Discrete dislocations in graphene

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\textbf{Abstract}

In this work, we present an application of the theory of discrete dislocations of Ariza and Ortiz (2005) to the analysis of dislocations in graphene. Specifically, we discuss the specialization of the theory to graphene and its further specialization to the force-constant model of Aizawa et al. (1990). The ability of the discrete-dislocation theory to predict dislocation core structures and energies is critically assessed for periodic arrangements of dislocation dipoles and quadrupoles. We show that, with the aid of the discrete Fourier transform, those problems are amenable to exact solution within the discrete-dislocation theory, which confers the theory a distinct advantage over conventional atomistic models. The discrete dislocations exhibit 5–7 ring core structures that are consistent with observation and result in dislocation energies that fall within the range of prediction of other models. The asymptotic behavior of dilute distributions of dislocations is characterized analytically in terms of a discrete prelogarithmic energy tensor. Explicit expressions for this discrete prelogarithmic energy tensor are provided up to quadratures.

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1. Introduction

Graphene is a one-atom-thick carbon material with carbon atoms packed densely in a hexagonal honeycomb lattice arrangement, which has been observed to be stable in two dimensions on a variety of substrates (Novoselov et al., 2004) or in free-standing form (Meyer et al., 2007). Owing to its anomalous electronic behavior and remarkable mechanical characteristics (Novoselov et al., 2005; Silvestrov and Efetov, 2007; Castro Neto et al., 2009; Geim and Novoselov, 2007; Bunch et al., 2007), graphene has recently been identified as a promising novel semiconducting material with numerous potential applications including chemical sensing instruments, flexible displays, biosensors, nanomechanical devices and others. However, graphene sheets grown in the laboratory are observed to contain a variety of defects (Rutter et al., 2007; Hashimoto et al., 2004). Defects can also be introduced extrinsically by a variety of means including electron-beam irradiation (Hashimoto et al., 2004; Telling and Heggie, 2007; Meyer et al., 2008), adatoms (Ewels et al., 2002; Li et al., 2005), mono and multi-vacancies (Xu et al., 1993; Li et al., 2005; Jeong et al., 2008) and others. Conversely, thermal annealing or chemical treatment can restore graphene to its pristine defect-free state (Elias et al., 2009; Geim, 2009). The presence of defects in graphene modifies its physical and chemical properties and plays a key limiting role in applications. This deleterious effect motivates the need for a fundamental mechanistic understanding of the equilibrium and kinetic properties of defects in graphene.

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One of the most widely studied defects of graphene and single-wall carbon nanotubes consists of two pentagon–heptagon (5–7) ring pairs obtained by rotating a single atomic bond through 90°. This mechanism was first studied by Stone and Wales (1986) and, consequently, this type of defect is commonly referred to as Stone–Wales (SW) defect. The SW mechanism is widely believed to be a key unit process underlying a variety of structural transformations in carbon-based materials (e.g., Lee et al., 2006). Hashimoto et al. (2004) observed 5–7 pairs attached to a missing zig-zag chain of atoms giving rise to a dislocation dipole. Jeong et al. (2008) have studied the stability of dislocation dipoles with 5–7 core structure using density-functional theory. Their calculations show 5–7 dipoles are energetically more stable than a haecelkite structure composed of three 5–7 pairs. These pairs have also been observed to form more complex defect structures (Hashimoto et al., 2004). More recently, Meyer et al. (2008) have observed defect configurations and their real-time dynamics and conclude that the dynamics of defects in two-dimensional graphene sheets are different from those arising in closed-shell structures such as nanotubes or fullerenes.

In addition to first-principles calculations, interatomic potentials have also been widely used for modeling carbon structures in general and graphene in particular (Wirtz and Rubio, 2004; Falkovsky, 2008; Mounet and Marzari, 2005; Grüneis et al., 2002; Tersoff, 1988; Brenner, 1990; Aizawa et al., 1990; Stuart et al., 2000; Tewary and Yang, 2009). The simplest types of potential are harmonic and are defined in terms of force constants. For instance, Aizawa et al. (1990) developed force-constant models up to second-nearest neighbors. A new parametrization of the Aizawa et al. (1990) potential has been obtained by Wirtz and Rubio (2004) from density-functional theory within the generalized-gradient approximation. A widely used fully nonlinear empirical potential is Tersoff’s (1988) potential. Recently, Tewary and Yang (2009) have developed a generalization of Tersoff’s potential that extends the range of interaction up to fourth nearest neighbors. More general bond-order interatomic potentials include the reactive empirical bond-order REBO potential developed by Brenner (1990). The addition of torsion, dispersion and non-bonded repulsion interactions to the latter potential resulted in a new hydrocarbon potential (AIREBO) that is suitable for studying reactivity in molecular condensed phases (Stuart et al., 2000).

Despite their widespread appeal, first-principles or empirical-potential atomistic simulations are not without intrinsic limitations. Thus, first-principles calculations are exceedingly costly and thus necessarily limited to very small periodic cells or supercells. This limitation is particularly onerous in the study of isolated lattice defects such as dislocations, which interact through long-range elastic fields. Often, atomistic models are based on explicit dynamics, in which case the time step is limited by numerical stability and the calculations are necessarily restricted to short time intervals. Almost invariably, atomistic schemes are numerical in nature and do not lead to an analytical understanding of the mechanics of defects in crystals. Efforts to make contact with linear elasticity often resort to awkward artifacts such as core-cutoff radii in order to sidestep the logarithmic singularity of linear-elastic dislocations at the core. Perhaps more fundamentally, conventional atomistic models regard crystal lattices as point lattices devoid of any additional topological or differential structure. By nature, the fundamental understanding of topological defects requires a rather more expanded view of crystal lattices that generalizes the familiar differential operators and integral identities of differential calculus. For instance, the Burgers circuit construction leading to the definition of dislocations as topological defects cannot be applied in a discrete setting unless crystal lattices are endowed with a discrete differential structure (Ariza and Ortiz, 2005). The definition of other familiar relations and operations of dislocation mechanics requires a similarly extended structure. Circulations, fluxes, Kröner’s (1958) formula for the definition of Nye’s (1953) dislocation density from the elastic distortions of the lattice and the conservation of Burgers vector along dislocations, are cases in point.

In this work, we present an application of the theory of discrete dislocations of Ariza and Ortiz (2005) to the analysis of dislocations in graphene. The theory overcomes the aforementioned limitations of conventional atomistic models by: endowing crystal lattices with a discrete differential structure that generalizes the common differential operators and integral identities of differential calculus; formulating a theory of discrete defects by recourse to the theory of eigendeformations, which leads to a precise and unambiguous characterization of topological defects, including dislocations and an exactly solvable equilibrium problem; and applying analytical tools, such as asymptotic and Γ−convergence analysis, to the elucidation of limits of interest such as the dilute and continuous limit.

The theoretical aspects of constructing a discrete mechanics of defective crystal lattices have been discussed at length in Ariza and Ortiz (2005). In Sections 2–4 we briefly review the essential elements of the theory, its specialization to graphene and its further specialization to the force-constant model of Aizawa et al. (1990), which we use in all subsequent examples. In Section 5, the ability of the discrete-dislocation theory to predict dislocation core structures and energies is critically assessed. We specifically analyze periodic arrangements of dislocation dipoles and quadrupoles. Such arrangements have been extensively considered in other studies of defects in graphene (Li et al., 2005; Kaxiras and Pandey, 1988; Xu et al., 1993; Los et al., 2005; Jeong et al., 2008) and thus lend themselves to detailed comparisons. We show that, with the aid of the discrete Fourier transform, those problems are amenable to exact solution within the discrete-dislocation theory. This exact solvability constitutes a distinct advantage of the theory over conventional atomistic models. The discrete-dislocation theory predicts 5–7 ring core structures that are consistent with observation and dislocation energies that fall within the range of prediction of other models. Indeed, the ability of the discrete-dislocation theory to predict defect core structures and formation energies is found to be well within the range of accuracy of present theoretical capability.

Finally, in Section 6 we turn to the analytical characterization of the asymptotic behavior of dilute distributions of dislocations. The dilute limit is of practical interest since even small numbers of defects, such as expected at low
temperatures, may have a substantial deleterious effect on device performance (Novoselov et al., 2005). Furthermore, the
direct numerical simulation of dilute dislocation distributions requires large computational cells, which is exceedingly
costly or unfeasible for very dilute distributions. We show that the asymptotic behavior of very dilute dislocation
distributions can be fully characterized analytically in terms of a discrete prelogarithmic energy tensor (cf., e.g., Barnett
and Swanger, 1971; Bacon et al., 1979 for the linear-elastic counterpart). Explicit expressions for this discrete
prelogarithmic energy tensor are provided up to quadratures. The dilute asymptotic limit is directly verified numerically
for increasingly dilute periodic arrangements of quadrupoles.

2. Graphene as a discrete differential complex

Following Ariza and Ortiz (2005), we regard a graphene lattice as a cell-complex $\mathcal{C}$ (cf., e.g., Munkres, 1984 for general
background on cell complexes), i.e., as a collection of interconnected atoms, atomic bonds and elementary areas. When
regarded as members of the graphene cell complex, we shall refer to those objects as $p$-cells, where $p$ is the dimension of
the cell. Thus, an atom is a 0-cell $e_0$, an atomic bond is a 1-cell $e_1$, and each of the hexagonal cells of graphene defines a
2-cell $e_2$. We shall denote by $E_p$ the set of $p$-cells of the lattice.

In order to facilitate calculations, a convenient cell-labeling scheme needs to be defined. To this end, we begin by
regrouping each cell of the same dimension by one type of 2-cells, or hexagonal cells. As already mentioned, the sets of cells of the same type are arranged in space as the figure, the graphene cell complex contains two types of 0-cells, or atoms, three types of 1-cells, or atomic bonds and
2-cells $e_2$. We shall denote by $E_p$ the set of $p$-cells of the lattice.

The states of graphene will be described in terms of discrete vector-valued forms $\phi : E_p \to \mathbb{R}^m$. We shall denote by $\mathcal{O}(\mathcal{C})$ the set of all $p$-forms over $\mathcal{C}$. We shall additionally refer to linear functions on discrete forms as discrete currents: A $p$-current $A$ has the representation

$$A(\phi) \equiv \langle A, \phi \rangle = \sum_{e \in E_p} \langle A(e_p), \phi(e_p) \rangle$$

Fig. 1. Cell-complex representation of the graphene lattice, classification of cells into types and Bravais lattice indexing scheme, with $l = (l^1, \lambda) \in \mathbb{Z}^2$, $e_1 = (1, 0)$, $e_2 = (0, 1)$ and $e_3 = -e_1 + e_2 = (-1, 1)$.\[1\]
for some coefficients \( \{ A(e_p), e_p \in E_p \} \). Thus, in the present context discrete \( p \)-currents can be identified simply with functions \( A : E_p \to \mathbb{R}^m \). We shall denote by \( \Omega_p(C) \) the set of all \( p \)-currents over \( C \).

In order to facilitate the formulation of a discrete mechanics of graphene, we proceed to endow the cell-complex just defined with a *differential structure*. This differential structure encodes once and for all the orientation, incidence and adjacency relations between cells of various dimensions and will enable the writing of field equations in a particularly compact and ‘structure-independent’ way. A cell complex is given a differential structure by defining a *differential operator* \( d : \Omega^p \to \Omega^{p+1} \) and a *codifferential operator* \( \delta : \Omega_p \to \Omega_{p-1} \) with the properties

\[
d^2 = 0, \quad \delta^2 = 0, \quad \langle A, d\omega \rangle = \langle \delta A, \omega \rangle .
\]

The last defining property expresses that \( d \) and \( \delta \) are the adjoints of each other. For graphene, an unambiguous definition of these operators follows from the fact that the Poincaré dual of the graphene cell-complex is simplicial, namely, the simplicial complex defined by its 2-cells. The differential structure of the graphene cell-complex then follows by duality from the canonical simplicial-complex structure of its dual. Adopting the cell-orientation conventions shown in Fig. 1, the resulting differential and codifferential operators are

\[
d\omega_0(l, 1) = \omega_0(l, 1) - \omega_0(l + e_2, 2), \quad \delta\omega_0(l, 1) = \omega_0(l, 1) - \omega_0(l + e_2, 2), \quad \delta\omega_0(l, 3) = \omega_0(l, 1) - \omega_0(l + e_2, 2), \quad \delta\omega_1(l) = \omega_1(l, 2) - \omega_1(l + e_1, 3) - \omega_1(l + e_1, 2) + \omega_1(l - e_3, 1) - \omega_1(l - e_3, 3),
\]

\[
\delta A^1(l, 1) = A^1(l, 1) + A^1(l, 3), \quad \delta A^1(l, 2) = -A^1(l - e_2, 1) - A^1(l, 2) - A^1(l - e_3, 3), \quad \delta A^2(l, 1) = -A^2(l) + A^2(l + e_3), \quad \delta A^2(l, 2) = A^2(l) - A^2(l - e_1), \quad \delta A^2(l, 3) = A^2(l - e_1) - A^2(l + e_3).
\]

In these expressions, \( \omega_p \) denotes a general \( p \)-form and \( A^p \) a general \( p \)-current. The properties (2) can be verified directly from the definitions. A precis of properties of discrete differential operators and integrals may be found in Ariza and Ortiz (2005). In particular, it is possible to define a wedge product between forms and formalize lattice sums such as appear in definition (1) into a general and self-contained theory of integration with all the familiar properties of the integral operators from differential calculus in \( \mathbb{R}^n \), including integration by parts and a Stokes’ theorem.

The discrete Fourier transform (DFT) provides a convenient—and computationally efficient—means of exploiting the translation invariance of lattice complexes. Recall that the discrete Fourier transform of the \( p \)-form \( \omega \in \Omega^p \) is (cf. Appendix A.1)

\[
\hat{\omega}(\theta, x) = \sum_{l \in \mathbb{Z}^2} \omega(l, x) e^{-i\theta l} \quad \text{and its inverse is}
\]

\[
\omega(l, x) = \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \hat{\omega}(\theta, x) e^{i\theta l} d\theta_1 d\theta_2.
\]

The Fourier and inverse Fourier transform of currents may be defined likewise. A summary of the properties of the DFT is collected in Appendix A.1. These properties include a discrete convolution theorem and a discrete Parseval identity. The corresponding DFT representation of the differential is of the form

\[
\hat{d}\omega(\theta, x) = \sum_{\beta = 1}^{N_x} Q\left(\frac{\theta}{x\beta}\right) \hat{\omega}(\theta, \beta).
\]
where the coefficients $Q(x, \theta)$ now encode the differential structure of the complex. For the graphene differential structure defined in (3) we have

$$Q_1(\theta) = 
\begin{pmatrix}
1 & -e^{i\theta_2} \\
1 & -1 \\
1 & -e^{-i\theta_1}
\end{pmatrix},$$

$$Q_2(\theta) = (e^{i\theta_1} - 1, 1 - e^{i\theta_1}, e^{i\theta_1} - e^{i\theta_1}),$$

where we write

$$\theta_3 = \theta_2 - \theta_1,$$

define the differentials of 0 and 1-forms in their Fourier representation, respectively. It follows directly from (2c) and the discrete Parseval identity that the codifferential operator has the Fourier representation

$$\tilde{\delta}A(\theta, x) = \sum_{\beta = 1}^{N_y} P\left(\frac{\theta}{\alpha}, \beta\right)\tilde{A}(\theta, \beta),$$

where

$$P\left(\frac{\theta}{\alpha}, \beta\right) = Q^*\left(\frac{\theta}{\alpha}, \beta\right),$$

or, for short,

$$P(\theta) = Q^{*T}(\theta) \equiv Q^T(\theta),$$

i.e., the $P(\theta)$ is the Hermitian transpose of $Q(\theta)$.

In the study of discrete dislocations the discrete Poisson problem

$$\Delta \omega = x$$

will play a central role. Here, $\Delta = d_\delta + \delta d$ is the discrete Laplace–deRham operator $\Delta : \Omega^2 \rightarrow \Omega^2$ (Ariza and Ortiz, 2005) and $v = A^{-1}\delta \beta$. For graphene, a straightforward calculation gives

$$\tilde{A}(\theta) = Q_2P_2 = 2(3 - \cos\theta_1 - \cos\theta_2 - \cos\theta_3),$$

where $\theta_3$ is defined as in (8). The symmetry of the graphene lattice is clearly reflected in the expression (13) of the discrete Laplace–deRham operator. Of particular concern is whether the discrete Poisson problem (12) is well-posed in the sense of existence and uniqueness of solutions. For graphene, this well-posedness may be elucidated directly from (13), which shows that $\Delta(\theta) \neq 0$ for $\theta \in [-\pi, \pi]^2 \setminus 0$. In general, the well-posedness of the discrete Poisson problem (12) rests on certain homological properties of the lattice complex. In particular, the invertibility of $\Delta$ is equivalent to the non-existence of non-trivial harmonic functions, which in turn is equivalent to the homology of the lattice complex being trivial (Ariza and Ortiz, 2005). Lattice complexes satisfying a discrete Poincaré lemma of that type were termed perfect, or defect-free, by Ariza and Ortiz (2005), who also showed that computation of the homology of a lattice complex and, in particular, the determination of whether a lattice complex is perfect, reduces to the investigation of the kernels and images of the matrices $Q(\theta)$. In particular, the graphene lattice complex is perfect since, for fixed $\theta \neq 0$, we have $\ker P_1(\theta) = \operatorname{im} P_2(\theta)$, where $\ker$ denotes the kernel of a mapping and $\operatorname{im}$ its image. Indeed, these conditions may be verified directly from (11) and (7).

As already mentioned, the description of the graphene lattice as a differential complex provides a powerful tool for formulating a discrete mechanics of graphene in a particularly compact and convenient way. From a practical point of view, the great benefit of defining differential and codifferential operators is that the structure of the lattice is encoded once and for all in a convenient tabular form and all the field equations describing the discrete mechanics of the lattice are subsequently ‘insulated’ from the details of the lattice structure. In applications, the use of the discrete Fourier transform further reduces the field equations to compact matrix forms that are amenable to efficient algebraic manipulation.

We additionally note that the metric properties of the graphene lattice do not enter in the definition of its differential complex, which is entirely algebraic. In particular, we carefully refrain from defining derivatives, e.g., by means of divided-difference expressions. While such definitions may at first seem appealing for purposes of ‘mapping’ the discrete mechanics of the lattice to a continuum formulation, e.g., through an application of the Cauchy–Born rule, they may result in loss of essential lattice information if implemented naively. For instance, a continuum model of graphene patterned, e.g., after linear elasticity necessarily loses much of the discrete structure of the lattice that plays a key role in determining the core structure of defects. For purposes of retaining that information, it proves more convenient to define the differential structure of the lattice strictly in algebraic terms and to encode all metric properties of the lattice, such as bond lengths and angles, into the interaction potential.
3. The harmonic graphene lattice

We begin by formulating the discrete elasticity of a perfect lattice within the framework of discrete differential complexes and the harmonic approximation. As a representative example of application to graphene we reformulate the harmonic model of Aizawa et al. (1990) within that framework. The main difference between the discrete differential representation of a harmonic lattice energy and the conventional force-constant representation is that the former exploits the invariance of the energy under translations in order to express it in terms of bondwise force-constants and the differential $du$ of the displacement field. For present purposes, the main interest of this reformulation rests in that provides a foundation for the description of discrete lattice defects, including dislocations, within an eigendeformation framework (Mura, 1987). This extension is pursued in Section 4.

3.1. Discrete elasticity of harmonic lattices

We recall that, by invariance under translations, the energy of a harmonic lattice can be expressed in the form (Ariza and Ortiz, 2005)

$$E(u) = \frac{1}{2} \sum_{\varepsilon_i} \sum_{\varepsilon_j} B_{ij}(\varepsilon_i, \varepsilon_j) du_i(\varepsilon_i) du_j(\varepsilon_j) \equiv \frac{1}{2} \langle B du, du \rangle,$$

where $B_{ij}(\varepsilon_i, \varepsilon_j)$ are bondwise force constants giving the interaction energy resulting from a unit differential displacement in the $j$ th coordinate direction at bond $\varepsilon_j$ and a unit differential displacement in the $i$ th coordinate direction at bond $\varepsilon_i$. By the linearity of the differential operator, the energy (14) can alternatively be expressed as

$$E(u) = \frac{1}{2} \sum_{\varepsilon_i} \sum_{\varepsilon_j} A_{ij}(\varepsilon_i, \varepsilon_j) u_i(\varepsilon_i) u_j(\varepsilon_j) \equiv \frac{1}{2} \langle Au, u \rangle,$$

where the conventional force constants $A_{ij}(\varepsilon_i, \varepsilon_j)$ give the interaction energy resulting from a unit displacement in the $j$ th coordinate direction at atom $\varepsilon_j$ and a unit displacement in the $i$ th coordinate direction at atom $\varepsilon_i$. In addition, by the translation invariance of the lattice, the harmonic energy can be expressed in convolution form (cf. Appendix A) as

$$(Bdu)(l, z) = \sum_{\varepsilon_i} \sum_{j} \Psi_{\varepsilon_i}^{l-m} \chi^j du_j(m, \beta) \equiv (\Psi \ast du)(l, z),$$

$$(Au)(l, z) = \sum_{\varepsilon_i} \sum_{j} \Phi_{\varepsilon_i}^{l-m} \chi^j u_j(m, \beta) \equiv (\Phi \ast u)(l, z),$$

where the reduced bondwise force constants $\Psi_{\varepsilon_i}^{l-m}$ give the interaction energy resulting from a unit differential displacement in the $j$ th coordinate direction at bond $\varepsilon_j$ and a unit differential displacement in the $i$ th coordinate direction at bond $\varepsilon_i(l, z)$, whereas the reduced force constants $\Phi_{\varepsilon_i}^{l-m}$ give the interaction energy resulting from a unit displacement in the $j$ th coordinate direction at atom $\varepsilon_j(m, \beta)$ and a unit displacement in the $i$ th coordinate direction at atom $\varepsilon_i(l, z)$. We recall that for graphene $N_\beta = 2$, since there are two types of atoms and $N_1 = 3$, since there are three types of bonds. Conveniently, since Eqs. (16a) and (16b) are in convolution form, an application of Parseval’s identity and the convolution theorem (cf. Appendix A) yields the DFT representations

$$E(u) = \frac{1}{2(2\pi)^2} \int_{-\pi, \pi} \frac{1}{2} \langle \hat{\Psi}(\theta) \hat{du}(\theta), \hat{du}^* (\theta) \rangle d\theta,$$

$$E(u) = \frac{1}{2(2\pi)^2} \int_{-\pi, \pi} \frac{1}{2} \langle \hat{\Phi}(\theta) \hat{u}(\theta), \hat{u}^* (\theta) \rangle d\theta,$$

where, here and subsequently, we write

$$\langle \hat{\Psi}(\theta) \hat{du}(\theta), \hat{du}^* (\theta) \rangle = \sum_{\varepsilon_i} \sum_{j} \hat{\Psi}_{\varepsilon_i}^{l-m} \hat{du}_j(m, \beta) \hat{du}_j^*(m, \beta),$$

$$\langle \hat{\Phi}(\theta) \hat{u}(\theta), \hat{u}^* (\theta) \rangle = \sum_{\varepsilon_i} \sum_{j} \hat{\Phi}_{\varepsilon_i}^{l-m} \hat{u}_i(m, \beta) \hat{u}_j^*(m, \beta).$$

The preceding representations show that the force-constant fields are related as

$$\hat{\Phi}_{\varepsilon_i}^{l-m} = \sum_{\mu = 1}^{N_\beta} \sum_{\nu = 1}^{N_\beta} \Theta_\mu^{l, \nu} Q_{\nu}^{l, \nu} \hat{\Psi}_{\varepsilon_i}^{\mu, \nu}.$$
or, in matrix form,
\[
\tilde{\Phi}_{ij} = Q_i^T \tilde{\Psi}_g Q_j^*.
\]

where \( Q_i \) is the matrix that provides the DFT representation of the differential operator for 1-forms, cf. Eq. (7).

The stable equilibrium configurations of the crystal are represented by displacement fields that minimize the potential energy
\[
F(u) = E(u) - \langle f, u \rangle,
\]

where \( f \in \Omega_0 \) denotes a 0-current consisting of forces applied on the atoms of the lattice. The corresponding equilibrium problem is
\[
Au = f.
\]

A harmonic lattice is said to be stable if the equilibrium problem (22) is well-posed, i.e., if the equilibrium displacement field exists and is unique up to rigid-body displacements. In general, well-posedness rests on the stability properties of the force constants. General conditions for the well-posedness of the equilibrium problem (22) are provided by Ariza and Ortiz (2005). Thus, if the force constants \( \Phi \) have finite support, if Green’s function \( G(\ell) = \tilde{\Phi}(\ell) \) exists in the perforated Brillouin zone \([−π, π]^2\times 0\), i.e., if the lattice has no soft modes, if \( \tilde{\Phi}^{-1}(\ell) \in L^1(−π, π]^2\) and if \( f \) has finite support then \( u = G * f \) is a solution of the equilibrium problem (22). Furthermore, the solution is unique modulo rigid-body displacements. This strict convexity of \( E(u) \) in turn follows if the \( \tilde{\Phi}(\ell) \) is strictly positive definite in \([−π, π]^2\times 0\), i.e., if the phonon speeds are well-defined at all wavelengths.

3.2. Example: the potential of Aizawa et al.

A convenient—and fairly representative—example of force constants for graphene is provided by the potential of Aizawa et al. (1990). This model consists of six energy terms (Fig. 2)
\[
E(u) = V_1 + V_2 + V_3 + V_4 + V_5 + V_6,
\]

where \( V_1 \) and \( V_2 \) account for nearest-neighbor and next-to-nearest neighbor interactions, respectively, \( V_3 \) for three-body in-plane bending, \( V_4 \) for four-body out-of-plane bending, \( V_5 \) for twisting and \( V_6 \) for bonding to the substrate. The precise expressions of these energy terms are
\[
V_1 = \frac{\gamma_1}{2a^2} \sum_{e_i \in \mathcal{E}_1} (du(e_i) \cdot dx(e_i))^2,
\]
\[
V_2 = \frac{\gamma_2}{6a^2} \sum_{e_i \in \mathcal{E}_1} \sum_{e_i' \in \mathcal{E}_1} [(du(e_i) + du(e_i')) \cdot (dx(e_i) + dx(e_i'))]^2,
\]

where \( e_i \) and \( e_i' \) share an atom in common and \( a \) is the lattice parameter,
\[
V_3 = \frac{\gamma_3}{2a^2} \sum_{e_i \in \mathcal{E}_1} \sum_{e_i' \in \mathcal{E}_1} [(du(e_i) \times dx(e_i))^2 - (du(e_i') \times dx(e_i'))^2],
\]

where \( z \) denotes the component perpendicular to the graphene plane,
\[
V_4 = \frac{\gamma_4}{2a^2} \sum_{e_i \in \mathcal{E}_1} \sum_{e_i' \in \mathcal{E}_1} \sum_{e_i'' \in \mathcal{E}_1} (du(e_i) + du(e_i') + du(e_i''))^2,
\]

where \( e_i, e_i' \) and \( e_i'' \) share an atom in common,
\[
V_5 = \frac{\delta}{6a^2} \sum_{e_i \in \mathcal{E}_1} \sum_{e_i' \in \mathcal{E}_1} \sum_{e_i'' \in \mathcal{E}_1} \sum_{e_i''' \in \mathcal{E}_1} [(du(e_i') - du(e_i''))^2 - (du(e_i') - du(e_i''))^2],
\]

\[\text{Fig. 2. Schematic representation of bondwise interactions considered in the force-constant model of Aizawa et al. (1990). (a) Nearest-neighbor, next-to-nearest neighbor and three-body in plane bending interactions; (b) four-body out-of-plane bending and (c) twist interactions.}\]
where $e_1$ and $e_1'$ have an atom $e_0$ in common, $e_1'$ and $e_1''$ share an atom $e_0'$ and $e_0$ and $e_0'$ are the end atoms of a common bond and

$$V_6 = \frac{2}{3} \sum_{e_0,e_0'} (\hat{u}(e_0'))^2.$$  \hfill (29)

Two different parametrizations of Aizawa's model for graphene are tabulated in Table 1, including the original parametrization of Aizawa et al. (1990) and a more recent parametrization by Wirtz and Rubio (2004) obtained by fitting to density-functional theory (generalized-gradient approximation) quantum-mechanical calculations of the phonon dispersion curves of graphene. In addition, throughout this work we adopt the widely accepted value $a = 1.42$ Å of the lattice constant of graphene at room temperature. The DFT representation of the bondwise force-constants corresponding to the Aizawa et al. (1990) are tabulated in Tables 2 and 3 for ease of reference. In this table we use the nomenclature: $c_1 = \gamma_1/a^2$, $c_2 = \gamma_2/a^2$, $d = \delta/a^2$ for shorthand.

A conventional means of ascertaining the fidelity and stability of force-constant models is by comparison to experimental phonon dispersion curves. In this vein, Fig. 3 shows two comparisons between the phonon dispersion curves computed from the Aizawa et al. (1990) model with the parametrizations of Aizawa et al. (1990) and of Wirtz and Rubio (2004) and the experimental data of Nicklow et al. (1972), Oshima et al. (1988), Siebentritt et al. (1997), Grünies et al. (2002) and Yanagisawa et al. (2005). As may be seen from this comparison, the model captures the rough outline and much of the fine structure of the experimental phonon-dispersion data. Both parametrizations afford comparable fidelity.

### Table 1

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<tr>
<td>$x_1$ (dyn/cm)</td>
<td>3.64 x 10^5</td>
<td>3.99 x 10^5</td>
</tr>
<tr>
<td>$x_2$ (dyn/cm)</td>
<td>0.62 x 10^5</td>
<td>0.57 x 10^5</td>
</tr>
<tr>
<td>$\gamma_1$ (erg)</td>
<td>8.30 x 10^{-12}</td>
<td>6.08 x 10^{-12}</td>
</tr>
<tr>
<td>$\gamma_2$ (erg)</td>
<td>3.38 x 10^{-12}</td>
<td>3.28 x 10^{-12}</td>
</tr>
<tr>
<td>$\delta$ (erg)</td>
<td>3.17 x 10^{-12}</td>
<td>3.46 x 10^{-12}</td>
</tr>
</tbody>
</table>

### Table 2

DFT of bondwise force constants $\tilde{\Psi}_b^{(a,b)}$ corresponding to the Aizawa et al. (1990) graphene potential, part I: in-plane components.

<table>
<thead>
<tr>
<th>$(\alpha,\beta)$</th>
<th>(11)</th>
<th>(22)</th>
<th>(12)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1,1)</td>
<td>$x_1 + 2x_2$</td>
<td>$x_2 + 4c_1$</td>
<td>0</td>
</tr>
<tr>
<td>(1,2)</td>
<td>$\frac{3}{4}x_2(1 + e^{-i\theta})$</td>
<td>$-\frac{1}{4}(2c_1 - 2c_1(1 + e^{-i\theta}))$</td>
<td>$-\frac{3}{4}x_2(1 + e^{-i\theta})$</td>
</tr>
<tr>
<td>(1,3)</td>
<td>$\frac{3}{4}x_2(1 + e^{-i\theta})$</td>
<td>$-\frac{1}{4}(2c_1 - 2c_1(1 + e^{-i\theta}))$</td>
<td>$\frac{3}{4}x_2(1 + e^{-i\theta})$</td>
</tr>
<tr>
<td>(2,2)</td>
<td>$\frac{1}{2}x_1 + \frac{1}{2}(x_2 + 2c_1)$</td>
<td>$\frac{1}{2}x_1 + \frac{1}{2}x_2 + c_1$</td>
<td>$\frac{1}{2}x_1 + \frac{1}{2}(x_2 + 2c_1)$</td>
</tr>
<tr>
<td>(2,3)</td>
<td>$\frac{3}{4}x_1(1 + e^{-i\theta})$</td>
<td>$-(x_2 + \frac{1}{2}c_1)(1 + e^{-i\theta})$</td>
<td>$\frac{3}{4}x_1(1 + e^{-i\theta})$</td>
</tr>
<tr>
<td>(3,3)</td>
<td>$\frac{1}{4}(x_1 + 6(x_2 + 2c_1))$</td>
<td>$\frac{1}{2}x_1 + \frac{1}{2}x_2 + \frac{1}{4}\gamma_1$</td>
<td>$\frac{1}{4}(x_1 + 6(x_2 + 2c_1))$</td>
</tr>
</tbody>
</table>

The columns collect the non-zero components of $\tilde{\Psi}_b^{(a,b)}$ by component $(ij)$.

### Table 3

DFT of bondwise force constants $\tilde{\Psi}_b^{(a,b)}$ corresponding to the Aizawa et al. (1990) graphene potential, part II: out-of-plane components.

<table>
<thead>
<tr>
<th>$(\alpha,\beta)$</th>
<th>(33)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1,1)</td>
<td>$2(c_2 + \frac{1}{2}(2 - \cos \theta_1 + \cos \theta_2)d)$</td>
</tr>
<tr>
<td>(1,2)</td>
<td>$\frac{2}{3}e^{-i\theta_2} \left( \cos \theta_1 \frac{\theta_2}{2} + (3c_2 - d \cos \theta_2) \frac{\theta_2}{2} \right)$</td>
</tr>
<tr>
<td>(1,3)</td>
<td>$\frac{2}{3}e^{-i\theta_2} \left( 3c_2 - d \cos \theta_2 \frac{\theta_2}{2} + d \cos \theta_2 \frac{\theta_2}{2} \right)$</td>
</tr>
<tr>
<td>(2,2)</td>
<td>$\frac{1}{3}(3c_2 + 2d - d \cos \theta_1 + \cos \theta_2)$</td>
</tr>
<tr>
<td>(2,3)</td>
<td>$\frac{1}{3}(3c_2 - d + e^{-i\theta_2}(3c_2 + (-1 + e^{i\theta_2})d))$</td>
</tr>
<tr>
<td>(3,3)</td>
<td>$\frac{1}{3}(3c_2 + 2d - d \cos \theta_1 + \cos \theta_2)$</td>
</tr>
</tbody>
</table>

The columns collect the non-zero components of $\tilde{\Psi}_b^{(a,b)}$ by component $(ij)$. 

---

However, the ability of the first-principles calculations of Wirtz and Rubio (2004) to accurately and predictively inform an empirical force-constant model is quite remarkable.

The stability of the Aizawa et al. (1990) potential, in the sense of the well-posedness of the equilibrium problem (22), also follows directly from the computed phonon-dispersion curves shown in Fig. 3. In particular, we verify from Fig. 3 that the phonon speeds are well-defined at all wavelengths and, in particular, that the lattice has no soft modes.

4. Discrete dislocations in graphene

A strictly harmonic description of graphene, such as presented in the foregoing, results in a quadratic energy that does not account for lattice defects. A standard device for effecting the requisite generalization is provided by Mura’s theory of eigendeformations (Mura, 1987; Ariza and Ortiz, 2005). In this section, we adapt this theory to the representation of discrete dislocations in graphene.

4.1. Discrete dislocations as eigendeformations

Lattice eigendeformations are affine mappings that leave the lattice invariant and, hence, cost no energy (Mura, 1987). Suppose that we refer position vectors to the basis $a_i$ of the Bravais lattice of the atoms. Then, in components $x=x_ia_i$ and $y=y_ia_i$, an affine mapping can be expressed as

$$y_i = F_{ij}x_j$$  \hspace{1cm} (30)

in terms of a matrix of coefficients $F$. Within this representation, a classical theorem of Ericksen (1979) then states that an affine mapping is lattice invariant if the coefficients $F_{ij}$ are integer and $\det(F) = \pm 1$. A particular type of lattice
eigendeformation consists of lattice-invariant shears of the form

\[ y_i = x_i + \frac{\zeta}{d} b_i m_j x_j \]  

(31)

or

\[ F_{ij} = \delta_{ij} + \frac{\zeta}{d} b_i m_j, \]  

(32)

where \( b_i \) are the components on the Bravais basis \( a_i \) of a translation vector of the lattice, or Burgers vector, \( m_j \) are the components on the dual Bravais basis of a unit vector normal to a crystallographic plane, \( d \) is the interplanar distance and \( \zeta \in \mathbb{Z} \) is an integer multiplicity. Since \( b \) is a translation vector of the lattice it follows that its components \( b_i \) on the Bravais basis are integer. In addition, it can be shown that \( m_i/d \) are the Miller indices of the plane, which are also integer. Hence it follows that the matrix \( F \) of the affine transformation has itself integer components. If, in addition, we assume \( b \) and \( m \) to be orthogonal, corresponding to a crystallographic shear, then \( \det F = 1 \) and the conditions of Ericksen’s theorem are met, showing that (31) indeed defines a lattice invariant transformation. The corresponding linearized eigendeformation 1-form is

\[ \beta_1(e_1) \approx F_{ij} d\xi_j(e_1) - d\xi_i(e_1) = \zeta b_i, \]  

(33)

where we have used the identity \( d\xi(e_1) \cdot m = d \), which applies whenever the bond vector \( d\xi(e_1) \) is transverse to the slip plane. In general crystals, slip planes may contain bonds in which case the representation (33) must be generalized slightly. However, as we shall see all bonds in graphene are transverse to its slip lines and representation (33) suffices from present purposes. The general eigendeformation 1-form resulting from the activation of the slip system defined by \( b \) and \( m \) is obtained by localizing (33) bondwise, with the result

\[ \beta_s(e_1) = \zeta(e_1) b_i, \]  

(34)

where now \( \zeta \in \Omega^1(\mathbb{Z}) \) is an integer-valued 1-form. Suppose now that crystallographic slip can occur on \( N \) crystallographic systems defined by Burgers vectors and normals \( (b^s, m^s) \), \( s = 1, \ldots, N \), respectively. Then, the most general eigendeformation 1-form is of the form

\[ \beta_s(e_1) = \sum_{s=1}^{N} \zeta^s(e_1) b^s, \]  

(35)

where the integer-valued 1-form \( \zeta^s \in \Omega^1(\mathbb{Z}) \) is the discrete slip field on slip system \( s \). Eq. (35) provides a general representation of the eigendeformations that can be achieved by the activation of \( N \) slip systems of the lattice. Evidently, the set of all such eigendeformations is parameterized by the discrete slip field \( \zeta \equiv \{ \zeta^s, s = 1, \ldots, N \} \in \Omega^1(\mathbb{Z}^N) \).

A general theory of crystallographic defects can be constructed in the spirit of the theory of eigendeformations by assuming that exact, or compatible, eigendeformations of the general form (35) cost no energy. Within a linearized kinematics framework, this assumption is equivalent to postulating an energy of the form

\[ E(u, \beta) = \frac{1}{2} \zeta \mathcal{B}(ddu - \beta), (du - \beta) \],  

(36)

which replaces representation (14) in the presence of eigendeformations. The equilibrium problem (22) is also replaced by

\[ Au = f + \delta \mathcal{B} \beta. \]  

(37)

We see that the effect of the eigendeformations is to introduce an additional force system \( \delta \mathcal{B} \beta \) (cf., e.g., Gallego and Ortiz, 1993). This equivalence generalizes the well-known correspondence between plastic deformations and body forces in continuum models of plasticity. Provided that the lattice is stable, in the sense of the well posedness of the equilibrium problem (22), the equilibrium displacements of the lattice follow formally as

\[ u = A^{-1} (f + \delta \mathcal{B} \beta), \]  

(38)

possibly up to rigid-body displacements, or, in DFT terms,

\[ \tilde{u}(\theta) = \tilde{\Phi}^{-1} (\theta) (\tilde{\mathcal{F}}(\theta) - Q^T_1 (\theta) \tilde{\mathcal{P}}(\theta) \tilde{\beta}(\theta)), \]  

(39)

which for a given eigendeformation gives the equilibrium displacement in closed form up to quadratures.

Evidently, if \( \beta = dv \), i.e., if the eigendeformations are exact, or compatible, it follows from (36) that the energy-minimizing displacements are \( u = v \) and \( E = 0 \). However, because the eigendeformations are crystallographically constrained, i.e., \( \beta \) must necessarily be of the form (35), they are not compatible in general. By virtue of this lack of compatibility, a general distribution of slip induces residual stresses in the lattice and a nonvanishing elastic energy, or stored energy. For perfect lattices in the sense of Ariza and Ortiz (2005), a form is exact if and only if it is closed, i.e., \( \beta = dv \) if and only if \( d\beta = 0 \). Hence, a measure of the incompatibility of \( \beta \) is given by the discrete dislocation density tensor

\[ \alpha = d\beta. \]  

(40)
This simple relation may be regarded as the discrete version of Kröner’s (1958) formula and \( \mathbf{\alpha} \) may be regarded as a discrete version of Nye’s (1953) dislocation density tensor. From (40) it follows immediately that

\[
d \mathbf{\alpha} = 0, \tag{41}
\]

which generalizes the conservation of Burgers vector identity. For a two-dimensional lattice such as graphene, Eq. (41) must be understood in the sense of the augmentation map of zero-dimensional homology (cf., e.g., Munkres, 1984). Explicitly, condition (41) requires that

\[
\sum_{l \in \mathbb{Z}^2} \mathbf{\alpha}(l) = 0, \tag{42}
\]

which in turn ensures the existence of an eigendeformation 1-form \( \mathbf{\beta} \) such that (40) is verified. From its definition (40) it follows that \( \mathbf{\alpha} \) is a 2-form taking values in the lattice \( \mathcal{A} = \bigoplus_{l=0}^{N-1} \mathbb{Z}\mathbf{b}^l \) consisting of integer linear combinations of the Burgers vectors of the lattice. Using the properties of the discrete linking number, it is also possible to extend the Burgers-circuit construction to lattices (Ariza and Ortiz, 2005), which provides an alternative means of defining discrete dislocation equivalences to (40).

In the theory of continuously distributed elastic dislocations, a result of Mura (1963) shows that the energy \( E(\mathbf{\beta}) \) can in fact be expressed directly as a function \( E(\mathbf{\alpha}) \) of the dislocation density field \( \mathbf{\alpha} \) and is independent of the choice of slip distribution \( \mathbf{\beta} \) used to define \( \mathbf{\alpha} \). In particular, two distributions of slip which differ by an exact form and, hence, represent the same dislocation density have the same stored energy. In linear elasticity, this situation also arises in the theory of cut surfaces, where an application of Stokes’ theorem shows that the energy is independent of the choice of cut (Bacon et al., 1979). The corresponding discrete analog may be derived as follows. By virtue of the discrete Hodge–Helmholtz decomposition for perfect lattices (Ariza and Ortiz, 2005) we have the representation

\[
\mathbf{\beta} = d\mathbf{\nu} + \delta \mathbf{\Delta}^{-1} \mathbf{\alpha}, \tag{43}
\]

where \( \mathbf{\Delta} \) is the discrete Laplace–deRham operator (13). Inserting this representation in (36) and redefining \( u - v \) as \( u \), a straightforward derivation gives

\[
E(\mathbf{\alpha}) = \frac{1}{2} \left\langle B\delta\mathbf{\Delta}^{-1}\mathbf{\alpha}, \delta\mathbf{\Delta}^{-1}\mathbf{\alpha} \right\rangle - \frac{1}{2} \left\langle A^{-1}\delta B\delta\mathbf{\Delta}^{-1}\mathbf{\alpha}, \delta B\delta\mathbf{\Delta}^{-1}\mathbf{\alpha} \right\rangle \equiv \frac{1}{2} \left\langle \mathbf{\Gamma}^{\mathbf{\alpha}} \right\rangle, \tag{44}
\]

where \( \mathbf{\Gamma}(l) \) is twice the interaction energy between a unit dislocation at the origin \( e_2(0) \) and another unit dislocation at \( e_2(l) \). In applications we shall work often with the discrete Fourier transform representation

\[
E(\mathbf{\alpha}) = \frac{1}{2\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \frac{1}{2} \left\langle \mathbf{\tilde{\Gamma}}(\theta) \mathbf{\tilde{\alpha}}(\theta), \mathbf{\tilde{\alpha}}^*(\theta) \right\rangle d\theta_1 d\theta_2, \tag{45}
\]

where

\[
\mathbf{\tilde{\Gamma}}(\theta) = \mathbf{\Delta}^{-1} \mathbf{Q}_2^x \mathbf{\Psi} \mathbf{Q}_2^x \mathbf{\Delta}^{-1} - \mathbf{\Delta}^{-1} \mathbf{Q}_2^x \mathbf{\Psi} \mathbf{Q}_2^x \mathbf{\Delta}^{-1} \mathbf{Q}_2^x \mathbf{\Psi} \mathbf{Q}_2^x \mathbf{\Delta}^{-1}. \tag{46}
\]

If, as in the potential of Aizawa et al. (1990), the force constants are of finite range, i.e., if \( \mathbf{\Phi} \) and \( \mathbf{\Psi} \) vanish for all but a finite number of sites, then the sum (A.1) that gives its DFT is finite and it follows that \( \mathbf{\Phi}, \mathbf{\Psi} \in C^\infty((-\pi, \pi)^2) \). If, in addition, the lattice is stable and has no soft modes, then \( \mathbf{\Phi} \) and \( \mathbf{\Psi} \) are invertible in the perforated Brillouin zone \([-\pi, \pi)^2 \) (0) and, hence, \( \mathbf{\Phi}^{-1}, \mathbf{\Psi}^{-1} \) and, by extension, \( \mathbf{\Gamma}(l) \) are likewise smooth in that set. Since the set \( E_2 \) of 2-cells in graphene defines a centrosymmetric Bravais lattice, it follows that \( \mathbf{\tilde{\Gamma}}(0) = \mathbf{\tilde{\Gamma}}(\theta) \), i.e., \( \mathbf{\tilde{\Gamma}}(0) \) is even. In addition, since \( \mathbf{\Gamma}(\theta) \) is the DFT of a real-valued function we have \( \mathbf{\tilde{\Gamma}}^*(\theta) = \mathbf{\tilde{\Gamma}}(-\theta) = \mathbf{\tilde{\Gamma}}(\theta) \), whence it follows that \( \mathbf{\tilde{\Gamma}}(0) \) is itself real valued.

In all the above expressions we have tacitly assumed that the discrete Poisson problem (12) and the equilibrium problem (22) are well-posed. The well-posedness of the discrete Poisson problem (12) has been verified in Section 2 for the graphene lattice complex defined therein. Conditions for the well-posedness of the equilibrium problem have been given in Section 3.1 and verified in Section 3.2 for the potential of Aizawa et al. (1990).

### 4.2. The discrete dislocations of graphene

The fundamental lattice-invariant shear for graphene that we consider in this work is depicted in Fig. 4a. The deformation shears the graphene lattice through a displacement of length \( |b| = \sqrt{3}a \). The corresponding slip systems are shown in Fig. 4b. Every bond can shear in the direction normal to itself and in two additional directions at 60° to the normal, namely,

\[
b_1(e_1) = \sqrt{3}R(-\pi/3) dx(e_1), \tag{47a}
\]

\[
b_2(e_1) = \sqrt{3}R(-\pi/2) dx(e_1), \tag{47b}
\]

\[
b_3(e_1) = \sqrt{3}R(-2\pi/3) dx(e_1), \tag{47c}
\]
Fig. 4. (a) Fundamental lattice-preserving shear deformation of graphene considered in this work; (b) resulting slip lines and Burgers vectors, defining the operative slip systems of graphene.

where $R(\theta)$ denotes a two-dimensional rotation through an angle $\theta$. Thus, the most general eigendeformation resulting from these slip systems is of the form

$$\beta_i(e_1) = \zeta_1(e_1)b_1(e_1) + \zeta_2(e_1)b_2(e_1) + \zeta_3(e_1)b_3(e_1),$$

(48)

where $\zeta_s(e_1) \in \mathbb{Z}, s=1,2,3, \text{is an integer slip field that keeps track of the multiplicity of the bondwise lattice invariant shears.}$

The corresponding discrete dislocation density follows from (48) by an application of the discrete Kröner formula (40). This representation can be given a compelling geometrical interpretation by writing the eigendeformation field in the form

$$\beta_i = \sum_{e_1 \in E_1} \beta_i(e_1)e^1,$$

(49)

where $e^1$ denotes the elementary 1-form associated with the 1-cell $e_1$, namely,

$$e^1(e_1) = \begin{cases} 1 & \text{if } e_1 = e_1, \\ 0 & \text{otherwise.} \end{cases}$$

(50)

Evidently, these elementary forms supply a basis of $\Omega^1$, the space of all 1-forms over the lattice. Applying the discrete Kröner formula (40)–(49) gives

$$z_i = \sum_{e_1 \in E_1} \beta_i(e_1)de^1.$$  

(51)

Thus, the set $\{de^1, e_1 \in E_1\}$ of elementary dislocation cycles, or loopons, supplies a basis for all the dislocation densities that can be supported by the lattice. For graphene, the three types of loopons $de^1(l,1), de^1(l,2)$ and $de^1(l,3)$, corresponding to the three types of bonds of the lattice, are shown in Fig. 5.

It follows from representation (49) that the local dislocation densities $z_i(e_2)$ take values in the triangular lattice

$$A = \{\xi_1b_1 + \xi_2b_2 + \xi_3b_3, \xi_1, \xi_2, \xi_3 \in \mathbb{Z}, \xi_2, \xi_3 \in \mathbb{Z} \}.$$

(52)

This renders the problem of determining energy-minimizing dislocation distributions a discrete optimization problem. These problems are combinatoric in nature and known to be NP-complete, which renders the low-energy dislocation structure (LEDs) problem exceedingly challenging.

5. Core-energies and structures

The ansatz eigendeformation energy (36) and crystallographic kinematics (48) constitute uncontrolled approximations whose validity must be carefully assessed by some appropriate means. By construction, the discrete mechanics framework accounts for harmonic lattice elasticity exactly and, hence, the main questions regarding the fidelity of the theory concern its ability to predict core structures. In this section, we address those questions by examining the dislocation cores of the discrete dislocations for the Aizawa et al. (1990) potential and by critically comparing them to experimental observations and the dislocation cores predicted by other theories.

We specifically consider dipolar and quadrupolar periodic arrangements of dislocations in cells of sizes ranging from $192$ to $3200$ atoms. For this latter size, the asymptotic regime of dilute dislocations characterized analytically in Section $6$ is fully established. Typical unit cells used in calculations are shown in Figs. 6 and $10$. The unit cells consist of a subset of lattice sites of the form $Y = \{l \in \mathbb{Z}^2, l^1 = 1, \ldots, N_1, l^2 = 1, \ldots, N_2\}$ relative to the Bravais basis $(a_1, a_2)$ defined in Section 2, with the property that the vectors $A_1 = N_1a_1$ and $A_2 = N_2a_2$ are translation vectors of the lattice. Conveniently, for periodic problems the inverse discrete Fourier transform is expressed in terms of a finite sum (cf. Appendix A.2)—instead of an integral—and, therefore, the equilibrium displacements and stored energies can be evaluated exactly. Specifically, the
equilibrium displacements and the stored energy per unit cell become

$$\tilde{u}(\Theta) = \tilde{\Phi}^{-1}(\Theta)\tilde{f}(\Theta) - Q^T(\Theta)\tilde{\Psi}(\Theta)\tilde{\beta}(\Theta)$$  \(53\)

and

$$E(\varepsilon) = \frac{1}{|Y|} \sum_{\Theta \in Z} \frac{1}{2} \left\langle \tilde{\Gamma}(\Theta)\tilde{z}(\Theta), \tilde{z}^*(\Theta) \right\rangle,$$ \(54\)

which replace (39) and (45), respectively. In these expressions, the points \(\Theta\) range over the finite lattice \(Z\) of size \(|Y| = N_1 \times N_2\) in reciprocal space defined as the intersection of the lattice spanned by the basis reciprocal to \(A_i\) and \([-\pi, \pi]^2\). Evidently, the evaluation of (53) and (54) entails finite sums that can be carried out exactly, which effectively furnishes an exact explicit solution of periodic-cell problems.

It should be carefully noted that the distribution of eigendeformations that gives rise to a given dislocation density is not unique. However, the discrete Kröner’s formula (45) ensures that the stored energy depends only on the dislocation density and not on the particular choice of eigendeformations. By contrast, the displacement field—and the resulting deformed configuration of the lattice—does depend on the particular choice of eigendeformations. For the slip systems assumed to operate for graphene, Eqs. (47) and (48), it is possible to construct eigendeformation distributions that are dislocation-free, i.e., there exist eigendeformations \(\beta \neq 0\) such that \(d\beta = 0\). Consequently, for a fixed dislocation density and even after taking crystallographic slip constraints into account, it is possible to construct—through different choices of eigendeformations—a multiplicity of cores all resulting in the same stored energy (44). This situation is in analogy to linear-elastic dislocations, where the energy of a given dislocation loop is independent of the choice of cut surface used to describe the dislocation. By contrast, the displacement field and, hence, the ‘core structure’, of a linear-elastic dislocation does depend on the choice of cut plane and, consequently, it cannot be uniquely determined by considerations of energy alone within the framework of linear elasticity.

**Fig. 5.** Elementary dislocation dipoles that provide a basis for the dislocation densities of graphene.

**Fig. 6.** Periodic dipolar arrangement of discrete dislocations, unit periodic cell. (a) Distribution of eigendeformations \(\beta_i(e_1)\) defining one dipole, consisting of a constant Burgers vector over a zig-zag chain of 1-cells. (b) Dislocation density \(\varepsilon_i(e_2)\) describing the resulting dipole.
The question thus naturally arises as to how to select eigendeformations describing a given dislocation density and simultaneously resulting in the most physically relevant cores. Within a strict energy-minimization framework, one physically meaningful selection criterion is to require that the discrete-dislocation cores be metastable with respect to a full atomistic potential. The simplest way to exercise this ancillary condition is simply to choose eigendeformations resulting in discrete-dislocation cores in the same class as the core structures that are either computed using full atomistic potentials or observed experimentally. This approach was followed in Ramasubramaniam et al. (2007) to validate the core structures predicted by the discrete-dislocation theory in bcc metals. The ancillary stability criterion provides an effective guiding principle for selecting appropriate distributions of eigendeformations in graphene. For instance, a commonly observed and computed core structure in graphene (Kaxiras and Pandey, 1988; Xu et al., 1993; Hashimoto et al., 2004; Los et al., 2005; Li et al., 2005; Meyer et al., 2008; Jeong et al., 2008) exhibits a characteristic pentagon–heptagon ring (5–7) structure. Therefore, in all subsequent examples we choose eigendeformations that, while satisfying the crystallographic slip constraints and resulting in a prescribed dislocation density, give rise to 5–7 core structures.

In order to facilitate the visualization and interpretation of the computed dislocation cores, in all subsequent calculations we reconstruct the atomic bonds over the deformed configuration according to a minimum-length criterion.

5.1. Dislocation dipole

We begin by considering periodic discrete-dislocation dipoles of increasing length embedded in periodic cells of increasing size. Fig. 6 shows typical assumed unit cells and discrete dislocation dipoles. The distribution of eigendeformations \( \beta_i(e_1) \) that defines one dipole consists of a constant Burgers vector supported over a zig-zag chain of 1-cells, Fig. 6a. The corresponding dislocation density \( \alpha_i(e_2) \) is shown in Fig. 6b.

The core structure of the shortest possible discrete dipole, consisting of a full Burgers vector applied on a single 1-cell, is shown in Fig. 7 for the Aizawa et al. (1990) potential. As may be seem from the figure, the core of the dipole exhibits pentagon–heptagon ring (5–7–7–5) SW structure. The core structure of a longer dipole is shown in Fig. 8 and consists of pentagon–heptagon rings (5–7). Finally, the energy of the periodic dipole arrangement per unit periodic cell, which may be

![Fig. 7. Core structure of shortest discrete dipole for the Aizawa et al. (1990) potential, exhibiting pentagon–heptagon ring (5–7–7–5) SW structure. (a) Undeformed and deformed lattices for a 192-atom unit cell. (b) Detail of the bond rotation \( \theta = 52^\circ \) resulting in the SW structure.](image)

![Fig. 8. Discrete dipole core structure for the Aizawa et al. (1990) potential, exhibiting double pentagon–heptagon ring (5–7) structure.](image)
regarded as an energy per dipole, is shown in Fig. 9 as a function of the dislocation separation and unit-cell size. As expected, for dislocation separations much smaller than the cell size the energy per dipole is ostensibly independent of the cell size and depends on the size of the dipole only. Except for the smallest dipoles, the dipole energy depends logarithmically on dipole size, in agreement with the asymptotic analysis of Section 6. When the dipole size becomes comparable with the cell size, dipole–dipole interactions become important and the dependence of the dipole energy on dipole size deviates increasingly from the logarithm behavior.

The SW-defect formation energy predicted by the present discrete mechanics approach for the Aizawa et al. (1990) potential follows from Fig. 9 as 11.92 eV. This formation energy and bond-rotation angle of 52° are in consistent with the available experimental evidence and with other theoretical predictions. For instance, Meyer et al. (2008) have reported that nearly planar graphene sheet are more stable under electron-beam irradiation than single-walled carbon nanotubes. They concluded that the maximum energy of 15.6 eV that can be transferred to a carbon atom by electron-beam irradiation is sufficient to form SW defects. Thus, our computed SW-defect formation of 11.92 eV is consistent with this observation. Li et al. (2005) obtained an SW-defect formation energy of 9.2 eV and a bond-rotation angle \( \theta = 45° \) in a single layer of graphite from density-functional theory calculations within the generalized gradient approximation (GGA). In earlier work, Kaxiras and Pandey carried out \textit{ab initio} calculations in a two-dimensional super-cell of 18 atoms using plane-wave pseudopotentials and obtained a formation energy of 14 eV and a bond rotation angle of 55°. Tight-binding calculations by Xu et al. (1993) in a two-dimensional cell containing 112 atoms give a formation energy of 9.8 eV and a bond-rotation angle of 50°. Recently, Los et al. (2005) performed calculations based on an improved long-range carbon bond-order potential (LCBOII) using a 576-atom periodic cell and obtained an SW formation energy of 8 eV and a bond-angle of 50°. From this comparison it seems fair to conclude that the ability of discrete mechanics to predict defect core structures and formation energies is well within the range of accuracy of present theoretical capability.

5.2. Quadrupolar arrangement

As a second validation example we consider a periodic arrangement of discrete-dislocation quadrupoles of increasing size embedded in periodic cells also of increasing size. Fig. 10 shows typical assumed unit cells and discrete-dislocation quadrupoles. The distribution of eigendeformations \( \psi_i(e_1) \) that defines one quadrupole consists of two constant and opposite Burgers vectors supported on two zig-zag chain of 1-cells, Fig. 10 a. The corresponding dislocation density \( \alpha_i(e_2) \) is shown in Fig. 10 b.

Two deformed configurations corresponding to 448-atom and 1144-atom periodic cells are shown in Fig. 11 for the Aizawa et al. (1990) potential. The discrete-dislocation cores exhibit pentagon–heptagon ring (5–7) core structures similar to those found in dipoles. This structure is consistent with the observations of Hashimoto et al. (2004) of pairs of pentagon–heptagons attached to a missing row of atoms in a zig-zag chain in electron-beam irradiated single-walled carbon nanotube of large diameter. Jeong et al. (2008) performed density functional theory calculations of graphene sheets containing zig-zag chains of vacancies of different lengths. After atomic relaxation, they observed the formation of two 5–7 pair defects at both ends of the missing chain. This structure arises when the number of vacancies is eight or more. For purposes of comparison, we have plotted in Fig. 12 the discrete-dislocation formation energies obtained for different periodic-cell sizes together with those calculated by Jeong et al. (2008) for a 448-atom periodic cell. As may be seen from
Finally, the energy of the periodic quadrupole arrangement per unit periodic cell is shown in Fig. 13 as a function of the dislocation separation and unit-cell size. As in the case of a periodic arrangement of dipoles, for dislocation separations much smaller than the cell size the energy per quadrupole is ostensibly independent of the cell size and depends on the size of the quadrupole only. Except for the smallest quadrupoles, the quadrupole energy depends logarithmically on quadrupole size, in agreement with the asymptotic analysis of Section 6. When the quadrupole size becomes comparable with the cell size, quadrupole–quadrupole interactions become important and the dependence of the quadrupole energy on quadrupole size deviates increasingly from the logarithm behavior.

6. The dilute limit

Given that dislocations in graphene are rather energetic defects, it is reasonable to expect that the equilibrium dislocation concentrations be relatively low except at very high temperatures. However, device performance is also expected to be highly sensitive to defects and even small numbers of defects may have a substantial deleterious effect on device performance (Novoselov et al., 2005). Consequently, a precise understanding of the energetics of dilute dislocation densities, or dilute limit, is of particular practical interest. Unfortunately, the direct numerical simulation of dilute dislocation distributions requires large computational cells, which renders the analysis unfeasible for very dilute distributions. In addition, the analysis of isolated dislocations is inherently multiscale. Thus, while their core properties are dominated by the discreteness of the lattice, their far field is dominated by continuum elasticity. In this section we present a formal asymptotic analysis of the limiting energy of dilute dislocation distributions in graphene that effectively balances these demands and produces explicit results.

For purposes of analysis we identify discrete-dislocation distributions with functions $\alpha : \mathbb{Z}^2 \rightarrow \Lambda$, obtained by representing the set $E_2$ of hexagonal cells as a simple Bravais lattice. The triangular lattice $\Lambda$ in which $\alpha$ takes values is
Fig. 11. Deformed configurations of periodic quadrupolar arrangement of discrete dislocations for the Aizawa et al. (1990) potential exhibiting pentagon–heptagon ring (5–7) core structures. (a) 448-Atom periodic cell. (b) 1144-Atom periodic cell.

Fig. 12. Comparison of discrete dislocation-pair formation energies for the Aizawa et al. (1990) potential with those computed by Jeong et al. (2008) from density functional theory, showing convergence of results 8 lattice units, when both the discrete and the density-functional theory dislocation cores begin to exhibit 5–7 ring cores.
defined in (52). The corresponding discrete Fourier representation of the dislocation density is, cf. (A.1),

\[ \tilde{\alpha}(\theta) = \sum_{l \in \mathbb{Z}^2} \alpha(l) e^{-i\theta l}, \quad \theta \in [-\pi, \pi]^2, \]  

(55)

with inverse, cf. (A.2),

\[ \alpha(l) = \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \tilde{\alpha}(\theta) e^{i\theta l} d\theta_1 d\theta_2. \]  

(56)

We recall that the stored energy of a distribution of dislocations is given by (45). As we shall see, the long wavelength limit of the kernel,

\[ \tilde{\Gamma}_0(\theta) = \lim_{L \to +0} \sqrt{L} \tilde{\Gamma}(\theta) \]  

(57)

plays a central role in the dilute limit. The kernel \( \Gamma_0(x) \) measures the linear elastic interaction energy between two point dislocations with relative position vector \( x \). For instance, for the potential of Aizawa et al. (1990) described in Section 3.2, a lengthy but straightforward computation gives

\[ (\tilde{\Gamma}_0)_{11}(\theta) = \frac{122872}{\theta_1^2 + \theta_2^2 + \theta_3^2} + \frac{276000\theta_2^2}{(\theta_1^2 + \theta_2^2 + \theta_3^2)^2}, \]  

(58a)

\[ (\tilde{\Gamma}_0)_{22}(\theta) = \frac{306872}{\theta_1^2 + \theta_2^2 + \theta_3^2} - \frac{276000\theta_2^2}{(\theta_1^2 + \theta_2^2 + \theta_3^2)^2}, \]  

(58b)

\[ (\tilde{\Gamma}_0)_{12}(\theta) = \frac{159349(\theta_1^2 - \theta_2^2)}{(\theta_1^2 + \theta_2^2 + \theta_3^2)^2}, \]  

(58c)

where all the constants are in dyn/cm. We note that \( \Gamma_0(\theta) \) is homogeneous of degree \(-2\) in \( \theta \). That this scaling holds in general may be verified directly as follows:

\[ \tilde{\Gamma}_0(\lambda \theta) = \lim_{\varepsilon \to 0} \varepsilon^2 \tilde{\Gamma}(\varepsilon \lambda \theta) = \lambda^{-2} \lim_{\eta \to 0} \eta^2 \tilde{\Gamma}(\eta \theta) = \lambda^{-2} \tilde{\Gamma}_0(\theta), \]  

(59)

provided that the limits are well-defined.

We shall be interested in the asymptotic behavior of the energy when a fixed dislocation mass becomes increasingly dilute. The basic asymptotic behavior that underlies this dilute limit is described by the following lemma. The proof of the lemma is straightforward but somewhat lengthy and is consigned to Appendix C for clarity of exposition.

**Lemma 1.** Suppose that \( \tilde{\Gamma}(\theta) \) is real-valued and smooth in \([-\pi, \pi]^2\) \( \setminus \{0\} \) and \( \tilde{\Gamma}(\theta) - \tilde{\Gamma}_0(\theta) \) is bounded in \([-\pi, \pi]^2\), where \( \tilde{\Gamma}_0(\theta) \) is the long-wavelength limit (57) of \( \tilde{\Gamma}(\theta) \). Let \( \varepsilon \in \tilde{\Gamma}(\mathbb{Z}^2) \) have finite energy and let \( \varepsilon_n \) be the sequence of increasingly dilute

---

**Fig. 13.** Energy of periodic dislocation quadrupoles for the Aizawa et al. (1990) potential as a function of dislocation separation and unit-cell size. The dislocations in the quadrupole are equally spaced so that the length of the dipoles and their distance is the same in all cases.
dislocation densities

\[ x_0(l) = \begin{cases} 
  a(l/h) & \text{if } l \in h\mathbb{Z}^2, \\
  0 & \text{otherwise.} 
\end{cases} \]  

(60)

Then

\[ \lim_{h \to \infty} \frac{E(x_h)}{\log h} = \frac{1}{4\pi} \langle Kx, x \rangle_{p(x^2)}, \]  

(61)

where

\[ K = \int_{[-\pi,\pi]^2} \hat{F}_0(\theta) \, d\theta \]  

(62)

is the prelogarithmic energy tensor.

The asymptotic limit (61) implies that the energy of a dilute distribution of dislocations in graphene takes, to leading order, the remarkably simple form

\[ E(x) \sim \frac{\log h}{4\pi} \langle Kx, x \rangle_{p(x^2)} = \frac{\log h}{4\pi} \sum_{l \in \mathbb{Z}^2} \langle Kx(l), x(l) \rangle, \]  

(63)

where \( h \) measures the minimum distance between pairs of dislocations. Thus, asymptotically each individual dislocation contributes to the total energy in proportion to its individual prelogarithmic factor (cf., e.g., Barnett and Swanger, 1971; Bacon et al., 1979).

For graphene, with \( F_0 \) given by (57), a straightforward calculation gives the prelogarithmic energy tensor as

\[ K = \begin{pmatrix} 248113 & 0 \\ 0 & 248113 \end{pmatrix}, \]  

(64)

in units of dyn/cm. The asymptotic behavior predicted by Lemma 1 is illustrated in Fig. 14, which shows the energy \( E(x_h) \) of an increasingly dilute dislocation quadrupole \( x_h \) normalized by \( \log h \), with \( h \) taken as the number of 2-cells between the dislocations in the quadrupole. According to (63), we should have the limiting behavior \( E(x_h)/\log h \to \langle Kb, b \rangle/\pi = 29.818 \) ergs, where we have used the prelogarithmic energy tensor (64), corresponding to the potential of Aizawa et al. (1990), in calculating the numerical value of the limit. This limiting behavior is clearly apparent in Fig. 14.

Finally, we note that the dilute limit formally characterized by Lemma 1 may equivalently be regarded as a continuum limit in which the lattice is allowed to become increasingly finer, Fig. 15. Thus, the energy of the sequence (60) of increasingly dilute dislocations is

\[ E(x_h) = \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \frac{1}{2} \langle \hat{F}(\theta)\hat{x}(h\theta), \hat{x}^*(h\theta) \rangle \, d\theta_1 \, d\theta_2. \]  

(65)

Fig. 14. Energy of an increasingly dilute dislocation quadrupole normalized by \( \log h \), where \( h \) is the number of 2-cells between the dislocations of the quadrupole. The energy is calculated using the potential of Aizawa et al. (1990). The curve exhibits the limiting behavior \( E(x_h)/\log h \to \langle Kb, b \rangle/\pi = 29.818 \) ergs typified by Lemma 1.
Effecting the change of variables \( \eta = h\theta \) we obtain

\[
E(\mathbf{x}_h) = \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \frac{1}{h^2} \left( \frac{\hbar}{1} \hat{\mathcal{F}}(\hbar^{-1} \eta, \hat{\mathbf{a}}(\eta), \hat{\mathbf{a}}^*(\eta)) \right) \, d\eta_1 \, d\eta_2 \equiv E_h(\mathbf{x}).
\]

But \( E_h(\mathbf{x}) \) is the energy of a fixed dislocation density supported on increasingly finer lattices, Fig. 15. This reinterpretation of the dilute limit as a continuum limit has the advantage of defining a sequence of functionals \( E_h \) to which the tools of \( \Gamma \)-convergence can be applied. \( \Gamma \)-convergence is a powerful form of variational convergence of functionals which, in particular, implies convergence of minimizers (cf., e.g., Dal Maso, 1993). Lemma 1 falls short of being a \( \Gamma \)-convergence in that the limiting energy (61) can be further relaxed by decomposing dislocations optimally. This lowers the energy further to a form that scales linearly with the dislocation density, instead of quadratically (Ponsiglione, 2007). However, the mathematical complexity of \( \Gamma \)-convergence is well beyond the scope of the present work and no such enhancements will be attempted here.

7. Summary and conclusions

We have presented an application of the theory of discrete dislocations of Ariza and Ortiz (2005) to the analysis of dislocations in graphene. We have shown that, by a systematic application of the discrete Fourier transform, the equilibrium problem is amenable to exact solution within the discrete-dislocation theory, which confers the theory a distinct advantage over conventional atomistic models. Explicit expressions have been given for the stored energy and the exactly solvable equilibrium displacement field that defines the deformed configuration of the lattice for the force-constant model of Aizawa et al. (1990). Those explicit expressions are ready for application to general dislocation structures. The ability of the discrete-dislocation theory to predict dislocation core structures and energies has been critically assessed for periodic arrangements of dislocation dipoles and quadrupoles and through comparisons to other work (Li et al., 2005; Kaxiras and Pandey, 1988; Xu et al., 1993; Los et al., 2005; Jeong et al., 2008). By a judicious choice of eigendeformations, the discrete dislocations exhibit 5–7–7–5 ring core structures that are consistent with observation and result in dislocation energies that fall within the range of prediction of other models. Finally, we have turned to the elucidation of the asymptotic behavior of dilute distributions of dislocations and shown that it can be characterized analytically in terms of a discrete prelogarithmic energy tensor. Explicit expressions for this discrete prelogarithmic energy tensor have been provided up to quadratures.

The present application to graphene effectively showcases many of the distinct advantages of the discrete-dislocation theory, some theoretical, some calculational, to wit: a self-contained discrete mechanics of defects in crystals free of spurious devices such as core-cutoffs; a precise definition of dislocations as topological defects of the lattice complex; the explicit solvability of the equilibrium problem; and the analytical tractability of limits of interest such as the dilute and continuum limits.

We close by pointing out limitations of the theory that suggest directions of future research. We begin by noting that in this work we have considered in-plane deformations of free-standing graphene sheets only. Under these conditions, the terms \( V_4 \), \( V_5 \) and \( V_6 \) in the Aizawa et al. (1990) potential, Eq. (23), do not come into play. Whereas these simplifying assumptions are often in analyses of defects in graphene, it is conceivable that out-of-plane displacements might have a significant influence on the structure and energy of defects and effect that should be carefully assessed.
Whereas the theory in its present form can predict reasonable dislocation core structures and energies, such predictions are limited by the choice of crystallographic eigendeformations described in Section 4.2. A richer diversity of defect structures—and an increased ability to match experimental observation—might be obtained by extending the set of slip systems, e.g., to include dislocation partials and stacking faults representative of a complex γ- curve.

Moreover, it should be carefully noted that in the present work we have confined our attention to the elucidation of dislocation structures in static equilibrium. To this end, the dislocation density of interest has been presumed given. A far richer class of problems concerns the characterization of low-energy dislocation structures, in which the dislocation structure is itself unknown. Rigorous I- convergence analyses necessarily entail the identification of some optimal dislocation structures as part of the definition of recovery sequences (Conti and Ortiz, 2005).

We also recall that the distribution of eigendeformations that gives rise to a given dislocation density is not uniquely determined by crystallographic slip constraints or energy considerations alone within the discrete-dislocation theory and we have appealed to stability with respect to a full atomistic potential as an ancillary criterion for selecting the most physically relevant cores. In this paper we have exercised this ancillary criterion simply by comparison with results of fully atomistic calculations and experimental observations. A more direct way of assessing the metastability of discrete-dislocation cores is to use the discrete-dislocation solution to seed a molecular statics calculation based on a full potential and verify that the discrete dislocation structure remains unchanged upon relaxation. This approach was applied by Gallego and Ortiz (1993) to Lomer dislocations in silicon. In that case, the Lomer dislocation core structure predicted by the discrete theory was shown to be stable with respect to the full Stillinger–Weber potential.

Finally, the questions of long-term dynamic stability of dislocation cores and thermodynamic properties of dislocation ensembles have been entirely eschewed in the present work. However, it is known that dislocation cores that are in mechanical equilibrium at zero temperature may anneal over time at finite temperature (Carpio and Bonilla, 2008; Carpio et al., 2008). In order to gain insight into these questions, we have used discrete-dislocation solutions to mechanically equilibrium at zero temperature may anneal over time at finite temperature (Carpio and Bonilla, 2008; Carpio et al., 2008). In order to gain insight into these questions, we have used discrete-dislocation solutions to

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**Appendix A. The discrete Fourier transform**

**A.1. Definition and fundamental properties**

The discrete Fourier transform of \( f : \mathbb{Z}^n \to \mathbb{R} \) is

\[
\hat{f}(\theta) = \sum_{l \in \mathbb{Z}^n} f(l) e^{-i \theta \cdot l}.
\]

(A.1)

In addition we have

\[
f(l) = \frac{1}{(2\pi)^n} \int_{[-\pi,\pi]^n} \hat{f}(\theta) e^{i \theta \cdot l} d^n \theta,
\]

(A.2)

which is the inversion formula for the discrete Fourier transform. It follows from this expression that \( f(-l) \) is the Fourier-series coefficient of \( f(\theta) \). Defining the discrete convolution as

\[
f \ast g(l) = \sum_{l \in \mathbb{Z}^n} f(l-l') g(l')
\]

(A.3)

we have the identity

\[
\hat{f} \ast \hat{g} = \hat{f} \hat{g},
\]

(A.4)

which is often referred to as the convolution theorem. Suppose in addition that \( f, g \) are square-summable. Then

\[
\sum_{l \in \mathbb{Z}^n} f(l) g^*(l) = \frac{1}{(2\pi)^n} \int_{[-\pi,\pi]^n} \hat{f}(\theta) \hat{g}^*(\theta) d^n \theta,
\]

(A.5)

which is the Parseval identity for the discrete Fourier transform.
A.2. Periodic functions

The extension of the Fourier transform formalism to periodic functions is of particular interest in applications. Consider a set \( Y \subset \mathbb{Z}^n \), the unit cell, such that the translates \( \{ Y + lA_i, l \in \mathbb{Z}^n \} \), for some translation vectors \( A_i \in \mathbb{Z}^n \), \( i = 1, \ldots, n \), define a partition of \( \mathbb{Z}^n \). Let \( A' \) be the corresponding dual basis, \( B' = 2\pi A' \) the reciprocal basis. A lattice function \( f : \mathbb{Z}^n \to \mathbb{R} \) is \( Y \)-periodic if \( f(l) = f(l + lA) \), for all \( l \in \mathbb{Z}^n \). The discrete Fourier transform of a \( Y \)-periodic lattice function can be written in the form

\[
\hat{f}(\theta) = \sum_{l \in \mathbb{Z}^n} f(l) e^{-i(\theta \cdot l + \Theta)} = \left\{ \frac{1}{|Y|} \sum_{l \in \mathbb{Z}^n} f(l) e^{i(\theta \cdot l)} \right\} \left\{ |Y| \sum_{l \in \mathbb{Z}^n} e^{i(\theta \cdot lA)} \right\},
\]

where \(|Y|\) is the number of points in \( Y \). But

\[
|Y| \sum_{l \in \mathbb{Z}^n} e^{i(\theta \cdot lA)} = (2\pi)^n \delta(\theta - HlB')
\]

and, hence,

\[
f(l) = \frac{1}{|Y|} \sum_{\theta \in \mathbb{Z}^n} \hat{f}(\theta) e^{i(\theta \cdot l)}.
\]

For periodic functions, Parseval’s identity takes the form

\[
\sum_{l \in \mathbb{Z}^n} f(l) \bar{g}(l) = \frac{1}{|Y|} \sum_{\theta \in \mathbb{Z}^n} \hat{f}(\theta) \bar{\hat{g}}(\theta).
\]

Likewise, let \( f \) and \( g \) be complex-valued lattice functions, the latter periodic. Inserting representation (A.8) into the convolution theorem gives

\[
(f * g)(\theta) = \hat{f}(\theta) \left( \frac{2\pi)^n}{|Y|} \sum_{\theta \in \mathbb{Z}^n} \hat{g}(\theta) \delta(\theta - \Theta) \right)
\]

whence it follows that

\[
(f * g) = \hat{f}(\theta) \hat{g}(\Theta).
\]

Finally, the average of a periodic function follows as

\[
\langle f \rangle = \frac{1}{|Y|} \sum_{l \in \mathbb{Z}^n} f(l) = \frac{1}{|Y|} \int \hat{f}(\theta) d\theta.
\]

Appendix B. Weak limits of rapidly oscillatory periodic functions

As a dislocation distribution becomes increasingly dilute, the discrete Fourier transform of its density becomes rapidly oscillatory. Under these conditions, the following property of rapidly oscillatory periodic functions plays a central role (cf., e.g., Cioranescu and Donato, 1999).

**Theorem 2.** Let \( f \) be a \( Y \)-periodic function in \( L^1(Y) \). Set

\[
f_\epsilon(x) = f\left( \frac{X}{\epsilon} \right) \quad \text{a.e. in } \mathbb{R}^n
\]

Then, as \( \epsilon \to 0 \),

\[
f_\epsilon - \frac{1}{|Y|} \int_Y f(x) \, dx \quad \text{in } L^1(\mathbb{R}^n).
\]

We recall that \( f_\epsilon \) converges weakly to \( f \), denoted \( f_\epsilon \rightharpoonup f \), in \( L^1(\Omega) \) if

\[
\int_{\Omega} f_\epsilon \varphi \, dx \to \int_{\Omega} f \varphi \, dx
\]
for all \( \varphi \in L^\infty(\Omega) \). Thus, when integrating a highly oscillatory sequence of functions of the form (B.1) against a bounded function, theorem (2) enables the oscillatory sequence to be replaced by its mean.

**Appendix C. Proof of Lemma 1**

**Proof.** Define \( \tilde{\varphi}_h(\theta) = \tilde{\varphi}(h\theta) \), where \( \tilde{\varphi}(\theta) \) is regarded as \([-\pi, \pi]^2\) - periodic. Then, we have

\[
E(\tilde{\varphi}_h) = \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \tilde{\varphi}'(\theta) \cdot f(h^2 \theta) \, d\theta_1 \, d\theta_2,
\]

where

\[
f(\theta) = \frac{1}{2} \tilde{\varphi}'(\theta) \otimes \tilde{\varphi}'(\theta) + \tilde{\varphi}'(\theta) \otimes \tilde{\varphi}(\theta)
\]

is a \([-\pi, \pi]^2\) - periodic real-valued function in \(L^1([-\pi, \pi]^2)\) and we have made use of the symmetry and real-valuedness of \( \tilde{\varphi}(\theta) \). In addition, \( f(-\theta) = f(\theta) \), i.e., \( f(\theta) \) is an even function. It therefore follows from these properties that the function \( f(h^2 \theta) \) becomes rapidly oscillatory over \([-\pi, \pi]^2\) as \( h \to \infty \), which suggests using Theorem 2 of Appendix B in order to characterize the limiting behavior of the sequence \( E(\tilde{\varphi}_h, \tilde{\varphi}_h) \). However, the kernel \( \tilde{\varphi}(\theta) \) is not essentially bounded at the origin and the theorem does not apply directly. In order to overcome this difficulty, we resort to the usual device of *extracting the singularity*, i.e., expressing

\[
E(\tilde{\varphi}_h) = E_1(\tilde{\varphi}_h) + E_2(\tilde{\varphi}_h),
\]

where

\[
E_1(\tilde{\varphi}_h) = \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} (\tilde{\varphi}(\theta) - \tilde{\varphi}_0(\theta)) \cdot f(h^2 \theta) \, d\theta_1 \, d\theta_2
\]

and

\[
E_2(\tilde{\varphi}_h) = \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \tilde{\varphi}_0(\theta) \cdot f(h^2 \theta) \, d\theta_1 \, d\theta_2.
\]

Since, by assumption, \( \tilde{\varphi}(\theta) - \tilde{\varphi}_0(\theta) \) is bounded we can now apply Theorem 2 of Appendix B to \( E_1(\tilde{\varphi}_h) \), with the result,

\[
\lim_{h \to \infty} E_1(\tilde{\varphi}_h) = \left\{ \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} (\tilde{\varphi}(\theta) - \tilde{\varphi}_0(\theta)) \, d\theta_1 \, d\theta_2 \right\} \cdot \left\{ \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} f(\theta) \, d\theta_1 \, d\theta_2 \right\},
\]

which is bounded. It remains to determine the asymptotic behavior of \( E_2(\tilde{\varphi}_h) \). To this, we proceed to exploit the homogeneity of the function \( \tilde{\varphi}_0(\theta) \). We expect \( E_2(\tilde{\varphi}_h) \) to exhibit logarithmic scaling. In order to characterize this scaling we define the new sequence

\[
E_2(\tilde{\varphi}_{h+1}-\tilde{\varphi}_h) = \frac{1}{(2\pi)^2} \int_{[-(1+1/\pi,1+1/\pi)^2]} \tilde{\varphi}_0(\theta) \cdot f(h^2 \theta) \, d\theta_1 \, d\theta_2,
\]

where we have used the homogeneity of \( \tilde{\varphi}_0(\theta) \). To within terms that become negligible upon scaling we find

\[
E_2(\tilde{\varphi}_{h+1}) - E_2(\tilde{\varphi}_h) \sim \frac{2}{(2\pi)^2} \int_{Q_{\theta}^+} \tilde{\varphi}_0(\theta) \cdot f(h^2 \theta) \, d\theta_1 \, d\theta_2 + \frac{2}{(2\pi)^2} \int_{Q_{\theta}^-} \tilde{\varphi}_0(\theta) \cdot f(h^2 \theta) \, d\theta_1 \, d\theta_2,
\]

(C.1)

where \( Q_{\theta}^+ = \{ \theta_j \in [-\pi, \pi] : j \neq i, \theta_i \in [\pi, \pi+\pi/h] \} \) and \( Q_{\theta}^- = \{ \theta_j \in [-\pi, \pi] : j \neq i, \theta_i \in [\pi, -\pi-\pi/h] \} \). Introducing the new variable \( \zeta_1 = (\theta_1-\pi)h \)

\[
\frac{1}{(2\pi)^2} \int_{Q_{\theta}^+} \tilde{\varphi}_0(\theta) \cdot f(h^2 \theta) \, d\theta = \frac{h^{-1}}{(2\pi)^2} \int_{0}^{\pi} \int_{-\pi}^{\pi} \tilde{\varphi}_0(\pi+\zeta_1/h, \theta_2) \cdot f(\zeta_1 + h\pi, h\theta_2) \, d\theta_2 \, d\zeta_1,
\]

which by the \([-\pi, \pi]^2\) - periodicity of \( f \) further reduces to

\[
\frac{1}{(2\pi)^2} \int_{Q_{\theta}^+} \tilde{\varphi}_0(\theta) \cdot f(h^2 \theta) \, d\theta = \frac{h^{-1}}{(2\pi)^2} \int_{0}^{\pi} \int_{-\pi}^{\pi} \tilde{\varphi}_0(\pi+\zeta_1/h, \theta_2) \cdot f(\zeta_1, h\theta_2) \, d\theta_2 \, d\zeta_1.
\]

For large \( h \) we have

\[
\frac{1}{(2\pi)^2} \int_{Q_{\theta}^-} \tilde{\varphi}_0(\theta) \cdot f(h^2 \theta) \, d\theta \sim \frac{h^{-1}}{(2\pi)^2} \int_{0}^{\pi} \int_{-\pi}^{\pi} \tilde{\varphi}_0(\pi, \theta_2) \cdot f(\zeta_1, h\theta_2) \, d\theta_2 \, d\zeta_1.
\]

Finally, an application of Theorem 2 of Appendix B gives

\[
\frac{h}{1} \int_{Q_{\theta}^-} \tilde{\varphi}_0(\theta) \cdot f(h^2 \theta) \, d\theta \sim \left\{ \frac{1}{2\pi} \int_{-\pi}^{\pi} \tilde{\varphi}_0(\pi, \theta_2) \, d\theta_2 \right\} \cdot \left\{ \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} f(\theta) \, d\theta_1 \, d\theta_2 \right\}.
\]
where we have used the evenness of \(f(\theta)\). Treating the remaining terms in (C.1) likewise and collecting the corresponding asymptotic estimates we obtain

\[
E_{2}(2k_{i}+1) - E_{2}(2k) \sim \frac{1}{4\pi h} \langle K \hat{\mathbf{\varepsilon}}, \hat{\mathbf{\zeta}} \rangle_{L^{2}(\pi \times \pi)}^{2},
\]

(C.2)

where \(K\) is the prelogarithmic energy tensor (64). Finally, from the recursion relation (C.2) we arrive at the identity

\[
\lim_{h \to 0} \frac{E_{2}(n)}{\log h} = \frac{1}{4\pi} \langle K \hat{\mathbf{\varepsilon}}, \hat{\mathbf{\zeta}} \rangle_{L^{2}(\pi \times \pi)}^{2},
\]

(C.3)

as required. We note that the bounded part \(E_{i}\) of the energy drops out in taking the limit (C.3) and only the logarithmically divergent part \(E_{2}\) contributes to that limit. □

References


