

## Ab Initio Studies of Defect Structures and Deformation

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### ABSTRACT AND BACKGROUND

The primary goal of this project is to study the material-specific mechanical and thermodynamic properties. We use *ab initio* calculations, combined with tight-binding and embedded atom model (EAM) potentials to examine lattice stability and the structure and energy of lattice distortions, including elastic deformations, phonon modes, dislocations and other defect structures.

One area of interest is atomistic modeling of dislocation core structures, energies, and mobilities. In recent years, there has been a strong interest in the fundamental description of plastic deformation of real materials. The difficulty in rigorously understanding the mechanisms that contribute to the deformation behavior is due to the fact that dislocation motion depends upon the atomic structure of the dislocation core, the energies of kinks along the dislocation and the Peierl's stress required to move the dislocation or kinks in the materials. These various competing effects are determined by energetics at the atomic scale, in addition to the stress field usually associated with the dislocations. We have performed calculations to study two important fundamental classes of materials: the bcc metals and the diamond-structure materials. Mo and Si have been studied as the prototype of these materials in our calculations.

We are also interested in behavior of materials at high temperature, high radiation, and corrosive

environments, in particular the dynamics of defect at high temperature. We have performed tight-binding molecular dynamics and *ab initio* calculations to study the diffusion, coalescence, and reconstruction of vacancy defects in graphene layers. We will also study the vacancy formation and diffusion in bulk Al in the presence of hydrogen alone and in the presence of metallic impurities such as Cu and Pb. Such information will be very useful as inputs into kinetic Monte Carlo simulations to understand the void formation in Al under corrosive environment.

Tight-binding potentials have emerged as an important class of potentials bridging the gap between the *ab initio* methods and empirical classical potentials for materials simulations. Tight-binding molecular dynamics, in combination the anisotropic elastic theory to treat the long-ranged elastic interactions, is a very powerful approach to tackle the very complex subject of mechanical properties of materials. Our group has pioneered the development and application of tight-binding potentials. We have developed accurate tight-binding potentials for C, Si and Mo, and recently for simple metallic systems such as Al and Pb.

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### TECHNICAL HIGHLIGHTS

- Calculated the structure and competing energetics of possible  $\{10\bar{1}2\}$  twin boundaries in hexagonal-close-packed metals, suggesting a new structure for such defects.
- Calculated the role of grain size on strengthening of materials, using dislocation dynamics.
- Calculated the structure and properties of amorphous carbon using tight-binding molecular dynamics
- Performed tight-binding molecular dynamics calculates to study the  $\langle 111 \rangle$  screw dislocation core structure and Peierl's stress in bcc Mo.
- Discovered a double-period glide set dislocation structure for Si screw dislocation based on tight-binding and *ab initio* calculations.

- Performed tight-binding molecular dynamics and ab initio calculations to study the diffusion, coalescence and reconstruction of vacancy defects in graphene layers.

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### INTERACTIONS WITH OTHER PROJECTS AND PROGRAMS

These studies were carried out in closely collaboration with J. R. Morris at Oak Ridge National Laboratory. The calculations and modeling of dislocation structures are performed in collaboration with J. Li at Ohio State University, and with S. Yip of Massachusetts Institute of Technology. Work on mesoscopic modeling of mechanical properties is in collaboration with S.B. Biner's effort "Mechanics and Mechanisms of Deformation". The work on amorphous carbon is done in collaboration with G. Kopidakis and P. C. Kelires of University of Crete, Greece. The work on diffusion and coalescence of vacancy defects in graphene is done in collaboration with Gun-Do Lee of Seoul National University, South Korea. Some of the work by J. R. Morris is supported through the "Alloy Behavior and Design" project supported by BES through Oak Ridge National Laboratory.

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### SELECTED PUBLICATIONS

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J.R. Morris, Y.Y. Ye, and M.H. Yoo, "An ab initio Calculation of the Structure and Energies of {1012} Twin Boundaries in Zr, Ti and Mg," *Phil. Mag.*, **85**, 233 (2005).

C.Z. Wang and K.M. Ho, "Tight-binding Molecular Dynamics for Carbon and

Applications to Nanostructure Formation," *J. Computational and Theoretical Nanoscience*, **1**, 1 (2004).

C. Mathioudakis, G. Kopidakis, P.C. Kelires, C.Z. Wang, and K.M. Ho, "Physical Trends in Amorphous Carbon: a Tight-binding Molecular Dynamics Study," *Phys. Rev. B*, **70**, 125202 (2004).

J. Li, C.Z. Wang, J.-P. Chang, W. Cai, V. Bulatov, K.M. Ho, and S. Yip, "Core Energy and Peierls Stress of Screw Dislocation in Molybdenum: a Periodic Cell Tight-binding Study," *Phys. Rev. B*, **70**, 104113 (2004).

C.Z. Wang and K.M. Ho, "Environment-Dependent Tight-binding Models," *Handbook of Materials Modeling*, **1**, 307, Ed. S. Yip (Springer, 2005).

G.-D. Lee, C.Z. Wang, E. Yoon, N.-M. Hwang, D.-Y. Kim, and K.M. Ho, "Diffusion, Coalescence and Reconstruction of Vacancy Defects in Graphene Layers," *Phys. Rev. Lett.* (accepted).

## Atomistic Modeling of Dislocation Core Structures in Mo and Si

**Personnel:** C.Z. Wang (PI) and K.M. Ho (PI)

### Scope:

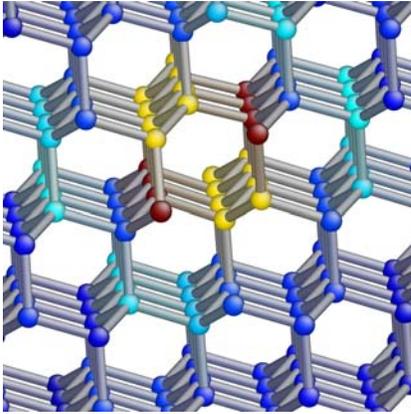
Defects such as dislocations, dislocation jogs and kinks determine the mechanical behavior of materials at the smallest length scales. The dislocation core structures along with their Peierls stresses are critical for understanding plastic deformation, but may only be examined at the atomistic scale. Using a combination of *ab initio* calculations and accurate empirical tight-binding molecular dynamics, we calculate the properties of these defects, including their atomistic structure, energies, and barriers of motion. By providing an accurate, material-specific description of the structures and energies of these defects, we will greatly further understanding of the mechanical properties of specific materials. Prototype systems being studied include Si and Mo, where there is both fundamental interest as well as important technological importance.

### Research Highlights:

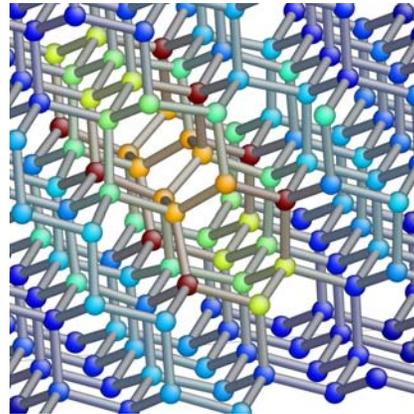
Calculation of Dislocation Properties in Mo. The bcc metals, which include Fe, Mo, and Ta, provide a prototypical system in which the dislocation cores are important in determining the plastic response. In particular, the  $b=1/2\langle 111 \rangle$  screw dislocations are the key limiting factor in plastic deformation of these metals. The dislocation cores may have two structures: the "unpolarized" core in which the [101] dyad symmetry of the bcc crystal is preserved, and the "polarized" core in which the symmetry is broken with the core spreading along the  $\{112\}$  planes. The structure of these cores, and their ease of motion for slip on the  $\{110\}$  or  $\{112\}$  planes, determine the primary deformation mechanism as well as the likelihood of cross-slip of the dislocation between these planes. In collaboration with Prof. Ju Li at Ohio State University and Prof. Sidney Yip at MIT, we have studied the structure and mobility of a screw dislocation in the bcc transition metal Mo. In our studies, the long-range anisotropic elastic energy is taken into account rigorously using methods developed at MIT. Using the environment-dependent tight-binding potential of Mo developed by us, we have performed tight-binding molecular dynamics calculations to study the atomistic structure of the  $\langle 111 \rangle$  screw dislocation core in Mo. Comparison with available LDA calculation results indicates that the core structure predicted from our tight-binding calculations accurately describes the atomic configuration of the system. The tight-binding equilibrium core structure has zero polarity. The Peierls stress is calculated to be 3.8 GPa. Our results suggest that such a large Peierls stress in Mo is due to the non-planar to planar transition of the core rather than a direct effect of the equilibrium core polarity.

Discovery of New Core Structure for Si Screw Dislocation. A second class of material in which the core structure is known to play an important role is the diamond-structure system, most notably silicon, as well as carbon, germanium and the III-V compounds. In this case, the primary slip system is associated with  $\{111\}$  planes moving along the  $b=1/2\langle 110 \rangle$  direction. Most of the large number of previous atomistic computations were devoted to partial glide dislocations, with particular attention to reconstructions of the  $30^\circ$  and  $90^\circ$  partials. While the partial dislocations of the glide set have been observed in experiments at high temperatures, recent studies show that plastic deformation occurring at room temperature under high pressure ( $\sim 5$ GPa) involves the formation of undissociated dislocations. This new discovery has stimulated a lot of theoretical studies in the past several years, using both empirical potentials and first-principles calculations. The core structure of the undissociated dislocation was proposed to belong to the shuffle set (called shuffled A core) as shown in Fig. 1. In collaboration with Prof. Ju Li at Ohio State University and Prof. Sidney Yip at MIT, we have performed tight-binding molecular dynamics calculation, in combination with anisotropic elastic theory, to study the core structure of the perfect screw dislocations in silicon. We found that the glide set dislocation with double period reconstruction along the

dislocation line as show in Fig. 2 has a much lower energy ( $\sim 0.6$  eV per Burgers vector) than the shuffle-set A dislocations, which were previously thought to be the lowest energy structure. Our results by tight-binding molecular dynamics simulation were confirmed by first-principles total energy calculations.



**Fig. 1** Shuffle set dislocation A in Si.



**Fig. 2** Double-period glide set dislocation in Si.

### **Impact:**

Our discovery of the double-period glide set dislocation core structure in silicon will stimulate further theoretical and experimental studies to re-exam the pathways of dislocation motions and plastic deformation mechanisms in this class of materials. Our calculations of dislocation properties in molybdenum demonstrate that the tight-binding approach is a very promising method for studying the complex mechanical behaviors in bcc transition metals.

### **Future Work:**

We will continue to perform tight-binding and first-principles calculations to study the Peierls stress associated with the perfect dislocations and the formation and migration energies of dislocation kinks in silicon. Such calculations require significantly larger systems than those required for the perfectly straight dislocation core, and therefore the tight-binding description will be essential for quantitative descriptions of these defects. In addition, the speed of the tight-binding approach is sufficient to allow us to simulate the motion at finite temperatures. These calculations will help establish the mechanisms of motion of the dissociated dislocation cores in silicon.

### **Interactions:**

This work is done in collaboration with Prof. Ju Li at Ohio State University and Prof. Sidney Yip at MIT. The work on Mo screw dislocation is also done in collaboration with Drs. V. V. Bulatov and W. Cai at Lawrence Livermore National Laboratory.

# Diffusion, Coalescence and Reconstruction of Vacancy Defects in Graphene Layers

**Personnel:** C.Z. Wang (PI) and K.M. Ho (PI)

## Scope:

The scope of this study is to ultimately understand the behavior of materials under extreme energy environments, particularly the defects generation, diffusion, coalescence, and reconstruction at high temperatures, high radiation, and corrosive conditions, as well as the unique electronic, magnetic, and mechanical properties caused by the defects.

## Research Highlights:

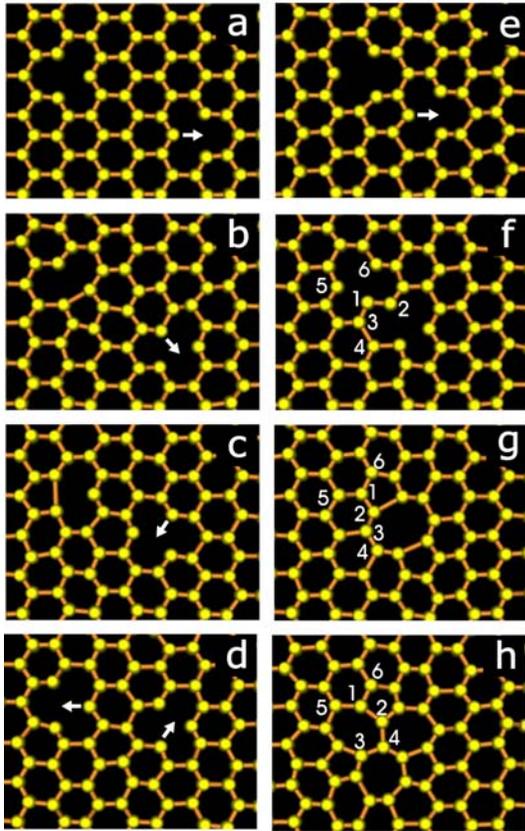
Recent experimental observation of magnetic ordering in graphite induced by proton irradiation of the graphite surface has focus interest on graphite vacancies. Several theoretical calculations have been performed to clarify the origin of the magnetism. One basic assumption in these theoretical studies is that the vacancies can be removed quickly by the fast diffusion of carbon adatoms due to the small energy barrier. However, using high-resolution transmission electron microscopy (HR-TEM), Hashimoto et al. reported that vacancies in a graphene layer such as single wall carbon nanotube can be very stable. Indeed, the structure and diffusion of vacancy defects in a graphene layer have been investigated by a number of theoretical calculations. However, a detailed study of the overall diffusion and formation process of vacancy defects in graphite is still lacking. We have performed tight-binding molecular dynamics (TBMD) simulations to study the diffusion and coalescence of vacancy defects in a single graphene layer using the environment dependent tight-binding (EDTB) carbon potential. First principles total energy calculations are performed to verify the TBMD results for the formation energies and energy barriers for some important configurations and structural transitions. We identify the atomistic pathway for two separated single vacancies in a graphene layer to coalesce into a 5-8-5 defect. On further annealing we found that the 5-8-5 defect reconstructs into a new 555-777 defect, which can be the precursor of the hexagonal ( $H_{5,6,7}$ ) haeckelite structure, by a Stone-Wales type transformation. The new defect is energetically much more stable than earlier structures considered for the divacancy system.

## Impact:

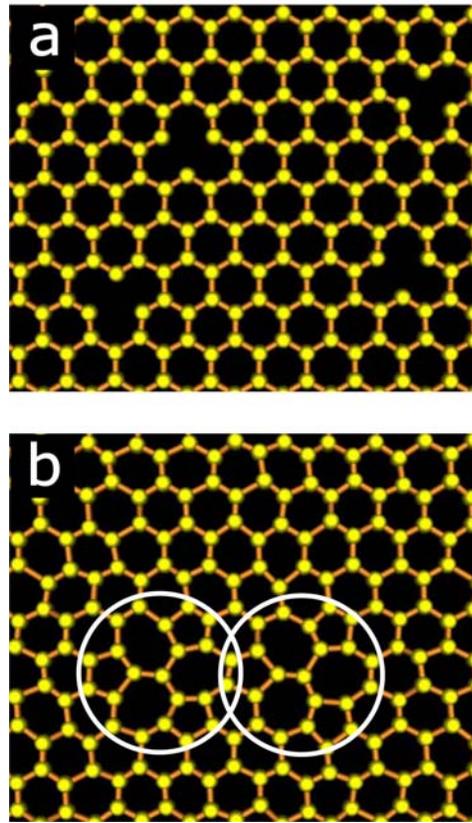
Vacancy defects generated by ion or electron irradiations of graphite or carbon nanotubes have been the subject of many studies. Vacancy reconstructions lead to the formation of various types of nanotube junctions such as Y-junction, T-junction, and X-junction necessary for the manufacture of multiterminal electronic devices. Vacancy defects created by electron irradiations can also induce structural changes within carbon nanotubes. Knowledge about the diffusion and coalescence of the vacancy defects at the details of atomic level would be very useful for understanding the structure reconstruction of graphene layers and carbon nanotubes induced by irradiation damages.

## Future Work:

This work indicates that our method is well-suited for further investigation of vacancy effects in more complicated carbon systems like nanotubes and nanotube junctions. We will also study the vacancy formation energy in bulk Al in the presence of hydrogen alone and also how the vacancy formation energy is altered by the presence of metallic impurities such as Cu and Pb. We will also calculate the diffusion pathways and barriers of vacancy in bulk Al and to study how these properties are affected by hydrogen and metallic impurities.



**Fig. 1** Atomic processes from TBMD simulation for vacancy diffusion in a graphene layer. **a**, 0 K (at time  $t=0$  ps), **b**,  $\sim 3,000$  K ( $t = 2.7$  ps), **c**,  $\sim 3,000$  K ( $t = 3.0$  ps), **d**,  $\sim 2,900$  K ( $t = 3.3$  ps), **e**,  $\sim 3,000$  K ( $t = 5.0$  ps), **f**,  $\sim 3,100$  K ( $t = 6.0$  ps). **g**,  $\sim 3,100$  K ( $t = 6.5$  ps). **h**,  $\sim 3,800$  K ( $t = 125$  ps). White arrows indicate the direction for the carbon atom to jump in the next step. The atoms involved in the diffusion process are labeled with the numbers.



**Fig. 2** (a) Initial and (b) final geometry in TBMD simulation for the graphene layer containing four separated single vacancies. Circles in b indicate the 555-777 defect structure.

### Interactions:

This work is done in collaboration with Dr. Gun-Do Lee at Seoul National University, South Korea. The defects and diffusion in Al will be carried out in collaboration Kurt Hebert's experimental group in the Department of Chemical Engineering at Iowa State University on the project, "Void Formation and Corrosion in Al."

# Environment-Dependent Tight-Binding Potentials for Metallic Systems

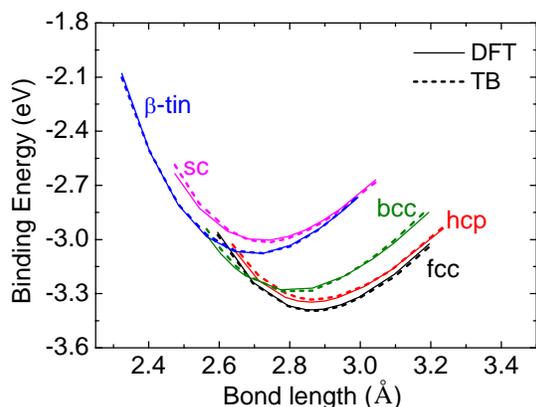
**Personnel:** C.Z. Wang (PI) and K.M. Ho (PI)

## Scope:

The scope of this project is to develop accurate and transferable tight-binding potentials suitable for molecular dynamics simulation studies of defects and deformations in the materials of interest.

## Research Highlights:

Over the past three decades, first principle techniques such as density functional calculations have been well developed and can produce reliable results for a wide variety of systems. As the methods mature, they are readily accessible to the general research community. However, with the increasing complexity encountered in modern materials science, there are many problems that are too computationally intensive to tackle with these techniques alone. There is a need for interatomic potentials that can describe the system accurately in a broad range of environments. The tight-binding (TB) method has attracted increasing attention recently due to the development of tight-binding total energy models that can provide accurate interatomic forces for molecular dynamics simulations of materials. The simplicity of the tight-binding description of electronic structures makes the method very economical for large scale electronic calculations and atomistic simulations. However, simulations of complex systems require the tight-binding parameters to be "transferable", i.e, should be able to describe accurately the electronic structures and total energies of a material at different bonding configurations. Although tight-binding molecular dynamics has been successfully applied to a number of interesting systems such as carbon fullerenes and carbon nanotubes, the transferability of tight-binding potentials is still a major obstacle to the wide spread application of the method to more materials of current interest.



**Fig. 1** The cohesive energies as a function of nearest neighbor distance for Al in different crystalline structures calculated using the environment-dependent TB model are compared with the results from the first-principles DFT-LDA calculations. The dashed curves are the TB results and the solid curves are the DFT results.

In the last fifteen years, our group has pioneered the development of transferable tight-binding potentials for atomistic simulation of materials. In particular, the orthogonal environment-dependent tight-binding total energy models developed by our group incorporate environment-dependent scaling functions not only for the diagonal matrix elements, but also for the off-diagonal hopping integrals and the repulsive energy in the tight-binding total energy expression, providing a mechanism to include important effects that have been ignored in the conventional tight-binding models such as the effects arising from the variation of the local minimal basis set with environment and three-center interactions, and effects due to Löwdin orthogonality. The environment-dependent tight-binding models have been demonstrated to describe well the properties of both the lower-coordinated covalent structures as well as the higher-coordinated metallic structures of carbon and silicon. The environment-dependent tight-binding model has also been successfully applied to the transition metal Mo. Recently we have extended the environment-dependent tight-binding total energy model to the free-electron like Al and Pb metallic systems. We showed that the model describes well the

band structures, cohesive energies, and vibrational properties of the crystalline structures of Al and Pb. The tight-binding potentials also give an accurate description of the surfaces of these materials. Some of these results can be seen from Fig.1 and Table I.

**Impact:**

The tight-binding potentials developed by our group have been widely adopted by researchers in the areas of physics, chemistry and materials science. In particular, one of our carbon potential papers has been listed as one of the five **Most Cited Papers in the Journal of Physics: Condensed Matter**.

**Future Work:**

We will continue to develop accurate and transferable tight-binding potentials for materials of interest, especially for intermetallic systems. Currently, the tight-binding parameters are determined by fits to the electronic structures of a number of standard geometries. The fitting procedure is quite laborious if we want to study a broad range of materials as well as compound systems where many sets of interactions have to be determined simultaneously from a given set of electronic structures. Therefore, we have recently developed, in collaboration with Klaus Ruedenberg’s group in quantum chemistry at Ames Laboratory, a method for extracting a minimal-basis Hamiltonian starting from *ab initio* calculation results using large converged basis sets. This provides a clear way to separate the electronic structure into different component interactions among the atomic orbitals in the system, and provides the basis for developing a systematic scheme to simplify the potential generation process and make the problem much faster and more tractable especially when we are dealing with compound systems.

**Interactions:**

The tight-binding potential development was carried out in collaboration with Prof. Wencai Lu (visiting scientist from Jilin University, China) and Prof. Mingsheng Tang (visiting scientist from Zhenzhou University, China) as part of the “Electronic and Magnetic Properties of Solids” project within the Condensed Matter Physics Program within the Ames Laboratory. Recently, we have also collaborated with Prof. Klaus Ruedenberg in quantum chemistry at Ames Laboratory in developing a method for extracting a minimal-basis Hamiltonian starting from *ab initio* calculations. Also, the tight binding potentials developed will be used for molecular dynamics simulation studies in the liquid metals project.

	TB	DFT	Exp.
$a(\text{\AA})$	4.06		4.05
$c_{11}-c_{12} (10^{12}\text{erg/cm}^3)$	0.51		0.46
$C_{44} (10^{12}\text{erg/cm}^3)$	0.27		0.28
$\nu_{\text{TA}(x)} (\text{TH}_z)$	5.95	5.83	5.78
$\nu_{\text{LA}(x)} (\text{TH}_z)$	9.48	9.51	9.69
$\gamma_{111} (\text{eV}/(1\times 1))$	0.48	0.48	
$\gamma_{100} (\text{eV}/(1\times 1))$	0.54	0.56	
$\gamma_{110} (\text{eV}/(1\times 1))$	0.88	0.89	

**Table I** Results of the Al EDTB model for the equilibrium lattice constant  $a_0$ , the elastic constants  $c_{11}-c_{12}$  and  $c_{44}$ , vibration frequencies, and the surface energies of (111), (100), and (110) surfaces, in comparison with results from ab-initio (DFT) calculations and experimental data.