One of the long-lasting challenges in materials study is how to effectively tackle the complex structural and dynamical phenomena involving multiple spatial and temporal scales. Of particular importance is the bridging between atom-level microstructural details and mesoscopic, nonequilibrium characteristics, such as mesoscale surface patterns or interface structures that are governed by system elasticity and plasticity and by diffusional or displacive dynamic processes. This requires novel theoretical efforts, particularly those based on coarse-graining methods beyond the traditional single-scale atomistic or continuum approaches. Among them much work has been devoted to the development of density-field-based schemes across different scales, as featured by the incorporation of crystalline and microscopic attributes into the probability density description [1–4].

Many of these field-based models can be connected to the classical density functional theory (CDFT) [5,6]. Through coarse graining or “smoothing” the local density field over atomic vibrational scales, the small-scale limitation of CDFT can be mitigated, resulting in a continuum field theory with the lattice symmetry controlled by microscopic length scales [1,2,7–14,24–26]. They are applicable to metallic-type materials or colloidal systems with excluded volume or steric interactions that are dependent on interparticle distance, but would be a crude approximation if applied to a broader range of material systems with directional interactions depending on both bond lengths and angles. It is thus important to build the bond (or particle-neighboring) angle dependency into continuum modeling which, however, is nontrivial, given that microscopically the corresponding interparticle interactions are anisotropic, while rotational invariance of the whole system must be maintained in the free-energy functional.

In the traditional density-field approach based on Landau theory, an additional bond-orientational order parameter and the associated rotationally invariant orientational free energy were introduced for glassy [27] or quasicrystalline [28] systems. On the other hand, in principle, the orientational information should already be incorporated in the density functional and direct correlation functions, although it is challenging to identify and control. The related attempts are rather limited, and are usually accompanied by some specific assumptions, as in two types of angle-dependent PFC models developed recently. The first one [29] adopts some nonlinear free-energy gradient terms introduced in previous studies of the square convection pattern [30,31], while the second type is built on some presumed infinite series expansions of the three-point direct correlation function $C^{(3)}$, either through a separation of $C^{(3)}$ in real space [32] or in terms of Legendre polynomials in Fourier space [33].

Here, we provide a systematic study of angular dependence and orientation control in a density field formulation. Our analysis is based on the property of the isotropic tensor and the complete Fourier expansion of any $n$-point direct correlation function $C^{(n)}$ that satisfies the condition of rotational invariance, without any preassumptions. Our results show that any finite-order contributions of $C^{(3)}$ expansion to the rotationally invariant free energy are always angle independent, as a result of the resonant condition of the wave-vector triads, while those from at least a four-point correlation are needed to explicitly incorporate the dependency on the angle between neighboring constituent particles. Applications of this PFC-type model...
include some examples of three-dimensional (3D) structure modeling (such as simple cubic and diamond cubic phases) via a single length scale combined with angle-dependent effects, and, importantly, the achievement of continuous angle control in both two-dimensional (2D) and 3D crystalline structures such as 2D rhombic and square and 3D simple monoclinic and orthorhombic phases, which demonstrates the advantage of this angle-adjustable density field approach.

In CDFT the free-energy functional is expanded via direct correlation functions [5,6], i.e.,

$$
\Delta F / k_B T = \rho_0 \int d\mathbf{r} (1 + n) \ln(1 + n) - \sum_m \frac{1}{m} \rho_0^m \\
\times \int \prod_{j=1}^m d\mathbf{r}_j C^{(m)}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_m) \\
\times n(\mathbf{r}_1)n(\mathbf{r}_2)\cdots n(\mathbf{r}_m),
$$

where \( n = (\rho - \rho_0) / \rho_0 \) is the density variation field, with \( \rho \) the local atomic number density and \( \rho_0 \) a reference state density. The condition of rotational invariance needs to be maintained for any \( m \)-point direct correlation function \( C^{(m)} \) and its Fourier transform \( \hat{C}^{(m)}(q_1, q_2, \ldots, q_{m-1}) \). If expanding \( \hat{C}^{(m)} \) as a power series of wave vector \( q_i \), the resulting terms are of the form \( \prod_{i=1}^{m-1} \prod_{\alpha=\{x,y,z\}} q_i^{n_\alpha} \) (\( n_\alpha = 0, 1, 2, \ldots \)), the majority of which are, however, not rotationally invariant. Alternatively, this expansion can be expressed in an equivalent form, \( \hat{C}^{(m)}(q_1, q_2, \ldots, q_{m-1}) = \sum_K \sum_{\beta=1}^{m-1} \sum_{\alpha=\{x,y,z\}} C_1 a_1 i_1 k_1 a_2 i_2 k_2 \cdots a_{m-1} i_{m-1} k_{m-1} \), where \( T^{(K)}(k_1 a_1, \ldots, a_{m-1} i_{m-1}) = \hat{q}_1 a_1 \cdots \hat{q}_{m-1} i_{m-1} \) can be viewed as components of a tensor \( T^{(K)} \) of rank \( K \). Thus the rotational invariance condition of this expansion would be satisfied if these tensor components are invariant under a proper orthogonal group \( O(2) \) or \( O(3) \) transformation (i.e., 2D or 3D rotation), which is the definition of an isotropic Cartesian tensor. Given the property of isotropic tensors which can be written as linear combinations of the products of Kronecker deltas \( \delta_{\alpha a_i} \) (for even rank \( K \)) or their product with only one Levi-Civita permutation tensor \( \epsilon_{a_1 a_2 a_3} \) (for odd \( K \)) with \( \{a_1, a_2, a_3\} = \{x, y, z\} \) in 2D or 3D Euclidean space [34–36], the corresponding rotationally invariant form of \( \hat{C}^{(m)} \) expansion can be expressed in terms of \( q_i \cdot q_j \) and \( (q_i \times q_j) \cdot q_j \), i.e.,

$$
\hat{C}^{(m)}(q_1, q_2, \ldots, q_{m-1}) = \sum_{\mu_{11}=0}^{\infty} \sum_{l, j=1}^{m-1} \hat{C}_{\mu_{11}}^{(m)} q_i q_j \mu_{11} + \sum_{k, l, p=1}^{m-1} \sum_{v_1=1}^{\infty} \hat{C}_{v_1}^{(m)} q_k q_l \mu_{11},
$$

with coefficients \( \hat{C}_{\mu_{11}}^{(m)} \) and \( \hat{C}_{v_1}^{(m)} \). Note that this is a general form of expansion but not an irreducible one.

For a two-point correlation, from Eq. (2) with \( m = 2 \) the only available expansion form is \( (q_i \cdot q_j)^2 M = q^2 M \), i.e., \( \hat{C}^{(2)}(q) = \hat{C}_0 + \sum_{M=1}^{\infty} \hat{C}_M q^{2M} \). Its contribution to the free-energy functional is given by (after rescaling)

$$
\Delta \mathcal{F}^{(2)} = \int d\mathbf{r} \left\{ -\frac{\epsilon}{2} n^2 + \lambda \frac{\hbar n}{2} \sum_{i=0}^{N-1} \left[ (\nabla^2 + Q^2) + b_i \right] \right\},
$$

where \( \epsilon, \lambda, Q_i, \) and \( b_i \) can be expressed via the expansion coefficients \( \hat{C}_M \). This leads to the multimode PFC model presented in Ref. [10], with wave numbers \( Q_i \) determining \( N \) different length scales (bond lengths).

When \( m = 3 \), the general form of \( \hat{C}^{(3)}(q_1, q_2) \) reads

$$
\hat{C}^{(3)}(q_1, q_2) = \hat{C}_0^{(3)} + \sum_{M=1}^{\infty} \left[ \hat{C}_1^{(3)} q_1^{2M} + \hat{C}_2^{(3)} q_2^{2M} \\
+ \sum_{\mu=1}^{M-1} \hat{C}_{\mu_{11}}^{(3)} q_1 q_2^{2M-2\mu} \\
+ \sum_{\mu=0}^{M-1} \sum_{\nu=0}^{M-1-\mu} \hat{C}_{\mu\nu}^{(3)} q_1 q_2 q_3^{2M-2\mu-2\nu} \right],
$$

with the corresponding free-energy contribution given by [see the Supplemental Material (SM) [37] for the derivation]

$$
\Delta \mathcal{F}^{(3)} = \int d\mathbf{r} \left\{ -\frac{1}{3} D_0 n^3 + \sum_{M=1}^{\infty} \left[ D_M n^2 (\nabla^2)^M n \\
+ \sum_{\mu=1}^{M-1} D_{M\mu} n (\nabla^2)^{M-\mu} n \\
+ \sum_{\mu=1}^{M-1} \sum_{\nu=1}^{M-1-\mu} D_{M\nu,\mu} n (\nabla^2)^{M-\mu-\nu} n \\
\times (\nabla^2)^{\nu} n (\nabla^2)^{M-2\mu-2\nu} n \right] \right\},
$$

where parameters \( D \)'s are dependent on the \( \hat{C}^{(3)} \) coefficients. Interestingly, Eq. (5) shows that any terms of the \( \hat{C}^{(3)} \) free-energy contribution are always angle independent and isotropic (except for some special infinite series of \( \hat{C}^{(3)} \) expansion [32,33]; see the SM [37]). This can be attributed to the fact that the cubic energy terms are governed by the resonant triads of reciprocal lattice vectors [10,38], i.e., \( q_i + q_j + q_k = 0 \), and the side lengths of this vector triangle (\( |q_i|, |q_j|, |q_k| \), i.e., lattice length scales) uniquely determine all three angles between the wave vectors and hence the bond (neighboring) orientations.

Thus we need a four- or higher-order direct correlation to obtain the explicit angle dependence, given that angles of a wave-vector polygon or skew polygon of more than three sides (with resonant condition \( \sum_{i=1}^{m} q_i = 0, m \geq 4 \)) cannot be uniquely determined by the side lengths. For \( \hat{C}^{(4)} \) all the free-energy terms are derived in the SM, including two types of isotropic terms, \( n^2 \) and \( n (\nabla^2)^{m} n (\nabla^2)^{M-2\mu-2\nu} n \) (with integers \( \mu, \nu \geq 0, M \geq \mu + \nu \)), and three types of angle-
dependent terms,

\[
f^{(4)}_{a1} = [\nabla^2 \mu (n \nabla^2 n)](\nabla^2 n)(\nabla^2 M - 2 \mu \nabla^2 - 2 \omega n),
\]

\[
f^{(4)}_{a2} = \sum_{\alpha_i, \beta_j = x, y, z} \left[ (\nabla^2 n)^2 \sum_{i=1}^{\kappa} \sum_{j=1}^{\tau} \partial_{\alpha_i} \partial_{\beta_j} n \right] \times \left( \nabla^2 n \prod_{j=1}^{\tau} \partial_{\beta_j} n \right),
\]

\[
f^{(4)}_{a3} = n \sum_{\alpha_i, \beta_j = x, y, z} \epsilon_{\alpha \beta \gamma} \left( \nabla^2 n \prod_{j=1}^{\tau} \partial_{\alpha_i} \partial_{\beta_j} n \right) \times \left( \nabla^2 n \prod_{j=1}^{\tau} \partial_{\beta_j} n \right),
\]

where \( \alpha_i, \beta_j, \gamma \) are \( x, y, z \). For the example of \( f^{(4)}_{a1} \) terms (with integers \( \mu \geq 1, \nu, \omega \geq 0 \) and \( M \geq \mu + \nu + \omega \)), if expanding the density field as \( n = n_0 + \sum_j A_j \exp(iq_j \cdot \mathbf{r}) \),
with the average density \( n_0 \) and amplitudes \( A_j(q_j) = A^2 \hat{A}(-q_j) \),
given a system of volume \( V \), we have

\[
\frac{1}{V} \int \mathbf{d}r \frac{f^{(4)}_{a1}}{n_{_{0}=0}} = (-1)^M \sum_{j=1}^{m} \left| q_j \right|^2 \nu^2 \left( \nabla^2 + q_j^2 \right) A_j^4,
\]

\[
\times \left( \nabla^2 n \prod_{j=1}^{\tau} \partial_{\beta_j} n \right),
\]

\[
\times \left( \nabla^2 n \prod_{j=1}^{\tau} \partial_{\beta_j} n \right),
\]

\[
\times \left( \nabla^2 n \prod_{j=1}^{\tau} \partial_{\beta_j} n \right),
\]

The resonant condition \( q_1 + q_2 + q_3 + q_4 = 0 \) is satisfied by three types of wave-vector combinations \([10,39]\): collinear \((q_1 - q_2 + q_3 - q_4 = 0)\), pairwise \((q_1 - q_2 + q_3 - q_4 = 0)\), and nonpairwise closed loops. For Eq. (6), the collinear contribution \( f^{(4)}_{a1} \) from \( n_q \) wave vectors yields \( f^{(4)}_{a1} = (-1)^M \sum_{j=1}^{m} q_j \left| q_j \right|^2 \nu^2 \left( \nabla^2 n \prod_{j=1}^{\tau} \partial_{\beta_j} n \right) \), while the angle dependence arises from the factor \( \left| q_j + q_k \right|^2 \mu \) if \( \mu \geq 2 \) for pairwise resonant tetrads and \( \mu \geq 2 \) for nonpairwise ones.

For some crystalline structures (e.g., five 2D Bravais lattices and some 3D ones) the pairwise contributions would be sufficient in determining the phase stability. Given any pair \( (q_i, q_j) \) with angle \( \theta \) and \( q_i = \nu q_j \), \( \theta = \nu \) (i.e. \( j \)), the pairwise \((P)\) contribution of Eq. (6) gives

\[
\frac{1}{V} \int \mathbf{d} \frac{\left| \nabla^2 n \right|^2}{n_{_{0}=0}} = 2(-1)^M \left[ (1 + \nu^2 + 2 \nu \cos \theta)^M + (1 + \nu^2 - 2 \nu \cos \theta)^M \right] \times q_j^2 \left( \nabla^2 n \prod_{j=1}^{\tau} \partial_{\beta_j} n \right) \left( \nabla^2 n \prod_{j=1}^{\tau} \partial_{\beta_j} n \right),
\]

\[
(7)
\]

the minimization of which leads to \( \cos \theta = 0 \) when \( (-1)^M > 0 \). A similar outcome is obtained for all other angle-dependent \( C^{(4)} \) contributions \([37]\), indicating that a single quartic gradient term would favor only the \( \pi/2 \) orientation when considering pairwise wave vectors.

To verify this result we study a 3D example with only one length scale (i.e., one mode with \( q_0 = 1 \) and \( \nu = 1 \)).

\[
\mathbb{F} = \int \mathbb{d}r \left[ -\frac{1}{2} \nu^2 + \frac{1}{2} \lambda \left( \nabla^2 + q_0^2 \right) - \frac{1}{4} \partial_{\theta} n^4 \right]
\]

\[
+ E_1 n^3 \nabla^2 n + E_A n^2 \nabla^2 n^2 \]

(8)

where the only angle-dependent term is \( n^2 \nabla^4 n^2 \) (i.e., \( M = 2 \) and \( \nu = 0 \)), reproducing that used previously in 2D square pattern formations \([30,31]\). From the above analysis, the simple cubic (sc) phase, characterized by a bond angle \( \theta = \pi/2 \) and basic wave vectors \((1,0,0), (0,1,0), (0,0,1)\), should be stabilized for \( n_0 \) close to 0. This is consistent with our numerical result in Fig. 1(b), for which the simulation starts from a homogeneous state with random initial condition and follows the dynamics \( \partial n/\partial t = \nabla^2 \mathbb{F}/\partial n \). The phase diagram is given in Fig. 1(a), as calculated via a one-mode approximation.

To model structures characterized by other angles, the parameters need to be chosen such that the contributions from nonpairwise wave vectors would be important. For the example of a diamond cubic (dc) phase, in the first mode with amplitude \( A_i, q_i = q_0(-1,1,1)/\sqrt{3}, q_2 = q_0(0,1,-1)/\sqrt{3}, q_3 = q_0(1,1,-1)/\sqrt{3} \), and \( q_4 = q_0(-1,1,1)/\sqrt{3} \), thus \( q_1 + q_2 + q_3 = 0 \), leading to \( \cos \theta = -1/3 \) and \( \theta = 109.47^\circ \). The corresponding nonpairwise contribution of Eq. (6) is then given by \((-1)^M \frac{1}{4} \frac{1}{48} \frac{1}{2} \nu^2 \left( 1 + \cos \theta \right)^4 |A|^4 \). Combining with Eq. (7), we can identify the parameters minimizing \( \mathbb{F} \) of Eq. (8) that favor the dc structure, with results (including the phase diagram and a simulated structure emerging from initial homogeneous state) shown in Figs. 1(c)–1(f). Note that due to the incorporation of angle dependence, only one mode is needed to generate a sc or dc phase, different from previous isotropic PFC models where three \([8]\) or two \([24]\) modes are required.

An important feature of this approach is the ability to continuously control the characteristic angles of the crystalline phases, as achieved by combining angle-dependent gradient terms, e.g., \( \sum_k E_k n (\nabla^2 n)^2 (\nabla^2 n - 2 \nu^2 n) \), so that the angle
can be tuned via coefficients $E_k$. For the case of a single adjustable angle $\theta$ between any pair of wave vectors $(q_i, q_j)$, the simplest combination is $E_1 n (\nabla V_\mu n^2 / (\nabla V_\mu n) \mid_{n=0}^{(P)}) + E_2 n (\nabla V_\mu n^2 / (\nabla V_\mu n) \mid_{n=0}^{(P)})$. For the structures dominated by pairwise and collinear wave vector contributions, Eq. (7) gives

$$f_P = \frac{1}{V} \int d\mathbf{r} \sum_{k=1}^2 \left[ E_k n (\nabla V_\mu n^2 / (\nabla V_\mu n)) \mid_{n=0}^{(P)} + E_2 n (\nabla V_\mu n^2 / (\nabla V_\mu n)) \mid_{n=0}^{(P)} \right]$$

which gives $\sin \theta = 0$ or

$$E_2 / E_1 = (1 + \gamma^2 + 2\gamma \cos \theta)^{\mu_{i+1}} - (1 + \gamma^2 + 2\gamma \cos \theta)^{\mu_{i-1}}$$

while the collinear contribution is angle independent, i.e., $f_C = \sum_{k=1}^2 (-1)^{M_k} q_i q_j [A_i A_j]^2$. By minimizing $f_P$ we get $\sin \theta = 0$ or

$$E_2 / E_1 = (1 + \gamma^2 + 2\gamma \cos \theta)^{\mu_{i+1}} - (1 + \gamma^2 + 2\gamma \cos \theta)^{\mu_{i-1}},$$

where $E_2 = (-1)^{M_k} q_i q_j$ and $M_k = 1, 2$. It is straightforward to show that the lowest-order terms giving adjustable values of nonzero $\theta$ for $f_P$ minimization are of $\mu_1 = 4$ and $\mu_2 = 2$, when $(-1)^{M_k} E_1 > 0$ and $(-1)^{M_k} E_2 < 0$, thus $\cos \theta = (3(1 + \gamma^2)^2 + 4\gamma^2 \cos \theta) / 4\gamma^2$ from Eq. (10). To ensure the results are independent of wave number $q$, we set $M_1 = M_2 = M$ and to lowest order $M = \mu_1 = 4, \mu_2 = 2$, leading to the combination $E_1 n^2 (\nabla^2 n^2 + E_2 n (\nabla^2 n^2))$ and

$$E_2 / E_1 = -4 \frac{3(1 + \gamma^2)^2 + 4\gamma^2 \cos \theta}{1 + \gamma^2}, \quad E_1 > 0,$$  

i.e., at least eighth-order gradient terms are needed to obtain the angle control in structures governed by pairwise resonant wave vectors. The free-energy functional is then

$$\mathcal{F} = \int d\mathbf{r} \left[ \frac{\epsilon}{2 n^2} + \frac{\lambda}{2} \sum_{n=0}^{N-1} \frac{1}{(\nabla^2 + Q^2)^2 n} + E_1 n^2 (\nabla^2 n^2) \right.$$

$$+ E_2 n (\nabla^2 n^2) (\nabla^2 n^2) + E_3 n (\nabla^2 n^2) (\nabla^2 n^2) + \frac{E_0}{4} n^4 \left. \right],$$

where the $E_3$ term is angle independent for pairwise wave vectors and is introduced for structure stability.

We first apply the above analysis to the modeling of 2D rhombic and square phases with continuous angle selection ($0 < \theta \leq \pi/2$), using one mode with $N = Q_0 = \gamma = 1$ and the basic wave vectors $q_{1,2} = \pm [\cos \theta / 2, \sin \theta / 2]$. Some simulation results are illustrated in Fig. 2, for five sample rhombic structures with $\theta = 30^\circ, 45^\circ, 55^\circ, 70^\circ, 85^\circ$, starting from a homogeneous initial state. The parameter ratio $E_2 / E_1$ is chosen according to Eq. (11), and $E_3 = 0$. The resulting structures with desired angles are corroborated by the associated diffraction patterns (Fig. 2 insets), indicating the capability of angle control via nonlinear gradient terms.

Similar outcomes of continuous angle control can be obtained in 3D from Eqs. (11) and (12), with an example of simple monoclinic phase presented in Fig. 3. Three modes, $Q_0 : Q_1 : Q_2 = 1 : 1.16 : 1.24$, based on the prediction of Eq. (11). A portion of the simulated system and the diffraction pattern are shown for each angle, with $n_0 = 0, \epsilon = 0.01, E_0 = 1.2, E_1 = 1.240, E_2 = 5/32, \lambda = 5 \times 10^6$ for $\theta = 66.22^\circ$ and $5 \times 10^5$ for $\theta = 74.41^\circ, 80.72^\circ, 84.21^\circ$. 

FIG. 2. Angle control for the rhombic phase, based on the prediction of Eq. (11) for $E_2 / E_1$ vs $\theta$ (solid curve). Simulated structures and diffraction patterns are obtained with $n_0 = 0, \epsilon = 0.01, E_0 = 1/3, E_3 = 0$, and $(\lambda, E_1) = (600, 1/750)$ for $\theta = 85^\circ$ and $70^\circ, (2 \times 10^5, 1/800)$ for $\theta = 55^\circ, (6 \times 10^5, 1/800)$ for $\theta = 45^\circ$, and $(6 \times 10^4, 1.104 \times 10^{-3})$ for $\theta = 30^\circ$.

FIG. 3. Angle control for simple monoclinic structures with $Q_0 : Q_1 : Q_2 = 1 : 1.16 : 1.24$, based on the prediction of Eq. (11). A portion of the simulated system and the diffraction pattern are shown for each angle, with $n_0 = 0, \epsilon = 0.01, E_0 = 1/2, E_1 = 1/240, E_2 = 5/32, \lambda = 5 \times 10^6$ for $\theta = 66.22^\circ$ and $5 \times 10^5$ for $\theta = 74.41^\circ, 80.72^\circ, 84.21^\circ$. 

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phases, such as rhombohedral (trigonal) or a more complex
case of triclinic (with three modes and three tunable angles). All
these results thus verify the effect of angle tuning and control
on the emergence of crystalline phases through contributions of
quartic coupling.

It is also important to note that although the model in-
troduced above involves high-order nonlinear gradient terms,
the related computational cost is modest when using the
pseudospectral numerical algorithm, particularly for the cases
of weak segregation (i.e., small $\epsilon$) simulated here. In addition,
such a format with spatial gradient terms has the advantage of
being more feasible for the construction of amplitude equa-
tion formalism describing slowly varying mesoscopic scales
[13,14,18,22], which is important for large-scale simulations
with high computational efficiency and is the subject of our
future research.

In summary, we have constructed a complete density field
formulation integrating the microscopic property of interpar-
cle bond-angle anisotropy and the requirement of global-
scale system rotational invariance. Our results demonstrate
that effects of angle dependency and adjustment are incor-
porated explicitly through quartic correlation in the system,
but not through any finite-order cubic coupling which instead
implicitly affects angle selection via lattice length scales.
The resulting nonlinear gradient terms of the atomic density
field have been utilized to model various crystalline phases
and, importantly, their bond-angle control. Since the model
developed here already incorporates system elasticity and
plasticity as in other PFC-type models, it can be readily applied
to the study or prediction of a broad range of crystalline or
polycrystalline material systems and more complex phases
with bond anisotropy, their elastoplastic and defect properties,
and nonequilibrium phenomena during crystallization and
growth. This approach is built on the full-order expansion of
direct correlation functions and the application of isotropic
Cartesian tensors, and is thus of a generic nature and applicable
to different types of ordering or self-assembling systems with
varying atomistic details.

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