Liquid to solid nucleation via onion structure droplets

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We study homogeneous nucleation from a deeply quenched metastable liquid to a spatially modulated phase. We find, for a general class of density functional theories, that the universally favored nucleating droplet in dimensions \( d \geq 3 \) is spherically symmetric with radial modulations resembling the layers of an onion. The existence of this droplet has important implications for systems with effective long-range interactions, and potentially applies to polymers, plasmas, and metals.

I. INTRODUCTION

Modulated pattern formation occurs in a wide variety of systems. Examples include cholesteric liquid crystals [1], hydromagnetic instabilities [2], superconducting vortices [3], block copolymers [4], as well as many others [5]. In recent years, there has been considerable renewed interest in the dynamical process of a first-order phase transition from a uniform (liquid) phase to a modulated (solid) phase following a quench [6–12]. If the supercooled liquid phase is long-lived, rare metastable equilibrium fluctuations locally initiate the phase transformation dynamics. The nucleation barrier is the free energy cost of the nucleating droplet, a saddle point solution of the effective free energy functional. Gibbs’ theory of homogeneous nucleation, valid near liquid-solid coexistence, postulated nucleating droplets as isolated regions of homogeneous nucleation from a deeply quenched metastable liquid to a spatially modulated phase by a sharp interface [13]. Subsequent refinements to this theory apply to deeper quenches within the metastable phase [14–16]. Near the spinodal (the limit at which the metastable phase becomes unstable) nucleating droplets differ dramatically from the stable phase [17], a phenomenon sometimes called the “Ostwald step rule” [18].

In liquid to solid nucleation, even the lattice symmetry of the nucleating droplet may differ from the stable solid phase. Using classical density functional theory (DFT) [19], Alexander and McTague predicted that a solid phase with a small density difference \( \psi(r) \) from the liquid phase would have hexagonal or bcc symmetry [20–21]. It was subsequently observed that such solid phases, being derived from a free energy functional of order \( \psi^3 \), are actually unstable [22]. The Alexander-McTague argument may, however, be used to characterize unstable nucleating droplets [23]. That is, nucleating droplets near the spinodal are expected to have hexagonal or bcc symmetry.

In this work, we demonstrate a new symmetry consistent with a \( \psi^3 \) free energy functional and not considered by Alexander and McTague: a spherically symmetric droplet with radial modulations reminiscent of layers in an onion. We show that for deep quenches near the spinodal, where a \( \psi^3 \) theory is valid, this onion structure droplet is in fact universally favored for a broad class of DFT models. Our argument applies when the metastable liquid phase is sufficiently long-lived, so that nucleation is well described by a saddle point approximation. For deep quenches, this approximation may be valid when fluctuations are damped by averaging over an effective long interaction range, e.g., the radius of gyration for block copolymer melts [24] or the effective screening length for plasmas [25].

There is much related work on liquid to solid nucleation. Our theory applies to an especially simple DFT, the phase field crystal model (PFC) [26], which has been the subject of much recent interest. Numerical calculation of PFC saddle points, which represent nucleating droplets, has been performed in two and three dimensions [8, 9]. In dynamical PFC studies, the metastable liquid was found to contain an amorphous precursor, which promotes the growth of bcc nuclei [9, 10]. These and other PFC results are reviewed in Ref. 12. Several studies suggest that nucleation is affected by the presence of a nearby (pseudo) spinodal [27–29]. In molecular dynamics (MD) of Lennard-Jones systems quenched not too close to the spinodal, evidence was found for nucleating droplets with an fcc core and a high degree of bcc ordering at the interface [30]. Consistent results were found in DFT studies of Lennard-Jones [31]. Subsequently, droplets of various other structures have been observed [32, 34], indicating that nucleation phenomena in these models of atomistic crystallization is not fully controlled by proximity to a spinodal.

The rest of this paper is structured as follows. In Sec. I[1] we define the DFT model and reduce it to a \( \psi^3 \) theory when liquid phase fluctuations are small. In Sec. III[11] we review the theory of lattice structure nucleating droplets derived by Klein and Leyvraz [23]. In Sec. IV[12] we demonstrate the existence of an onion structure droplet with qualitatively new scaling behavior. In Sec. V[13] we calculate the free energy scaling of the lattice and onion structure droplet types and conclude that onion structure droplets are favored in \( d \geq 3 \) dimensions, independent of the details of the model. Our result is valid for systems with effective long-range interactions, and for quenches near the spinodal.
II. PRELIMINARIES

We assume that the effective free energy of the density field $\rho(x)$ has the form,

$$F[\rho] = \int \left[ \frac{1}{2} \rho(x)(C \ast \rho)(x) + f(\rho(x)) - h\rho(x) \right] d^4x,$$

where the convolution operation is denoted as

$$(C \ast \rho)(x) = \int C(x' - x)\rho(x') d^3x'.$$  

In (metastable) equilibrium, fluctuations are Boltzmann distributed,

$$P[\rho] \propto \exp(-F[\rho]/k_B T),$$

with $k_B$ the Boltzmann constant and $T$ the temperature. The term $f(\rho(x))$ represents a local free energy cost and the quantity $h$ represents the chemical potential. We choose a symmetric Kac potential $[35]$ with characteristic length scale $R$,

$$C(x) = R^{-d}\Lambda(|x|/R).$$

The free energy functional in Eq. (1) can be used to model a variety of pattern forming systems $[5]$. In classical DFT of atomistic systems, $C(x)$ is interpreted as a direct correlation function $[59]$. Alternatively, this free energy can be rigorously justified for the clump model $[37, 38]$, in which a system of particles interact via the long-range repulsive step function potential

$$\Lambda(|x|) = \Theta(R - |x|)$$

with $R \rightarrow \infty$. Perhaps counterintuitively, the particles minimize potential energy by forming “clumps” of characteristic separation distance $R$ $[39]$. The temperature controls the magnitude of local entropic free energy,

$$f(\rho(x)) = T\rho(x)\ln\rho(x),$$

and drives a phase transition between a liquid phase of uniform $\rho(x) = \rho_0$ and a clump phase of modulated $\rho(x)$. It is convenient to work with dimensionless lengths,

$$r = x/R, \quad \phi(r) = \rho(x).$$

The parameter $R$ damps fluctuations by setting an overall energy scale,

$$F[\phi] = R^d\int \left[ \frac{1}{2} \phi(r)(\Lambda \ast \phi)(r) + f(\phi(r)) - h\phi(r) \right] d^4r.$$  

Equilibrium states are solutions to the Euler-Lagrange equation

$$\frac{\delta F}{\delta \phi(r)} = (\Lambda \ast \phi)(r) + f'(\phi(r)) - h = 0,$$

where $f'(\phi(r))$ denotes the ordinary derivative $df(y)/dy$ evaluated at $y = \phi(r)$. We assume that one such solution is a metastable liquid phase of uniform density, $\phi(r) = \phi_0$. When $R$ is large, we expect fluctuations about the liquid phase, $\psi(r) = \phi(r) - \phi_0$, to be small, and we expand $F$ in powers of $\psi(r)$ with

$$F_0 = R^d\int \left[ \frac{1}{2} \phi_0(\Lambda \ast \phi_0) + f(\phi_0) - h\phi_0 \right] d^4r$$

$$F_1 = R^d\int [\Lambda \ast \phi_0 + f'(\phi_0) - h]\psi(r) d^4r$$

$$F_2 = R^d\int \left[ \frac{1}{2} (\Lambda \ast \psi)(r) + \frac{1}{2} f''(\phi_0)\psi^2(r) \right] d^4r$$

$$F_3 = R^d\int \frac{1}{3!} f'''(\phi_0)\psi^3(r) d^4r.$$  

$F_0$ is independent of $\psi(r)$ and can be ignored. $F_1$ is zero because $\phi_0$ satisfies the Euler-Lagrange equation. The two relevant leading order terms are

$$F = F_2 + F_3 + \mathcal{O}(\psi^4).$$

Analysis proceeds most easily in Fourier space,

$$F_2 = \frac{1}{2} R^d \int A(\{|k|\})|\psi(k)|^2 d^4k$$

$$F_3 = \frac{-b}{3} R^d \int \psi(k)\psi(k')\psi(-k - k') d^4k d^4k',$$

where

$$\psi(k) = \int e^{ikr}\psi(r) d^4r$$

$$A(|k|) = \frac{1}{(2\pi)^d} \left( \int e^{ikr}\Lambda(|r|) d^4r + f''(\phi_0) \right)$$

$$b = -\frac{1}{(2\pi)^d} \frac{f''''(\phi_0)}{2},$$

and $b > 0$ by assumption. Note that $\psi(k) = \psi^*(-k)$, because $\psi(r)$ is real-valued. Also, $A(|k|)$ is real because $A(|x|)$ is real and symmetric.

The cost of small perturbations about the liquid phase, $\psi(k) = \phi - \phi_0$, scales as $A(|k|)^{1/2}|\psi(k)|$. The largest fluctuations occur at the angular frequency $|k| = k_0$ that minimizes $A(|k|)$. Our interest is nucleation into a modulated phase, and we choose the potential $\Lambda(x)$ such that $k_0 > 0$. We expand about this minimum,

$$A(|k|) = \epsilon + \sigma^2(|k| - k_0)^2 + \mathcal{O}((|k| - k_0)^3),$$

where

$$\epsilon = A(k_0)$$

$$\sigma^2 = A''(k_0)/2.$$  

The parameter $\epsilon$ determines the stability of the system. When $\epsilon < 0$ the liquid phase is unstable to fluctuations.
ψ(\(k\)) with angular frequency \(|k| = k_0\). For \(\epsilon > 0\) sufficiently small, the liquid phase is metastable. We study nucleating droplets near the limit of metastability (spinodal) of the liquid phase, where \(0 < \epsilon \ll 1\). In this limit, we will show that the truncations in Eqs. (14)–(20) are self-consistent. That is, near the liquid phase spinodal, only the small set of parameters \{\(\epsilon, \sigma, k_0, b\}\) is relevant. We assume that nucleation is controlled by the saddle point approximation \(\psi \sim \psi_0\), which is valid when \(R^d \gg 1\) such that the metastable phase is long-lived \(22\).

We seek nucleating droplets as saddle point solutions of the Euler-Lagrange equation expressed in Fourier space,

\[
A(|k|)\psi(k) = b(\psi \ast \psi)(k) + O(\psi^3). \quad (23)
\]

Nucleation occurs through localized droplet objects within a background of the liquid phase (\(\psi = 0\)). In this work, we compare two types of nucleating droplets. The first type (introduced by Klein and Leyvraz \(23\), building on the symmetry arguments of Alexander and McTague \(20\)), is a ramified droplet with a lattice structure at its core. The second type (not previously considered) is a spherically symmetric solution with concentric shells of modulated density. We will call these two types lattice structure and onion structure droplets.

Our strategy is as follows. We propose a scaling ansatz for both lattice structure and onion structure droplet types. By substituting these ansatze into the Euler-Lagrange equation, we show that both may be self-consistent solutions. However, we find that the free energies of the two droplet types scale differently. Our analysis, which is valid near the spinodal, predicts that lattice structure droplets are favored in two dimensions, while onion structure droplets are favored in three and higher dimensions.

III. LATTICE STRUCTURE DROPLETS

Following Klein and Leyvraz \(23\), we seek lattice structure droplet solutions to the Euler-Lagrange equation. We work with the ansatz

\[
\psi_{LS}(k) = \frac{\epsilon}{bm} \sum_{i=1}^{n} \left( \frac{\sigma}{\epsilon^{1/2}} \right)^d f_i \left( \frac{\sigma}{\epsilon^{1/2}} (k - q_i) \right), \quad (24)
\]

valid at leading order in \(\epsilon \ll 1\), the distance from the spinodal. The parameters \(k_0, \sigma,\) and \(b\) are as before, while the constant \(m\) and functions \(f_i(k)\) are to be determined. The \(n\) reciprocal lattice vectors \{\(q_i\)\} all have magnitude \(|q_i| = k_0\), consistent with minimal droplet free energy cost, Eq. (15).

The functions \(f_i\) are peaked at the origin and scaled such that, in the spinodal limit,

\[
\psi_{LS}(k) \to \frac{\epsilon}{bm} \sum_{i=1}^{n} \delta(k - q_i) \text{ as } \epsilon \to 0, \quad (25)
\]

where \(\delta(k)\) is the Dirac \(\delta\)-function. For \(\epsilon\) positive but small, the ansatz \(\psi_{LS}(k)\) is a sum of highly peaked terms.

Following Alexander and McTague \(20\), we use symmetry arguments to constrain the possible symmetries of the reciprocal vectors \{\(q_i\)\}. For this argument, we work with the asymptotic representation of Eq. (25), valid at leading order in \(\epsilon \ll 22\). We insert the ansatz \(\psi_{LS}(k)\) into the Euler-Lagrange equation \(23\), and expand the right-hand side using the identity

\[
g(k - q_i) * h(k - q_i) = (g * h)(k - q_i) - q_i. \quad (26)
\]

The left-hand side of Eq. \(22\) is approximately \(A(k_0)\psi_{LS}(k) = c\psi_{LS}(k)\), a sum of \(\delta\)-functions at the reciprocal vectors \{\(q_i\)\}. The right-hand side contains approximate \(\delta\)-functions at \(\{q_j + q_k\}\) for all pairs \(j, k\). The \(i\)th left-hand side term must be matched by corresponding ones on the right-hand side,

\[
\epsilon \left[ \frac{\epsilon}{bm} \delta(k - q_i) \right] = \sum _{j,k=1}^{n} \left( \frac{\epsilon}{bm} \right)^2 (\delta \ast \delta)(k - q_j - q_k). \quad (27)
\]

Using \((\delta \ast \delta)(k) = \delta(k)\), we find that every \(q_i\) on the left-hand side must be matched by \(m\) ordered pairs \(\{q_j, q_k\}\) satisfying \(q_j + q_k = q_i\) on the right-hand side. What about unmatched terms on the right-hand side of Eq. \(23\), for which \(p = q_j + q_k\) is different than all \(q_i\)? There are two possibilities. If \(|p| \neq k_0\), then these terms can be accounted for by higher order corrections, \(\psi_{LS} \to \psi_{LS} + \delta \psi_{LS}\). Namely, we balance the left- and right-hand sides, \(A(|p|)\delta\psi(|p|) \sim (\psi \ast \psi)(|p|)\), where \(\psi(|p|) \sim \epsilon\) and \(A(|p|) \sim 1\), and find that \(\delta\psi(|p|) \sim \epsilon^2\) is a higher order correction. The second case, \(|p| = k_0\), is disallowed because \(A(|p|) \sim \epsilon\), and it is not possible to satisfy the Euler-Lagrange equation.

We conclude that the reciprocal lattice vectors \{\(q_i\)\}, each of magnitude \(k_0\), must form equilateral triangles. The possible closed, symmetric sets of equilateral triangles are shown in Fig. 1. The simplest solution is the set of \(n = 6\) edge vectors of a single triangle. In direct space, this solution represents a triangular lattice (in 2d) or close packed rod-like structures (in 3d). There are only three polyhedra composed of equilateral triangles. The \(n = 12\) unique edge vectors of the octahedron and tetrahedron are equivalent, and correspond to a bcc lattice in direct space. The \(n = 30\) unique edge vectors of the icosahedron correspond to a quasicrystal in direct space. These finite sets complete the classification given by Alexander and McTague \(20\), and are the basis of the lattice structure droplets we will describe in the remainder of this section. In Sec. XIV we consider instead the \(continuum\) set of vectors \{\(q\)\} with magnitude \(|q| \approx k_0\).

For simplicity, we used the asymptotic scaling of Eq. \(25\) to derive the Alexander-McTague symmetry constraints. Now we return to the full ansatz Eq. \(24\), where \(\psi_{LS}(k)\) has sharp but non-singular peaks at \{\(q_i\)\}. By symmetry, we may focus on one particular \(q_i\), without loss of generality. For \(k\) in the neighborhood of \(q_i\), we
We seek smooth, non-singular solutions $f_i(\mathbf{v})$ of Eq. (32). For such solutions, the ansatz $\psi_{LS}(\mathbf{k})$ would potentially represent a nucleating droplet appearing in the metastable liquid phase. In direct space, this droplet would have spatial scale $\ell \sim R \sigma / \epsilon^{1/2}$. We expect droplet solutions to inherit the symmetries of the reciprocal lattice vectors $\{\mathbf{q}_j\}$. In particular, all point group symmetries $\mathcal{R}\{\mathbf{q}_j\} = \{\mathbf{q}_j\}$ should be represented by the droplet, $\psi_{LS}(\mathbf{k}) = \psi_{LS}(R\mathbf{k})$, and the envelope functions $\{f_i\}$ should satisfy,

$$f_i(\mathbf{k}) = f_j(R\mathbf{k}) \quad \text{if} \quad \mathbf{q}_j = R\mathbf{q}_i. \quad (33)$$

In direct space, the full nucleating droplet solution will exhibit anisotropic faceting due to the term $\mathbf{v} \cdot \mathbf{q}_i$ appearing on the left-hand side of Eq. (32). Analytical solution appears difficult. The substitution $(\mathbf{v} \cdot \mathbf{q}_i / k_0)^2 \rightarrow \mathbf{v}^2$ would restore isotropy and yield a theory analogous to that of ferromagnetic nucleation, but approximation is uncontrolled [17].

Numerical solutions to the non-truncated Euler-Lagrange equation (3) are shown in Fig. 2. We applied the string method \cite{11,12,13} to find saddle points of minimum free energy for the clump model, Eqs. (3) and (6). Up to a simple rescaling, the clump model is independent of the liquid phase density $\phi_0$. The spinodal temperatures are $T^{3d}_{s} = 0.13228 \phi_0$ and $T^{3d}_{s} = 0.08617 \phi_0$ in two and three dimensions, respectively. We used $\epsilon = (T - T_s) / \phi_0 = 0.01$ to calculate the droplets shown in Fig. 2. In two dimensions we find, for all $\epsilon$, that the nucleating droplets have an extended core with triangular lattice symmetry. For small $\epsilon$, we observe scaling consistent with the ansatz $\psi_{LS}(\mathbf{k})$. In three dimensions and intermediate values of $\epsilon$, we observe droplets with an icosahedral core. This result is non-universal in the sense that other models may have a different structure. Closer to the spinodal ($\epsilon \lesssim 0.005$ for the clump model) we instead find the onion structure droplets that we describe in the next section.
such that $\psi$ shell of radius $\{\psi < \epsilon$ and $g$ The parameters $k$ symmetry of the droplet depends on the distance $\epsilon$ from the spinodal. In numerical studies of the clump model, Eqs. (5) and (6), at intermediate $\epsilon$, we find a droplet core containing 13 close packed spheres with icosahedral symmetry (two slices are shown).

IV. ONION STRUCTURE DROPLETS

In this section, we propose a new kind of nucleating droplet composed of all vectors $\{q\}$ satisfying $|q| = k_0$. This continuum set may be interpreted as a degenerate solution to the Alexander-McTague symmetry constraints, Fig. 1(d). In direct space, this solution becomes a spherically symmetric, radially modulated density field that resembles the layers of an onion.

Our full ansatz for onion structure droplets is,

$$\psi_{\text{OS}}(|k|) = \gamma g\left(\frac{\sigma}{\epsilon^{1/2}}(|k| - k_0)\right). \quad (34)$$

The parameters $k_0$ and $\sigma$ are as before. At leading order in $0 < \epsilon \ll 1$, we will self-consistently solve for $\gamma$ and $g(u)$. The latter is centered and normalized such that

$$\int g(u) \, du = 1,$$ \hspace{1cm} (35)$$

and

$$\psi_{\text{OS}}(|k|) \rightarrow \frac{\epsilon^{1/2} \gamma}{\sigma} \delta(|k| - k_0) \quad \text{as} \quad \epsilon \rightarrow 0. \quad (36)$$

Whereas $\psi_{\text{LS}}(k)$ was composed of sharp peaks at the discrete set of vectors $\{q_i\}$ [cf. Eq. (25)], the new solution $\psi_{\text{OS}}(|k|)$ shows a non-zero spectral density along the full shell of radius $k_0$.

We anticipate restricting $|k|$ to the neighborhood of $k_0$, such that

$$u = \frac{\sigma}{\epsilon^{1/2}}(|k| - k_0)$$ \hspace{1cm} (37)$$

is of order unity [cf. Eq. (40)]. In particular, for small $\delta k = |k| - k_0$ we may write

$$A(|k|) = \epsilon(1 + u^2) + \mathcal{O}(\epsilon^{3/2}). \quad (38)$$

The left-hand side of Eq. (23) becomes

$$A(|k|)\psi_{\text{OS}} = \epsilon(1 + u^2)\gamma g(u) + \mathcal{O}(\epsilon^{3/2}). \quad (39)$$

We now turn to the right-hand side of Eq. (23). As a first approximation, we use the asymptotic representation of Eq. (36).

$$(\psi_{\text{OS}} * \psi_{\text{OS}})(|k|) \approx \frac{\epsilon \gamma^2}{\sigma^2} \int \delta(|k'| - k_0)\delta(|k - k'| - k_0) \, d^d k'. \quad (40)$$

This convolution corresponds to the integrated overlap between the two shells, illustrated in Fig. 3(a). The overlap area is $p^{d-2} S_{d-2}$ where

$$p = \sqrt{k_0^2 - |k|^2}/4, \quad (41)$$

and $S_n$ is the surface area of the $n$-sphere,

$$S_n = \frac{2\pi^{n+1}/2}{\Gamma((n + 1)/2)} = \begin{cases} 2 & n = 0 \\ 2\pi & n = 1 \\ 4\pi & n = 2 \end{cases}. \quad (42)$$

To evaluate $\psi_{\text{OS}} * \psi_{\text{OS}}$ more precisely, we return to the full ansatz, Eq. (34). In a local region $\Omega_i$ of overlap, Fig. 3(b), we treat the shells as (hyper)planes with surface normals satisfying $\hat{n}_a \cdot \hat{n}_b = \cos \theta$. The integral in Eq. (40) becomes a sum over many such regions,

$$(\psi_{\text{OS}} * \psi_{\text{OS}})(|k|) = \gamma^2 \sum_i \int_{\Omega_i} \frac{g(v_a) \, g(v_b)}{\sigma} \, d^d k' + \mathcal{O}(\epsilon^{3/2}), \quad (43)$$

where

$$v_{\{a,b\}} = \frac{\sigma}{\epsilon^{1/2}} k' \cdot \hat{n}_{\{a,b\}}. \quad (44)$$

Curvature effects are negligible because the shells have width $\mathcal{O}(\epsilon^{1/2})$. In each region $\Omega_i$ we select an orthogonal
coordinate system \( \{ \mathbf{e}_1, \mathbf{e}_2, \ldots, \mathbf{e}_d \} \) in which the surface normals are \( \mathbf{n}_i = \mathbf{e}_1 \) and \( \mathbf{n}_i = \cos \theta \mathbf{e}_1 + \sin \theta \mathbf{e}_2 \). The integrand then depends only on the first two components, \( k'_1 \) and \( k'_2 \), of \( \mathbf{K}' \). After two applications of the normalization condition, Eq. \( (35) \), we find
\[
\int g(v_a) g(v_b) \, dk'_1 \, dk'_2 = \frac{\epsilon^{1/2}}{\sigma \sin \theta} \int g(v) \, dk'_1 \quad (45)
\]
The remaining \( (d - 2) \) orthogonal integrations, summed over all regions \( \Omega_i \), evaluate to the area of overlap,
\[
\sum_i \int_{\Omega_i} \prod_{j=2}^d \, dk'_j = p^{d-2} S_{d-2}. \quad (46)
\]
The full convolution becomes
\[
(\psi_{\text{OS}} \ast \psi_{\text{OS}})(|k|) = \frac{\epsilon^2 \sigma^{d-2}}{2} S_{d-2} + O(\epsilon^{3/2}). \quad (47)
\]
Inspection of Fig. 3 gives the geometric identity,
\[
\sin \theta = k p / k_0^2,
\]
and, at leading order in \( \delta k \sim \epsilon^{1/2} \),
\[
(\psi_{\text{OS}} \ast \psi_{\text{OS}})(|k|) = \frac{\epsilon^2 \sigma^{d-3} k_0^2}{k} S_{d-2} + O(\epsilon^{3/2})
= \frac{\epsilon^2 \sigma^2}{2} \left( \frac{3}{4} \right) k_0^{d-2} S_{d-2} + O(\epsilon^{3/2}). \quad (48)
\]
With Eqs. \( (39) \) and \( (48) \), we satisfy the Euler-Lagrange equation \( \Box \) at leading order in \( \epsilon \) with
\[
g(u) = \frac{1}{\pi (1 + u^2)} \quad (49)
\]
\[
\gamma = \frac{\sigma^2}{b \pi (3/4)^{d-3} k_0^{d-2} S_{d-2}}. \quad (50)
\]
Note that \( g \) is properly normalized, Eq. \( (35) \). This self-consistent solution justifies the ansatz \( \psi_{\text{OS}}(|k|) \) at small \( \delta k \). Our final expression for the onion structure droplets in Fourier space is
\[
\psi_{\text{OS}}(|k|) = \frac{\sigma^2}{b \pi (3/4)^{d-3} k_0^{d-2} S_{d-2}} (1 + u^2)^{-1}, \quad (51)
\]
where \( u \) is defined in Eq. \( (37) \).
We can also express the onion structure droplets in real space by the inverse Fourier transformation,
\[
\psi_{\text{OS}}(|r|) = (2\pi)^{-d} \int e^{-ik \cdot r} \psi_{\text{OS}}(|k|) \, dk. \quad (52)
\]
In the following, we use the shorthand notation \( r = |r| \).
In spherical coordinates we have
\[
d^d k = \, |dk| \, ((k \sin \theta)^{d-2} \, d\theta) \, [k \, d^{d-2} \phi], \quad (53)
\]
where \( k \) is the distance from the origin and \( \theta \) is the zenith angle. The remaining \( d - 2 \) surface angles \( \phi \) are the remaining \( d - 2 \) surface angles \( \phi \) satisfy
\[
\int d^{d-2} \phi = \pi \nu \sin \nu \, d\theta, \quad (62)
\]
to obtain a result valid when \( r \ll \epsilon^{1/2} \),
\[
\psi_{\text{OS}}(r) \approx \alpha \beta \frac{\pi^{1/2} \Gamma(d/2)}{k_0 r^{d/2-1}} J_{d/2-1}(k_0 r). \quad (63)
\]
The neglected \( \epsilon \) dependence in Eq. \( (61) \) damps \( \psi_{\text{OS}}(r) \) on the scale \( r \sim \epsilon^{1/2} \). In \( d = 3 \) the full leading order result is
\[
\psi_{\text{OS}}^d = \exp\left[-\frac{\epsilon^{1/2}}{\sigma} \left( \frac{2 \sin k_0 r}{k_0 r} \right) \right], \quad (64)
\]
which is equivalent to Eq. (63) with an exponential damping factor. By substituting definitions from Eqs. (50), (56), and (58), we obtain our final droplet solution,

$$\psi_{\text{OS}}^3(r) = \exp\left[-\epsilon \sigma^{-1} r\right] \frac{\sqrt{2} \sigma k_0}{\pi^2 b} \left(\frac{\sin k_0 r}{k_0 r}\right).$$  

(65)

We numerically calculated the free energy saddle point using non-truncated Euler-Lagrange equation (9) for the clump model near the spinodal, $\epsilon \approx 0.6$, and found the onion structure droplet $\psi_{\text{OS}}(r)$ shown in Fig. 4.

V. DROPLET FREE ENERGIES

When large fluctuations about the metastable liquid phase are rare, nucleation occurs via the saddle point of minimum free energy. Both lattice structure $[\psi_{\text{LS}}, \text{Eq. (24)}]$ and onion structure $[\psi_{\text{OS}}, \text{Eq. (34)}]$ solutions are possible nucleating droplets. In this section, we compute their free energies to predict the preferred nucleating droplet structure.

The $\epsilon$-scaling of $\psi_{\text{LS}}$ and $\psi_{\text{OS}}$ ensures that $\mathcal{O}(\rho^3)$ free energy terms are negligible in the limit $\epsilon \ll 1$. The two terms $F_2$ and $F_3$ in Eq. (14) remain. For droplets $\psi$ satisfying the Euler-Lagrange equation (23), the two terms are related,

$$F_3 = -\frac{b}{3} R^d \int \psi(k) \psi(k') \psi(-k-k') d^d k d^d k'$$

$$= -\frac{1}{3} R^d \int \psi(k) [b(\psi \ast \psi)(-k)] d^d k$$

$$= -\frac{1}{3} \frac{1}{2} R^d \int \psi(k) [A(k) \psi(-k)] d^d k = -\frac{2}{3} F_2. $$  

(66)

The total free energy becomes

$$F = F_2 + F_3 = \frac{1}{3} F_2. $$  

(67)

We now evaluate the free energy of onion structure droplets,

$$F[\psi_{\text{OS}}] = \frac{R^d}{6} A(|k|) \psi_{\text{OS}}(|k|) |d^d k. $$  

(68)

Because $\psi_{\text{OS}}(|k|)$ is sharply peaked at $k_0$, we expand $|k| = k_0 + \delta k$ for $\delta k \sim 1/\epsilon$, truncate the expansion of $A(|k|)$, Eq. (50), and extend the bounds of integration,

$$F[\psi_{\text{OS}}] = \frac{R^d}{6} k_0^{d-1} S_{d-1} \int_{-\infty}^{+\infty} \epsilon (1 + u^2) \psi_{\text{OS}}^3(k) d\delta k, $$  

(69)

where $u$ is defined in Eq. (67). We insert the solution $\psi_{\text{OS}}^3(|k|)$ from Eqs. (34), (49), and (50) and evaluate the integral to get our final result

$$F[\psi_{\text{OS}}] = \frac{\epsilon^{3/2} \sigma R^d}{b^2 k_0^{d-3}} \frac{S_{d-1}}{6 \pi^{3/4}} S_{d-2}. $$  

(70)

Next we consider the lattice structure droplets. Assuming that solutions to Eq. (32) exist, the droplet free energy is

$$F[\psi_{\text{LS}}] = \frac{R^d}{6} \int A(|k|) \psi_{\text{LS}}(|k|)^2 d^d k. $$  

(71)

The ansatz $\psi_{\text{LS}}(k)$ in Eq. (24) is a sum of $n$ symmetrically-equivalent peaks $f_i$, Eq. (33). At the $i$th peak, the relevant scale $\delta k = |k - q_i|$ is $\mathcal{O}(1/\epsilon)$, and we can truncate the expansion of $A(|k|)$ in Eq. (31). The free energy from all $n$ peaks becomes

$$F[\psi_{\text{LS}}] = \frac{R^d n}{6} \int \epsilon (1 + (v \cdot e_i)^2) \left[ \frac{\epsilon}{bn} \left(\frac{\sigma}{\epsilon^{1/2}}\right)^d f_i(v) \right]^2 d^d k, $$  

(72)

where $v$ is defined in Eq. (30). After a change of variables and some algebra, we find

$$F[\psi_{\text{LS}}] = \frac{\epsilon^{d/2} \sigma R^d}{b^2} \frac{cn}{6m^2}, $$  

(73)

with

$$c = \int (1 + (v \cdot q_i/k_0)^2) f_i(v)^2 d^d v. $$  

(74)

As before, $m$ represents the number of ordered pairs of reciprocal lattice vectors ($q_j$, $q_k$) that sum to a specific $q_i$. The possible values of $n$ and $m$ are listed in Fig. 2. Although the solution $f_i$ of Eq. (32) (if it exists) is not known analytically, by construction it is a dimensionless function independent of the model parameters. It is therefore natural to assume that $c$ is of order unity.

The free energy costs of the onion structure ($F[\psi_{\text{OS}}]$ in Eq. (70)) and lattice structure ($F[\psi_{\text{LS}}]$ in Eq. (73)) droplets allow us to make predictions for nucleation near the spinodal ($\epsilon \ll 1$) when the metastable liquid phase is long lived ($R \gg 1$).
● In $d = 1$ both $\psi_{\text{OS}} \sim 1/S_{d-2}$ and $\psi_{\text{LS}} \sim 1/m$ are ill-defined. Note that $m = 0$ because a single wave vector cannot form an equilibrium structure. This absence of nucleating droplets is consistent with the continuous phase transition allowed by the “Landau rules” and predicted in Ref. 20.

● In $d = 2$ the droplet free energies scale as $F[\psi_{\text{OS}}] \sim \epsilon^{3/2}$ and $F[\psi_{\text{LS}}] \sim \epsilon^2$. Lattice structure droplets are therefore preferred when $\epsilon \ll 1$. The reciprocal lattice vectors form a single triangle, Fig. 1(a). In direct space, the droplet core has a hexagonal lattice structure with amplitude $O(\epsilon)$. This is the droplet we observe numerically, Fig. 2(a).

● In $d = 3$ the droplet free energies scale identically in all model parameters ($\epsilon, \sigma, b, F^d, \kappa_0$). The universal ratio,

$$\frac{F[\psi_{\text{LS}}]}{F[\psi_{\text{OS}}]} = \frac{cn\pi^d}{m^2},$$

then determines the preferred droplet structure. Of the possible lattice structure droplets shown in Fig. 1, bcc is preferred because it minimizes $n/m^2 = 12/4^2$. If the constant $c$ were 1, $F[\psi_{\text{LS}}]$ would be 73 times greater than $F[\psi_{\text{OS}}]$! Our numerical efforts to calculate $c$ have failed, suggesting that the ansatz $\psi_{\text{LS}}$ does not exist in the spinodal limit, $\epsilon \ll 1$. Instead, we always find onion structure droplets near the spinodal, Fig. 3. At temperatures away from both the spinodal and liquid/solid coexistence, the droplet structure depends on model details. For the clump model, we find droplets with an icosahedral core, Fig. 2(b).

● In $d \geq 4$ the onion structure droplets have lower free energy, $F[\psi_{\text{OS}}] \sim \epsilon^{3/2}$, than the lattice structure ones, $F[\psi_{\text{LS}}] \sim \epsilon^{3-d/2}$, when $\epsilon \ll 1$. Our theory of nucleation to a modulated phase (frequency $k_0 > 0$) is qualitatively different than classical results for the ferromagnet ($k_0 = 0$). In ferromagnetic nucleation, universality breaks down at $d \geq 6$, the upper critical dimension of a $\phi^3$ theory. In contrast, onion structure droplets have no such critical dimension.

VI. CONCLUSIONS

We have demonstrated a new type of nucleating droplet to describe nucleation in supercooled liquids with effective long-range interactions. This onion structure droplet is spherically symmetric and modulated in the radial direction. In two dimensions, droplets with a hexagonal lattice structure, Fig. 2(a), have a lower free energy barrier than onion structure ones. In three dimensions, in contrast, our scaling arguments and numerical results indicate that onion structure droplets, Fig. 3, are universally favored for a general class of DFT models when quenched near the spinodal.

For shallower quenches the structure of the nucleating droplet depends sensitively on model details. In our numerical study of the clump model away from the spinodal we find a droplet with icosahedral symmetry to be the lowest free energy saddle point solution, Fig. 2(b). We find that, in its initial growth, this icosahedral droplet develops onion structure modulations away from the core. In studies of atomistic crystallization, a variety of non-universal droplet structures have been observed [30–34]. For such systems, DFT models of nucleation near the spinodal may be inapplicable.

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[1] S. A. Brazovskii, Sov. Phys.–JETP 68, 175 (1975).
[2] J. Swift and P. C. Hohenberg, Phys. Rev. A 15, 319 (1977).
[3] P. Pardo, F. de la Cruz, P. L. Gammel, E. Bucher, and D. J. Bishop, Nature 396, 348 (1998).
[4] C. Harrison, D. H. Adamson, Z. Cheng, J. M. Sebastian, S. Sethuraman, D. A. Huse, R. A. Register, and P. M. Chaikin, Science 290, 1558 (2000).
[5] M. Seul and D. Andelman, Science 267, 476 (1995).
[6] S. van Teeffelen, C. N. Likos, and H. Löwen, Phys. Rev. Lett. 100, 108302 (2008).
[7] G. Tegze, L. Gránásy, G. I. Tóth, F. Podmaniczy, A. Jaatinen, T. Ala-Nissila, and T. Pusztai, Phys. Rev. Lett. 103, 035702 (2009).
[8] R. Backofen and A. Voigt, J. Phys.: Condens. Matter 22, 364104 (2010).
[9] G. I. Tóth, G. Tegze, T. Pusztai, G. Tóth, and L. Gránásy, J. Phys.: Condens. Matter 22, 364101 (2010).
[10] G. I. Tóth, T. Pusztai, G. Tegze, G. Tóth, and L. Gránásy, Phys. Rev. Lett. 107, 175702 (2011).
[11] G. I. Tóth, G. Tegze, T. Pusztai, and L. Gránásy, Phys. Rev. Lett. 108, 025502 (2012).
[12] L. Gránásy, G. Tegze, G. I. Tóth, and T. Pusztai, Philos. Mag. 91, 123 (2011).
[13] J. W. Gibbs, Collected Works, Vol. 1 (Yale University Press, New Haven, 1948).
[14] J. W. Cahn and J. E. Hilliard, J. Chem. Phys. 31, 688 (1959).
[15] J. S. Langer, Ann. Phys. (N.Y.) 41, 108 (1967).
[16] J. Gunton, J. Stat. Phys. 95, 903 (1999).
[17] C. Unger and W. Klein, Phys. Rev. B 29, 2698 (1984).
[18] W. Ostwald, Z. Phys. Chem. 22, 289 (1897).
[19] D. W. Oxtoby, in Proceedings of the Les Houches Summer School, Session LI, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (Elsevier, Amsterdam, 1991) p. 147.
[20] S. Alexander and J. Mctague, Phys. Rev. Lett. 41, 702 (1978).
[21] P. Chaikin and T. Lubensky, “Principles of condensed matter physics,” (Cambridge University Press, Cambridge, 1995) Chap. 4.7.
[22] W. Klein, Phys. Rev. E 64, 056110 (2001).
[23] W. Klein and F. Leyvraz, Phys. Rev. Lett. 57, 2845 (1986).
[24] J. G. E. M. Fraaije, B. A. C. van Vlimmeren, N. M. Maurit, M. Postma, O. A. Evers, C. Hoffmann, P. Altevogt, and G. Goldbeck-Wood, J. Chem. Phys. 99, 9202 (1993).
[25] J. E. Hammerberg, B. L. Holian, and R. Ravelo, Phys. Rev. E 50, 1372 (1994).
[26] K. R. Elder and M. Grant, Phys. Rev. E 70, 051605 (2004).
[27] J.-x. Yang, H. Gould, and W. Klein, Phys. Rev. Lett. 60, 2665 (1988).
[28] J.-x. Yang, H. Gould, W. Klein, and R. D. Mountain, J. Chem. Phys. 93, 711 (1990).
[29] V. Talanquer and D. W. Oxtoby, J. Chem. Phys. 109, 223 (1998).
[30] P. R. ten Wolde, M. J. Ruiz-Montero, and D. Frenkel, Phys. Rev. Lett. 75, 2714 (1995).
[31] Y. C. Shen and D. W. Oxtoby, Phys. Rev. Lett. 77, 3585 (1996).
[32] P. R. ten Wolde and D. Frenkel, Phys. Chem. Chem. Phys. 1, 2191 (1999).
[33] F. J. Cherne, M. I. Baskes, R. B. Schwarz, S. G. Srinivasan, and W. Klein, Model. Simul. Mater. Sci. Eng. 12, 1063 (2004).
[34] H. Wang, H. Gould, and W. Klein, Phys. Rev. E 76 (2007).
[35] M. Kac, G. E. Uhlenbeck, and P. C. Hemmer, J. Math. Phys. 4, 216 (1963).
[36] T. V. Ramakrishnan and M. Yussouff, Phys. Rev. B 19, 2775 (1979).
[37] N. Grewe and W. Klein, J. Math. Phys. 18, 1729 (1977).
[38] N. Grewe and W. Klein, J. Math. Phys. 18, 1735 (1977).
[39] W. Klein, H. Gould, R. A. Ramos, I. Clejan, and A. I. Mel'cuk, Physica A 205, 738 (1994).
[40] W. E. W. Ren, and E. Vanden-Eijnden, J. Chem. Phys. 126, 164103 (2007).
[41] W. Ren and E. Vanden-Eijnden, J. Chem. Phys. 138, 134105 (2013).
[42] L. D. Landau and E. M. Lifshitz, Statistical physics, 3rd ed. (Pergamon, Oxford, 1980).
[43] C. B. Muratov and E. Vanden-Eijnden, J. Stat. Phys. 114, 605 (2004).