

Chapter 1

Phenomenological Theories of Nucleation

©2012 by William Klein, Harvey Gould, and Jan Tobochnik
16 September 2012

1.1 Introduction

These chapters discuss the problems of nucleation, spinodal decomposition and continuous ordering, and domain growth. The first and most obvious question that we will address is “What is the nature of these processes?” We will begin with simple theories that yield most of the physics correctly, but many of the details are not quite right. We will compare these theories with data from experiments and computer simulations. In many cases we will need to use simulations because the relevant data is too difficult to extract from experiments.

We begin by looking at the phenomenology of these processes and taking a broad brush view of the data generated by both simulations and laboratory experiments. We first consider the van der Waals equation of state for a simple one-component fluid:

$$P = \frac{kT\rho}{1 - b\rho} - a\rho^2, \quad (1.1)$$

In Eq. (1.1) T is the temperature, P is the pressure, ρ is the number density, and a and b are parameters. Equation (1.1) is a generalization of the ideal gas law $PV = NkT$ or $P = kT\rho$, where V is the volume. One way to motivate the van der Waals equation is to replace the volume V by $V - Nb$ in the ideal gas law to account for the finite size of the molecules. The weak attractive interaction is modeled by the term $-a\rho^2$. The van der

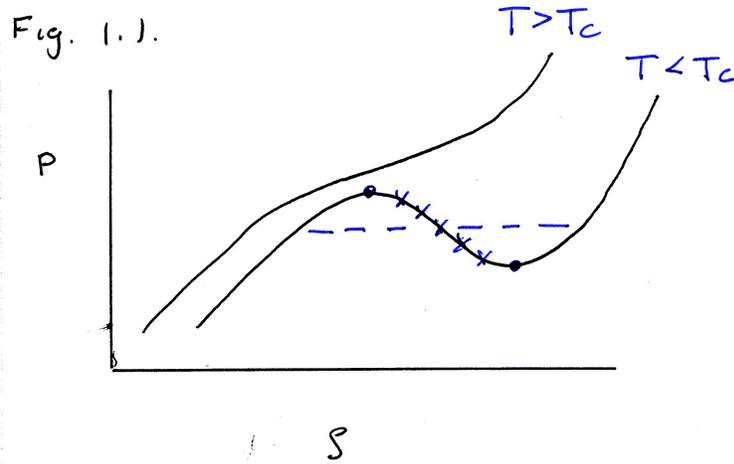


Figure 1.1: The pressure versus density as given by the van der Waals equation of state for $T < T_c$. The dashed line is found by the Maxwell construction. The crosses represent the unstable states. The metastable states are between each filled dots and the intersection of the van der Waals equation with the Maxwell construction line

Waals equation is an example of a *mean-field* theory, which becomes exact in the limit of an infinitely long range but infinitely weak potential.

A plot of the pressure P versus the density ρ for $T < T_c$, $T = T_c$, and $T > T_c$ where T_c is the critical temperature, is shown in Fig. 1.1. The solid line represents the equilibrium gas (small ρ) and liquid (large ρ) phases. The dashed line is found by the Maxwell construction and is the equilibrium coexistence line between the liquid and the gas. Our range of interest is represented by the line of dots and the line of crosses.

The line of crosses represents a region of instability. On this line the isothermal compressibility κ_T defined as

$$\kappa_T = (1/\rho[\partial p/\partial \rho]_T^{-1}) \quad (1.2)$$

is negative. This property of κ_T implies that an increase in the pressure would lower the density, an unphysical prediction that results because we are trying to describe the system by an equilibrium theory in a region of rapid time development.

The dotted lines represent metastable states. In this region there is no obvious contradiction generated by the use of equilibrium methods. To understand the metastable state we will use a slightly different thermodynamic point of view. Recall that the chemical potential μ is the Gibbs free energy per particle [Callen 1985, Gould and Tobochnik 2010].

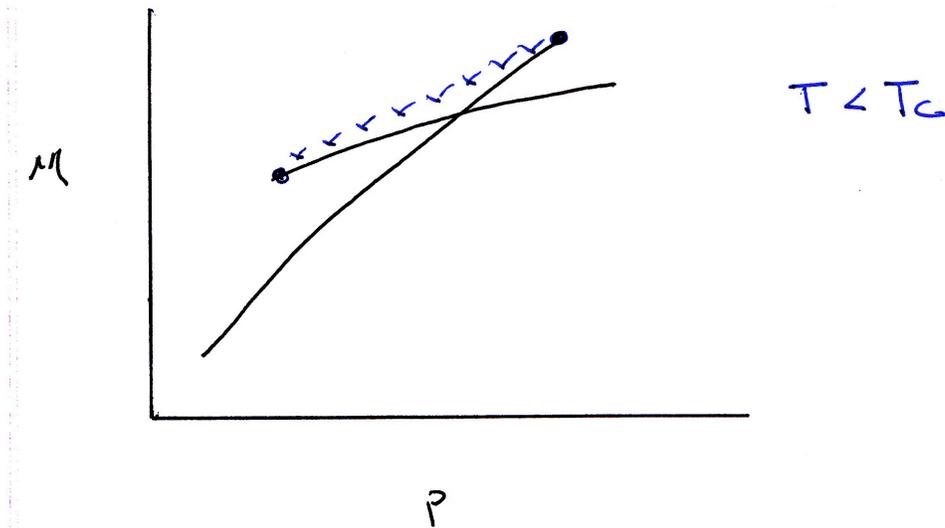


Figure 1.2: The chemical potential as a function of the pressure P for $T < T_c$. The solid lines represent stable and metastable states. The solid lines show two values of μ for each value of P . The higher values represent the metastable states; the lower values represent the stable states. The crosses represent unstable states.

In the van der Waals limit μ is given by

$$\mu = \int^P v(P') dP' + \phi(T), \quad (1.3)$$

where $v(P) = \rho^{-1}$, and $\phi(T)$ is an undetermined function of the temperature. We can use the van der Waals equation (1.1) to obtain $v(P)$ and hence the (Gibbs) free energy versus pressure relation as shown schematically in Fig. 1.2.

Note that the dotted line obtained by an integration of the negative κ_T region shown in Fig. 1.1 is concave; this property again indicates that this region is unstable. The rest of the curve is convex. That is, in the metastable and stable regions of the Gibbs free energy is a convex function of the pressure indicating a positive response function or compressibility. However, the part of the curve represented by the dashed line lies above the solid line. Hence the region we have labeled metastable has a higher free energy than the stable phase. Because thermodynamic states (stable, metastable state, and even unstable) are associated with free energy extrema, the metastable state is a local rather than a global minimum of the free energy. We will return to this point shortly.

We can learn more terminology by returning to Fig. 1.1 and noting the two points where the dotted lines and lines of crosses meet. At these points $\kappa_T \rightarrow \infty$. These points are known as *spinodal* points, the characteristics of which we will discuss in detail in later

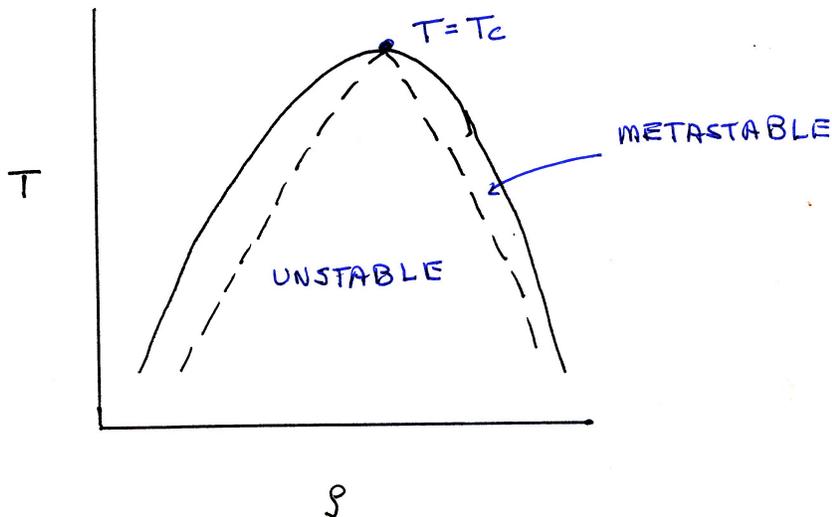


Figure 1.3: The coexistence (solid line) and spinodal curves (dashed line).

chapters. Here we note that spinodals are critical points, which not only have a divergent compressibility, but also have many of the same as usual critical points. (One difference is that the usual critical point has two relevant scaling fields, but spinodals have only one.)

We plot in Fig. 1.3 the loci of the spinodal points (dashed line) and the end points of the Maxwell construction (solid line). The loci of the spinodal points represent the *spinodal curve*, which separates the metastable region from the unstable region in a mean-field description of the phase transition. The coexistence curve separates the metastable region from the stable fluid region.

Because neither the unstable or metastable state corresponds to an absolute minimum of the free energy, the system can not remain in either state forever. Consequently, if we prepare a system in one of these states a decay process must occur which eventually brings the system into equilibrium.

Although our considerations so far have been based on the liquid-gas transition, our considerations are quite general. If, for example, we want to describe the phase separation of a binary mixture of two different molecules A and B , the same diagrams can be used with a relabeling of the axes. In Fig. 1.3, for example, the x axis would correspond to the difference in concentration of the two components, $\Delta\rho_{AB}$, rather than the density. The only difference in the two diagrams is the definition of the *order parameter*. The order parameter is the physical quantity that specifies the structure of the phase transition and is nonzero in the ordered phase. If the order parameter is discontinuous at the phase transition, then the transition is called *first-order*. If the derivative of the order parameter

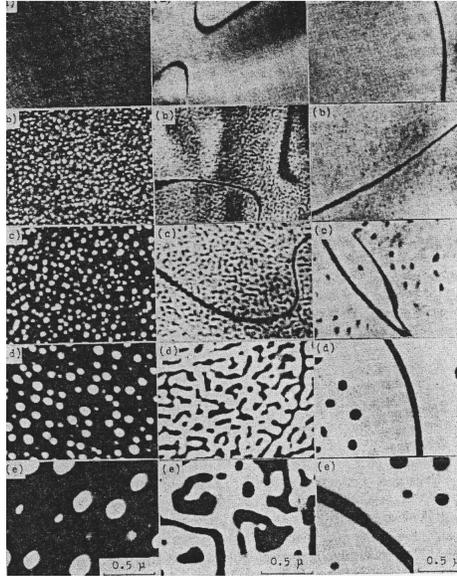


Figure 1.4: Temporal evolution of an iron-aluminum alloy quenched into the metastable (outer columns) and unstable (center column) regions [from Gunton et al. 1983].

is discontinuous at the transition, then the transition is *continuous*, although we frequently denote the transition as second-order. A well known example of the latter transition is the gas-liquid critical point.

We next look at pictures of decay processes. In Fig. 1.4 we have reproduced pictures obtained from a transmission electron microscope study of an iron aluminum alloy undergoing phase separation [Gunton et al. 1983]. The outer two columns illustrate the temporal evolution (from top to bottom) subsequent to a quench (a sudden lowering of the temperature) to two different points in the metastable region. The middle column is the result of a quench into an unstable state. The outer columns are characterized by the appearance some time after the quench of isolated droplets which then grow. The quench into the unstable region is followed by the appearance of an interconnected structure. These interconnected structures grow and coarsen. For late times, evolution from both the metastable and unstable region evolves into the growth of large isolated droplets. In this state the system has lost all memory of the initial quench.

We can now define the processes that we will be studying. *Nucleation* is the mechanism by which the metastable state decays and is characterized by the appearance at sometime after the quench of isolated regions or droplets that grow and become the stable phase. *Late stage domain growth* is the way these droplets or regions (we will also refer to them as clusters) grow in the very late stages of their evolution. *Spinodal decomposition* is the

mechanism by which the unstable state begins to decay if the order parameter is conserved and *continuous ordering* is the same process when the order parameter is not conserved.

In the next three sections we will construct some simple theories to describe these processes. Although these theories are crude, they yield much of the physics correctly and will be our starting points for the more sophisticated approaches to follow in later chapters.

1.2 Classical nucleation

The metastable state is not characterized by the absolute or global minimum of the free energy, but there does not appear to be any contradiction when we describe the metastable state by equilibrium methods.

To obtain more insight into the properties of this state and to develop a foundation for more sophisticated theoretical approaches, we will consider the Ising model and another approach based on the *Landau-Ginzburg* theory. The Ising model is of particular interest because much simulation data is available for it.

Consider a lattice with a spin at each vertex (see Fig. 1.5). These spins can be in one of two directions, up or down. The variable that describes the spins is s_i , where i labels the vertex and $s_i = \pm 1$. The Hamiltonian is given by

$$-\beta H = \sum_{ij} K_{ij} s_i s_j + h \sum_i s_i \quad (1.4)$$

where $\beta = 1/k_B T$, k_B is Boltzmann's constant, and h represents an applied uniform magnetic field. Note we have absorbed a minus sign into H . The first sum is over pairs of spins but they need not be nearest neighbors. We will assume $K_{ij} > 0$, that is, the interaction between spins is ferromagnetic.

This Ising model has been studied extensively and we will return to it often. For now we simply note that the identification of, for example, an up spin with an occupied site and a down spin with an empty one gives a simple model for the liquid-gas transition. In a similar manner, the identification of an up spin with an A atom and a down spin with a B atom gives us a model for a binary system. The Ising model itself is a model for a uniaxial magnet.

Figure 1.6 is a schematic plot of the magnetization as a function of the magnetic field h for $T < T_c$ for the mean-field approximation to the Ising model. Figure 1.3 shows the corresponding coexistence curve and spinodal.

Although the Ising model is conceptually simple and much is known about its equilibrium properties, it is difficult to understand in the metastable and unstable regions. We

will look at an even simpler model obtained from the Ising model by the process of *coarse graining*. The idea is to take the lattice in Fig. 1.5 and block it into squares of length b on a side. We will refer to b as the coarse graining size. We now introduce a local coarse grained order parameter, $\psi(\vec{x})$, which is the sum of the local microscopic variables over the box centered at \vec{x} . The quantity $\psi(\vec{x})$ will be our fundamental variable rather than s_i . In the Ising model for example we define $\psi(\vec{x})$ by the equation

$$\psi(\vec{x}) = \frac{1}{b^d} \sum_{i \in b(\vec{x})} s_i, \quad (1.5)$$

where $b(\vec{x})$ is a box of size b centered at \vec{x} . Our aim is to develop a description of the phenomena of interest in terms of $\psi(\vec{x})$. If this description is to make any sense, then we must require that $b \gg a$, where a is the fundamental microscopic length in the problem. For the Ising model a would be the lattice constant. We must also require that $b \ll \ell$, where ℓ is the dominant statistical length in the problem. We require the latter condition so that the physics of interest is not washed away in the coarse graining procedure. We require the former condition so that the fluctuations of the $\psi(\vec{x})$ are small and can be ignored.

It is important to understand that ℓ need not be the correlation length. For example in nucleation ℓ would be the size of the critical droplet, which can be significantly larger than the correlation length.

We now postulate the form of the phenomenological Helmholtz free energy $F(\psi)$ of a system in contact with a heat bath. We again use the Ising model as our paradigm. The postulated form of the free energy is [Callen 1985]

$$F(\psi) = -h \int \psi(\vec{x}) d\vec{x} - \frac{1}{2} \iint K(|\vec{x} - \vec{y}|) \psi(\vec{x}) \psi(\vec{y}) d\vec{x} d\vec{y} - k_B T \int [1 + \psi(\vec{x})] \ln(1 + \psi(\vec{x})) d\vec{x} - k_B T \int [1 - \psi(\vec{x})] \ln(1 - \psi(\vec{x})) d\vec{x} \quad (1.6)$$

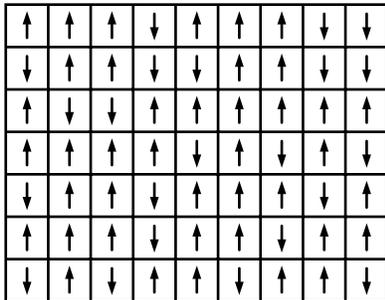


Figure 1.5: The square lattice with an Ising spin at each vertex.

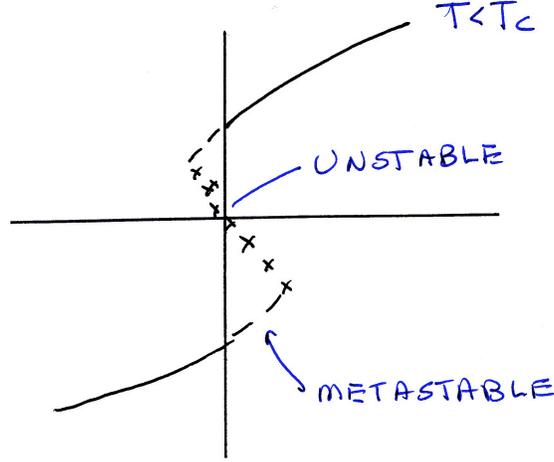


Figure 1.6: The magnetization as a function of magnetic field for $T < T_c$.

The first term is the interaction of the coarse grained $\psi(\vec{x})$ with an external magnetic field. The second term is the interaction between coarse grained blocks which we have assumed to depend only on the distance between blocks. The last two terms are the entropy, which can be obtained by considering the (natural) log of the number of states in a coarse grained volume and by using Stirling's approximation. Note that the up-down symmetry for $h = 0$ of the Ising model is preserved. (See Gunton et al. 1983 for a further discussion.)

The model free energy in Eq. (1.6) is simpler than the Ising model free energy obtained from the log of the partition function, but we will simplify it still more by making two additional assumptions. First we will assume that $\psi(\vec{x})$ is small so that the logarithms can be expanded and the expansion truncated after the second order term. Our second assumption can be best understood by going into Fourier space using Parseval's theorem and writing the interaction between blocks as

$$\frac{1}{2} \int \hat{K}(|\vec{k}|) \hat{\psi}(\vec{k}) \psi(-\vec{k}) d\vec{k}. \quad (1.7)$$

If we expand $\hat{K}(|\vec{k}|)$ in a power series in $k = |\vec{k}|$ such that $\hat{K}(k) = \hat{K}(0) + (1/2)k^2 \hat{K}''(k)|_{k=0}$, we obtain upon returning to \vec{x} space

$$\hat{K}(0) \int \psi(\vec{x}) \psi(\vec{x}) d\vec{x} + \frac{1}{2} R^2 \int [\vec{\nabla} \psi(\vec{x})]^2 d\vec{x}, \quad (1.8)$$

where $R^2 \propto \int x^2 K(x) dx$, $x = |\vec{x}|$, and we have done an integration by parts. The truncation of the power series in k assumes that the $\psi(\vec{x})$ are slowly varying so that significant changes can occur only over large distances.

With these assumptions our model free energy becomes

$$F(\psi) = \int d\vec{x} [R^2 [\nabla\psi(\vec{x})]^2 + \epsilon\psi^2(\vec{x}) + \psi^4(\vec{x}) - h\psi(\vec{x})], \quad (1.9)$$

with

$$\epsilon = k_B T - \hat{K}(0). \quad (1.10)$$

This form of $F(\psi)$ is the Landau-Ginzburg free energy. Alternative derivations of Eq. (1.9) can be found in Gunton et al. 1983, Lifshitz and Pitaevskii 1980, and Ma 1976. Because the original interaction is positive, the interaction between blocks is also positive and hence $\hat{K}(0) > 0$. Also note that the Landau-Ginzburg form in Eq. (1.10) can be easily modified to be applicable to the other models we have mentioned.

We emphasize that Eqs. (1.6) and (1.9) correspond to a mean-field model. The reason is that the free energy, unlike the Hamiltonian, is a thermodynamic quantity. Thus it is necessary to interpret $\psi(\vec{x})$ as an average quantity, that is, averaged over time or ensembles. The definition of $\psi(\vec{x})$ in Eq. (1.5) does not use either of these averages. Consequently the only way we can make a thermodynamic free energy consistent with an unaveraged $\psi(\vec{x})$ is to assume that only one configuration is important and hence averaging is unnecessary. The implication is that we can ignore fluctuations, which corresponds to a mean-field model. Therefore we should expect that the Landau-Ginzburg free energy will produce results consistent with mean-field theory.

We now return to consideration of the metastable state in the mean-field approximation. You might know that the van der Waals equation without the Maxwell construction is “derived” with the condition of spatial uniformity. This condition is what gives rise to the van der Waals loop. With this same assumption the free energy in Eq. (1.9) becomes

$$f(\psi) = \frac{F(\psi)}{V} = \epsilon\psi^2 + \psi^4 - h\psi, \quad (1.11)$$

where V is the volume of the system. The free energy per unit volume (or per spin) has the form shown in Fig. 1.7, where from Eq. (1.10), it is clear that $\epsilon > 0$ for high temperature.

From Fig. 1.7 we see that there is one minimum at $\psi = 0$. As T is lowered, the critical temperature T_c corresponding to $\epsilon = 0$ is reached. If $h = 0$ this point is the critical point. It is simple to obtain the static critical exponents for this model [Stanley 1971] and to confirm that they have mean-field values as expected.

If T is lowered below T_c , then $f(\psi)$ develops three extrema, two minima and a maximum (see Fig. 1.8).

To make contact with Fig. 1.2 think of fixing the temperature and generating a change in the pressure P . You will move along the curve $\mu(p)$ in Fig. 1.2. The same change in pressure generates, in the language of Fig. 1.8, a change in the shape of the free energy

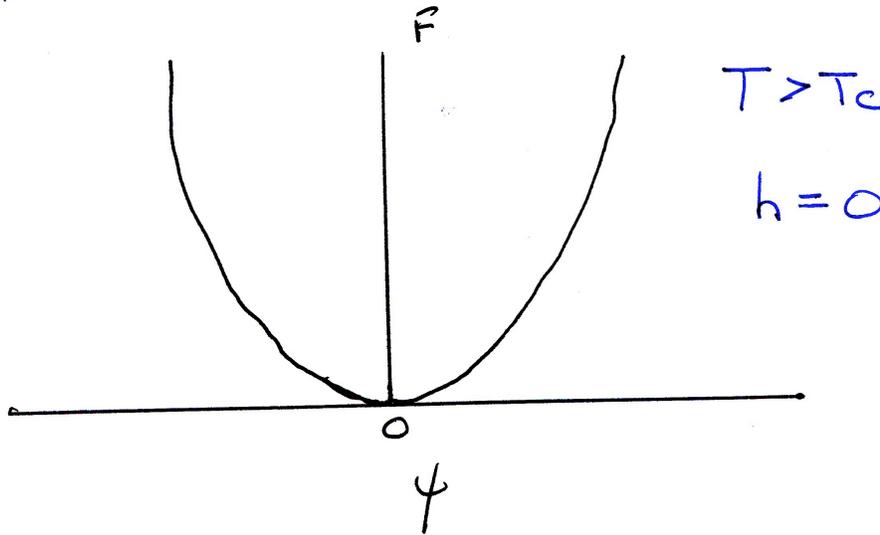


Figure 1.7: The free energy density as given by Eq. (1.11) as a function of the order parameter ψ for high T and $h = 0$.

versus ψ curve. The absolute minimum tracks the stable part of the curve in Fig. 1.2, the relative minimum tracks the metastable branch, and the relative maximum tracks the unstable branch. When the relative minimum and the maximum come together in Fig. 1.8, the spinodal is reached in Fig. 1.2.

The metastable state is a relative minimum of the free energy. It will act like a thermodynamically stable state until a fluctuation probes the thermodynamic space far enough away from the local minimum so that the system “knows” there is a lower free energy elsewhere. At this point the decay of the metastable state begins. We now make a rather strong assumption. That is, the fluctuations that initiate the decay of the metastable state can be treated as equilibrium fluctuations about the metastable local minimum of the free energy. This assumption can only hold if the metastable state lasts long enough that metastable equilibrium is attained. How long is that? No one knows. We will return to this point later.

Let us accept this assumption for now and see where it leads us. We know experimentally that the metastable state lasts a long time if we are close to the coexistence curve. In this region we can also see that the number of droplets that appear and grow in some time interval is small and the droplets are isolated, that is, non-interacting. Near the coexistence curve the droplets also appear to be compact, that is, not stringy or seaweed-like. They are also large enough to be treated with macroscopic ideas such as free energy and surface tension. These observations lead to the following assumptions.

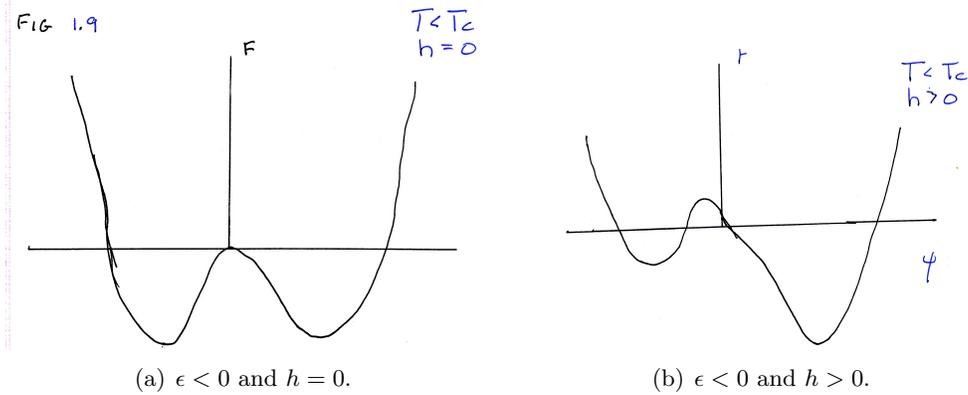


Figure 1.8: The free energy per unit volume versus the order parameter ψ .

1. Nucleation is initiated by isolated, non-interacting droplets that can be treated as fluctuations about metastable equilibrium.
2. The droplets are compact with a surface and interior that can be considered separately.
3. The interior and surface free energy density are well defined.
4. The surface free energy density (surface tension) is insensitive to quench depth.
5. The interior free energy density is equal to the free energy density of the stable phase.

These are the assumptions that go into the *classical theory of nucleation*.

We can determine the free energy cost ΔF to produce a critical or nucleating droplet. From the above assumptions ΔF will have two contributions: a surface term that raises the free energy (because it costs free energy to have a boundary between two different phases) and a bulk term that lowers it. We write

$$\Delta F = -|\Delta f|r^d + \sigma r^{d-1}, \quad (1.12)$$

where σ is the surface tension, Δf the interior free energy density difference between the metastable state and the droplet interior (assumed negative), r is the droplet radius, and d is the dimension of space.

From the plot of ΔF versus r in Fig. 1.9 we can see that systems become trapped in metastable states because small fluctuations (small r) tend to decay rather than to grow. In contrast, sufficiently large fluctuations tend to grow because growing lowers the free

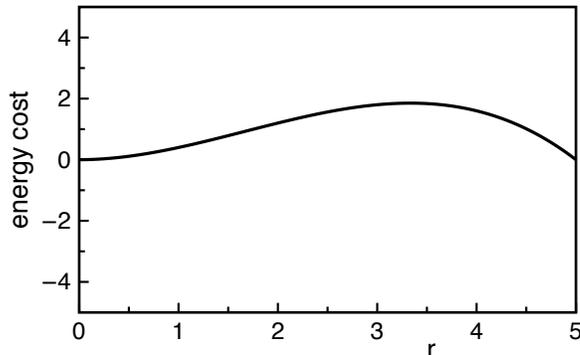


Figure 1.9: Sketch of the free energy cost as a function of the radius of a droplet.

energy. The critical droplet is the one for which growth and decay are equally likely. From Fig. 1.9 we see that the critical droplet has a radius corresponding to the maximum of ΔF .

The critical radius r_c , that is, the radius of the critical droplet, is obtained by differentiating ΔF and setting the derivative equal to zero. From Eq. (1.12) we have

$$r_c \propto \frac{\sigma}{\Delta f}, \quad (1.13)$$

and

$$\Delta F_c \propto \frac{\sigma^d}{\Delta f^{d-1}}, \quad (1.14)$$

where ΔF_c is the free energy cost of a critical droplet.

Because the droplets are assumed to be noninteracting equilibrium fluctuations, the probability of finding a critical droplet is inversely proportional to the time τ spent in the metastable state before one appears. This time is roughly the lifetime of the metastable state.

$$\tau \propto e^{\Delta F_c/k_B T}. \quad (1.15)$$

If the quench into the metastable state terminates near the coexistence curve, then $\Delta f \ll 1$ and the lifetime of the metastable state is large. We assumed that the system would settle into metastable equilibrium before the critical droplet initiates the decay, and for large τ this assumption is reasonable. However, suppose that the quench takes the system far from the coexistence curve. From Fig. 1.8 we see that the free energy difference Δf increases and hence ΔF_c decreases. For many systems ΔF_c can become the order of a few $k_B T$. If these systems undergo a deep quench, the metastable state cannot be maintained long enough for the assumption of metastable equilibrium to be

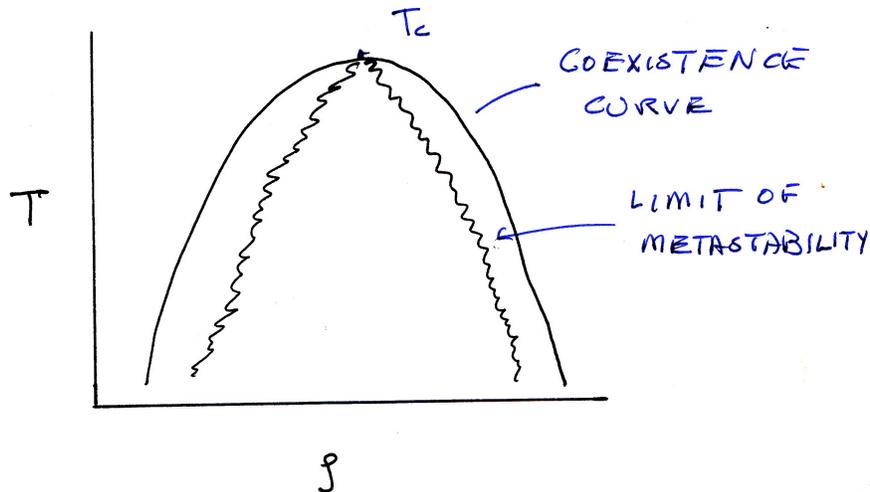


Figure 1.10: The coexistence curve and the Becker-Döring limit.

valid. The quench depth at which this takes place is often called the *limit of metastability* or sometimes the Becker-Döring limit (see Fig. 1.10).

For many systems the limit of metastability is not the spinodal. Often there is no divergent susceptibility (compressibility) at this limit. Secondly, in such systems the limit is not a well defined line but is a crossover region with a finite width where the system goes from quench depths where equilibrium ideas work well to one where they do not work at all. For these systems the spinodal presents us with a real problem. Because it is an equilibrium concept, it has no meaning past the limit of metastability and it cannot exist between the Becker-Döring limit and the coexistence curve. For now we leave this problem as one to be resolved when we return to the consideration of nucleation with more powerful tools. It is also important to note that while we motivated treating the metastable state by equilibrium methods and the use of mean-field theory, the analysis that led to the classical nucleation theory was not mean-field. There were, to be sure, several assumptions but they were not assumptions associated with the mean-field limit.

Before leaving nucleation to consider the other problems we have raised, let us look at a test of the classical theory. The test is a numerical simulation of a $d = 3$ nearest-neighbor Ising model [Heermann et al. 1984]. What is measured? Remember that the probability of finding a critical droplet is τ^{-1} , where τ is given by Eq. (1.15). We have assumed that the critical droplets were non-interacting. This assumption is based on the experimental observation that the number of droplets is small enough for shallow quenches so that they are well separated. Roughly there is a volume V inside which there is at most one droplet with probability τ^{-1} . Therefore τ^{-1} is the number of critical droplets per unit volume per

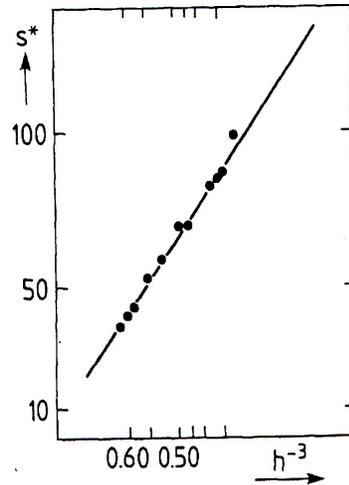


Figure 1.11: Nucleation rate vs h^{-2} for the $d = 3$ nearest-neighbor Ising model [from Heermann et al. 1984]. The solid line is the prediction of the classical theory.

unit time. This quantity is called the nucleation rate and is one of the variables measured in experiments.

Equation (1.15) gives us the classical prediction for the nucleation rate. To compare the theory with the measurement, we need to provide three factors: the constant of proportionality, the surface tension σ , and ΔF_c . The proportionality constant is too complicated for the simple theory we have developed, and will have to wait until we return to nucleation in more detail. However, it is not important for the level of comparison of theory and experiment we will do now. The surface tension is, by assumption, not sensitive to the quench depth and therefore can be taken as the surface tension between two coexisting bulk phases [Heermann et al. 1984]. Finally we adopt for ΔF_c the strategy that the free energy is well approximated by the energy for low temperatures. In this case the free energy difference between the two phases, stable and metastable, is proportional to h . These considerations lead to the prediction that the log of the number of critical droplets per unit volume per unit time when plotted against h^{-2} in $d = 3$ should be a straight line with a slope proportional to the surface tension. In Fig. 1.11 we have reproduced a plot of the log of the nucleation rate versus h^{-2} for $T = 0.59T_c$ [see Heermann et al. 1984]. As you can see, the fit is consistent with the theoretical prediction. There certainly are some questions, particularly about the deviations at small values of h , but that is a subject for another chapter.

Suggestions for Further Reading

- Herbert B. Callen, *Thermodynamics and an Introduction to Thermostatistics*, 2nd edition, John Wiley & Sons (1985).
- Harvey Gould and Jan Tobochnik, *Statistical and Thermal Physics with Computer Applications*, Princeton University Press (2010).
- 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).
- D. W. Heermann, A. Coniglio, W. Klein, and D. Stauffer, “Monte Carlo simulation of metastable states in 3D Ising models,” *J. Stat. Phys.* **36**, 447–470 (1984).
- K. Huang, *Statistical Mechanics*, 2nd edition, John Wiley & Sons (1978).
- M. Kac, G. E. Uhlenbeck, and P. C. Hemmer. “On the van der Waals theory of the vapor-liquid equilibrium. I. Discussion of a one-dimensional model,” *J. Math. Phys.* **4**, 216–228 (1963). The authors show that the van der Waals equation and the Maxwell equal-area construction becomes exact in the mean-field limit.
- E. M. Lifshitz and L. P. Pitaevskii, *Statistical Physics*, 3rd edition, Part 1, Pergamon Press (1980).
- S.-k. Ma, *Modern Theory of Critical Phenomena*, Benjamin (1976).
- H. E. Stanley, *Phase Transitions and Critical Phenomena*, Oxford (1971).