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Multiscale Modeling of Point Defects and Free Surfaces in Semi-infinite Solids

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ABSTRACT

A Green's function method is described for multiscale modeling of point defects such as vacancies and interstitials at the atomistic level and extended defects such as free surfaces and interfaces at the macroscopic continuum level in a solid. The point defects are represented in terms of Kanzaki forces using the lattice-statics Green's function, which can model a large crystallite containing a million atoms without excessive CPU effort. The lattice-statics Green's function reduces to the continuum Green's function in the asymptotic limit which is used to model the extended defects by imposing continuum- model boundary conditions. Numerical results are presented for the displacement field on the free surface due to a vacancy in semi-infinite fcc copper.

INTRODUCTION

We describe a Green's function method for multiscale modeling of point defects such as vacancies and interstitials and extended defects such as free surfaces and interfaces in thin films and semi-infinite solids . Our model treats the point defects at the atomistic level and extended defects at a macroscopic level in the same formalism. We use the lattice-statics Green's function for atomistic modeling of a point defect and the elastic continuum Green's function for modeling an extended defect. In contrast to direct computer simulation methods for lattice statics which are CPU intensive, the advantage of the Green's function method is that it is semi-analytic. Our method can model a large crystallite containing a million atoms without excessive CPU effort. The lattice-statics Green's function reduces asymptotically to the continuum Green's function that we use to model the extended defects. We use our method to calculate strain fields in the solid that contains both point and extended defects.

Many physical properties of thin films and semi-infinite solids depend upon the strains caused by the point defects near the free surfaces and the interfaces. Strain is a macroscopic quantity that can be measured near a free surface. In order to interpret the experimental results, one needs a model to calculate the strains caused by the point defects in the presence of the free surface. Whereas the continuum model is adequate to represent macroscopic extended defects in solids, it is not fully reliable for modeling point defects where the discrete atomistic structure of the crystal lattice is very important (see, for example, [1,2]). It is therefore necessary to use a multiscale model that accounts for the discrete lattice structure of the solid near a point defect and the macroscopic effects near an extended defect. This explains the upsurge of current interest in multiscale modeling of solids.

Recent papers on multiscale modeling are based upon purely numerical techniques using the finite element method and/or computer simulation of the lattice

structure ([3,4]; for an excellent review and other references, see [5]). The purely numerical techniques can be very accurate but they are CPU intensive and are not convenient for parametric design studies. The Green's function method gives accurate results, is computationally convenient, and can provide quick 'what if' answers which is useful for design of experiments.

In this paper we describe the salient features of the Green's function method. For the purpose of illustration, we apply the method to calculate the displacement field at the free surface of a semi-infinite copper crystal containing a vacancy. This paper is a preliminary report of our ongoing work on multiscale modeling of point defects in thin films of metals and semiconductors. Details will be published elsewhere.

THEORY

We consider a monatomic Bravais lattice with a point defect at the origin. We assume a Cartesian frame of reference with an atomic site as origin. We denote the lattice sites by vector indices **l, l'** etc. A vector index **l** has 3 components denoted by l_1, l_2, and l_3. The three-dimensional (3D) force constant matrix between atoms at **l** and **l'** is denoted by $\boldsymbol{\phi}^*(\mathbf{l}, \mathbf{l'})$. The force on atom **l** and its displacement from equilibrium position will be denoted, respectively, by **F(l)** and **u(l)**, which are 3d column vectors. The displacement vectors **u(l)** at each lattice site give the relaxation of the lattice or the lattice distortion caused by the defect.

The force constant matrices for each pair of atoms are 3x3. They are obtained from the interatomic potential as follows:

$$[\boldsymbol{\phi}^*(\mathbf{l}, \mathbf{l'})]_{ij} = \partial^2 V(x)/ \partial x_i \, \partial x_j, \qquad (1)$$

where V(x) is the interatomic potential (assumed to be central) between the pair of atoms **l** and **l'** separated by vector distance **x.** Similarly, the force at the atom **l** due to the atom at the origin at a distance **x** is given by

$$[\mathbf{F(l)}]_i = - \partial V(x)/ \partial x_i. \qquad (2)$$

Following the method given in [1,2], we obtain

$$\mathbf{u(l)} = \Sigma_{l'} \, \mathbf{G}^*(\mathbf{l}, \mathbf{l'}) \, \mathbf{F(l')}, \qquad (3)$$

where, **G*** is the defect lattice Green's function defined by

$$\mathbf{G}^* = [\boldsymbol{\phi}^*]^{-1}. \qquad (4)$$

The sum in eq. (3) is over all lattice sites and Cartesian coordinates which have not been shown explicitly for notational brevity.

In the representation of lattice sites, $\mathbf{G}^*$ and $\boldsymbol{\phi}^*$ are 3N x 3N matrices where N is the total number of lattice sites in the Born von Karman supercell. For a perfect lattice in

equilibrium without defects, **F(l)** is 0 for all **l** and the force constant and the Green's function matrices have translation symmetry. We denote these matrices by ϕ and **G**, respectively. When a defect is introduced in the lattice, **F(l)** becomes, in general, non-zero and the force constant matrix changes. So

$$\phi^* = \phi - \Delta\phi, \tag{5}$$

where $\Delta\phi$ denotes the local change in the force constant matrix ϕ. From eqs. (4) and (5), we obtain the following Dyson equation

$$\mathbf{G}^* = \mathbf{G} + \mathbf{G}\,\Delta\phi\,\mathbf{G}^*, \tag{6}$$

where

$$\mathbf{G} = [\phi]^{-1}, \tag{7}$$

is the perfect lattice Green's function. In the same representation, we can write eq. (3) in the following matrix notation:

$$\mathbf{u} = \mathbf{G}^*\,\mathbf{F}. \tag{8}$$

Using eq. (6), we rewrite eq. (8) as

$$\mathbf{u} = \mathbf{G}\,\mathbf{F}^*, \tag{9}$$

where

$$\mathbf{F}^* = \mathbf{F} + \Delta\phi\,\mathbf{u}. \tag{10}$$

Equation (9) gives the displacement in terms of the perfect lattice Green's function and an effective force denoted by **F*,** the so called Kanzaki force [1]. From eq. (10), we can identify it as the force due to the defect on relaxed lattice sites in contrast to **F** which denotes the force at the unrelaxed original lattice site. Equation (9) is applicable to any point defect such as a vacancy, an interstitial, or a substitutional impurity.

For the perfect lattice, **G(l,l')** has translation symmetry and therefore can be labeled by a single index **l-l'**. It is calculated by using the Fourier representation

$$\mathbf{G(l)} = (1/N)\,\Sigma_{\mathbf{q}}\,\mathbf{G(q)}\,\exp[\,\iota\mathbf{q}.\mathbf{l}], \tag{11}$$

where $\iota = \sqrt{-1}$, N is the total number of atoms,

$$\mathbf{G(q)} = [\phi(\mathbf{q})]^{-1}, \tag{12}$$

$\boldsymbol{\phi}(\mathbf{q})$ is the Fourier transform of the force constant matrix, and **q** is a vector in the reciprocal space of the lattice. For brevity of notation, we shall use the same symbol for a function and its Fourier transform, the distinguishing feature being the argument of the function. Since $\mathbf{G}(\mathbf{q})$ and $\boldsymbol{\phi}(\mathbf{q})$ are 3 x 3 matrices, eqs. (11) and (12) can be used to calculate the perfect lattice-statics Green's function **G(l,l')**.

We define the defect space as the vector space generated by **l,l'** for which $\Delta\boldsymbol{\phi}$ is non-vanishing. We solve the Dyson equation for the defect Green's function by using the matrix partitioning technique [1]. The reduced Dyson equation in defect space is given by

$$\mathbf{g}^* = \mathbf{g} + \mathbf{g}\,\Delta\boldsymbol{\phi}\,\mathbf{g}^*, \tag{13}$$

where **g**, $\mathbf{g}^*$ are components of **G** and $\mathbf{G}^*$ in defect space. The matrices in eq. (13) are 3n x 3n matrices, where n is the number of atoms in the defect space. For point defects, n is small so eq. (13) can be solved by direct matrix inversion as given below:

$$\mathbf{g}^* = (\mathbf{I} - \mathbf{g}\,\Delta\boldsymbol{\phi})^{-1}\mathbf{g}, \tag{14}$$

where **I** is the unit matrix.

For an fcc lattice in which the defect interacts up to its second neighbor atoms, the matrices in eq. (14) are 57x57. Since a point defect such as a vacancy retains the local point-group symmetry of the lattice, we can use group theory to simplify eq. (14) considerably. In the above case of a vacancy in an fcc lattice, eq. (14) can be reduced to a 2x2 matrix equation.

By definition, the force matrix defined by eq. (2) is nonvanishing only in the defect space. Using eqs. (8) and (13), we obtain for all atoms in the defect space

$$\mathbf{u} = \mathbf{g}^*\,\mathbf{F}. \tag{15}$$

After calculating **u** for all atoms in the defect space, we calculate the Kanzaki force in the defect space by using eq. (10). Then the displacement of all atoms in the solid is given in terms of the perfect lattice Green's function by using eq. (9). The Kanzaki force contains the full contribution of the discrete lattice structure in the defect space.

It can be shown [1] that the perfect lattice Green's function reduces asymptotically to the continuum Green's function. For this purpose, we make **l** and **q** continuous variables and replace the summation in eq. (11) by integration over the reciprocal space. In conformity with the continuum model notation, we replace **l** by **x** for large l, which will denote the position vector corresponding to the lattice site **l**. Thus, in the limit $x \to \infty$,

$$\mathbf{G}(\mathbf{x}) = (1/2\pi)^3 \int \mathbf{G}_c(\mathbf{q}) \exp(\imath\mathbf{q}.\mathbf{x})\, \mathbf{dq}, \tag{16}$$

where, keeping terms up to q^2 in $\boldsymbol{\phi}(\mathbf{q})$,

$$\mathbf{G_c(q)} = \mathrm{Lim}_{q\to 0}\, \mathbf{G(q)} = \mathrm{Lim}_{q\to 0}\, [\boldsymbol{\phi}(\mathbf{q})]^{-1} = [\boldsymbol{\Lambda}(\mathbf{q})]^{-1}. \qquad (17)$$

In eq. (17), $\boldsymbol{\Lambda}$ is the Christoffel matrix, which is defined in terms of **c**, the elastic constant tensor, as follows:

$$\Lambda_{ij}(\mathbf{q}) = c_{ikjl}\, q_k\, q_l, \qquad (18)$$

where i,j,k,l, etc. are Cartesian indices that assume the values 1-3. Summation over repeated indices is implied.

Equation (9) is our master equation for multscale modeling. At large distances from the point defect, we replace **G** by the continuum Green's function defined by eq. (17) but use the lattice value of **F*** as defined in terms of the lattice Green's function by eqs. (8) and (9). Thus the displacement field in our multiscale model at the position vector **x** is given by the following sum over the defect space:

$$\mathbf{u(x)} = \Sigma_{\mathbf{l'}}\, \mathbf{G_c(x-l')}\, \mathbf{F^*(l')}. \qquad (19)$$

Since the distance between the lattice sites in the defect space over which **F*** is distributed, is much less than x, $\mathbf{G_c(x-l')}$ can be calculated in terms of the derivatives of the continuum Green's function.

We can now incorporate the effect of extended defects in $\mathbf{G_c}$ by imposing appropriate boundary conditions using the standard techniques of the continuum model. As an example, we will consider a semi-infinite solid with a free surface. We choose a frame of reference in which the origin and the X- and Y- axes are on the free surface and the positive Z-axis points into the solid. The zero-traction boundary condition at the free surface, which is taken to be the plane at $x_3=0$, is given by

$$\tau_{i3}(\mathbf{x}) = c_{i3jk}\, e_{jk}(\mathbf{x}) = 0 \qquad (x_3=0), \qquad (20)$$

where

$$e_{jk} = \partial u_j(\mathbf{x})/\partial x_k, \qquad (21)$$

e and $\boldsymbol{\tau}$ denote the strain and stress tensors respectively.

Various computationally efficient representations of the continuum Green's function for anisotropic semi-infinite solids are available in the literature [6,7]. In this paper, since our objective is just to illustrate the multi-scale modeling technique, we will assume for simplicity that the solid is elastically isotropic. The solution for the isotropic continuum case was obtained by Mindlin [8]. The result for the displacement field at the free surface at a radial distance r from the origin is quoted below:

$$4\pi u_r/f = -rh/R^3 + \mu r/[(\lambda+\mu)(R-h)R], \qquad (22)$$

and

$$4\pi u_z/f = (R^2 + h^2)/R^3 + \mu/[(\lambda+\mu)R], \qquad (23)$$

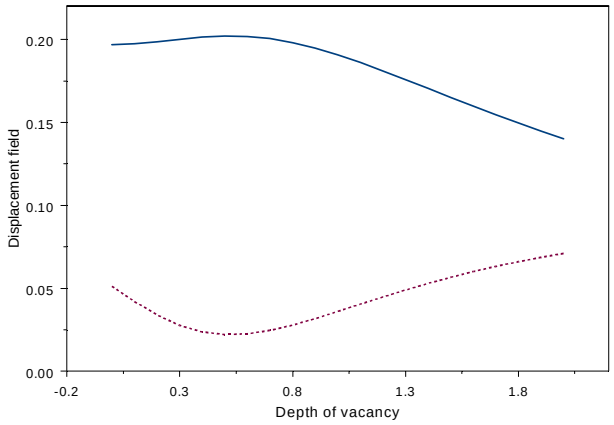

Figure 1 Displacement field at the free surface of fcc copper due to a vacancy as a function of h, the distance of the vacancy from the free surface. Solid line- u_z, the Z-component; broken line- u_r, the radial component in cylindrical coordinates.

where we have used cylindrical coordinates, u_r and u_z are, respectively, the radial and the Z-components of the displacement field, f is the magnitude of the force in units of $8\pi\mu$ $(\lambda +2\mu)/(\lambda +\mu)$ acting at at (0,0,h), λ and μ are the Lame constants, and $R^2 = (r^2 + h^2)$.

RESULTS AND CONCLUSIONS

Figure (1) gives the calculated values of u_r and u_z as a function of h at the free surface at r=1 due to a vacancy at (0,0,h) in fcc copper. The free surface is taken to be a (1,0,0) plane. We assumed a simple model interatomic potential due to Bullough and Hardy (see [1]) extending up to second neighbors. The lattice-statics Green's function is calculated for a million-atom model using the method given in [1], which gives **F***. The defect space consists of the vacancy, its 12 nearest neighbors, and 6 second neighbors.

The main conclusion of this paper is that the Green's function method for multiscale modeling can be used to model a large crystallite at the atomistic level without excessive CPU effort and, in the same formalism, include the macroscopic defects such as free surfaces and interfaces using the standard techniques of the continuum model.

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