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Breakup of Universality in the Generalized Spinodal Nucleation Theory

Cyrill B. Muratov[1] **and Eric Vanden-Eijnden**[2,3]

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The problem of nucleation near spinodal is revisited. It is shown that the standard scaling argument due to Unger and Klein [*Phys. Rev. B* **29**:2698–2708 (1984)] based on neglecting all but the first two terms of the Taylor expansion of the potential in the free energy functional is only valid below critical dimension. At critical dimension, the nucleating droplet has a bigger amplitude and a smaller spatial extent than predicted by the standard scaling argument. In this case the structure of the droplet is determined in a nontrivial fashion by the next order term in the expansion of the potential. Above critical dimension, the amplitude of the nucleating droplet turns out to be too big to justify expanding the potential in Taylor series, and no universality is to be expected in the shape and size of the droplet. Both at and above critical dimension, however, the free energy barrier remains finite, which indicates that the nucleation rate does not vanish at spinodal as predicted by the standard scaling argument.

KEY WORDS: Non-classical nucleation; spinodal; critical droplet; matched asymptotics; scaling.

1. INTRODUCTION

First-order phase transitions are dynamical barrier crossing events.(1) This is why a metastable phase, even though it is not thermodynamically preferred, may persist over long periods of time before decaying to the stable phase. Small fluctuations of the metastable phase tend to disappear, and a fluctuation of critical size—a nucleating droplet—must be created from which the system can quickly transform to the stable phase. The free

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[1] Department of Mathematical Sciences, New Jersey Institute of Technology, Newark, New Jersey 07102; e-mail: muratov@njit.edu

[2] Courant Institute of Mathematical Sciences, New York University, New York, New York 10012.

[3] Institute for Advanced Study, Princeton, New Jersey 08540.

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energy of this nucleating droplet determines the rate k of the transformation via Arrhenius law (for a recent review, see ref. 2):

$$k = \nu \exp(-\Delta F / k_B T). \tag{1}$$

Here ν is a prefactor which contains information about the kinetics of the system, and $\Delta F / k_B T$ is the ratio of the free energy cost of a nucleating droplet to the thermal energy $k_B T$; (1) is valid when this ratio is large. The shape of the nucleating droplet gives information about the mechanism of the transformation. In the simplest situations when classical nucleation theory applies, the nucleating droplet can be described as an island of the stable phase which appears within the metastable one, and can therefore be described in terms of its radius as a single parameter; the size of the nucleating droplet is such that the free energy gained by creating this volume of the stable phase balances exactly the free energy spent in sustaining the interface of the droplet.(2, 3) In many situations, however, classical nucleation theory is insufficient because the droplet differs significantly from an homogeneous island of the new stable phase and requires more parameters for its description.(1)

Nonclassical nucleation theory, pioneered by Cahn and Hilliard(4) and based on a mean-field description as briefly summarized in the next paragraphs, identifies the nucleating droplet as the saddle point of some suitably defined free energy functional. Under appropriate circumstances, namely near the spinodal point (a point at which the metastable phase becomes thermodynamically unstable), Cahn and Hilliard,(4) and then Unger and Klein(5) have concluded that the nucleating droplet displays universal characteristics. However, some of the conclusions of the spinodal nucleation theory are paradoxical at and above some critical spatial dimension (see below). Our purpose is to generalize this theory, obtain the nucleating droplet near spinodal, and resolve the paradoxes mentioned above by establishing under which circumstances this droplet is or is not universal. As in refs. 4 and 5, we proceed within the framework of a simple mean-field theory based on a free energy functional of Ginzburg–Landau type, which we briefly summarize first. Note that this type of description can be systematically derived for long-range Ising models or systems of particles interacting via a long-range Kac potential after resorting to gradient expansion (see, for example, refs. 6–10). Also note that related questions may also arise in the context of quantum field theories (see, for example, ref. 11).

Within mean-field theory, the state of the system undergoing a simple first-order phase transition is represented by a scalar order parameter ϕ

defined in the domain $\Omega \subset \mathbb{R}^d$, together with the free energy functional (see, for example, ref. 12)

$$F = \int_\Omega \left(\tfrac{1}{2}\,|\nabla\phi|^2 + V(\phi)\right) dx. \tag{2}$$

The first term in (2) penalizes the spatial fluctuations of the order parameter, while the second favors to minimize the effective potential $V(\phi)$ (which also depends on the control parameters, such as temperature, etc.). Different phases are then defined as the local minima of $V(\phi)$; when $V(\phi)$ has more than one minimum, the system can sustain more than one phase. The lowest energy phase is thermodynamically stable, while all the other phases are metastable.

The dynamics of such a system may be described via the noisy gradient flow(13)

$$\phi_t = -M\,\frac{\delta F}{\delta\phi} + \eta(x, t). \tag{3}$$

Here $\delta F/\delta\phi$ is the Frechet derivative of $F[\phi]$, M is the generalized mobility (for example, one may have $M = 1$ for continuous ordering or $M = -\Delta$ for spinodal decomposition in the context of Ginzburg–Landau theories(12)), and $\eta(x, t)$ is the noise appropriately defined so that the equilibrium distribution associated with (3) is formally the Gibbs distribution proportional to $e^{-F[\phi]/k_B T}$; note that there are technical difficulties in giving a precise mathematical meaning to (3) with such a noise.(14) When the noise is small (i.e., if the thermal energy $k_B T$ is much smaller than the typical free energy barriers in the system), there is metastability: the system remains for long periods of time in one phase before being driven to another phase by thermal fluctuations. Motivated by large deviation theory,(15) one then deduces that the dynamical paths by which the system undergoes a phase transformation lie within a small tube around the (time-reversed) heteroclinic orbit connecting the lowest-lying saddle point of F with the metastable and stable equilibria; this orbit is obtained from the deterministic (zero noise) version of (3), whereas the saddle point of the free energy functional(4) is a solution of the Euler–Lagrange equation associated with (2):

$$\Delta\phi = V'(\phi), \tag{4}$$

where Δ is the d-dimensional Laplacian. The saddle point determines the shape of the nucleating droplet and also allows to calculate the free energy barrier ΔF and hence the leading order contribution to the nucleation rate in (1). This is the problem which we shall focus on here, leaving a more refined analysis leading also to the prefactor ν in (1) for the future.

In an extended system, the saddle point associated with the phase transformation from a higher energy phase to that of lower energy must be a localized nucleating droplet. Back in ref. 4, Cahn and Hilliard showed that near spinodal in $d = 3$ the amplitude of the nucleating droplet should be small; therefore, the droplet can be determined by expanding in Taylor series the potential in (2) and (4):

$$V(\phi) = \frac{b_2}{2}\phi^2 + \frac{b_3}{3}\phi^3 + O(\phi^4). \tag{5}$$

Here b_n are expansion coefficients (generally, depending on the control parameters) and it is assumed that $\phi = 0$ is the metastable state out of which the nucleation takes place. The spinodal corresponds to $b_2 \to 0^+$ upon variation of the control parameters as the spinodal is approached. Generically, when the order parameter does not have any special symmetries, the coefficient b_3 will not vanish at the spinodal; in this case, the nucleating droplet can be obtained by neglecting all the terms in the expansion except the first two.(4)

Unger and Klein generalized these arguments to arbitrary space dimensions.(5) Using the truncated potential where only the first two terms at the right hand side of (5) are kept, they observed that the amplitude of the nucleating droplet decreases, and its spatial extent increases as one approaches spinodal; they also observed that, below the critical dimension $d_c = 6$, the free energy barrier decreases in this limit, whereas it tends to a finite constant when $d = d_c$ and it blows up above critical dimension, $d > d_c$. This conclusion is actually paradoxical, since (1) then implies that the rate of phase transformation vanishes when spinodal is approached, even though the metastable phase corresponding to $\phi = 0$ must disappear at spinodal.

As mentioned earlier, in this paper we revisit the spinodal nucleation theory(4, 5) and extend it to potentials admitting a more general expansion than in (5). The precise shape and scaling of the nucleating droplet are obtained using careful matched asymptotics expansion techniques. In particular, we establish that the conclusions of standard nucleation theory are only valid below the critical dimension. At critical dimension, the amplitude of the nucleating droplet is bigger, and its spatial extent smaller, so that the next term in the Taylor expansion of the potential in (5) must be accounted for. Furthermore, above critical dimension, the amplitude of the nucleating droplet becomes too big to justify Taylor expanding the potential as in (5). In this case, the nucleating droplet depends more sensitively on the full shape of $V(\phi)$ and does not display universal features near spinodal. Both for $d = d_c$ and $d > d_c$, however, the free energy barrier remains finite as one approaches spinodal, which ensures that the nucleation rate in (1) does not vanish at the spinodal.

The remainder of this paper is organized as follows. In Section 2 we generalize the scaling argument of the classical spinodal nucleation theory and establish its precise range of validity. In Section 3 we refine the scaling analysis at and above critical dimension, and resolve the paradoxes observed in ref. 5. Some concluding remarks are then given in Section 4. Finally, we devote the appendix to the situation of special physical interest when $d = 3$ which is relevant for nucleation near a tricritical point.

2. THE STANDARD SCALING ARGUMENT AND ITS RANGE OF VALIDITY

Here we generalize the arguments of Unger and Klein for the situation in which at spinodal the first non-zero coefficient in the Taylor expansion of $V(\phi)$ is b_p, $p > 2$, with $b_p < 0$ (this assumption is inessential for p odd, but is needed for p even in order for spinodal nucleation out of the $\phi = 0$ state to be possible). We also focus on the case of an infinite domain, $\Omega = \mathbb{R}^d$; the argument can be easily generalized to finite domains provided they are large enough—see below. After appropriate dimensional reduction, the free energy in (2) can be written as

$$F = \int_{\mathbb{R}^d} \left(\frac{1}{2} |\nabla\phi|^2 + \frac{1}{2} \varepsilon\phi^2 - \frac{1}{p} \phi^p + \tilde{V}(\phi) \right) dx, \tag{6}$$

where $\varepsilon \to 0^+$ as the spinodal is approached, and $\tilde{V}(\phi) = o(\phi^p)$ as $\phi \to 0$. Rescaling the order parameter and length:

$$\phi \to \varepsilon^{1/(p-2)}\phi, \qquad x \to \varepsilon^{-1/2}x, \tag{7}$$

leads to

$$F = \varepsilon^{\frac{d_c - d}{2}} \left(\int_{\mathbb{R}^d} \left(\frac{1}{2} |\nabla\phi|^2 + \frac{1}{2} \phi^2 - \frac{1}{p} \phi^p \right) dx + o(1) \right), \tag{8}$$

where

$$d_c = \frac{2p}{p-2}, \tag{9}$$

is the critical dimension associated with p. In particular, for $p=3$ (generic case without symmetries) we have $d_c=6$,(5) and for $p=4$ (generic case in the presence of reflection symmetry) we have $d_c=4$, the usual upper critical dimension of the Ginzburg–Landau theory.(16) Note that from the mathematical point of view d_c is the critical dimension of the continuous embedding of the Sobolev space $H^1(\Omega) \hookrightarrow L^p(\Omega)$ with bounded Ω and is intimately related to the extremal properties of F.(17)

From (7), it follows that the radial extent of the droplet grows as $\varepsilon^{-1/2}$ (the correlation length) and its amplitude decreases as $\varepsilon^{1/(p-2)}$ when $\varepsilon \to 0^+$. Also, from (8) one can see that for $d<d_c$ the free energy cost of the droplet goes to zero as $\varepsilon^{(d_c-d)/2}$ when $\varepsilon \to 0^+$. In other words, for $d<d_c$ it becomes easier for a system to nucleate as the spinodal is approached. Surprisingly, this argument also suggests that for $d>d_c$ the free energy cost associated with the nucleating droplet goes to infinity as $\varepsilon \to 0^+$, implying that it becomes harder for the system to nucleate close to the spinodal (at which the metastable phase disappears). This conclusion, however, is incorrect, because the argument above does not apply above critical dimension, as we show now.

Neglecting the $o(1)$ term in (8) for small ε, one obtains the Euler–Lagrange equation:

$$\Delta\phi = \phi - \phi^{p-1}. \tag{10}$$

Thus, in the vicinity of the spinodal the nucleating droplet may be obtained from the nontrivial solution of (10) that vanishes at infinity. Where the scaling argument may fail, however, is that there is no guarantee that (10) has a nontrivial solution for arbitrary d.

Existence of solutions of Eqs. (4) and (10) was studied in great detail and leads to a classical variational problem.(17–23) For sufficiently large bounded domains positive solutions of (10) were proved to exist for any $p>2$ in $d \leqslant 2$, as well as for $d<d_c$ when $d \geqslant 3$ (see, for example, ref. 17). Similarly, these solutions were proved to exist under the same assumptions when $\Omega = \mathbb{R}^d$.(17, 20, 21, 23) In fact, when $\Omega = \mathbb{R}^d$ and $d \geqslant 3$ the obtained solutions have the lowest free energy out of all nontrivial solutions of (10),(19, 23) so they should indeed correspond to nucleating droplets. These existence results imply, in particular, that the solution of (10) indeed exists in the case of the standard spinodal nucleation in $d=3$,(4, 5, 24) and that in general the scaling argument presented above holds in $d<d_c$.

On the other hand, the variational argument fails for $d \geqslant d_c$. In fact, in this case it can be shown that there are *no* nonzero solutions to (10) in

$d \geqslant 3$.(18, 23) To see this, we use the identity due to Pokhozhaev, which the solutions of (10) decaying appropriately at infinity must satisfy:(17, 18, 23)

$$\frac{d-2}{2}\int_{\mathbb{R}^d} |\nabla\phi|^2\,dx+\frac{d}{2}\int_{\mathbb{R}^d} \phi^2\,dx-\frac{d}{p}\int_{\mathbb{R}^d} \phi^p\,dx=0. \tag{11}$$

This identity is obtained from (10) upon multiplication by $x\cdot\nabla\phi$ and a number of integrations by parts. Next we calculate the integral of ϕ^p by multiplying (10) by ϕ, integrating by parts, and combining it with (11) to obtain

$$\int_{\mathbb{R}^d} \phi^2\,dx+\frac{d-d_c}{d}\int_{\mathbb{R}^d} |\nabla\phi|^2\,dx=0. \tag{12}$$

For $d \geqslant d_c$ both terms at the left hand-side are positive and this equation cannot be satisfied with a nonzero ϕ. Therefore, the scaling argument presented above fails to predict the parameters of the nucleating droplet in this situation, and a more subtle analysis of the free energy functional in (2) is necessary.

Notice also that the arguments above can be generalized to a finite domain Ω provided the radial size of Ω is much larger than the size of the nucleating droplet, which is $O(\varepsilon^{-1/2})$ from (7) (see also ref. 20). In particular, (12) is modified by including a boundary term which does not help to satisfy this equation.(17)

3. A REFINED SCALING ANALYSIS

When (10) has no nontrivial solutions, the natural generalization is to take into account the next term in the expansion of the potential $V(\phi)$ in (6) and check two things. First, that the corresponding Euler–Lagrange equation does indeed have a solution in this case; second, that this solution has a sufficiently small amplitude so that truncation of the series expansion of $V(\phi)$ is justified. At critical dimension, it turns out that both requirements can be satisfied, as shown next. Above critical dimension, however, only the first requirement can be satisfied: the solution of the corresponding Euler–Lagrange equation exists, but it is too big in amplitude to justify Taylor expanding $V(\phi)$ in (2). In this case, the full potential must be accounted for, and the droplet profile near spinodal is non-universal.

To see this, let us explicitly include the next-order term in the expansion of the free energy from (6) which is stabilizing for positive values of ϕ. After a suitable dimensional reduction, (2) can be written as

$$F=\int_{\mathbb{R}^d}\left(\frac{1}{2}\,|\nabla\phi|^2+\frac{1}{2}\,\varepsilon\phi^2-\frac{1}{p}\,\phi^p+\frac{1}{q}\,\phi^q+\hat{V}(\phi)\right)dx, \tag{13}$$

where $q > p$ and we have again assumed than $\Omega = \mathbb{R}^d$ (which is fine as long as the radial size of the spinodal droplet remains much smaller than that of Ω). Here $\hat{V}(\phi) = o(\phi^q)$ as $\phi \to 0$; we will first neglect this term in the manipulations below, then verify whether it gives a negligible contribution to the saddle point of (13) (which, as mentioned earlier, will turn out to be true for $d = d_c$, but not for $d > d_c$).

Neglecting $\hat{V}(\phi)$, we arrive at the following canonical Euler–Lagrange equation describing the nucleating droplet

$$\Delta\phi = \varepsilon\phi - \phi^{p-1} + \phi^{q-1}. \tag{14}$$

The first thing to note with this equation is that it leads to an identity similar to (12) but which may now be satisfied in any dimension. Indeed, the Pokhozhaev identity for (14) reads

$$\frac{d-2}{2}\int_{\mathbb{R}^d} |\nabla\phi|^2\, dx + \frac{\varepsilon d}{2}\int_{\mathbb{R}^d} \phi^2\, dx - \frac{d}{p}\int_{\mathbb{R}^d} \phi^p\, dx + \frac{d}{q}\int_{\mathbb{R}^d} \phi^q\, dx = 0. \tag{15}$$

Using (14) multiplied by ϕ and integrated yields (compare with (12))

$$\varepsilon\int_{\mathbb{R}^d} \phi^2\, dx + \frac{d-d_c}{d}\int_{\mathbb{R}^d} |\nabla\phi|^2\, dx = \frac{d_c(q-p)}{pq}\int_{\mathbb{R}^d} \phi^q\, dx. \tag{16}$$

Since $q > p$, the right hand-side is positive whenever the last integral in (16) is positive, and unlike (12) this identity does not imply $\phi = 0$.

Let us now get back to (14). The existence of positive solutions of (14) was studied in great detail by many authors.(17, 19, 21–23) In particular, it follows from the results of Berestycki and Lions that a positive solution of (14) exists for all $d \geqslant 3$, as long as ε is small enough.(21) Moreover, this solution is radially-symmetric, monotonically decreasing with asymptotic exponential decay, and has the lowest free energy out of all possible positive solutions of (14).(19, 23) A straightforward extension of the argument of refs. 19 and 23 also shows that for q even this solution is in fact the lowest free energy saddle point solution out of *all* solutions of (14) and therefore is the correct nucleating droplet.

So, we look for a radially symmetric solution of (14) centered around a point which can be taken as the origin with no loss of generality, i.e., we consider

$$\phi'' + \frac{d-1}{r}\phi' = \varepsilon\phi - \phi^{p-1} + \phi^{q-1}, \tag{17}$$

augmented by the boundary conditions $\phi'(0)=\phi(+\infty)=0$. We treat the cases $d=d_c$ and $d>d_c$ separately; the case $d=3$, which is of special physical interest is also treated in more detail in the appendix. We also note that the calculations presented below were checked and confirmed by direct numerical solution of (17).

3.1. Universal Droplet at Critical Dimension

Different terms in (17) dominate in different ranges of r which, at $d=d_c$, leads to a singular perturbation problem and therefore requires a rather subtle asymptotic analysis in the limit $\varepsilon\to 0^+$. The analysis proceeds in a number of steps below.

Outer Layer Solution. For large r (in the outer layer, to be specified later), when the amplitude of the droplet decays to zero, the first term in the right-hand side dominates. Based on this assumption, one arrives at the outer layer equation for $\phi=\phi_{\text{out}}$:

$$\phi''_{\text{out}}+\frac{d-1}{r}\phi'_{\text{out}}=\varepsilon\phi_{\text{out}}, \tag{18}$$

whose exact solution that decays at infinity is

$$\phi_{\text{out}}(r)=br^{1-\frac{d}{2}}K_{\frac{d}{2}-1}(\varepsilon^{1/2}r), \tag{19}$$

where $b>0$ is a constant to be fixed later by matching, and $K_{\frac{d}{2}-1}(z)$ is the modified Bessel function of the second kind. Using the properties of $K_{\frac{d}{2}-1}(z)$, one has

$$\phi_{\text{out}}(r)\sim b\Gamma\left(\frac{d-2}{2}\right)2^{\frac{d-4}{2}}\varepsilon^{\frac{2-d}{4}}r^{2-d} \qquad \text{when} \quad \varepsilon^{1/2}r\ll 1, \tag{20}$$

$$\phi_{\text{out}}(r)\sim b\pi^{1/2}2^{-1/2}\varepsilon^{-1/4}r^{\frac{1-d}{2}}e^{-\varepsilon^{1/2}r} \qquad \text{when} \quad \varepsilon^{1/2}r\gg 1, \tag{21}$$

where $\Gamma(z)$ is the Gamma-function; here and below, $f\sim g$ indicates that $f/g\to 1$ in the appropriate limit.

Inner Layer Solution. For small r (in the inner layer, to be specified later), i.e., in the core of the nucleating droplet where its amplitude is maximal, the second term at the right-hand side must dominate. Based on this assumption (to be checked a posteriori) and using (9), one arrives at the equation for $\phi=\phi_{\text{in}}$ in the inner layer:

$$\phi''_{\text{in}}+\frac{d-1}{r}\phi'_{\text{in}}=-\phi_{\text{in}}^{\frac{d+2}{d-2}}. \tag{22}$$

This equation has a continuous one-parameter family of positive solutions decaying at infinity:

$$\phi_{\text{in}}(r) = a\varphi(r/r_0), \qquad a r_0^{\frac{d-2}{2}} = 1, \tag{23}$$

where φ is explicitly given by (see, e.g., ref. 23)

$$\varphi(r) = \left(\frac{\sqrt{d(d-2)}}{1+r^2} \right)^{\frac{d-2}{2}}, \tag{24}$$

and the second equation in (23) expresses the obvious scaling symmetry of (22). The values of a and r_0 characterize the amplitude and radial size of the solution, respectively.

As can be seen from (23) and (24), when r increases the solution of (22) behaves as

$$\phi_{\text{in}}(r) \sim \frac{(d(d-2))^{\frac{d-2}{4}}}{a} r^{2-d} \qquad \text{when} \quad r \gg r_0. \tag{25}$$

Comparing (20) with (25), one concludes that

$$b = \frac{2^{\frac{4-d}{2}} (d(d-2)\,\varepsilon)^{\frac{d-2}{4}}}{a\Gamma\left(\frac{d-2}{2}\right)}, \tag{26}$$

and it only remains to fix the constant a. This is done using (16) by evaluating various integrals consistent with the inner-outer expansion above; the different integrals are dominated either by ϕ_{out} or ϕ_{in}, and this is what selects a particular inner solution out of the continuous family in (23). Notice also that it is here that the term ϕ^{q-1} in (14) matters for our refined scaling analysis.

Matching. For $d = d_c$ the second term at the left hand-side of (16) vanishes, and we are left with the following two terms. First, we obtain

$$\varepsilon \int_{\mathbb{R}^d} \phi^2\, dx \sim \begin{cases} 2\pi\sqrt{3}\,\varepsilon^{1/2} a^{-2} & \text{when} \quad d = 3, \\ 8\pi^2 \varepsilon a^{-2} \ln r_0^{-2} \varepsilon^{-1} & \text{when} \quad d = 4, \\ \dfrac{\varepsilon \pi^{d/2} (d(d-2))^{\frac{d-2}{2}}\, \Gamma\left(\frac{d-4}{2}\right) a^2 r_0^d}{\Gamma(d-2)} & \text{when} \quad d > 4, \end{cases} \tag{27}$$

as $\varepsilon \to 0^+$. The integral is dominated by ϕ_{out} for $d=3$, the tail of ϕ_{in} for $d=4$, and by ϕ_{in} for $d>4$. Note that for completeness we included the results for arbitrary $d \geqslant 3$; within the context of the expansion (5) p is an integer, so the relevant situations here are: $d_c = 3, 4, 6$, see (9).

Second, we have

$$\int_{\mathbb{R}^d} \phi^q \, dx \sim \frac{\pi^{d/2} (d(d-2))^{\frac{q(d-2)}{4}} \, \Gamma\left(\dfrac{dq-d-2q}{2}\right) a^q r_0^d}{\Gamma\left(\dfrac{d-2}{2} q\right)} \tag{28}$$

as $\varepsilon \to 0^+$; this integral is dominated by ϕ_{in}. Therefore, comparing (27) and (28), we conclude from (16) that

$$a = \begin{cases} \left(\dfrac{4\varepsilon^{1/2} q \Gamma\left(\dfrac{q}{2}\right)}{3^{\frac{q-2}{4}} \pi^{1/2} (q-6) \, \Gamma\left(\dfrac{q-3}{2}\right)} \right)^{\frac{1}{q-4}} & \text{when } d=3 \\ \left(\dfrac{q\Gamma(q) \, \varepsilon \ln \varepsilon^{-1}}{8^{\frac{q-2}{2}} (q-2) \, \Gamma(q-2)} \right)^{\frac{1}{q-2}} & \text{when } d=4, \\ (d(d-2))^{\frac{2-d}{4}} \left(\dfrac{2\varepsilon q \Gamma\left(\dfrac{d-4}{2}\right) \Gamma\left(\dfrac{d-2}{2} q\right)}{(qd-2q-2d) \, \Gamma(d-2) \, \Gamma\left(\dfrac{qd-2q-d}{2}\right)} \right)^{\frac{1}{q-2}} & \text{when } d>4. \end{cases} \tag{29}$$

Similarly, the leading order contribution to the free energy cost ΔF of the nucleating droplet can be obtained from (13) and (14) (multiplied by ϕ and integrated by parts; the obtained integral is dominated by ϕ_{in})

$$\Delta F \sim \frac{1}{d} \int_{\mathbb{R}^d} \phi_{\text{in}}^p \, dx = \frac{\pi^{d/2} d^{\frac{d-2}{2}} (d-2)^{d/2} \, \Gamma\left(\dfrac{d}{2}\right)}{\Gamma(d)}, \tag{30}$$

which indicates that ΔF becomes independent of ε as $\varepsilon \to 0^+$. These results for a few choices of p and q are shown in Table I. A more detailed matched asymptotics analysis of the case $p=6$ and $q=8$ is also presented in the appendix.

Validation. We now validate the assumptions used to obtain these results. First, the separation of the solution into the inner and outer layers

Table I. Scaling of the Droplet Amplitude, a, Its Radial Size, r_0, and Its Free Energy Cost ΔF in the Limit $\varepsilon \to 0^+$ for $p = 3, 4, 6$ and $d = d_c$.

d_c	p	q	a	r_0	ΔF
3	6	8	$\varepsilon^{1/8}$	$\varepsilon^{-1/4}$	$\pi^2\sqrt{3}/4$
4	4	6	$(\varepsilon \ln \varepsilon^{-1})^{1/4}$	$(\varepsilon \ln \varepsilon^{-1})^{-1/4}$	$8\pi^2/3$
6	3	4	$\varepsilon^{1/2}$	$\varepsilon^{-1/4}$	$192\pi^3/5$

is justified if the characteristic length scale r_0 of the inner solution is much smaller than that of the outer: $r_0 \ll \varepsilon^{-1/2}$. From (29) and (23) we obtain that

$$r_0 = \begin{cases} O(\varepsilon^{-\frac{1}{q-4}}) & \text{when} \quad d = 3, \\ O((\varepsilon \ln \varepsilon^{-1})^{-\frac{1}{q-2}}) & \text{when} \quad d = 4, \\ O(\varepsilon^{-\frac{2}{(q-2)(d-2)}}) & \text{when} \quad d > 4. \end{cases} \tag{31}$$

It is not difficult to see from this that the assumption $r_0 \ll \varepsilon^{1/2}$ is always satisfied: case $d = 3$ is verified by direct inspection, and for $d \geqslant 4$ observe that in view of (9) we have (apart from inessential logarithmic terms) $\varepsilon^{1/2} r_0 = O(\varepsilon^{(q-p)/(2(q-2))}) \ll 1$, since $q > p$. Based on this, one also sees that the outer solution ϕ_{out} must be valid in the

$$\text{outer layer} = \begin{cases} r\colon \varepsilon r^{q-4} \gg 1 & \text{when} \quad d = 3 \\ r\colon \varepsilon \ln \varepsilon^{-1} r^{q-2} \gg 1 & \text{when} \quad d = 4, \\ r\colon \varepsilon^2 r^{(q-2)(d-2)} \gg 1 & \text{when} \quad d > 4, \end{cases} \tag{32}$$

whereas the inner solution ϕ_{in} must be valid in the

$$\text{inner layer} = \{r\colon \varepsilon r^2 \ll 1\}. \tag{33}$$

Naturally, a matching layer $r_0 \ll r \ll \varepsilon^{-1/2}$ where both solution are valid necessarily exists.

Second, we need to check that various terms that were dropped in (18) and (22) are indeed negligible. It is easy to see from (29) that both $\phi_{\text{in}} \ll 1$ and $\phi_{\text{out}} \ll 1$ in the domains of their validity, so the term ϕ^{q-1} is small compared to ϕ^{p-1} both in the inner and the outer layers. Note that this also justifies neglecting $\hat{V}(\phi)$ in (13). To see when the term $\varepsilon\phi$ becomes important, we estimate the value r_c for which $\varepsilon\phi$ and ϕ^{p-1} are of the same order. Using (25), for $d = 3$ we obtain $r_c = O(\varepsilon^{-(q-2)/(4(q-4))})$, so it is easy to see that indeed $r_0 \ll r_c \ll \varepsilon^{-1/2}$ for $q > 6$. Similarly, for $d \geqslant 4$ we obtain (apart from the possible logarithmic terms), using (9), (25), and (31), that $r_0 = O(\varepsilon^{-(p-2)/(2(q-2))})$ and $r_c = O(\varepsilon^{-(q+p-4)/(4(q-2))})$, and it is easy to see that for $q > p$ we again have $r_0 \ll r_c \ll \varepsilon^{-1/2}$.

We conclude that at critical dimension the radial extent of the nucleating droplet increases and its amplitude decreases in accordance with universal equations (29) and (31) as $\varepsilon \to 0^+$. These scalings are different from the ones in (7); they show that the size of the droplet grows much slower as $\varepsilon \to 0^+$, and its amplitude also remains substantially larger than below critical dimension.

3.2. Breakup of Universality above Critical Dimension

The above analysis simplifies when $d > d_c$ because (17) leads to a regular perturbation problem as $\varepsilon \to 0^+$. Indeed, Berestycki and Lions have proven that (17) has a nontrivial solution with the right decay at infinity even if the term $\varepsilon\phi$ is set to zero;(23) this solution, whose large r behavior is in fact given by (25), is the leading order approximation to the solution with the term $\varepsilon\phi$ included, which indicates that both the amplitude of the droplet and its radial extension are $O(1)$ in the limit as $\varepsilon \to 0^+$. This is confirmed by the identity (16) in which the first term at the left hand-side is always a small correction (except in $d = 3$ where it is possible to show that it is $O(1)$; this does not affect the argument) and to leading order ($O(1)$ in ε) the second term at the left-hand side balances the right-hand side. This also implies that the free energy barrier reaches a finite constant value in this limit, so the nucleation rate does not have to vanish as $\varepsilon \to 0^+$.

Let us emphasize, however, that the Euler–Lagrange equation in (17) is associated with the free energy where the term $\hat{V}(\phi)$ in (13) is absent; yet, neglecting this term is illegitimate if ϕ is $O(1)$ as $\varepsilon \to 0^+$. In other words, for $d > d_c$, one needs to solve the full equation (4) even in the limit of $\varepsilon \to 0^+$ to obtain the actual shape of the droplet and the value of the free energy barrier. It is important to note that, since the argument based on Taylor expanding the potential $V(\phi)$ is inconsistent, it automatically implies that both the amplitude of the droplet, its radial extension, and its free energy are $O(1)$ in the limit as $\varepsilon \to 0^+$ provided only that

$$\Delta\phi = \varepsilon\phi + \mathscr{V}'(\phi), \tag{34}$$

has a nontrivial solution when $\varepsilon = 0$ (here $\mathscr{V}(\phi) = V(\phi) - \frac{\varepsilon}{2}\phi^2$, so $\mathscr{V}(\phi) = o(\phi^{2d/(d-2)})$ as $\phi \to 0$, and it is assumed that $\mathscr{V}$ has no minimum at zero, consistent with $\phi = 0$ becoming thermodynamically unstable as $\varepsilon \to 0^+$);

yet, the specific properties of the nucleating droplet near spinodal depend on the details of the full potential $V(\phi)$ (or $\mathcal{V}(\phi)$) and are non-universal.

4. CONCLUDING REMARKS

To summarize, we have re-examined the problem of nucleation near spinodal within the general framework of the expansion (13). We found that the properties of nucleating droplets differ qualitatively below, at, and above critical dimension, given by (9). Below critical dimension a simple scaling argument which takes into account only the first two terms in the expansion in (13) and generalizes the arguments of Unger and Klein(5) predicts that the size of the droplet grows as the correlation length and its amplitude decreases when spinodal is approached; the free energy cost of such a droplet decreases also. In this case the characteristics of the droplet are universal and are given by the scaling in (7) and (8).

On the other hand, at critical dimension the situation changes. In this case the simple scaling argument fails because the Euler–Lagrange equation for the reduced problem no longer has non-trivial solutions. The scaling argument, however, can be modified by including the next-order term in the expansion and leads to a set of unusual exponents describing the main characteristics of the nucleating droplet (see (29) and (31)). As spinodal is approached, the size of the droplet grows and the amplitude shrinks, but much slower than below critical dimension. Thus, the properties of the nucleating droplets at critical dimension again turn out to be universal, but with a different set of exponents. Note that in this situation the asymptotic shape of the nucleating droplet, as well as the height of the free energy barrier, can be computed analytically.

Finally, above critical dimension the Taylor expansion used in (13) breaks down because both the size and the amplitude of the nucleating droplet remain of order 1 even right at spinodal. Therefore, in this case one needs to solve the Euler–Lagrange equation (4) for the full problem, so the properties of the droplet will depend on the details of the potential and will therefore be non-universal. Let us point out, however, that in all these cases the free energy barrier associated with the droplet does not diverge, implying that the nucleation rate never vanishes at spinodal. This resolves the apparent paradox of the scaling argument in ref. 5.

APPENDIX: NUCLEATION NEAR TRICRITICAL POINT

Here we present a more detailed investigation of the nucleating droplet in the physically relevant case when $d = 3$, with $p = 6$ and $q = 8$ in the limit

$\varepsilon \to 0^+$. In this case the canonical Euler–Lagrange equation describing a radially symmetric nucleating droplet is

$$\phi'' + \frac{2}{r}\phi' = \varepsilon\phi - \phi^5 + \phi^7. \tag{35}$$

Below we obtain a formal asymptotic series expansion for the solution of (35) using matched asymptotics (see, for example, refs. 25 and 26); this analysis is complimentary to the leading order analysis presented in Section 3.

Before proceeding any further, we note that the situation corresponding to (35) can in fact be easily realized in practice near tricritical point. Indeed, for the order parameter with the reflection symmetry only the even powers of ϕ will enter the expansion in (5). Near tricritical point both b_2 and b_4 are of order $\varepsilon \sim (T - T_c)/T_c$, where T_c is the tricritical temperature. In this case for small ϕ the fourth-order term in (5) is uniformly smaller than the second-order term and therefore can be neglected. Then, if the ϕ^6 term in (13) is destabilizing, $b_6 < 0$, (otherwise we are dealing with a second-order or weakly first-order phase transition at T_c) and the next term ($q = 8$) in the expansion is stabilizing, $b_8 > 0$, we have precisely the situation discussed in Section 3.

To study (35) it is convenient to introduce a new variable $u = r\phi$ and rewrite this equation as

$$u'' - \varepsilon u + r^{-4}u^5 - r^{-6}u^7 = 0, \tag{36}$$

with boundary conditions

$$u(0) = u(+\infty) = 0. \tag{37}$$

Motivated by the arguments in Section 3, we separate u into the inner and outer solutions, with

$$u_{\text{in}}(r) = \varepsilon^{-1/8}(v_0(\varepsilon^{1/4}r) + \varepsilon^{1/4}v_1(\varepsilon^{1/4}r) + \varepsilon^{1/2}v_2(\varepsilon^{1/4}r) + \cdots), \tag{38}$$

and

$$u_{\text{out}}(r) = \varepsilon^{-1/8}(w_0(\varepsilon^{1/2}r) + \varepsilon^{1/4}w_1(\varepsilon^{1/2}r) + \varepsilon^{1/2}w_2(\varepsilon^{1/2}r) + \cdots). \tag{39}$$

Introducing the fast and slow variables

$$\rho = \varepsilon^{1/4}r, \qquad R = \varepsilon^{1/2}r, \tag{40}$$

respectively, expanding the nonlinearity, and collecting the terms with the like powers of $\varepsilon^{1/4}$, we obtain a hierarchy of equations for v's:

$$v_0'' + \rho^{-4} v_0^5 = 0, \tag{41}$$

$$v_1'' + 5\rho^{-4} v_0^4 v_1 - \rho^{-6} v_0^7 = 0, \tag{42}$$

$$\dots$$

and w's:

$$w_0'' - w_0 = 0, \tag{43}$$

$$w_1'' - w_1 = 0, \tag{44}$$

$$w_2'' - w_2 + R^{-4} w_0^5 = 0, \tag{45}$$

$$\dots$$

with the boundary conditions

$$v_0(0) = 0, \qquad v_1(0) = 0, \dots \tag{46}$$

$$w_0(+\infty) = 0, \qquad w_1(+\infty) = 0, \dots . \tag{47}$$

Observe that for bounded v_0 the solutions of (41), (42), etc., behave like

$$v_n \sim a_n + b_n \rho \qquad \text{as} \quad \rho \to +\infty. \tag{48}$$

This, together with the same behavior of w_n as $R \to 0^+$ obtained from the usual Taylor expansion, translates to the following matching conditions (recall (40)):

$$b_0 = 0, \qquad a_0 = w_0(0), \qquad b_1 = w_0'(0), \dots . \tag{49}$$

The obtained hierarchy of equations can be solved exactly. Below we compute the leading order terms and show that they agree with the results of Section 3. Let us start with (41). This is a particular case of the Emden–Fowler equation which can be integrated in quadratures (see, for example, ref. 27; see also Section 3). The solution of (41) that satisfies the first of (46) has the form

$$v_0 = \frac{3^{1/4} c_0 \rho}{\sqrt{1 + c_0^4 \rho^2}}, \qquad \text{with} \quad a_0 = 3^{1/4} c_0^{-1}, \quad b_0 = 0, \tag{50}$$

where c_0 is an arbitrary (positive) constant that arises due to the scaling symmetry of (41). Then, the solution w_0 of (43) that satisfies the second condition in (49) is

$$w_0 = 3^{1/4} c_0^{-1} e^{-R}. \tag{51}$$

Next, (42) can be solved by the method of variation of parameters. To do that, we need to know the two linearly independent solutions $v^{(1)}$ and $v^{(2)}$ of the homogeneous part of (42), with v_0 given by (50). One such solution can in fact be easily obtained by noting that differentiation of (41) with v_0 given by (50) with respect to c_0 gives the homogeneous equation (42) with $v_1 = dv_0/dc_0$. Then, using reduction of order, we obtain

$$v^{(1)} = \frac{\rho(1-c_0^4\rho^2)}{\sqrt{(1+c_0^4\rho^2)^3}}, \qquad v^{(2)} = \frac{1-6c_0^4\rho^2+c_0^8\rho^4}{\sqrt{(1+c_0^4\rho^2)^3}}. \tag{52}$$

Substituting these into the formula of variation of parameters for (42) and using the second of (46), we obtain

$$v_1 = \frac{3^{3/4}c_0[19c_0^2\rho - 3c_0^6\rho^3 - 3(1-6c_0^4\rho^2+c_0^8\rho^4)\arctan(c_0^2\rho)]}{64\sqrt{(1+c_0^4\rho^2)^3}} + c_1 v^{(1)}, \tag{53}$$

where c_1 is an arbitrary constant and

$$a_1 = -\frac{c_1}{c_0^2}, \qquad b_1 = -\frac{3^{7/4}\pi c_0^3}{128}. \tag{54}$$

Now, using the third of (49), we fix the value of c_0:

$$c_0 = 2\left(\frac{64}{27\pi^2}\right)^{1/8}. \tag{55}$$

The constant c_1 carries over to the equation for w_1 through the matching condition; it is then fixed analogously in the equation for v_2. This procedure can be continued to all orders.

As they should, the results above agree with those of Section 3. In particular, the explicit expressions for the droplet amplitude and free energy cost are asymptotically

$$\phi(0) \sim u'_{\text{in}}(0) = 2\left(\frac{64\varepsilon}{3\pi^2}\right)^{1/8}, \qquad \Delta F \sim \frac{4\pi}{3}\int_0^\infty \rho^{-4} v_0^6 \, d\rho = \frac{\pi^2\sqrt{3}}{4}. \tag{56}$$

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