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Multiscale modeling of polycrystalline graphene: A comparison of structure and defect energies of realistic samples from phase field crystal models

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We extend the phase field crystal (PFC) framework to quantitative modeling of polycrystalline graphene. PFC models are ideal for finding the ground state configurations of large realistic samples that can be further used to study their mechanical, thermal or electronic properties. By fitting to density functional theory (DFT) calculations, we show that PFC models are able to predict realistic formation energies of grain boundaries. We provide an in-depth comparison of the formation energies between our PFC, DFT and molecular dynamics (MD) calculations. To ensure perfect comparability, our DFT and MD calculations are initialized using atomic configurations estimated from PFC ground states. Finally, we use PFC to explicitly construct large realistic polycrystalline samples and characterize their properties using MD simulations to demonstrate their quality.

I. INTRODUCTION

Graphene is a widely studied material due to its remarkable mechanical strength, and thermal and electronic conductivities [1-4]. Graphene-based devices and interconnects often require high quality samples, whereas large graphene patches typically grown by the industry-standard chemical vapor deposition (CVD) result in polycrystalline structures [5-6]. Polycrystalline graphene is a quilt consisting of pristine graphene domains in various crystalline orientations that are separated by grain boundary defects comprised of dislocations that accommodate the lattice mismatch between neighboring crystals. It is the grain boundaries that largely determine the properties of the material, such as out-of-plane relaxation, weakening its mechanical strength at low-angle tilt boundaries, altering the electronic structure and limiting the carrier mobility [7,11]. Many of the features of the grain boundaries stem from the early stages of formation, where the graphene grains nucleate in certain orientations that are partly determined by the substrate. This results in a rich variety of possible grain tilt angles and grain boundary topologies, each having their own characteristic properties.

Modeling realistic systems of polycrystalline graphene has remained a challenge due to the multiple length and time scales involved. Of the conventional methods, density functional theory (DFT) is limited to small sample sizes with a few thousand atoms, whereas the time scales of tracing atomic vibrations in molecular dynamics (MD) simulations are too short to capture dislocation dynamics. Constructing model systems with grains and grain boundaries has, therefore, typically been approached as a multi-step process, using for instance cut and paste, iterative grain growth, thermalization and cooling of the grain boundaries by applying local relaxation, and probing stability by adding additional atoms [12,13]. For constructing symmetric grains, the coincidence site lattice (CSL) theory can be applied [9,14]. In the general case, however, there still are obvious problems in the construction of realistic samples regarding especially the non-local properties such as determining how many carbon atoms are needed at the grain boundary, and whether the low-stress ground state configuration has been reached. Furthermore, one commonly restricts to the 5/7 dislocation defects with adjacent pentagon-heptagon pairs in the graphene backbone that have been seen in experiments using transmission electron microscopy techniques [5,9]. However, in some tilt angles and conditions there could be other interesting defect types present, such as 5|8|7 defects that have been shown to have finite spin moments [15]. Other polygons and more complex chains are possible in principle as well, but the number of structural permutations corresponding to reasonable grain boundaries is too large to be sampled by conventional methods.

Our solution to multiscale modeling of polycrystalline graphene is to apply phase field crystal (PFC) models [16]. They are ideally suited to deal with large system sizes required by the polycrystalline nature of graphene. Namely, PFC is a continuum approach to microstructure evolution and elastoplasticity in crystalline materials. It models a time-averaged atomic number density field over long, diffusive time scales, while retaining atomic resolution. Due to the simplicity of PFC models, and the numerically convenient smoothness of the density fields, mesoscopic length scales are easily attained. Therefore,
PFC models can be used to construct even large realistic systems without a priori knowledge of the atomic positions. The multiscale characteristics of the PFC framework allow access to new modeling regimes that fall beyond the reach of conventional techniques.

In this paper, we demonstrate a thorough evaluation of four different two-dimensional PFC models by studying graphene grain boundary structures and energies at varying tilt angles and with different defect types. Such structure and energetics calculations have been performed previously with MD, DFT, and MD methods. In this work, MD was used to calculate formation energies of grain boundaries. The formation energies of grain boundaries were also evaluated using PFC, DFT and MD.

To further validate the use of PFC models to study polycrystalline graphene, we show ground state configurations of grain boundaries and the distribution of different defect or dislocation types produced by the PFC models. While 5|7 grain boundaries are the most prominent, one of the PFC models produces a rich variety of alternate dislocation types in certain tilt angle regimes. Furthermore, we explicitly show that the PFC models can be used to construct large (~100 nm) and low-stress polycrystalline graphene systems for further mechanical, thermal or electronic transport calculations. Here, we characterize the formation energies and height fluctuations in such realistic systems of varying size.

This paper is organized as follows. Sec. II introduces the DFT, MD and PFC models. In Sec. III, the PFC models are fitted to DFT, and are used to study both the formation energy and topology of grain boundaries. In Sec. IV, we construct large polycrystalline samples and demonstrate their quality by characterization of their properties. Sec. V concludes.

II. METHODS

A. Density functional theory calculations

In the Born-Oppenheimer approximation, the electronic structure and the nuclear configuration are solved separately. Density functional theory solves the quantum-mechanical electronic structure of a material, after which the atomic geometry can be relaxed using the forces evaluated from the DFT total energy gradients. While this constitutes a highly accurate ab initio description, the system sizes are limited.

The DFT calculations were performed using the all-electron FHI-aims package [23]. It uses numerical atom-centered basis functions for each atom type. The default light basis sets were employed together with the GGA-PBE functional [24]. During the course of the calculation, the self-consistent cycle was considered converged if, among other things, the total energy had converged up to $10^{-6}$ eV between consecutive iterations. The atom geometries were relaxed in each case until the forces acting on the atoms were smaller than $10^{-2}$ eV/Å.

B. Molecular dynamics calculations

Molecular dynamics (MD) methods demonstrate further coarse-graining compared to DFT by replacing the electronic structure with effective interatomic potentials. As a consequence, computational complexity is reduced and very large systems with millions of atoms can be handled. However, tracing atomic vibrations at femtosecond time-scales becomes the stumbling block. That is, processes such as microstructure formation and evolution that occur over long, diffusive time scales cannot usually be addressed. Constructing large polycrystalline samples with low stress also becomes a difficult task, since the relaxed structure can be nontrivial and hence not known a priori.

In this work, MD was used to calculate formation energies of grain boundaries and to characterize the properties of large polycrystalline samples constructed using PFC. The grain boundary formation energies were evaluated by MD calculations using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) software [25]. Two potentials were used to define the interactions of carbon atoms: the adaptive intermolecular reactive empirical bond order (AIREBO) potential [26] and the Tersoff potential [27]. We employed the parameters provided by S. J. Stuart et al. [28] for the AIREBO potential and the parameters provided by J. Tersoff [29] for the Tersoff potential. The Polak-Ribiere version of the conjugate gradient algorithm [29] was used in all of the minimizations. All minimizations were carried out until one of these criteria was met: The energy change between two successive iterations is less than $10^{-6}$ times its magnitude, or length of the global force vector is less than $10^{-6}$ eV/Å, or when the step distance becomes zero.

The formation energies of grain boundaries were also evaluated using a MD code implemented fully on graphics process units (GPUs) [30, 31], which can be two orders of magnitude faster than a serial code for relatively large systems. This code uses the Tersoff potential [29], but with optimized parameters provided by L. Lindsay and D. A. Broido [32], which are better suited for modeling graphene. In the calculation of the grain boundary formation energies, we performed MD simulations at a low temperature of 1 K with a total simulation time of 100 ps, up to which the systems become fully relaxed.

The relative efficiency of the Tersoff potential com-
pared to the AIREBO potential and its acceleration by GPUs allowed us to simulate large-scale polycrystalline graphene samples with long simulation times. Here, a room temperature of 300 K was chosen and the in-plane stress was required to be around zero. All simulations of polycrystalline graphene samples were performed up to 1000 ps to ensure full convergence of out-of-plane deformations. In all the MD simulations with the GPU code, we adopted the Verlet-velocity integration method with a time step of 1 fs.

C. Phase field crystal models

PFC is a continuum approach that models crystalline matter via a classical density field, $\psi = \psi (r)$ [16]. The density field is governed by a free energy functional, $F = F[\psi]$, that is chosen to be minimized by a periodic solution to $\psi$. The relaxed configuration corresponding to a particular initial state can be solved via energy minimization. Details of the functional determine the symmetries in the ground state that can be matched with the desired crystal structure. The standard relaxation dynamics for PFC capture dynamics on diffusive time scales only. Thereby the atomic vibrations captured by MD are effectively coarse-grained into time-averaged smooth peaks in $\psi$ describing the lattice. Furthermore, atomic relaxation is retained while the smoothness of $\psi$ facilitates numerical modeling of systems with millions of atoms. While its diffusive description of matter neglects some microscopic details, such as atomic vibrations and vacancies, PFC resolves the length and time scale limitations of DFT and MD, respectively [16, 17].

We investigate here the suitability of four PFC variants for modeling of polycrystalline graphene samples: the one-mode model (PFC1), the amplitude model (APFC), the three-mode model (PFC3) [33] and the structural model (XPFC) [22]. For the convenience of the reader, more comprehensive details of these models, such as present model parameter choices, method of relaxation, etc., are provided in Appendices [4] and [3].

PFC1 is the standard PFC model [16], but instead of the close-packed triangular lattice formed by its density field maxima, we relate the hexagonal arrangement of density field minima to atom positions. In practice, we choose model parameters to invert the density field to yield a hexagonal (triangular) set of maxima (minima). The PFC1 free energy functional is given by

$$F_1 = c_1 \int dr \left( \frac{\psi L_1 \psi}{2} + \tau \psi^3 + \psi^4 \right), \quad (1)$$

where

$$L_1 = \epsilon + (q_0^2 + \nabla^2)^2 \quad (2)$$

is a rotation-invariant Hamiltonian describing non-local contributions. The parameter $\epsilon$ is related to temperature, $q_0$ controls the equilibrium lattice constant and $\tau$ sets the average density. The coefficient $c_1$ allows controlling the energy scale of the model.

APFC is an amplitude expanded reformulation of PFC1 [34] where the density field is replaced by three smooth, complex-valued amplitude fields, $\eta_j$, for increased numerical performance. The APFC functional is written

$$F_A = c_A \int dr \left( \frac{\Delta B}{2} A^2 + \frac{3v}{4} A^4 \right) - 2\tau \left( \prod_{j=0}^2 \eta_j + \text{c.c.} \right) \quad (3)$$

$$+ \sum_{j=0}^2 \left( B^2 |G_j \eta_j|^2 - \frac{3v}{2} |\eta_j|^4 \right),$$

where

$$\Delta B = B^l - B^c, \quad (4)$$

$$G_j = \nabla^2 + 2i g_{j} \cdot \nabla \quad (5)$$

and

$$A^2 = 2 \sum_j |\eta_j|^2. \quad (6)$$

The parameters $B^l$ and $B^c$ are related to the compressibility of the liquid state and the elastic moduli of the crystalline state, respectively, whereas the magnitude of the amplitudes and the liquid-solid miscibility gap depend on the choice of $t$ and $v$ [35]. The complex conjugate is denoted by c.c. and the lowest-mode set of reciprocal lattice vectors by $g_{j}$, for $g_0 \cdot g_1 \cdot g_2 = (-\sqrt{3}/2, -1/2), (0, 1), (\sqrt{3}/2, -1/2)$. The coefficient $c_A$ controls the energy scale of the model. The real-space density field can be reconstructed from the complex amplitudes as

$$\psi (r) = \sum_j \eta_j e^{ig_j \cdot r} + \text{c.c.}. \quad (7)$$

It must be noted that this model is limited to relatively small orientational mismatch between neighboring crystals, see Ref. [36] for details.

PFC3 is a generalization of PFC1 that incorporates not just one, but three controlled length scales, or modes. The free energy reads

$$F_3 = c_3 \int dr \left( \frac{\psi L_3 \psi}{2} + \frac{\psi^4}{4} + \mu \psi \right), \quad (8)$$

with

$$L_3 = \epsilon + \lambda \left( b_0 + (q_0^2 + \nabla^2)^2 \right) \left( b_1 + (q_1^2 + \nabla^2)^2 \right) \times \left( b_2 + (q_2^2 + \nabla^2)^2 \right), \quad (9)$$
where a chemical potential term replaces the third-order term and assumes its role in fixing the average density to a constant value. The third-order term is often omitted from PFC formulations and this choice is argued further in Ref. 37. The parameters $\lambda, b_0, b_1$ and $b_2$ weight the competing modes controlled by $q_0, q_1$ and $q_2$. Again, the coefficient $c_3$ controls the energy scale.

The XPFC free energy can be expressed as a sum of three contributions: ideal free energy, $F_0$, two-point interactions, $F_\perp$, and three-point interactions, $F_\Delta$,

$$F_X = c_X (F_0 + F_\perp + F_\Delta),$$

where $c_X$ sets the energy scale. The ideal free energy is given by

$$F_0 = \int dr \left( \frac{\psi^2}{2} - \eta \frac{\psi^3}{6} + \chi \frac{\psi^4}{12} + \mu \psi \right),$$

where $\eta$ and $\chi$ are phenomenological parameters and $\mu$ again the chemical potential. The two-point term is given by

$$F_\perp = -\frac{1}{2} \int dr \left( \psi \mathcal{F}^{-1} \left\{ \hat{C}_2 \hat{\psi} \right\} \right),$$

where the caret and $\mathcal{F}^{-1}$ denote (inverse) Fourier transforms, and

$$\hat{C}_2 = -2R J_1 \frac{r_0 k}{r_0 k},$$

where $R$ and $r_0$ set the magnitude and range of the interaction, respectively, $J_1$ is a Bessel function of the first kind and $k$ is the magnitude of the Fourier space $k$-vector. The three-point term reads

$$F_\Delta = -\frac{1}{3} \int dr \left( \psi \sum_{i=1}^{2} \left( \mathcal{F}^{-1} \left\{ \hat{C}_s^{(i)} \hat{\psi} \right\} \right)^2 \right),$$

where

$$\hat{C}_s^{(1)} = X i^m \cos (m \theta_k) J_m (ka_0)$$

and

$$\hat{C}_s^{(2)} = X i^m \sin (m \theta_k) J_m (ka_0).$$

Here, $X$ sets the interaction strength, $i$ is the imaginary unit, $m = 3$ indicates the three-fold rotational symmetry that is desired, $\theta_k$ is the polar coordinates angle in Fourier space and $a_0$ controls the lattice constant.

We apply these models in two dimensions where a number of different phase structures can be produced depending on the model in question and the set of model parameters employed. A phase diagram can be constructed by dividing the parameter space of a model into domains based on the most stable phase. Phase diagrams also indicate the possible coexistences and transitions between neighboring phases. We fixed the parameters of each

![FIG. 1. (Color online) The appearance of PFC density fields in equilibrium: (a) PFC1, (b) APFC, (c) PFC3 and (d) XPFC. All density fields have been mapped linearly to grayscale values with the maxima (minima) appearing as white (black). Density profiles along the red lines intersecting local maxima and minima are shown on top in arbitrary units.]

**III. GRAIN BOUNDARIES**

**A. Construction of grain boundaries**

Extensive calculations of graphene grain boundary topologies and formation energies were performed to benchmark the four PFC models. These results are compared against DFT and MD calculations of identical grain boundaries from both the present and previous works. To simplify the analysis, we considered only symmetrically tilted grain boundaries in systems that were both free-standing and planar. Free-standing systems were treated to facilitate comparison to previous theoretical works and two-dimensionality is a limitation of the PFC models investigated. On the other hand, graphene
is typically grown on a substrate [3] forcing a planar atomic configuration. Periodic boundary conditions were employed to eliminate edge effects.

A bicrystalline layout was used for the grain boundary calculations, because it is the simplest that satisfies periodic boundary conditions. Fig. 2 demonstrates a bicrystal with two grains and two grain boundaries. The tilt angle, $2\theta$, is the difference in crystallographic orientation between the bicrystal halves rotated by $\pm \theta$, see Fig. 2 (a). We take $2\theta \rightarrow 0^\circ$ and $2\theta \rightarrow 60^\circ$ to correspond to armchair and zigzag grain boundaries, respectively, and refer collectively to both limits as small tilt angles.

The symmetrically tilted, hexagonal crystals were constructed into a rectangular, two-dimensional computational unit cell. The initial hexagonal state shown in Fig. 2 (a) was obtained using the one-mode approximation [17] where

$$\psi(x, y) = \cos (q x) \cos \left(\frac{q y}{\sqrt{3}}\right)$$

$$- \cos \left(2q y/\sqrt{3}\right)/2,$$

(17)

where $2\pi/q$ is the lattice constant. While rotating $\psi$ is trivial, the rotated equilibrium state in APFC is given by

$$\eta_j (\mathbf{r}, \theta) = \phi_{eq} \exp \left(i (\mathbf{g}_j (\theta) - \mathbf{g}_j (0)) \cdot \mathbf{r}\right),$$

(18)

where

$$\phi_{eq} = \frac{t - \sqrt{t^2 - 15v (B^2 - B^z)}}{15v}$$

(19)

and

$$\mathbf{g}_j (\theta) = \left(\cos (\theta) - \sin (\theta) \sin (\theta) \cos (\theta) \right) \mathbf{g}_j (0).$$

(20)

Here, $\mathbf{g}_j (0)$ are the non-rotated reciprocal lattice vectors, recall Eq. [3]. The lattice constant is $4\pi/\sqrt{3}$. The continuity of the density and amplitude fields was ensured at the edges of the periodic unit cell.

Due to the model’s limitation to small rotations, two sets of APFC calculations were carried out to investigate both the armchair (APFC(AC)) and zigzag (APFC(ZZ)) grain boundary limits. This was achieved by rearranging the adjacent bicrystal halves—such as in Fig. 2 (a)-(c)—with one on top of each other, thereby replacing vertical armchair grain boundaries in one set with horizontal zigzag grain boundaries in the other.

As shown in Fig. 2 (a), narrow strips along the grain boundaries in the density field (amplitude fields) were in most cases set to its average value (to zero)—corresponding to a disordered phase—to give the grain boundaries some additional freedom to seek their ground state configuration.

All computational unit cell sizes used for PFC calculations of grain boundaries were greater than 10 nm in the direction perpendicular to the grain boundaries. This was verified to eliminate finite size effects to a high degree, see Appendix C for details.

To ensure perfect comparability between PFC, DFT and MD calculations of grain boundaries, the initial atomic configurations for the latter two were obtained from relaxed PFC density fields that were converted to discrete sets of atom coordinates, see Fig 2 (b) and (c), respectively. PFC3 was used, because it appears capable of producing all the same topologies as the other PFC models, and more. The primary maxima of the density field were treated as atom positions, and their exact coordinates were estimated via quadratic interpolation around local maximum values in the discretized density field. The atom coordinates were rescaled to take into account the equilibrium bond lengths given by DFT and MD potentials.

We verified the validity of the atomic configurations extracted from PFC3 by relaxing them further using DFT. Since the PFC models are two-dimensional, we relaxed the geometries in two ways using DFT, constrained on plane $(z = 0)$ (DFT(2D)) and also, for comparison, freely in three dimensions (DFT(3D)), using small random initial values of $z$ or folding the grain boundaries with small angles. The lattice vectors were allowed to relax but their relative angles were kept perpendicular to each other. As the rectangular-shaped systems were rather large, a grid of $3 \times 10 \times 1 \text{ k-points}$ was enough to obtain sufficiently convergent results.
Using LAMMPS, the atomic configurations extracted from PFC3 were minimized freely in two and three dimensions. For three-dimensional calculations, the initial z coordinates were assigned small random values. These calculations, however, resulted in planar structures, and Ref. 39 reports similar findings with LAMMPS. The formation energies of grain boundaries in these systems are identical to those from the corresponding two-dimensional AIREBO(2D) and Tersoff(2D) calculations—to the precision given by the convergence criteria. To obtain data for three-dimensionally buckled structures, we applied also the GPU code for evaluation of formation energies of grain boundaries (Tersoff(3D)).

### B. Calculation of formation energies

The formation energies of grain boundaries are calculated by subtracting from the total energy of the defected system that of a corresponding pristine system. Grain boundary energy, \( \gamma \), i.e., formation energy of a grain boundary per unit length, can be calculated exploiting a periodic, bicrystalline PFC system with two grain boundaries (note the factor 1/2) as

\[
\gamma = \frac{1}{2} \left( f - f_{eq} \right)
\]

where \( f \) and \( f_{eq} \) are the average free energy densities of the bicrystalline system and the single-crystalline equilibrium state, respectively. Here, \( f = F/A \), where \( F \) is the free energy and \( A \) the total area of the PFC system in question. The quantity \( l_\perp \) is the system size in the direction perpendicular to the grain boundaries. Alternatively, \( \gamma \) can be calculated via atomistic methods as

\[
\gamma = \frac{E - N_C E_C}{2l_\parallel},
\]

where \( E \) is the total energy of the defected system, \( N_C \) is the number of carbon atoms in the defected system, \( E_C \) is the energy per atom of a pristine system of any size in equilibrium and \( 2l_\parallel \) is the combined length of the two grain boundaries in a bicrystal system.

### C. Fitting to density functional theory

The energy scale of each PFC model was fitted to DFT. There is no unique way to carry out the fitting. We tried, for example, fitting the elastic behavior of each model to the Young’s modulus of graphene, but found the most consistent results by fitting with respect to the grain boundary energy of a particular small-tile angle system. In the small-tile angle limit, the separation between dislocations, \( s \), diverges as \( s \propto 1/\theta \). This limit is ideal for PFC models that are not expected to describe adjacent dislocations perfectly. Fig. 15 in Appendix D shows the system with 5/7 grain boundaries at \( 2\theta \approx 4.4^\circ \), that was chosen because it is close to this limit and yet feasibly small to be studied using DFT. Our PFC calculations are two-dimensional which is why the DFT atomic configuration was also constrained to a plane.

The grain boundary energies given by PFC1, PFC3 and XPFC for the aforementioned system were matched to the grain boundary energy given by DFT for the very same system via the respective coefficients \( c_1 \), \( c_3 \) and \( c_X \). These datapoints are shown in Fig. 3 alongside other values calculated for lowest-energy 5/7 grain boundaries found in the armchair limit. The tilt angles for APFC are not exactly the same as for the other PFC models, because the smooth amplitude fields need not satisfy the geometric constraints given by the real-space crystal lattice. In the small-tile angle limit, where grain boundaries reduce to arrays of non-interacting dislocations, the grain boundary energy can be expressed with the Read-Shockley equation as

\[
\gamma = \frac{b Y_{2D}}{8 \pi} \theta \left( \frac{3}{2} - \ln \left( 2 \pi \theta \right) \right),
\]

where \( b \) is the size of a dislocation core and \( Y_{2D} \) is the two-dimensional Young’s modulus. We fitted this expression to the DFT datapoint via \( b Y_{2D} \) and equated the APFC grain boundary energy at \( 2\theta \approx 4.6^\circ \) to this curve via \( c_A \). The Read-Shockley curve and APFC values are also plotted in Fig. 3. For PFC1, APFC, PFC3 and XPFC, \( c_1 \), \( c_A \), \( c_3 \) and \( c_X \) take values 97, 117, 462 and 48 \text{ eV/nm}, respectively. The grain boundary energy values demonstrate an excellent agreement with the Read-Shockley curve, validating the fitting approach used.
Having fitted the energy scales of the models, we determined for PFC1, PFC3 and XPFC the following two-dimensional Young’s moduli, $Y_{2D} \approx 252, 359$ and 309 N/m, respectively. The moduli of PFC3 and XPFC agree best with the experimental value ca. 340 N/m\textsuperscript{[41]}. As an aside, a similar fitting to DFT(3D) would have resulted in half lower values. The following Poisson’s ratios were also determined: $\nu \approx 0.334, 0.370$ and 0.161, respectively. The XPFC model parameter $X$ was in fact chosen to yield a reasonable Poisson’s ratio for the model $\nu$. Details of these calculations are given in Appendix \textsuperscript{[2].

D. Energetics of grain boundaries

1. Phase field crystal calculations

Fig. 4 collects the grain boundary energies, $\gamma$, of lowest-energy grain boundary configurations found using the four PFC models. The grain boundary energies of lowest-energy PFC3 $\{7\}$ grain boundary configurations relaxed further using DFT(2D), DFT(3D), AIREBO(2D) and Tersoff(3D) are also given. For APFC both the armchair (AC) and zigzag (ZZ) grain boundary limits were investigated by two independent sets of calculations, corresponding to the two sets of APFC values present. While the other PFC models give $\{7\}$ grain boundaries practically exclusively, PFC3 produces also grain boundaries containing alternative dislocation types, that are discussed further in Sec. IIIE. The grain boundary energies of such alternative grain boundaries are plotted separately in cases where their energy is lower than that of $\{7\}$ grain boundaries at the same tilt angle. Due to symmetry arguments, the efficient diffusive relaxation of the PFC models and our extensive calculations, the PFC configurations corresponding to the lowest-energy grain boundary energy values plotted are expected to be ground states, or to exhibit very similar energies.

More comprehensive data is tabulated in supplemental material, indicating the tilt angle, system size, initialization type, relaxation details, GB energy and dislocation types present in the relaxed GBs for each PFC calculation. Energies of the corresponding DFT and MD calculations are given as well.

PFC1, PFC3 and XPFC give the correct grain boundary energy trend as a function of the tilt angle. Starting from a single-crystalline state at zero tilt, $2\theta = 0^\circ$, increasingly dense arrays of dislocations are encountered as the tilt angle is grown and the grain boundary energy rises. At large tilt angles, the grain boundary energy dips as high-symmetry grain boundaries are approached at $2\theta_1 \approx 21.8^\circ$ and $2\theta_{11} \approx 32.2^\circ$, giving characteristic kinks to the energy curve. Finally, at $2\theta \to 60^\circ$, the grain boundaries grow sparse with dislocations and the grain boundary energy plunges to zero as the single-crystalline state is again restored. As expected, APFC is not applicable at large tilt angles as its grain boundary energy saturates. However, together the two grain boundary energy sets trace the correct trend. Furthermore, APFC does not capture the characteristic kinks in grain boundary energy.

The energy scale of each PFC model was fitted to DFT at $2\theta \approx 4.4^\circ$, and in both small-tilt angle limits, all PFC models are in an excellent mutual agreement. At around $2\theta \approx 10^\circ$, the respective grain boundary energy values begin to branch, and come again together around $2\theta \approx 50^\circ$. The grain boundary energy predicted by PFC3 at large tilt angles is the lowest, leveling roughly at 5 eV/nm between $2\theta \approx 15^\circ$ and $50^\circ$. PFC1 and XPFC follow a mutually similar trend in grain boundary energy, and compared to PFC3, both give higher grain boundary energies at large tilt angles. PFC1 and XPFC values reach roughly 7 eV/nm, PFC1 peaking ca. 1 eV/nm higher than XPFC. Before their saturation, both sets of APFC values follow PFC1 data closely.

2. Comparison to other methods

Of the PFC models, the grain boundary energies given by PFC3 are the most consistent with our primary benchmark DFT(2D), see Fig. 4. At large tilt angles, PFC1, APFC and XPFC agree only qualitatively with DFT(2D) whose grain boundary energy declines slightly at large tilt angles. At large tilt angles, the grain boundaries become crowded with dislocations that screen each other’s bipolar elastic fields. The PFC models are likely to capture such short-wavelength properties incompletely, resulting in the elevated grain boundary energies observed.

Between $2\theta \approx 4.4^\circ$ and $13.2^\circ$, PFC3 is in an excellent agreement with DFT(2D). At larger tilt angles, however, PFC3 values lie roughly 1 eV/nm higher in energy compared to DFT(2D), and at $2\theta_1$ and $2\theta_{11}$, it overestimates the grain boundary energy somewhat more. Overall, PFC3 is in a good quantitative agreement with DFT(2D).

Due to the further relaxation achieved via three-dimensional buckling of the graphene sheet\textsuperscript{[4]}, DFT(3D) calculations demonstrate lower energies compared to DFT(2D). At $2\theta_1$ and $2\theta_{11}$, however, planar structures are preferred resulting in equal energies between DFT(2D) and DFT(3D) calculations. The difference in grain boundary energy between DFT(2D) and DFT(3D) is very small at large tilt angles between $2\theta \approx 20^\circ$ and $40^\circ$. Although PFC3 is less consistent with DFT(3D), both demonstrate qualitative mutual agreement in that the grain boundary energy levels at large tilt angles.

Our primary benchmark DFT is limited to systems with relatively few atoms. Another benchmark is therefore needed for large samples. AIREBO(2D) is very well in line with PFC3 throughout the tilt angle range, similarly exceeding DFT(2D) values at large tilt angles. At $2\theta_{11}$, the kink given by AIREBO(2D) is a bit deeper than that of PFC3.

Using the Tersoff potential, we observed that both LAMMPS and the GPU code give mutually consistent
FIG. 4. (Color online) The grain boundary energy as a function of the tilt angle. The values are given by PFC1, APFC, PFC3, XPFC, DFT(2D), DFT(3D), AIREBO(2D) and Tersoff(3D). The values correspond to lowest-energy grain boundary configurations found that are comprised of 5|7 dislocations. An exception is the dataset PFC3* that gives the energy of grain boundaries containing other dislocation types in addition to 5|7 dislocations or exclusively. For APFC, two separate sets of data are plotted corresponding to the armchair (APFC(AC)) and zigzag (APFC(ZZ)) grain boundary limits.

but high grain boundary energies for systems forced to a plane. Namely, the Tersoff(2D) values peak at ca. 10 eV/nm and their slope at small tilt angles is significantly steeper than those of other 2D data. While these deviant points are not shown in Fig. 4, the results from Tersoff(3D) simulations are plotted. In the armchair grain boundary limit, these data are consistent with DFT(3D), whereas at large tilt angles they agree better with PFC3.

3. Comparison to previous works

Fig. 4 shows that our calculations using PFC3 are consistent with present DFT(2D) and DFT(3D) calculations. Fig. 5 validates these results by comparing the corresponding grain boundary energy values to ones reported in previous works employing DFT [9, 12, 14, 20, 43], MD [7, 12, 14, 39] and disclination-structural unit (DSU) model [44] calculations. To avoid unnecessary clutter, the AIREBO(2D) and Tersoff(3D) values have been left out.

Grain boundary energy values from previous works have been accepted into this comparison only if we have been able to make sure, with high confidence, that the grain boundary topologies of the corresponding systems are identical to those of the present systems. Despite this, significant scatter is observed. Different relative translations between the two grain boundaries—in the case of periodic bicrystal systems—and the different techniques used, explain much of the scatter that is present. It is understandable that the MD potentials fitted for various purposes yield deviant values for the grain boundary energy. However, a much narrower spread is expected for DFT values. This indicates that not all previous grain boundary energy analyses have been performed consistently.

Most of the grain boundary energy data available in the literature is for systems free to buckle in three dimensions. However, Ref. [9] provides a set of grain boundary energy values from planar DFT systems. As can be seen in Fig. 5, present DFT(2D) calculations of 5|7 grain boundaries are in a perfect agreement with these values, validating our DFT benchmark and moreover the atomic configurations extracted from PFC3.

Three-dimensional buckling allows grain boundaries to relax further [9], which explains why the grain boundary energy values from planar PFC3 systems remain at the high-end of the data spectrum. While there is some scatter, present DFT(3D) calculations are well in line with those of previous works. The low energy given by DFT(3D) demonstrates that even for three-dimensionally buckled systems realistic in-plane structures can be extracted from planar PFC3 configurations. Furthermore, PFC3 grain boundary energy is in a reasonable agreement with DFT(3D). There is a large amount of scatter in previous MD(3D) results, and the present AIREBO(2D)
A comparison of grain boundary energies to previous works. Present PFC3, DFT(2D) and DFT(3D) datasets are depicted alongside previous DFT(2D) [9], DFT(3D) [9, 12, 14, 20, 43], MD [7, 12, 14, 39] and disclination-structural unit (DSU) values. Systems with grain boundary topology identical to the present ones have been included. All systems have \( 5|7 \) grain boundaries and are expected to be ground states, excluding the PFC3 5|7 systems at \( 2\theta \approx 4.4^\circ \) and 42.1\(^\circ \) where a minimally lower energy is given to alternative grain boundary structures.

and Tersoff(3D) values are consistent with this spectrum, compare with Fig. 4. The few DSU datapoints agree very well with DFT(3D).

### E. Topology and dislocation types

#### 1. Topology of grain boundaries

When constructing large polycrystalline graphene samples, one has to pay attention to the topology of the grain boundaries, and what kind of dislocations there are, since the grain boundaries largely determine the physical properties of the whole system. Here, we determine how suitable the PFC models are to constructing realistic samples in their ground state configurations. Namely, in addition to having evaluated the grain boundary energies of \( 5|7 \) dislocation arrays, we have determined for each PFC model the topologies of the expected ground state grain boundary configurations as a function of the tilt angle.

Of the four PFC models studied, PFC1 and XPFC produce \( 5|7 \) dislocations exclusively in their expected ground state grain boundary configurations at all tilt angles. Of these two models, PFC1 appears to exhibit faster and more robust relaxation, and is computationally more light-weight. It is, therefore, the more convenient alternative of the two models that can be applied to constructing realistic systems with \( 5|7 \) dislocations. We will focus on PFC1 over XPFC for the remainder of this work. On the other hand, PFC3 that gives the best estimates of the grain boundary energies, also supports \( 5|8|7 \) dislocations and more exotic defects with several under- and over-coordinated carbon atoms. Such exotic grain boundary topologies are coined as ‘incompatible’ with the underlying hexagonal lattice, see Fig. 6 for an example. In certain tilt angle ranges, these alternative grain boundary structures demonstrate near-identical energies to \( 5|7 \) grain boundaries. Lastly, the topology of APFC dislocations cannot always be determined unambiguously from the imperfect reconstruction of the density field. Furthermore, all APFC calculations were carried out using very low spatial resolution, ruling out topological analysis.

Examples of ground state configurations of grain boundaries from the PFC1 and PFC3 models are shown in Fig. 7. Excluding Fig. 7 (h), the depicted grain boundaries consist of \( 5|7 \) dislocations that come closer together when the tilt angle is increased. The grain boundaries are highly symmetric with periodic arrays of dislocations, which typically indicates low energy. For tilt angles, where geometrical constraints necessitate that the dislocations cannot be stacked both linearly and with equal spacings, we find that the PFC models prefer slightly meandering arrangements with equal spacings, see Fig. 7 (c) and (j).

Towards the zigzag grain boundary limit, \( 2\theta \to 60^\circ \), \( 5|7 \) dislocations become alternatingly slanted. Previous works have typically considered paired configurations of slanted \( 5|7 \) dislocations [12], but our boundaries exhibit disperse arrangements, see Fig. 7 (g) and (n). Ref. [9] reports lower energies for disperse arrangements in two dimensions and for paired arrangements in three dimensions, settling the discrepancy. Present DFT calculations concur at \( 2\theta_{III} \approx 42.1^\circ \) with \( \gamma \approx 4.41, 5.09, 4.33 \) eV/nm.
The lowest-energy configurations of grain boundaries found using the PFC1 (a)-(g) and PFC3 models (h)-(n), where the grain boundary tilt angles are \(2\theta \approx 4.4^\circ\) in (a) and (h), \(2\theta \approx 9.4^\circ\) in (b) and (i), \(2\theta \approx 16.4^\circ\) in (c) and (j), \(2\theta_I \approx 21.8^\circ\) in (d) and (k), \(2\theta \approx 27.8^\circ\) in (e) and (l), \(2\theta_{II} \approx 32.2^\circ\) in (f) and (m), and \(2\theta \approx 46.8^\circ\) in (g) and (n), respectively. The atomic positions are determined from the density field \(\psi\) that is shown around 5/7 and 5/8|7 dislocations as insets. In (n), 5/7 dislocations from systems relaxed using DFT(2D) (yellow background) and AIREBO(2D) (red background) are embedded.

The topologies of the symmetric large-tilt angle cases at \(2\theta_I \approx 21.8^\circ\), shown in Fig. 7 (d) and (k), and \(2\theta_{II} \approx 32.2^\circ\), shown in Fig. 7 (f) and (m), match those studied in, e.g., Ref. [9]. Furthermore, the less symmetric case at \(\theta \approx 27.8^\circ\) shown in Fig. 7 (e) and (l) has the same topology as studied in Ref. [12]. The quality and consistency of the configurations further validate the use of especially the PFC1 model to constructing large polycrystalline samples.

Fig. 7 (g) and (n) compare the PFC1 and PFC3 den-
FIG. 8. (Color online) A stacked area chart of the proportions of 5|7, 5|8|7 and incompatible dislocations in lowest-energy PFC3 grain boundary configurations found. No data is available for small tilt angles due to non-exhaustive small-tilt angle PFC3 calculations that excluded non-5|7 grain boundaries, see Appendix B.

sity fields and the corresponding atomic configurations extracted from them and relaxed using DFT(2D) and AIREBO(2D), in the vicinity of 5|7 dislocations. The PFC models are different from the conventional methods in that they produce slightly more elongated heptagons. The PFC1 pentagons are also noticeably large. All bond lengths are fairly similar in both DFT(2D) and AIREBO(2D) 5|7 dislocations. Furthermore, the DFT(2D) and AIREBO(2D) geometries cannot readily be told apart with the naked eye.

2. Distribution of dislocation types in PFC3

The distribution of dislocation types present in the lowest-energy PFC3 configurations found is shown in Fig. 8 as a function of the tilt angle. The proportions between dislocation types are determined by their contribution to the magnitude of the Burgers vector of the grain boundary. Between $2\theta \approx 9.4^\circ$ and $38.2^\circ$—some corresponding cases are shown in Fig. 7 (b)-(f) and (i)-(m)—both PFC1 and PFC3 prefer similar arrays of 5|7 dislocations. However, for PFC3 the smallest-tilt angle ground states with stable 5|7 grain boundaries are found at $2\theta \approx 9.4^\circ$ and $2\theta \approx 46.8^\circ$ and are depicted in Fig. 7 (i) and (n), respectively. We expect that the 5|8|7 dislocation, see Fig. 7 (h), becomes the energetically favorable dislocation type—albeit with a minimal energy difference to corresponding 5|7 boundaries—in both small-tilt angle limits in PFC3, see Appendix B. This is challenging to confirm or refute using DFT, because infeasibly large computational unit cells are needed at small tilt angles. However, at larger tilt angles the 5|8|7 formation energies are higher than for 5|7 dislocations [15, 43]. Furthermore, at $2\theta \approx 4.4^\circ$, AIREBO(2D) gives a noticeably higher 0.5 eV/nm for 5|8|7 grain boundaries.

Between $2\theta \approx 40^\circ$ and $55^\circ$ PFC3 can produce incompatible grain boundary configurations with low energies. Here, up to three different dislocation types (5|7, 5|8|7 and incompatible) are encountered with very similar energies. This complicates the analysis greatly, and in general, the ground state configurations cannot be guaranteed. The high-symmetry 4|5|6|7|8 grain boundary at $2\theta_{III}$ shown in Fig. 9 has a slightly lower (significantly lower) energy than a disperse (paired) 5|7 boundary, and therefore is the PFC3 ground state. In fact, in this configuration the carbon atom connecting a tetragon and a pentagon appears to have four nearest-neighbor carbon atoms, which is not energetically preferred in an otherwise planar sp$^2$-hybridized structure. Further DFT relaxation of the geometry results in one of the nearest-neighbor carbon atoms at the tetragon to recede, while the octagon transforms into two pentagons, leaving two under-coordinated carbon atoms at the defect. The DFT(2D) formation energy is roughly 7 eV/nm higher compared to a grain boundary with only 5|7 dislocations at the same tilt angle. Also AIREBO(2D) reveals this structure as unstable with a similar excess in grain boundary energy. This shows that even if highly symmetric, the grain boundary structures extracted from PFC3 can prove metastable, requiring additional attention and processing.

The results presented in this subsection suggest that the PFC3 model is not readily suited for constructing realistic graphene samples in their ground state grain boundary configurations with arbitrary tilt angles. In Appendix B, advanced techniques are introduced that can be used for constructing PFC3 samples with more realistic defect topologies, but that have practical limitations. On the other hand, PFC3 can be used to generate varied, metastable structures that can be of interest regardless. For instance, divacancy chains containing segments of 4|8 polygon pairs and terminating in pentagons have been observed directly in electron irradiation stud-
ies of graphene [15, 16]. PFC3 produces metastable grain boundaries with related 5[8]4[8]4...7 dislocations, and also 5[8]7 and 5[6]7 dislocation types that have been studied by previous theoretical works [7, 9, 13, 15, 20, 43, 47].

IV. POLYCRYSTALLINE SAMPLES

A. Construction

Now we demonstrate the construction of large and realistic polycrystalline graphene samples that can be used for further mechanical, thermal or electrical calculations. Detailed results of such further calculations will be published elsewhere, but a comprehensive characterization of the samples is carried out employing both PFC1 and the Tersoff potential to demonstrate the quality of these samples. The PFC1 model was chosen, because it displays robust relaxation and produces ground states with 5[7] dislocations. The XPFC model was also found suited for this task, but it has somewhat greater computational complexity. On the other hand, the XPFC grain boundary energy at large tilt angles is slightly more realistic than that of PFC1, recall Fig. 3. The Tersoff potential was chosen, because it gives realistic grain boundary energies and because a high-performance GPU code is available that employs this potential [30, 31].

Polycrystalline samples produced by PFC1 were studied in three sizes, the number of carbon atoms being ca. 22500, 90000, and 360000. The samples were almost square-shaped and their linear sizes ca. 24 nm, 48 nm and 97 nm, respectively. The samples were prepared by first initializing the PFC1 density field to a constant, disordered state. In each sample, 16 small, randomly distributed and oriented, hexagonal crystallites were introduced, of which 11 crystals on average survived the crystallization phase, the modified model was chosen, because it gives realistic grain boundary energies and because a high-performance GPU code is available that employs this potential [30, 31].

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When growing large hexagonal PFC1 crystals from a constant state, the metastable stripe phase may solidify faster and leave dislocations in its recrystallizing wake. It was found more straightforward to control the growth of crystals by replacing the third order term in Eq. 1 with a linear chemical potential term

\[ F_1^* = c_1^* \int d\mathbf{r} \left( \frac{\psi L_1 \psi}{2} + \frac{\psi^4}{4} + \mu \psi \right). \]  

To achieve slow, more stable growth of large crystals during the crystallization phase, the modified model (PFC1*) was brought close to the liquid-solid coexistence with \( \mu = -0.2 \). Once fully solidified, the chemical potential was set to \( \mu = -0.15 \) for a more stable hexagonal phase and the systems were further relaxed. For quantitative calculations, the energy scale of PFC1* was fitted to DFT similarly to the other PFC models, yielding \( c_1^* \approx 400 \text{ eV/nm} \). The diffusive fading of global stress was sped up using the unit cell size optimization algorithm described briefly in Appendix 3.

The fact that there are no clear peaks at the maxima in the mesh-like PFC1 density field occasionally results in 5[7] dislocations where there is no local maximum at one of the nodal points that indicate atom positions. The result is a missing atom when the density field is converted into atom coordinates. This issue was resolved by locating all triads of local minima whose members are the closest neighbors to one another, and by treating the average of their coordinates as an atom position.

These atomic configurations were relaxed further in three dimensions at 300 K using the GPU code with the Tersoff potential.

B. In-plane structure and energetics

Fig. 10 exemplifies the distribution of grains and their orientation in the largest sample size. In Fig. 10 (a), the crystals are color coded to reveal the local crystallographic orientation in the PFC1* density field, whereas in Fig. 10 (b), the system has been relaxed using MD and the atoms are lit up based on their energy, as given by the Tersoff potential. Individual dislocation cores are visible and they trace fairly straight grain boundaries between the grains. The spacings between dislocations along the grain boundaries, \( s \propto 1/\theta \) [10], reveal that there are grain boundaries of varying tilt angles. As expected, no noticeable changes are observed in the microstructure between the PFC1* (a) and Tersoff (b) configurations after a simulation of 1 ns.

Detailed experimental analyses of the distribution of crystal orientations in polycrystalline graphene have been presented in Ref. [3, 6]. Comparability with present samples is not perfect due to the absence of a substrate in our simplified calculations. PFC density fields, however, can be coupled to external fields emulating the substrate [50]. Furthermore, local irregularities acting as nucleation sites can be incorporated into this field, resulting in more realistic, heterogeneous nucleation instead of the simultaneous introduction of pristine crystallites.

The distributions of grains and grain boundaries are inseparable. The characteristic grain size can be estimated as

\[ \bar{d} = \sqrt{\frac{A}{n}}, \]  

where \( A \) is the total area of the sample and \( n \) the number of grains in it. As the characteristic grain size is increased, the total grain boundary length scales linearly while grain boundary energy—per unit length—remains constant. Grain boundary formation energy per unit area, or grain boundary energy density, \( \Gamma \), however, scales as \( \Gamma \propto 1/\bar{d} \).

Fig. 11 demonstrates the grain boundary energy densities calculated using PFC1* and extracted from MD simulations as a function of the characteristic grain size. From the information provided in Ref. [48, 49], we estimated also the grain boundary energy densities in ran-
dom polycrystalline graphene systems studied previously using the AIREBO and Tersoff potentials. The present Tersoff values are somewhat lower in energy compared to PFC1*. This was expected, because in Fig. 4 the grain boundary energy given by Tersoff(3D) is consistently lower than that of PFC1. Despite some scatter, the scaling of both present datasets is very close to the expected $1/d$, implying low stress in the samples. Our results line up almost perfectly with those of the previous works.

C. Height fluctuations

During the MD simulations, the polycrystalline samples gradually deviate from their initial flat configurations and become corrugated. Fig. 12 (a) illustrates the relaxed three-dimensional structure of the 97 nm sample shown in Fig. 10. Fig. 12 (b) again gives the in-plane microstructure with the crystallographic orientations colored. This helps demonstrate the connection between the in-plane and out-of-plane structures, namely, the sharp folds in the buckled graphene sheet that are commensurate with grain boundaries. An interesting detail is the isolated dislocation core at bottom-right in Fig. 10 (a) and (b), that causes noticeable buckling in the atomic sheet visible in Fig. 12 (a).

We used the root mean square of the out-of-plane displacements of the atoms

$$h_{\text{rms}}(t) = \sqrt{\frac{1}{N} \sum_i \left(z_i(t) - z_i(0)\right)^2}$$

(26)

to quantify the magnitude of height fluctuations. Here, $N$ is the number of atoms and $z_i(t)$ is the $z$ coordinate of the $i$th atom at time $t$. Fig. 13 (a) shows that the magnitude of height fluctuations in three different-sized samples increases with evolution time $t$ and converges when $t > 100$ ps. A larger sample requires a longer time to achieve convergence. The time scale for the convergence of height fluctuations is one order of magnitude larger than that observed for the convergence of grain boundary energy density (not shown), which reflects the fact that grain boundary energy is a local property while the magnitude of the height fluctuations is a global one.

The converged values of the magnitude of the height fluctuations in polycrystalline graphene increase roughly linearly with increasing sample size, which is similar to the case of pristine graphene shown in the inset of Fig. 13 (a). However, for a given sample size, the magnitude of the height fluctuations in polycrystalline graphene is about twice as large as that in pristine graphene. Qualitatively, this can be understood by the fact that the corrugation in pristine graphene is solely induced by the thermal motions of the atoms, while that in polycrystalline graphene is also driven by minimizing of the GB energy. In fact, as can be seen by comparing the buckled three-dimensional structure and the in-plane microstructure of the sample shown in Fig. 12 (a) and (b), respec-
FIG. 11. (Color online) Scaling of grain boundary energy density in random polycrystalline graphene samples as a function of the characteristic grain size. The values are given by PFC1* calculations, extracted from MD simulations using the Tersoff potential, and estimated from Ref. [48]a and [49]b. Two power curves fitted to PFC1* and Tersoff(3D) data are also plotted.

respectively, there is a strong correlation between the out-of-plane deformation and the locations of the grain boundaries.

The global nature of the height fluctuations can be seen more clearly from the time-evolution of the distribution of the out-of-plane displacements, as shown in Fig. 13 (b). At a small time scale of 1 ps, the distribution is Gaussian, resulting from the random thermal motions of the atoms, while at larger time scales, the distribution does not follow a simple function. When the system is fully relaxed, the distribution does not change much any more because the system has already found a minimum energy configuration. While this is probably a local minimum rather than the global one, the system is not likely to jump into another minimum within a finite simulation time.

V. CONCLUSIONS

The applicability of four phase field crystal (PFC) models to modeling polycrystalline graphene was studied. The three-mode model (PFC3) was found well-suited for quantitative modeling of grain boundaries in graphene. This was determined by fitting each model to density functional theory (DFT), and by carrying out a detailed comparison of the formation energies of grain boundaries calculated using PFC, DFT and molecular dynamics (MD). Present results were compared to previous works. The one-mode model (PFC1) proved ideal for constructing large samples of polycrystalline graphene, since this model exhibits efficient relaxation and produces realistic grain boundaries comprised of 5/7 dislocations. We successfully constructed large polycrystalline samples and demonstrated their quality by characterizing their properties using MD simulations.

All four PFC models were found to agree with DFT in terms of the formation energy of small-tilt angle grain boundaries. At large tilt angles, the formation energies given by PFC3, DFT and MD calculations are all fairly consistent with each other reaching roughly 4-5 eV/nm, whereas PFC1, the amplitude model (APFC) and the structural model (XPFC) peak roughly between 7-8 eV/nm. In terms of grain boundary topologies, the other PFC models produce 5|7 dislocations exclusively, whereas PFC3 gives rise to alternative low-energy dislocation types in certain tilt angle ranges. The polycrystalline samples were characterized by an inspection of the distribution of grains and grain boundaries, and by studying the scaling of height fluctuations and the formation energy of grain boundaries in them as a function of the sample size. We observed expected scaling behavior. Realistic Young’s moduli of 359 and 309 N/m were determined for PFC3 and XPFC, respectively.

The PFC1 model provides a straightforward approach to constructing low-stress samples without a priori knowledge of the atomistic details of defect structures. Such realistic samples can be exploited for further mechanical, thermal and electronical calculations using conventional techniques. Similarly, the PFC3 model that produces a rich variety of alternative defect types could be used for sample generation for the study of metastable defect structures, such as encountered under electron irradiation [45, 46]. While neither PFC1 nor PFC3 are ideal for modeling both the topology and energetics of grain boundaries, it is likely that the performance of PFC3 and XPFC can be improved in both respects. Namely, the model parameter spaces of both models remain largely uncharted with respect to grain boundary structures and their energies.

VI. ACKNOWLEDGMENTS

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FIG. 12. (Color online) (a) An aerial view of a relaxed 97 nm sample from MD simulation. The height fluctuations are colored with the highest (lowest) z coordinates appearing as yellow (blue). The scale of all axes is equal. (b) The in-plane structure of (a) color coded based on the local crystallographic orientation.

FIG. 13. (Color online) (a) Magnitude of height fluctuations $h_{\text{rms}}$ in three polycrystalline samples of linear size ca. 24, 48 and 97 nm as a function of simulation time in the molecular dynamics simulations. The inset shows the corresponding results for three similarly-sized samples of pristine graphene. The approximate characteristic grain sizes of the polycrystalline samples are 8, 13, 26 nm. (b) Evolution of the distribution of height fluctuations in a 49 nm sample from 1 ps to 1000 ps.

Appendix A: PFC models: Further details

For the parameters of the PFC1 model, recall Eq. (1), we chose $(\epsilon, q_0, \tau) = (-0.15, 1, -0.5/\sqrt{0.98/3})$. Similarly, for APFC, recall Eq. (3), $(B_l, B_x, t, v) = (1, 0.98, -1/2, 1/3)$, which conforms to PFC1 via $\tau = t/\sqrt{B^3}$ [30]. For PFC3, recall Eq. (8), we chose $(\epsilon, \lambda, q_0, q_1, q_2, b_0, b_1, b_2, \mu) = (-0.15, 0.02, 1, \sqrt{3}, 2, 0, -0.15, 0.2, 0.56915)$. The choice of $\mu$ gives an average density of $\bar{\psi} = -0.2$. For XPFC, recall Eq. (10), we used $(\eta, \chi, r_0, m, X^{-1}, a_0, \mu) =$
While defected PFC1 and PFC3 systems retain their respective average densities ($\bar{\rho}$ corresponding XPFC systems decreases slightly at large tilt angles, reaching $\Delta \bar{\rho} \approx 0.9$ %). We verified, by carrying out conserved dynamics calculations for certain tilt angle cases, that the resulting deviation in grain boundary energy is negligible.

The PFC systems studied were driven to equilibrium by employing non-conserved, dissipative dynamics as

$$\frac{\partial \phi}{\partial t} = -\frac{\delta F}{\delta \phi} = -\mathcal{L}\phi + \mathcal{N}, \quad (A1)$$

where $\phi$ denotes either the density field, $\psi$, or the APFC amplitude fields, $\eta_j$, and $\delta / \delta \phi$ is a functional derivative with respect to $\phi$ and $\mathcal{L} (\mathcal{N})$ is the Hamiltonian (nonlinear terms). While non-conserved dynamics allows the number of particles to fluctuate, this choice speeds up calculations via larger time steps becoming numerically stable. The non-conserved dynamics for PFC1, APFC, PFC3 and XPFC can be expressed as

$$\frac{\partial \psi}{\partial t} = -\mathcal{L}_1\psi - \tau \psi^2 - \psi^3, \quad (A2)$$

$$\frac{\partial \eta_j}{\partial t} = -\left( \Delta B + B^* \mathcal{G}_j^2 + 3\nu \left( A^2 - |\eta_j|^2 \right) \right) \eta_j + 2t \prod_{k \neq j} \eta_k, \quad (A3)$$

$$\frac{\partial \psi}{\partial t} = -\mathcal{L}_3\psi - \psi^3 - \mu \quad (A4)$$

and

$$\frac{\partial \psi}{\partial t} = -\psi + \frac{\psi^2}{2} - \frac{\psi^3}{3} - \mu + \mathcal{F}^{-1} \left\{ \hat{C}_2\psi \right\}$$

$$+ \frac{1}{3} \sum_{i=1}^2 \left( \left( \mathcal{F}^{-1} \left\{ \mathcal{C}_s^{(i)} \hat{\psi} \right\} \right)^2 \right)$$

$$-2\mathcal{F}^{-1} \left\{ \mathcal{C}_s^{(i)} \mathcal{F} \left\{ \psi \mathcal{F}^{-1} \left\{ \mathcal{C}_s^{(i)} \hat{\psi} \right\} \right\} \right\}$$

respectively. Above, * denotes a complex conjugate, whereas the cares and $\mathcal{F}^{-1}$ (inverse) Fourier transforms.

The PFC systems were propagated using the numerical method from Ref. [30]. Although this method requires entering the Fourier space, it comes with the benefit of gradients reducing to algebraic expressions. Furthermore, it allows large time steps due to its numerically stable, implicit nature [30]. This method approximates the solution to Eq. (A1) at a time $t + \Delta t$ as

$$\dot{\phi} (t + \Delta t) \approx e^{-\hat{\mathcal{L}}\Delta t} \dot{\phi} (t) + \frac{e^{-\hat{\mathcal{L}}\Delta t} - 1}{\hat{\mathcal{L}}} \mathcal{N} (t). \quad (A6)$$

### Table I. Numerically stable maximum values for spatial and temporal discretization parameters

<table>
<thead>
<tr>
<th>Model</th>
<th>$\Delta x$, $\Delta y$</th>
<th>$\Delta t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFC1</td>
<td>0.8</td>
<td>1.0</td>
</tr>
<tr>
<td>APFC</td>
<td>2.0</td>
<td>3.0</td>
</tr>
<tr>
<td>PFC3</td>
<td>0.75</td>
<td>3.0</td>
</tr>
<tr>
<td>XPFC</td>
<td>0.08</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Suitable step size $\Delta t$, as well as spatial resolution $\Delta x$ and $\Delta y$, were determined by trial and error. These values for all four PFC models are given in Table I. Note that the energy scale coefficients of the models, $c_1$, $c_A$, $c_3$ and $c_X$, have no effect on the dynamics and the relaxed structures. These coefficients have been taken into account only when calculating the energies of already relaxed systems.

### Appendix B: PFC models: Advanced initialization and relaxation techniques

Despite the advantageous properties of the PFC models, finding the ground state grain boundary configurations is not always trivial. We exploited the following techniques to gain more control over the PFC systems. The bicrystal systems were initialized with or without disordered grain boundaries ("melted" and "naive" initializations, respectively), recall Fig. 2(a), or the initial grain boundary configuration was set up using image processing software to predetermined the relaxed topology ("soldered" initialization).

Additionally, the relaxation of PFC systems was modified by incorporating higher-level algorithms. When feasible, the strain energy of PFC systems was minimized using a simple iterative optimization algorithm. This algorithm stretches the systems carefully, relaxes them according to Eq. (A2)-(A5) and uses the resulting free energy densities to estimate, via quadratic interpolation, the unit cell size that eliminates global strain. Each individual relaxation step was considered converged if the change in average free energy density was less than $10^{-9}$ between two consecutive evaluations.

For the majority of PFC3 calculations, 25 cycles of simulated annealing were applied to probe for the ground state grain boundary configuration. The simulated annealing noise was set to decay exponentially and each cycle lasted until $t = 40000$. We developed a spectral defect detection (SDD) algorithm to focus the annealing noise directly on the dislocations comprising the grain boundaries. This technique proved superior to the other approaches tried for finding low-energy configurations. A brief description of the SDD algorithm is given in Appendix E.

Bicrystal systems that were not optimized or annealed, were typically relaxed until $t = 100000$. In supplemental material, we tabulate the grain boundary energies and other data of present grain boundary calculations, and
indicate which initialization and relaxation types have been used for each calculation.

For APFC, all grain boundary systems were initialized with melted grain boundaries and relaxed normally without optimization or annealing. While the majority of corresponding PFC1 and XPFC systems were initialized with melted grain boundaries, they were relaxed employing the optimization algorithm. At small tilt angles, annealing of PFC3 systems was observed to cause extensive slip of dislocations, even annihilations. Furthermore, in the armchair grain boundary limit, the model has a tendency to produce metastable 5|8|4|8|4|...|7 dislocations. These issues were resolved by soldering the grain boundaries with 5|7 dislocations and by applying normal relaxation. The predetermined, symmetrical arrangement of 5|7 dislocations is expected to be metastable with a minimally higher energy compared to a similar arrangement with 5|8|7 dislocations. Due to being asymmetrical and their ground state arrangement therefore less trivial, 5|8|7 dislocations were not soldered into small-tilt angle grain boundaries. This explains the lack of small-tilt angle data in Fig. 8. Due to the relatively large computing effort, small-tilt angle XPFC systems were not optimized either. Additionally, for PFC1, PFC3 and XPFC, higher-symmetry grain boundaries were soldered with different types of dislocations and optimized to compare reliably the stability and energies of alternative dislocation types.

Appendix C: Finite size effect analysis

Grain boundaries are comprised of dislocations giving rise to long-range elastic fields. In periodic bicrystal systems such as exploited in this work, there are two grain boundaries that can interact with each other, or with their periodic images [51], via screening of these bipolar fields in a finite system. For consistent results, we considered the large-grain limit where such finite size effects become negligible. All computational unit cell sizes used for PFC calculations were greater than 10 nm in the direction perpendicular to the grain boundaries, which was verified to eliminate finite size effects to a high degree. Fig. 14 gives an example of the quick and consistent convergence of grain boundary energy as a function of the bicrystal width. The grain boundary energy value estimated in the large-grain limit, $\gamma(\infty)$, was found by requiring an optimal linear fit in logarithmic units. The relative error in grain boundary energy with respect to $\gamma(\infty)$ was $\leq 1\%$ for all PFC models. No finite size effects were observed with respect to the direction parallel to the grain boundaries, nor for the amplitude model in general. Because PFC models capture long-length scale elastic interactions well [30], the PFC finite size effect analysis is sufficient also for the DFT and MD calculations that used the same bicrystal topologies.

![Image of table]

FIG. 14. The convergence of grain boundary energy as a function of a bicrystal system’s width. Both the perpendicular dimension and tilt angle are held constant. The horizontal and vertical axes give the width (nm) and deviation of grain boundary energy (eV/nm) from the large-grain limit, respectively, in logarithmic scale. The depicted case is a PFC3 system at $2\theta \approx 13.2^\circ$ with 5|7 dislocations comprising the grain boundaries.

Appendix D: Fitting system

The full periodic system used for fitting the energy scales of the PFC models to DFT is shown in Fig. 15. The total width of the system is approximately 6.4 nm and it has 780 atoms.

Appendix E: Calculation of elastic coefficients

Contribution of non-shearing elastic deformation to the free energy density of a two-dimensional system can be expressed as

$$\Delta f = \frac{C_{11}}{2} (\varepsilon_x^2 + \varepsilon_y^2) + C_{12} \varepsilon_x \varepsilon_y, \quad (E1)$$

where $C_{11}$ and $C_{12}$ are stiffness coefficients, and $\varepsilon_x$ and $\varepsilon_y$ the two strain components [32]. We calculated the elastic free energy density landscape for single-crystalline PFC systems in the small deformation limit by applying varying combinations of uniform strain in the $x$ and $y$ directions. The stiffness coefficients were obtained from the least squares fit of Eq. (E1) to the measured free energy density values. From $C_{11}$ and $C_{12}$, the elastic modulus: bulk modulus $B$, shear modulus $\mu$ and two-dimensional Young’s modulus $Y_{2D}$, and Poisson’s ratio $\nu$ can be solved as

$$B = \frac{C_{11} + C_{12}}{2}, \quad (E2)$$

$$\mu = \frac{C_{11} - C_{12}}{2}, \quad (E3)$$

$$Y_{2D} = \frac{4B\mu}{B + \mu}, \quad (E4)$$
and

$$\nu = \frac{B - \mu}{B + \mu}. \quad (E5)$$

### Appendix F: Spectral defect detection

We developed a frequency filtering-based spectral defect detection algorithm for focusing simulated annealing noise directly to lattice imperfections. Fig. [16] presents a flowchart that illustrates the steps of the algorithm and gives the mathematical formulations thereof: Make a copy of the density field and compute its discrete Fourier transform. The bulk of the two bicrystal halves results in two sets of peaks in the amplitude spectrum, whose positions \(k_i\) are determined by the structure and rotation of the lattice. Filter out these peaks using smooth functions, e.g., Gaussians. Alternatively and especially for polycrystalline systems, instead of \(k_i\), filter out the full frequency bands \(k = |k_i|\). While still in Fourier space, take the Laplacian and then perform an inverse Fourier transform. Next, take the absolute value and apply some smoothing. We carried out this step by a Gaussian convolution in Fourier space. The steps described above result in a set of smooth bumps that are commensurate with the defects in the original density field. Then, normalize and threshold appropriately to obtain a binary mask \(m = m(r)\) that indicates the defected regions. Finally, use this mask to set the lattice imperfections to a disordered state or to focus annealing noise on them.

FIG. 16. Flowchart representation of the spectral algorithm for finding lattice defects. Position and time are denoted by $r$ and $t$, respectively, while $k$ is the Fourier space $k$-vector. The binary mask is denoted by $m$ and $\zeta$ describes random noise sampled from a uniform distribution $U$. 