Materials Defects: Tutorial and Workshop Overview

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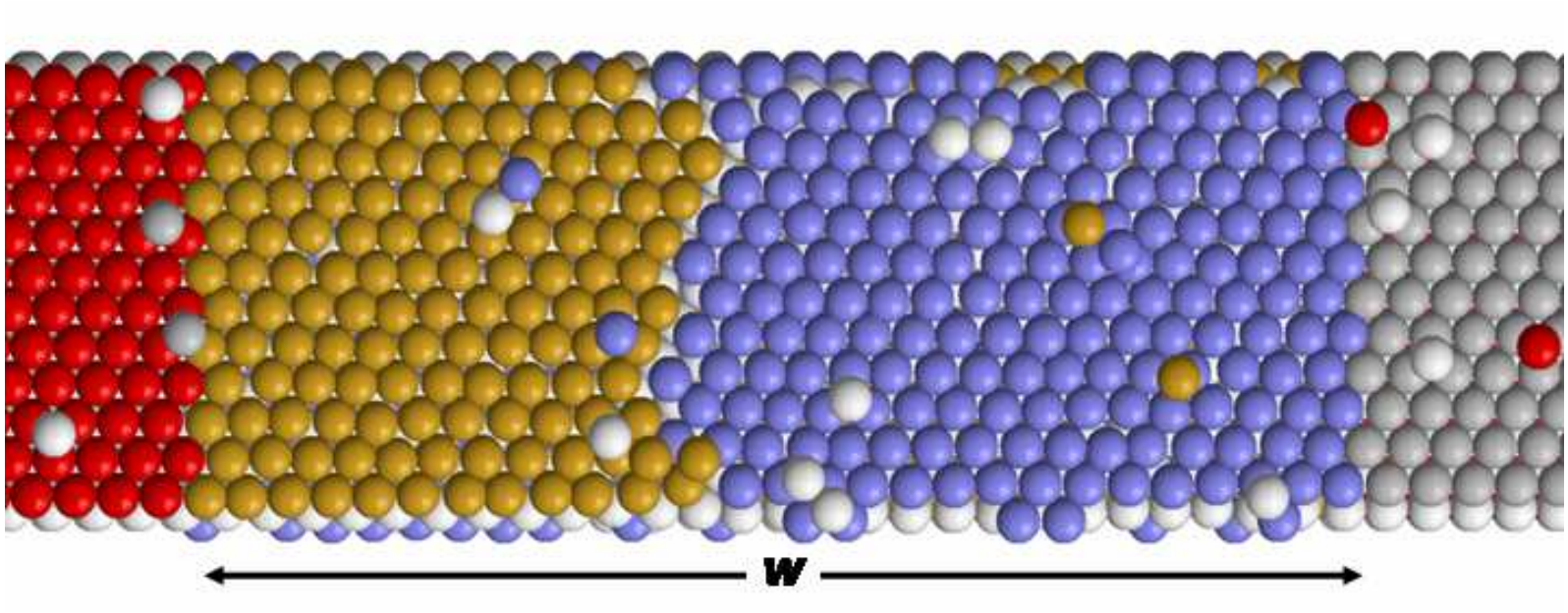
Program Overview

The program is built around two major themes:

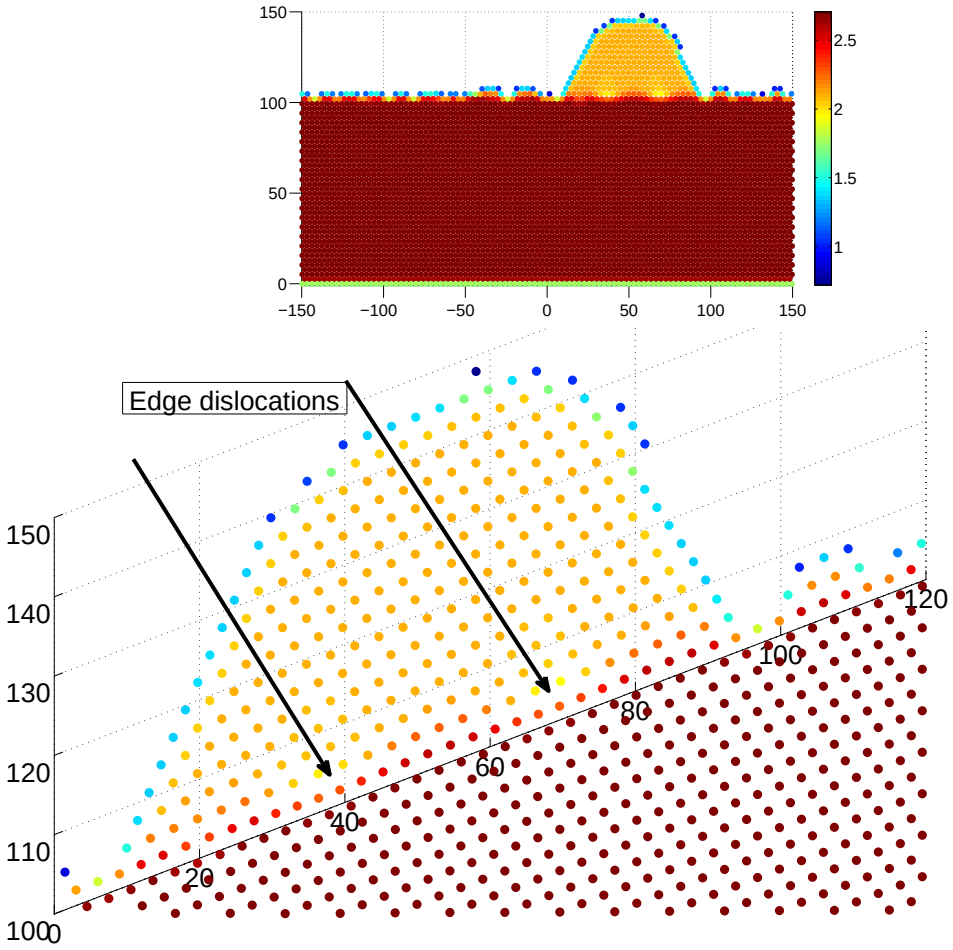
- Materials Defects:
  - Defects are those things we often neglect so that our calculations are easier.
  - Defects present a huge challenge for mathematical modeling and simulation, as anything that breaks up the regular, homogeneous structure of a calculation requires special consideration.
  - Examples include grain boundaries, dislocations, cracks, surface reconstructions, impurities, vacancies, . . .
- Multiscale Modeling and Computation

Grain Boundaries



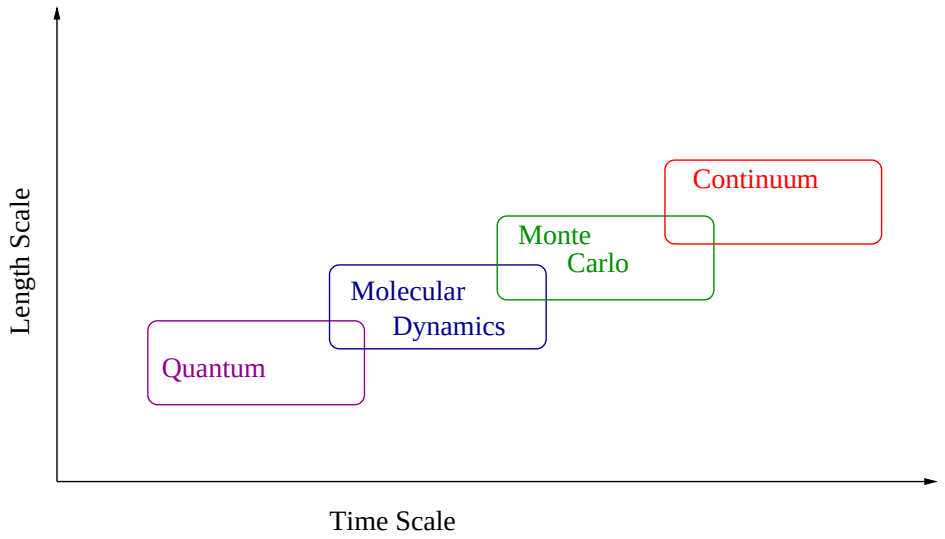
Zoontjens, Schulze, Hendy *PRE* 2008

Dislocations



Boateng, Smereka, Schulze

Multiscale Modeling Paradigms



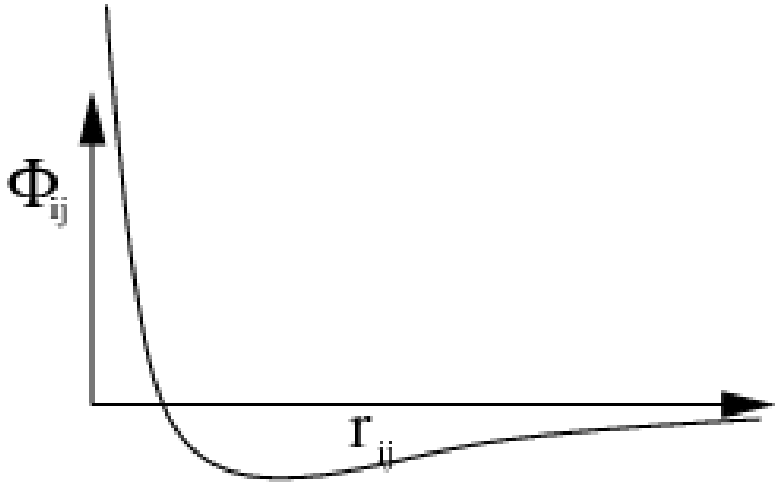
- Quantum Mechanics and DFT
- Classical Mechanics and MD
- Statistical Mechanics and MC
- Continuum Mechanics and Numerical PDE

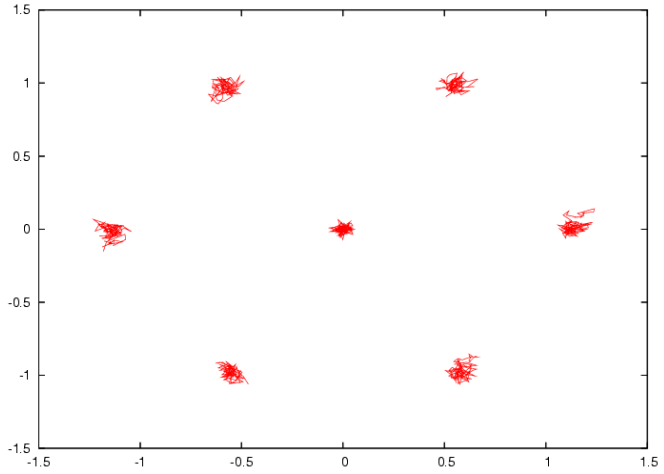
Molecular Dynamics

- In the classical regime, MD is the fundamental model

$$m_i \ddot{\mathbf{x}}_i = -\nabla_i \Phi\left(\{\mathbf{x}_i\}\right) \qquad i = 1, 2, \ldots, N.$$

$$\Phi(\{\mathbf{x}_i\}) = \sum_{i \neq j} \Phi_{ij} = 4\epsilon \sum_{i \neq j} \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right]$$





Failure of MD at Small Scales

- MD would be sufficient for Materials Science applications at small scales if the potentials $\phi(\mathbf{x})$ were accurate.

- One reason these fail, is that they are limited to two-, three-, etc. body interactions:

$$\phi = \sum_{ij} \phi_{ij} + \sum_{ijk} \phi_{ijk} + \dots$$

- They are typically fit to model particular materials in particular regimes, and they do not transfer well to other scenarios.

- When new potentials are being fit, new regimes are encountered or greater accuracy is desired, one must turn away from this empirical approach and use a "first principles" approach.

Electronic Structure

- This means solving some version of the many-body Schrodinger equation.

- In the Born-Oppenheimer approximation, the heavy, atomic nuclei are treated as classical, stationary point particles, and only the relatively light electrons are treated in the non-localized, quantum mechanical way.

- This reduces the many-body problem to:

$$\hat{H}_{bo}\Psi = E\Psi,$$

$$\hat{H}_{bo} = -\sum_{i}^{N_e}\frac{1}{2}\nabla_i^2 - \sum_{i}^{N_e}\sum_{j}^{N_n}\frac{Z_j}{r_{ij}} + \sum_{i}^{N_e}\sum_{j>i}^{N_e}\frac{1}{r_{ij}}.$$

  where Ψ is a function of the coordinates of *just* the electrons, i.e. a 3*(number of electrons) dimensional eigenvalue problem!

Variational Principle

- The expected value of the energy is a functional of the many-body wavefunction:

$$E[\Psi] = \frac{\int \Psi^* \hat{H} \Psi d\mathbf{x}}{\langle \Psi | \Psi \rangle} \equiv \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

- If one takes Ψ_0 to be the ground-state, one can use this to construct a "first-principles" energy landscape.

- It is easy to show, that for any choice of Ψ, one has

$$E[\Psi] \geq E_0.$$

Density Functional Theory

- Solving the electronic structure problem is hopeless for large systems of particles.

- The vast majority of materials science energy-landscape calculations approximate the ground state energy via the *electron density*:

$$\rho(\mathbf{r}_1) = N \int \int \dots \int ||\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)||^2 ds_1 d\mathbf{x}_2 \dots d\mathbf{x}_N.$$

- The function $\rho \geq 0$ is the number-density of electrons.

- The Hohnberg-Kohn theorems guarantee the existence of functionals that are equivalent to the many-body Schrodinger electronic structure problem:

$$E_v[\rho] \geq E_0.$$

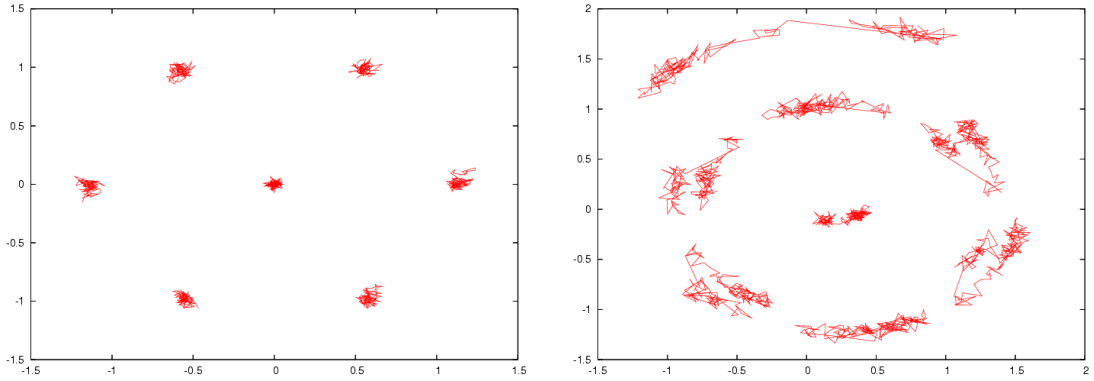
- While standard approximations are widely used, the functionals are not actually known, nor are there any rigorous estimates of their accuracy.

Failure of MD at Large Scales

- MD would be sufficient for Materials Science applications at large scales if it were faster.

- The reason for the failure is the extremely small time-steps that are needed to resolve the chaotic motion that invariably arises with many body interactions:

- This makes determining even the equilibrium behavior difficult, and nonequilibrium even harder.



Monte Carlo

There are two broad classes of statistical approaches:

- (Equilibrium) Monte Carlo
- Dynamic or Kinetic Monte Carlo

Often, these methods are appropriate for bridging length and time scales between MD and Continuum Mechanics.

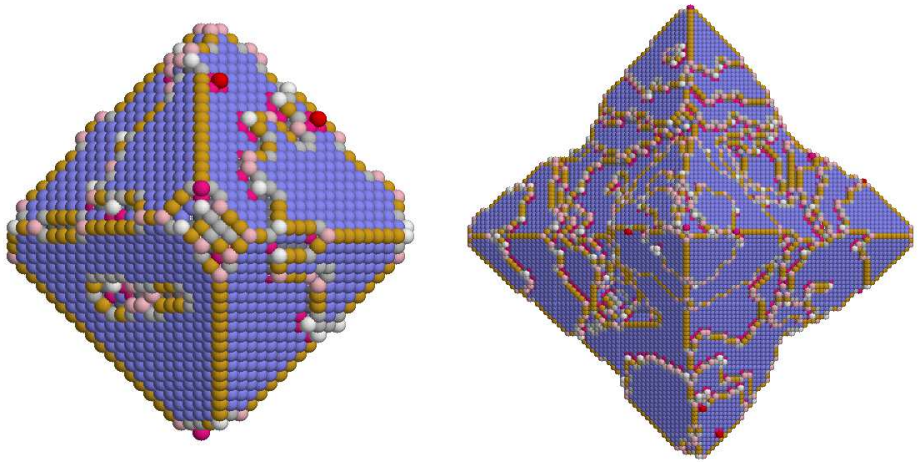
Equilibrium Monte Carlo

This approach is based directly on statistical mechanics and allows one to compute average properties of a collection particles, producing thermodynamic quantities.

- *Canonical Ensemble* This is by far the most common type of simulation, aiming to evaluate the average properties of a collection of N particles in a volume V interacting with an environment at a fixed temperature T.

- Other commonly used ensembles include the *micro-canonical Ensemble* ($N-V-E$) and *Grand/ macro-canonical* ($\mu-V-T$) ensemble.

Kinetic Monte-Carlo Simulations



- Configuration space is typically discrete, e.g. occupation arrays for a fixed lattice.
- Dynamics are imposed via a Markov Chain model
- Transition rates are based on configuration changes
- Example: $q_i = \nu \exp\left(-\frac{\Delta\phi}{k_b T}\right), \quad \Delta\phi = E_S + mE_N$

Continuum Models

- Includes fluid dynamics, elasticity, thermodynamics, diffusion processes, porous media, . . .

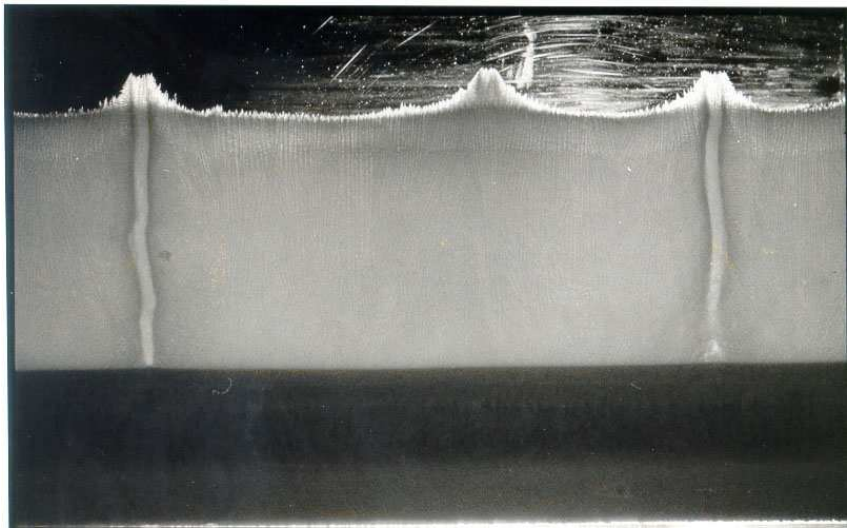
- Common threads are
  - a *continuum assumption*—the idea that mass, velocity, etc. can be represented at each point in space by a continuous and smoothly varying field rather than a discrete system of particles.
  - one or more *conservation laws*.

- Similarly, *interfaces* are often modeled as smooth curves or "phase" fields.

- $\Rightarrow$ PDE's in 3D space & time

- The bulk of traditional applied math/numerical analysis/front tracking methods are focused on this regime.

Larger Scale Defects



- At larger scales, models are often further coarse-grained.
- For example, *mushy zones* are arrays of dendrites.
- These are often modeled as reactive porous media.
- *Chimneys* are sold-free channels caused by convection.
- This leaves behind larger scale defects known as *freckles*.

Tutorial Schedule

- Peter Voorhees (Northwestern University) "Line and Planar Defects in Materials"
- Danny Perez (Los Alamos National Laboratory) "Introduction to Molecular Dynamics"
- Kristen Fichthorn (Pennsylvania State University) "An Introduction to Theoretical Methods for Describing Rare Events"
- Tony Lelivre (Ecole des Ponts ParisTech) "Monte Carlo methods in molecular dynamics"
- Maria Emelianenko (George Mason University) "Mathematical modeling of interfacial dynamics in polycrystals"
- Peter Smereka (University of Michigan) "Theory and Application of Simplified Kinetic Monte Carlo Models"
- Gabor Csanyi (University of Cambridge) "State of the art: a broad-brush survey of interatomic potentials"

Program

- Materials Defects: Tutorials. September 11 - 14, 2012.
- Workshop I: Quantum and Atomistic Modeling of Materials Defects. October 1 - 5, 2012.
- Workshop II: Atomistic and Mesoscale Modeling of Materials Defects. October 22 - 26, 2012.
- Workshop III: Mesoscale and Continuum Scale Modeling of Materials Defects. November 13 - 16, 2012.
- Workshop IV: Computational Methods for Multiscale Modeling of Materials Defects. December 3 - 7, 2012.
- Culminating Workshop at Lake Arrowhead (by invitation only). December 9 - 14, 2012.