



An atomistic and non-classical continuum field theoretic perspective of elastic interactions between defects (force dipoles) of various symmetries and application to graphene

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Abstract

Force multipoles are employed to represent various types of defects and physical phenomena in solids: point defects (interstitials, vacancies), surface steps and islands, proteins on biological membranes, inclusions, extended defects, and biological cell interactions among others. In the present work, we (i) as a prototype simple test case, conduct quantum mechanical calculations for mechanics of defects in graphene sheet and in parallel, (ii) formulate an enriched continuum elasticity theory of force dipoles of various anisotropies incorporating up to second gradients of strain fields (thus accounting for nonlocal dispersive effects) instead of the usual dispersion-less classical elasticity formulation that depends on just the strain (c.f. Peyla, P., Misbah, C., 2003. Elastic interaction between defects in thin and 2-D films. *Eur. Phys. J. B.* 33, 233–247). The fundamental Green's function is derived for the governing equations of second gradient elasticity and the elastic self and interaction energies between force dipoles are formulated for both the two-dimensional thin film and the three-dimensional case. While our continuum results asymptotically yield the same interaction energy law as Peyla and Misbah for large defect separations ($\sim 1/r^n$ for defects with n -fold symmetry), the near-field interactions are qualitatively far more complex and free of singularities. Certain qualitative behavior of defect mechanics predicted by atomistic calculations are well captured by our

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enriched continuum models in contrast to classical elasticity calculations. For example, consistent with our atomistic calculations of defects in isotropic graphene, even two dilation centers show a finite interaction (as opposed to classical elasticity that predicts zero interaction). We explicitly find the physically consistent result that the self-energy of a defect is equivalent to half the interaction energy between two identical defects when they “merge” into each other. The atomistic, classical elastic and the enriched continuum predictions are thoroughly compared for two types of defects in graphene: Stone-Wales and divacancy.

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1. Introduction

In analogy with electrostatics, the field effects of defects in elastic solids can be expanded in terms of multipoles. Force multipoles (which can be employed to mimic a variety of defects) are of fundamental importance in condensed matter physics and mechanics of materials (Love, 1944; Teodosiu, 1982; Eshelby, 1956; Siems, 1968). In various contexts, defects often control and/or dramatically alter not only microscopic but also the coarse-grained macroscopic behavior of solids. Dislocations (Hirth and Lothe, 1982; Gutkin, 2000), point defects (interstitials, vacancies (Bitter, 1931; Bullough and Hardy, 1968)), surface islands and steps (Ronda and Berbezier, 2004; Kukta et al., 2002a,b), inclusions (Eshelby, 1957, 1959; Mura, 1987) are all example of defects that can be modeled using juxtaposition of distribution of forces (Fig. 1) and their multipoles. Interestingly, the concept of force dipoles has also found applications in biological physics (Bischofs et al., 2004; Bischofs, 2004; Peyla and Misbah, 2003; Marchenko and Misbah, 2005; Schwarz and Safran, 2002; Ghim and Park, 2002; Schwarz et al., 2002). Cell–cell long range interactions have been analyzed using the classical elastic theory of force dipoles (Bischofs et al., 2004; Bischofs, 2004; Marchenko and Misbah, 2005; Schwarz and Safran, 2002). Proteins in biological membranes can also be considered as point defects.

The multipole representation of defects has already been explored by many authors. Historically, perhaps the most widely cited treatments are those due to Eshelby (1956), Bullough and Hardy (1968), and Teodosiu (1982), which are predicated on classical elasticity. Unfortunately, the latter suffers from several deficiencies and, as will be demonstrated in more detail in Section 6, yields some results that are inconsistent with atomistic calculations: (i) by their very definition, force dipoles in classical elasticity admit singular displacement fields (ii) interaction energies between force dipoles are singular as separation distance approaches zero (iii) assuming isotropic media, isotropic defects exhibit zero *direct* interaction¹ while atomistic simulations and other studies indicate a weak but nonetheless finite attraction (Bullough and Hardy, 1968; Tewary, 1973) (iv) compared with atomistic calculations, classical elasticity often predicts the opposite sign (i.e. attraction or repulsion) when defects are very close. By its very conception, elasticity is a long-wavelength theory and ill designed to capture phenomena near defect cores or for close defect separations so these deficiencies are hardly surprising. While atomistic simulations can be employed to remedy these aforementioned shortcomings, a field

¹There is an indirect induced term that varies as inverse sixth power of separation distance (Tewary, 1973).

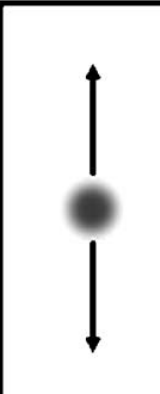
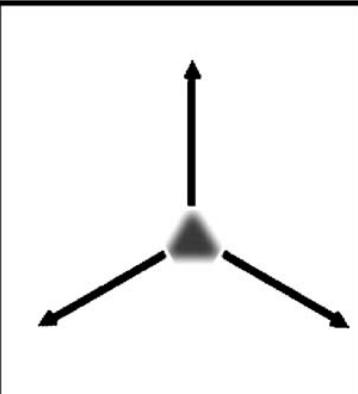
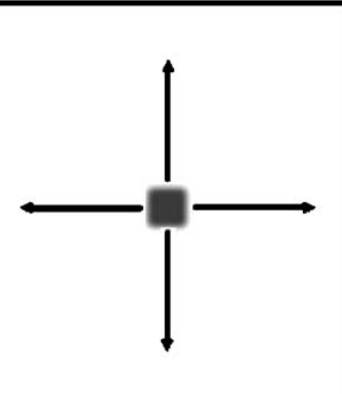
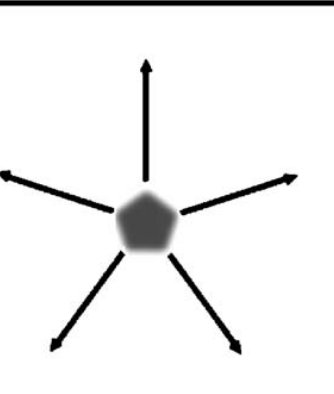
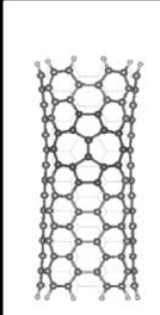
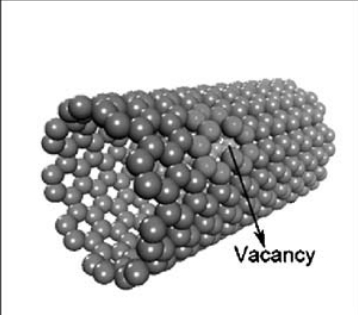
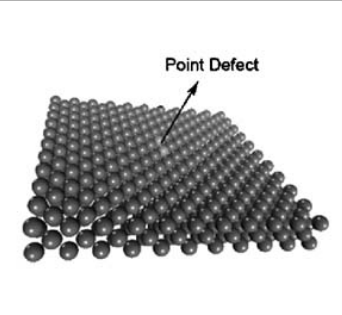
			
			
dipole (Stone–Wales)	Tripole (vacancy on CNT)	Quadrupole (Interstitial/vacancy in cubic crystal)	Pentapole (unknown higher order defect)

Fig. 1. Different point defects with n -fold symmetries.

theoretic approach that faithfully replicates the qualitative insights afforded by atomistics is highly desirable as well. Field theoretic solutions can be then complementarily employed with (numerical) atomistic simulations to parameterize the effect of defects (Li et al., 2005). The utility of the latter is demonstrated in Section 6 where we apply our theoretical formulation to the study of Stone–Wales and divacancy defects in graphene sheet. Recently, Garikipati et al. (2006) have made an elegant reconciliation of atomistic and continuum viewpoints of energetics of point defects.

This concept and the prevalence of nonlocal effects (which are especially strong near defects) have led several authors to propose nonlocal theories of elasticity. In the latter (at least one version of it), higher order gradients of strain are incorporated in a Ginzburg–Landau-type expansion of the elastic energy. Some researchers also advocate an “integral nonlocal theory” (e.g. Gairola, 1976; Eringen, 2002) which is not considered in the present work. Recently, higher-order theories of elasticity that incorporate not just the strain but also the strain gradients are en vogue to capture the elastic size-effects prevalent at the nanoscale. Several works (Reid and Gooding, 1992; Zhang and Sharma, 2005a; Gutkin, 2000; Aifantis, 1999, 2003) are available in the literature that address, among other issues, defects via strain gradient elasticity. The first strain gradient theory (which incorporates first gradients of strain in addition to the strain itself) has been very successful in addressing extended defects such as dislocations and disclinations (Gutkin, 2000; Gutkin and Aifantis, 1999a, b; Lazar et al., 2005). The derivations of the present authors, however, indicate that the first gradient theory (contrary to the case of dislocations) is unable to remove singular behavior in the case of force dipoles (see

Appendix A for the relevant derivations concerning first gradient theory). Since dislocations, and indeed any defect may be mimicked via superposition of force multipoles (i.e. point defects of various symmetries), a physical consistent, atomistically faithful field theoretic framework for force multipoles is desirable and pursued in this paper.

We present here a *second gradient elasticity formulation for force dipoles* that will be shown to well-describe the qualitative features of defect interactions as predicted by atomistic studies even for extremely close separations.² Thus, in the present work, despite the attendant mathematical complexity, we successfully employ an elastic energy expansion correct to *second gradients in strain*. The derivation of the necessary equations for such a second gradient theory, its fundamental solutions (Green's function), explicit and closed-form formulation of the interaction energies between defects of different symmetries for both thin film and three-dimensional (3-D) case, and a discussion of the ensuing physical insights and a comparison with atomistic calculations are the major objectives of the present work.

The outline of this paper is as follows: first, in Section 2, the classical elasticity approach towards force multipoles is briefly recapitulated and some essential notions are discussed. In Section 3, we describe the second gradient elasticity theory. The Green's functions for both the two-dimensional (2-D) thin film case as well as the 3-D case are derived in this section while the general form of the interaction energy is formulated in Section 4. Analytical and numerical results for various symmetries of the force dipoles are presented in Sections 5. An application of the developed models is made on two types of defects in graphene sheet in Section 6 and a comparison is drawn with atomistic calculations. We finally conclude in Section 7.

2. Essential background and classical elasticity based analysis of defect multipoles

Consider a localized defect centered at $\mathbf{X}$ in a d -dimensional medium (where $d = 2$ or 3). Various (n) point forces acting around this point defect at $\mathbf{x} + \mathbf{l}^{(n)}$ are denoted by $\mathbf{f}^{(n)}$. In analogy with electrostatics, a multi-polar tensor, $\mathbf{P}$, can be defined:

$$\mathbf{P}^{(m)} = \sum_n \mathbf{f}^{(n)} \otimes \underbrace{\mathbf{l}^{(n)} \otimes \dots \otimes \mathbf{l}^{(n)}}_m, \quad (1)$$

where, superscript m denotes the order of expansion. The first expansion $\mathbf{P}^{(0)}$ is the monopole, $\mathbf{P}^{(0)} = \sum_n \mathbf{f}^{(n)}$, which vanishes due to force equilibrium. The second-order expansion $\mathbf{P}^{(1)}$ (denoted by $\mathbf{P}$ here and below) is the dipole tensor: $\mathbf{P}^{(1)} = \sum_n \mathbf{f}^{(n)} \otimes \mathbf{l}^{(n)}$. Higher-order expansions such as tripole, quadropole and so forth are similarly defined. Following Peyla and Misbah (2003), only defects with inverse symmetry are considered here. In this case, the point defects can be treated only by force dipoles without moment ($\mathbf{M} = \sum_n \mathbf{l}^{(n)} \times \mathbf{f}^{(n)} = 0$) and in particular, odd tensors vanish, e.g. tripole term is zero. Historically, as well as from the point of view of wide-applicability, dipoles are the most oft studied defects and thus shall also be the focus of the present work. There is, however, little difficulty in extending the results we present to defects that lack centrosymmetry simply by incorporating higher-order expansion terms like elastic tripole or yet higher effects for centrosymmetric ones (via quadropoles). In particular, the tripole term is expected to be

²During advanced stages of publication of this manuscript, Professor Lazar kindly brought to our attention his recent work that also employs an identical form of second gradient elasticity to analyze dislocations (Lazar et al., 2006).

useful for certain types of defects like triangular vacancies, 5–7 (1/2) Stones–Wales defect in carbon nanotubes among others (Samsonidze et al., 2002).

Insofar as dipoles are concerned, they can be subject to various classifications. Love (1944), classified them as isotropic dipoles, anisotropic dipoles without moment and anisotropic dipoles with moment (Bischofs et al., 2004; Bischofs, 2004; Schwarz and Safran, 2002). A juxtaposition of forces with equal dipole strength in each direction is the isotropic dipole. For this isotropic defect, the dipole tensor is $\mathbf{P} = A\mathbf{I}$. Here the constant “ A ”, has units of energy and characterizes the strength of the dipole, and must be determined from either experimental or atomistic considerations. The isotropic force dipole may be used to mimic dilation centers and is thus ideal for spherically or circularly symmetric vacancies and interstitials. Clearly the isotropic dipolar tensor is diagonal.

A juxtaposition of forces with average dipole strength pointing in a direction n is described by a non-diagonal but symmetrical tensor, $\mathbf{P} = B\mathbf{n} \otimes \mathbf{n}$. “ B ”, analogous to “ A ”, is the directional strength of the force dipole (Fig. 2). This kind of force dipole is utilized to simulate anisotropic defects, like proteins (Ghim and Park, 2002), ellipsoidal inclusions (Eshelby, 1956), probing force patterns of cells (Bischofs et al., 2004; Bischofs, 2004) among others. Following (Peyla and Misbah, 2003) we will employ the completely anisotropic dipole tensor duly decomposed into a dilatation (isotropic) part and a directional part that is trace-free:

$$\mathbf{P} = A\mathbf{I} + B\left(\mathbf{n} \otimes \mathbf{n} - \frac{1}{2}\mathbf{I}\right). \quad (2)$$

Obviously, the elastic dipole tensor in Eq. (2) can be denoted by a symmetrical matrix, which means the defects should be inverse-symmetrical or the defects are moment free. In some special cases, a non-symmetrical dipole tensor is required (Bischofs et al., 2004).

The 3-D linear static equation for classical isotropic elastic medium is:

$$\mu\Delta\mathbf{u} + (\mu + \lambda)\nabla \otimes (\nabla \cdot \mathbf{u}) = -\mathbf{f}\delta(\mathbf{r}). \quad (3)$$

Here, μ is shear modulus and λ is lame modulus. The Green’s functions that solve Eq. (3) for the 2-D and 3-D cases are, respectively (cf. Love, 1944):

$$4\pi\mathbf{G}^{\text{cl}}(R) = \frac{(1+v)^2}{Eh} \left[\frac{v-3}{1+v} \ln RI + \frac{\mathbf{x} \otimes \mathbf{x}}{R^2} \right], \quad (4)$$

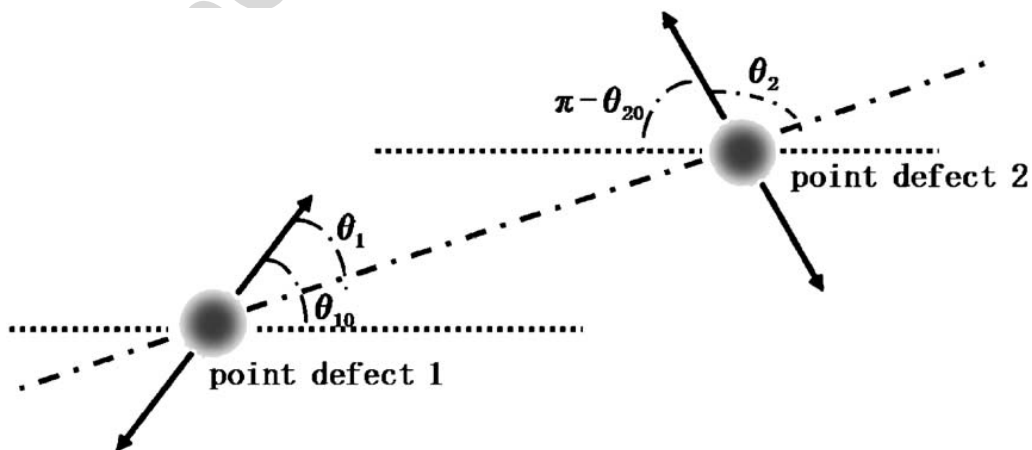


Fig. 2. Two-fold symmetrical anisotropic point defect with anisotropic direction n .

$$4\pi\mathbf{G}^{\text{cl}} = \frac{1}{\mu R}\mathbf{I} - \frac{\mu + \lambda}{\mu(2\mu + \lambda)}\nabla\nabla\frac{R}{2} \quad R = |\mathbf{x} - \mathbf{x}'|. \quad (5)$$

Incidentally, Eq. (4) may be obtained by integrating Eq. (5) in the third direction and imposing plane stress conditions (Mura, 1987). Here, E is 3-D Young's modulus with dimension N/m^2 . Eh (where “ h ” is the thickness of the film) can be considered to be the 2-D Young's modulus. The superscript “cl” serves to remind us that the Green's functions in Eqs. (4) and (5) correspond to classical elasticity.

The displacement field of a single point defect (or force dipole) is (Siems, 1968; Teodosiu, 1982):

$$\mathbf{u} = -(\nabla \otimes \mathbf{G}) : \mathbf{P}^T. \quad (6)$$

Several researchers, including (in a more modern setting), Peyla and Misbah (2003) have derived the interaction energy between two point defects as

$$U_{\text{int}} = \mathbf{P}^1 : (\nabla \otimes \mathbf{G} \otimes \nabla) : \mathbf{P}^2, \quad (7)$$

where, $\mathbf{P}^1$ and $\mathbf{P}^2$ are dipole strength for two point defects depicted in Fig. 2. Consider now an isotropic point defect (i.e. $B = 0$). For the 3-D case, the displacement field is then:

$$\mathbf{u}(\mathbf{r}) = -\frac{A}{2\mu + \lambda}\nabla\left(\frac{1}{r}\right) \quad r = |\mathbf{r}|. \quad (8)$$

It is now trivial to verify that the divergence of the displacement in Eq. (8) (which is simply the strain dilatation) is zero everywhere except at the point where the defect is located. Thus, we note the well-known notion that the field external to a dilatation center is pure shear. Physically, this implies that two dilation center will not interact (at least directly—as alluded to earlier, there is an induced indirection interaction; e.g. Tewary, 1973). This is also easily checked (for both 3-D and 2-D) case by directly using Eq. (7) and the appropriate Green's functions. To summarize, predicated on linearized isotropic elasticity, two isotropic point defects have zero direct interaction energy in both two and three dimensions i.e.:

$$U_{\text{int}} = A^2\nabla^2\text{tr}(\mathbf{G}) = 0. \quad (9)$$

In the more general case of anisotropic defects (even though the medium may be isotropic),³ Eq. (9) is no longer true. Peyla and Misbah (2003) provide the following expression for the general anisotropic case (in 2-D):

$$U_{\text{int}}^{\text{cl}} = \frac{g(\theta)}{4\pi Eh}\left(\frac{1}{R^2}\right),$$

$$g(\theta) = -(M - N)A_2B_1\cos 2\theta_1 - (M - N)A_1B_2\cos 2\theta_2 + \frac{1}{2}MB_1B_2\cos 2(\theta_1 + \theta_2), \quad (10)$$

where, M and N are combination of material parameters defined as: $M = 2(1 + \nu)^2$ and $N = 4(1 + \nu)$. Subscripts “1” and “2” denote two different defects. Here, R is the distance between two defects. $\alpha_1 = A_1/B_1$ and $\alpha_2 = A_2/B_2$ represent the extent of anisotropy of the defect. $\theta_1 = \theta - \theta_{10}$, $\theta_2 = \theta - \theta_{20}$ are the angles of inclination, where θ is the angle between

³This relation also does not hold when defects are located near a free surface or an interface. Even isotropic defects then may interact through “image” defects.

horizontal direction and the line joining the two defects. θ_{10} and θ_{20} are anisotropic directions of respective defects.

The $\sim 1/R^2$ interaction law is manifest.⁴ More generally, Peyla and Misbah (2003) show that the interaction law is $\sim 1/R^n$ for a defect with n -fold symmetry. The isotropic case of zero direct interaction energy is easily recovered by setting $B = 0$. Clearly, the interaction energy becomes singular as the defects approach infinitesimally close to each other.

3. Second-order strain gradient elasticity and derivation of Green's function

Changes in energy due to elastic deformation are parameterized by the elastic material constants. The fundamental variable on which the elastic stored energy depends is the displacement field $\mathbf{u}$. The elastic energy is invariant under the Euclidean group $SO(3) \triangleright T(3)$ i.e. the semi-direct product of the rigid rotation group $SO(3)$ and the rigid translation group $T(3)$. This invariance ensures that the elastic energy can only depend on the first and higher derivatives of the displacement: $\nabla \otimes \nabla \dots \mathbf{u}$ and not displacement itself $\mathbf{u}$. Further, invariance under rigid rotations specifies that (in case of the first derivative) only the symmetric part of the displacement gradient $\text{sym}(\nabla \otimes \mathbf{u})$ contributes to the elastic energy expression. Thus, for example, for an isotropic medium, the classical linearized elastic strain energy density is written as

$$W = \frac{1}{2} \sigma : \varepsilon = \mu \varepsilon : \varepsilon + \frac{1}{2} \lambda \text{tr}(\varepsilon)^2, \quad (11a, b)$$

$$\varepsilon = \text{sym}(\nabla \otimes \mathbf{u}).$$

There is, however, no requirement that the strain energy be dependent only on the strain. Higher-order strain gradient contributions are indeed admissible in an expansion of the energy in terms of the strains (provided of course that the usual invariance under the Euclidean group and the material symmetry are observed). Mindlin (1965) presented the following expansion for the elastic energy correct to second strain gradients:

$$W = \underbrace{\frac{1}{2} \lambda \varepsilon_{ii} \varepsilon_{jj} + \mu \varepsilon_{ij} \varepsilon_{ij}}_{\text{classical elasticity}} + \underbrace{a_1 \varepsilon_{ijj} \varepsilon_{ikk} + a_2 \varepsilon_{iik} \varepsilon_{kjj} + a_3 \varepsilon_{iik} \varepsilon_{jjk} + a_4 \varepsilon_{ijk} \varepsilon_{ijk} + a_5 \varepsilon_{ijk} \varepsilon_{kji}}_{\text{1st gradient elasticity}} + \underbrace{b_1 \varepsilon_{ijj} \varepsilon_{kkll} + b_2 \varepsilon_{ijkk} \varepsilon_{ijll} + b_3 \varepsilon_{ijjk} \varepsilon_{jkll} + b_4 \varepsilon_{iijk} \varepsilon_{llkj} + b_5 \varepsilon_{iijk} \varepsilon_{lljk} + b_6 \varepsilon_{ijk} \varepsilon_{ijk} + b_7 \varepsilon_{ijk} \varepsilon_{kji} + c_1 \varepsilon_{ij} \varepsilon_{jjk} + c_2 \varepsilon_{ij} \varepsilon_{ijk} + c_3 \varepsilon_{ij} \varepsilon_{kkj} + b_0 \varepsilon_{ijj}}_{\text{2nd gradient elasticity}}. \quad (12)$$

Interestingly, in this model, surface tension is also automatically incorporated (see also, Wu, 1992).⁵ While we do not elaborate further on this, Mindlin's original model (1965) yield governing equations that are wickedly complex to solve sometimes even for simple 1D problems. In a spirit similar to Koiter (2005), Kleinert (1989) and Aifantis (2003) (who proposed simplified versions of the first strain gradient theory),⁶ we propose to employ a simpler version of Mindlin's second gradient formulation. We assert for now (and proved

⁴ $1/R^3$ for the 3-D.

⁵The surface effects manifest through the constant b_0 . In the present work, as will be noted in due course, this term will be dropped, as it is not of significance in the present context.

⁶The reader is referred to Zhang et al. (2005) who compare various first-order strain gradient theories.

later in Section 6 via atomistic calculations) that such a framework is an appropriate field theoretic model that qualitatively and (once parameterized) quantitatively mimics the same behavior as obtained from atomistics while retaining an enormous advantage of computational simplicity and often yielding analytical results.

We employ the following elastic strain energy density that incorporates the essential effects of including second-order strain gradients and yet simpler to pursue mathematically (as compared to Mindlin's complete expansion):

$$W = \frac{1}{2} \lambda \varepsilon_{ii} \varepsilon_{jj} + \mu \varepsilon_{ij} \varepsilon_{ij} + \frac{1}{2} s_1^2 \lambda \varepsilon_{ii,k} \varepsilon_{jj,k} + s_1^2 \mu \varepsilon_{ij,k} \varepsilon_{ij,k} + \frac{1}{2} s_2^4 \lambda \varepsilon_{ii,kl} \varepsilon_{jj,kl} + s_2^4 \mu \varepsilon_{ij,kl} \varepsilon_{ij,kl}. \quad (13)$$

Here, s_1 and s_2 are two higher-order coupling material constants. During advanced stages of publication of this manuscript, one of the authors of the present work was kindly informed by Professor Lazar of an identical expression to Eq. (13) recently introduced and used in his work that analyzes the elastic behavior of dislocations (Lazar et al., 2006).

Invoking the standard field theoretic method to derive governing equations, (via Euler–Lagrange formalism), we obtain:

$$-\nabla[(1 - s_1^2 \nabla^2 + s_2^4 \nabla^4)(\lambda \text{tr}(\varepsilon) \mathbf{I} + 2\mu \varepsilon)] + \mathbf{f} = 0, \quad (14)$$

where $\mathbf{f}$ represents body forces. Eq. (14) can be rewritten as

$$-\nabla[(1 - l^2 \nabla^2)(1 - l_1^2 \nabla^2)(\lambda \text{tr}(\varepsilon) \mathbf{I} + 2\mu \varepsilon)] + \mathbf{f} = 0, \quad (15)$$

where $s_1^2 = l^2 + l_1^2$ and $s_2^4 = l^2 l_1^2$. l and l_1 are two internal length scales and characteristic of the material. These can be determined either through experimental phonon dispersion curves or as we have done in the present work, via using atomistic calculations (see Section 6). The reader is also referred to the works of and references in Chen et al. (2003, 2004) and a recent ones of Zhang and Sharma (2005a, b) that shed some light on determination of the higher-order strain gradient elasticity constants.

We now proceed to derive the Green's function for Eq. (15), which will later be employed to compute the interaction energies. Using the strain–displacement relation (11b), Eq. (15) can be rewritten as

$$-[(1 - l^2 \nabla^2)(1 - l_1^2 \nabla^2)(\lambda u_{k,k} \delta_{ij} + \mu u_{i,j} + \mu u_{j,i})]_{,j} + f_i = 0. \quad (16)$$

The Fourier transform of Eq. (16) yields:

$$(1 + l^2 \mathbf{q}^2)(1 + l_1^2 \mathbf{q}^2) \left[\mu \mathbf{q}^2 \left(\delta_{ij} - \frac{q_i q_j}{\mathbf{q}^2} \right) \hat{u}_i + (2\mu + \lambda) \mathbf{q}^2 \left(\frac{q_i q_j}{\mathbf{q}^2} \right) \hat{u}_j \right] = \hat{f}_i, \quad (17)$$

where $\mathbf{q}^2 = q_i q_i$. We have split the expression in the square brackets into two parts $\delta_{ij} - q_i q_j / \mathbf{q}^2$ and $q_i q_j / \mathbf{q}^2$ corresponding to two orthogonal projections. On the basis of Eq. (17), the dynamical matrix can be determined by coefficients of $\hat{u}_i$ in its matrix form. Eq. (17) gives the following expansion form for the dynamical matrix: $D(\mathbf{q}) = A_{ij} q_i q_j + B_{ijkl} q_i q_j q_k q_l + O(q^4)$, which is close to the form shown by discrete lattice theory. (Tewary, 1973). This observation has also been noted elsewhere (e.g. Zhang and Sharma (2005a, b); Reid and Gooding, 1992).

In the Fourier space, the displacement then can be obtained by a simple inversion of Eq. (17):

$$\hat{u}_i = \hat{G}_{ij} \hat{f}_j, \quad (18)$$

where the Fourier space Green's function is:

$$\hat{G}_{ij} = \frac{1}{\mu \mathbf{q}^2 (1 + l^2 \mathbf{q}^2) (1 + l_1^2 \mathbf{q}^2)} \left(\delta_{ij} - \frac{q_i q_j}{\mathbf{q}^2} \right) + \frac{1}{(2\mu + \lambda) \mathbf{q}^2 (1 + l^2 \mathbf{q}^2) (1 + l_1^2 \mathbf{q}^2)} \frac{q_i q_j}{\mathbf{q}^2}. \quad (19)$$

The following Fourier transform pairs will be of use:

$$\frac{1}{\mathbf{q}^2} \sim \frac{1}{4\pi R}; \quad \frac{1}{\mathbf{q}^4} \sim -\frac{R}{8\pi}; \quad \frac{1}{(\mathbf{q}^2 + 1/l^2)} \sim \frac{e^{-R/l}}{4\pi R}. \quad (20)$$

After some manipulations, the real-space Green's function is found to be:

$$4\pi G_{ij}(R) = \frac{1}{\mu} \left[\frac{1}{R} - \frac{l^2}{l^2 - l_1^2} \frac{e^{-R/l}}{R} + \frac{l_1^2}{l^2 - l_1^2} \frac{e^{-R/l_1}}{R} \right] \delta_{ij} - \frac{\mu + \lambda}{\mu(2\mu + \lambda)} \partial_i \partial_j \times \left[\frac{R}{2} + l_1^2 \left(\frac{1 - e^{-R/l_1}}{R} \right) + l^2 \left(\frac{1}{R} - \frac{l^2}{l^2 - l_1^2} \frac{e^{-R/l}}{R} + \frac{l_1^2}{l^2 - l_1^2} \frac{e^{-R/l_1}}{R} \right) \right]. \quad (21)$$

Analogous to the 3-D expression in Eq. (21), we can derive an expression for the 2-D case also. Alternatively, one may simply integrate Eq. (21) and impose plane stress conditions to obtain:

$$4\pi G_{ij}^{\text{sg}} = 4\pi G_{ij}^{\text{cl}} + \frac{4(1+\nu)}{Eh} \left[-\frac{l^2}{l^2 - l_1^2} K_0\left(\frac{R}{l}\right) + \frac{l_1^2}{l^2 - l_1^2} K_0\left(\frac{R}{l_1}\right) \right] \delta_{ij} + \frac{2(1+\nu)^2}{Eh} \partial_i \partial_j \left\{ \begin{aligned} & l_1^2 \left[K_0\left(\frac{R}{l_1}\right) + \text{Log} R \right] \\ & + l^2 \left[\frac{l^2}{l^2 - l_1^2} K_0\left(\frac{R}{l}\right) + \text{Log} R - \frac{l_1^2}{l^2 - l_1^2} K_0\left(\frac{R}{l_1}\right) \right] \end{aligned} \right\}, \quad (22)$$

where, $K_0(R)$ is the zeroth-order modified Bessel's function of the second kind. Note that the Green's function has been separated into two parts (classical part and an additional term arising from second gradient effects). This decomposition will facilitate subsequent comparison with classical elasticity based analysis.

4. General defect multipole analysis in second gradient elasticity

For isothermal thermoelastic process, the free energy of the continuum medium is just the elastic strain energy:

$$W = \frac{1}{2} \int_V \sigma_{ij} \varepsilon_{ij} dv + \frac{s_1^2}{2} \int_V \sigma_{ij,k} \varepsilon_{ij,k} dv + \frac{s_2^4}{2} \int_V \sigma_{ij,kl} \varepsilon_{ij,kl} dv. \quad (23)$$

The energy expression in Eq. (23) coincides with internal energy for isothermal thermo elastic process, regardless of whether the defect is in an isolated system or open system. We assume that the boundaries of the solid or thin film are sufficiently far away from the defect that any boundary contributions can be discarded. Therefore, after integrating by parts, a more convenient form (24) may be obtained as

$$W = -\frac{1}{2} \int_V (\sigma_{ij,j} - s_1^2 \sigma_{ij,kk,j} + s_2^4 \sigma_{ij,kk,ll,j}) u_i dv = \frac{1}{2} \int_V f_i u_i dv. \quad (24)$$

The interaction energy between two elastic fields $[\mathbf{u}^1, \boldsymbol{\varepsilon}^1, \boldsymbol{\sigma}^1]$ and $[\mathbf{u}^2, \boldsymbol{\varepsilon}^2, \boldsymbol{\sigma}^2]$ is exactly the interaction enthalpy. For closed system, it is written as Eq. (24) with $\mathbf{f}$ and $\mathbf{u}$ in different superscripts indicating different fields. However, for open system, which is the concern of this paper, the interaction energy needs to be subtracted an extra part (Eq. (25)) as the force multipoles model introduces external forces into the system (Teodosiu, 1982).

$$\Phi_E = W - \int_V f_i u_i dv = -\frac{1}{2} \int_V f_i u_i dv. \quad (25)$$

Hence, the interaction energy is

$$\Phi_E^{\text{int}} = -\frac{1}{2} \int_V f_i^1 u_i^2 dv. \quad (26)$$

Interestingly, Eq. (26) is in the form as what Teodosiu (1982), Siems (1968) and Peyla and Misbah (2003) derived for interaction energy even in the classical elasticity case. This interaction energy is also called direct interaction energy in contrast to indirect induced interaction of two point defects (Tewary, 1973).

The displacement field referred to in Eq. (26) can be derived from Eq. (6) by Taylor expansion.

$$u_i(\mathbf{x}) = \sum_a G_{ij}(|\mathbf{x} - \mathbf{r}_A - \mathbf{l}^a|) f_j(\mathbf{r}_A + \mathbf{l}^a). \quad (27)$$

Here $\mathbf{x}$ and $\mathbf{r}_A$ are defined in Fig. 2. $\mathbf{l}^a$ is local distribution coordinate of point loads.

Self-energy can be obtained similarly. For discrete force multipoles, Eq. (24) is written in summation form as

$$W = \frac{1}{2} \sum_a f_i(\mathbf{l}^a) u_i(\mathbf{l}^a). \quad (28)$$

After Taylor's expansion and only retaining dipole term, Eq. (28) can be expanded to:

$$W = \frac{1}{2} \sum_a f_i(\mathbf{l}^a) \left[l_j^a u_{ij}(0) \right] = \frac{1}{2} P_{ij} u_{ij}(0). \quad (29)$$

With the aid of Eq. (6), the self-formation energy can now be expressed as

$$W = \frac{1}{2} P_{il} P_{jk} G_{ij,kl}(R=0) = -\frac{1}{2} \Phi_E^{\text{int}}(R=0) \Big|_{\text{identical}}. \quad (30)$$

Eq. (30) implies that self-energy of a point defect is equivalent to half the interaction energy between two identical point defects when they “merge” into each other. This is consistent with physically intuition. This result is not readily apparent in classical elasticity due to singularities of the fields when defect separation distance approaches zero. However, this result can be made transparent if carried out in Fourier space. In Eq. (30), there is no boundary effect. It needs to be emphasized that Eqs. (26) and (30) are independent of the type or form of gradient elasticity chosen.

5. Defect interactions in thin films: explicit expressions and results

In the present section, the displacement field of a point defect is split into two parts: a classical elastic part (which is known) and the new terms arising from the second gradient

theory:

$$\mathbf{u} = \mathbf{u}^{\text{cl}} + \mathbf{u}^{\text{sg}}. \quad (31)$$

The classical displacement fields have been evaluated by Peyla and Misbah (2003) and are:

$$\begin{aligned} \frac{4\pi Ehu_x}{B} &= \frac{1}{2R^4} \left[\begin{aligned} &-2(M-N)xR^2a + [ux^3 + (-2M+N)xy^2] \cos 2\theta_0 \\ &+ [(M+N)x^2y - (M-N)y^3] \sin 2\theta_0 \end{aligned} \right], \\ \frac{4\pi Ehu_y}{B} &= \frac{1}{2R^4} \left[\begin{aligned} &-2(M-N)yR^2a + [2Mx^2\bar{y} - NyR^2] \cos 2\theta_0 \\ &+ [(M+N)xy^2 - (M-N)x^3] \sin 2\theta_0 \end{aligned} \right], \end{aligned} \quad (32)$$

where, $a = A/B$ represents isotropic/anisotropic ratio. $M = 2(1+\nu)^2$ and $N = 4(1+\nu)$ are two constants related to material properties. θ_0 is self-angle of one point defect.

The higher-order terms are more tedious to derive. Using the derived Green's function in Section 3, Eq. (22) and after several manipulations and simplifications we finally obtain:

$$\frac{4\pi Ehu_x^{\text{sg}}l}{B} = C_1(\bar{x}, \bar{y})f_1(r) + C_2(\bar{x}, \bar{y})f_2(r), \quad (33)$$

$$\frac{4\pi Ehu_y^{\text{sg}}l}{B} = C_3(\bar{x}, \bar{y})f_3(r) + C_4(\bar{x}, \bar{y})f_4(r), \quad (34)$$

where f_1 and f_2 are

$$f_1(r) = \frac{K_1(r) - (1/s)K_1(rs)}{1 - (1/s^2)}. \quad (35)$$

$$f_2(r) = \frac{(sr)^2 K_2(r) - r^2 K_2(rs) + (2/s^2) - 2s^2}{s^2 - 1}. \quad (36)$$

The four coefficients, C_1 , C_2 , C_3 and C_4 are

$$\begin{aligned} C_1(\bar{x}, \bar{y}) &= \frac{(M-N)\bar{x}a}{r} \\ &+ \frac{\{[(M-N)\bar{x}^3 - (M+N)\bar{y}^2\bar{x}] \cos 2\theta_0 + [2M\bar{x}^2\bar{y} - N\bar{y}r^2] \sin 2\theta_0\}}{2r^3}. \end{aligned} \quad (37)$$

$$C_2(\bar{x}, \bar{y}) = \frac{M[(\bar{x}^3 - 3\bar{y}^2\bar{x}) \cos 2\theta_0 + (3\bar{x}^2\bar{y} - \bar{y}^3) \sin 2\theta_0]}{r^6}. \quad (38)$$

$$\begin{aligned} C_3(\bar{x}, \bar{y}) &= \frac{(M-N)\bar{y}a}{r} \\ &- \frac{\{[(M-N)\bar{y}^3 - (M+N)\bar{x}^2\bar{y}] \cos 2\theta_0 + [N\bar{x}^3 + (N-2M)\bar{y}^2\bar{x}] \sin 2\theta_0\}}{2r^3}. \end{aligned} \quad (39)$$

$$C_4(\bar{x}, \bar{y}) = -\frac{M[(\bar{y}^3 - 3\bar{x}^2\bar{y}) \cos 2\theta_0 + (\bar{x}^3 - 3\bar{y}^2\bar{x}) \sin 2\theta_0]}{r^6}. \quad (40)$$

Here, $K_2(r)$ is second-order modified Bessel function of the second kind. s is ratio between l and l_1 : $s = l/l_1$. For the second strain gradient elasticity to be physically meaningful, “ s ” is constrained to be not equal to unity (see Eqs. (21) and (22)).

The displacement results are illustrated via contour plots (Figs. 3(a)–(d)). Poisson ratio is chosen to be 0.3 and “ s ” is chosen to be 2. The radial displacement is depicted: $u = \sqrt{u_x^2 + u_y^2}$. Fig. 3 shows the radial displacement field distribution around single point defect. Due to the anisotropy of the defect, the displacement is strongly angle-dependent (even though the medium itself is isotropic). Anisotropy factor is decreased from Figs. 3(a)–(c). Between Figs. 3(b) and (c), the self-angles are different. It can be seen from the two figures that the displacement fields simply differ by a rotation of $\pi/4$. Fig. 3(d) is for a perfectly isotropic point defect (i.e. a dilation center). The displacement field for the latter has infinite numbers of axis of symmetry.

Other parameters, such as ν and s , do not change the deformation pattern qualitatively. The role of s can be seen from Figs. 4(a)–(d). $s = 0$ corresponds to first-order strain gradient result, which (as claimed in Section 1) still cannot remove the singularity at defect center. With increase of s , the length scale of second-order strain gradient becomes larger.

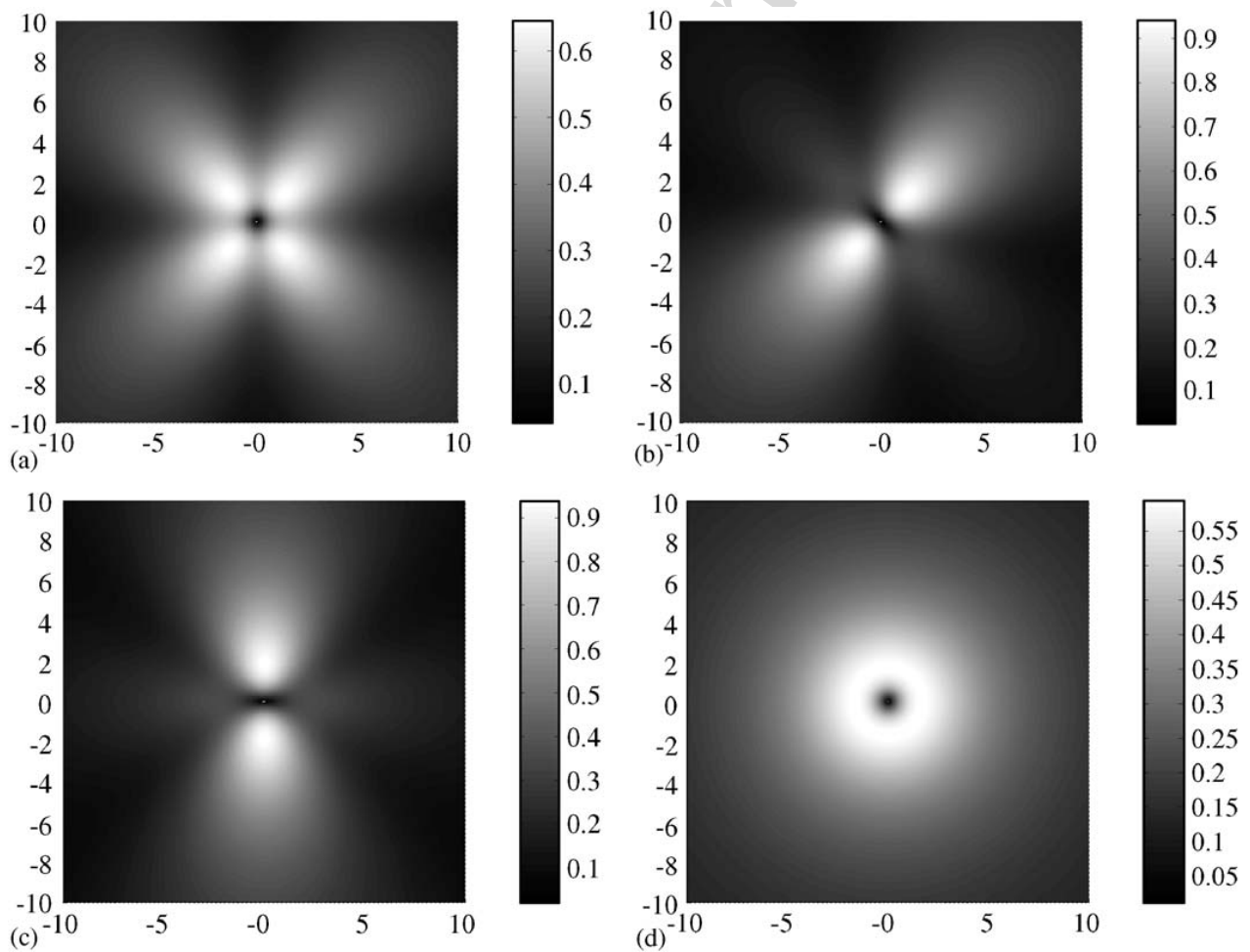


Fig. 3. (a) Displacement field around one single point defect with self-angle $\pi/4$. Anisotropic effect is chosen to be $\alpha = 0$. “ x ” and “ y ” are normalized with respect to “ l ”. Displacement is normalized as $4\pi E h l u/B$. (b) Self-angle is $\pi/4$. Anisotropic effects is chosen to be $\alpha = 1/2$. (c) Self-angle is $\pi/2$ and anisotropic effect is $\alpha = 1/2$. (d) Single isotropic point defect.

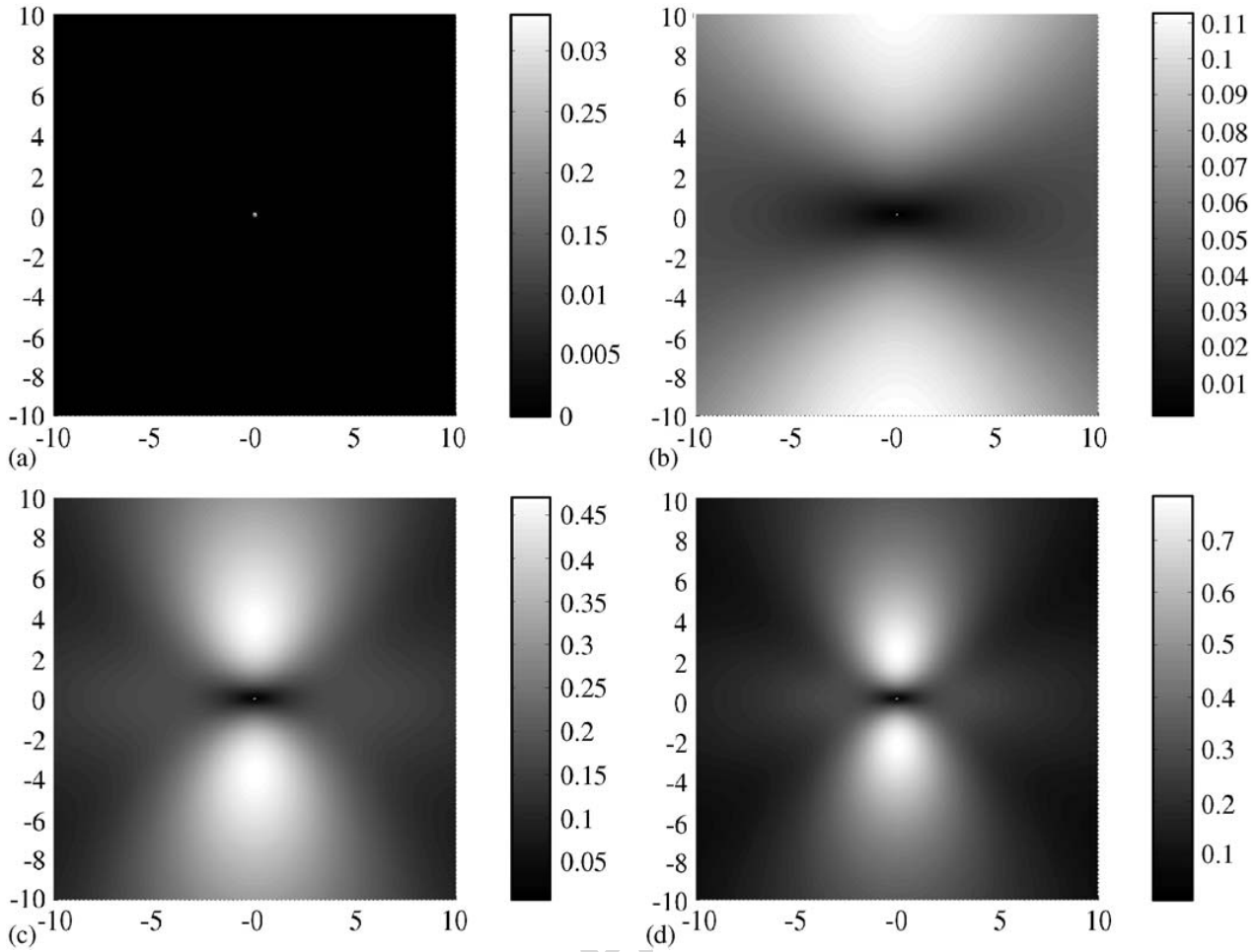


Fig. 4. Displacement field around single point defect with $\nu = 0.3$, self-angle is set to $\pi/2$, isotropic/anisotropic ratio is $1/2$ and (a) $s = 0$, (b) $s = 0.1$, (c) $s = 0.5$, (d) $s = 1.5$.

We now proceed to elaborate on the interaction energy between two defects. As with displacements, we can decompose the total interaction energy into the classical part and strain gradient part.

$$U_{\text{int}} = U_{\text{int}}^{\text{cl}} + U_{\text{int}}^{\text{sg}}. \quad (41)$$

$U_{\text{int}}^{\text{cl}}$ is known from Peyla and Misbah (2003) as

$$\frac{4\pi Eh U_{\text{int}}^{\text{cl}}}{B_1 B_2} = \left\{ \begin{array}{l} -(M - N) \cos 2\theta_1 \alpha_2 \\ -(M - N) \cos 2\theta_2 \alpha_1 + \frac{1}{2} M \cos 2(\theta_1 + \theta_2) \end{array} \right\} \frac{1}{R^2}. \quad (42)$$

$U_{\text{int}}^{\text{sg}}$, like the corresponding displacements presented earlier is tedious to derive, however, we succeed in obtaining lengthy albeit completely close-form expressions:

$$\frac{U_{\text{int}}^{\text{sg}} 4\pi Eh (l^2 - l_1^2)}{B_1 B_2} = H_1 + H_2 + H_3 + H_4. \quad (43)$$

H_1 , H_2 , H_3 and H_4 are

$$H_1 = \frac{M - N}{2} \{ 2\alpha_1 \alpha_2 [K_0(r) - K_0(sr)] + \alpha_1 \cos 2\theta_2 [K_2(r) - K_2(sr)] \}. \quad (44)$$

$$H_2 = -6 \cos 2(\theta_1 + \theta_2) M \left(\frac{1}{r^4} - \frac{1}{(sr)^4} \right). \quad (45)$$

$$H_3 = [(M - N) \cos 2\theta_1 \alpha_2 + M \cos 2(\theta_1 + \theta_2)] \left[\frac{K_1(r)}{r} - \frac{K_1(sr)}{sr} \right] \\ + 6m \cos 2(\theta_1 + \theta_2) \left[\frac{K_1(r)}{r^3} - \frac{K_1(sr)}{(sr)^3} \right]. \quad (46)$$

$$H_4 = \frac{1}{8} \left[\begin{aligned} &4(M - N) \cos 2\theta_1 \alpha_2 + M \cos 2(\theta_1 + \theta_2) \\ &+ (M - 2N) \cos 2(\theta_1 - \theta_2) \end{aligned} \right] [K_0(r) - K_0(sr)] \\ + 4M \cos 2(\theta_1 + \theta_2) \left[\frac{K_0(r)}{r^2} - \frac{K_0(sr)}{(sr)^2} \right]. \quad (47)$$

Asymptotically, for large defect separations, the gradient part of the interaction energy fall to zero very rapidly and thus the total interaction energy behaves classically in the far field. In the near field, the interaction energy is more complex. As expected, singularities are eliminated and in particular, at $r = 0$, the interaction energy is well defined and a constant:

$$4\pi Eh U_{\text{int}}^{\text{Limit}}(0) = \frac{\text{Log}(l) - \text{Log}(l_1)}{8(l^2 - l_1^2)} \left[\begin{aligned} &8(M - N)A_1A_2 \\ &+ (M - 2N) \cos 2(\theta_1 - \theta_2)B_1B_2 \end{aligned} \right]. \quad (48)$$

Based on Eq. (30), the self-energy is related to limit of interaction energy. Hence, the self-energy of one single point defect can be expressed in analytical form as

$$4\pi Eh U_{\text{self}}(0) = \frac{\text{Log}(l) - \text{Log}(l_1)}{16(l^2 - l_1^2)} [8(N - M)A^2 + (2N - M)B^2], \quad (49)$$

where the self energy is positive due to $M < N$. The same conclusion can be alternatively obtained by finding the limit of strain dilation as in Eq. (29). In yet another way, independently of Eq. (49), employing the usual integral of the energy density we arrive at this exact same expression thus confirming this relation.

Some numerical results are presented below. In Figs. 5(a) and (b) we plot the interaction energy between two defects.

We note a significant deviation between the classical results and our model when the defect separation is less than $r = 5$ i.e. ~ 5 times the fundamental length constant, $5l$. l varies from material to material. For metals, it is expected to be quite small (to the order of $\frac{1}{4}$ th of the lattice parameter, “ a ”). For example, Shibutani (1998) and Shibutani et al. (1998) indicated l to be roughly $0.25a$ while Eringen (2002) quotes a value of $0.39a$ for FCC material. A simple Born–Karman-type model yields $a/2$ (see also discussions in the Zhang and Sharma (2005a, b) and Chen et. al. (2003, 2004). Thus for these materials, the deviation from classical elasticity is only significant for separations of about 0.75 nm. The situation changes dramatically for some other systems. Reid and Gooding (1992) indicate l to be 3.4 nm for graphite thus make graphitic systems an ideal application area for this work. Based on the work of DiVincenzo (1986) we may roughly estimate l to be 0.8 nm for GaAs. Thus, we can expect the gradient effects to prevail up to about 4 nm for the latter.

In Fig. 5(a), our model and classical elasticity-based calculation both predicts attractive interaction between the point defects. However, for different isotropic/anisotropic ratios,

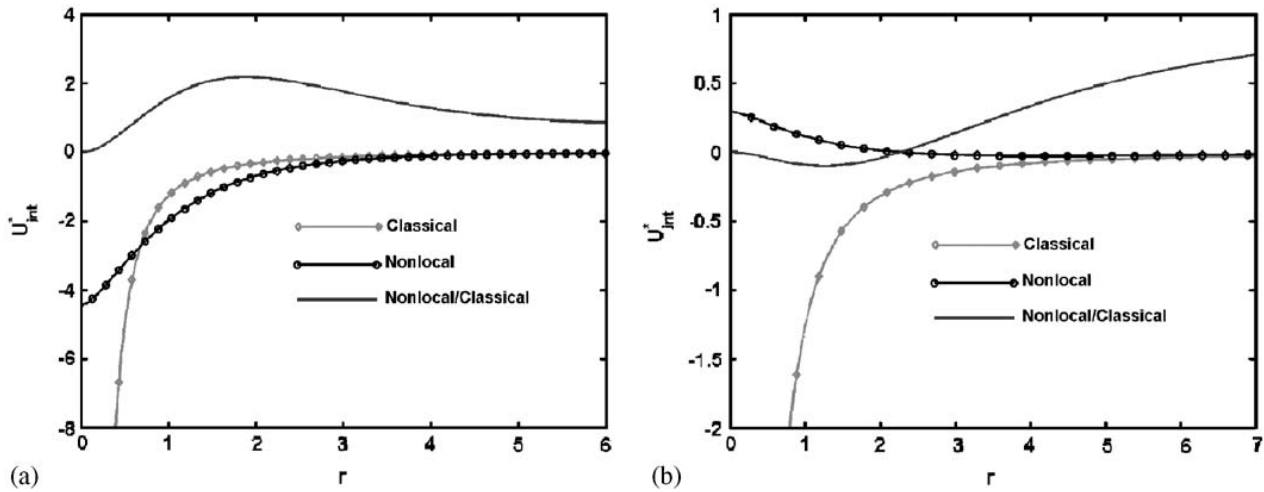


Fig. 5. (a) Plot of the interaction energy between two point defects with inclination angles $\theta_1 = \pi/2$ and $\theta_2 = 0$. Poisson ratio is chosen as $\nu = 0.3$. Strain gradient ratio is chosen to be $s = 2$. Isotropic/anisotropic extent ratio is chosen as $\alpha_1 = \alpha_2 = 2$. (b) Plot of interaction energy between two point defects with inclination angles $\theta_1 = \pi/2$ and $\theta_2 = 0$. Poisson ratio is chosen to be $\nu = 0.3$. Strain gradient ratio is chosen as $s = 2$. Isotropic/anisotropic extent ratio is chosen to be $\alpha_1 = \alpha_2 = 1/2$.

the results between second strain gradient elasticity and classical elasticity can be completely different, as shown in Fig. 5(b). Collectively from Figs. 5(a) and (b), it can be concluded that strain gradient length scale effects predominate in the length range $< 8l$. Above such length range, strain gradient effect diminishes rapidly and the interaction energy converges to the classical result.

The repulsive/attractive interactive behavior of two point defects is best illustrated using contour plots since (for the anisotropic case) the nature of the force is strongly direction dependent. Such plots are depicted in Figs. 6(a)–(d) for various cases. In all these figures, the position of defect 1 is fixed at the center (0,0). The contour is interaction energy between defect 1 and a second defect 2 at a given location. Darker shade represents attraction. Once again, strain gradient ratio s is chosen to be 2 and the adopted Poisson ratio is 0.3.

Fig. 6(a) shows the interaction energy between two point defects with different self-angles ($\theta_{10} = \pi/4$ and $\theta_{20} = 0$). The point defects are completely anisotropic. Fig. 6(b) indicates the interaction energy when changing the self-angle. $\theta_{10} = \pi/2$. Similarly, Figs. 6(a)–(d) are interaction energy patterns for different choices of parameters. From Figs. 6(a) and (b), we conclude that self-angles of the point defects are the most important factor in the determination of the symmetry properties of the interaction pattern. The point defects isotropic/anisotropic ratios do not change the interaction energy pattern qualitatively.

Finally, Figs. 7(a) and (b) displays interaction energy between purely isotropic defects. As mentioned before, two isotropic point defects do not interact in classical elasticity. Our results indicate that there is weak, nevertheless nonzero, attractive interaction between two such defects. To clarify the role of s , Fig. 7(b) shows the interaction energy between two isotropic point defects for different values of “ s ”. The ratio s of first-order strain gradient length scale and second order strain gradient constant indicates their respective relative strength. Increase of s implies the first-order strain gradient effect is taking predominant

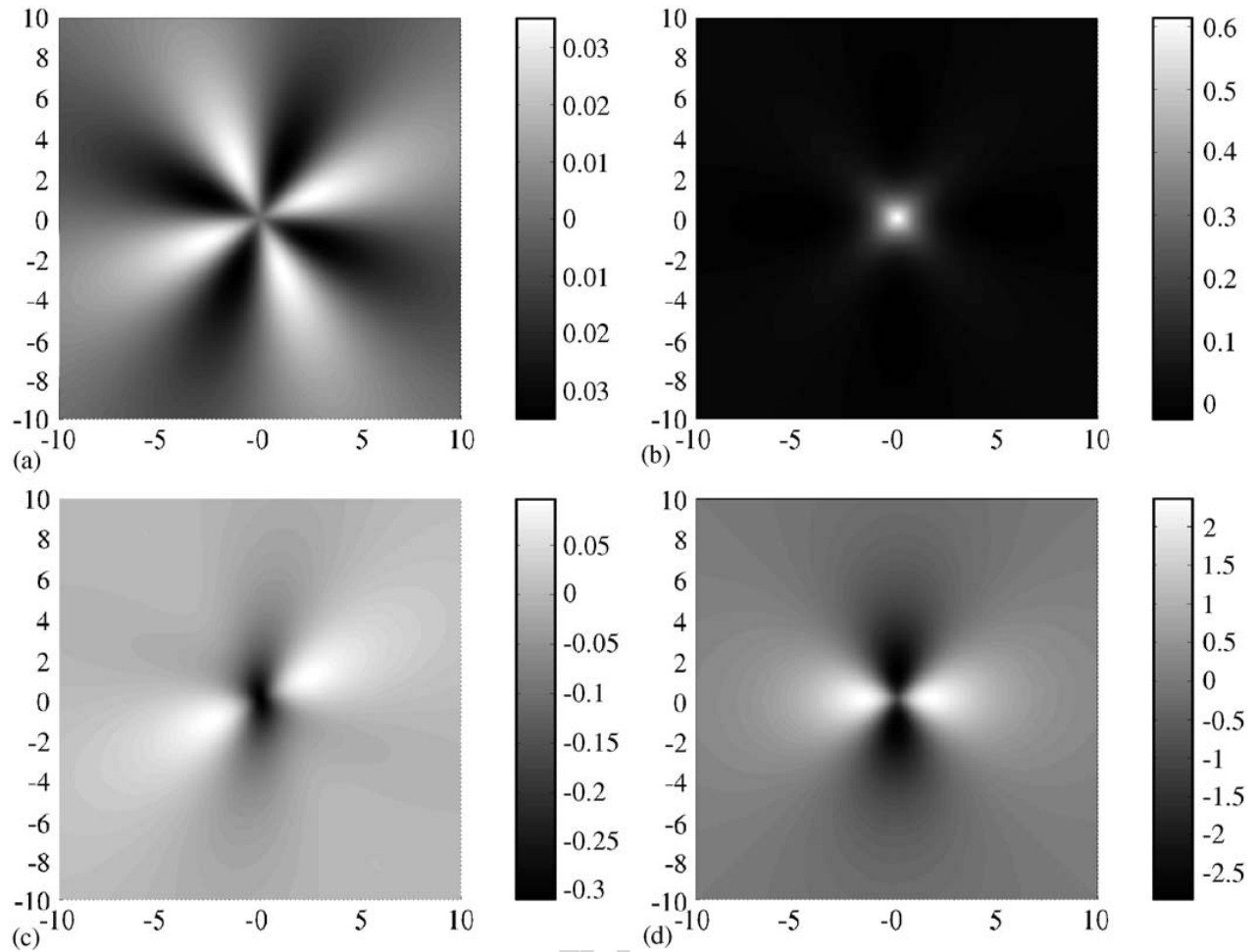


Fig. 6. (a) Interaction energy between point defect 1 (self-angle $\pi/4$) with fictitious point defect 2 (self angle 0). Isotropic extents are $\alpha_1 = \alpha_2 = 0$. (b) Interaction energy between point defect 1 (self-angle $\pi/2$) with fictitious point defect 2 (self angle 0). Isotropic extents are $\alpha_1 = \alpha_2 = 0$. (c) Interaction energy between point defect 1 (self-angle $\pi/3$) with fictitious point defect 2 (self-angle 0). Isotropic extents are $\alpha_1 = 1$ and $\alpha_2 = 1/2$. (d) Interaction energy between point defect 1 (self-angle $\pi/3$) with fictitious point defect 2 (self-angle 0). Isotropic extents are $\alpha_1 = 20$ and $\alpha_2 = 1/20$.

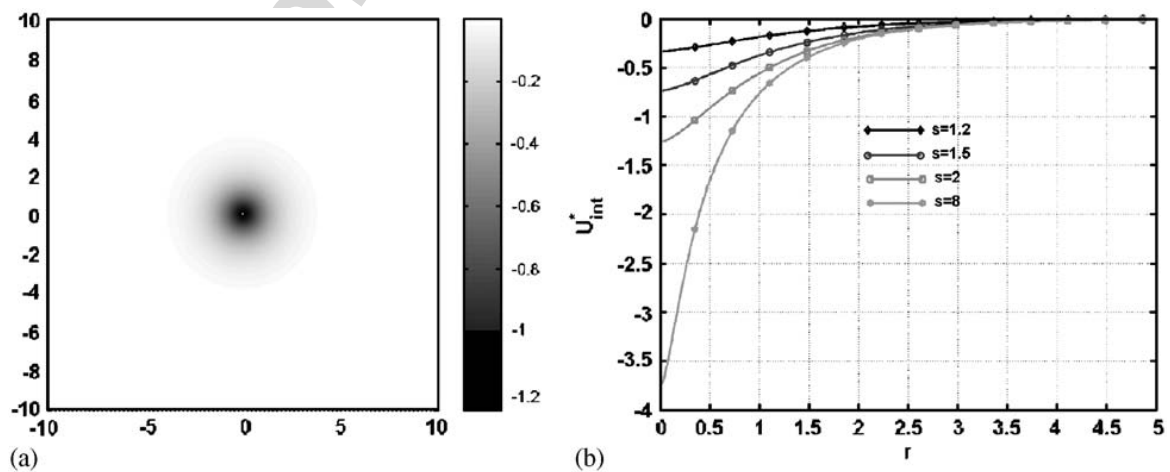


Fig. 7. (a) Interaction energy between two isotropic point defects 1 and 2, with $s = 2$, $v = 0.3$. (b) Interaction energy between two isotropic point defects along one direction.

role. Thus, the result converges to first-order strain gradient result for larger values of s (see Appendix A).

6. Atomistic calculations for defects in graphene sheet and comparison with continuum results

Among the various defects in carbon graphene sheet, Stone–Wales, divacancy, addimer, and oxygen functional group are known to have two-fold symmetry (Fig. 8).

The nucleation and relaxation of Stone–Wales defects (90° bond-flip) are related with the so-called plasticity and brittle-ductile transition in nanotubes, as discussed from atomistic standpoint in early papers (Yakobson, 1997; Yakoson, 1998; Nardelli et al., 1998). Comprehensive analysis of the strength is also recently achieved (Dumitrica et al., 2006). Other researchers have approached this from a continuum viewpoint as well (Jiang et al., 2004; Zhang et al., 2004).

Epoxy bridge group is a chemical group that forms on the graphene sheet, where a single oxygen atom bonds to two adjacent carbon atoms, forming a triangle (Ajayan and Yakobson, 2006). In recent paper (Li et al., 2006) describe how the stress generated by these epoxy bridges leads to unraveling of the graphite lattice. Each epoxy bridge is severely strained, and the geometry of graphene sheet has changed to a 3-D shape.

In order to evaluate the “strength” of the discussed defects, we compute the exact atomic displacements in the vicinity of defect, to be matched with the displacement field in the

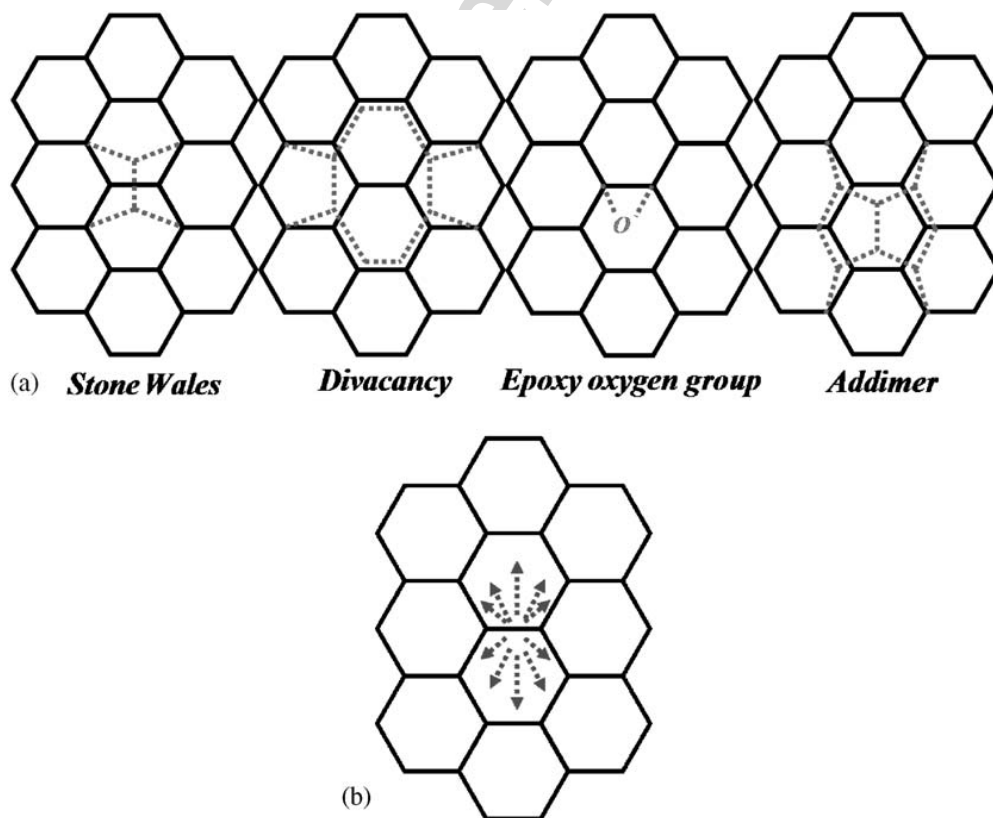


Fig. 8. (a) Schematic description of four kinds of point defects on carbon graphene layer. (b) Force dipoles acting on graphene sheet.

Table 1

Multipole parameters for the Stone–Wales and divacancy defects in graphene

	SW defect	Divacancy	Length scales	
A (eV)	8.49	−97.36	l (Å)	1.23
B (eV)	−105.81	237.07	l_1 (Å)	2.46

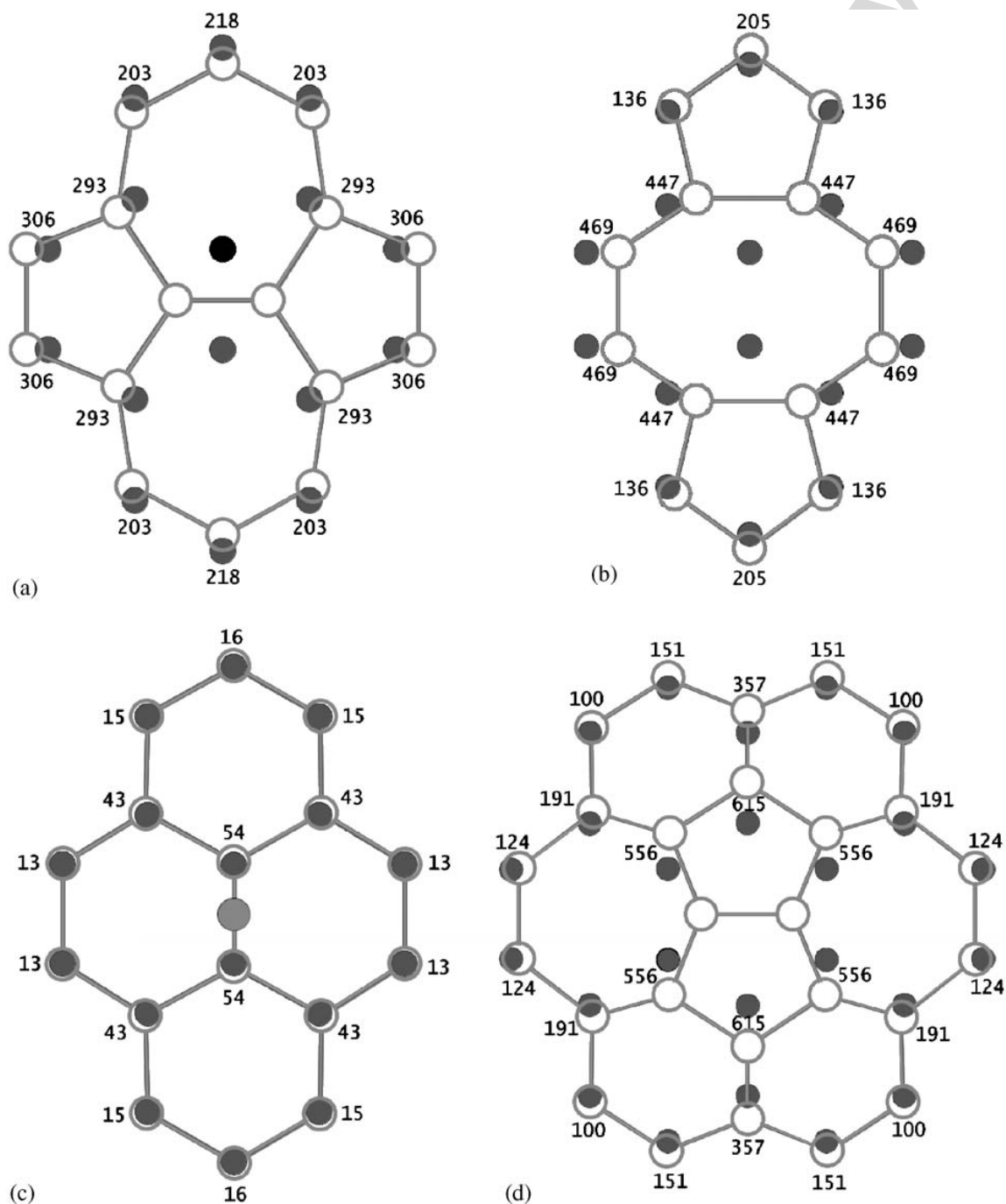


Fig. 9. The displacements of the core part in four different types of defects, in units of 10^{-13} m (0.001 Å). Hollow circles represent the defect structures, dark gray circles and lines/bonds represent perfect graphite lattice, and red circle represents oxygen atom. (a) Stone–Wales defect, (b) divacancy, (c) oxygen atom as epoxy group, (d) addimer, that is two interstitial carbon atoms. Larger vicinity of (a) and (b) are presented in Figs. 10(a) and (b). Oxygen defect and addimer defect are under further study.

continuum representation. Semi-empirical quantum mechanical method PM3 (Stewart, 1989) was used for such evaluation. PM3 is one of the most common semi-empirical methods. It uses the same NDDO functional form with that of AM1. The PM3 method aims to simultaneously optimize the overlap integral parameters for more atoms based on larger data set than AM1 uses. The main improvement of PM3 is that the optimization algorithms applied in this method permitted an efficient search of parameter space, which brings the possibility that the PM3 parameter set may actually be the global minimum in the parameter space. Due to the above reasons, PM3 is a very good method for the geometry purpose use.

All atomic calculations were performed within GAMESS package (Schmidt et al., 1993). In our calculations, perfect graphite sheet was represented by the finite cluster containing 132 carbon atoms and 36 hydrogen atoms, which is sufficiently large, so that the displacements at the edges do not change with the further increase of cluster size. Here, four different types of defects were investigated. After energy optimization, we compare those defects structures with perfect graphite sheet to obtain the displacement vectors, i.e. the strain field. We find that the Stone–Wales bond-flip and the divacancy are exact 2-D defects, where the absence of the off-plane displacements makes it easy to obtain the in-plane strain. On the other hand, oxygen and addimer defects are 3-D, and then we only account for and calculate the displacements in X – Y plane. Hence, oxygen and addimer defects are not appropriate in our 2-D layer model and they are under further investigation and will be presented in future works. The following pictures (Fig. 9) present these displacements.

Corresponding to Samsonidze et al., (2002), the Young's modulus is chosen to be $E = 1020$ GPa with Poisson's ratio of $\nu = 0.33$. In the second-order strain gradient elasticity, there are two length scales l and l_1 . In a previous work of two of the present authors, which dealt with SW defect through dislocations (Li et al. 2005), the first length scale l was fitted to be 1.23 Å. The displacement field obtained by classical elasticity and

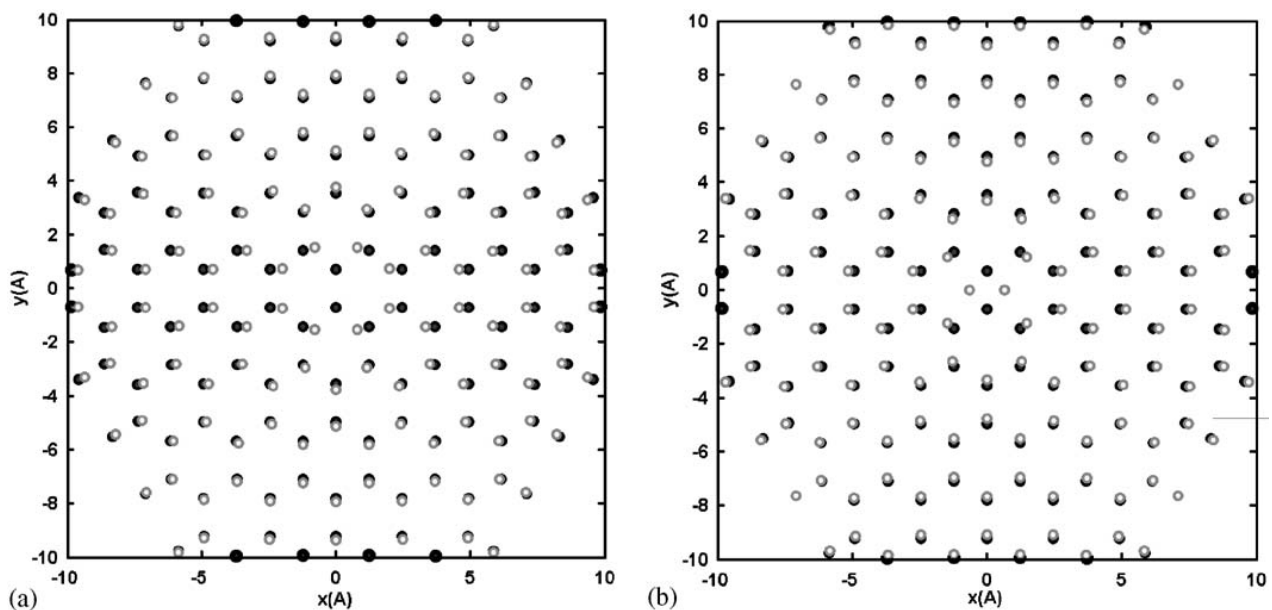


Fig. 10. (a) The positions of atoms of graphene sheet before (blue dots) and after (yellow dots) formation of a single Stone–Wales defect. (b) The positions of atoms of graphene sheet before (blue dots) and after (yellow dots) formation of a single divacancy defect.

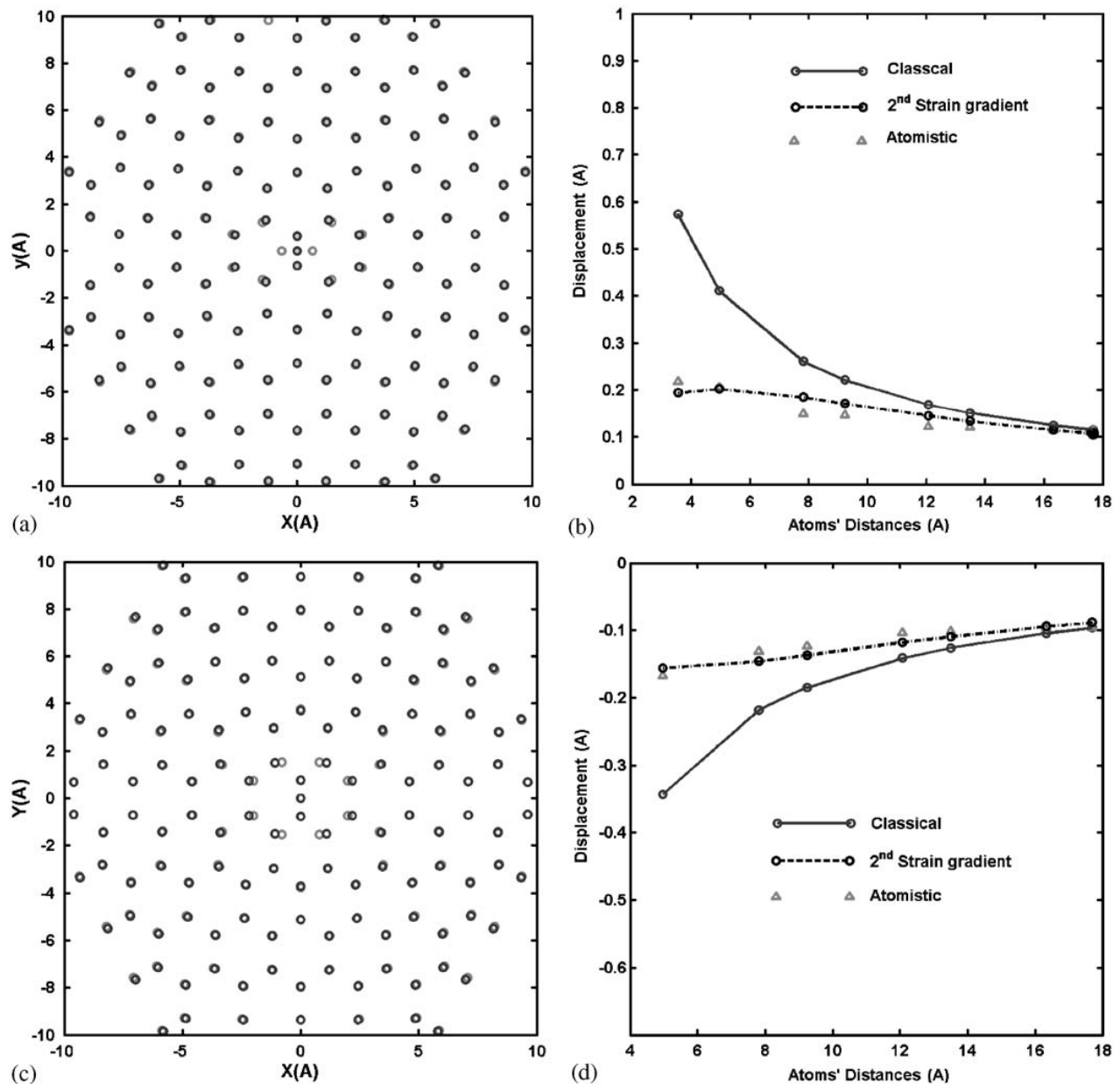


Fig. 11. Comparison of atoms' position predicted by second order strain gradient elasticity, classical elasticity and atomistic simulation: (a) and (c) are atoms' positions predicted by second-order strain gradient elasticity (blue dots) and atomistic result (red dots) for Stone–Wales defect (a) and divacancy (c). (b) and (d) are comparison between the three methods by plotting displacement field along y + direction for Stone–Wales defect (b) and divacancy (d).

second-order strain gradient elasticity must converge at far field. Hence, we can fit the components of force dipole matrix by using far field classical solution directly. The only parameter needs to be fitted is the second length scale l_1 . Since these parameters are material properties not defect properties, such an exercise must be performed only once for a given material. All parameters obtained from the atomistic calculations are tabulated in Table 1.

The displacement results obtained from our continuum model and the atomistic calculations are compared in Figs. 9–11 for Stone–Wales and divacancy defects. The atoms' positions predicted by classical elasticity deviate significantly from atomistic results

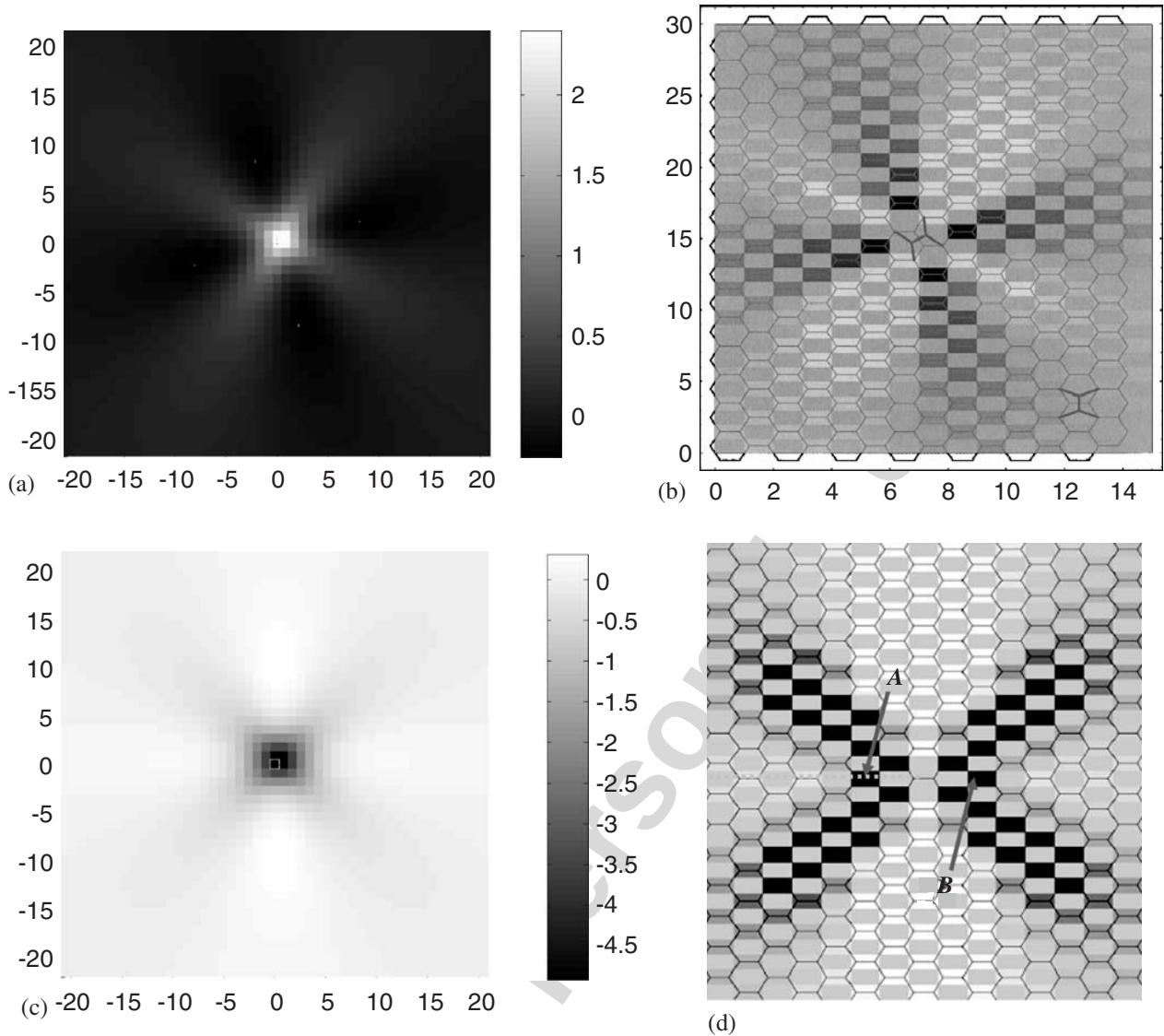


Fig. 12. Interaction energy between two SW defect (of self-angles $\pi/6$ and $\pi/2$, respectively) predicted by strain gradient result (a) and atomic simulation result (b). Interaction energy between two SW defect (of self-angles $\pi/2$ and $\pi/2$, respectively) predicted by strain gradient result (c) and atomic simulation result (d).

in the near field, while they match very well in the far field. In contrast, the displacement field predicted by our enriched continuum model is reasonably close to the atomistic values even for points close to the defect core.

With the obtained defect multipole parameters for SW defect, we can now easily compute the interaction energy between two SW defects which is available in literature (Yakobson et al., 2000; Samsonidze, et al., 2002).

The contour plots of the interaction energy are shown in Fig. 12. Figs. 12(b) and (d) are results from the atomistic calculations. Our model shows excellent match with atomistic results and is extremely fast to implement as the relations are essentially analytical while the atomistic maps of the interaction energy plots shows in Figs. 12(b) and (d) require enormous computational effort. The self-formation energy of a single Stone–Wales defect is easily obtained by Eq. (49). The formation energy is predicted to be 2.86 eV based on our model, which is very close to atomistic result (~ 2.7 eV). Thus the parameters A and B for

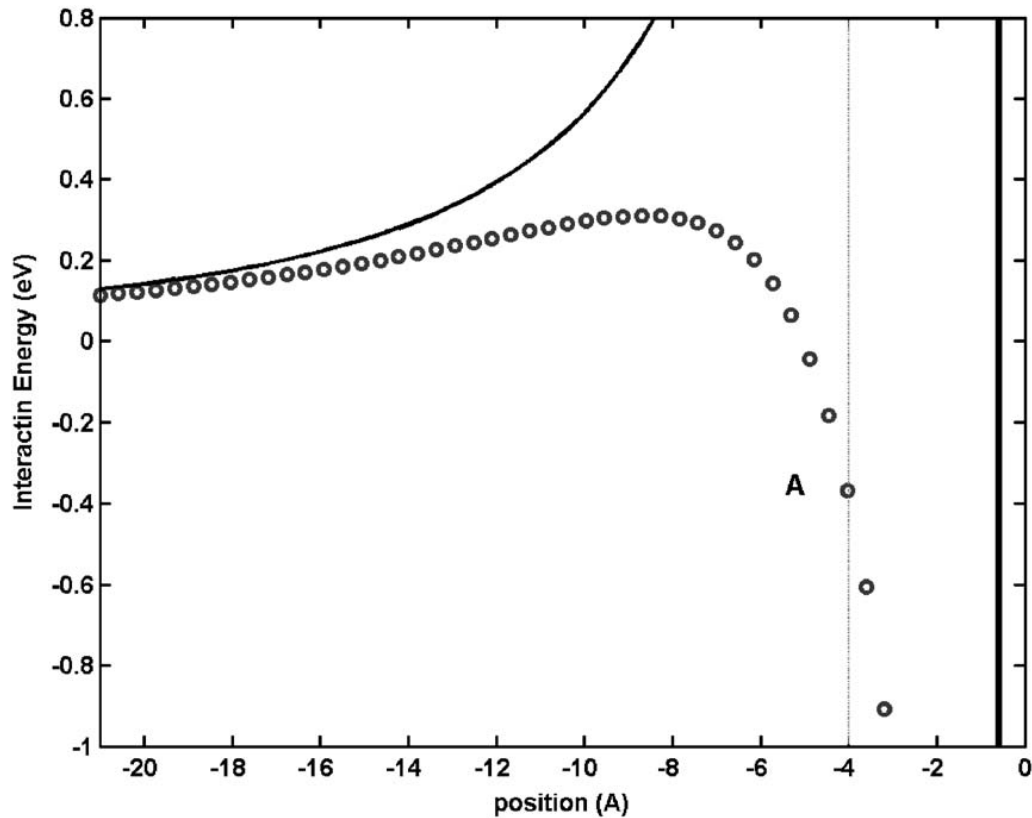


Fig. 13. Interaction energy plot along dashed line in Fig. 12(d). Solid line is classical result and circles correspond to second strain gradient result.

the SW defect need be calculated only once from a simple atomistic calculation and thereafter any number of complex interactions (such as in Fig. 12) may then be faithfully studied using a computationally simpler model developed in the present work rather than a repeat of the atomistic simulations.

In Fig. 12(d), the interaction energies at A and B are not predicted precisely by classical elasticity. To further emphasize the deficiency of classical elasticity, in Fig. 13, the interaction energy is plotted along the dashed line shown in Fig. 13(d). Classical result shows that the interaction energy at A is repulsive, while both our model and atomistics indicate attraction.

We finally note here as an interesting aside that rigorously speaking, while the perfect lattice Green's function asymptotically approaches that of classical elasticity (in the limit of vanishing lattice spacing), the defect Green's function does not (Tewary, 1973). Formally, by resorting to the concept of Kanzaki forces, this may be remedied (Tewary, 1973, 2004). In essence, our fitting of the phenomenological parameters of second gradient elasticity through atomistic simulations is tantamount of finding these forces. A formal derivation relating these two concepts would be an interesting future endeavor.

7. Closure

To summarize, we have formulated a theoretical continuum field framework that addresses defect energetics of different symmetries. Comparison with atomistic calculations, applied in particular to the Stone–Wales and divacancy defect in graphene, yields

qualitative results that are in accord with atomistics; in contrast to the classical elasticity framework, which fails on several accounts. The formal framework and the derived analytical relations, predicated on second strain gradient elasticity, are of interest in its own right and in addition provide a facile atomistically faithful method to parameterize defects of any kind so that atomistic calculations need be performed only once and the more computationally favorable continuum model may be employed for further studies on defect interactions. Such a framework has broad implications beyond what is presented in the present paper e.g. technologically important interactions between functional groups in carbon nanotubes may be mimicked via the same framework. The latter is expected to be pursued by the authors in their future work.

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Appendix A. First strain gradient results for force dipoles

The first strain gradient elasticity is based on first order modification of elastic energy density:

$$W = \frac{1}{2} \lambda \varepsilon_{ii} \varepsilon_{jj} + \mu \varepsilon_{ij} \varepsilon_{ij} + \frac{1}{2} s_1^2 \lambda \varepsilon_{ii,k} \varepsilon_{jj,k} + s_1^2 \mu \varepsilon_{ij,k} \varepsilon_{ij,k}, \quad (50)$$

Euler–Lagrangian equations are:

$$[(1 - l^2 \nabla^2) (\lambda u_{k,k} \delta_{ij} + \mu u_{i,j} + \mu u_{j,i})]_{,j} + f_i = 0, \quad (51)$$

Green's function can be obtained easily by using Fourier transformation:

$$4\pi G_{ij}(R) = \frac{1}{\mu} \left[\frac{1}{R} - \frac{e^{-(R/l)}}{R} \right] \delta_{ij} - \frac{\mu + \lambda}{\mu(2\mu + \lambda)} \partial_i \partial_j \left[\frac{R}{2} + l^2 \left(\frac{1}{R} - \frac{e^{-(R/l)}}{R} \right) \right]. \quad (52)$$

Therefore, the Green's function in 2-D case can be derived as:

$$4\pi G_{ij}^{\text{sg}} = 4\pi G_{ij}^{\text{cl}} + \frac{4(1+v)}{Eh} \left[-K_0 \left(\frac{R}{l} \right) \right] \delta_{ij} + \frac{2(1+v)^2}{Eh} \partial_i \partial_j \left\{ l^2 \left[K_0 \left(\frac{R}{l} \right) + \text{Log } R \right] \right\}. \quad (53)$$

By using above Green's function, interaction energy between point defects can be presented as

$$F_{\text{int}} = \frac{a^2 f^2 (1+v)}{4\pi E h R^2} g, \quad (54)$$

where, g is defined as: $g = g^c + g^{sg}g^c = 4(1 - \nu)(\cos 2\theta_1 + \cos 2\theta_2) + 4(1 + \nu)\cos 2(\theta_1 + \theta_2)$ classical

$$g^{sg} = \frac{1}{r^2} \left\{ \begin{array}{l} -48(1 + \nu)\cos 2(\theta_1 + \theta_2) \\ +4rK_1(r) \left[(12 + 2r^2)(1 + \nu)\cos 2(\theta_1 + \theta_2) + r^2(\nu - 1)(\cos 2\theta_1 + \cos 2\theta_2) \right] \\ +r^2K_0(r) \left[\begin{array}{l} 2r^2(\nu - 1)\cos 2\theta_1 + (24 + r^2)(1 + \nu)\cos 2(\theta_1 + \theta_2) \\ +2r^2(-1 + \nu)(1 + \cos 2\theta_2) + r^2(-3 + \nu)\cos 2(\theta_1 - \theta_2) \end{array} \right] \end{array} \right\}. \quad (55)$$

It can be easily verified that the interaction energy in Eq. (55) would still diverge when R approaches 0. The approaching speed is the same as $K_0(R)$ ($e^{-R/l}/R$ for 3-D), rather than $(1/R^2)$ ($(1/R)$ for 3-D) as classical result.

Physically, the Green's function represents the displacement due to point load. In classical elasticity, the Green's function diverges at the point of load application, which means point load induces infinite displacement at loading point. This is physically unreasonable. First order strain gradient elasticity provides a converging Green's function. Therefore, the displacement given by first order strain gradient elasticity also converges. Unfortunately, strain field does not (for a point force at least—unlike a line defect). This is still physically unreasonable. Meanwhile, second order strain gradient elasticity, as evident from the present work, yields displacement, strain/stress and strain gradient that are regular at origin.

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