Chair of Condensed Matter Physics
Institute of Theoretical Physics
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Summer Semester 2014

Lecture

Modeling of Nanostructures and Materials

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Modeling of Nanostructures and Materials

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Lecture 6 – *March 31, 2014*

- **Molecular Dynamics & Coarse-Graining**
- **Tight-Binding Methods**
  - ❖Tight-Binding Hamiltonian
  - ❖Tight-Binding Molecular Dynamics
  - ❖ Applications

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Molecular Dynamics

- **Equations of motion for the particles and the thermostat's degree of freedom**

$$\frac{d^2\vec{R}_I}{dt^2} = \frac{\vec{F}_I}{M_I s^2} - \frac{2}{s}\frac{ds}{dt}\frac{d\vec{R}_I}{dt}$$

$$Q\frac{d^2 s}{dt^2} = \sum_J s M_J \left(\frac{d\vec{R}_J}{dt}\right)^2 - k_B T\frac{1+f}{s}$$

Value of Q is arbitrary, can be fixed by trial and error.

- $\vec{F}_I = -\nabla_I V_{eff}(\{\vec{R}_I\})$
  - **Classical MD**
  - ***Ab initio* MD (AIMD)**

MD and Time Averages

- **From MD simulations, one gets**

$\{R_I(t)\}$	$\{\vec{v}_I(t)\}$	$\{E_{kin,I}(t)\}$	$E_{pot}(t)$
trajectories	**velocities**	**kinetic energies**	**potential energy**

- These quantities maybe used for performing time averages

$$C_{AB}(t) = <\delta A(t)\delta B(0)>$$

MD and Structural Quantities

- MD provides us with structural quantities such as the **pair correlation function**, which gives the distribution of distances between pairs of atoms
- **The structure factor** $S(k)=\frac{1}{N}<\rho(k)\rho(-k)>$

  can be measured in neutron-scattering experiments
- **The Time Correlation Functions** between two quantities $C_{AB}(t)=<\delta A(t)\delta B(0)>$

  ⟹ **Response Functions,** such as
  - diffusion coefficient,
  - viscosity,
  - compressibility,
  - electrical and heat conductivities,
  - dynamical structure factor.

MD – limitations system size and time scales

Ab initio **(Car-Parrinello) MD**

size: 100 – 200 atoms (workstations)

100 000 atoms (multiprocessor supercomputers)

time: 10 ps

Classical MD

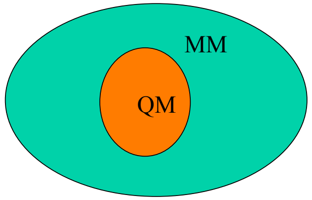
size: up to 18 x 10^9 atoms (supercomputers) ▶

time: 10 ns

- **Both methods – atomistic scale methods**
- **Advantage of AIMD – bond formation and bond breaking**
- **Simulation of materials properties – larger scales needed**

Hybrid QM/MM approaches: quantum-mechanics/molecular-mechanics

- Systems of interest in computational biology are too large for a full AIMD treatment
- The system is divided in two subsystems: an inner region (QM) where quantum-mechanics is used and an outer region (MM) where a classical field is used, interacting with each other



MM = classical MD
QM = AIMD

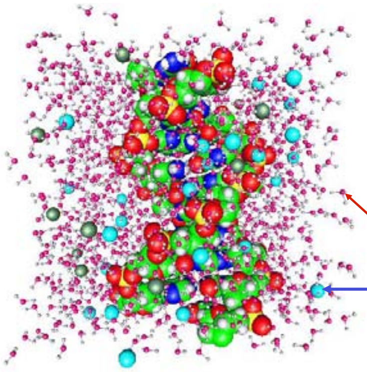
Large scale modeling - Coarse-Graining

- For large scale modeling, one may introduce alternative approaches using simplified ***coarse-grained models*** (lattice gas models)
- These models can be treated with the methods used commonly in statistical mechanics such as
  - **mean-field theory**,
  - **the cluster variation method (CVM),**
  - **Monte Carlo methods**.
- **Question: how to provide a link between atomistic calculations (*ab initio*, classical potentials) and the potential parameters suitable for coarse-grained models.**

Why do we need coarse-grained modeling?

An Example

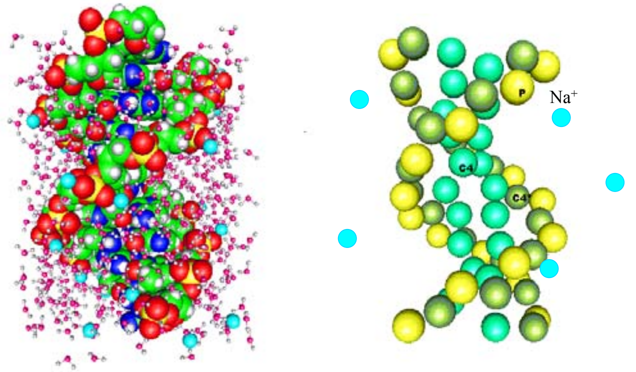
Polyelectrolyte problem: ions around DNA



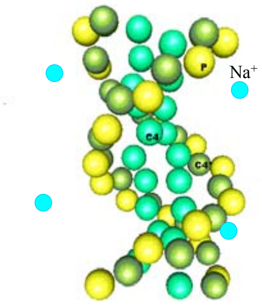
Atomistic MD
not really possible to
sample distances
30 – 40 A from DNA

Coarse-grained model for ions around DNA

All-atom model **Coarse-grained model**

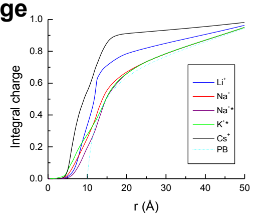


Coarse-grained model for ions around DNA

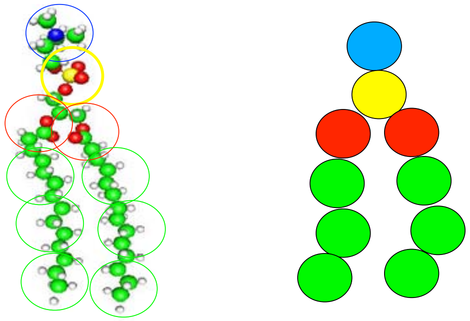


- 🟩 **Ions interacting with DNA by effective solvent-mediated potentials**
- 🟩 **Different potentials for various parts of DNA**
- 🟩 **No explicit water**

➡ **density profile and integral charge**



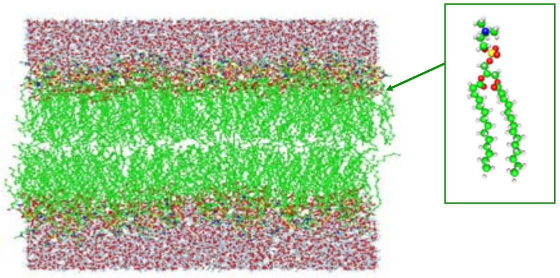
Another example: Coarse-grained lipid model



All-atom model
118 atoms

Coarse-grained model
10 sites

Lipid bilayer in water

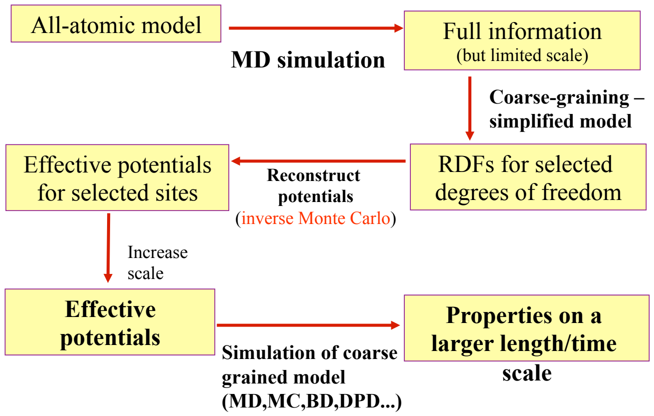


Picture contains 50000 atoms

Minimal, reasonable piece of bilayer for **atomistic MD**

72 lipids + at least 20 H_2O per lipid = 13000 atoms

Multi-scale approach



All-atomic model

MD simulation

Full information
(but limited scale)

Coarse-graining – simplified model

RDFs for selected degrees of freedom

Reconstruct potentials (inverse Monte Carlo)

Effective potentials for selected sites

Increase scale

Effective potentials

Simulation of coarse grained model (MD,MC,BD,DPD...)

Properties on a larger length/time scale

Tight Binding Method

The Kohn- Sham Method –
The Kohn-Sham Equations

- **Schrödinger-like equations with local potential**

$$\upsilon_H(\vec{r}) = \frac{\delta U}{\delta\rho} = \int d\vec{r}\,' \frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \qquad \frac{\delta E_x[\rho]}{\delta\rho} \qquad \frac{\delta E_c[\rho]}{\delta\rho}$$

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + \upsilon_{ext}(\vec{r}) + \upsilon_H(\vec{r}) + \upsilon_x(\vec{r}) + \upsilon_c(\vec{r})\right]\varphi_i(\vec{r}) = \varepsilon_i\varphi_i(\vec{r})$$

$$\upsilon_{ext}(\vec{r}) = -e^2\sum_{s,n}\frac{Z_s}{|\vec{r}-\vec{\tau}_s-\vec{R}_n|}$$

$$\rho(\vec{r}) = \sum_{i=1}^{N}\varphi^*_i(\vec{r})\varphi_i(\vec{r})$$

- **These equation are nonlinear and must be solved iteratively (self-consistently)**

Solution of the Kohn-Sham Equations

- **Expansion of the Kohn-Sham orbitals in a basis** $\{\chi_{\alpha\vec{k}}(\vec{r})\}$

$$\varphi_{n\vec{k}}(\vec{r}) = \mathbb{N}\sum_{\alpha} c_{\alpha}(n,\vec{k})\chi_{\alpha\vec{k}}(\vec{r})$$

$$\left[\sum_{\alpha'} \left\langle \chi_{\alpha\vec{k}} \left| -\frac{\hbar^2}{2m}\vec{\nabla}^2 + \upsilon_{KS}(\vec{r}) \right| \chi_{\alpha'\vec{k}} \right\rangle - \varepsilon_n(\vec{k})\left\langle \chi_{\alpha\vec{k}} | \chi_{\alpha'\vec{k}} \right\rangle\right] c_{\alpha'}(n,\vec{k}) = 0$$

Hamiltonian matrix elements

Overlap integrals

$$[H_{\alpha\alpha'}(\vec{k}) - \varepsilon_n(\vec{k})S_{\alpha\alpha'}(\vec{k})]c_{\alpha'}(n,\vec{k}) = 0$$

Eigenvalueproblem $\det[H_{\alpha\alpha'}(\vec{k}) - \varepsilon_n(\vec{k})S_{\alpha\alpha'}(\vec{k})] = 0$

➡ $\varepsilon_n(\vec{k})$ **Bandstructure**

LCAO (Linear Combination of Atomic Orbitals)

$$\varphi_n(\vec{r}) = \mathbb{N}\sum_{\alpha} c_{\alpha n}\phi_{\alpha}^{at}(\vec{r} - \vec{X}_{\alpha})$$

All atoms in the system

ϕ_{α}^{at} - ‘Atomic’ Kohn-Sham orbitals:

$$[\frac{\hat{\vec{p}}^2}{2m} + \upsilon_{KS}^{at}]\phi_{\alpha}^{at} = \varepsilon_{\alpha}^{at}\phi_{\alpha}^{at}$$

Kohn-Sham orbitals in periodic systems $\varphi_{n\vec{k}}(\vec{r}) = \mathbb{N}\sum_{\alpha} c_{\alpha}(n,\vec{k})\chi_{\alpha\vec{k}}(\vec{r})$

$$\chi_{\alpha\vec{k}}(\vec{r}) = \sum_{\vec{R}_l} e^{i\vec{k}\cdot\vec{R}_l}\phi_{\alpha}^{at}(\vec{r} - \vec{R}_l - \vec{\tau}_{s(\alpha)})$$

$\{\vec{\tau}_s\}$ Basis atoms
$\{\vec{R}_l\}$ Primitive translations

$\{\chi_{\alpha\vec{k}}\}$ - fulfill Bloch’s theorem $\chi_{\alpha\vec{k}}(\vec{r} + \vec{R}_n) = e^{i\vec{k}\cdot\vec{R}_n}\chi_{\alpha\vec{k}}(\vec{r})$

Problems

- Minimal Basis, i.e., one orbital per electron, is not sufficient
- Results depend on the chosen basis

Tight-Binding Formalism

$$\varphi_n(\vec{r}) = \sum_{\alpha,i} c_n^{\alpha i}\chi_{\alpha i}(\vec{r})$$

index of orbital **index of atom**

$\{\chi_{\alpha i}\}$ orthogonal set of functions

➡ **NOT ATOMIC ORBITALS !**

$$\varepsilon_n = <\varphi_n | H | \varphi_n> = \sum_{i\alpha}\sum_{j\beta}(c_n^{\alpha i})^* c_n^{\beta j} <i\alpha | H | j\beta>$$

Tight –binding Hamiltonian

$$H = \sum_{\alpha i}\varepsilon_{i\alpha} | i\alpha >< i\alpha | + \sum_{\alpha i,\beta j} t_{i\alpha,j\beta} | i\alpha >< j\beta |$$

on-site

hoping TB-parameters

Tight-Binding Hamiltonian

$$H = \sum_{\alpha i}\varepsilon_{i\alpha}c_{i\alpha}^{\dagger}c_{i\alpha} + \sum_{\alpha i,\beta j} t_{i\alpha,j\beta}c_{i\alpha}^{\dagger}c_{j\beta}$$

creation & anihilation operators

- ***On-site energies*** **are not atomic eigenenergies**
  They include on average the effects of neighbors

➡ **Problem:** ***Transferability***
E.g., **Si** in diamond lattice (4 nearest neighbors) & in fcc lattice (12 nearest neighbors)

- **Dependence of** ***the hopping energies*** **on the distance between atoms**

Tight-Binding Formalism – Overlap Integrals

- In the general case orbitals will not be an orthonormal set and we define the ***overlap integrals*** as

$$S_{i\alpha j\beta} = \langle i\alpha | j\beta \rangle = \int \phi^*_{i\alpha}\phi_{j\beta}\,d\mathbf{r}$$

- In orthogonal-TB schemes S reduces to the unit matrix.

One needs to solve $\sum_{j\beta}(H_{i\alpha j\beta} - \epsilon S_{i\alpha j\beta})c_{j\beta} = 0$

Parameters to be determined

➡ **Semiempirical Tight-Binding Method**

Tight-Binding Formalism – Parameters

- **The TB parameters:**
    - **on-site,**
    - **hopping**
    - **(overlap integrals)**

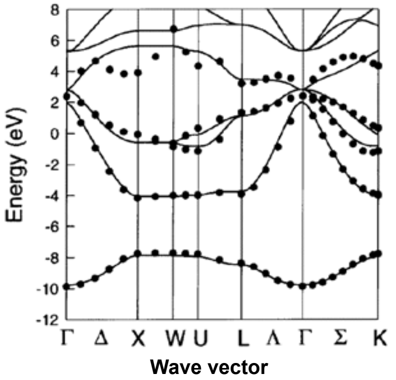
  are usually determined empirically by fitting TB energies (eigenvalues) to the *ab initio* (experimantal) ones.
- One could also try to calculate them directly by performing the same calculation for a localized basis set exactly

  e.g., F. Liu, Phys. Rev. B **52**, 10677 (1995)
- **Simple version of the TB method – universal parameters**

  W. Harrison, *Electronic structure and the properties of solids* (Dover, New York, 1980)
    - not very transferable and not accurate enough
    - **allow to extract qualitative physics**

Tight-Binding Formalism – Parameters

Fitting the *ab initio* band structure



LDA (●) and **tight-binding** (——) band structures for **GaAs** in the zinc-blende structure

Tight-Binding Formalism – Physical meaning of the on-site energies

$$H = \sum_{\alpha i}\varepsilon_{i\alpha}c^{\dagger}_{i\alpha}c_{i\alpha} + \sum_{\alpha i,\beta j} t_{i\alpha,j\beta}c^{\dagger}_{i\alpha}c_{j\beta}$$

- Anderson has shown that there exists a pseudoatomic Hamiltonian that has as its eigenstates the basis states $|i\alpha>$, but this Hamiltonian is not an atomic one and depends yet again on neighboring atoms.

$$H_i|i\alpha> = (T + V_i + \sum_{j\neq i,\beta} V_j - |j\beta><j\beta|V_j)|i\alpha> = \varepsilon_{i\alpha}|i\alpha>$$

- Similar procedure to the construction of the pseudopotential

P. W. Anderson, Phys. Rev. Lett. **21**, 13 (1968)
Phys. Rev. **181**, 25 (1969)

Tight-Binding Formalism – Physical meaning of the on-site energies

- The expression for the pseudo-Hamiltonian of atom i

$$H_i\,|i\alpha> = (T + V_i + \sum_{j\neq i,\beta} V_j - |j\beta><j\beta|V_j)\,|i\alpha> = \varepsilon_{i\alpha}\,|i\alpha>$$

- In the pseudopotential one projects out core states
- Here one projects out the states of the neighboring atoms which overlap with the atomic basis function.
- This is where the dependence on the environment comes from in this atomic pseudo-Hamiltonian

Tight-Binding Formalism – Dependence of the hopping integrals on atomic distance

Calculations for systems with distorted lattice

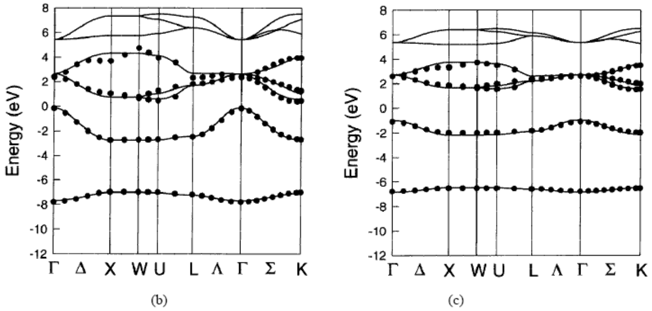
The dependence of the hopping integrals on the inter-atomic distance

- Harrison's ~d^{-2} dependence
- Exponential dependence $t = t_0\, exp(-\beta r)$
- $t_{\alpha\beta}(R_{ij}) = t_{\alpha\beta}(r_0) f(R_{ij})$

$$f(r) = \begin{cases} \left(\dfrac{r_0}{r}\right)^n exp\left\{ n\left[-\left(\dfrac{r}{r_c}\right)^{n_c} + \left(\dfrac{r_0}{r_c}\right)^{n_c} \right]\right\} & r < r_1 \\ c_0 + c_1(r - r_1) + c_2(r - r_2)^2 + c_3(r - r_2)^3 & r \geq r_1 \end{cases}$$

C. Xu *et al*., J. Phys. Condens. Matter **4**, 6047 (1992)

Tight-Binding Formalism – Dependence of the hopping integrals on atomic distance

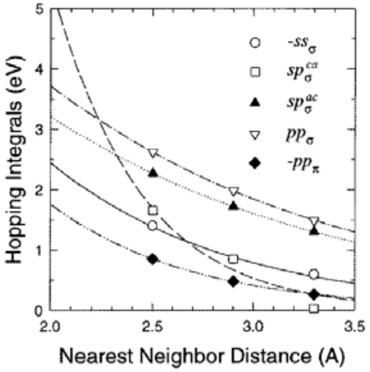


(b) (c)

LDA (●) and **tight-binding** (——) band structures for **GaAs** in the zinc-blende structure for two different bond lengths (b) 2.9 Å, and (c) 3.3 Å

Tight-Binding Formalism – Dependence of the hopping integrals on atomic distance

Minimal sp basis used



Tight-binding hopping integrals with the functional dependence

$$t = t_0\, exp(-\beta r)$$

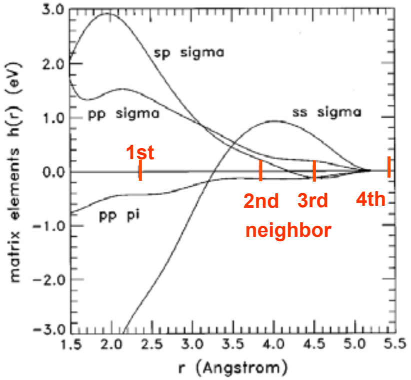
(lines) as functions of the interatomic distance for **GaAs** in the zinc-blende structure. Optimum fits of the LDA band structure at selected nearest-neighbour distances are given by the data points.

Y. P. Feng, C. K. Ong, H. C. Poon and D. Tomanek, J. Phys.: Condens. Matter **9,** 4345 (1997).

Tight-Binding Formalism – Dependence of the hopping integrals on atomic distance

Highly optimized tight-binding model of silicon

Matrix elements $h_{ss\sigma}(r),\ h_{sp\sigma}(r),\ h_{pp\sigma}(r)\ \&\ h_{pp\pi}(r)$



The matrix elements are defined whenever *r* is greater than 1.5 Å.
The distances corresponding to the first four neighbor shells in the diamond structure are marked by short vertical lines; each matrix element goes smoothly to zero between the third and fourth neighbor shells.

T. J. Lenosky et al.,
Phys. Rev. B **55**, 1528 (1996)

Tight-Binding Formalism – Band Energy

$$\boxed{U_{\text{band}} = 2\sum_{\text{occ}} \epsilon_s = 2\sum_{s} n_s \epsilon_s}$$

- This energy term is called the ***band energy***, and is usually attractive and responsible for the cohesion.
- In fact, if atoms get closer their overlap increases, the range of the eigenvalues increases and, since only the lowest energy states are occupied, the energy decreases (bonding increases).

⟹ **“Real” description of solids requires repulsive term** (to prevent colaps)

Tight-Binding Formalism – The Total Energy

- However, the TB formalism shown above describes only bonding due to the outer electrons.
- If one brings two atoms close together, inner shells will start to overlap and bring additional energy (in the form of a strong repulsion) that is not included in the band energy term.
- The total energy will therefore be given as

$$\boxed{E = U_{\text{rep}} + U_{\text{band}}}$$

an empirical repulsive energy term

Tight-Binding Formalism – The Repulsive Energy

In most cases this is modeled simply as a sum of ***two-body repulsive potentials*** between atoms

$$\boxed{U_{\text{rep}} = \frac{1}{2}\sum_{ij} v_R(r_{ij})}$$

but many-body expressions such as

$$\boxed{U_{\text{rep}} = \sum_i g\left[\sum_j \Phi(r_{ij})\right]}$$

(where g is a non-linear embedding function, which can be fitted by a polynomial) have also been proposed.

Φ has similar dependence on the R_{ij} as hopping integrals

Tight-Binding Formalism – The Total Energy

$$E = \sum_{k,n} \epsilon_n(k) + \sum_{l=2}^{N}\sum_{l'=1}^{l-1} E_{rep}(|\boldsymbol{R}_l - \boldsymbol{R}_{l'}|) + U\sum_{l=1}^{N}(q_l - q_l^0)^2$$

Band structure energy

Repulsive energy

Charge transfer energy

- The ***total repulsive energy*** contains ion–ion repulsion, exchange–correlation energy, and accounts for the double counting of electron–electron interactions in the band-structure energy term.
- The last term imposes an energy penalty on large inter-atomic charge transfers → ***Charge transfer energy***

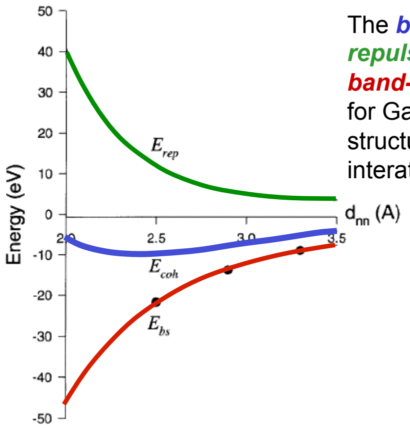
Typical $U \sim 1eV$

Tight-Binding Formalism – Parametrization of the repulsive term

- **Using the interpolated hopping integrals, the tight-binding band-structure energy can be obtained for any geometry and inter-atomic distance.**
- We then *define* the repulsive energy as the difference between the 'exact' binding energy, obtained using *ab initio* calculations, and the tight-binding band-structure energy
- Several crystallographic phases of a material are usually used

⟹ **Structure independent parametrization of the repulsive terms**

Tight-Binding Formalism – The Total Energy



The ***binding energy*** (***E***$_{coh}$), ***repulsive energy*** (***E***$_{rep}$), and ***band-structure energy*** (***E***$_{bs}$) for GaAs in the zinc-blende structure, as functions of the interatomic distance.

Tight-Binding Formalism – Molecular Dynamics

The molecular dynamics proposed by Car and Parrinello **'fictitious Lagrangian**'

$$L = \frac{1}{2}\mu\sum_{i,l,\alpha}(\dot{c}^i_{l\alpha})^2 + \frac{1}{2}\sum_{l} M_l\dot{\boldsymbol{R}}_l^2 - E(\{\boldsymbol{R}_l\},\{c^i_{l\alpha}\})$$

The orthonormality of the occupied states requires the following constraints $\sum_{l\alpha} c^i_{l\alpha} c^j_{l\alpha} = \delta_{ij}$

i,j - indicate occupied states

l - indicate atoms

α - describes types of localized orbitals

Tight-Binding Formalism – Molecular Dynamics

Equations of motion for the ionic and electronic coordinates

$$\boxed{M_l \ddot{\boldsymbol{R}}_l = -\frac{\partial}{\partial \boldsymbol{R}_l} E(\{\boldsymbol{R}_l\}, \{c^i_{l\alpha}\})}$$

$$\boxed{\mu \ddot{c}^i_{l\alpha} = -\frac{\partial}{\partial c^i_{l\alpha}} E(\{\boldsymbol{R}_l\}, \{c^i_{l\alpha}\}) + \sum_j \Lambda_{ij} c^j_{l\alpha}}$$

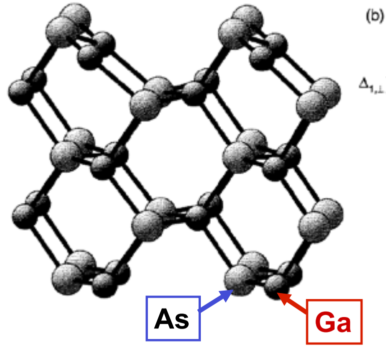
Lagrange multipliers

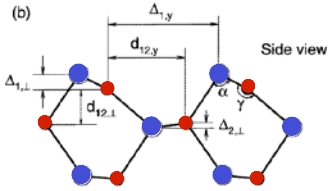
$$\Lambda_{ij} = \sum_{l\alpha}\left(\frac{1}{2}\frac{\partial E}{\partial c^i_{l\alpha}} c^j_{l\alpha} + \frac{1}{2}\frac{\partial E}{\partial c^j_{l\alpha}} c^i_{l\alpha} - \mu \ddot{c}^i_{l\alpha} \dot{c}^j_{l\alpha}\right)$$

F. S. Khan & J. Q. Broughton, Phys. Rev. B **39,** 3688 (1989)

Tight-Binding Formalism – Molecular Dynamics Applications (1)

Fully relaxed atomic structure of the topmost few layers of the GaAs(110) surface.

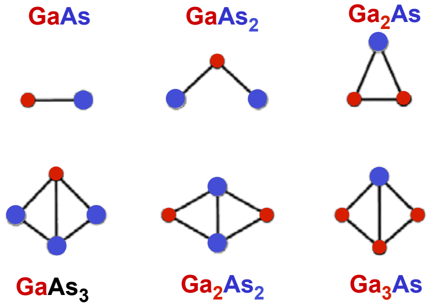




Good agreement with LDA and experiment

Tight-Binding Formalism – Molecular Dynamics Applications (2)

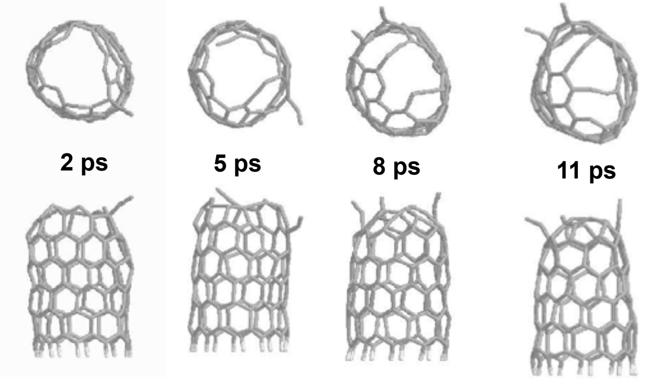
Ground-state geometries of small semiconductor clusters



- **TBMD method is also able to predict the relative stability of GaAs clusters.**

Tight Binding Molecular Dynamics Studies of Nanotube Growth

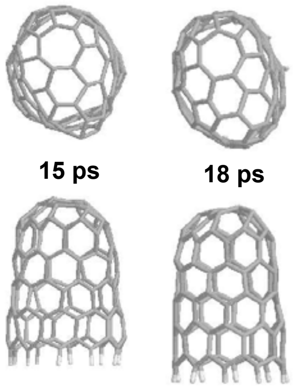
Different stages of the closure of the (10,0) nanotube at 2500 K.



E. Hernandez et al., arXiv:cond-mat/0006230 v1

Tight Binding Molecular Dynamics Studies of Nanotube Growth

Different stages of the closure of the (10,0) nanotube at 2500 K.

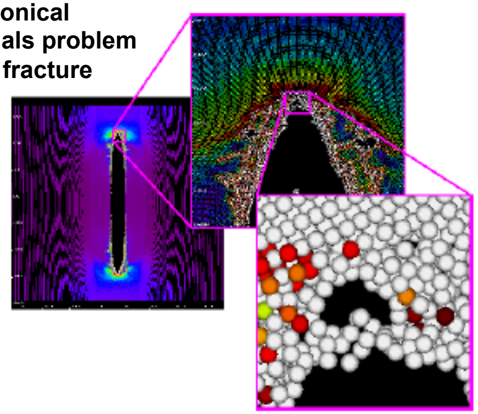


15 ps

18 ps

Atomistic simulation of fracture in Silicon

Fracture: the canonical multiscale materials problem brittle vs. ductile fracture

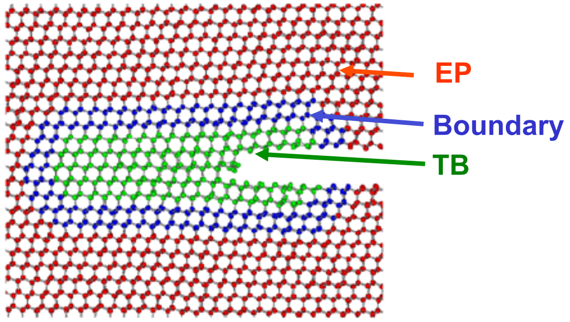


Fracture with Tight-Binding

Coupled empirical potential (EP) and TB

~50000 EP atoms and ~1000 TB atoms

400 A × 250 A × 12 A, (80 A × 65 A shown)



(Bernstein and Hess PRL 2003)

Examples of Computational Simulations

Melting A Diamond Crystal with Tight Binding Molecular Dynamics

Melting A Diamond Crystal with Tight Binding Molecular Dynamics

- Well beyond its value for jewelry, **diamond is invaluable as the hardest known substance**.
- Fine diamond particles are the ultimate abrasive, and wear resistant diamond coatings are used on tools from saw blades to surgical instruments.
- But who would consider melting diamond?
- Materials scientists and engineers who are searching for cheaper and more robust processing routes to the synthesis of diamond coatings could use the thermodynamic phase diagram of carbon as a guide.
- **The conditions that it takes to melt diamond are too extreme for careful laboratory experimentation**.

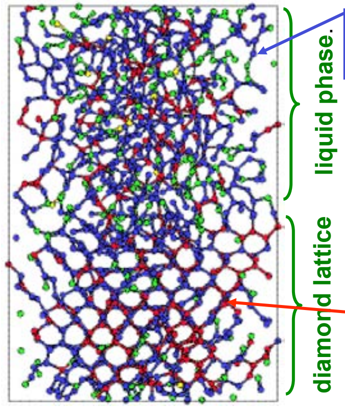
Melting A Diamond Crystal with Tight Binding Molecular Dynamics

➡ ***Melting diamond on a computer***, **makes it possible to determine the complete pressure-temperature phase diagram.**

- Quantum mechanical tight binding (TB) molecular dynamics calculations were run with a parallel code and an algorithm that scales linearly with the system size.
- A highly efficient implementation permits the calculation of the electronic structure and forces for systems of up to ***10 000 atoms***
- The empirical parameters for the TB code were determined by fits to the results from extensive first principles calculations for many static geometries.

Melting A Diamond Crystal with Tight Binding Molecular Dynamics

A snapshot of 2000 carbon atoms (T>6000 K)



Blue atoms indicate three-fold (graphitic) bonded atoms

● ● two-fold and five-fold coordinated atoms

Red atoms indicate four-fold bonded (diamond-like) atoms

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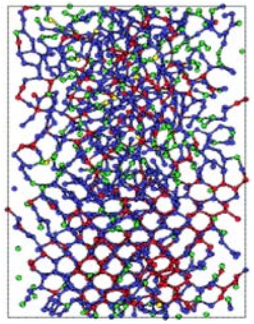

- The large number of three-fold atoms is an indication that the liquid phase is less dense than the four-fold diamond phase.
- By changing temperature and/or pressure, the interface between the solid and liquid will move (e.g., the solid fraction increases below the melting point).

Such simulations permit the accurate determination of the melting temperature of diamond as a function of pressure.

Melting A Diamond Crystal with TB Molecular Dynamics - Significance

- By including the essential quantum nature of the electrons and their chemical bonds, the ***tight binding calculations*** form a natural ***bridge*** leading from first principles electronic structure calculations ***to the mesoscopic regime***.

➡ Extension of the quantum mechanical treatment to even larger numbers of atoms in order to investigate more complex nanoscale phenomena involving extended defects.

- **This would illuminate the fundamental relationship between *microstructure* and important *macroscopic materials properties*.**

Tight-Binding Methods - Summary

- ***Classical MD*** is not accurate enough
- **Ab initio MD** prohibitive (system size)

➡ **T-B MD**

The End – Thank You