

Chapter 5

Nucleation Near Coexistence

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5.1 Introduction

In this chapter we will continue our discussion of nucleation for $h \approx 0$, that is, near the coexistence curve. We will also begin a study of nucleation near the spinodal. The latter topic will require a substantial digression into percolation theory.

5.2 Classical nucleation continued

The variation that led to Eq. (4.35) was incomplete because to obtain an equation that we could solve without resorting to a computer we were forced to set $h = 0$ in Eq. (4.30). However, we can obtain information about the nucleation rate and the droplet size if we are willing to accept some plausible hand waving. To obtain this information we again follow Langer [1987].

First we note that by an integration by parts

$$\frac{1}{2} \int [\nabla \phi(r)]^2 d\vec{r} = -\frac{1}{2} \int \phi(r) \nabla^2 \phi(r) d\vec{r}. \quad (5.1)$$

If we use Eqs. (5.1) and (4.9), we have

$$-\frac{1}{2} \int \bar{\phi}(r) \nabla^2 \bar{\phi}(r) d\vec{r} = \int \bar{\phi}(r) \left[-\epsilon \bar{\phi}(r) - 2\bar{\phi}^3(r) + \frac{h}{2} \right] d\vec{r}, \quad (5.2)$$

where $\bar{\phi}(r)$ refers to the solution of Eq. (4.9) for an arbitrary value of h , not just to the solution for $h = 0$ in Eq. (4.35).

For $\phi(r) = \bar{\phi}(r)$ the Hamiltonian $H(\phi)$ becomes $H(\bar{\phi})$. We use Eq. (4.3) to obtain

$$-\beta H(\bar{\phi}) = -\beta R^d \int [\bar{\phi}^4(r) + \frac{h}{2}\bar{\phi}(r)] d\vec{r}. \quad (5.3)$$

Remember that the solution to Eq. (4.9) is the metastable state plus the isolated droplet. As we have seen, there is a solution to Eq. (4.9) which is just the metastable state, that is, ϕ'_{0+} . Because ϕ'_{0+} is a solution to Eq. (4.9), the energy associated with this spatially uniform saddle point can also be written in the form of Eq. (5.3). The energy associated only with the droplet, the energy cost of the droplet ΔH , is

$$-\beta \Delta H = -\beta R^d \int [(\bar{\phi}^4(r) - \phi'^4_{0+}) + \frac{h}{2}(\bar{\phi}(r) - \phi'_{0+})] d\vec{r}. \quad (5.4)$$

We now use the idea that the interior of the critical droplet can be treated separately from its surface and resembles the stable phase. This idea was assumed in Chapter 1 and made plausible in Chap 4 in the discussion following Eq. (4.35). If this assumption is valid, then the bulk contribution to the energy cost per unit volume of the critical droplet ΔE_B is

$$-\Delta E_B = (\phi_{0-}^4 - \phi'^4_{0+}) + \frac{h}{2}(\phi_{0-} - \phi'_{0+}), \quad (5.5)$$

where ϕ_{0-} is the stable phase saddle point.

To obtain ϕ_{0-} and ϕ'_{0+} , we start with $h = 0$ so that $\phi_{0-} = -\sqrt{\epsilon}/2$ and $\phi'_{0+} = \sqrt{\epsilon}/2$. We now assume that the change in these saddle point values generated by a small field in the negative h direction is also small. If we substitute $\phi = \pm\sqrt{|\epsilon|}/2 + \delta$ in Eq. (4.10) with $\epsilon < 0$, we obtain

$$2\epsilon \left[\pm \sqrt{\frac{|\epsilon|}{2}} + \delta \right] + 4 \left[\pm \sqrt{\frac{|\epsilon|}{2}} + \delta \right]^3 - h = 0, \quad (5.6)$$

where δ is assumed to be small.

We linearize Eq. (5.6) with respect to δ and obtain

$$\delta = \frac{h}{4|\epsilon|}. \quad (5.7)$$

Therefore for small h

$$\phi_{0-} = -\sqrt{\frac{|\epsilon|}{2}} + \frac{h}{4|\epsilon|} \quad \text{and} \quad \phi'_{0+} = \sqrt{\frac{|\epsilon|}{2}} + \frac{h}{4|\epsilon|}. \quad (5.8)$$

From Eqs. (5.5) and (5.8) we find to first order in h

$$\Delta E_B = 2h\sqrt{\frac{|\epsilon|}{2}}. \quad (5.9)$$

This result is the energy change per unit volume due to the bulk or interior of the droplet. Note that this term is proportional to the magnetic field h as was assumed in the simple theory in Chapter 1, and we have temporarily ignored the R^d term in Eq. (5.4).

Next we consider the surface or droplet interface term. To calculate the surface energy cost per unit area, we again view the problem as a particle moving on a potential surface. In particular, the surface contribution comes from the motion from the larger to the smaller peak. In the limit $h \rightarrow 0$, we can ignore the friction term Eq. (4.32). Moreover, we should expect no magnetic field h -dependence, because h controls only how long the particle stays close to the higher peak. With these considerations we obtain the energy cost per unit area from the surface ΔE_S by substituting the solution for $\bar{\phi}(r)$ for $h = 0$ given in Eq. (4.35) into Eq. (5.4), neglecting the term proportional to h , and integrating only over the radial coordinate.

$$\Delta E_S \approx \int_{-\infty}^{\infty} \frac{|\epsilon|^2}{4} [1 - \tanh^4 \sqrt{2}|\epsilon|^{1/2}(r - r_0)] dr = \frac{\sqrt{2}|\epsilon|^{3/2}}{3}. \quad (5.10)$$

If we substitute ΔE_S and ΔE_B into Eq. (5.4), perform the required integrals (we have already done the radial part of the integral over ΔE_S), and remember that h is negative, we obtain

$$-\beta\Delta H \approx -\beta R^d \left[-2|h|\sqrt{\frac{|\epsilon|}{2}} \frac{4}{3}\pi r_0^3 + \frac{\sqrt{2}|\epsilon|^{3/2}}{3} 4\pi r_0^2 \right]. \quad (5.11)$$

To obtain the critical droplet, we need to complete the variational procedure that we did not complete before because we could not solve Eq. (4.30) for $h \neq 0$. From Eq. (5.11) it is clear that we will again obtain results for the critical droplet radius and for the free energy cost of the critical droplet which are essentially the same as obtained in Chapters 1 and 3.

It is useful to comment a bit more on the integral in Eq. (5.10). It is clear why we did not perform the integral over the angles at this time, but why did we not use the r^2 part of the volume differential, $d\vec{r} = r^2 \sin(\theta) dr d\theta d\phi$? The answer lies again in the separation of the surface and bulk terms in the limit $h \rightarrow 0$. The parameter r_0 , which locates the center of the droplet surface, is assumed to be large if the droplet center is placed at the origin. The magnitude of r_0 will be seen to be of order h^{-1} in the following. We can write $r = r_0[1 + (r - r_0)/r_0]$. The term $1 - \tanh^4[\sqrt{2}|\epsilon|^{1/2}(r - r_0)]$ restricts $r - r_0$ to be small compared to h^{-1} so we can ignore the $(r - r_0)/r_0$ term and set $r^2 = r_0^2$ in the volume differential.

5.3 Nucleation rate

We now consider the nucleation rate. As we saw with the droplet model in Chapter 3, the nucleation rate is associated with the jump across the branch cut obtained from the analytic continuation to negative values of the magnetic field. In the droplet model this analytic continuation was performed explicitly. The Landau-Ginsburg-Wilson (LGW) model is not as simple to analyze.

One difference between the two models is that the stable state for $h > 0$ and the metastable state for $h < 0$ are not specified for the droplet model. We know only that they correspond to the droplet parameter $\ell = 0$. In the LGW model the metastable and stable states are specified. Moreover, the LGW model is rich enough so that these states can be determined as functions of h and ϵ .

The other difference, which is more mathematically complicated, is that in the droplet model the integral over fluctuations is reduced to a simple integral in one direction in the space of fluctuations. All fluctuations are assumed to be simple spherical compact droplets which can be varied only by changing their radius. In the LGW model this simplification is not present, and the integral is to be performed in an infinite dimensional function space. Consequently, it is not possible to carry out the program of analytic continuation explicitly in the LGW model.

However, we can make certain physically based arguments using the classical droplet model as a paradigm. In the classical droplet model there are two saddle points for $d \geq 2$. The one on which we concentrated corresponded to the critical droplet, that is, Eq. (3.33). However, there is also a saddle point at $\ell = 0$. This saddle point corresponds to the metastable state for $\alpha = -1$ in Eq. (3.31). As we discussed, there is no saddle point in this simple model that corresponds to the stable state for $h < 0$. Note that it is the saddle point associated with the droplet that we integrate over in the droplet model to obtain the imaginary part of the free energy and hence the nucleation rate.

By using the droplet model as a paradigm we will use the saddle point associated with the droplet in the LGW model to obtain the nucleation rate. That is, we want the part of the solution of Eq. (4.9) corresponding to the critical droplet. Remember that the complete solution of Eq. (4.9) also contains the metastable state. If we could obtain this solution directly for arbitrary h , we would simply substitute it into the LGW Hamiltonian to obtain the exponential factor of the nucleation rate. We could then expand in a functional Taylor series about the critical droplet saddle point and do the Gaussian integral to obtain the prefactor [see Eq. (3.34)].

As we discussed we cannot solve Eq. (4.9) for arbitrary values of h . However, we have obtained the energy cost of the droplet using a plausible argument due to Langer. To obtain the exponential part of the nucleation rate we return to Eq. (5.11). We differentiate

with respect to r_c and set the derivative equal to zero, and obtain

$$r_c = \frac{2}{3} \frac{|\epsilon|}{|h|}. \quad (5.12)$$

If we substitute this value for r_c into Eq. (5.11), we obtain

$$-\beta\Delta H = -\beta R^d \sqrt{2} \left(\frac{8}{9}\right)^2 \frac{\pi}{27} \frac{|\epsilon|^{7/2}}{|h|^2}. \quad (5.13)$$

From Eq. (4.4) and our analogy with the droplet model we obtain the nucleation rate J

$$J = \lambda_s \exp \left[-\beta R^d \sqrt{2} \left(\frac{8}{9}\right)^2 \frac{\pi}{27} \frac{|\epsilon|^{7/2}}{|h|^2} \right]. \quad (5.14)$$

The exponential part of the nucleation rate is consistent with that obtained from the Becker-Döring theory. The prefactor λ_s is very difficult to obtain. We will return to the prefactor in the context of nucleation near the spinodal where the same techniques are used as in the classical case, but the calculation is a bit more transparent, although still quite involved. We turn to the spinodal case next.

5.4 Nucleation near the spinodal

We begin by returning to Eq. (4.10) which we repeat here for convenience.

$$-2|\epsilon|\phi + 4\phi^3 - h = 0, \quad (5.15)$$

and we have assumed a negative value for ϵ . The solutions to Eq. (5.15) are either the metastable or stable minima or an unstable maximum. Suppose we differentiate the left-hand side of Eq. (5.15) and set this second derivative of the Landau-Ginsburg free energy equal to zero to obtain the value of ϕ at the spinodal. We obtain

$$-2|\epsilon| + 12\phi^2 = 0. \quad (5.16)$$

The solution to Eq. (5.16) locates the inflection points in the Landau-Ginsburg free energy. It is the point where the free energy ceases to be convex (see Fig. 5.1).

If we fix $|\epsilon|$ and require that both Eqs. (5.15) and (5.16) be satisfied simultaneously we locate the point at which the metastable minimum vanishes. At this point the metastable minimum, the maximum, and the inflection point coalesce. We designate the value of the order parameter at this point as ϕ_s and the value of the magnetic field as h_s . Both of these quantities depend on the temperature.

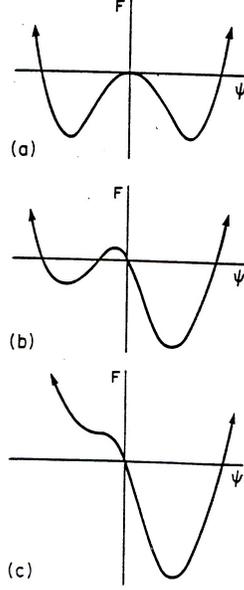


Figure 5.1: Landau-Ginsburg free energy for (a) $h = 0$, (b) $0 < h < h_s$ and (c) $h = h_s$.

We now define a new field

$$\tilde{\psi}(\vec{r}) \equiv \phi(\vec{r}) - \phi_s. \quad (5.17)$$

We can rewrite the LGW Hamiltonian by substituting $\phi(\vec{r}) = \tilde{\psi}(\vec{r}) + \phi_s$ obtained from Eq. (5.17) into Eq. (4.2) to obtain

$$-\beta H(\tilde{\psi}) = -\beta H(\phi_s) - \beta R^d \int \left[\frac{1}{2} [\nabla \tilde{\psi}(\vec{r})]^2 + \Delta h \tilde{\psi}(\vec{r}) - \sqrt{6} |\epsilon| \tilde{\psi}^3(\vec{r}) + \tilde{\psi}^4(\vec{r}) \right] d\vec{r}, \quad (5.18)$$

where $\Delta h = h_s - h$, and $H(\phi_s)$ is the LGW Hamiltonian at $\phi(\vec{r}) = \phi_s$. We will ignore ϕ_s because it will produce only an overall constant.

Because we will stay away from the critical point, $|\epsilon| \neq 0$. However, as we approach the spinodal, Δh will vanish. We might also expect that $\tilde{\psi}(\vec{r})$ will also be small near the spinodal. The reason is that the spinodal is a critical point as discussed in Chapter 3. At the spinodal we expect that any fluctuations, including critical droplets, are not compact objects with large differences in the order parameter between the droplet interior and the metastable state background, but are diffuse objects. We will see that this assumption is correct. We make this assumption for now and neglect the $\tilde{\psi}^4(\vec{r})$ term in Eq. (5.18) because it is small compared to the $\tilde{\psi}^3(\vec{r})$ term [Cahn and Hilliard 1958, Cahn and Hilliard 1959, Klein and Unger 1983, Unger and Klein 1984].

We will make one more alteration to Eq. (5.18). We have expanded Eq. (4.3) about the spinodal by setting $\phi(\vec{r}) = \tilde{\psi}(\vec{r}) + \phi_s$. Note that the first functional derivative of $-\beta H(\tilde{\psi})$ does not vanish unless $\Delta h = 0$, but the second derivative vanishes for all values of Δh at $\tilde{\psi}(\vec{r}) = 0$, that is, at $\phi(\vec{r}) = \phi_s$. For several reasons it will be more convenient to expand instead about the metastable minimum. To do so we define a new field

$$\psi(\vec{r}) \equiv \tilde{\psi}(\vec{r}) + a, \quad (5.19)$$

where a is a constant to be determined. We then insert $\tilde{\psi}(\vec{r}) = \psi(\vec{r}) - a$ and determine a so that the coefficient of $\psi(\vec{r})$ vanishes. We obtain

$$\begin{aligned} -\beta H(\psi) = & -\beta H(\phi_s) - L^d \beta R^d \frac{1}{3} \sqrt{3} |\Delta h|^{3/2} |\epsilon|^{1/4} \\ & - \beta R^d \int \left[\frac{1}{2} [\nabla \psi(\vec{r})]^2 + 2\sqrt{3} |\epsilon|^{1/4} (\Delta h)^{1/2} \psi^2(\vec{r}) - 6|\epsilon|^{1/2} \psi^3(\vec{r}) \right] d\vec{r}. \end{aligned} \quad (5.20)$$

The first functional derivative vanishes at $\psi(\vec{r}) = 0$, but the second derivative vanishes only when $\Delta h = 0$ as well. The value of a is such that the order parameter $\psi(\vec{r}) = \phi(\vec{r}) - \phi_m$, where ϕ_m is the value of the order parameter obtained from Eq. (5.15) at the metastable minimum. The first two terms on the right-hand side of Eq. (5.20) are independent of $\psi(\vec{r})$ and can be ignored for the present.

Before proceeding to investigate the nucleation process near the spinodal we need to investigate the thermodynamics of the metastable state near the spinodal. We begin by finding the expression for the equilibrium order parameter when we fix the value of $\psi(\vec{r}) = L^{-d}$ at $r = 0$. This is simply the pair correlation function, which is the probability that there is a particle at \vec{r} given that there is a particle at another fixed site that we have chosen to be $\vec{r} = 0$. In the $\beta R^d \gg 1$ limit this correlation function can be found by finding the extrema of the LGW Hamiltonian using a Lagrange multiplier with the condition that $\psi(\vec{r} = 0) = L^{-d}$. Specifically we need the functional derivative of

$$\int \left[\frac{1}{2} [\nabla \bar{\psi}(\vec{r})]^2 + 2\sqrt{3} |\epsilon|^{1/4} (\Delta h)^{1/2} \bar{\psi}^2(\vec{r}) - 6|\epsilon|^{1/2} \bar{\psi}^3(\vec{r}) - \lambda(\delta(\vec{r}) \bar{\psi}(\vec{r}) - L^{-d}) \right] d\vec{r}, \quad (5.21)$$

which results in the Euler-Lagrange equation

$$-\nabla^2 \bar{\psi}(\vec{r}) + 4\sqrt{3} |\epsilon|^{1/4} (\Delta h)^{1/2} \bar{\psi}(\vec{r}) - 18|\epsilon|^{1/2} \bar{\psi}^2(\vec{r}) = \lambda \delta(\vec{r}). \quad (5.22)$$

We expect the correlation function $\bar{\psi}(\vec{r})$ to be of the form [Ma 1976]

$$\bar{\psi}(\vec{r}) = \frac{\exp -r/\xi}{r^{d-2+\eta}}, \quad (5.23)$$

where ξ is the correlation length.

For large r , $\bar{\psi}(\vec{r})$ is small. Consequently we can neglect the $\bar{\psi}^2(\vec{r})$ term in Eq. (5.22). We then want to solve

$$-\nabla^2 \bar{\psi}(\vec{r}) + 4\sqrt{3}|\epsilon|^{1/4}(\Delta h)^{1/2} \bar{\psi}(\vec{r}) = \lambda \delta(\vec{r}). \quad (5.24)$$

We take the Fourier transform and obtain

$$\hat{\bar{\psi}}(\vec{k}) = \frac{\lambda}{k^2 + 4\sqrt{3}|\epsilon|^{1/4}(\Delta h)^{1/2}}. \quad (5.25)$$

The Fourier transform of the correlation function is the structure factor $\hat{\bar{\psi}}(k)$, where the structure factor is a function of the magnitude $|\vec{k}|$ only. The critical exponent η is obtained [Ma 1976] by setting $\Delta h = 0$ and asking how the structure factor diverges as $k \rightarrow 0$. The divergence we expect is

$$\hat{\bar{\psi}}(k) \approx k^{-(2-\eta)}. \quad (5.26)$$

From Eqs. (5.25) and (5.26) we conclude that $\eta = 0$.

To obtain the susceptibility exponent γ defined by

$$\chi_T \approx (\Delta h)^{-\gamma}, \quad (5.27)$$

where χ_T is the isothermal susceptibility, we set $k = 0$ and ask how the susceptibility diverges as $\Delta h \rightarrow 0$. From Eqs. (5.25) and (5.27) we obtain $\gamma = 1/2$.

We obtain the correlation length exponent,

$$\xi \approx (\Delta h)^{-\nu}, \quad (5.28)$$

by taking the inverse Fourier transform of $\hat{\bar{\psi}}(k)$ in Eq. (5.25). In $d = 3$

$$\bar{\psi}(r) = \frac{\pi}{r} \int_{-\infty}^{\infty} \frac{k \sin(kr)}{k^2 + 4\sqrt{3}|\epsilon|^{1/4}(\Delta h)^{1/2}}. \quad (5.29)$$

The integral is done as a contour integral by breaking up $\sin(kr)$ into two exponentials and closing the contour in the upper half complex k plane for the e^{ikr} term and in the lower half plane for the e^{-ikr} term. We let $\omega^2 = 4\sqrt{3}|\epsilon|^{1/4}$ and obtain

$$\bar{\psi}(r) = \pi^2 \frac{\exp[-\omega(\Delta h)^{1/4}r]}{r}. \quad (5.30)$$

From Eq. (5.30) we immediately obtain $\nu = 1/4$. We also obtain $\eta = 0$ by comparison with Eq. (5.23), consistent with our earlier result. To obtain the precise asymptotic form for the correlation length remember that $r = x/R$. Therefore in unscaled units $\xi \approx R(\Delta h)^{-1/4}$.

We need two more critical exponents. We want to obtain the exponent β (not to be confused with $(k_B T)^{-1}$), which specifies the way $\phi_m - \phi_s \rightarrow 0$ as $\Delta h \rightarrow 0$. We defined $\tilde{\psi}(\vec{r})$ in Eq. (5.17) as the difference between the order parameter and the spinodal value ϕ_s . To obtain β we restrict $\tilde{\psi}(\vec{r})$ to be a spatial constant $\tilde{\psi}$ and define β through

$$\tilde{\psi} \approx (\Delta h)^\beta. \quad (5.31)$$

To obtain β we return to Eq. (5.18), assume $\tilde{\psi}(\vec{r}) = \tilde{\psi}$, differentiate $-\beta H(\tilde{\psi})$ with respect to $\tilde{\psi}$, and obtain

$$\tilde{\psi} \approx (\Delta h)^{1/2}, \quad (5.32)$$

where we neglected the term in $\tilde{\psi}^4$. Therefore $\beta = 1/2$.

The last critical exponent we wish to determine is the one that specifies the free energy cost of a critical fluctuation the size of the correlation length. We can find this exponent by substituting Eq. (5.32) into Eq. (5.18). The partition function is

$$z = \int \delta\tilde{\psi} \exp[-\beta H(\tilde{\psi})]. \quad (5.33)$$

In the limit $\beta R^d \gg 1$ we can do the integral using steepest descent and obtain the free energy per unit volume f as

$$f(|\epsilon|, |\Delta h|) \approx (\Delta h)^{3/2}. \quad (5.34)$$

The exponent corresponding to this quantity is $2 - \alpha$. The free energy cost ΔF of a fluctuation of linear dimension ξ is

$$\Delta F = f(|\epsilon|, |\Delta h|) \xi^d \approx R^d (\Delta h)^{\frac{3}{2} - \frac{d}{4}}, \quad (5.35)$$

In summary, we have obtained the critical exponents at the spinodal as

$$\eta = 0, \quad \gamma = 1/2, \quad \beta = 1/2, \quad \nu = 1/2, \quad \text{and } 2 - \alpha = 3/2. \quad (5.36)$$

These exponents satisfy all of the scaling laws. For example, we should have

$$2\beta + \gamma = 2 - \alpha, \quad (5.37)$$

which is satisfied by the exponents in Eq. (5.36). We will return to the subject of scaling shortly.

What do these considerations have to do with nucleation near the spinodal? Let's return to Eqs. (5.20) and (5.33) and apply the same methods that we used in the classical case. The metastable order parameter, with the critical droplet, is the solution of the differential equation

$$-\nabla^2 \psi(\vec{r}) + 4\sqrt{3}|\epsilon|^{1/4}(\Delta h)^{1/2} \psi(\vec{r}) - 18|\epsilon|^{1/2} \psi^2(\vec{r}) = 0. \quad (5.38)$$

As with the classical case this equation is difficult to solve. However, here we can take advantage of scaling. If we assume that the function $\psi(\vec{r})$ is of the form

$$\psi(\vec{r}) = (|\Delta h|)^{1/2} \psi'(\vec{r}(\Delta h)^{1/4}) \quad (5.39)$$

we obtain an equation for ψ' independent of Δh . Equation (5.39) implies that the critical droplet has an amplitude proportional to $(\Delta h)^{1/2}$. That is, the density at the center of the droplet goes to zero in the same way the order parameter goes to zero [see Eq. (5.32)]. Again using the unscaled length variable we see that Eq. (5.39) also implies that the linear dimension of the droplet is proportional to $R(\Delta h)^{-1/4}$, that is, the correlation length (see Eq. (5.30) and the following discussion).

Finally, we can substitute Eq. (5.39) into Eq. (5.20) to obtain the nucleation rate, or at least the way it scales. To do so we should first subtract from the solution in Eq. (5.39) the value as $r \rightarrow \infty$, which will be the spatially constant metastable value of the order parameter. As an example, we will consider nucleation near the spinodal in one dimension in Chapter 6, where we will see explicitly how this calculation works. Here, we will use the fact that we only want the scaling behavior and that the droplet is the size of the correlation length. Then we can do the spatial integration in Eq. (5.20) by assuming that the droplet $\psi(x/\xi)$ is a spatial constant up to $x \sim \xi$ and is zero for larger values of x . By using the same arguments we employed in the classical case near the coexistence curve we obtain for the nucleation rate J

$$J = \tilde{\lambda}_s \exp[-C\beta R^d (\Delta h)^{\frac{3}{2} - \frac{d}{4}}], \quad (5.40)$$

where C is a constant. If we compare Eq. (5.40) with the Becker-Döring nucleation rate (Eq. (3.18) and the simple theory in Chapter 1, we are lead to identify the argument of the exponential in Eq. (5.40) with the free energy cost of the critical droplet. This expression is the same as that of the cost of a critical phenomenon fluctuation near the spinodal given in Eq. (5.35).

So far our analysis has shown that the critical droplet, which initiates the decay of the metastable state, has the linear dimension, and free energy cost, of fluctuations near the spinodal critical point, and a density which vanishes at the spinodal with the same critical exponent as the order parameter. These properties lead to the idea that the critical droplet is a critical fluctuation near the spinodal. We will expand on this point in Chapter 6. For now we want to make three points about the argument of the exponential term in Eq. (5.40).

1. The fact that nucleation near the spinodal occurs with droplets that are critical fluctuations indicates that nucleation near the spinodal is not a “tunneling” from the bottom of the metastable well to the bottom of the stable well as it is in the classical case. Rather, it is a “tunneling” from the bottom of the metastable well to the top of the stable one as $\Delta h \rightarrow 0$.

2. The spinodal is at $\Delta h = 0$. The free energy barrier to nucleation ΔF_c from Eq. (5.40) is of the form

$$\Delta F_c \approx C\beta R^d (\Delta h)^{\frac{3}{2} - \frac{d}{4}}. \quad (5.41)$$

If we want to study nucleation, we must have ΔF_c large, that is, $\Delta F_c \sim 10$. If $\Delta h \ll 1$, we must have $R \gg 1$, which implies that spinodal nucleation (nucleation near the spinodal) can only be a valid description of the nucleation process for systems undergoing deep quenches with long-range interactions. How long-range do the interactions have to be? The answer depends on the constant C , which varies from system to system. However, in simulations of Ising models in $d = 3$ with a varying range of interaction, non-classical effects were seen in systems with interaction ranges as short as four lattice constants [Heermann and Klein, 1983].

3. Equation (5.41) predicts that $d = 6$ is the upper critical dimension. Above $d = 6$ it appears even for $R = 1$ that the nucleation rate is extremely small for small Δh . This point was tested by Ray [1991] and is consistent with his results.

Suggestions for Further Reading

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