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InAs/GaAs QUANTUM DOTS AND NANOMESAS: MULTIMILLION-ATOM MD SIMULATIONS ON PARALLEL ARCHITECTURES

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Physics and Astronomy

by

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B.Eng., Tsinghua University, 1991
M.Eng., Tsinghua University, 1993
May 2001

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To my late father, Su Zhimao
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ABSTRACT

Multimillion-atom molecular dynamics (MD) simulations have been performed to study the flat InAs overlayers with self-limiting thickness on GaAs square nanomesas. The in-plane lattice constant of InAs layers parallel to the InAs/GaAs(001) interface starts to exceed the InAs bulk value at 12\textsuperscript{th} monolayer (ML) and the hydrostatic stresses in InAs layers become tensile above ~ 12\textsuperscript{th} ML. As a result, it is not favorable to have InAs overlayers thicker than 12 ML. This may explain the experimental findings of the growth of flat InAs overlayers with self-limiting thickness of ~ 11 ML on GaAs nanomesas. We have also examined the lateral size effects on the stress distribution and morphology of InAs/GaAs square nanomesas using parallel molecular dynamics. Two mesas with the same vertical size but different lateral sizes are simulated. For the smaller mesa, a single stress domain is observed in the InAs overlayer, whereas two stress domains are found in the larger mesa. This indicates the existence of a critical lateral size for domain formation in accordance with recent experimental findings. The InAs overlayer in the larger mesa is laterally constrained to the GaAs bulk lattice constant but vertically relaxed to the InAs bulk lattice constant, consistent with the Poisson effect. Moreover, we have calculated surface energies of GaAs and InAs for the (100), (110), and (111) orientations. Both MD and the conjugate gradient method are used and the results are in excellent agreement. Surface reconstructions on GaAs(100) and InAs(100) are studied via the conjugate gradient method. We have developed a new model for GaAs(100) and InAs(100) surface atoms. Not only this model reproduces well the surface energies for the (100) orientation, it also yields (1\times2) dimer lengths in accordance with \textit{Ab initio} calculations. Finally, a series of molecular dynamics simulations are performed to investigate the behavior under load of several <001> and <011> symmetrical tilt grain boundaries.
(GBs) in diamond. These MD simulations are based on the bond-order analytic potential. Crack propagation in polycrystalline diamond samples under an applied load is simulated, and found to be predominantly transgranular rather than intergranular.
CHAPTER 1

INTRODUCTION

With the rapid development of computer technology in recent years, computer simulations have become increasingly important in both science and engineering. Computer simulations are considered the third branch of scientific research, bridging the gap between laboratory experiments and analytical theories. Laboratory experiments provide first-hand observations of complex natural phenomena, from which analytical theories are developed. For large, complex systems, the analytical theories usually involve very complicated mathematical equations, which have no analytical solutions. However, computer simulations can solve these equations numerically in their full complexity, and the results of the simulations may be compared with those of real experiments. This is also a test of the underlying theory used in a computer simulation. If the theory is a successful one, the simulation result may offer insights to experimentalists and assist in the interpretation of new results.

Atomistic simulations have played a key role in studying various properties and phenomena relevant to material science at the microscopic level. Based solely on equations of quantum mechanics, *ab-initio* electronic structure calculations provide the most fundamental description of materials without using any empirical parameters. Density-functional theory (DFT) with local density approximation (LDA) simplifies the problem and makes it suitable for computer simulations. The complicated many-electron Schrödinger equation is replaced by a set of effective single-particle equations which are solved self-consistently [1,2]. However, in these first-principles calculations, we need to diagonalize large matrices representing single-particle Hamiltonians over a certain basis. As a result, the computation time scales as $N^3$, where $N$ is the number of atoms. In 1985,
Car and Parrinello [3] proposed an \textit{ab-initio} molecular dynamics method which combines the DFT-LDA treatment of electrons with molecular-dynamics approach for atomic nuclei. The underlying assumption is that electronic wavefunctions can adjust instantaneously to each new atomic configuration because the electronic degrees of freedom relax much more rapidly than atomic nuclei. In the Car and Parrinello method, the electronic degrees of freedom are represented by a fictitious Lagrangian with sufficiently small fictitious masses so that the electronic degrees of freedom rapidly adjust to each new position of the atoms. The major computational challenge of the \textit{ab-initio} MD is the orthogonalization of single-particle wavefunctions. Another atomistic simulation approach which includes electronic effects is the tight-binding molecular-dynamics (TBMD) method [4,5]. In this approach, the electronic degrees of freedom are represented by an effective tight-binding Hamiltonian over a limited basis. The matrix elements of this Hamiltonian are fitted to reproduce the band structure and total energy calculated by first-principles methods.

In many circumstances, there is no need to follow the time evolution of electronic wavefunctions, and instead the motion of atoms can be well described by effective interatomic potentials. Consequently, for a 3-dimensional system, the problem is reduced to solving a system of $3N$ coupled Newton's equations of motion. This molecular dynamics (MD) approach allows simulations of very large systems. Over the years, MD methods have been widely used by physicists, chemists, biologists, and engineers. As a result, MD has introduced great degrees of cross-fertilization in various fields. MD simulation provides phase-space trajectories (positions and velocities of all atoms at all times), which are then analyzed using classical statistical mechanics. This gives us critical information of how atomistic processes determine macroscopic materials' properties. With the emergence of highly efficient space-time multiresolution algorithms, massively
parallel computers, and reliable interatomic potential models, atomistic simulation based on MD can now be used to perform real-materials simulations.

In MD simulations, a reliable and realistic interatomic potential is an essential ingredient. In recent years, a great deal of progress has been made in developing realistic interatomic potentials, such as (1) Vashishta's potential for silica [6] and silicon nitride [7,8], (2) Tersoff's potential for carbon [9], silicon [10] and germanium [11], (3) Stillinger-Weber potential for silicon [12], (4) Brenner's hydrocarbon potential [13,14], and (5) Embedded Atom Model (EAM) for metals and alloys [15,16]. Experimental data and results of *ab-initio* calculations are used to fit the parameters in these potentials and these interatomic potentials are designed to capture the essential features of the real material. Usually these realistic potentials have complicated functional forms and hence they are computationally expensive. As a result, efficient algorithms are developed to minimize the cost of computing of forces and interaction energies.

In this dissertation we focus on (1) surface energies of GaAs and InAs, and reconstructions on GaAs(100) and InAs(100) surfaces, (2) million-atom molecular dynamics simulation of flat InAs overlayers with self-limiting thickness on GaAs square nanomesas, (3) critical lateral size for stress domain formation in InAs/GaAs square nanomesas, and (4) atomistic simulations of grain boundary fracture in diamond. We have also investigated structural, dynamical, and mechanical properties of InAs, GaAs and grain boundaries (GBs) in diamond.

In recent years, quantum dots have attracted much attention due to their importance for study of electronic behavior in zero dimension and applications in electronic and optoelectronic devices [73,74]. The structure consists of coherently strained three-dimensional (3D) islands formed in semiconductor overlayers having high lattice-mismatch with underlying substrates, such as Ge on Si and InAs on GaAs. The role and manipulation of stress in the formation of such nanostructures have been
systematically examined through a study of the growth of InAs on planar and patterned GaAs(001) substrate, these systems having a large lattice mismatch of ~ 7%. On stripe mesas of sub-100-nm widths on GaAs(001) substrates, deposition of InAs is shown to allow self-assembly of three, two, and single chains of InAs 3D island quantum dots selectively on the stripe mesa tops for widths decreasing from 100 nm down to 30 nm [64]. Growth of InAs overlayers on GaAs(001) nanoscale square mesas of linear dimensions < 100 nm has been shown to give a remarkable suppression of the 2D-to-3D morphology change of the overlayer due to the significant strain relief provided by the free surfaces of the overlayer itself and the strain accommodation by the underlying GaAs square mesa [63]. The square and stripe mesas, together with the studies on planar surfaces, bracket the entire regime of length scales of significance to stress relaxation and manipulation leading to control of the island number (and hence density) on chosen nanoscale area arrays.

The large lattice mismatch and associated strain at InAs/GaAs(001) interfaces have recently been utilized to fabricate a number of nanostructures [60-64]. On infinite planar substrates, the strain relief leads to the formation of coherent three-dimensional island structures above a critical amount, ~ 1.6 ML, of InAs deposition. When InAs is deposited on <100> oriented GaAs square mesas of size ≤ 75 nm, on the contrary, the island morphology is suppressed and, instead, a continuous film with flat morphology is observed. This InAs film growth is, however, self-limiting and stops at ~ 11 ML [63]. In order to understand the self-limiting nature of the InAs film growth, it is important to know atomistic information about mechanical stress and the in-plane lattice constant of InAs layers in the InAs/GaAs square nanomesas.

Recently, chemical vapor deposited (CVD) diamond films have received considerable attention for applications requiring hard, wear-resistant coatings, due to their extremely high strength and fracture toughness [96]. However, relationships between
specific values for the properties, microstructure and crack propagation mechanisms, are not well understood. Moreover, the tendency for diamond to deposit as a polycrystalline film with a high density of GBs and related defects degrade many of its desirable properties. Mechanical properties of CVD diamond films can be affected by the presence of GBs and particularly depend on GBs structures. It is known that different types of GBs can behave differently under applied load, e.g., they may have different resistance to crack propagation [97,98]. Hence, studying the mechanical properties of different types of GBs can helps us predict what types of microstructures provide the highest toughness of the film.

This dissertation is organized as follows. Chapter 2 describes the multiresolution MD algorithms and their parallel implementation. Chapter 3 focuses on surface energies and surface reconstructions of GaAs and InAs. In Chapter 4 we deal with multimillion-atom molecular dynamics simulation of flat InAs overlayers with self-limiting thickness on GaAs square nanomesas. Chapter 5 describes the critical lateral size for stress domain formation in InAs/GaAs square nanomesas. Atomistic simulations of grain boundary fracture in diamond are reported in Chapter 6. Finally, Chapter 7 gives conclusions.
In this Chapter we discuss the concepts of molecular dynamics (MD), the interatomic potentials used in MD simulations, physical properties calculation in MD simulations, the implementation of parallel MD, and the multiresolution MD method in time and space.

2.1 Molecular Dynamics Method

Molecular dynamics is a technique to compute the equilibrium, non-equilibrium, and transport properties of a classical many-body system. In this context, the word "classical" means that the nuclear motion of the constituent particles obeys the laws of classical mechanics. For a wide range of materials, this is an excellent approximation. Consider a system of $N$ atoms with coordinates $\{r_i\}_{i=1,\ldots,N}$ and momenta $\{p_i\}_{i=1,\ldots,N}$. The system can be described by a classical Hamiltonian,

$$H = \sum_i \frac{p_i^2}{2m_i} + V(r_1, r_2, \ldots, r_N),$$  \hspace{1cm} (2.1)

where $m_i$ is the mass of the $i$-th atom and $V$ is the potential energy.

The potential function $V$ is sometimes approximated by a simple two-body potential,

$$V = \frac{1}{2} \sum_{i,j} v_{ij}(r_{ij}),$$  \hspace{1cm} (2.2)

where the pair potential $v_{ij}$ depends on the interatomic distance $r_{ij} = |r_i - r_j|$ and the atomic species. Using the Hamiltonian equations of motion, we have,
\[
\dot{x}_i = \frac{\partial H}{\partial p_i}, \\
\dot{p}_i = -\frac{\partial H}{\partial x_i}. \\
\]

The above equations are reduced to Newton's second law for classical Hamiltonian (2.1),

\[
m_i \ddot{x}_i = -\frac{\partial V(x_1, x_2, \ldots, x_N)}{\partial x_i}.
\]  

(2.4)

In the MD approach, we obtain the system's phase-space trajectories (positions are velocities at all times) from numerical solution of Newton’s equation (2.4). By taking averages over phase-space trajectories we can compute equilibrium properties of the system. This lets us study how atomistic processes determine materials' macroscopic properties. MD simulations can also be used to study non-equilibrium processes, such as dynamic fracture and thermal transport.

In MD simulations, we usually place atoms in a simulation box and apply periodic boundary conditions (PBC) at the box boundaries. The introduction of PBC is equivalent to considering an infinite space-filling array of identical copies of the simulation region. This technique allows us to simulate bulk solid and liquid properties with a small number of atoms (say, \(N = 1,000\)) by eliminating surface effects. Note that for 1,000 atoms arranged in a \(10 \times 10 \times 10\) cube, the number of surface atoms is \(10^3 - 8^3 = 488\). In other words, nearly half the atoms are at the surface. Since these surface atoms are in very different environment from the bulk atoms, the average properties computed for this system are very different from bulk properties.

Periodic boundary conditions are implemented by replicating a simulation box of size \(L_x \times L_y \times L_z\) to form an infinite lattice. Figure 2.1 shows a schematic of PBC in 2 dimensions. Note that we assume atoms to be contained in a rectangular simulation box. As an atom moves in the original simulation box, all the images move in a concerted
manner by the same amount. Since all the images are just shifted copies of an original
atom, we need to keep only the coordinates of the original (central) image as a
representative of all images. When an atom leaves the central box by crossing a
boundary, attention is switched to the image just entering the central box; see Figure 2.2.

At every MD step, we require that an atomic coordinate satisfy

\[ 0 \leq x_i < L_x, 0 \leq y_i < L_y, 0 \leq z_i < L_z. \]

If \( \vec{r}_i(t) \) is in the central box and time increment \( \Delta \) is small, \( \vec{r}_i(t + \Delta) \) is at most in
the neighbor image. In this case, an atom can reenter the central box by

\[
\begin{align*}
  x_i &\leftarrow x_i - \text{SignR}\left( \frac{L_x}{2}, x_i \right) - \text{SignR}\left( \frac{L_x}{2}, x_i - L_x \right) \\
  y_i &\leftarrow y_i - \text{SignR}\left( \frac{L_y}{2}, y_i \right) - \text{SignR}\left( \frac{L_y}{2}, y_i - L_y \right) \\
  z_i &\leftarrow z_i - \text{SignR}\left( \frac{L_z}{2}, z_i \right) - \text{SignR}\left( \frac{L_z}{2}, z_i - L_z \right)
\end{align*}
\]

(2.5)

where

\[
\text{SignR}\left( \frac{L_x}{2}, x_i \right) = \begin{cases} 
  \frac{L_x}{2} & x_i > 0 \\
  -\frac{L_x}{2} & x_i \leq 0
\end{cases}
\]

(2.6)

and this means

\[
\begin{align*}
  L_x < x_i &\quad x_i - \frac{L_x}{2} - \frac{L_x}{2} = x_i - L_x \\
  0 < x_i \leq L_x &\quad x_i - \frac{L_x}{2} + \frac{L_x}{2} = x_i \\
  x_i \leq 0 &\quad x_i + \frac{L_x}{2} + \frac{L_x}{2} = x_i + L_x
\end{align*}
\]

(2.7)
Figure 2.1 Periodically repeated images of an original simulation box (shaded) in 2 dimensions.

Figure 2.2 Change of the representative atom due to boundary crossing of the atom.
Furthermore, atoms near the boundaries of the MD box interact with atoms in the appropriate periodic images of the box and only the closest image atom is taken into account. This is also known as the minimum image convention. In principle, an atom interacts with all the images of another atom (and even with its own images except for itself); see Figure 2.3.

![Diagram of the minimum image convention in 2 dimensions.](image)

Figure 2.3 Schematic of the minimum image convention in 2 dimensions.

Consider a box of size $L_x \times L_y \times L_z$ centered at atom $i$, and this atom interacts only with other atoms in this imaginary box. Then, we have,

$$\begin{align*}
-\frac{L_x}{2} & \leq x_i < \frac{L_x}{2} \\
-\frac{L_y}{2} & \leq y_i < \frac{L_y}{2} \\
-\frac{L_z}{2} & \leq z_i < \frac{L_z}{2}
\end{align*}$$

(2.8)

during the computation of forces. This can be achieved by
MD simulations generate information at the microscopic level (atomic positions, velocities, etc.) and the conversion of this very detailed information into macroscopic terms (pressure, internal energy, etc.) needs statistic mechanics. For a system which has Hamiltonian (2.1) and contains $N$ atoms, we can use a microcanonical ($NVE$) ensemble, in which the total energy ($E$), the number of atoms ($N$), and the system volume ($V$) are conserved. However, other thermodynamic quantities (pressure, $P$, temperature, $T$, etc.) fluctuate around their average values. Obviously the microcanonical ensemble is the most natural choice for MD simulations, but certain physical situations require that the MD simulations be carried out at constant pressure or temperature (for example, dynamic fracture simulations).

In order to perform constant-temperature MD simulations, several different techniques were developed [17-21]. In these techniques, the equations of motion are modified so that the instantaneous temperature defined in (2.10) is either constant or the average temperature is controlled at a desired value $T_{req}$,

$$T = \frac{2K}{3Nk_B} = \frac{1}{3Nk_B} \sum_{i=1}^{N} |p_i|^2 / m_i$$  \hspace{1cm} (2.10)

$$\langle T \rangle = T_{req}. \hspace{1cm} (2.11)$$

There is an easy yet widely used way to control the instantaneous temperature, $T$. Namely, the atom velocities are scaled to the desired temperature $T_{req}$,

$$\dot{\mathbf{r}}_i \rightarrow \dot{\mathbf{r}}_i \sqrt{\frac{T_{req}}{T}}, \hspace{1cm} (2.12)$$
where \( \dot{r}_i \) is the velocity of the \( i \)-th atom. The criterion is whenever the absolute value of the relative difference between the instantaneous temperature and desired temperature exceeds a certain small value \( \varepsilon \), the atom velocities are subject to scaling (2.11).

A canonical ensemble can be accurately simulated by employing an extended system, developed by Nosé [17, 21]. Namely, a heat bath in contact with the system is simulated by introducing fictitious degrees of freedom into the original Hamiltonian. The extended Hamiltonian \( H_{ex} \) is defined as

\[
H_{ex} = \sum_i \frac{p_i^2}{2m_i s^2} + V + \frac{p_s^2}{2Q} + (f + 1)k_b T_{eq} \ln s,
\]

where \( s \) and \( p_s \) are the generalized coordinate and momentum of the heat bath, \( Q \) is the fictitious mass of the heat bath, and \( f \) is the number of degrees of freedom. Plug in the above Hamiltonian into equations of motion (2.3), we have

\[
\ddot{x} = \frac{f_i}{m s^2} - 2 \frac{\dot{s} \dot{x}}{s},
\]

\[
Q \ddot{s} = \sum_i m s^2 \dot{x}_i^2 \frac{(f + 1)k_b T_{eq}}{s}.
\]

When the variable \( s \) varies slowly enough, the extended-system approach may be used to simulate a canonical ensemble. In order to maintain the temperature control, the fictitious mass \( Q \) is chosen so that \( s \) changes as slow as possible.

For an isobaric (\textit{NPE}) ensemble, similar methods can be employed [19]. Atomic coordinates and the size of the MD box are periodically scaled to maintain constant pressure. In addition, an extended system technique was developed to simulate an isobaric (\textit{NPE}) ensemble [22, 23]. In this technique, both the size and shape of the MD box may be changed during MD simulations. The MD box is a parallelepiped, defined by three vectors \((h_1, h_2, h_3)\). Figure 2.4 shows a schematic of the MD box. A matrix \( H \)
(called $h$-matrix) is defined using the three vectors $(h_1, h_2, h_3)$ to make coordinate transformation,

$$
H = \begin{pmatrix}
  h_{1x} & h_{2x} & h_{3x} \\
  h_{1y} & h_{2y} & h_{3y} \\
  h_{1z} & h_{2z} & h_{3z}
\end{pmatrix}.
$$  \hfill (2.15)

Atomic positions $r_i = (r_{ix}, r_{iy}, r_{iz})$ are mapped to a new vector space defined by vectors $(h_1, h_2, h_3)$. Hence, reduced coordinates $s_i = (s_{i1}, s_{i2}, s_{i3})$ are obtained,

$$
 r_i = s_{i1}h_1 + s_{i2}h_2 + s_{i3}h_3.
$$  \hfill (2.16)

Figure 2.4 In constant-pressure variable-shape MD, $(h_1, h_2, h_3)$ are base vectors of the MD box. The shape and size of the box may change during the simulations.

In the extended Lagrangian, the components of the $h$-matrix and the reduced coordinates $s_i$ represent the degrees of freedom,

$$
L = \sum_i \frac{m_i}{2} (H\dot{s}_i)^2 - V + \frac{W}{2} \text{Tr}(\dot{HH}^T) - P_{\text{ext}} V_b,
$$  \hfill (2.17)
where $V_b$ is the volume of the box and $W$ is the fictitious mass associated with the box variables. Given the stress tensor matrix $\hat{\sigma} = (\sigma_{ab})$ and the external stress tensor $\hat{\sigma}^{(ext)}$, the equations of motion become

$$m_i \ddot{s}_i = H^{-1}f_i - m_i G^{-1} \hat{\sigma} \dot{s}_i,$$

$$W \ddot{H} = (\hat{\sigma} - \hat{\sigma}^{(ext)}) V (H^{-1})^T,$$

where $G = hh^T$.

2.2 Interatomic Potentials

Interatomic potentials are essential ingredients of MD simulations. A good interatomic potential accurately as well as reliably describes a real system. Originally proposed for liquid argon, Lennard-Jones (LJ) potential is the simplest yet widely used model. It contains only two-body terms,

$$\nu(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right], \quad r \leq r_c$$

where parameter $\varepsilon$ governs the strength of the interaction and $\sigma$ defines a length scale. The first term in (2.19) represents steric repulsion and the second term corresponds to van der Waals interaction. The interaction repels at close range, then attracts, and is eventually cut off at some limiting separation $r_c$. Although this potential provides a reasonable model for solid and liquid argon, it can not realistically describe most other materials.

Although monatomic systems with close-packed structures can be reasonably described by two-body potentials, for materials with strong covalent bonds, the two-body approximation gives poor results. Hence, three-body terms should be included in the potentials,

$$V = \frac{1}{2} \sum_{i,j} V^{(2)}_{ij} (r_{ij}) + \frac{1}{2} \sum_{i,j,k} V^{(3)}_{ijk} (r_{ij}, r_{ik}, \cos \theta_{jk}),$$

(2.20)
where $\theta_{ijk}$ is the angle formed by $r_{ij}$ and $r_{ik}$. Obviously the three-body part introduces an explicit dependence on bond angles $\theta_{ijk}$. This is important for realistic descriptions of covalent materials. One of the most widely used three-body potential models was proposed by Stillinger and Weber [12]. The Stillinger-Weber potential has the following three-body part:

$$V^{(3)}_{ijk}(r_{ij}, r_{ik}, \cos \theta_{ijk}) = B_{ijk} f_{ij}(r_{ij}) f_{ik}(r_{ik}) [\cos \theta_{ijk} - \cos \bar{\theta}_{ijk}]^2, \quad (2.21)$$

where $\bar{\theta}_{ijk}$ is a constant, $B_{ijk}$ is the strength of the interaction, and function $f_{ij}(r)$ is defined as

$$f_{ij}(r) = \begin{cases} \exp \left[ \frac{l}{(r - r_o)} \right], & \text{for } r < r_o, \\ 0, & \text{for } r \geq r_o \end{cases} \quad (2.22)$$

where $l$ is a parameter, and $r_o$ is the cutoff distance which is chosen to be slightly larger than the length of the covalent bond. The function $f_{ij}(r)$ becomes zero whenever atoms $i$ and $j$ are out of the cutoff distance.

**2.2.1 Reactive Empirical Bond-Order Potentials for Hydrocarbons**

Brenner et al. developed Reactive Empirical Bond-Order (REBO) potentials for hydrocarbons [13,14]. A unique feature of this potential is that it treats covalent bonding in molecular and solid-state structures with a single classical expression. In addition, Brenner’s potentials can be used to describe chemical processes (for example, bond formation and breaking). The fitting database for the potential includes experimental values and first-principle calculations of bond lengths, bond energies, and force constants for several solid-state and molecular systems. The REBO model has been shown to provide a good description of properties outside the fitting database. For instance, the
model gives a good description for in-plane elastic properties of graphite and vibrational spectra of diamond [24-27]. Brenner's potential has been employed in MD simulations [28] of liquid and amorphous carbon with good agreements with experiment [29], first-principles and tight-binding molecular dynamics calculations [30-32].

The REBO potential is expressed as follows

\[ V = \frac{1}{2} \sum_{i,j} \left[ V_{ij}^{(R)}(r_{ij}) - b_i V_{ij}^{(A)}(r_{ij}) \right], \tag{2.23} \]

where the attractive \( V_{ij}^{(A)} \) and repulsive \( V_{ij}^{(R)} \) are defined as

\[ V_{ij}^{(R)}(r) = f_{ij}^{s}(r) \left( 1 + \frac{Q_{ij}}{r} \right) A_{ij} e^{\alpha r}, \]
\[ V_{ij}^{(A)}(r) = f_{ij}^{s}(r) \sum_{n=1}^{3} B_{ijn} e^{\beta_{ijn} r}. \tag{2.24} \]

In the above expressions, the subscripts \( i \) and \( j \) represent atomic species (either C or H) and \( f_{ij}^{s}(r) \) is the switching function which changes smoothly from 1 to 0, restricting the range of covalent bonding.

The bond-order parameter \( b_{ij} \) has the following form:

\[ b_{ij} = \frac{1}{2} \left( p_{ij}^{\sigma} + p_{ij}^{\pi} \right) + p_{ij}^{\sigma}, \tag{2.25} \]

where \( p_{ij}^{\sigma} \) and \( p_{ij}^{\pi} \) are functions of the bond angles and local coordinations of atoms \( i \) and \( j \). The term \( p_{ij}^{\sigma} \) can be written as:

\[ p_{ij}^{\sigma} = \pi_{ij}^{\sigma} + \pi_{ij}^{\sigma}, \tag{2.26} \]

where \( \pi_{ij}^{\sigma} \) is contribution from the conjugated bond and radical energetics, and \( \pi_{ij}^{\sigma} \) is the energetics of rotation around the dihedral angles for carbon-carbon double bonds.

The term \( \pi_{ij}^{\sigma} \) has the following form:
where $F_{ij}(x,y,z)$ is a function and $N'_i$ is the total number of neighbors of atom $i$ without counting $j$.

The term $N'^{\text{conf}}_{ij}$ depends on the local conjugation of the bond between atoms $i$ and $j$.

\[
N'^{\text{conf}}_{ij} = 1 + \left[ \sum_{k \in C} f^{\alpha}_{ii}(r_{ik}) \Phi(N'^{\text{tr}}_{ik}) \right]^2 + \left[ \sum_{l \in C} f^{\alpha}_{jl}(r_{jl}) \Phi(N'^{\text{tr}}_{jl}) \right]^2, \tag{2.28}
\]

where $\Phi(N'^{\text{tr}}_{ik})$ is a switching function. It goes from one to zero smoothly as $N'^{\text{tr}}_{ik}$ increases from three to four.

The dihedral term, $\pi^{\text{dih}}_{ij}$, in (2.26) is defined as follows

\[
\pi^{\text{dih}}_{ij} = T_{ij}(N'^{\text{tr}}_{ij}, N'^{\text{tr}}_{ij}, N'^{\text{conf}}_{ij}) \sum_{k \in C} \sum_{l \in C} f^{\alpha}_{ik}(r_{ik}) f^{\alpha}_{jl}(r_{jl}) (1 - \cos^2 \Omega_{ijkl}). \tag{2.29}
\]

where the function $T_{ij}(N'^{\text{tr}}_{ij}, N'^{\text{tr}}_{ij}, N'^{\text{conf}}_{ij})$ represents the barrier for rotation.

2.2.2 GaAs and InAs Potentials

Recently, new interatomic potentials have been developed for GaAs and InAs [33, 34]. These potentials involve both two-body and three-body terms,

\[
V = \sum_{i<j} V_{ij}^{(2)}(r_{ij}) + \sum_{i<j<k} V_{ijk}^{(3)}(r_{ij}, r_{ik}). \tag{2.30}
\]

The two-body terms include effects of steric repulsion, charge-transfer between atoms, charge-dipole interactions, and van der Waals interactions:

\[
V_{ij}^{(2)}(r_{ij}) = \frac{H_{ij}}{r_{ij}^{1}} + \frac{Z_i Z_j}{r_{ij}^{1}} e^{-r_{ij}/a} - \frac{D_{ij}}{r_{ij}^{4}} e^{-r_{ij}/b} - \frac{W_{ij}}{r_{ij}^{6}}, \tag{2.31}
\]
The first term represents steric repulsion. It contains two parameters $H_{ij}$ and $\eta_{ij}$.

The second term is the Coulomb interaction due to charge transfer and contains the effective atomic charges $Z_i$ as parameters. The third term corresponds to the charge dipole interaction due to large polarizability of negative ions. The last term is the induced dipole-dipole interaction, containing the parameter $W_{ij}$. Covalent effects are represented by three-body bond-bending and bond-stretching terms. The three-body term $V_{ijk}^{(3)}$ includes bond angles and has the form:

$$V_{ijk}^{(3)}(r_{ij}, r_{ik}) = \beta_{ijk} \exp \left( \frac{\gamma}{r_{ij}} + \frac{\gamma}{r_{ik}} \right) \left( \frac{\cos \theta_{jik} - \cos \bar{\theta}_{jik}}{1 + C \left( \cos \theta_{jik} - \cos \bar{\theta}_{jik} \right)} \right)^2 \Theta(r_0 - r_{ij}) \Theta(r_0 - r_{ik}),$$

(2.32)

where $B_{ijk}$ is the strength of the interaction, $\Theta(r_0 - r_{ij}) \Theta(r_0 - r_{ik})$ are step functions, and $\bar{\theta}_{jik}$ is a constant. Here $\theta_{jik}$ is the angle formed by $r_{ij}$ and $r_{ik}$.

The adjustable parameters in Eqs. (2.31) and (2.32) are determined so that a set of experimental data and first-principle calculations of electronic structures are reproduced. These potentials reproduce well the experimental crystalline lattice constants, cohesive energies, elastic constants, surface energies [35-37], high-pressure structural transitions, phonon density-of-states, and neutron-scattering data for liquid and amorphous structures.

Recently, MD simulations of a-GaAs are performed based on the new interatomic potential [34]. The calculated static structure factor, including the intermediate-range correlations, is in excellent agreement with X-ray diffraction experiments. The correlation beyond nearest-neighbor distances in a-GaAs is analyzed in terms of the distribution of
predominantly 6-membered rings. The calculated energy difference between crystalline and amorphous GaAs is in good agreement with electronic-structure calculations.

2.3 Physical Properties Calculation in MD Simulations

In MD simulations, a wide range of techniques are used to analyze the results. Usually, a large amount of data is generated during a MD simulation, but such data is often not of particular interest in itself. The important thing is to extract meaningful information from such a large data set. For homogeneous systems at equilibrium, averages corresponding to thermodynamics quantities are easy to measure. Such MD averages can be related to their thermodynamic counterparts, and the ergodic hypothesis can be employed to justify equating trajectory averages to ensemble-based thermodynamic properties [38].

In statistical mechanics, there is no knowledge of trajectories of atoms. Therefore basically it cannot deal with quantities that are defined in terms of atomic motions. In contrast, MD simulations provide all such information of trajectories of atoms. If the system is spatially inhomogeneous, all quantities must be based on localized measurements. Furthermore, if the system is also non-stationary over time, long-term time averaging is invalid since it would obliterate the effects being studied [38].

2.3.1 Structural Correlations

There are well defined structural correlations, which can be measured experimentally to provide important details about the average molecular organization in a material. A material’s structural properties can be characterized by various correlation functions, such as the pair distribution function. The treatment of structural correlations begins with the completely general pair-distribution function:

\[
g_{\alpha\beta}(r_1, r_2) = \frac{V^2}{N_\alpha N_\beta} \left( \sum_{\{i\in[\alpha]\}} \sum_{j\neq i} \delta(r_{1i} - r_j) \delta(r_{2i} - r_j) \right),
\]  

(2.33)
where \( \alpha, \beta \) are atomic species, \( V \) is the volume of the system, and \( \langle \ldots \rangle \) is an ensemble average. In the case of spatially homogeneous systems, only relative atomic separation is meaningful, leading to a sum over atom pairs:

\[
g_{\alpha\beta}(r) = \frac{V}{N_{\alpha}N_{\beta}} \left\langle \sum_{i \in \{\alpha\}} \sum_{j \neq i} \delta(r - r_{ij}) \right\rangle,
\]  

(2.34)

where \( r = r_{1} - r_{2} \). If the system is also isotropic, the function can be averaged over angles without loss of information. The result is the radial distribution function \( g(r) \), which describes the spherically averaged local organization around any given atom,

\[
g_{\alpha\beta}(r) = \frac{V}{4\pi r^2 N_{\alpha}N_{\beta}} \left\langle \sum_{i \in \{\alpha\}} \sum_{j \neq i} \delta(r - r_{ij}) \right\rangle,
\]  

(2.35)

where \( r = |r| \). This equation can be used in the evaluation of \( g(r) \) by computer simulations. In practice, the delta function is replaced by a function which is non-zero in a small range of separations, and a histogram is compiled of all pair separations falling within each such range.

The radial distribution function \( g(r) \) is related to the experimentally measurable static structure factor, \( S_{\alpha\beta}(q) \), by Fourier transformations. The static structure factor is a key quantity in interpreting X-ray scattering measurements and it has the following definition:

\[
S_{\alpha\beta}(q) = \left( N_{\alpha}N_{\beta} \right)^{-1/2} \left\langle \rho_{q\alpha} \rho_{-q\beta} \right\rangle,
\]  

(2.36)

where \( \rho_{q\alpha} \) is the Fourier transformation of the number density of species \( \alpha \),

\[
\rho_{q\alpha} = \sum_{i \in \{\alpha\}} e^{iq \cdot r_{i}}.
\]  

(2.37)
In a general case, not assuming isotropy, the structure factor is related to the pair correlation function, \( g_{ab}(r) \), by the following equation

\[
S_{ab}(q) = \delta_{ab} + \left( c_a c_\beta \right)^{\frac{1}{2}} \int g_{ab}(r) e^{iqr} d^3r,
\]

(2.38)

where \( c_a = N_a / N \). If the system is isotropic, the structure factor and the pair correlation function do not depend on angle. Equation (2.38) can be further simplified into

\[
S_{ab}(q) = \delta_{ab} + 4\pi \left( c_a c_\beta \right)^{\frac{1}{2}} N V \int [g_{ab}(r) - 1] \frac{\sin(qr)}{qr} r^2 dr.
\]

(2.39)

This equation provides an important link between MD simulations and the real world. Furthermore, \( S_{ab}(q) \) can be used in calculating the static structure factor \( S_N(q) \) measured by neutron scattering [39],

\[
S_N(q) = \frac{\sum_{a,b} b_a b_\beta \left( c_a c_\beta \right)^{\frac{1}{2}} \left[ S_{ab}(q) - \delta_{ab} + \left( c_a c_\beta \right)^{\frac{1}{2}} \right]}{\left[ \sum_a b_a c_a \right]^2},
\]

(2.40)

where \( b_a, b_\beta \) are the coherent neutron-scattering lengths of species \( \alpha, \beta \), respectively.

Beside the pair-correlation function, there are higher-order correlations that can be used to characterize the structure of materials. For instance, the bond-angle distribution function is an important three-particle correlation. In MD simulations, a cutoff distance \( r_c \) is usually defined. Atoms \( i \) and \( j \) are considered to form a bond if \( r_{ij} < r_c \). First, the histogram of all the bond angles is computed by going over all the appropriate triplets of particles. Then, the bond-angle distribution is calculated based on such histogram. In addition, other structural correlations (such as porosity of the material) can be studied. These structural properties are calculated in such a way that the atomistic level information is coarse-grained by converting it into a two-dimensional array of pixel values or a three-dimensional array of voxels.

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2.3.2 Dynamic Correlations

In MD simulations, time correlation functions can be used to characterize the dynamics of a system. For instance, time correlation function for two quantities $X$ and $Y$ is the following

$$C_{xy}(t) = \langle X(t)Y(0) \rangle,$$  \hspace{1cm} (2.41)

where $\langle \ldots \rangle$ denotes an average taken over a sufficiently long phase-space trajectory. For example, velocity autocorrelation function is an important time correlation function,

$$Z_\alpha(t) = \frac{\langle v(t)v(0) \rangle_\alpha}{\langle v(0)^2 \rangle_\alpha},$$  \hspace{1cm} (2.42)

where the averages are taken over all atoms of species $\alpha$. Time correlation functions can be related to transport coefficients. For instance, $Z_\alpha(t)$ can be used to compute the diffusion coefficient,

$$D_\alpha = \frac{k_B T}{m_\alpha} \int_0^\infty Z_\alpha(t) \, dt.$$  \hspace{1cm} (2.43)

In addition, the diffusion coefficient can be calculated from the mean-square displacement $R_\alpha(t)^2$, which measures how far an atom has traveled on average from time 0 to time $t$,

$$R_\alpha(t)^2 = \langle [r(t) - r(0)]^2 \rangle_\alpha.$$  \hspace{1cm} (2.44)

For large $t$, we have the Einstein expression,

$$D_\alpha = \lim_{t \to \infty} \frac{R_\alpha(t)^2}{6t}.$$  \hspace{1cm} (2.45)

Note that for a finite system, $t$ cannot become too large because the allowed displacements are bounded. Eventually this asymptotic result will break down, so that after reaching a plateau $D$ will begin to drop to zero. A reliable estimate of $D$ as well as other transport
coefficients requires that the trajectories be computed relatively accurately for as long as the velocities remain correlated.

2.3.3 Thermodynamics Quantities

Consider a one-component macroscopic system. The thermodynamic state of such a system is usually defined by a small set of parameters (such as the number of particles \( N \), the temperature \( T \), and the pressure \( P \)). These quantities are computed by simply averaging the corresponding instantaneous quantities over the phase trajectory. Other thermodynamic quantities (such as density \( \rho \), chemical potential \( \mu \), specific heat, \( C_v \)) can be derived by the fundamental equations of thermodynamics. For instance, the thermodynamic temperature is defined as

\[
T = \frac{2\langle K \rangle}{3Nk_B}.
\]

where \( \langle K \rangle \) is the average kinetic energy.

Some thermodynamic quantities can be derived from Root Mean Square (RMS) fluctuations. For instance, the RMS of a thermodynamic quantity \( A \) is defined as

\[
\langle \delta A^2 \rangle = \langle A^2 \rangle - \langle A \rangle^2,
\]

where \( \langle \ldots \rangle \) denotes an average taken over a sufficiently long phase-space trajectory. The RMS fluctuation of some thermodynamic variables can be used to extract other thermodynamic variables. For instance, in the microcanonical ensemble, the specific heat, \( C_v \), can be derived from the fluctuation of the total kinetic energy [40]:

\[
\frac{\langle \delta K^2 \rangle}{\langle K \rangle} = k_B T \left[ 1 - \frac{3k_B}{2C_v} \right].
\]

2.3.4 Mechanic Quantities

The internal stress tensor for a system of atoms may be derived using the virial theorem,
where $\alpha$ and $\beta$ are Cartesian indices, and the forces $f_i$ contain only the internal contributions due to the interaction among the atoms in the system. All external forces that keep the system under stress are excluded. If the system is subjected to periodic boundary conditions and no external forces are present, the equation is further simplified into:

$$\sigma_{\alpha\beta} = \frac{1}{V} \left\langle \sum_i \left[ m_i v_i^\alpha v_i^\beta + \frac{1}{2} \sum_j r_{ij}^\alpha f_{ij}^\beta \right] \right\rangle. \quad (2.50)$$

where $r_{ij}^\alpha$ is normalized using the minimum-image convention. In this case, the stresses are independent of the origin of the coordinates. Let us assumed that the potential is has a two-body form, then we have

$$f_i = \sum_j f_{ij}, \quad (2.51)$$

$$f_{ij} = -\frac{\partial v_j(r_{ij})}{\partial r_{ij}} \frac{r_{ij}}{r_{ij}}. \quad (2.52)$$

If the interatomic potential allows the decomposition (2.51) with $f_{ij} = -f_{ji}$, equation (2.50) can still be used. However, the expression (2.49) cannot be generally used for simulations with periodic boundary conditions. The reason is that the minimum-image convention is not followed.

At the atomic level, the local stress can be determined by calculating the interatomic forces arising from interactions among neighboring atoms. In this approach, the stress is either assigned to small regions of space or to individual atoms. However, the stresses are not uniquely defined on the atomistic level because stress is inherently related to the assumption of continuity. In MD simulations, stresses need to be calculated over length scales of few atomic spacings. So we can either abandon this concept.
completely or define a quantity that reasonably extrapolates the continuum definition of stress to atomistic length scales. However, such a quantity should be equivalent to macroscopic stress for a sufficiently large region of space. In addition, the symmetry of the stress tensor has to be preserved. Furthermore, the atomistic stress should vanish for systems which are expected to be under zero stress (for example, an ideal crystal in equilibrium).

Atomic-level stresses can be defined using the virial approach. Namely, the local stress is calculated using (2.50)

\[
\sigma_{\alpha\beta}^{\Omega} = \frac{1}{\Omega} \left( \sum_{i,r \in \Omega} m_i \nu_i^\alpha \nu_i^\beta + \frac{1}{2} \sum_{i,r \in \Omega} \sum_j r_{ij}^\alpha f_{ij}^\beta \right),
\]

where the summation over \( i \) is restricted to atoms within a certain region of space, \( \Omega \). On the other hand, stresses \( \sigma_{\alpha\beta}^{i} \) may be assigned to individual atoms:

\[
\sigma_{\alpha\beta}^{i} = \frac{1}{\Omega_i} \left( m_i \nu_i^\alpha \nu_i^\beta + \frac{1}{2} \sum_j r_{ij}^\alpha f_{ij}^\beta \right),
\]

where \( \Omega_i \) is atomic volume.

Atomic-level stresses can also be defined using the direct mechanical approach, in which the stresses are assumed to act on surface elements [41]. The MD box is divided into cells and the stress on each cell is defined in terms of stresses acting on its faces. The momentum transfer associated with an atom leaving or entering a cell results in a force acting for a short time interval. Such a force is assumed to be applied to the surface intersected by this atom. This approach is solely based on mechanical formulation without assuming the local thermodynamic equilibrium.

The elastic constants can be calculated by applying a certain strain to a system and examining the resultant stress. Let us consider the six components of a strain tensor
(u_x, u_y, u_z, u_y, u_z, u_x). We apply a strain by appropriately modifying the h-matrix.

The h-matrix of a rectangular MD box is:

\[
H^{(o)} = \begin{pmatrix}
  h_x & 0 & 0 \\
  0 & h_y & 0 \\
  0 & 0 & h_z
\end{pmatrix},
\]  

(2.55)

then the h-matrix is modified into

\[
H = \begin{pmatrix}
  h_x (1 + u_x) & u_x h_x h_y / (h_x + h_y) & u_x h_z h_y / (h_z + h_y) \\
  u_y h_x h_y / (h_x + h_y) & h_y (1 + u_x) & u_y h_z h_z / (h_y + h_z) \\
  u_z h_x h_z / (h_x + h_z) & u_z h_z h_y / (h_z + h_y) & h_z (1 + u_x)
\end{pmatrix}.
\]  

(2.56)

Finally, the system is relaxed via the conjugate-gradient method and stress is calculated.

The elastic constants \( C_{\alpha \beta \gamma \delta} \) are determined by using the Hooke’s law,

\[
\sigma_{\alpha \beta} = C_{\alpha \beta \gamma \delta} u_{\gamma \delta}
\]  

(2.57)

2.4 Multiresolution Molecular Dynamics Method

In a molecular dynamics simulation of a system consisting of \( N \) atoms, we integrate the \( 3N \) coupled equations of motion numerically with respect of time. The \( 3N \) coupled equations of motion are differential equations where time has continuous values. To perform computer simulations, however, these continuous equations must be cast into discrete algebraic forms that can be solved numerically on digital computers. In such a numerical solution, time is discretized into a sequence of time steps, which are denoted as \( \Delta t \). The time step should be sufficiently small so that the time derivatives are well approximated by the finite-difference expressions. At each time step, the forces for all the atoms are calculated and the atoms' coordinates are updated using appropriate finite-difference algorithms. For the microcanonical ensemble, an effective way to test the soundness of an integration algorithm is to check if the energy of a system is conserved during a MD simulation. In this case, the energy should be conserved to a reasonable
accuracy (typically, $\sim 10^{-5}$) during the MD simulations. Usually, $\Delta t$ is determined through a trial and error process in which we choose the largest value that yields reasonable accuracy of energy conservation. Typically, the value of time step is in the order of a femto second ($10^{-15}$ s). This value is about an order of magnitude smaller than the typical time scale of atomic oscillations. In a typical MD simulation, the number of time step may range from $10^3$ to $10^6$, which is basically limited by available computing resources.

In MD simulations, the major part of computation time is spent on the calculation of interatomic forces at each time step. For a system consisting of $N$ atoms, the calculation of two-body forces among all atom pairs requires $O(N^2)$ CPU time. If the number of atoms is relatively small (say hundreds of atoms) the computation time is still acceptable. However, as the number of atoms increases to a certain amount (say millions of atoms) the computation time is $O(10^{12})$, which is intractable even using the most powerful supercomputers in the world. In order to tackle this problem, multiresolution algorithms have been developed in recent years to efficiently manage multiple lengths and time scales. These algorithms have dramatically improved the performance MD simulations. For instance, finite-range potentials and forces can be computed in $O(N)$ time using the linked-cell list algorithm [19]. On the other hand, $O(N)$ algorithms have also been developed for the long-range Coulomb interaction using divide-and-conquer techniques for a hierarchy of cells. For example, the fast multipole method (FMM) [42] is designed to compute long-range contributions to the forces using truncated multipole expansion. The FMM technique groups distant atoms together and treats them collectively. Hierarchical grouping is facilitated by recursively dividing the physical system into smaller cells, hence generating a tree structure. The FMM method uses the truncated multipole expansion and the local Taylor expansion of the electrostatic potential.
field. The computation of both expansions is performed recursively for the hierarchy of cells, and hence the electrostatic energy is of \(O(N)\) complexity [43].

In order to represent accurately the fastest characteristic oscillations of a simulated system, the time step \(\Delta t\) in MD simulations must be small enough. However, many important physical processes are slow and the characterized time scales are many orders of magnitude larger than \(\Delta t\). As a result, MD simulations of such processes require extremely long computing time. This severely restricts the applicability of MD simulations. To speed up MD simulations, we took advantage of the multiple time scale (MTS) techniques [44,45], which uses different time steps for different force components to reduce the number of force calculations. Namely, the force experienced by an atom is separated into a rapidly varying primary component and a slowly varying secondary component. Typically, short-range forces belong to the primary component, and the long-range contributions are included in the secondary part. While the primary forces are evaluated at every time step, the secondary interactions are calculated only for a certain number of time steps. This technique may be extended to include several different time scales. For instance, a hierarchy of dynamics including rigid-body motion of atomic clusters can be employed [43].

In the last decade, parallel-computing technology has become a powerful tool to extend the scope of computer simulations in terms of size of simulated systems. MD simulations involving billions of atoms have become possible with the emergence of advanced massively parallel architectures. However, algorithms developed for serial computers must be appropriately modified in order to run efficiently on parallel computers. To utilize parallel computing, a computation task needs to be decomposed into subtasks that are mapped to multiple processors. In terms of MD simulations, such a spatial decomposition leads to a divide-and-conquer approach. Large-scale MD simulations are naturally suited for parallelization by domain decomposition. Namely, a
system is decomposed into subdomains, which are assigned to multiple processors. The data associated with atoms in a subdomain is assigned to the corresponding processor. In the evaluation of forces for all atoms in a subdomain, the data of the atoms in the boundaries of neighbor subdomains must be cached from the corresponding processors. The inter-processor communication time is short relative to the total computation time, since the number of atoms near the boundaries of the subdomains is small compared to the total number of atoms in the system.

2.4.1 Multiresolution Scheme in Space

In MD simulations, an interatomic potential may be short-ranged, i.e., there is no force between any pair of atoms if their distance is greater than a cutoff distance, \( r_c \). In this case, there is no need to calculate forces between all pairs of atom in the system. Force evaluations are needed only for atoms within the cutoff distance. This leads to the linked-cell list algorithm for short-range potentials. The MD box is divided into equal sized cells, as shown in Figure 2.5. The atoms are sorted into the cells and the data associated with the atoms is stored in a linked list. To simplify the process, the decomposition into cells is defined in the reduced space, \( s = (s_1, s_2, s_3) \), where the MD box is a unit cube. The cell size in real space, \( a \), is usually set to be

\[
a = r_c + \delta,
\]

where \( \delta \) is a small number, also called a “skin”. The purpose of adding such a “skin” is to avoid recomputing the link-cell list at every time step, since the link-cell list is still valid while atoms do not move by more than \( \delta/2 \). The evaluation of the force on an atom only needs to add the contributions from atoms in the neighboring cells, as schematically illustrated in Figure 2.6 for a two dimensional case. As a result, the computation time scales as \( MN \), where \( M \) is the average number of atoms involved in evaluating the force on an atom. The value of \( M \) can be estimated as
\[ M = 27\rho(\tau + \delta)^{3}. \]  

(2.59)

where \( \rho \) is the average number density in the system. Consequently, the linked-cell method is an \( O(N) \) algorithm. Moreover, according Newton's third law, the force exerted on atom \( i \) by atom \( j \) is of the same magnitude but opposite direction compared with the force exerted on atom \( j \) by atom \( i \). Taking advantage of this fact, the computation can be further reduced by a factor of two, since we evaluating the force between two atoms only once, instead of twice previously.

An improvement to the link-cell method is to set the cell size smaller than the cutoff distance, i.e., choose the cell size as

\[ a = \frac{1}{k}(\tau + \delta), \]  

(2.60)

where \( k > 1 \). Then, \( M \) is decreased into

\[ M = \left(2 + \frac{1}{k}\right)^{3}\rho(\tau + \delta)^{3}. \]  

(2.61)

However, there are certain limitations for this approach. For instance, the cell size should not be overly small to avoid the creation of too many empty cells, in which case considerable computation overhead will be produced.

There is still another efficient method for the evaluation of forces, namely, the neighbor list approach. In this method, a list of neighbor atoms lying within a radius of \( (\tau + \delta) \) from each atom is generated. This neighbor list is stored in an array, which is usually large since each atom has a certain number of neighbor atoms. When evaluating the force exerted on an atom, only the atoms in the neighbor list are used. The neighbor list does not need to be updated until atoms move by more than \( \delta/2 \). With the help of the neighbor list, \( M \) can be further reduced to

\[ M = 4.2\rho(\tau + \delta)^{3}. \]  

(2.62)
Figure 2.5 MD box decomposition into cells in reduced space in two dimensions. The MD box is divided into equal sized cells.
However, the major drawback of the neighbor list approach is the requirement of huge memory, especially when the number of atoms is large. Generally speaking, there is always a tradeoff between speed and memory in computation. Some algorithms may be slower but occupy less memory, while others may occupy more memory but faster. The neighbor list approach falls into the latter category since it obtains speedup by using more memory. When the system size is relatively small and memory is large, the neighbor list approach can be a good choice.

In parallel MD simulations, a MD box with $N$ atoms is decomposed into subdomains, which are mapped to $P$ processors, or nodes. Each node has 26 neighbor
nodes, which are located in 6 directions. Usually, these directions are denoted as east, west, north, south, up and down, respectively. In each node, the corresponding subdomain is divided into cells and a link-cell list is generated. The data associated with all atoms in a subdomain is stored in the corresponding processor. However, when evaluating forces for all atoms in a node, the data of the atoms in the boundaries of all neighbor nodes must be transferred via message passing.

In each node, the message passing to its 26 neighbor nodes is completed in six steps, in which the boundary atom information is sent to east, west, north, south, up and down, sequentially. In terms of boundary atoms at the corners and edges, they are first forwarded to other neighbor nodes, and then copied to the proper node. Since the coordinates of all atoms are updated in each time step, some atoms may cross a node boundary. In other words, these atoms migrated from one node to another node. In this case, they have to be reassigned to the new node, and all the data associated with them have to be sent to the corresponding node. In terms of spatial decomposition, the computation time scales as $N/P$, while the communication time scales as $(N/P)^{2/3}$. As a result, when $N$ is much larger than $P$, the communication overhead becomes less significant. This is exactly the case of parallel MD simulations, which typically have $N = 10^6 \sim 10^9$ and $P = 10^2 \sim 10^3$ [43,46].

In parallel MD simulations, ideally a system being simulated should be evenly distributed in space, in which case the system is divided into equal sized subdomains and each processor is assigned a subdomain with nearly equal number of atoms. In other words, the computation and communication loads are evenly divided among processors through a straightforward equal-sized space decomposition. However, such a situation only occurs for some simple, static system in the real world. Many systems studied by parallel MD simulations are characterized by irregular atomic distributions, such as
dynamic fracture with multiple branches. In these cases, atomic distributions may change over time. If a straightforward equal-sized decomposition space decomposition is applied to a system with irregular atomic distribution, a problem of load imbalance will set in. Consequently, the parallel efficiency is degraded considerably. The load imbalance problem can be solved by partitioning the system in a computational space related to the physical space, instead of partitioning the system in the physical Euclidean space. Recently, a load-balancing technique has been developed using a curvilinear coordinate transformation [47]. In this approach, the computational space shrinks where the workload density is high and expands where the density is low, so that the workload is uniformly distributed. Minimization of the load-imbalance and communication costs is performed to obtain the optimal coordinate system [43].

In practice, the passing of information of atoms that migrate from one node into another node is performed when periodic boundary conditions are applied. Usually, this procedure is not performed at every time step, since the linked-cell list does not have to be updated for several time steps. In each node, all atoms in the cells adjacent to the node boundaries are checked to see if any of them have moved outside the node boundaries. Subsequently, periodic boundary conditions are enforced and information is collected for all atoms that have moved outside the node boundaries. The information of all these migrated atoms (including species, coordinates, velocities, identity tag, etc.) are packed into an array and sent to appropriate nodes using massage passing. In each node, the arrays that store the information of all atoms may have empty slots due to the migration of atoms. On the other hand, each node may receive some migrated atoms from other nodes. Therefore, the empty slots each node may be filled with the information of those received atoms. If the number of atoms received exceeds the number of the available slots, the extra atoms are appended to the end of the arrays. Otherwise, the extra slots are filled with the atoms taken successively from the end of the arrays. Not only does this
procedure maintains a simple array structure, it requires a minimum rearrangement of atoms. However, this technique has a side effect of reordering atoms in the arrays during the simulations. As a result, the build-in ordering of atoms' identities in the arrays is no longer valid. An additional array has to be created to store information of all the atoms' identities.

In the following, we discuss the detailed implementation of the parallel MD. We use simple 3D-mesh decomposition or torus decomposition due to the periodic boundary conditions. Figure 2.7 shows schematically the subsystems that are arranged in a 3D array of dimensions $P_x \times P_y \times P_z$. Each subsystem is a parallelepiped of size $L_x \times L_y \times L_z$. Accordingly, processors or nodes are also logically arranged in such a 3D array.

Each processor is given a unique processor ID, $p$, whose range is $[0, P-1]$, where $P = P_x \times P_y \times P_z$ is the total number of processors; see Figure 2.8. We also define a vector processor ID $\vec{p} = (p_x, p_y, p_z)$, where $p_x = 0, ..., P_x-1$; $p_y = 0, ..., P_y-1$; and $p_z = 0, ..., P_z-1$. The relation between the sequential and vector ID’s is

$$p_x = p / (P_y P_z)$$
$$p_y = (p / P_z) \mod P_y$$
$$p_z = p \mod P_z$$

or

$$p = p_x P_y P_z + p_y P_z + p_z.$$

For each processor, the six face-shared neighbor are identified by a sequential index ($\kappa = 0, ..., 5$). For each neighbor, $\kappa$, the shift-length vector $\vec{\Delta} = (\Delta_x, \Delta_y, \Delta_z)$ denotes the position of the neighbor subsystem relative to itself. Table 2.1 lists the six neighbors, where an integer vector $\vec{\delta} = (\delta_x, \delta_y, \delta_z)$ specifies the relative location of each neighbor.
Figure 2.7 Schematic of a 3D-mesh decomposition in which subsystems are arranged in a 3D array of dimensions $P_x \times P_y \times P_z$. Each subsystem is a parallelepiped of size $L_x \times L_y \times L_z$. 

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Figure 2.8 Schematic of a unique processor ID $\mathbf{p}$ and a vector processor ID $\mathbf{\bar{p}} = (p_x, p_y, p_z)$.
Table 2.1 The six face-shared neighbors for each processor.

<table>
<thead>
<tr>
<th>Neighbor ID, $\kappa$</th>
<th>$\vec{\delta} = (\delta_x, \delta_y, \delta_z)$</th>
<th>$\vec{\Delta} = (\Delta_x, \Delta_y, \Delta_z)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (east)</td>
<td>(-1, 0, 0)</td>
<td>(-Lx, 0, 0)</td>
</tr>
<tr>
<td>1 (west)</td>
<td>(1, 0, 0)</td>
<td>(Lx, 0, 0)</td>
</tr>
<tr>
<td>2 (north)</td>
<td>(0, -1, 0)</td>
<td>(0, -Ly, 0)</td>
</tr>
<tr>
<td>3 (south)</td>
<td>(0, 1, 0)</td>
<td>(0, Ly, 0)</td>
</tr>
<tr>
<td>4 (up)</td>
<td>(0, 0, -1)</td>
<td>(0, 0, -Lz)</td>
</tr>
<tr>
<td>5 (down)</td>
<td>(0, 0, 1)</td>
<td>(0, 0, Lz)</td>
</tr>
</tbody>
</table>

The sequential processor ID, $p'(\kappa)$ is obtained by

$$p'_\alpha (\kappa) = [p_\alpha + \delta_\alpha (\kappa)] \mod P_\alpha (\alpha = x, y, z) \quad (2.64)$$

and

$$p' (\kappa) = p'_{x} (\kappa) \times P_{y} P_{z} + p'_{y} (\kappa) \times P_{x} P_{z} + p'_{z} (\kappa)$$  \quad (2.65)$$

Using the periodic boundary conditions, every node has 26 neighbor nodes, which share either a corner, an edge, or a face with it. We express atomic coordinates relative to the origin of each node, i.e., $0 < x_\kappa < L_\alpha (\alpha = x, y, z)$. In other words, each node thinks that it is the center of the world.

In order to compute interatomic interaction in a node with cut-off length $r_c$, atomic coordinates of 26 neighbor nodes which are located within $r_c$ from the node boundary are copied to this node, as illustrated in Figure 2.9.

After the coordinates of all atoms in a node are updated at each time step, some resident atoms may have moved out of the subsystem boundary. The data of these migrated atoms must be transferred to the proper processors. This is also called "atom migration", as illustrated in Figure 2.10.
Figure 2.9 To compute interatomic interaction in a node, the atomic coordinates of the 26 neighbor nodes that are located within $r_c$ from the node boundary needed to be copied to this node.
2.4.2 Multiresolution Scheme in Time

In MD simulations, the equations of motion are integrated numerically. Over the years, a wide variety of numerical integration algorithms have been developed. An integration algorithm is desirable for MD simulations if it permits larger time steps and maintains sufficient accuracy and stability, since the calculation of forces at each time step is computationally intensive. An important criterion to judge an integration scheme is to check its long-time behavior. Since any two phase-space trajectories with a small difference in the initial conditions diverge exponentially after sufficiently long time, no integration algorithm will provide an exact solution over a long time interval. However, such an exact solution is not necessary in MD simulations because of the statistical nature of the simulated system. There are basically two characteristics for a good
integration algorithm used in MD simulations: on short time scales, it should have an accurate approximation of the differential equations; on long time scales, it should provide conservation of the constants of motion such as total energy and momenta. The first characteristic is not difficult to satisfy. There are some sophisticated high-order finite-difference algorithms that can be used to improve the short-time accuracy. But, a sophisticated high-order finite-difference algorithm does not necessarily guarantee good long-time behavior. For instance, the complicated Gear's predictor-corrector algorithm performs much less stable over long time scales than the simple velocity-Verlet algorithm [19,50,51]. Therefore, most MD simulations are based on the velocity-Verlet algorithm instead of a high-order finite-difference algorithm.

The good long-time behavior of the velocity-Verlet algorithm is due to the fact that it is a symplectic integration scheme. On the other hand, Gear's predictor-corrector scheme does not have this property. A symplectic (or canonical) integration scheme [48,49] preserves certain invariants of Hamiltonian systems. In an integration algorithm, variables (such as atoms' positions $x$ and momenta $p$) are transformed at each time step

$$(x, p) \rightarrow (X, P),$$

(2.66)

where

$$x = (r_1, r_2, \ldots, r_N),$$

$$p = (p_1, p_2, \ldots, p_N).$$

(2.67)

Such a transformation is considered to be symplectic if it defines a canonical transformation of variables in the following way,

$$
\begin{bmatrix}
\frac{\partial X}{\partial x} & \frac{\partial X}{\partial p} \\
\frac{\partial P}{\partial x} & \frac{\partial P}{\partial p}
\end{bmatrix}
\begin{bmatrix}
0 & I \\
-I & 0
\end{bmatrix}
\begin{bmatrix}
\frac{\partial X}{\partial x} & \frac{\partial X}{\partial p} \\
\frac{\partial P}{\partial x} & \frac{\partial P}{\partial p}
\end{bmatrix}
= \begin{bmatrix}
0 & I \\
-I & 0
\end{bmatrix},
$$

(2.68)
where $I$ is a unit matrix. This symplectic transformation provides good long-time scale performance because it conserves the phase space volume. In addition, the error due to discretizing the time interval can be interpreted as an error in the Hamiltonian. Consequently, a symplectic scheme represents an essentially exact algorithm for some modified Hamiltonian, except for computer truncation error.

Let us discuss how the velocity-Verlet algorithm works. Consider a system at a certain time $t$, with atomic positions $r_i(t)$, velocities $v_i(t)$, and accelerations $a_i(t)$. First the velocities at the mid-point are calculated,

$$v_i(t + \frac{\Delta t}{2}) = v_i(t) + a_i(t)\frac{\Delta t}{2}.$$  

Subsequently, the atomic positions at time $t + \Delta t$ are updated,

$$r_i(t + \Delta t) = r_i(t) + v_i(t + \frac{\Delta t}{2})\Delta t.$$  

Then, at the new atomic positions, values of forces $f_i(t + \Delta t)$ and accelerations $a_i(t + \Delta t)$ are computed. Finally, the velocities at time $t + \Delta t$ are determined by

$$v_i(t + \Delta t) = v_i(t + \frac{\Delta t}{2}) + a_i(t + \Delta t)\frac{\Delta t}{2}.$$  

At this point, new values of positions, velocities, and accelerations at time $t + \Delta t$ are generated. In MD simulations, the above expressions are employed recursively to calculate the phase-space trajectory of all atoms over a certain period of time.

In the following, we discuss the multiple time scale (MTS) approach, which was originally proposed by Streett et al. [44]. In their MTS approach, the force on an atom is divided into two parts:

$$f_i = f_i^p + f_i^s.$$  

where $f_i^p$ is a rapid-varying primary force and $f_i^s$ is a slow-varying secondary force. The primary force is usually the short-range contribution, and the secondary force represents
the long-range interaction; see Figure 2.11. A large time step $\Delta t$ is equally divided into $n$ smaller steps, $\Delta \delta t = \Delta t/n$. The primary forces are evaluated at each small time step. On the other hand, the secondary forces $f_i'(t)$ and their time derivatives are calculated only at each large time step $\Delta t$. These values are then extrapolated by applying a truncated Taylor series,

$$f_i'(t + k \delta t) = f_i'(t) + (k \delta t) \dot{f}_i'(t) + \frac{1}{2} (k \delta t)^2 \ddot{f}_i'(t) + \ldots \quad (2.73)$$

Although this approach has been successfully applied to molecular systems, there are some difficulties to deal with. First, the evaluation of the time derivatives requires considerable programming effort and computational time. Moreover, it is difficult to treat atoms crossing over from the secondary shell to the primary shell. Furthermore, this approach sacrifices the time-reversibility of the algorithm. As a result, the integration algorithm is quite unstable, unless a relatively small time step is used. Consequently, this approach is useful when the secondary forces vary much slower than the primary forces. If the two time scales are comparable, a stable symplectic integrator (such as the velocity-Verlet algorithm) actually performs better.

Recently, a time-reversible integrator has been developed using the Trotter factorization of the Liouville operator and a reversible reference system propagator algorithm (RESPA) has been derived by employing the formulation [45]. Several improvements to the original MTS approach are achieved by the RESPA methods. For example, the RESPA integrators are symplectic and time-reversible, which greatly improves the long-time scale stability. In addition, the RESPA methods do not need to compute the time derivatives, which are required in the original MTS scheme. This makes the RESPA methods computationally efficient and easy to implement. Furthermore, this approach provides a single framework to treat various time-scale problems and the separation of long- and short-range forces.
Following Tuckerman et al. [45], the Liouville operator $L$ for a Hamiltonian system is denoted as

$$iL = \{..., H\}, \quad (2.74)$$

where $H$ is the Hamiltonian function and $\{..., \}$ is the Poisson bracket. The Liouville operator corresponding to the Hamiltonian (2.1) is

$$iL = \sum_i \left[ v_i \frac{\partial}{\partial r_i} + f_i \frac{\partial}{\partial p_i} \right]. \quad (2.75)$$

Let us define the state of the system as $\Gamma(t) = \{r_i, p_i\}$. Using the Liouville operator, a formal solution for the Hamiltonian equations of motion (2.3) can be obtained.
\[ \Gamma(t) = e^{iH} = U(t) \Gamma(0), \]  
(2.76)

where \( U(t) = e^{iH} \) is the classical propagator. Decompose the Liouville operator into two parts,

\[ iL = iL_p + iL_s. \]  
(2.77)

Then, apply the Trotter factorization, we have

\[ U(\Delta t) = e^{iL_p \Delta t/2} e^{iL_s \Delta t/2} + O(\Delta t^3). \]  
(2.78)

Decompose the time interval \([0, t]\) into a number of small intervals \(\Delta t\), then the state of the system at time \(t\) may be obtained by successive applications of the propagator \(U(\Delta t)\).

The decomposition (2.77) may be used to separate rapidly varying primary forces \(f'_p\) and slowly varying secondary forces \(f'_s\), and this leads to the MTS algorithms:

\[ iL = iL_p + iL_s, \]

\[ iL_p = \sum_i \dot{x}_i \frac{\partial}{\partial x_i} + f'_p \frac{\partial}{\partial p_i}, \]  
(2.79)

\[ iL_s = \sum_i f'_s \frac{\partial}{\partial p_i}. \]

Apply the Trotter expansion, we have

\[ U(\Delta t) = U_p \left( \frac{\Delta t}{2} \right) U_s \left( \frac{\Delta t}{2} \right), \]  
(2.80)

where the propagator \(U_s(\Delta t/2)\) increments the velocities due to secondary forces:

\[ U_s(\Delta t): \quad v_i \rightarrow v_i + \frac{f'_s}{m_i} \left( \frac{\Delta t}{2} \right). \]  
(2.81)

Divide the time step \(\Delta t\) into \(n\) smaller time steps \(\delta t\). Then the primary part \(U_p(\Delta t)\) can be further factorized into \(U_p(\delta t)\), with each of the elementary propagators \(U_p(\delta t)\) be approximated by the velocity-Verlet integrator.
In the MTS algorithm, the secondary forces are computed at time $t$, and the velocities are incremented using (2.81). Then, the velocities and positions are updated by applying the usual velocity-Verlet integrator for $n$ small time steps $\Delta t$, using only the primary forces. Subsequently, the velocities are again incremented using the secondary forces evaluated at the new atomic positions.

Given an interatomic potential of the form (2.30), the two-body potential (2.31) is divided into short and long range parts using a switching function $f(r)$:

\begin{align}
V^{(2)}(r) &= V^{(2)}_{sh}(r) + V^{(2)}_{lo}(r), \\
V^{(2)}_{sh}(r) &= f(r) V^{(2)}(r), \\
V^{(2)}_{lo}(r) &= [1 - f(r)] V^{(2)}(r).
\end{align}

where

\begin{equation}
f(r) = \begin{cases} 
1, & r < r_{sh} - \Delta \\
1 + \frac{(r - r_{sh} + \Delta)^3}{2(r_{sh} - \Delta)^2}, & r_{sh} - \Delta < r < r_{sh} \\
0, & r > r_{sh}
\end{cases}
\end{equation}

Usually, the primary forces are derived from the short-range part of the two-body potential; while the secondary forces are given by the long-range two-body potential and the three-body potential, namely
\[ V_p = V_{st}^{(2)}, \]
\[ V_s = V_{st}^{(2)} + V^{(3)}. \] (2.87)

The MTS technique is very effective and efficient, especially when the simulated system contains a large number of atoms, e.g., multimillion-atom MD simulations.
CHAPTER 3

SURFACE ENERGIES AND RECONSTRUCTIONS OF GaAs AND InAs

This Chapter focuses on the calculation of surface energies of GaAs and InAs for the (100), (110), and (111) orientations. Both MD and the conjugate gradient method are used and the results are in excellent agreement. In addition, surface reconstructions on GaAs(100) and InAs(100) are studied via the conjugate gradient method. We have developed a new model for GaAs(100) and InAs(100) surface atoms. Not only this model reproduces well surface energies for the (100) orientation, it also yields (1x2) dimer lengths in accordance with \textit{Ab initio} calculations.

3.1 Introduction

Surface energies of GaAs and InAs play a major role in the formation of islands during heteroepitaxy. For instance, the Molecular Beam Epitaxy (MBE) growth of InAs on GaAs(100) planar substrate is in the Stranski-Krastanov (SK) mode. Since the surface energy of InAs is lower than that of GaAs, first a uniform wetting layer forms. Further deposition of InAs will lead to the formation of InAs three-dimensional islands, which relieve part of the stain energy stored in the InAs layer.

Using an energy density formalism with the first-principles pseudopotential density-functional approach, Moll et al. [36,37] have calculated the surface energies of GaAs and InAs for the (100), (110), and (111) orientations. They have calculated the absolute surface energies for different orientations directly and consistently with the same set of parameters and pseudopotentials, without introducing a reference surface. The surface energies are determined via total-energy calculations using density-functional theory. Qian et al. [35] carried out \textit{Ab initio} total-energy density functional calculations to study the reconstruction of GaAs(100) surfaces as a function of Ga and As surface
coverage. Equilibrium atomic geometry and energies for Ga- and As-stabilized 1×2, 2×1, and 2×2 surfaces consisting of various combinations of dimers and vacancies were determined.

GaAs(100) surface is the most technologically important surface within the family of zinc-blende III-V semiconductors, due to its importance for electronic and optoelectronic devices. As a result, in the past decade, numerous state-of-the-art techniques from both theory and experiment have focused on uncovering the atomic structure of such surface [53-59]. A general consensus has been achieved concerning the structural details of the As-stabilized reconstruction, most notably the 2×4 and c(4×4) phases. In particular, the atomic structure of the As-rich GaAs(100)-β2(2×4) surface is determined using Scanning Tunneling Microscopy (STM) and first-principles electronic-structure calculations [54].

3.2 GaAs and InAs Surface Energies (without Modeling Surface Atoms)

We have used MD simulations to calculate GaAs and InAs surface energies for the (100), (110), and (111) orientations. In the beginning, we use interatomic potentials of the form (2.30) for GaAs and InAs, without modeling surface atoms. In other words, the surface atoms are treated as bulk atoms and surface reconstructions are not taken into account. Due to the surface reconstruction on GaAs and InAs surfaces, we don't expect this simple treatment will yield the correct surface energies. However, this simple treatment may provide valuable information to guide us in the modeling of GaAs and InAs surface atoms.

Let us start with the surface energy calculation of GaAs(100). A MD box of size 28.266Å × 28.266Å × 38.266Å (i.e., 5×5×5 unit cells) is constructed and the system contains 1,000 atoms. The Z-axis is (001) oriented and a 10Å gap is inserted in the Z-direction to create two GaAs(100) surfaces, which are As- and Ga- terminated,
respectively. Periodic boundary conditions are applied only in X- and Y- directions, which are (100), (010) oriented, respectively. Equations of motion are integrated using a reversible symplectic algorithm with a time step $\Delta t = 2.0$ fs. The system is first quenched to 0K every $10\Delta t$ for $200\Delta t$, i.e., the velocities of all atoms are set to zero every $10\Delta t$. Subsequently, we quench the system with a factor of 0.3 every $10\Delta t$ for $200\Delta t$, i.e., the velocities of all atoms are multiplied by a factor of 0.3 every $10\Delta t$. Then, the system is quenched with a factor of 0.6 every $10\Delta t$ for $200\Delta t$, followed by a quenching with a factor of 0.9 every $10\Delta t$ for $400\Delta t$. Finally, the system is allowed to relax around 0.0001K for $13,000\Delta t$. At this point, the system is in an equilibrium state and we can calculate the energy $\langle E \rangle$, which corresponds to the GaAs cubic with two GaAs(100) surfaces.

The GaAs(100) surface energy is calculated using the following expression:

$$\gamma = \frac{\langle E \rangle - \langle E \rangle_{\text{bulk}}}{2A},$$

(3.1)

where $\langle E \rangle_{\text{bulk}}$ is the GaAs bulk energy and $A$ is the surface area.

We have also used the conjugate gradient method to calculate GaAs(100) surface energy using the same setup as the MD simulation, and we want to compare the result with that of the MD simulation.

Similarly, we have calculated surface energies of GaAs for the (110) and (111) orientations using both MD simulations and the conjugate gradient method; the results are listed in Table 3.1. From Table 3.1 we find that the MD results of GaAs surface energies agree very well with those of the conjugate gradient method. It is also found that the MD results of GaAs surface energies for the (110) and (111) orientations are reasonable compared with the $Ab initio$ calculations (with about 25% difference). The MD result of GaAs(110) surface energy is also in reasonable agreement with experimental values from fracture experiments [52]. It turns out that GaAs(110) surface is stoichiometric, i.e., there are equal numbers of Ga and As atoms on the surface. The
(110) plane is the cleavage plane of III-V semiconductors. Such a cleavage surface does not reconstruct, and only a relaxation of surface atomic positions within the (1×1) surface unit cell is observed. On the other hand, there is a big difference between the MD result for GaAs(100) surface energy and the \textit{Ab initio} calculation (with about 63% difference). The reason is that the (100) surface is polar, i.e., the planes parallel to the surface consist of either only Ga or only As atoms. As a result, the stable surface structure displays various reconstructions which distinctly differ from those found on the (100) faces of the covalent group-IV semiconductors.

Table 3.1 MD, the conjugate gradient method, \textit{Ab initio} calculations, and experiment results for GaAs surface energies for the (100), (110) and (111) orientations.

<table>
<thead>
<tr>
<th>Orientations</th>
<th>(110)</th>
<th>(100)</th>
<th>(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD †</td>
<td>0.621 J/m²</td>
<td>1.692 J/m²</td>
<td>0.722 J/m²</td>
</tr>
<tr>
<td>Conjugate gradient †</td>
<td>0.621 J/m²</td>
<td>1.692 J/m²</td>
<td>0.722 J/m²</td>
</tr>
<tr>
<td>\textit{Ab initio} *</td>
<td>0.83 J/m²</td>
<td>~1.0 J/m²</td>
<td>~0.96 J/m²</td>
</tr>
<tr>
<td>Experiment **</td>
<td>0.87±0.1 J/m²</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

† Without modeling surface atoms
* Reference [36]
** Reference [52]

Using the same MD simulation procedure for determining GaAs surface energies, we have also calculated InAs surface energies for the (100), (110), and (111) orientations. Similar to the GaAs case, we have also employed the conjugate gradient method to calculate InAs surface energies using the same setup as the MD simulations. These results are shown in Table 3.2.
Table 3.2 MD, the conjugate gradient method, *Ab initio* calculations, and experiment results for InAs surface energies for the (100), (110) and (111) orientations.

<table>
<thead>
<tr>
<th>Orientations</th>
<th>(110)</th>
<th>(100)</th>
<th>(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD †</td>
<td>0.333 J/m²</td>
<td>1.126 J/m²</td>
<td>0.464 J/m²</td>
</tr>
<tr>
<td>Conjugate gradient †</td>
<td>0.333 J/m²</td>
<td>1.125 J/m²</td>
<td>0.463 J/m²</td>
</tr>
<tr>
<td><em>Ab initio</em></td>
<td>0.656 J/m²</td>
<td>-0.704 J/m²</td>
<td>-0.672 J/m²</td>
</tr>
<tr>
<td>Experiment</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

† Without modeling surface atoms  
* Reference [37]

To our best knowledge, there are no experimental values of InAs surface energies for the (100), (110) and (111) orientations. From Table 3.2 we find that the MD results of InAs surface energies agree well with those of the conjugate gradient method. It is also found that the MD results of InAs surface energies for the (110) and (111) orientations are reasonable compared with *Ab initio* calculations. However, there is a big difference between the MD result for InAs(100) surface energy and *Ab initio* calculations (with about 60% difference). The reason for this discrepancy is similar to that of the GaAs(100) case, which is described in a previous paragraph.

3.3 A New Model for GaAs(100) and InAs(100) Surface Atoms

In the last section, we have calculated the GaAs and InAs surface energies for the (100), (110), and (111) orientations, without modeling surface atoms. We find that the MD results of GaAs and InAs surface energies for the (110) and (111) orientations are reasonable compared with *Ab initio* calculations. But, there are big differences between the MD results for GaAs(100) and InAs(100) surface energies and *Ab initio* calculations (with about 60% difference). Therefore, atoms at the GaAs(100) and InAs(100) surface
should be properly modeled in order to reproduce the correct surface energy. Furthermore, the surface reconstruction on these surfaces should also be taken into account. Based on both the *Ab initio* calculations and experimental measurements, such as surface energies and dimer lengths, we have developed a new model for GaAs(100) and InAs(100) surface atoms. Not only this model reproduces well surface energies for the (100) orientation, it also yields dimer lengths in accordance with *Ab initio* calculations.

This new model for GaAs(100) and InAs(100) surface atoms works in the following way. There are four different types of surface atoms: Ga, As of GaAs, In, and As of InAs. All the atoms are denoted as follows: Ga1 for bulk Ga, Ga2 for surface Ga, As1 for bulk As, As2 for surface As, In1 for bulk In, In2 for surface In. Each type of surface atom is treated as a new species of atoms, different from its bulk counterpart. The two body interactions for bulk atoms of GaAs and InAs are described in (2.31). The two body interactions between surface atoms, as well as those between surface atoms and bulk atoms, are also in the form of (2.31), but with different parameters. These parameters include the effective atomic charges, the ionic radii, and the van der Waals strengths. The effective atomic charges of surface atoms are chosen to be $1/\sqrt{2}$ of that of their bulk counterparts. Other parameters, namely, the ionic radii and the van der Waals strengths, are determined through a trail and error process. In terms of three body interactions, the surface atoms behave the same as their bulk counterparts, as described in (2.32).

Figure 3.1 shows two body interactions between GaAs(100) surface atoms. A minimum is found at a distance of $\sim 2.4\,\text{Å}$, which is roughly the dimer length. Figure 3.2 shows the two body interactions between GaAs(100) surface and bulk atoms compared to the two body interactions between bulk atoms in GaAs. We find that the bulk potential is lower than the potential between surface and bulk atoms. Similar observations are found for InAs(100), see Figure 3.3 and Figure 3.4.
Figure 3.1 Two body interactions between GaAs(100) surface atoms. $V(\text{Ga}_2-\text{Ga}_2)$ is the interatomic potential between Ga surface atoms, and $V(\text{As}_2-\text{As}_2)$ is the interatomic potential between As of GaAs surface atoms.
Figure 3.2 Two body interactions between GaAs(100) surface and bulk atoms compared to the two body interactions between bulk GaAs. \( V(Ga_1-As_1) \) is the interatomic potential between bulk Ga and As, \( V(Ga_2-As_1) \) is the interatomic potential between surface Ga and bulk As, and \( V(As_2-Ga_1) \) is the interatomic potential between surface As of GaAs and bulk Ga.
Figure 3.3 Two body interactions between InAs(100) surface atoms. $V(\text{In}_2-\text{In}_2)$ is the interatomic potential between In surface atoms, and $V(\text{As}_2-\text{As}_2)$ is the interatomic potential between As of InAs surface atoms.
Figure 3.4 Two body interactions between InAs(100) surface and bulk atoms compared to the two body interactions between bulk InAs. $V(\text{In}_1, \text{As}_1)$ is the interatomic potential between bulk In and As, $V(\text{In}_2, \text{As}_1)$ is the interatomic potential between surface In and bulk As, and $V(\text{As}_2, \text{In}_1)$ is the interatomic potential between surface As of InAs and bulk In.
The new model for GaAs(100) and InAs(100) surface atoms reproduces well the surface energies; see Tables 3.3 and 3.4. There is only 3% difference between the MD result of GaAs(100) surface energy and Ab initio calculations. The MD result of InAs(100) surface energy differs the Ab initio calculations for 8%.

Table 3.3 The new model for GaAs(100) surface atoms, Ab initio calculations, and experimental results for GaAs surface energies for the (100), (110) and (111) orientations.

<table>
<thead>
<tr>
<th>Orientations</th>
<th>(110)</th>
<th>(100)</th>
<th>(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>The new model</td>
<td>0.621 J/m²</td>
<td>1.03 J/m²</td>
<td>0.722 J/m²</td>
</tr>
<tr>
<td>for surface atoms</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ab initio*</td>
<td>0.83 J/m²</td>
<td>~1.0 J/m²</td>
<td>~0.96 J/m²</td>
</tr>
<tr>
<td>Experiment **</td>
<td>0.87±0.1 J/m²</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

* Reference [36]
** Reference [52]

Table 3.4 The new model for InAs(100) surface atoms, Ab initio calculations, and experimental results for InAs surface energies for the (100), (110) and (111) orientations.

<table>
<thead>
<tr>
<th>Orientations</th>
<th>(110)</th>
<th>(100)</th>
<th>(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>The new model</td>
<td>0.333 J/m²</td>
<td>0.640 J/m²</td>
<td>0.463 J/m²</td>
</tr>
<tr>
<td>for surface atoms</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ab initio*</td>
<td>0.656 J/m²</td>
<td>~0.704 J/m²</td>
<td>~0.672 J/m²</td>
</tr>
<tr>
<td>Experiment</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

* Reference [37]
In addition, the new model yields (1x2) dimer on both the GaAs(100) and InAs(100) surfaces. Figures 3.5 shows a cross-sectional view of the GaAs slab. As(1x2) and Ga(1x2) dimers are observed in the top and bottom, respectively. In Figures 3.6, a cross-sectional view of the InAs slab is shows. As(1x2) and In(1x2) dimers are found in the top and bottom, respectively.

The dimer lengths of As and Ga surface atoms on GaAs(100) are listed in Table 3.5. The MD simulations yield an As(1x2) dimer length of 2.45 Å, which agrees well with the value of 2.51 Å obtained from Ab initio calculations of the same dimer. The difference is only 2%. The MD result also compares well with Ab initio calculations of β2(2x4) dimer and α(2x4) dimer, which are 2.50 Å and 2.45 Å, respectively.

Figure 3.5 As (1x2) and Ga (1x2) dimers on GaAs(100) surfaces.

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Figure 3.6 As (1×2) and In (1×2) dimers on InAs(100) surfaces.

From Table 3.5, we also find that for the Ga(1×2) dimer, the MD result agrees well with *Ab initio* calculations. The MD simulations yield an Ga(1×2) dimer length of 2.39 Å, which agrees well with the value of 2.31 Å obtained from *Ab initio* calculations of the same dimer. The difference is only 3%. The MD result also compares well with *Ab initio* calculations of β2(2×4) dimer and α(2×4) dimer, which are 2.40 Å and 2.50 Å, respectively. The bond lengths and angles of As(1×2) and Ga(1×2) dimers are shown in Table 3.6. We find that the MD results are close to *Ab initio* calculations. For the InAs(100) surface, there are only *Ab initio* calculations for As(1×2) dimer, which agrees well with the MD result; see Table 3.7. Table 3.8 shows the MD results of bond lengths and angles of As(1×2) and In(1×2) dimer on InAs(100) surfaces.
Table 3.5 Dimer lengths of As(1×2) and Ga(1×2) on GaAs(100) surfaces.

<table>
<thead>
<tr>
<th></th>
<th>Atomistic*** (1×2) dimer</th>
<th>Ab initio* β2(2×4) dimer</th>
<th>Ab initio* α(2×4) dimer</th>
<th>Ab initio** (1×2) dimer</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(As2-As2)</td>
<td>2.45 Å</td>
<td>2.50 Å</td>
<td>2.45 Å</td>
<td>2.51 Å</td>
</tr>
<tr>
<td>d(Ga2-Ga2)</td>
<td>2.39 Å</td>
<td>2.40 Å</td>
<td>2.50 Å</td>
<td>2.31 Å</td>
</tr>
</tbody>
</table>

* Reference [36]
** Reference [35]
*** The new model for surface atoms

Table 3.6 Bond lengths and angles of As(1×2) and Ga(1×2) dimer on GaAs(100) surfaces.

<table>
<thead>
<tr>
<th></th>
<th>Ab initio* (1×2) dimer</th>
<th>Atomistic** (1×2) dimer</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(As2-Ga1)</td>
<td>2.40 Å</td>
<td>2.39 Å</td>
</tr>
<tr>
<td>θ(As2-Ga1-As1)-1</td>
<td>101.14°</td>
<td>102.29°</td>
</tr>
<tr>
<td>θ(As2-Ga1-As1)-2</td>
<td>118.20°</td>
<td>115.49°</td>
</tr>
<tr>
<td>θ(Ga1-As2-Ga1)</td>
<td>108.87°</td>
<td>113.66°</td>
</tr>
<tr>
<td>d(Ga2-As1)</td>
<td>2.30 Å</td>
<td>2.33 Å</td>
</tr>
<tr>
<td>θ(Ga2-As1-Ga1)-1</td>
<td>84.01°</td>
<td>96.49°</td>
</tr>
<tr>
<td>θ(Ga2-As1-Ga1)-2</td>
<td>122.05°</td>
<td>116.79°</td>
</tr>
<tr>
<td>θ(As1-Ga2-As1)</td>
<td>115.60°</td>
<td>118.02°</td>
</tr>
</tbody>
</table>

* Reference [35]
** The new model for surface atoms

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### Table 3.7 Dimer lengths of As(1×2) and In(1×2) on InAs(100) surfaces.

<table>
<thead>
<tr>
<th></th>
<th>As2-As2</th>
<th>In2-In2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomistic**</td>
<td>(1×2) dimer</td>
<td>2.44 Å</td>
</tr>
<tr>
<td>Experiment*</td>
<td>β2(2×4)</td>
<td>2.44 Å, 2.47 Å</td>
</tr>
</tbody>
</table>

* Reference [53]
** The new model for surface atoms

### Table 3.8 Bond lengths and angles of As(1×2) and In(1×2) dimer on InAs(100) surfaces.

<table>
<thead>
<tr>
<th></th>
<th>Atomistic*  (1×2) dimer</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(As2-In1)</td>
<td>2.63 Å</td>
</tr>
<tr>
<td>θ(As2-In1-As1)-1</td>
<td>102.75°</td>
</tr>
<tr>
<td>θ(As2-In1-As1)-2</td>
<td>118.27°</td>
</tr>
<tr>
<td>θ(In1-As2-In1)</td>
<td>108.79°</td>
</tr>
<tr>
<td>d(In2-As1)</td>
<td>2.65 Å</td>
</tr>
<tr>
<td>θ(In2-As1-In1)-1</td>
<td>101.16°</td>
</tr>
<tr>
<td>θ(In2-As1-In1)-2</td>
<td>119.42°</td>
</tr>
<tr>
<td>θ(As1-In2-As1)</td>
<td>107.91°</td>
</tr>
</tbody>
</table>

* The new model for surface atoms

### 3.4 Summary

Surface energies of GaAs and InAs for the (100), (110), and (111) orientations have been calculated. Both MD and the conjugate gradient method are used and the results are in excellent agreement. Surface reconstructions on GaAs(100) and InAs(100) are studied via the conjugate gradient method. We have developed a new model for
GaAs(100) and InAs(100) surface atoms. Not only this model reproduces well surface energies for the (100) orientation, it also yields (1×2) dimer lengths in accordance with *Ab initio* calculations.
CHAPTER 4
FLAT InAs OVERLAYERS WITH SELF-LIMITING THICKNESS ON GaAs SQUARE NANOMESAS

In this Chapter we discuss the parallel molecular dynamics simulations of InAs/GaAs nanomesas with self-limiting InAs overlayer thickness. The in-plane lattice constant of InAs layers parallel to the InAs/GaAs(001) interface starts to exceed the InAs bulk value at 12\textsuperscript{th} monolayer (ML) and the hydrostatic stresses in InAs layers become tensile above \sim 12\textsuperscript{th} ML. As a result, it is not favorable to have InAs overlayers thicker than 12 ML. This may explain the experimental findings of the growth of flat InAs overlayers with self-limiting thickness of \sim 11 ML on GaAs nanomesas.

4.1 Introduction

The large (6.6\%) lattice mismatch and associated strain at InAs/GaAs(001) interfaces have recently been utilized to fabricate a number of nanostructures [60-64]. On infinite planar substrates, the strain relief leads to the formation of coherent three-dimensional island structures above a critical amount, \sim 1.6 ML, of InAs deposition [60,61]. When InAs is deposited on \textless 100\textgreater oriented GaAs square mesas of size \leq 75 nm, on the contrary, the island morphology is suppressed and, instead, a continuous film with flat morphology is observed. This InAs film growth is, however, self-limiting and stops at \sim 11 ML [63]. In order to understand the self-limiting nature of the InAs film growth, it is important to know atomistic information about mechanical stress and the in-plane lattice constant of InAs layers in the InAs/GaAs square nanomesas. However, this atomistic information has so far been lacking. Recently, molecular dynamics as well as first-principle simulations have been widely used to study the dynamic, structural, electronic and mechanical properties of various...
structures, and environment-dependent interatomic potentials have been developed [65-
71]. In particular, atomic-level surface stresses and pressure distributions on
InAs/GaAs nanomesas have been studied via MD simulations [71].

In this Chapter, we report MD simulations of InAs/GaAs nanomesas with
<100> oriented square base and {101} sidewalls on GaAs(001) substrates. We have
investigated the mechanical stresses and the in-plane lattice constant of InAs layers
parallel to the InAs/GaAs(001) interface in the nanomesas.

4.2 Interatomic Potential for the Atoms at the Interface

The MD simulations are based on reliable interatomic potentials of the form
(2.30), which can successfully describe a wide range of physical properties of InAs and
GaAs. The potential parameters are determined so that a set of experimental data and
first-principle calculations of electronic structures for the bulk are reproduced. The
potentials reproduce well the experimental crystalline lattice constants, cohesive
energies, elastic constants, surface energies, high-pressure structural transitions,
phonon density-of-states, and neutron-scattering data for liquid and amorphous
structures.

In order to study the InAs/GaAs nanomesas, we need to develop an interatomic-
potential scheme to represent the mixed environment experienced by the atoms at the
InAs/GaAs interface. To this end, we have developed a scheme to combine
interatomic potentials of binary materials (InAs and GaAs) in such a way that the
resulting potential depends on the local chemical composition. For systems involving
Ga, In, and As, we use an environment-dependent linear interpolation scheme to
combine the interatomic potentials for GaAs and InAs. This scheme is adaptive in
which As atoms are classified into different types according to the number of Ga and In
neighbor atoms [72]:

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i) The two-body potential between different cations (Ga and In) is the average of the cation-cation interaction potentials in the pure compounds (GaAs and InAs),

$$V_{Ga-In}^{(2)} = \frac{V_{Ga-Ga}^{(2)} + V_{In-In}^{(2)}}{2}.$$  (4.1)

ii) The two-body interaction potential between As interpolates the potentials in the pure compounds, since the first neighbor shell of each cation is As, whereas the first neighbor of As is either Ga or In. Therefore, we have five different neighbor configurations for As, and consequently five different types of As in the alloy. Let As atom be labeled as As$_{wA}$ (n=0,...,4), where n is the number of In atoms around the As atom. The As-As interaction potential is then interpolated as

$$V_{As-As}^{(2)} = \frac{2 - x - y}{2} V_{As-As}^{(2)} + \frac{x + y}{2} V_{As-In}^{(2)}.$$  (4.2)

iii) The three-body interaction potential Ga-As-In is the average of those in the pure compounds

$$V_{Ga-As-In}^{(3)} = \frac{V_{Ga-As-Ga}^{(3)} + V_{In-As-In}^{(3)}}{2}.$$  (4.3)

All other interactions are the same as those in the pure compounds.

4.3 MD Setup and Results

Figure 4.1 shows a schematic of an InAs/GaAs nanomesa with a 12 ML InAs overlayer, <100> oriented square base and {101} sidewalls on a GaAs(001) substrate. Periodic boundary conditions are applied to the GaAs substrate of size $L = 474.9$ Å in both x and y directions. The GaAs mesa top size is $124.4$ Å $\times$ $124.4$ Å and the system consists of 2,205,157 atoms.
Figure 4.1 Schematic of an InAs/GaAs nanomesa with <100> oriented square base and \{101\} sidewalls on a GaAs (001) substrate.

The initial configuration of the InAs/GaAs nanomesa with a 16 ML InAs overlayer is constructed by setting the lattice constant of InAs the same as that of GaAs. Equations of motion are integrated using a reversible symplectic algorithm [45] with a time step $\Delta t$ of 2.0 fs. The system is first quenched to 0K for 10$\Delta t$, i.e., the velocities of all atoms are set to zero every $\Delta t$. Subsequently, we quench the system with a factor of 0.8 whenever the temperature of the system is higher than 3K, every 5$\Delta t$ for 5,000$\Delta t$. Figures 4.2, 4.3, and 4.4 show the atomic-level hydrostatic stress (defined as $[\sigma_{xx} + \sigma_{yy} + \sigma_{zz}]/3$) distributions of an InAs/GaAs nanomesa with a 16 ML InAs overlayer, after being quenched for 2,000$\Delta t$, 3,000$\Delta t$, and 5,000$\Delta t$, respectively.
Figure 4.2 Atomic-level hydrostatic stress distribution in an InAs/GaAs square nanomesa with a 16 ML InAs overlayer after being quenched for 2,000Δt. Negative pressure means tensile and positive pressure means compressive.
We find that the hydrostatic stresses in the InAs layer become tensile above ~12\textsuperscript{th} ML after the nanomesa has been quenched 5,000\textdegree, and cracks are developed on the top of the nanomesa, due to the tensile stress; see Figure 4.4. However, the hydrostatic stresses in the InAs layer lower than ~12\textsuperscript{th} ML is still compressive. We are interested in an InAs/GaAs square nanomesa with a 12 ML InAs layer, which has the InAs thickness observed in the experiment. So we remove the top 4 ML of InAs from the nanomesa with a 16 ML InAs overlayer, and quench the system to 0K in the same
time. Subsequently, we quench the system with a factor of 0.3 whenever the temperature of the system is higher than 0.5K, every $5\Delta t$ for $500\Delta t$. Then, the system is quenched with a factor of 0.8 whenever the temperature of the system is higher than 0.5K, every $5\Delta t$ for $29,500\Delta t$. At this point, the system is in a mechanically stable state and hence we obtain an InAs/GaAs nanomesa with a 12 ML InAs overlayer.

Figure 4.4 Atomic-level hydrostatic stress distribution in an InAs/GaAs square nanomesa with a 16 ML InAs overlayer after being quenched for $5,000\Delta t$. Negative pressure means tensile and positive pressure means compressive.
Figure 4.5 shows the atomic-level hydrostatic stress distribution of the InAs/GaAs nanomesa with a 12 ML InAs overlayer. Due to the lattice mismatch, a tensile stress well is formed in GaAs immediately below the InAs/GaAs interface. Figure 4.6 shows an enlarged cross-sectional view of the InAs/GaAs square nanomesa with a 12 ML InAs overlayer. It is found that the in-plane lattice constant of the InAs layer gradually increases with the number of InAs monolayer.

The lattice mismatch as well as the geometry of the nanomesa plays an important role in the relaxation of the InAs layers. We are more interested in the effect of lattice mismatch, since it is the fundamental cause for the relaxation of the InAs layers.

Figure 4.5 Atomic-level hydrostatic stress distribution in an InAs/GaAs square nanomesa with a 12 ML InAs overlayer. Negative pressure means tensile and positive pressure means compressive.
In order to isolate the effect of lattice mismatch, we construct a GaAs square nanomesa of exactly the same geometry as the InAs/GaAs square nanomesa, with the 12 ML InAs overlayer replaced by a 12 ML GaAs overlayer. Again, the system is quenched and relaxed by scaling atomic velocities for 35,000 time steps. Once the system reaches a mechanically stable state, the in-plane lattice constant of each monolayer of the 12 ML GaAs overlayer in the GaAs square nanomesa is calculated. For the 12 ML GaAs overlayer, the in-plane lattice constant shows small changes for the lower 5 ML and increases monotonically for the upper 7 ML, with value higher than the GaAs bulk lattice constant (5.6532 Å). The net increase of the in-plane lattice constant of the 12 ML GaAs overlayer with respect to the GaAs bulk value is caused by the geometry of the nanomesa. This net increase is subtracted from the in-plane...
lattice constant of the corresponding 12 ML InAs overlayer in the InAs/GaAs nanomesa, isolating the effect of lattice mismatch.

Figure 4.7 shows the in-plane lattice constant of each monolayer of the 12 ML InAs overlayer on the InAs/GaAs nanomesa, the net increase of in-plane lattice constant of the corresponding 12 ML GaAs overlayer on the GaAs nanomesa (see the inset), and the subtraction of the two. The subtracted in-plane lattice constant of the 12th InAs monolayer is 6.083 Å, which is slightly larger than the InAs bulk value (6.058 Å). Similar calculations are performed for InAs/GaAs square nanomesa with 10, 14, and 16 ML InAs overlayers. The subtracted in-plane lattice constants of the 10th, 14th, and 16th InAs monolayer are 5.975 Å, 6.122 Å, and 6.151 Å, respectively. The subtracted in-plane lattice constant of the 10th InAs monolayer is smaller, while those of the 14th and 16th InAs monolayer are larger, than the InAs bulk value. Moreover, the hydrostatic stresses in InAs layers are tensile above ~12th monolayer, in contrast to the compressive stresses in the InAs layers below ~12th monolayer. This change from compressive to tensile stress may underline the experimental findings of the growth of flat InAs overlayers with self-limiting thickness of ~11 ML on GaAs nanomesas [63].

4.4 Summary

Large-scale molecular dynamics simulations are performed to investigate the mechanical stresses in InAs/GaAs nanomesas with {101}-type sidewalls. The in-plane lattice constant of InAs layers parallel to the InAs/GaAs(001) interface starts to exceed the InAs bulk value at 12th monolayer and the hydrostatic stresses in InAs layers become tensile above ~12th ML. Hence, it is not favorable to have InAs overlayers thicker than 12 ML.
Figure 4.7 The in-plane lattice constant of each monolayer of the 12 ML InAs overlayer in the InAs/GaAs square nanomesa, the net increase of in-plane lattice constant of the corresponding 12 ML GaAs overlayer on the GaAs square nanomesa (see the inset), and the subtraction of the two.
CHAPTER 5

CRITICAL LATERAL SIZE FOR DOMAIN FORMATION IN InAs/GaAs SQUARE NANOMESAS

This Chapter focuses on the lateral size effects on the stress distribution and morphology of InAs/GaAs square nanomesas, which are investigated via parallel molecular dynamics [80]. Two mesas with the same vertical size but different lateral sizes are simulated. For the smaller mesa, a single stress domain is observed in the InAs overlayer, whereas two stress domains are found in the larger mesa. This indicates the existence of a critical lateral size for domain formation in accordance with recent experimental findings. The InAs overlayer in the larger mesa is laterally constrained to the GaAs bulk lattice constant but vertically relaxed to the InAs bulk lattice constant, consistent with the Poisson effect.

5.1 Introduction

In recent years, coherently strained three-dimensional (3D) islands formed in semiconductor overlayers having high lattice-mismatch with underlying substrates, such as Ge on Si and InAs on GaAs [73,74], have attracted much attention due to their importance for study of electronic behavior in zero dimension and applications in electronic and optoelectronic devices. The role and manipulation of stress in the formation of such nanostructures have been systematically examined through a study of the growth of InAs on planar and patterned GaAs(001) substrate, these systems having a large lattice mismatch of ~ 7% [60,63,64,75,76]. On stripe mesas of sub-100-nm widths on GaAs(001) substrates, deposition of InAs is shown to allow self-assembly of three, two, and single chains of InAs 3D island quantum dots selectively on the stripe mesa tops for widths decreasing from 100 nm down to 30 nm [64].
Growth of InAs overlayers on GaAs(001) nanoscale square mesas of linear dimensions < 100 nm has been shown to give a remarkable suppression of the 2D-to-3D morphology change of the overlayer due to the significant strain relief provided by the free surfaces of the overlayer itself and the strain accommodation by the underlying GaAs square mesa [63]. The square and stripe mesas, together with the studies on planar surfaces, bracket the entire regime of length scales of significance to stress relaxation and manipulation leading to control of the island number (and hence density) on chosen nanoscale area arrays. However, atomistic information about the morphology and mechanical stress on InAs/GaAs square nanomesas has so far been lacking. Recently, molecular dynamics has been used to study the behavior of energetics, atomic-level stress, and strain in coherent 3D Ge islands on Si(001) substrates and Ge overlayers on Si(001) nanomesas [77,78].

In this Chapter, we report MD simulations of InAs/GaAs nanomesas with ⟨100⟩ oriented square base and {101} sidewalls on GaAs(001) substrates. The simulations indicate the existence of a critical lateral size for stress domain formation. It is also found that, for InAs/GaAs nanomesas beyond a certain lateral size, the InAs overlayer is laterally constrained to the GaAs bulk near the interface but vertically relaxed to the InAs bulk, and this is consistent with the Poisson effect.

5.2 MD Setup and Procedure

In MD simulations, reliable interatomic potentials are essential ingredients. Our interatomic potentials for GaAs and InAs consist of two-body and three-body terms, which are defined in (2.31) and (2.32). In order to study InAs/GaAs mesas, it is crucial to develop an interatomic-potential scheme to represent the mixed environment experienced by the atoms at the InAs/GaAs interface. To this end, we have developed
a scheme to combine interatomic potentials of binary materials (InAs and GaAs) in such a way that the resulting potential depends on the local chemical composition [72].

Figure 5.1 shows a schematic of an InAs/GaAs mesa with a 12 monolayer (ML) InAs overlayer, <100> oriented square base and {101} sidewalls on a GaAs(001) substrate. Periodic boundary conditions are applied to the GaAs substrate of size \( L = 916 \, \text{Å} \) in both \( x \) and \( y \) directions. The GaAs mesa top size is \( 407 \, \text{Å} \times 407 \, \text{Å} \) and the system consists of 8.5 million atoms.

Figure 5.1 Schematic of an InAs/GaAs mesa with <100> oriented square base and {101} sidewalls on a GaAs(001) substrate.
We construct the initial configuration of the InAs/GaAs nanomesa with a 16 ML InAs overlayer by setting the lattice constant of InAs the same as that of GaAs. Equations of motion are integrated using a reversible symplectic algorithm [45] with a time step $\Delta t$ of 2.0 fs. The system is first quenched to 0K for $10\Delta t$, i.e., the velocities of all atoms are set to zero every $\Delta t$. Subsequently, we quench the system with a factor of 0.8 whenever the temperature of the system is higher than 3K, every $5\Delta t$ for 55,000$\Delta t$. We are interested in an InAs/GaAs square nanomesa with a 12 ML InAs layer, which has the InAs thickness observed in the experiment. So we remove the top 4 ML of InAs from the nanomesa with a 16 ML InAs overlayer, and quench the system to 0K. Then, we quench the system with a factor of 0.8 whenever the temperature of the system is higher than 0.5K, every $5\Delta t$ for 1,000$\Delta t$. At this point, the system is in a mechanically stable state and hence we get an InAs/GaAs nanomesa with a 12 ML InAs overlayer.

In order to investigate the effect of different lateral sizes on the stress distribution and morphology of the InAs/GaAs square nanomesas, we have also simulated an InAs/GaAs nanomesa with the same geometry but smaller size [71,79] in which the GaAs substrate size $L = 475 \, \text{Å}$ in both $x$ and $y$ directions, the GaAs mesa top size is $124 \, \text{Å} \times 124 \, \text{Å}$ and the system consists of 2.2 million atoms. The heights of both the GaAs substrate and the InAs/GaAs mesa are kept the same in these nanomesas.

### 5.3 Critical Lateral Size for Domain Formation

Recently, strain/stress relaxation and surface morphology in InAs/GaAs heteroepitaxy have been investigated via experimental measurements and computer simulations [81-91]. Strained-layer heteroepitaxial growth of semiconductor films is of major technological interest. One of the main obstacles that hamper high-structural-
quality InAs/GaAs heteroepitaxial growth is the limit of strain accommodation in the InAs overlayer film. Since stress is inherently related to strain, strain relaxation is equivalent to stress relaxation. Benabbas et. al [90] have used finite element (FE) analysis and transmission electron microscopy (TEM) observations to model stress relaxation in InAs quantum dots deposited on (001) GaAs. They found that elastic stress relaxation mainly occurs at the crest of the island and that the underlying substrate is under tension. Nosho et. al [83] have studied the surface morphology of InAs films grown on GaAs(111)A by scanning tunneling microscopy (STM). They found that the vertical surface displacement on the InAs films depend on the underlying GaAs buffer layer thickness and specifically, thin GaAs layers are observed to behave mechanically similar to compliant substrates. They have also performed atomistic simulations within a valence force field model to compare quantitatively how the InAs surface morphology depends on film thickness and the underlying GaAs layer thickness. The atomistic simulations and experimental results agree excellently over a range of film thickness where the misfit dislocation network at the semicoherent InAs/GaAs interface is fully developed.

In our case, InAs is deposited on GaAs(100) surface. Let us examine the effect of lateral size of InAs/GaAs nanomesa on the stress distribution in the nanomesa. Figure 5.2 shows the atomic-level hydrostatic stress in the vertical cross sections at the center of the 2.2 million-atom and 8.5 million-atom nanomesas. Due to the lattice mismatch, tensile stress wells are formed in GaAs immediately below the InAs/GaAs interfaces. It can be seen from Figure 5.2(a) that in the 2.2 million-atom nanomesa, the hydrostatic stress in the InAs overlayer is essentially homogeneous. However, in the 8.5 million-atom nanomesa, the hydrostatic stress in the InAs overlayer is inhomogeneous and consists of highly and less compressive domains: A highly
compressive domain is located at the center of the InAs overlayer, whereas the peripheral region of the InAs overlayer is less compressive; see Figure 5.2(b).

Figure 5.2 Atomic-level hydrostatic stresses in the cross sections through the center of the (a) 2.2 million-atom, and (b) 8.5 million-atom nanomesas.

Next, we discuss the morphology of the InAs overlayer near the InAs/GaAs interface. Figure 5.3 shows the vertical displacement of As atoms in the first As layer above the first In layer in the 2.2 million-atom and 8.5 million-atom nanomesas. The vertical displacement is measured with respect to the ideal bulk atomic plane of that As layer ($z = 0$). In order to show the details of the morphology of the layer, the vertical displacement of each atom has been magnified by a factor of 40. The morphology of the first InAs monolayer above the InAs/GaAs interface in the 2.2 million-atom
nanomesa, shown in Figure 5.3(a), resembles the morphology of the first Ge layer in coherent 3D Ge islands on Si(001) substrates [77].

![Figure 5.3](image)

Figure 5.3 Vertical displacement of As atoms in the first As layer above the first In layer in the (a) 2.2 million-atom, and (b) 8.5 million-atom nanomesas.

For the 2.2 million-atom nanomesa, the As layer is "dome" shaped, in which atoms have an upward displacement of ~0.8 Å at the center and a downward displacement of ~0.5 Å at the edges. In contrast, the As layer in the 8.5 million-atom nanomesa shows a "dimple" at the center of the mesa; see Figure 5.3(b). At the "rim" and "bottom" of the "dimple", atoms have upward displacements of ~1.0 Å and ~0.5 Å, respectively, while atoms at the edges have a downward displacement of ~1.6 Å. The "dimple" is located at roughly the same position as the enhanced compressive
stress domain shown in Figure 5.2(b). This provides clear evidence that there exists a critical lateral size for such stress domain formation, and the critical value is somewhere between 124 Å and 407 Å. A similar sensitivity of the number of islands to the lateral size of mesa has been observed in recent experiments [64]: deposition of InAs is shown to allow self-assembly of three, two, and single chains of InAs 3D island quantum dots selectively on the stripe mesa tops for widths decreasing from 100 nm down to 30 nm.

5.4 Structural Correlations in the InAs/GaAs Nanomesas

In the InAs/GaAs heteroepitaxy, strain relaxation play an important role in determining the structural and electronic properties of InAs overlays. Recently, Ohtake et al [81] have studied the strain relaxation process in InAs heteroepitaxy on GaAs(111)A using rocking-curve analysis of reflecting high-energy electron diffraction. They have performed in situ measurements of strain in the surface-normal direction during the InAs/GaAs heteroepitaxy. They found that the lattice constant in the direction normal to the surface remains almost unchanged below ~3ML.

To the best of our knowledge, there is no experimental measurements of the strain relaxation process in InAs heteroepitaxy on GaAs(100). However, structural correlations may provide valuable information on the strain relaxation process. We have analyzed the structural correlations in the InAs/GaAs nanomesas through a pair distribution function (PDF), $g(r)$. This function gives the probability of finding a pair of atoms a distance $r$ apart, relative to the probability expected for a completely random distribution at the same density. The In-In and In-As PDFs in the 2.2 million-atom and 8.5 million-atom nanomesas are shown in Figure 5.4.
For the 2.2 million-atom nanomesa, the In-In PDF has only one first-neighbor peak at 4.30 Å (which is close to the InAs bulk value, 4.28 Å); see Figure 5.4(a). This suggests that the lattice spacing in the InAs overlayer is mostly relaxed to its bulk value. For the 8.5 million-atom nanomesa, however, the first-neighbor peak of In-In PDF is split into two sub-peaks at 4.06 Å (which is close to the GaAs bulk value, 4.00 Å), and 4.31 Å (which is close to the InAs bulk value, 4.28 Å); see Figure 5.4(b). This indicates that the InAs overlayer is only partially relaxed to its bulk value. The In-As
PDFs in the two nanomesas, on the contrary, show that the first-neighbor peak positions are essentially the same as the InAs bulk value.

To understand the origin of the split first-neighbor peak of In-In PDF in the 8.5 million-atom nanomesa, the in-plane In-In PDF of InAs layer parallel to the InAs/GaAs(001) interface is calculated. The In-In PDF and the in-plane In-In PDF in the 12 ML InAs overlayer are shown in Figures Figure 5.5(a) and 5.5(b), respectively. It can be seen that the first sub-peak in Figure 5.5(a) coincides with the first peak in Figure 5.5(b). This shows that the first sub-peak of In-In PDF is entirely due to in-plane correlations. The second sub-peak in the In-In PDF is, on the other hand, contributed by the inter-plane correlations. In other words, the InAs overlayer is laterally constrained to the GaAs lattice near the interface but vertically relaxed to approach the InAs lattice. This is consistent with the Poisson effect.

5.5 Summary

We have performed multimillion-atom molecular dynamics simulations of InAs/GaAs square nanomesas with {101}-type sidewalls to study the lateral size effect on the stress distribution and morphology. The simulations indicate the existence of a critical lateral size for domain formation in accordance with recent experimental findings. A single stress domain is found in a smaller mesa, whereas a large mesa contains 2 stress domains. It is also found that, in the large nanomesa, the InAs overlayer is laterally constrained to the GaAs bulk near the interface but vertically relaxed to the InAs bulk, and this is consistent with the Poisson effect.
Figure 5.5 (a) The In-In pair distribution function and (b) the in-plane In-In pair distribution function of InAs layer parallel to the InAs/GaAs(001) interface, in the 12 ML InAs overlayer of the 8.5 million-atom nanomesa.
CHAPTER 6

ATOMISTIC SIMULATIONS OF GRAIN BOUNDARY FRACTURE IN DIAMOND

In this Chapter we report the results of molecular dynamics simulations which are performed to investigate the behavior under load of several \(<001>\) and \(<011>\) symmetrical tilt grain boundaries (GBs) in diamond [92-95]. The results indicate that special short-period GBs possess higher strengths and greater resistance to crack propagation than GBs in the nearby misorientation angles [92]. Crack propagation in polycrystalline diamond samples under an applied load is also simulated, and found to be predominantly transgranular rather than intergranular.

6.1 Introduction

In recent years, chemical vapor deposited (CVD) diamond films have received considerable attention for applications requiring hard, wear-resistant coatings, due to their extremely high strength and fracture toughness [96]. However, relationships between specific values for the properties, microstructure and crack propagation mechanisms, are not well understood. Moreover, the tendency for diamond to deposit as a polycrystalline film with a high density of GBs and related defects degrade many of its desirable properties. For example, defects in coatings can induce intermediate states in the band gap, and significantly reduce thermal conductivity due to phonon scattering. Mechanical properties of CVD diamond films may also be affected by the presence of GBs and particularly depend on GBs structures. It is known that different types of GBs can behave differently under applied load, e.g., they may have different resistance to crack propagation [97,98]. Hence, studying the mechanical properties of
different types of GBs may help us predict what types of microstructures provide the highest toughness of the film.

Recently, atomistic simulations have been used to provide important insights into the mechanisms of dynamic crack propagation in various systems [99-103]. In this Chapter, results from a series of molecular dynamics simulations designed to yield insight into the relationship between microstructural elements and crack propagation mechanisms in polycrystalline diamond are reported. The fracture properties of individual <001> and <011> symmetrical tilt GBs both with and without pre-existing flaws are studied in several sets of simulations. The simulations predict that special short-period GBs possess higher strengths than GBs in the nearby misorientation range, consistent with their enhanced energetic stability [92]. The simulations also predict that crack propagation in notched samples is primarily transgranular unless an initial crack is inserted directly into a GB.

In the MD simulations, we have used Brenner's reactive empirical bond-order potential, which has the form of (2.23). Fracture simulations are valuable tests of reliability of interatomic potentials since fracture properties usually are not included in the fitting database. During a crack propagation, atoms are subjected to different bonding environments. The atoms near a crack tip are under atomic environments that are far from ideal bond lengths and bond angles. Moreover, fracture properties are sensitive to the behavior of the interatomic potential near the inflection point and in the cutoff region. For a typical interatomic potential, the interaction has to be cut off before the second neighbor distance by using a suitable switching function. Usually the form of switching function does not affect most of the bulk and surface properties of materials and can be chosen arbitrarily rather than fitted to experiments. However, the switching function is crucial in describing bond breaking during fracture process.
If the switching function is not properly chosen, unphysical behaviors may be observed in atomistic fracture simulations, such as very high critical stresses and strains for diamond fractures.

In the initial version of the potential [13], a switching function cuts off the interaction between 1.7 and 2.0 Å. This choice is well justified by the nature of covalent bonding and works well for most equilibrium structures. However, as C-C bonds are stretched beyond 1.7 Å, things are different - it significantly influences the forces in the vicinity of the inflection point (~ 1.85 Å in diamond for the <111> direction). To avoid this problem, the cutoff distance is extended beyond the inflection point. A bond list using the original (2 Å) cutoff distance is constructed for the initial system and is left unchanged during the simulations. This *ad hoc* scheme solves the cutoff problem while still describing bond breaking and changes in the chemistry of the bond during cleavage. However, its application is restricted to phenomena that involve bond breaking but not new bond formation.

6.2 MD Setup and Procedure

We have performed three sets of simulations, each with a different type of initial structure. The first set consists of single symmetrical tilt GBs with <001> and <011> misorientation axes with no pre-existing flaws. The initial structures of these GBs are based on a coincident-site lattice model for group IV materials in which each atom is four-fold coordinated. Periodic boundary conditions are applied within the GB plane, and each system contains approximately 4,000 atoms. Equations of motion are integrated with a time step Δt of 1.0 fs. First, the GBs are gradually heated to 300K. Then, the crystals are strained at a rate of 2%/ps along the direction perpendicular to the GB plane until 20%. This is accomplished by moving two regions of atoms 3Å wide and 10 lattice parameters on both sides of the GB away from the interface.
During the simulations, the atomic positions within the end regions are held constant while the remaining atoms are allowed to move. The quantities considered in this set of simulations were the maximum fracture stresses of the GBs compared to the bulk, and the GB work for fracture defined by the areas under the stress-strain curves. Figure 6.1 shows a single symmetrical tilt GB with no pre-existing flaws, before and after fracture.

![Figure 6.1 A single symmetrical tilt GB with no pre-existing flaws, (a) before and (b) after fracture.](image)

In the second set of simulations, a surface notch $30\,\text{Å}$ long oriented perpendicular to the direction of strain is inserted into the GB; see Figure 6.2. Periodic boundary conditions are applied within the GB plane, and each system contains approximately 50,000 atoms. Equations of motion are integrated with a time step $\Delta t$ of 1.0 fs. After the notch is inserted, the conjugate gradient method is employed to relax the system. Then, the GB is gradually heated to $300K$ and strained at a rate of $2\%/\text{ps}$
along the direction perpendicular to the GB plane until 20%. Strain is applied to these systems as described above until a crack started to propagate, after which the coordinates of the atoms in the end regions are left unchanged.

Figure 6.2 A single symmetrical tilt GB with a surface notch 30Å long oriented perpendicular to the direction of strain is inserted into the GB, (a) before and (b) after crack propagation.

The third set of simulations is identical to the second except that different GB orientations with respect to the notch and applied strain are examined. The same simulation procedure is used as in the second set of simulations. GBs with different angle of inclination of the GB plane relative to the notch plane have been studied. These GBs are the following: 13-1, 13-2, 13-3, 13-4, 13-5, 450-3, 9-1, 9-2, 9-4, and 27-3, denoted according the GB type and the angle of inclination of the GB plane relative to the notch plane. Figures 6.3-6.7 show the snapshots of these GBs before and after crack propagation.
Figure 6.3 Snapshots of GBs 13-2 and 13-3, before and after crack propagation.
Figure 6.4 Snapshots of GBs 13-4 and 13-5, before and after crack propagation.
Figure 6.5 Snapshots of GBs 13-1 and 450-3, before and after crack propagation.
Figure 6.6 Snapshots of GBs 9-4 and 9-2, before and after crack propagation.
Crack Propagation

In general, when a crack reaches a GB, it can propagate within the GB (intergranular fracture), or penetrate into the second grain (transgranular fracture).

Figure 6.7 Snapshots of GBs 9-1 and 27-3, before and after crack propagation.

6.3 Crack Propagation

In general, when a crack reaches a GB, it can propagate within the GB (intergranular fracture), or penetrate into the second grain (transgranular fracture).
Within the second grain, the crack can keep moving in the initial direction of propagation or deviate into the easier cleavage plane. Figures 6.3-6.7 show that in most cases transgranular crack propagation is observed. These events depend on the GB cleavage energy, relative bulk cohesive energies of the first and second grains, and the inclination angle of the GB relatively to the initial plane of a crack propagation [92]. Unless an angle between a primary crack plane and a GB is small, the crack tends to cross the GB. Our molecular dynamic simulation results indicate predominantly a transgranular mode, rather than an intergranular mode, of fracture in polycrystalline diamond.

6.4 Summary

A series of molecular dynamics simulations have been performed to investigate the behavior under load of several <001> and <011> symmetrical tilt grain boundaries (GBs) in diamond. These MD simulations are based on the bond-order analytic potential. Crack propagation in polycrystalline diamond samples under an applied load is also simulated, and found to be predominantly transgranular rather than intergranular.
CHAPTER 7

CONCLUSIONS

In this dissertation, we have discussed the implementation of large-scale molecular dynamics (MD) simulations on parallel machines, which has been used to study the flat InAs overlayers with self-limiting thickness on GaAs square nanomesas, the critical lateral size for domain formation in InAs/GaAs square nanomesas, and the behavior under load of several <001> and <011> symmetrical tilt grain boundaries (GBs) in diamond. In addition, surface energies and surface reconstructions of GaAs and InAs have been examined using MD and the conjugate gradient method. The simulations are based on realistic interatomic potentials, which have been validated by comparing with experiments. Multiresolution algorithms which are of O(N) have been employed to compute interatomic interactions efficiently in these multi-million MD simulations.

We have calculated surface energies of GaAs and InAs for the (100), (110), and (111) orientations. Both MD and the conjugate gradient method are used and the results are in excellent agreement. Surface reconstructions on GaAs(100) and InAs(100) are studied via the conjugate gradient method. We have developed a new model for GaAs(100) and InAs(100) surface atoms. Not only does this model reproduce well surface energies for the (100) orientation, it also yields (1x2) dimer lengths in accordance with ab initio calculations.

Large-scale molecular dynamics simulations are performed to investigate the mechanical stresses in InAs/GaAs nanomesas with {101}-type sidewalls. The in-plane lattice constant of InAs layers parallel to the InAs/GaAs(001) interface starts to exceed the InAs bulk value at 12\textsuperscript{th} monolayer (ML) and the hydrostatic stresses in InAs layers become tensile above ~ 12\textsuperscript{th} ML. As a result, it is not favorable to have InAs overlayers...
thicker than 12 ML. This may explain the experimental findings of the growth of flat InAs overlayers with self-limiting thickness of ~ 11 ML on GaAs nanomesas.

We have also examined the lateral size effects on the stress distribution and morphology of InAs/GaAs square nanomesas using parallel molecular dynamics. Two mesas with the same vertical size but different lateral sizes are simulated. For the smaller mesa, a single stress domain is observed in the InAs overlayer, whereas two stress domains are found in the larger mesa. This indicates the existence of a critical lateral size for domain formation in accordance with recent experimental findings. The InAs overlayer in the larger mesa is laterally constrained to the GaAs bulk lattice constant but vertically relaxed to the InAs bulk lattice constant, consistent with the Poisson effect.

Finally, a series of molecular dynamics simulations have been performed to investigate the behavior under load of several <001> and <011> symmetrical tilt grain boundaries (GBs) in diamond. These MD simulations are based on the bond-order analytic potential. Crack propagation in polycrystalline diamond samples under an applied load is also simulated, and found to be predominantly transgranular rather than intergranular.
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