



Atomic-level computer simulation

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Abstract

This paper provides a broad overview of the methods of atomic-level computer simulation. It discusses methods of modelling atomic bonding, and computer simulation methods such as energy minimization, molecular dynamics, Monte Carlo, and lattice Monte Carlo.

1. Introduction

Atomic-level computer simulations of the structure and properties of different materials (metals, semiconductors, polymers, inert gases, etc.) have been carried out since the 1950s, and have become more powerful with the rapid development in computing facilities and efficient numerical algorithms. The purpose of this paper is to provide a broad overview of current research methods in the field, including both a discussion of the various models of atomic bonding, and the various methods which have been used to carry out atomic level computer simulations.

Atomic bonding can be simulated with either quantum mechanical or empirical models. The quantum mechanical methods involve the solution of Schrodinger's equation within certain approximations to determine the electronic structure, and thereby extract the forces on the atoms. Empirical methods involve the use of simpler models of interatomic bonding such as pair potentials in which the bond energy is only a function of the distance between atoms. The parameters describing these potentials are determined by fitting to experimental data, such as bond lengths, bond energies, and elastic constants. In the last decade, there have been rapid improvements in empirical methods for metallic and covalent systems [1]. The quantum mechanical methods are generally more reliable than the empirical methods, but are currently limited to small systems (less than 50 atoms versus millions for empirical methods).

Using these models of atomic bonding, several simulation methods are commonly used for atomic-level calculations, including energy minimization, molecular dynamics, Monte Carlo, and lattice Monte Carlo. Energy minimization involves moving atoms to minimize the net force acting on them, and thus is useful for determining the optimal structure at zero Kelvin. Molecular dynamics involves modelling the vibrations of atoms by solving force = mass \times acceleration ($F = ma$), and can therefore simulate systems at nonzero temperatures. Monte Carlo involves random sampling of various possible states of a system, to determine equilibrium structures and properties at finite temperatures. Finally, Lattice Monte Carlo is useful to model systems over long times, by ignoring atomic vibrations and only considering events which result in atom motion from one lattice site to another. Together, these methods provide a wide variety of choices in modelling systems at the atomic level.

A typical example of a computer simulation is a molecular dynamics simulation of the interaction of an energetic ion with a slab of atoms, resulting in a radiation damage cascade. The molecular dynamics simulations can determine the motion of all the atoms, from the initial trajectory to the final cascade, revealing the mechanisms of damage and the final defect distribution. However, the molecular dynamics model is only as realistic as the potentials used to describe the interatomic bonding, because the potentials determine, for example, the energy required to create Frenkel pairs or to allow atoms to diffuse.

In the following sections, we first discuss models of atomic bonding, with an emphasis on empirical models. Then, we explain the various types of simulation methods, and discuss the advantages and disadvantages of each. The following papers by other authors in this proceeding volume [2,3] describe applications of these methods to radiation damage.

2. Atomic Bonding

2.1. Electronic Structure Models

The basic idea of most electronic structure methods is to solve the Schrödinger equation in the presence of many electrons and ions (the “many-body” problem) within a set of simplifying assumptions. The primary assumptions are: (1) Born–Oppenheimer approximation: since the electrons move much faster than the nuclei, assume that the nuclei are fixed and solve for the electrons; then move the nuclei in a classical approximation ($F = ma$) and solve again for the electrons. (2) One-electron approximation: solve for each electron separately, assuming that its interactions with other electrons can be approximated with an average potential. Further assumptions are then made, leading to either the Hartree–Fock or density functional approaches. Both methods rely on a variational principle which states that the electron wave functions which yield the lowest total energy of the system are the correct ones. Thus, one assumes an initial set of trial wave functions for the electrons and, through an iterative process, determines the true electron wave functions which yield the lowest energy of the system. This also yields the forces acting on every atom.

In the Hartree–Fock approach (HF) [4], one assumes that the electron wave functions can be described as a combination of antisymmetric orbitals, typically Gaussians or atomic orbitals. The antisymmetry property ensures that exchange is properly described. It does not necessarily account properly for electron correlation effects (due to the many-body interactions of the electrons) due to the limited nature of the basis set. More exact variations of HF, such as configuration interaction (CI), can treat the correlation effect properly; thus, HF methods can be highly reliable, typically yielding bond lengths to within 1% accuracy and bond energies to within 10% accuracy. However, this method scales as N^4 , where N is the number of electrons in the simulation volume, so only small systems (less than about 15 atoms) can be treated. Also, due to the choice of basis set for the electrons, HF methods cannot in general treat periodic systems. Thus, HF methods are primarily used for the study of small molecules.

Density functional theory (DFT) [5] is based on the theorem that the ground state energy and properties of a system are uniquely determined by the electron density in the system only, regardless of which orbitals (s, p, d, etc.) contribute to it. The electronic equation thus contains terms for the electron–ion, kinetic, electron–electron repulsion and electron exchange and correlation energies. The exchange–correlation term contains the nonclassical contributions to the total energy and is a functional of the electron density but has an unknown form. This term can be computed using the local density approximation (LDA), in which a system with an inhomogeneous electron density is approximated as a set of many small regions of uniform electron density, since the exchange and correlation energy of a uniform electron gas have been determined. This approach is analogous to approximating a curve with a histogram. As with HF, there is a variational principle which says that the energy is minimum for the exact ground state. Thus, by assuming an initial charge distribution, one can iteratively solve for the ground state charge density, and thus determine the total energy of the system and the forces on the atoms. DFT/LDA bond-lengths are typically reliable to 1%, and bond energies are generally 10% higher than experimental values. However, nonground-state properties, such as energy gaps and ionization energies are not well described with LDA. LDA methods can treat periodic (bulk or surface) systems, and are generally limited to systems of 50 atoms or less, since they generally scale as N^3 .

2.2. Empirical models

2.2.1. Noble gas models (the Lennard–Jones potential)

The Lennard–Jones potential (LJP) [6] is a simple pair potential that can accurately model noble gases, yielding reliable bond energies and bond lengths. It has been widely used for modelling covalent and especially metallic systems. However, it can be quite inaccurate for those systems because the LJP does not include the environmental dependence of bonding. For example, a bond between two carbon atoms can be a single, double or triple bond depending on the presence of other atoms. The LJP derives its popularity from its mathematical simplicity and computational efficiency.

When considering the simplest of molecular crystals, in which the constituent atoms are noble gases, the atoms are only slightly distorted from their stable closed shell configurations. The attractive interactions between atoms are due to a fluctuating-dipole interaction which varies as the inverse sixth power of the inter-atomic distance. This weakly attractive interaction holds the Van der Waals solids together. However, when the atoms are too close to each other, the repulsion of ion cores and especially the repulsion of the

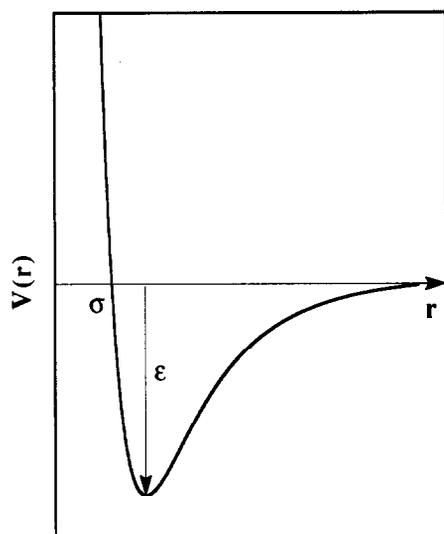


Fig. 1. The energy versus distance for a typical LJP.

filled electron shells (by Pauli's exclusion principle) come into play; this balance of repulsive and attractive forces defines the equilibrium interatomic distance. The repulsive interaction is strong at short distances, but decays rapidly, and is assumed to vary as the inverse twelfth power of the interatomic distance. It is customary to write the Lennard-Jones potential as

$$V^{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (1)$$

where r is the distance between any two atoms and ϵ and σ are parameters determined by fitting to known properties of the gas. ϵ represents the well depth (strength of the attraction) and σ represents the radius of the repulsive core (see Fig. 1). The radial distance corresponding to the bottom of the well determines the equilibrium bond distance, and the depth of the well determines the bond strength. The curvature of the minimum determines the "spring constant" in the atom-atom interaction.

Although the parameters are developed by fitting to gas phase data, they are found to accurately describe the bond energies and bond lengths of the solid state of the noble "gases".

2.2.2. Ionic models

Inorganic compounds combining alkali, alkali-earth and several transition metals with group VI and VII elements, show a strong tendency towards ionic bonding. This means that the compounds have low energy, filled-shell electronic orbitals which results in heavily-localized charge configurations. For many practical purposes, the interaction between ions can be described with a Born-Mayer potential, which is composed of a short range repulsive term, which acts only

between nearest neighbors, and a Coulomb term, which prevails over larger distances. The Coulomb term is treated as an electrostatic interaction between point charges, and can be described by Coulomb's law. Accordingly, the potential energy of a point charge $q_i = z_i e$ (where z is the electronic charge in units of e , the charge of an electron) located at a distance $|r_i| = |r_j - r_i|$ from a point charge $q_j = z_j e$ is

$$\phi_q(r) = \frac{z_i z_j e^2}{4\pi\epsilon |r|}, \quad (2)$$

where ϵ is the dielectric constant. The force that acts between the point charges is the negative derivative of ϕ with respect to r_{ij} .

In condensed matter, however, each ion interacts with many neighbors, and the total potential energy of the particle j is obtained by the summation

$$V_i^C = \frac{z_i e^2}{4\pi\epsilon} \sum_{j \neq i}^N \frac{z_j}{|r_{ij}|}. \quad (3)$$

Accordingly, the potential decreases as $1/r_{ij}$ but the number of particles that can be found at a distance r_{ij} increases as r_{ij}^2 . This makes the summation in Eq. (3) converge very slowly. That it converges at all is only due to the fact that coordination shells with oppositely charged ions follow in close proximity of each other, when r_{ij} becomes large. This slow convergence represents a central problem in the framework of computations that involve Coulomb interactions, since typical simulation ensembles do not contain a sufficient number of particles to attain convergence. Coulomb interactions are significant even over distances of several tens of interatomic spacings. An arbitrary truncation at a distance of about half of the side of the simulation box not only introduces an error in the evaluation of the total energy of the system, but it causes spurious effects with particles that cross this cutoff radius. These atoms tend to oscillate back and forth because when outside of the interaction sphere a repulsive component suddenly vanishes. Such behavior distorts the dynamics of the system.

Fortunately, this situation can be remedied. Perhaps the most widely used construct for this purpose is the Ewald summation method. The principal idea behind this method is to enhance each point charge with two mutually compensating Gaussian charge distributions, centered at the same position. Each point charge is now shielded by an oppositely charged Gaussian, and the combination is summed in real space, where it rapidly converges. The compensating Gaussian charge distributions are transformed into reciprocal space and the summation is carried out over periodic images. Finally, the reciprocal space part is transformed back into real space and both are added. Since this recipe includes the interaction of each particle with its own

periodic image, an important correction is the subtraction of this self term at the end. The final result then becomes,

$$V_{\text{tot}}^C = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \left(\frac{z_i z_j e^2 \operatorname{erfc}(\alpha r_{ij})}{|r_{ij}|} + \sum_{q \neq 0} z_i z_j e^2 \frac{e^{-\pi^2 q^2 / \alpha^2 L^2}}{|q|^2} \cos\left(\frac{2\pi}{L} q r_{ij}\right) \right) - \sum_{i=1}^N z_i^2 e^2 \alpha \pi^{-1/2}. \quad (4)$$

The adaptation of this formalism for molecular dynamic computer simulations took place in the early seventies. The Born-Mayer potential also includes a repulsive term, which mimics the increase of energy upon overlap of filled orbitals, i.e.,

$$\phi_{\text{B-M}}(r) = \frac{z_i z_j e^2}{4\pi\epsilon |r|} + A_{ij} \left(1 + \frac{z_i}{n_i} + \frac{z_j}{n_j} \right) e^{(\sigma_i + \sigma_j - r)/\rho_{ij}} \quad (5)$$

where n_i is the number of electrons in the outer shell of ion i , σ_i a parameter commensurate with the size of the ion, and ρ_{ij} an empirical parameter describing the “softness” of the electron cloud.

Initial work was carried out on crystalline and liquid salts (alkali halides), for which this approach proved to be very accurate. Thermodynamic, structural, and kinetic properties of these systems have been studied in great detail [7–10]. Another class of materials where this approach was fruitful are oxide glasses, in particular silicates. Using only central force interactions, tetrahedral coordination of silicon by oxygen could be achieved. This provided a powerful new technique for the investigation of amorphous structures [11]. Furthermore, it was possible to study thermodynamic and transport properties [12–14].

More recently the Born-Mayer formalism has been expanded to include noncentrosymmetric charge distributions or polarized ions [15]. The enhancement includes charge-dipole and dipole-dipole interactions, where the dipoles are located at the positions of atoms, ions or molecules. The potential energy of between a charge and a dipole, separated by r_{ij} is

$$\phi_{\text{c-d}} = \frac{z_i e}{4\pi\epsilon} \frac{\mu_j r_{ij}}{|r_{ij}|^3} \quad (6)$$

and that between two dipoles is

$$\phi_{\text{d-d}} = \frac{1}{4\pi\epsilon} \left((\mu_i r_{ij})(\mu_j r_{ij}) \frac{3}{|r_{ij}|^5} - \frac{\mu_i \mu_j}{|r_{ij}|^3} \right). \quad (7)$$

A dipole vector is defined as $\mu = \sum_{i=1}^n r_i z_i e$, and describes the asymmetry of a charge distribution. The

large group VI and VII anions are likely to be polarized, and ionic molecules are even more likely to be strongly polarized. Note that these interactions not only depend on the distance between charges and dipoles, but also on the orientation of the dipoles. As for point charges, the charge-dipole and dipole-dipole interactions are long-ranged, and require special treatment within limited size simulation configurations. The Ewald summation procedures for these interactions have been described [15].

Applications of this more detailed treatment of Coulomb interactions include the study of the structure and dynamics of simple crystalline salts [16], complexing binary molten salts [17], and liquid water [18]. Although the effects of polarization on the energy and forces are only of the order of a few percent of the nonpolarization energy, the vibrational properties of the substances can be affected quite drastically.

The parameters involved in describing the potentials are generally determined by fitting to experimental data, but there has been recent work on developing the parameters from quantum mechanics models [19]. This work is very promising, due to the rich variety of structures that can be simulated, providing a much richer database than available from experiment.

2.2.3. Covalent models

Determination of the energy of covalently bonded systems is much more difficult than for metals because the total energy of the system can be dominated by either changes in chemical bonding or by elastic strain effects. These two contributions are best simulated by fundamentally different methods. Chemical effects can only be modeled adequately by explicit solution of the Schrödinger equation to determine the molecular orbitals, resulting from the chemical interactions. Elastic strain effects can only be treated with very large simulation cells since strain effects decay very slowly around lattice defects. When developing a simulation of a covalent material it is critical to determine which of the two contributions dominates the energy before selecting a simulation technique.

Empirical potentials provide simple mathematical relationships between bond energies and the coordinates of atoms. They are generally unable to respond to changes in bonding, for example changes in interatomic electron transfer and orbital hybridization. However, because they can effectively model small deformation elastic behaviors and can handle very large simulation cells, empirical potentials simulate strain fields relatively effectively.

Empirical potentials can be subdivided into valence force potentials and many-body potentials. Several reviews have been published comparing the most popular empirical potentials for semiconductors [20]. The class of empirical methods known as valence-force poten-

tials are Taylor expansions of the system potential energy around the equilibrium structure and are designed to fit the phonon dispersion relations and small elastic deformation behaviors of the simulated structure. Such potentials are successful in limited applications but cannot be applied to systems which have large atomic displacements such as occur at dislocations, grain boundaries, and surfaces.

Many-body potentials expand the interatomic force terms in increasingly collective interactions (binary, three body, ...). This approach emphasizes long-range bonding effects. However, it is difficult to determine the relative contributions of each of the many-body interactions to the total bonding force between atoms from either first principles arguments or from measurements. Typical many-body semiconductor potentials are terminated at the three-body terms. Examples of three-body models for Si include the Stillinger-Weber (SW) [21] and Tersoff (TS) potentials [22]. The SW potential was fit to the bulk melting point of Si and is well-suited to modelling liquid-solid interfaces in Si. Because the SW potential does not allow any changes in its angular dependence, it does not adapt to undercoordinated configurations such as surfaces. The TS potential allows some modification of the effective bond hybridization in undercoordinated structures (see below) and as such should represent a better simulation of surfaces. The TS potential has been shown to fit bulk elastic properties, high pressure metastable amorphous states, some features of the surface reconstruction of Si (001) and polytypes of Si relatively well. The cohesive energies and bond lengths of these structures are also well reproduced. There are many other empirical potentials similar to the SW and TS models. Applications, critical evaluations, and descriptions of these potentials may be found in Ref. [20] and references therein.

We now present a brief description of the TS model as an illustration of the approach used in three-body potentials, how this potential can adapt to different coordination environments, and how the TS form is related to the semiconductors to be simulated. The TS model includes attractive and repulsive components which decay exponentially with distance from the central atom. This is justified on the basis of the radial exponential decay of wave functions in isolated atoms. As such it seems appropriate to treat the relatively large bond distances between Si atoms. The range of the attractive part of the potential is slightly larger than that of the repulsive part, yielding a net bonding energy at a fixed range. The attractive term includes an angular dependence which seeks to maintain an angle $\theta \sim 120^\circ$ between any two bonds while the repulsive part has spherical symmetry (angular dependent terms have also been considered). The potential includes a cutoff function which reduces all interactions to zero at

a distance of 0.285 nm from the atom for which the energy contribution is being determined. This cutoff eliminates second nearest neighbor interactions in bulk Si and consequently reduces computation time in molecular-dynamics simulations. Unfortunately, the cutoff function introduces substantial errors for surface calculations because surface atomic diffusion events may move atoms through the range where the potential is being cut off. This results in a large gradient in the system energy and consequently a large force on the atom.

The angle dependent attractive term is quadratic in $\cos \theta$ (where θ is the angle between bonds), with a form fit to the energies of metastable Si structures of different coordination number. This approximates re-hybridization of bonds as a function of lattice geometry. An exponential screening term simulating the electron density of the intervening lattice prevents atom “*i*” from influencing atom “*j*” when other atoms “*k*” lie closer to *i* than does *j*. The relative energy of a bond with respect to angle is adjusted such that three optimal bonds (angle 120°) are less favorable than four bonds with an angle of $\sim 109^\circ$, stabilizing the tetrahedral diamond structure. Because the angular dependence of the potential is asymmetric with respect to distortions around the tetrahedral value the potential favors distortions increasing the bond angle while it is relatively stiff as the bond angle decreases.

The TS model has been shown to provide excellent results for many bulk properties of Si and has been adapted to simulate Ge and C as well. While simulation of surface phenomena is hampered by the cutoff function, the general behavior of the energy of an adatom as a function of position on the Si(100) 2×1 surface agrees reasonably well with density functional theory results.

Overall, the most general conclusions which can be reached about modeling covalent materials are that relatively sophisticated methods such as density functional theories are probably necessary for problems involving changes in electron density or bonding. For problems concerned with long time scales (several atomic vibrations) or large systems (more than a few hundred atoms) it is necessary to use an empirical method. The best results will be obtained only with an empirical potential specifically optimized to handle the task at hand. Hence, the TS potential is best for generic bulk Si problems, while the SW potential is preferred for any system involving liquid-like properties. New potentials will probably be necessary to simulate surface processes.

2.2.4. Metallic models

From the 1950s to the 1980s, metals were primarily modelled with simple pair potentials, such as the Lennard–Jones, Morse, and empirical pair potentials

[23] constructed from cubic (or other) splines. These potentials were used because they could be fit to several physical properties. A review of these potentials can be found in Ref. [23]. Many studies of point defects, dislocations, grain boundaries and other systems were carried out with these potentials. Although this was acceptable for modelling small elastic distortions, it was unacceptable for major changes in the bonding environment, so that potentials that describe bulk bonds could not reliably describe surface bonds, and vice versa. The basic problem is that the loss of some bonds is partially compensated by increasing the strength of remaining bonds. In other words, a metallic bond between two atoms depends on the surrounding atoms.

In recent years, new many-body empirical models have been developed to overcome the limitations of simple pair potentials by including a many-body dependence [24–29]. One of the most commonly-used many-body methods, the embedded atom method (EAM) will be presented as a typical example. Many similar models have been developed from different starting assumptions. The effective medium theory [30–32] of Nørskov and coworkers, the corrective effective medium theory [33] of DePristo and Kress, the “glue model” [29] of Ercolessi, Tosatti and Parrinello, the Finnis–Sinclair models [27], and the equivalent crystal theory [34,35] of Smith and Banerjee are quite similar to the EAM, and have also been applied to a number of bulk and surface studies.

Daw and Baskes developed the embedded atom method (EAM) [24] to describe atomic interactions in metals. The EAM is a semiempirical method based on local electron density theory. In the EAM, a metal is thought of as a set of positively-charged nuclei embedded in an electron “sea.” Thus, the total energy of a system is assumed to be due to two sources: the total electronic energy and the electrostatic energy of core–core interactions. According to density-functional theory, the total electronic energy for an arbitrary arrangement of nuclei can be written as a unique functional of the total electron density. The electron density in a metal can be reasonably approximated by the linear superposition of contributions from the individual atoms. This leads to an approximation for the total energy in the EAM:

$$E_{\text{tot}} = \sum_i F(\rho_i) + \frac{1}{2} \sum_{i,j(i \neq j)} \Phi(R_{i,j}), \quad (8)$$

where $F(\rho)$ is the embedding energy that is required to embed atom i into the background electron density ρ_i , $\Phi(R)$ is the short-range electrostatic interaction between nuclei, and R is the distance between atoms. The sums in Eq. (8) are over all atoms. The background electron density ρ_i is approximated by the

linear superposition of atomic electron densities of nearby atoms,

$$\rho_i = \sum_{j(\neq i)} \rho_j^a(R_{ij}), \quad (9)$$

where $\rho_j^a(R_{ij})$ is the electron density contribution by atom j .

In order to compute the total energy according to Eq. (8), pair interactions, the embedding functions, and atomic densities must be known. These are generally determined for pure metals by fitting to experimental data, such as the equilibrium lattice constant, sublimation energy, bulk modulus, elastic constants, and vacancy-formation energy. These properties are generally fit to 5–10% accuracy.

The EAM has been shown to reliably describe FCC transition metals with filled or nearly filled d-bands (especially Ni and Cu column elements). Limited success has been obtained for BCC transition metals with partially-filled d-bands because the electron density is assumed to be spherically symmetric, so that the angular dependence of the partly-full d-orbitals is not adequately described [26,36,47]. Even though the EAM functions are typically fit only to perfect crystal properties, they are generally reliable for modelling crystal thermodynamics, crystal defects, surfaces and even liquids [37–40].

For alloys, the expression for the total energy also includes a term ϕ_{AB} , the pair potential describing the interactions between different types of atoms A and B. Unfortunately, there is usually little useful experimental data available to use for fitting this potential (often only the mixing enthalpies). Thus, alloys are often not as well described as the pure elements, although simulations of metallic alloys are still relatively-widely used. This is not necessarily an intrinsic flaw in the EAM, but rather primarily due to a lack of data. One promising approach to overcome this problem is to fit to a large set of quantum mechanical calculations [41]. However, mixtures of metallic and nonmetallic elements are not expected to be reliably described by the EAM, and new models need to be developed to handle such complex systems.

For the bcc transition metals with partially-filled d-bands, three and four body interactions contributing to the total energy are essential to more accurately describe the properties of materials. Recently Carlsson [42] developed a semiempirical model including angular force terms based on tight-binding theory. This model included both second and fourth moments of the electron density of states (the EAM is essentially a second moment model). This model and similar ones [43,44] have been shown to reliably model bulk and surface properties of bcc metals, albeit at a computational cost of about 200 times that of the simpler EAM. Moriarty has also developed a many-body model which

includes angular forces, and is quite reliable for many bulk properties [45,46].

3. Simulation Methods

There are four widely-used methods for carrying out atomic-level computer simulations based on the above bonding models. Energy minimization is used to study systems at 0 K, molecular dynamics is used to model atomic vibrations, Monte Carlo is used to sample equilibrium states, and lattice Monte Carlo is used to study long-time dynamics.

3.1. Energy minimization

Energy minimization is a method for finding the stable structures of materials at 0 K. It is based on the fact that a particle is in equilibrium when the forces acting on it are zero. The generalization of this result for N particles in three dimensions ($3N$ degrees of freedom) is that the equilibrium structure can be found by all the forces on all the atoms. Unfortunately, it can be very difficult to find the true minimum of a $3N$ dimensional function.

One simple method of minimizing a $3N$ dimensional function is the steepest decent algorithm [48]. It involves moving an atom in the direction of the force acting on it, until a minimum in that direction is reached. This process is repeated until every atom has been moved. Unfortunately, the movement of subsequent atoms changes the forces acting on each atom, so that the process must be repeated many times. Due to its lack of “memory” of previous steps, this algorithm has a tendency to zig-zag inefficiently through parameter space and may require many iterations to converge on a minimum. The widely-accepted alternative to steepest-descent is the conjugate-gradient method [48], which retains a limited memory of previous moves, and therefore executes a more efficient search.

The most obvious problem of any energy minimization method is the lack of any guarantee that the minimum located is the global minimum corresponding to the true lowest-energy structure. It is possible to become trapped in a local minimum which corresponds to some metastable state and as a result predict an incorrect structure. For example, if an interstitial atom is placed in an octahedral site, it will not move to a tetrahedral site (which may be lower energy) if there is an activation energy barrier to that motion.

An additional set of more subtle problems involves the treatment of the boundary conditions and cell volume. Most atomic simulations employ periodic boundary conditions. This simply means that the simulation cell is treated as if surrounded in all directions

by infinitely many copies of itself. Thus, an atom on the edge of the right side of a cell could interact with an atom on the left side. If the cell volume is too small, long-range interactions may not be properly computed. A general rule is that the length of a cell edge should be at least twice as large as the longest interaction, so that only neighboring cells need to be considered. (For ionic systems, this is not possible, and an Ewald summation method is used instead.)

The boundary conditions also determine whether the simulation models a system at constant volume (fixed boundaries) or at constant pressure (movable boundaries). A simulation of radiation damage, for example, is generally most useful if carried out at constant pressure. Not only are most experiments performed at constant pressure, but the process of radiation damage usually produces numerous interstitial and vacancy defects which add to the volume of the sample – a fact the simulation should reflect.

Energy minimization is widely used to study the structure of surfaces, bulk defects, and many other systems at 0 K. It can also be used to study dynamic processes, such as vacancy diffusion, by searching for the lowest energy pathway as an atom is forced from an initial state to a final state. This method can yield the activation energy for the process, and the attempt frequency for that event [49].

3.2. Molecular dynamics

The basic idea of molecular dynamics is to simulate the thermal vibrations of atoms in a classical manner, following Newton's laws. It involves the following steps: (1) assign an initial thermal velocity to each atom (usually according to a Boltzman distribution); (2) calculate the force on each atom, and hence determine the acceleration; (3) move all atoms according to their velocity and acceleration for a short time t ; (4) repeat steps 2 and 3.

There are several algorithms that can be used to solve the equations of motion, ranging from the simple Verlet algorithm to the complex predictor-corrector methods [50].

One problem is that as atoms move, forces change, so the time step t has to be very small, typically around 10^{-15} s, as compared to atomic vibrational frequencies of 10^{-13} s. Typical workstations (such as an IBM RS6000) can simulate 10 000 atoms for 10^{-10} s in a day, using empirical models of interatomic bonding. For density functional methods, typical simulations of 50 atoms for 10^{-13} s would require a day or longer. Thus, with empirical or especially with quantum mechanical methods, one is limited to very short simulations. This is sufficient to model many atomic vibrations, but insufficient to model most thermally acti-

vated processes. Thus, observing the diffusion of atoms in a crystal by a vacancy mechanism would be impossible, but a short radiation damage event occurring over 10^{-12} s could easily be simulated with empirical methods.

A second problem of molecular dynamics is that it is classical, hence phonons are not quantized. This is particularly important below the Debye temperature, when certain phonon modes would be frozen out, and zero-point motion would not be accounted for. Thus, thermal expansion and other thermodynamic properties will be slightly incorrect. Above the Debye temperature, this is a negligible effect.

Molecular dynamics may either be carried out at constant energy or constant temperature. In constant energy molecular dynamics, one solves $F = ma$ directly, and energy is conserved throughout the simulation. This is the method used for computing thermodynamic averages, such as the enthalpy of a crystal with a vacancy. It is also the correct method to use for modelling dynamic processes, such as energetic collisions, so that energy is transferred between atoms in a realistic manner.

Constant temperature molecular dynamics is generally used only to bring systems to a desired temperature. It involves periodically computing the kinetic energy of the system, and then modifying the acceleration or velocity in an artificial manner to maintain a constant temperature throughout the simulation. It is an unphysical way of simulating a classical system, but useful to move the system to a desired temperature. It cannot be used to correctly calculate thermodynamic averages, because the Boltzmann distribution of energy is periodically altered in an unphysical manner. This also means that dynamic processes will be incorrectly modelled, because activation energy barriers will be overcome incorrectly.

One special application of molecular dynamics is “simulated annealing”. In this case the MD simulation begins with the material at a high temperature and slowly cools the system by steadily removing kinetic energy. As the atoms vibrate, they can jump from metastable to global minima, but the reverse jump requires a higher activation energy barrier. Thus, as the system cools they tend to become trapped in the global minima. Whereas energy minimization tends to find local minima (regardless of whether or not it is the global minima), simulated annealing may escape from those local minima, thereby yielding the optimal structure of the system.

3.3. Monte Carlo simulations

As mentioned previously, energy minimization methods will generally find the local (not global) minima of a system. Molecular dynamics can often be

trapped in local minima as well if the simulation time is too short or the temperature is too low, as is often the case. Monte Carlo methods offer an alternative to sample the possible states of a system. In some cases Monte Carlo is a more efficient method for finding the true minima, particularly if the simulation involves phase separation.

The Monte Carlo (MC) method was developed by Von Neumann, Ulam, and Metropolis [51] in the 1940s. The term “Monte Carlo methods” refers to any of the multitudes of approaches to solving problems involving the use of random numbers to sample the ensemble. Many good review articles and books are available about the MC method [50,52–54]. The purpose of atomistic MC simulations is usually to determine thermodynamic equilibrium properties by generating numerous “typical” atomic configurations.

A normal procedure for MC simulations is to:

- (1) generate an initial arrangement of atoms;
- (2) change the system in one of several ways (discussed below);
- (3) calculate the change in total energy ΔE ;
- (4) retain the change if ΔE is negative; if ΔE is positive, then possibly accept the change with a probability proportional to $\exp(-\Delta E/kT)$;
- (5) repeat steps 2–4.

The above procedure is guaranteed to properly sample the thermodynamic states of the system in the limit that the number of steps is infinite.

During the MC simulations, each atom is typically moved 10^4 – 10^5 times. Typical types of atom moves are: (1) move an atom (usually ~ 0.2 Å); (2) swap atoms (A to B, or B to A); (3) change cell size (for constant pressure simulations); (4) remove or add an atom. Thus, although the instantaneous changes are approximate, the typical structures generated are thermodynamically correct.

The advantage of MC over MD is that it can simulate systems which do not equilibrate on MD time scales, such as segregation to a dislocation, phase separation, and rearrangement of a grain boundary structure by diffusion. The Monte Carlo method is particularly useful in efficiently modelling the effects of long-range diffusion, since atoms can be moved, created or destroyed in one step. The same process would generally never occur in a MD simulation, due to the short time simulated. Thus, MC is often more efficient than MD for generating optimal structures. The disadvantage of MC is that it does not model the physical dynamics of the systems.

3.4. Lattice Monte Carlo

The Monte Carlo method mentioned previously is typically used to find equilibrium structures. However, lattice Monte Carlo (LMC) can also be used to model

dynamic processes over long times. In LMC, one assumes that all atoms are on lattice sites, and one only considers events that transport atoms from one lattice site to another. The principle advantage of the LMC method is that it ignores atomic vibrations which do not in general change the structure; this dramatically reduces the number of events which must be considered. Thus, whereas MD is limited to time scales of 10^{-10} s, LMC simulates events at the rate at which they occur, which may be seconds or hours. The LMC methods, by definition, are unable to model amorphous or liquid systems, grain boundaries and dislocations, and other problems involving atoms not on bulk lattice sites.

One major use of LMC is the study of crystal growth from the vapor phase [55]. In these simulations atoms are deposited on the simulated surface and diffuse by specified routes. The most common LMC approach for modeling crystal growth is the solid-on-solid (SOS) form in which atoms are only allowed to lie on top of other atoms. Overhangs and vacancies below the surface are not permitted. This greatly simplifies representation of the solid (since only the height of the surface at a given location need be specified) and reduces the number of tests which must be performed to determine where the next event will occur.

During a typical LMC simulation, one must first tabulate the possible jump events (adatom moving on a flat surface, adatom, moving along a ledge, etc.), and the activation energy associated with it. Then, one event is picked randomly, with a weighting appropriate to the rate at which the event occurs. Thus, with LMC, one ignores atomic vibrations, which occur on a short time scale, in order to model dynamic processes such as thin film growth which occur on a much longer time scale.

It should be pointed out that LMC is limited by the understanding of the underlying events. If incorrect assumptions are made regarding which events occur, or the rate at which they occur, incorrect results will be obtained. In some cases, activation energies may be known experimentally or derived from atomic level simulations; alternatively, they may be assumed to have a certain value, and then by running the LMC simulation and comparing the resulting structures with experimental results, one can infer what the energetics should be. Typically, a combination of known and unknown processes are involved.

A possible application of LMC to radiation damage would be the study of cascade evolution. First, a molecular dynamics simulation of a cascade event could determine the position of vacancies and interstitials after a few picoseconds. Then, using that structure as the starting structure for a LMC calculation, one could study the diffusion of interstitials and vacancies, leading to their possible annihilation or clustering. Whereas

MD could only simulate the first few picoseconds, LMC could simulate the long-time evolution of the defects. However, in order for the LMC to be realistic, one would have to input defect migration rates, and possibly strain effects on those migration rates.

4. Summary

We have briefly summarized the methods of atomic-level computer simulation. Atomic bonding can be modelled with quantum mechanical models or with empirical models, depending on the trade-off between reliability and the number of simulated atoms. In general, empirical models accurately describe small strains, but are less accurate for major changes in the bonding environment such as on the surface, although many-body models are more successful in this regard. Quantum mechanical models can handle changes in chemical bonding quite accurately, but still meet difficulties in handling strains due to their small simulation cells.

Four methods of modelling atomic-level systems were reviewed, namely energy minimization, molecular dynamics (MD), Monte Carlo (MC), and lattice Monte Carlo (LMC). Energy minimization methods can be used to find the stable structure of a system, but are limited to zero Kelvin and are easily trapped in local minima. MD simulations can model phenomena on the time scale of picoseconds, but not longer. MC is used for finding an equilibrium structure but cannot model the physical dynamics of a system. LMC can be used for modelling a dynamic process over long time, but it is limited by the knowledge of the rate of jump events. In general, all these interatomic interaction models and simulation methods supply one with a variety of approaches to carry out computational studies for a wide variety of problems. In future, as computational power continues to grow rapidly, computer simulations will become more even more useful.

5. Reference

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