Multiscale modeling of quantum nanostructures using integrated Green's function and molecular dynamics[*]

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Summary

A multiscale mathematical model is described for a nanostructure in a semi-infinite anisotropic solid containing one free surface. A modified form of molecular dynamics is used to calculate the equilibrium configuration of atoms in and close to the nanostructure, which are coupled to the host lattice through the lattice statics Green's function. This gives a fully atomistic description of a nanostructure that includes the effect of nonlinear forces embedded in a large crystallite consisting of a million atoms or more. The lattice statics Green's function is then related to the anisotropic continuum Green's function that is used to model the free surface and also to relate the discrete lattice distortion to measurable continuum parameters such as the displacement and the strain fields at the free surface. The model is applied to a gold nanoisland embedded in fcc copper and a germanium quantum dot in silicon.

Introduction

A nanostructure is usually embedded in a lattice of a different material and can be treated as either a defect or an inclusion. A defect in a crystal lattice distorts the lattice. The lattice distortion is defined as the displacement of atoms from their equilibrium lattice sites and is a discrete variable. The corresponding quantity in the continuum model of a solid is the elastic strain. In order to interpret the measurement of strains, it is necessary to have a multiscale model that can relate parameters of the macroscopic continuum model to those of the discrete atomistic model of a solid.

A mathematical model for a nanostructure should account for at least one free surface in the solid since the measurements are usually made at or near a free surface. The model should satisfy the following criteria: (i) it must account for the discrete structure of the lattice in and around the nanostructure and, therefore, the crystallite must be sufficiently larger than the nanostructure, (ii) the crystallite must be large enough to include a free surface and for the lattice distortions to smear out into a continuum, so that the continuum parameters such as the strain and the displacement fields can be defined, (iii) the continuum parameters have to account for the elastic anisotropy since most materials of

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practical interest are anisotropic, (iv) the model must include nonlinear interactions between atoms inside and close to the nanostructure even if the host lattice is harmonic, and, finally, (v) the model should be computationally efficient.

The criteria (i), (ii), and (iii) require the model to be multiscale and bridge the length scales from the atomistic through to the macro continuum. The existing models (for an excellent review and other references, see, for example, [1,2]) do not meet all the above five criteria. The lattice statics Green's function (LSGF) method [3] is computationally efficient and can model large crystallites but does not account for the nonlinear interactions. Molecular dynamics (MD) accounts for nonlinear forces but is usually limited to crystallites of only a few hundred atoms. Powerful techniques based upon MD have been developed by Vashishta et al. [4] to model large crystallites but these techniques are computationally intensive. MD calculations using flexible boundary conditions derived from the Green's function [5] and purely numerical techniques [6] based upon finite element methods have been developed for some defect systems. No existing multiscale modeling technique has been applied to a nanostructure and a free surface in a large model crystallite consisting of a million or more atoms.

In an earlier paper [7] we presented a multiscale Green's function method that integrates the LSGF method for a million-atom crystallite with the continuum Green's function (CGF) in the macroscopic limit and applied it to model point defects and extended defects in metals. We have now integrated [8] this method with MD in the core of a nanostructure at the subnanometer scale. By incorporating MD in our model, we include the nonlinear effects in the core of the nanostructure and obtain a fast algorithm for modeling a large crystallite.

In our method the core of the defect or the nanostructure, where the nonlinear effects are significant, is modeled by using MD. This is the subnanometer scale region including a few hundred to a few thousand atoms, which can be easily handled by MD. The core is surrounded by a shell to which the core atoms are pegged in the MD calculations. The lattice beyond the core is modeled by using the LSGF method for a million-atom crystallite. This integrated method has the advantages of both techniques. It models a large crystallite and includes nonlinear effects in the core but without excessive computational requirements. The LSGF reduces to the CGF at large distances from the core. The CGF is then used to model a free surface as in the Mindlin problem [9]. Thus our model integrates MD, LSGF, and CGF and meets all the five criteria given above. We will refer to our model as the GFMD model.

This paper briefly reviews the GFMD model and the lattice distortion in and around a gold (Au) nanoisland in fcc copper. The details of the method will be published in [8]. Work on its application to a germanium quantum dot in silicon is in progress and will be reported at the conference.

Theory of the GFMD model

We consider the Born-von Karman model for the host lattice assuming short-range interatomic interactions. We assume a Cartesian frame of reference with an atomic site as origin and the coordinate axes parallel to the crystallographic axes. We denote the lattice sites by vector indices **l, l'** etc.

The potential energy of the crystal can be written as

$$W^* = \sum_{\mathbf{l}} W_{\mathbf{l}}(x_{\mathbf{l}}), \tag{1}$$

where

$$x_{\mathbf{l}} = r_{\mathbf{l}} + u_{\mathbf{l}} \tag{2}$$

denotes the instantaneous position of the atom **l, $r_{\mathbf{l}}$** its equilibrium lattice site, and $W_{\mathbf{l}}$ is its potential energy in the field of all other atoms. The sum over **l** in eq. (1) extends over all the atoms in the crystal. A perfect lattice with no defects has translation symmetry, so the form of the potential energy function $W_{\mathbf{l}}$ is independent of **l** for a perfect lattice.

We assume that n_A sites of the host lattice at the center of the supercell are occupied by foreign atoms. All the foreign atoms are assumed to fill all of the host lattice sites in a cube centered at the origin of the coordinates. We shall refer to this cube as the inner core. We further identify an outer cubic core that encloses the n_A foreign atoms and n_B host atoms. The size of the outer core is chosen such that it includes at least those atoms with which the atoms of the inner core interact directly. Obviously, in this model the atoms of the inner core will not directly interact with any atom of the host lattice outside the outer core. The core consisting of $n_A + n_B$ atoms is treated as a defect in our model.

We further identify a shell cube by drawing another cube containing n_C atoms that encloses the defect cube and is also centered at the origin of the coordinates. The size of the shell cube is assumed to be much smaller than the size of the Born von Karman supercell. The region of the supercell outside the shell is referred to as the host region.

Now we write the total potential energy of the crystal given by eq. (1) as

$$W^* = \sum^*_{\mathbf{l'}} W_h(x_{\mathbf{l'}}) + \sum^s_{\mathbf{l''}} W_{h'}(x_{\mathbf{l''}}) + \sum^c_{\mathbf{L}} W_c(x_{\mathbf{L}}), \tag{3}$$

where W_h is the potential function for a host atom, which is interacting only with other host atoms, $W_{h'}$ is the potential function for a host atom interacting with other host atoms as well as atoms in the defect cube, and W_c is the potential function of an atom in the defect cube interacting with other defect or host atoms. The superscripts *, s, and c over

the summation signs on the right hand side (RHS) of eq. (3) indicate that the summation is over a limited range of sites: the index $\mathbf{l'}$ goes over all lattice sites outside the shell cube. The index $\mathbf{l''}$ goes over all lattice sites in the shell region (excludes the inner and outer core), and $\mathbf{L}$ goes over all the lattice sites of the defect cube. In case of a many-body potential, which we assume in our calculations, each potential function depends upon the coordinates of many atoms.

We rewrite eq. (3) as follows:

$$W^* = W_0 + \Delta W, \tag{4}$$

where

$$W_0 = \sum_{\mathbf{l}} W_h(x_{\mathbf{l}}), \tag{5}$$

and ΔW contains the remaining terms in eq. (3). The sum in eq. (5) is over all the lattice sites of the perfect lattice. We define W_0 as the energy of the reference state and ΔW as the change in the energy of the reference state caused by the defect. The interaction between each atom in the reference state is assumed to be harmonic. The defect space, as defined in [3], consists of the coordinates of all the atoms in the defect cube and those atoms in the shell with which the atoms in the defect cube directly interact.

The atomic displacements at equilibrium are obtained by minimizing the total energy of the defect state given by eq. (4) which gives

$$\partial W_0(x_{\mathbf{l}})/\partial u_{\mathbf{l}} = F_t(\mathbf{l}), \tag{6}$$

where

$$F_t(\mathbf{l}) = -\partial[\sum_{\mathbf{l''}}^{s} \Delta W_{h'}(x_{\mathbf{l''}}) + \sum_{\mathbf{L}}^{c} \Delta W_c(x_{\mathbf{L}})]/\partial u_{\mathbf{l}} . \tag{7}$$

The solution of eq. (6) in matrix notation is

$$\mathbf{u} = \mathbf{G}\, \mathbf{F}_t , \tag{8}$$

where $\mathbf{G}$ is the Green's function matrix [3,7] for the reference state. The force $\mathbf{F}_t$ can be identified as the Kanzaki force defined in [3,7] and is nonvanishing only in the defect space. We calculate $\mathbf{F}_t$ by iteratively using MD and the Green's function. In each MD iteration, we treat the displacements of the atoms in the shell as fixed and then calculate these displacements by using the LSGF in the next iteration.

Once we obtain $\mathbf{F}_t$, we calculate the atomic displacements everywhere in the crystal by using the LSGF in eq. (8). The calculation and properties of the LSGF have been discussed in detail in [3]. Finally, to account for a free surface, we use the Mindlin CGF [9,10] for $\mathbf{G}$ in eq. (8), as has been done for a vacancy in copper [7]. By using the CGF, we can calculate the displacement and the strain fields at the free surface.

We have applied the GFMD technique to model a 63-atom Au nanoisland embedded in fcc Cu containing a free (1,0,0) surface. We used the many-body potential derived by Cleri and Rosato [11] in these calculations. In our model, $n_A = 63$, $n_B = 7750$, and $n_C = 10156$. The number of atoms in the Born von Karman supercell for the calculation of the LSGF was 10^6. Lattice distortion in the Au nanoisland is shown in Fig. 1. The filled circles denote the equilibrium positions of the atoms, whereas their original positions are denoted by empty circles. The diameter of the circles is chosen for visual convenience and has no physical significance. More numerical results on Au nanoisland in Cu and a Ge quantum dot in Si will be presented at the conference.

Conclusions

We have described the GFMD technique for modeling a nanostructure in a semi-infinite solid containing a free surface. The technique combines MD, LSGF, and CGF and thus links the length scales from atomistic (subnanometers) to macroscale without excessive computational requirements. The model enables us to relate discrete atomic displacements with measurable macroscopic elastic parameters such as the strain and the displacement fields at the free surface without any need for an arbitrary averaging ansatz.

Acknowledgements

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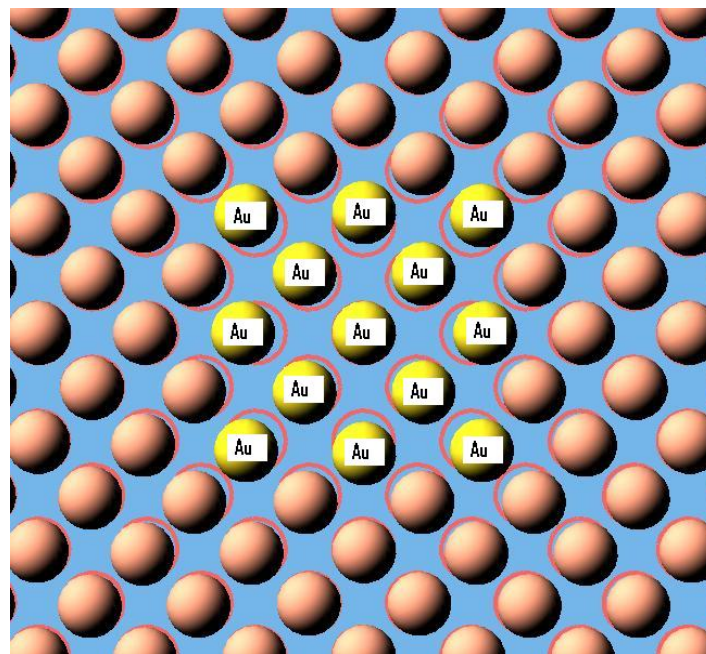
Fig. 1: Equilibrium position of the atoms in and around Au nanoisland in fcc Cu on the (0,0,1) plane. The empty circles denote the original lattice sites. Size of the circles is chosen arbitrarily for visualization. Au atoms as marked, Cu atoms unmarked.