Chapter 4

The Landau-Ginzburg Free Energy as a Hamiltonian

1 October 2012

4.1 Introduction

In this chapter we will follow the paradigm discussed in Chapters 1 and 3. Namely, we will use the Landau-Ginzburg free energy as a Hamiltonian or action. This approach is well known in field theory and critical phenomena [Ma 1976, Amit 1984], and is one of the most powerful tools known for describing phase transitions. Although these methods are useful for several classes of systems such as the x-y and Heisenberg models, superconductivity and fluidity, and percolation, we will restrict our considerations to Ising, binary, and fluid systems for now. For the processes we wish to study these systems are systems for which good numerical and laboratory data exists.

If you are interested in the details of how to convert from a Landau-Ginzburg free energy to a Landau-Ginzburg-Wilson Hamiltonian, see the books by Ma, Amit, or the article by Langer [1967].

Our point of departure is the partition function

$$z = \int \delta\phi \exp\big[-\beta H(\phi)\big], \tag{4.1}$$

where

$$-\beta H(\phi) = -\beta \int \Big[\frac{R^2}{2}\big[\nabla\phi(\vec{x})\big]^2 + \epsilon\phi^2(\vec{x}) + \phi^4(\vec{x}) - h\phi(\vec{x})\Big] d\vec{x}. \tag{4.2}$$

Equation (4.2) is the same as Eq. (1.9) except that here we are using it as a Hamiltonian rather than as a free energy. The integral in Eq. (4.1) is a functional integral over all functions $\phi(\vec{x})$. We define a new variable $\vec{r} = \vec{x}/R$ so that Eq. (4.2) becomes

$$-\beta H(\phi) = -\beta R^d \int \Big[\frac{1}{2}\big[\nabla\phi(\vec{r})\big]^2 + \epsilon\phi^2(\vec{r}) + \phi^4(\vec{r}) - h\phi(\vec{r})\Big] d\vec{r}. \tag{4.3}$$

The partition function becomes

$$z = \int \delta\phi \exp[-\beta R^d H(\phi)]. \tag{4.4}$$

If β or R is large, then the partition function can be well approximated using steepest descent techniques. We will assume that we are working in this limit. Therefore, we will take either $R \gg 1$ or $T \ll T_c$ or both.

4.2 Saddle points and Gaussian fluctuations

To evaluate the steepest descent integral we first find the saddle points. To find the saddle points we functionally differentiate the argument of the exponential in Eq. (4.4), that is, the Hamiltonian in Eq. (4.3).

To evaluate the derivative of a functional $H(\phi)$ we consider the functional $H(\phi(\vec{r}) + \theta(\vec{r}))$ where θ is a small perturbation. We write

$$H(\phi + \theta) \approx H(\phi) + \int H'(\phi)\theta(\vec{r}) d\vec{r} \tag{4.5}$$

Equation (4.5) defines the functional derivative $H'(\phi)$. From Eq. (4.3)

$$H(\phi+\theta) = R^d \int \Big[\frac{1}{2}\big[\nabla(\phi(\vec{r}) + \theta(\vec{r})\big]^2 + \epsilon(\phi(\vec{r}) + \theta(\vec{r}))^2 + (\phi(\vec{r}) + \theta(\vec{r}))^4 - h(\phi(\vec{r}) + \theta(\vec{r}))\Big] d\vec{r} \tag{4.6}$$

We expand the right-hand side of Eq. (4.6) and keep only up to linear terms and obtain

$$H(\phi + \theta) \approx H(\phi) + R^d \int \Big[\nabla\phi(\vec{r})\nabla\theta(\vec{r}) + 2\epsilon\phi(\vec{r})\theta(\vec{r}) + 4\phi^3(\vec{r})\theta(\vec{r}) - h\theta(\vec{r})\Big] d\vec{r} \tag{4.7}$$

The term $\int \nabla\phi(\vec{r})\nabla\theta(\vec{r}) d\vec{r}$ is not quite in the right form. To get it in the proper form we integrate by parts using the boundary conditions that $\theta(\vec{r}) \to 0$ as $|\vec{r}| \to \infty$ to obtain

$$H(\phi + \theta) \approx H(\phi) + R^d \int \big[-\nabla^2\phi(\vec{r}) + 2\epsilon\phi(\vec{r}) + 4\phi^3(\vec{r}) - h\big]\theta(\vec{r}) d\vec{r}. \tag{4.8}$$

The saddle point is the solution of

$$-\nabla^2\phi(\vec{r}) + 2\epsilon\phi(\vec{r}) + 4\phi^3(\vec{r}) - h = 0. \tag{4.9}$$

We first consider the solutions of Eq. (4.9) that are spatial constants. If we assume $\phi(\vec{r}) = \phi = \text{constant}$, Eq. (4.9) becomes

$$2\epsilon\phi + 4\phi^3 - h = 0 \tag{4.10}$$

For $\epsilon > 0$ there is one real solution to Eq. (4.10). For $\epsilon < 0$ there are three real solutions, one maximum and two minima. This behavior is reminiscent of the discussion in Chapter 1 following Eq. (1.11), and with good reason. As βR^d becomes large so that we can use the saddle point technique, the system becomes more mean-field as is illustrated in Fig. 3.3 for the susceptibility.

Let's look more closely at z for $\epsilon > 0$ and $h = 0$. To complete the steepest descent evaluation of the partition function we must evaluate the Gaussian integral about the saddle point. To do so we first need the second functional derivative of the functional $H(\phi)$ and the functional Taylor series expansion up to second order. To obtain these quantities we return to Eq. (4.5). The term $\int H'(\phi)\theta(\vec{r})d\vec{r}$ is first order in the small parameter $\theta(\vec{r})$. To have an equality rather than the approximate equality in Eq. (4.5) we should write

$$H(\phi + \theta) = H(\phi) + \int H'(\phi + \theta)\theta(\vec{r})\, d\vec{r} \tag{4.11}$$

We can now expand H' to first order in $\theta(\vec{r})$ to obtain

$$H(\phi + \theta) \approx H(\phi) + \int H'\theta(\vec{r})d\vec{r} + \int H''(\phi)\theta(\vec{r})\theta(\vec{r}')d\vec{r}d\vec{r}' \tag{4.12}$$

where we have kept terms up to second order in θ.

An equivalent, and perhaps easier way to obtain the functional derivative is to use a variable ω in the argument of the functional $H(\phi)$. We can then define the functional derivative through the relation [Volterra 1959]

$$\frac{d}{d\omega}H(\phi(\vec{r}) + \omega\theta(\vec{r})) = \int H'(\phi(\vec{r}))\theta(\vec{r})d\vec{r}. \tag{4.13}$$

The functional Taylor series can simply be seen in Eq. (4.12) up to second order. It is the functional Taylor series that is used to define the derivative. With these considerations we return to Eq. (4.6), and expand and keep terms up to second order and obtain

$$H(\phi) \approx H(\phi_0) + \int \Big[-\theta(\vec{r})\nabla^2\theta(\vec{r}) + 2\epsilon\theta^2(\vec{r}) + 12\phi_0^2\theta^2(\vec{r})\Big]d\vec{r}, \tag{4.14}$$

where ϕ_0 is the solution to Eq. (4.10).

The partition function integral in Eq. (4.4) reduces to

$$z \approx \exp[-\beta R^d H(\phi_0)] \int \delta\theta \exp[-\beta R^d] \int \big[-\theta(\vec{r})\nabla^2\theta(\vec{r}) + 2\epsilon\theta^2(\vec{r}) + 12\phi_0^2\theta^2(\vec{r})\big] d\vec{r}. \quad (4.15)$$

To do the functional Gaussian integral we diagonalize the Gaussian form in Eq. (4.15). Specifically we write

$$-\theta(\vec{r})\nabla^2\theta(\vec{r}) + 2\epsilon\theta^2(\vec{r}) + 12\phi_0^2\theta^2(\vec{r}) = \theta(\vec{r})\big[-\nabla^2\theta(\vec{r}) + 2\epsilon\theta(\vec{r}) + 12\phi_0^2\theta(\vec{r})\big]. \quad (4.16)$$

We return to the case $\epsilon > 0$ and $h = 0$ and write

$$\theta(\vec{r}) = \int \exp[i\vec{k}\cdot\vec{r}]\hat{\theta}(\vec{k})d\vec{k}. \quad (4.17)$$

Then the right-hand side of Eq. (4.16) becomes

$$\iiint e^{-i\vec{k}'\cdot\vec{r}} e^{i\vec{k}\cdot\vec{r}}\big[|\vec{k}|^2 + \epsilon\rangle\hat{\theta}^*(\vec{k}')\hat{\theta}(\vec{k})\big] d\vec{r}\, d\vec{k}\, d\vec{k}' = \int [k^2+\epsilon]|\hat{\theta}(\vec{k})|^2 d\vec{k}, \quad (4.18)$$

where we have used $k = |\vec{k}|$, and

$$\theta(\vec{r}) = \theta^*(\vec{r}) = \int e^{-i\vec{k}'\cdot\vec{r}}\hat{\theta}^*(\vec{k}')d\vec{k}'. \quad (4.19)$$

The $\vec{r}$ integration produces $\delta(\vec{k} - \vec{k}')$.

The functional integral in Eq. (4.15) can now be written as

$$\int \delta\hat{\theta}(\vec{k}) \exp\big[-\beta R^d \int (k^2+\epsilon)|\hat{\theta}(\vec{k})|^2 d\vec{k}\big]. \quad (4.20)$$

Because we expect radial symmetry we can take $\theta(\vec{r}) = \theta(|\vec{r}|)$, which implies that $|\theta(\vec{k})|^2 = \theta^2(k)$. Also note that we have written the functional integral with respect to $\theta(\vec{r})$ as an integral over the Fourier coefficients $\hat{\theta}(\vec{k})$. In this way we can do the integral in Eq. (4.20) as a product of Gaussian integrals in the scalar variables $\hat{\theta}(\vec{k})$ for each value of $\vec{k}$. In a sense the evaluation of the functional Gaussian integral is similar to the way the propagator is evaluated in a Feynman path integral representation of the quadratic Lagrangian [Schulman 1981].

The partition function in Eq. (4.15) can now be written as

$$z \approx \exp[-\beta R^d H(\phi_0 = 0)] \prod_{\vec{k}} \left[\frac{\pi}{(k^2+\epsilon)}\right]^{1/2}, \quad (4.21)$$

and the free energy can be expressed as

$$F = -k_B T \ln z \approx \frac{1}{2} k_B T \int d\vec{k} \ln[(k^2 + \epsilon)\pi^{-1}]. \tag{4.22}$$

We now briefly digress to ask how we can write the integral in Eq. (4.15) as the product of simple Gaussian integrals. The problem specifically is how to deal with the continuum of $\vec{k}$ values. The answer lies in doing the calculation in a finite volume L^d and then taking the limit $L \to \infty$. For finite L there is not a continuum of eigenvalues for the free particle Schrödinger operator in Eq. (4.16), and instead there is a discrete set with a density proportional to L^{-d}. The discrete set is the spectrum of a free particle in a box in quantum mechanics. We now have a sum over discreet values of $\vec{k}$ rather than an integral over the $\vec{k}$ continuum in Eq. (4.20). The upshot is that the expression for the free energy in Eq. (4.22) is modified by multiplication by the factor L^d. The critical exponent α can be calculated from the free energy in Eq. (4.22). We refer the interested reader to Ma [1976]. The relevant point for our purposes is that it is the small amplitude modes, which can be treated in the Gaussian approximation, that are responsible for the part of the equilibrium free energy due to fluctuations. Of course this conclusion holds only in the $R \to \infty$ or $T \to 0$ limit. Note also that the system is stable to these modes or fluctuations as can be seen from the positivity of the eigenvalues of the Schrödinger operator in Eq. (4.16). That is,

$$\lambda_k = k^2 + \epsilon. \tag{4.23}$$

For $\epsilon < 0$ there are three solutions to Eq. (4.10). As we saw in Chapter 1 two are minima and one is a maximum. For $h = 0$ the two minima are of equal depth, but for $h \neq 0$ one minimum is lower than the other. For the $\epsilon < 0$ case we take $h > 0$ initially. If we perform the functional integral for the partition function in Eq. (4.4) with the steepest descent technique, we obtain the dominant contribution from the saddle point at $\phi = \phi_{0+}$, where ϕ_{0+} is the solution of Eq. (4.10) for $h > 0$ and $\epsilon < 0$ corresponding to the absolute minimum.

What about the small amplitude Gaussian fluctuations? The same procedure we used for $\epsilon > 0$ and $h = 0$ can be used in the vicinity of the ϕ_{0+} saddle point but now the eigenvalues λ_k are given by

$$\lambda_k = k^2 - 2|\epsilon| + 12\phi_{0+}^2 \tag{4.24}$$

The positivity of λ_k in Eq. (4.24) is guaranteed by the fact that the system is in the stable state. In other words $\lambda_k > 0$ because we are restricting ourselves to considering only those values of h and ϵ for which the inequality holds. We considered those regions for which the inequality did not hold in Chapter 2.

4.3 4.3 Metastable states

We now consider $h < 0$. If we simply set h equal to some negative value, we expect, by symmetry, that the same considerations as before still apply except we would evaluate the partition function around the ϕ_{0-} saddle point. To some extent this evaluation is reminiscent of the droplet model in Chapter 3. In that case we could not set the magnetic field equal to a negative value and obtain another phase because the model was not rich enough. However, we could reach the metastable phase by analytic continuation.

We will follow the same procedure here. That is, we will analytically continue the free energy to negative values of h. To see what is happening consider the simple model obtained from Eq. (4.4) for the partition function by restricting the variable $\phi(\vec{r})$ to a constant ϕ. The partition function integral in this model is

$$\tilde{z} = \int d\phi \exp\big[- \beta R^d(-|\epsilon|\phi^2 + \phi^4 - h\phi)\big]. \tag{4.25}$$

There are now two saddle points of interest – the two minima. The deeper minimum dominates the saddle point integral so that in the limit $R \to \infty$ the stable state will dominate the partition function sum as expected. Suppose we now expand the argument of the exponential in Eq. (4.25) about the saddle point ϕ_{0+} with $h > 0$. We will refer to this saddle point as the positive magnetization saddle point. Equilibrium corresponds to $h > 0$ and $\phi_{0+} > 0$. Expansion about this saddle point gives

$$\begin{aligned} -|\epsilon|\phi^2 + \phi^4 - h\phi = & -|\epsilon|\phi_{0+}^2 + \phi_{0+}^4 - h\phi_{0+} \\ & + \frac{f''(\phi_{0+})}{2}(\phi - \phi_{0+})^2 + 2\phi_{0+}(\phi - \phi_{0+})^3 + (\phi - \phi_{0+})^4, \end{aligned} \tag{4.26}$$

where $f''(\phi_{0+})$ is the second derivative of the left-hand side of Eq. (4.26) evaluated at $\phi = \phi_{0+}$. Lets focus our attention on the cubic term. If we are close to the saddle point, the quadratic term dominates. If we increase —$(\phi - \phi_{0+})$—, the cubic term will eventually dominate the quadratic for $\phi - \phi_{0+} < 0$, and the presence of the other saddle point will be felt. If $h > 0$ so that ϕ_{0+} is the stable state, it will not matter that another saddle point exists because ϕ_{0+} will dominate. However, suppose that we analytically continue to $h < 0$. The saddle point at ϕ_{0+} will move slightly to, say, ϕ_{0+}^{∂}, but it will no longer be the dominant saddle point. The dominant saddle point will be at ϕ_{0-}. The cubic term in the expansion about ϕ_{0+}^{∂} will now indicate the presence of another, dominant saddle point. We can avoid the evaluation of the integral at the dominant saddle point, and hence obtain a description of the metastable state, by deforming the contour of integration in Eq. (4.25) so that the cubic term remains positive. We will not do this procedure here but note only that the method is similar to the procedure used in Chapter 3 for the classical

droplet model. We now want to evaluate the partition function in the neighborhood of the metastable saddle point having analytically continued as we have outlined previpously.

The small amplitude Gaussian fluctuations about the metastable saddle point ϕ^{∂}_{0+} for $h < 0$ can be handled in the same way we treated such fluctuations for $\epsilon > 0$ and $h = 0$. The eigenvalues λ_k are given by

$$\lambda_k = k^2 - \epsilon + 12\phi^{\partial 2}_{0+}. \tag{4.27}$$

As with the stable state saddle points, the eigenvalues in Eq. (4.27) are positive. This positivity distinguishes the metastable from the unstable states discussed in Chaper 2 where the λ_k are negative for some range of k.

4.4 Nucleation: general considerations

If the Gaussian fluctuations were the only ones, the metastable state would be stable. Some indication of what we might expect can be obtained by recalling that the critical droplet initiating the metastable state decay is associated with a saddle point in the classical droplet model. What kind of saddle point would we need to describe a critical droplet? Clearly it must be a spatially non-constant solution of Eq. (4.9). If we are looking for a solution of Eq. (4.9) what boundary conditions should we employ? As usual, the boundary conditions must come from the physics. First, we expect a radially symmetric solution. This expectation arises from the symmetry of the differential equation. With this assumption Eq. (4.9) becomes

$$-\frac{d^2\phi(r)}{dr^2} - \frac{(d-1)}{r}\frac{d\phi(r)}{dr} - 2|\epsilon|\phi(r) + 4\phi^3(r) - h = 0. \tag{4.28}$$

If $\phi(r)$, the solution of Eq. (4.28), is to represent the critical droplet, then for physical reasons we do not expect any kinks at $r = 0$. This physical condition implies the boundary condition

$$\left.\frac{d\phi(r)}{dr}\right|_{r=0} = 0. \tag{4.29}$$

The second boundary condition arises from the expectation that the critical droplets are localized in space. Specifically, as $r \to \infty$ we expect the order parameter (that is, $\phi(r)$) to approach the value of the metastable state background for large r. Note that the solution $\phi(r)$ to Eq. (4.28) is not just the critical droplet, but the order parameter of a system that contains an isolated critical droplet as well as the uniform metastable state.

Nonlinear differential equations are notoriously difficult to solve, and it is very difficult to obtain solutions to Eq. (4.28). Equation (4.28) has been solved numerically, and we

will look at these solutions shortly. However, it is possible to obtain a significant amount of insight into the physics by looking at two limits; $h \approx 0$ and deep quenches near the spinodal.

4.5 Classical nucleation

What can we learn about the solutions to Eq. (4.28) for $h \approx 0$ without actually solving the equation? Following Langer [1967] we can think of Eq. (4.28) as describing the motion of a particle in a displacement dependent potential. If we recall that the force is the negative gradient of the potential, we can rewrite Eq. (4.28) as

$$\frac{d^2\phi(r)}{dr^2} = -\frac{(d-1)}{r}\frac{d\phi(r)}{dr} - 2|\epsilon|\phi(r) + 4\phi^3(r) - h. \tag{4.30}$$

We interpret $\phi(r)$ as a time dependent displacement $x(t)$ and r as the time t and write

$$\frac{d^2x(t)}{dt^2} = -\frac{(d-1)}{t}\frac{dx(t)}{dt} - 2|\epsilon|x(t) + 4x^3(t) - h. \tag{4.31}$$

The left-hand side of Eq. (4.31) is mass times acceleration (unit mass). The right-hand side consists of a time dependent friction force,

$$-\frac{(d-1)}{t}\frac{dx(t)}{dt}, \tag{4.32}$$

and a displacement dependent force

$$-2|\epsilon|x(t) + 4x^3(t) - h. \tag{4.33}$$

The potential $V(x)$ associated with this force is plotted in Fig. 4.1.

The potential is the inverse of the free energy because the force is the negative gradient of the potential. The time is the variable r so that the boundary condition that $\phi(r)$ approaches the metastable order parameter as $r \to \infty$ translates into the particle coming to rest at the top of the smaller (metastable) hill in Fig. 4.1 as $t \to \infty$. The boundary condition that the derivative of $\phi(r)$ equals zero at $r = 0$ [Eq. (4.29)] becomes the condition that the initial velocity of the particle is zero. The motion we are looking for is that the particle starts at rest near the top of the higher hill (stable state minimum), rolls down the larger hill and up the smaller one and comes to rest at the top of the smaller hill (metastable minimum).

As $h \to 0$ the heights of the two hills become equal. Because the friction force is non-conservative, we must have that the effect of this non-conservative force also goes to

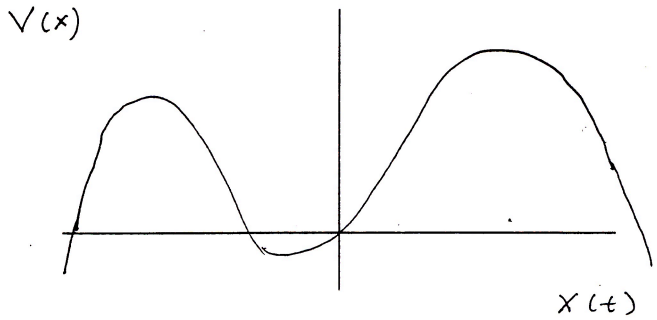

Figure 4.1: $V(x)$ as a function of $x(t)$ for $h \approx 0$. The hill on the left is lower than the hill on the right.

zero as $h \to 0$. The only way this can happen is that the particle start closer to the top of the bigger hill as $h \to 0$. This initial condition makes the initial acceleration smaller and keeps the particle near the top of the larger hill for a longer time. Because the friction force in Eq. (4.32) decays as t^{-1}, the longer the particle remains at the top of the larger hill, the less the effect of the friction during the motion from the smaller to the larger hill. As $h \to 0$ the particle spends a longer and longer time at the top of the larger hill, and in the limit $h = 0$, the time spent at the top diverges making the friction force irrelevant. This conclusion is clear because if the two hills are equal in height there must be no dissipation of energy via friction.

This analysis tells us three things. First, as the magnetic field becomes small and the coexistence curve is approached, the order parameter in the interior of the droplet approaches its stable state value. This conclusion is the result of converting back to the $\phi(r)$ language of the statement that the particle starts closer to the top of the larger hill as $h \to 0$. Secondly, the time spent near the top of the bigger hill diverges as $h \to 0$. This statement implies a divergent droplet radius as $h \to 0$. Finally, the interface between the droplet interior and the outside metastable state can be treated separately from the bulk or interior because the interface is the motion from peak to peak in Fig. 4.1, and the interior is the motion in the neighborhood of the bigger peak. This separation is not exact, but as the droplet radius diverges in the $h \to 0$ limit, the separation becomes exact. As a consequence the surface profile of the droplet can be well approximated in the $h \to 0$ limit by the solution to

$$-\frac{d^2\phi(r)}{dr^2} - 2|\epsilon|\phi(r) + 4\phi^3(r) = 0, \tag{4.34}$$

where we have set $h = 0$ and neglected the friction force. Equation (4.34) gives an accurate description of the surface profile for small h, but contains no information about the droplet size.

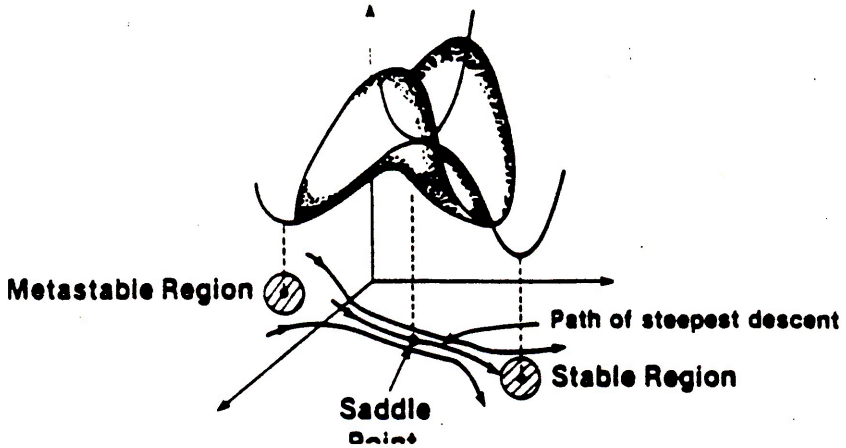

Figure 4.2: Schematic drawing of a saddle point in function space.

The picture we have discussed is that the system is trapped in a metastable state due to the fact that it is stable to small amplitude fluctuations, which we have been treating within the Gaussian approximation. However, there are large amplitude fluctuations which cannot be treated in the Gaussian approximation that allow the system to escape from the metastable trap. These fluctuations must overcome a barrier which manifests itself theoretically as a saddle point in function space for large βR^d. The meaning of the saddle point is twofold. The saddle point droplet is the critical droplet, that is, the smallest one that makes it. There are larger droplets, droplets larger than the critical size, as well as droplets with different shapes that will also grow and take the system out of the metastable state, but these are not given by the solution to Eq. (4.9) and in the limit $\beta R^d \to \infty$ are very improbable. The second meaning to the saddle point is that there are droplet modes or fluctuations, for example, surface deformations, that are orthogonal to the path of steepest descent down from the droplet saddle point. These modes may be important in calculating the metastable state lifetime, and we will have to examine them carefully.

It is also important to remember that the nucleation we are considering with these methods is the steady state nucleation described by the Becker-Döring theory discussed in Chapter 3.

The solution to Eq. (4.34) which satisfies our boundary conditions is

$$\bar{\phi}(r) = \pm\left[\frac{|\epsilon|}{2}\right]^{1/2} \tanh\left(\sqrt{2}|\epsilon|^{1/2}(r - r_0)\right), \tag{4.35}$$

where r_0 is the location of the center of the interface and is arbitrary. This solution satisfies the boundary conditions and is usually referred to as the kink solution or the classical droplet or bubble solution. Note that as $r - r_0 \to \pm\infty$, the solution approaches $\pm\sqrt{\epsilon}/\sqrt{2}$ which are the stable and metastable values of the order parameter as $h \to 0$.

Away from the critical point the droplet described by Eq. (4.35) is compact, resembles the metastable phase in its interior and has a distinct interior and surface. These characteristics are the same as assumed by the classical theory discussed in Chapter 1.

We can use the solution in Eq. (4.35) to obtain some information about the dependence of the droplet size as a function of h and about the nucleation rate. We will consider these problems in the next chapter.

S. K. Ma, *Modern Theory of Critical Phenomena*, Benjamin (1976).

D. Amit, *Field Theory, The Renormalization Group and Critical Phenomena*, World Scientific (1984).

V. Volterra, *Theory of Functionals and of Integral and Integro-Differential Equations*, Dover (1959).

L. Schulman, *Techniques and Applications of Path Integration*, John Wiley & Sons (1981).

J. S. Langer, "Theory of the condensation point," Ann. Phys. (NY) **41**, 108 (1967).