Multiscale Green’s function for silicene and its application to calculation of the strain field due to a vacancy[[1]](#footnote-1)

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ABSTRACT

The multiscale Green’s function method is extended to dual planar, two dimensional lattices and applied to calculate the lattice distortion and the strain field due to a vacancy in silicene. The method fully accounts for the discrete atomistic structure of the solid and links the atomistic and the macroscopic continuum scales seamlessly in the asymptotic limit.

INTRODUCTION

Since the advent of graphene, many new two-dimensional (2D) materials have been either fabricated or theoretically proposed [1]. The new monoelemental materials, called Xenes, have a dual planar structure and represent a revolutionary new development in the science and technology of materials. Silicene, a 2D allotrope of silicon, is one of these materials. It has highly unusual electronic and phononic characteristics. Hence, there is a strong international interest in silicene for potential applications in solid state devices for diverse applications such as thermal management, thermoelectric energy conversion, quantum computing, spintronic devices, and biosensors [2].

A reliable and robust mathematical model is necessary for industrial development of new materials via guiding characterization, system testing, and virtual experimentation for providing answers to “what if” type questions. Conventional modeling techniques based upon continuum approximations are not applicable to modern 2D materials. One obvious reason is that the solid has almost zero thickness. This introduces a discontinuity in the derivatives of field quantities, in the direction of the thickness (the Z-direction). Hence, the components of the standard continuum parameters, like stress and strain tensors, that depend upon spatial derivatives in the Z-direction, are not rigorously defined for 2D materials. Modeling 2D materials is, therefore, a multiscale many-body problem [3], which must be valid at the atomistic as well as at the macroscopic scales.

Another characteristic of 2D materials is that their response has a strong size dependence [4]. It is, therefore, necessary to model a large crystallite to avoid spurious contributions from the boundaries. Models using ab initio theories are certainly more accurate, but have a high computational cost, due to the need for including a large number of atoms.

The performance of Xenes is sensitive to the presence of vacancies [5] and other lattice defects, which induce strains in the solid. For example, the thermoelectric response of silicene can be ‘tuned’ via mechanical strain [6]. Calculation of the strain field due to a vacancy in silicene is, therefore, a subject of strong topical interest.

We have been developing computationally efficient multiscale modeling techniques for 2D materials using the multiscale Green’s functions (MSGF) [7]. These techniques are based upon the use of the lattice statics Green’s functions [8] and can model a crystallite containing even a million atoms on an ordinary desktop. The MSGF method also links the atomistic and the continuum scales seamlessly [7]. In a previous paper [3], henceforth referred to as Paper 1, we described the MSGF method for modeling a vacancy in graphene. In this paper, we extend the MSGF method to dual planar 2D lattices and apply it to calculate the strain field produced by a vacancy in silicene.

This paper is a snapshot of our work in progress and serves to illustrate the primary features of the MSGF technique for dual planar lattices. One important characteristic of the MSGF method is that it depends upon the interatomic force constants and not the details of the interatomic potential. [9]. This reduces some of the uncertainties in the calculation of the interatomic potential.

Many details given in Paper 1 are also applicable to this paper and will not be reproduced here. The basic theory of the MSGF method is described in Sec. 2. The calculations and the results, along with a brief discussion, are presented in Sec 3.



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**Fig. 1:** Lattice structure of silicene and the Cartesian frame of reference. The Z- axis is normal to the plane of the paper.

2. THEORY

The lattice structure of silicene is shown in Fig. 1 along with the Cartesian frame of reference. The structure has two sublattices A and B, each on a separate plane. Each corner is a lattice site. The vectors OB1 and OB6 are 2D primitive Bravais lattice vectors on the XY plane, which define a unit cell. The hexagonal Bravais lattice structure of silicene is the same as graphene, discussed in Paper 1. In Fig. 1, unlike graphene, the plane of the A atoms is displaced in the Z direction by +0.45 Å [10]. It implies that, unlike graphene, the displacement field will have a Z component. Unlike graphene, even in the harmonic approximations, the displacements in the X, Y and Z directions will be coupled. This affects the stress and strain components in the XY plane. This coupling is an important difference between silicene and graphene. The atomistic displacements in silicene have components along the Z axis but the Z axis itself is discontinuous. Hence, the derivatives of the displacement field in the Z direction and the corresponding elements of the strain tensor are still undefined.

We assume the Born von Karman model [11] for the silicene lattice with periodic boundary conditions. We denote the lattice sites by L, L’, and the Cartesian coordinates x, y, and z by the Greek indices α, β. The two basis atoms inside each unit cell will be denoted by κ, κ’. The atom at the origin of each unit cell is labelled as κ=0 (type B), whereas the second atom (type A) is κ=1. If N denotes the number of unit cells, the total number of the atoms in the lattice is 2N. We denote the α component of the force on atom Lκ by fα(Lκ), its displacement by uα(Lκ), and its position vector by Rα(Lκ). The force constant (FC) and the Green’s function (GF), which link two atoms Lκ and L’κ’, will be denoted by фαβ(Lκ,L’κ’) and Gαβ(Lκ,L’κ’) respectively. For brevity, we will suppress the indices when not needed.

The position vector of the atom Lκ (Fig. 1) is given by

Rα(Lκ) = Rα(L0) + rα(κ),   
  
where **r**(κ) is the position vector of the atom κ with respect to the origin of the cell, and **R**(L0) is the position vector of the origin of the unit cell L. The atom at **R**(L0) for all values of L are of type B and their Z-coordinate Rz(L0) is zero. The lattice vectors Rα(L0) also define a 2D reciprocal space in terms of reciprocal lattice vectors [9]. A vector in the reciprocal space is denoted by **k**, which is confined to the first Brillouin zone of the hexagonal lattice (Paper 1).

For a perfect lattice with full translation symmetry, **f** and **u** are zero for all Lκ and **ϕ** and **G** depend upon L and L’ only through their difference [9] (L’-L). It is possible, therefore, to express **ϕ**(L,L’) and **G**(L,L’) as a function of the single cell index (L’-L). It enables us to write **ϕ** and **G** in terms of discrete Fourier transforms of a single Fourier variable [7-9]. It is an extremely useful property, which is the basis of our MSGF method [7].

The Fourier transforms of **G** and **u** are defined as follows.

Gαβ(κ,κ’;**k**) = Σ**k** Gαβ(0κ,L’κ’) exp [ι**k**.**R(**L’**)**],

uβ(κ;**k**) = Σ**k** uβ(Lκ) exp [-ι**k.R(**L**)**],

where ι = √(-1). Similar equations are written for **ϕ** and **f or f\***. Their inverse transforms are given below.

uβ(Lκ)= (1/N) Σ**k** uβ(κ;**k**) exp [-ι**k.R(**L**)**].

Gαβ(0κ,Lκ’)= (1/N) Σ**k** Gαβ(κ;**k**) exp [ι**k.R(**L**)**],

Note the absence of the factor (1/N) in Eqs. and . We have used the same symbol for the Fourier transform of a function as for the function itself, the identifying feature being the dependence on **k** shown in the list of arguments.

If a point defect is introduced in an otherwise perfect lattice, it breaks the translation symmetry, changes the force constants to **ξ**, the GF to **U**, induces forces (**f** ≠ 0 ) on the atoms, and causes lattice distortion (**u** ≠ 0). The displacement of each atom defines the displacement field, which in the asymptotic continuum limit, gives the strain field. In this limit, we treat **R**(L0) as a continuous variable. The strain is then defined as the following symmetrized tensor:

ℇαβ = (1/2) [ ∂uα/∂Rβ + ∂uβ/∂Rα ]

In the vector space of the lattice sites, following Paper 1, we treat **G, U**, **ф**, **Δϕ, ξ** as square matrices, and **R**, **r**, **u**, and **f** as column matrices. They are given by:

**U** = (**ξ)**-1 ,

**G** = (**ф)-1** ,

**ξ** = **ф** – **Δф** ,

**U** = **G** + **G** **Δф** **U** ,

**f\* = f + Δф** **u**, .

**u** = **U f**.

Our objective is to calculate the displacement field or **u** for each atom at equilibrium. Equation gives the result in terms of the defect GF and the actual force. Using Eq, , Eq. can be written in the following exactly equivalent form:

**u** = **G f\***,

which gives the same result in terms of the perfect GF and an effective force. Of course, both the results require solution of the Dyson equation . Solution of the Dyson equation for lattice statics has been described in [7-9]. In our present calculations, we use Eq. .

In the Fourier space, Eqs. and reduce, respectively, to the following:

**G**(**k**) = [**ϕ**(**k**)]-1 ,

uα(κ;**k**) = Σ**κ’**βGαβ(κ,κ’;**k**) fβ\*(κ’;**k**).

The displacement field is then given by Eq. . To calculate the strain tensor, we consider the asymptotic limit given by k→0 [7, 8]. In this limit, the lattice sites merge into a continuum and R(L0) is treated as a continuous variable. From Eqs. and ,

ℇαβ[R(L0)]= Re [(ι/2N) Σ**k** [kβuα(0;**k**) + kαuβ(0;**k**)]exp [ι**k.R(**L0**)**]].

The displacements in Eq. are given only for κ=0, that is atoms in the sublattice B. A similar expression can be written for κ=1, the atoms in sublattice A.

Now we estimate the interatomic force constants for silicene by using a model potential for silicon, derived earlier [12, 13]. The underlying idea is that the near neighbor interactions in silicene as well as silicon are partly determined by the overlap of the outer electron wavefunctions and partly by the direct interaction between the ions. This is similar to that used by Davydov [14, 15] in a different context. The model potential extends up to second neighbors. It can reproduce the measured binding energy, elastic constants, and the Raman frequency of silicon. These are the most important measurable parameters of a solid, which determine its lattice statics characteristics such as the strain.

In the harmonic approximation, the lattice statics GF depends only upon the derivatives of the potential at the equilibrium lattice sites. We represent the force constants for silicon by a set of effective central and non-central force constants. We then extrapolate this set to silicene by scaling them with respect to appropriate distances. laThis set is only an extrapolation formula for the force constants and is not meant to be the interatomic potential in silicene.

Let V(r) denote the radial potential at an atom at **r** due to an atom at the origin, the elements of **ϕ** and **f** are given by [8, 9, 16]

ϕαβ = - (rα rβ/r2) (V2 – V1) – δαβ V1,

fα\* = - (rα)V1

where

V1 (r) = dV(r)/rdr,

V2(r) = d2V(r)/dr2,

and the derivatives are evaluated at the equilibrium locations of the atoms. Note that if **r** and ϕαβ for an atom at **r** are known, we can calculate V1 and V2 for that atom. Conversely, **ϕ** and **f**\* can be calculated from V1 and V2 for the same value of **r** without any need to know V(r) explicitly. For Si, we determine V1 and V2 for the first neighbor at aSi(1,1,1) and second neighbor at aSi(2,0,0), where 4aSi = 5.43 Å. We then assume, based upon the justification given above, that V1 and V2 have the same values for first and second neighbors for silicene (see Fig. 1), except for a scale facto, which we assume to be exponentialr. Thus, we estimate the following values of the force constants between the origin and its first two neighbors.  
Note: All **ϕ** matrices are symmetric. Matrix elements not given below are zero.  
Units: **ϕ** in ev/a2; F\* in ev/a; R in units of a, where 2a = 3.82 Å, lattice constant of silicene [10].

Atom A1 : R(Lκ) = (2/√3, 0, 0.23); Fx\* = 14.99; Fz\* = 2.99   
 фxx = -39.66; фyy = - 12.98; фzz = - 14.05; фxz = - 5.32;

Atom B2: R(Lκ) = (0, 2, 0); Fy\* = - 0.91;   
ϕxx = ϕzz = 0.46; ϕyy = - 4.90

RESULTS AND DISCUSSION

The components of the strain tensor for atoms in the Y-direction starting from the atom B9 are plotted in Fig. 2. These are the same atoms selected in Paper 1. The qualitative nature of the curves for silicene is similar to that of graphene. This is expected because the Brillouin zones of the two lattices are identical and the asymptotic behavior of the GF is largely determined by the behavior of the dynamical matrix near the center of the zone. Note that the curves are discrete for near neighbors and become continuous at large distances from the vacancy. This is consistent with the multiscale nature of our model.

The quantitative difference between the two arises because ϕxz ≠ 0 for silicene even in the harmonic approximation (see Eq. ). It introduces coupling between the Z component of the displacement field and its X and Y components. It also couples the off diagonal and the diagonal elements of the strain tensor.

Note that in the region where the curves appear to be discrete, the strain is not defined anyway, because the derivatives don’t exist for a discrete variable. As remarked earlier, the strain is essentially a continuum model parameter. This is also apparent from Eqs. and , which are valid only if **R** and **k** are continuous variables for the derivatives to exist. In the discrete region, the relevant physical parameter is the lattice distortion [8], given by the displacement field in Eq. .

Although our MSGF technique is rigorous, in this paper, we have used a rather crude parametric model for estimating the interatomic force constants and forces. More precise and detailed results, using a more realistic interatomic force constants, will be published later.



**Fig. 2**: Strain field due to a vacancy in silicene at the sites in the Y-directions. Distance from the origin in units of a=1.91 Å.

Conflict of interest: On behalf of all authors, the corresponding author states that there is no conflict of interest.

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