightarrow 0$, that is, as the critical point is approached, the growth of the unstable modes decreases down. Because the mode at $k = 0$ grows the fastest, we see that the characteristic time $\tau \sim \epsilon^{-1} \propto \xi^2$, where ξ is the correlation length. This behavior is an example of *critical slowing down*. In general, $\tau \sim \xi^z$ near a critical point, where z is different from 2. The value of $z = 2$ is the mean-field result for model A. The second point is that a off-critical quench is more difficult to describe. The reason is that in addition to the small perturbation, there is a large amplitude $k = 0$ mode for small time which cannot be treated linearly. For that reason we will delay our discussion of off-critical quenches to a later chapter. We next consider spinodal decomposition for both critical and off-critical quenches.

2.5 Spinodal decomposition

Spinodal decomposition is the evolution of a system with a conserved order parameter that is quenched into the unstable region. To describe this evolution we return to Eq. (2.8) with the addition of a noise term as we discussed for continuous ordering. We need to solve the equation

$$\frac{\partial \psi(\vec{x}, t)}{\partial t} = M \nabla^2 \left[-R^2 \nabla^2 \psi(\vec{x}, t) - 2|\epsilon| \psi(\vec{x}, t) + 4\psi^3(\vec{x}, t) \right] + \eta(\vec{x}, t), \quad (2.46)$$

where $\eta(\vec{x}, t)$ satisfies Eq. (2.34), and

$$\langle \eta(\vec{x}, t) \eta(\vec{x}', t') \rangle = -k_B T \nabla^2 \delta(\vec{x} - \vec{x}') \delta(t - t'). \quad (2.47)$$

We will follow a procedure which is almost identical to the procedure for continuous ordering. We first linearize Eq. (2.46) by assuming

$$\psi(\vec{x}, t) = \psi_0 + w(\vec{x}, t), \quad (2.48)$$

where $w(\vec{x}, t)$ is assumed to be small throughout the time period we are studying. We substitute Eq. (2.48) into Eq. (2.46) and keep only terms linear in $w(\vec{x}, t)$ and obtain

$$\frac{\partial w(\vec{x}, t)}{\partial t} = M \nabla^2 \left[-R^2 \nabla^2 w(\vec{x}, t) - 2|\epsilon| w(\vec{x}, t) + 12\psi_0^2 w(\vec{x}, t) \right] + \eta(\vec{x}, t). \quad (2.49)$$

Equation (2.49) can be solved by the same methods used for continuous ordering. For the order parameter we obtain

$$\hat{w}(\vec{k}, t) = \hat{d}(k)e^{\tilde{D}(k)t} + \int_0^t \eta(\vec{k}, t')\tilde{G}(t-t') dt', \quad (2.50)$$

where

$$\tilde{D}(k) = -k^2 M[R^2 k^2 - 2|\epsilon| + \psi_0^2], \quad (2.51)$$

and

$$\tilde{G}(t-t') = e^{(t-t')\tilde{D}(k)}. \quad (2.52)$$

For the structure factor we obtain

$$S(k, t) = S_0(k)e^{2\tilde{D}(k)t} + \frac{1}{2}\tilde{D}(k)[e^{\tilde{D}(k)t} - 1]. \quad (2.53)$$

If we compare Eq. (2.45) and Eq. (2.53), we see that the only difference is the form of the functions $D(k)$ and $\tilde{D}(k)$ given in Eqs. (2.20) and Eq. (2.26), respectively. For continuous ordering the fastest growing mode is at $k = 0$. In contrast, the fastest growing mode (for large t) in spinodal decomposition is at

$$k^2 = \frac{|\epsilon| - 6\psi_0^2}{R^2}. \quad (2.54)$$

Both theories predict that the growth of the structure factor is exponential. The difference at this point appears to be minor but, as we shall see, the later time evolution, which is described by a nonlinear theory, is quite different. We shall see that even in the linear regime there are significant differences.

We have introduced the linear theory, which assumes that $u(\vec{x}, t) \ll 1$ or $w(\vec{x}, t) \ll 1$. The linear theory is not valid for all times. As we shall see, the duration for which it is valid depends on the material or system under study. Some materials will be properly described by the linear theory up to $t_0 \gg 1$, but for others it is not clear that there is any time for which the linear theory is applicable.

2.6 Experimental data

In Figs. 2.5 and 2.6 we plot the structure factor as a function of k for various times after the quench. The data is for a two-dimensional Ising model with several values of the interaction range. The parameter q is the number of spins with which one spin interacts. Figure 2.5 is for continuous ordering and Fig. 2.6 is for spinodal decomposition. In Fig. 2.7

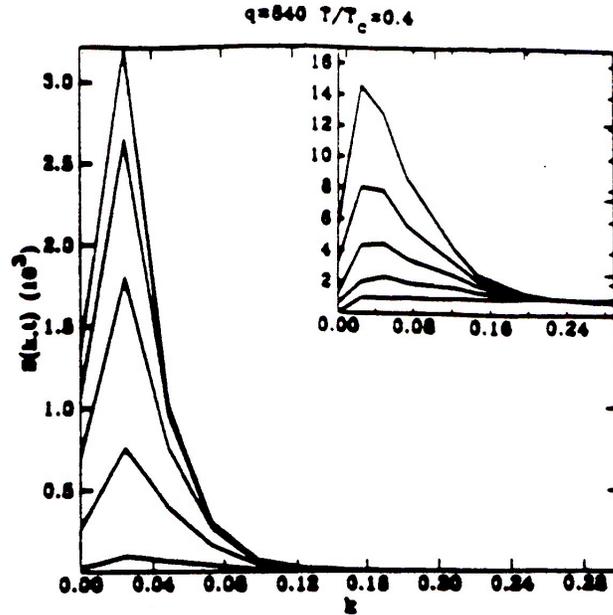


Figure 2.4: $S(k, t)$ for continuous ordering as a function of k for several times. The finite value of k at the peak is due to the finite system size.

the structure factor is plotted as a function of time for various values of k . The parameter n is related to k by $k = 2\pi n/L$, where the linear dimension of the square lattice is $L = 256$. The dots are the data and the lines are the linear theory. These figures are taken from Laradji's thesis.

Supplementary Notes

The structure factor is related to the Fourier transform of the pair correlation function. Let

$$g(\vec{x}, \vec{x}', t) = \langle \psi(\vec{x}, t) \psi(\vec{x}', t) \rangle - \langle \psi(\vec{x}, t) \rangle \langle \psi(\vec{x}', t) \rangle. \quad (2.55)$$

For the problems we are treating in this chapter the ensemble average

$$\langle \psi(\vec{x}, t) \rangle = \rho(t) \quad (2.56)$$

is time-dependent but spatially constant. Consequently there are delta functions, $\delta(\vec{k})$, which arise from the Fourier transform of the two terms on the right-hand side of Eq. (2.55). These delta functions will cancel. We will treat this $\vec{k} = 0$ divergence by ignoring the

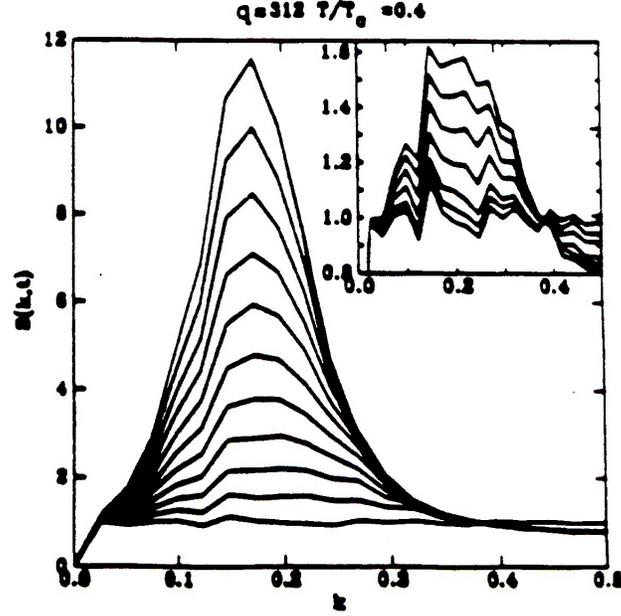


Figure 2.5: $S(k, t)$ for spinodal decomposition as a function of k for several times.

product $\langle \psi(\vec{x}, t) \rangle \langle \psi(\vec{x}', t) \rangle$, but always take the limit $\vec{k} \rightarrow 0$ when investigating the $\vec{k} = 0$ mode in the structure factor.

For a system with spherical symmetry we know that

$$g(\vec{x}, \vec{x}', t) = g(|\vec{x} - \vec{x}'|, t). \quad (2.57)$$

The structure factor in this case is given by

$$S(|\vec{k}|, t) = \frac{1}{V} \int g(|\vec{x} - \vec{x}'|) e^{-i\vec{k} \cdot (\vec{x} - \vec{x}')} d(\vec{x} - \vec{x}') d\vec{x}', \quad (2.58)$$

where the integral over \vec{x}' simply produces a factor of V . We can also write Eq. (2.58) as

$$S(k, t) = \frac{1}{V} \int g(|\vec{x} - \vec{x}'|) e^{-i\vec{k} \cdot \vec{x}} e^{-i\vec{k}' \cdot \vec{x}'} \delta(\vec{k} + \vec{k}') d\vec{x} d\vec{x}' d\vec{k}'. \quad (2.59)$$

From this discussion we can replace $g(|\vec{x} - \vec{x}'|)$ by $\langle \psi(\vec{x}) \psi(\vec{x}') \rangle$ so that Eq. (2.59) becomes

$$S(k, t) = \frac{1}{V} \int \langle \psi(\vec{x}) \psi(\vec{x}') \rangle e^{-i\vec{k} \cdot \vec{x}} e^{-i\vec{k}' \cdot \vec{x}'} \delta(\vec{k} + \vec{k}') d\vec{x} d\vec{x}' d\vec{k}', \quad (2.60)$$

or

$$S(k, t) = \frac{1}{V} \langle \hat{\psi}(\vec{k}) \hat{\psi}(-\vec{k}) \rangle. \quad (2.61)$$

Remember that we will ignore the delta function singularity at $k = 0$.

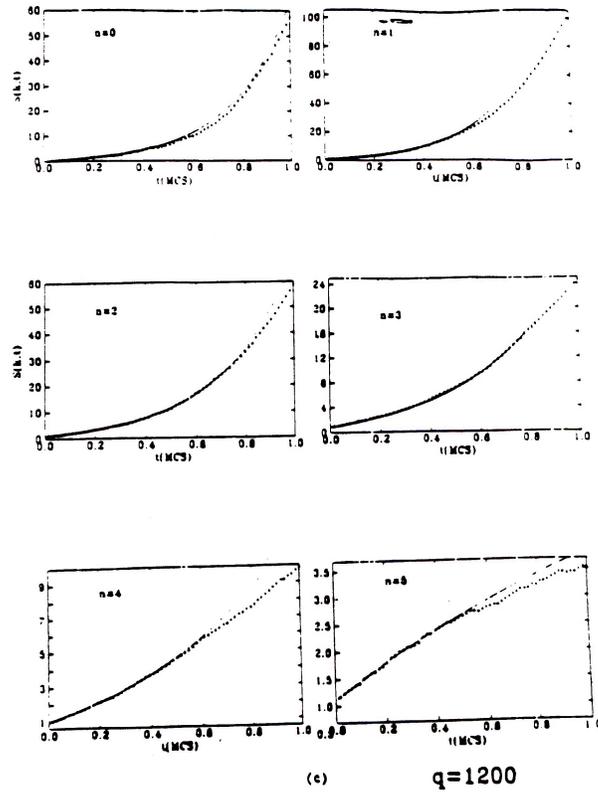


Figure 2.6: $S(k, t)$ as a function of time for several values of k for continuous ordering. The parameter q is the number of spins with which one spin interacts.

Suggestions for Further Reading

- J. W. Cahn, “On spinodal decomposition,” *Acta Metall.* **9**, 795–801 (1961).
- J. W. Cahn and J. E. Hilliard, “Free energy of a non-uniform system III: Nucleation in a two component incompressible fluid,” *J. Chem. Phys.* **31**, 688–699 (1959).
- H. E. Cook, “Brownian motion in spinodal decomposition,” *Acta Metall.* **18**, 297–306 (1970).
- Harvey Gould and Jan Tobochnik, *Statistical and Thermal Physics with Computer Applications*, Princeton University Press (2010), Chapter 8.
- J. D. Gunton, M. San Miguel, and P. S. Sahni, “The dynamics of first order phase transitions,” in *Phase Transitions and Critical Phenomena*, Vol. 8, edited by C. Domb and J. L. Lebowitz, Academic Press (1983).

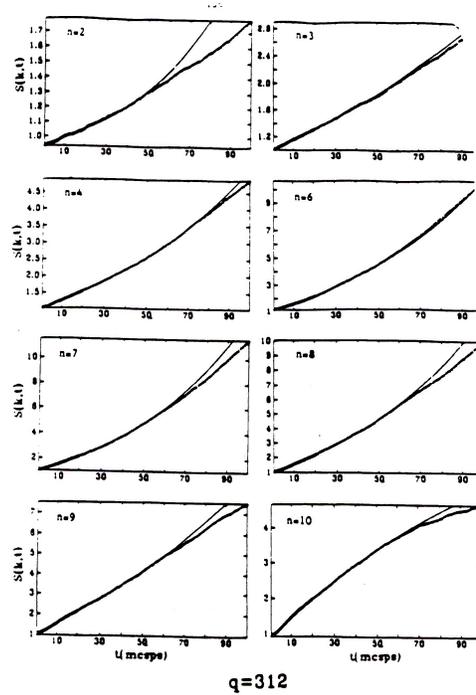


Figure 2.7: $S(k, t)$ for spinodal decomposition as a function of time for several values of k .

T. Hill, *Statistical Mechanics*, McGraw-Hill (1956).

P. Hohenberg and B. I. Halperin, “Theory of dynamical critical phenomena,” *Rev. Mod. Phys.* **49**, 435–479 (1977).

Mohamed Laradji, Ph.D. thesis, unpublished.

O. Penrose and J. L. Lebowitz, “Towards a rigorous molecular theory of metastability,” in *Fluctuation Phenomena*, edited by E. W. Montroll and J. L. Lebowitz, North-Holland (1976) and references therein.

G. Stell, “Cluster expansion for classical systems,” in *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frisch and J. L. Lebowitz, Benjamin (1964), pp. 171–267.