Faculty of Physics,
University of Warsaw

Summer Semester 2014

Lecture

Modeling of Nanostructures and Materials

Jacek A. Majewski

E-mail: Jacek.Majewski@fuw.edu.pl

Lecture 11 – *May 12, 2014*

Kinetic Monte Carlo Methods – Basics

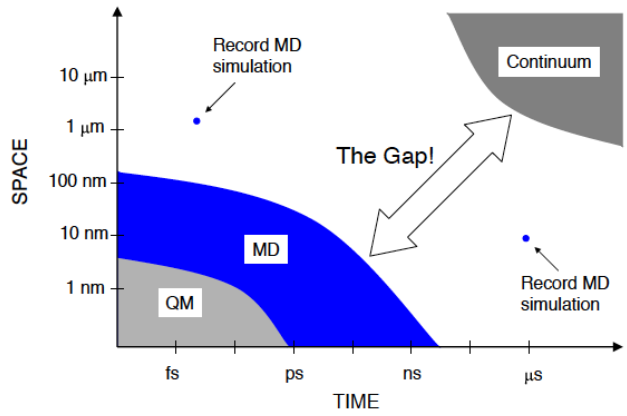
- Simulation of epitaxial crystal growth

Continuum Methods in Materials Science

- Composite Materials with Carbon Nanotubes
- Crack spreading
- Crystal Growth

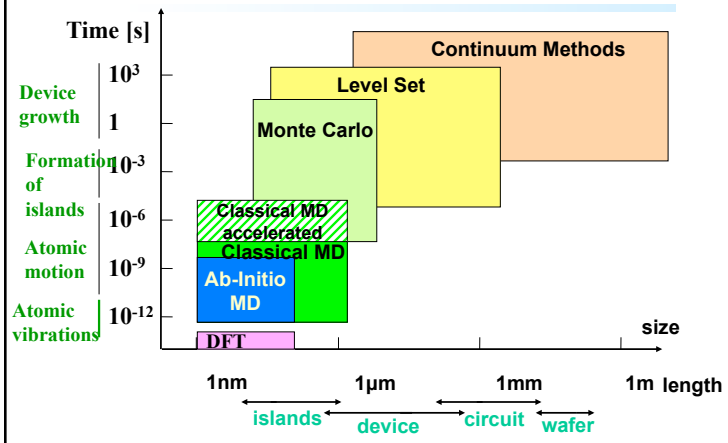
e-mail: Jacek.Majewski@fuw.edu.pl

Limitations of Atomistic Methods



Monte Carlo Methods

Hierarchy of Theoretical Approaches



Basics of the Monte Carlo Method

- In a macroscopic system, it is difficult to treat the motions of the all (microscopic) atoms or molecules
- Macroscopic properties of a systems (i.e., how the whole system behaves) are of interest

  ⟹ **Coarse-graining necessary**
- If the time evolution of the system is coarse-grained stochastically, one achieves one class of models, so-called ***stochastic models***.
- ***Monte Carlo Method*** **–** efficient method to realize this numerically on a computer
- Monte Carlo methods provide a powerful way to solve numerically the fluctuation or relaxation in a stochastic system

Stochastic Processes – Dynamical Variables at Equilibrium

One of the most important subjects in the ***Monte Carlo*** method

distribution of dynamical variables at thermal equilibrium of the system ?

- It is not necessary to examine the trajectory of the dynamical variable according to some deterministic equation.
- It is important to discuss the value of the dynamical variable at a certain place and a certain time

Markov Process

- Most algorithms used in simulating a realistic system by Monte Carlo methods, are based on the following ***Markov process***.
- $\Phi(q_0, t_0 \mid q, t)$ **is independent of any information about any time** t' **before** t_0
- All the history before time t_0 is contracted into the single piece of information that the system has the dynamic variable q_0 at the time t_0.

Markov Process

Master equation **– basis time-evolution equation**

$$p(q,t+\Delta t)-p(q,t)= \int dq_1\, p(q_1,t)W(q_1;q)-p(q,t)\Gamma(q)+O(\Delta t^2)$$

describes the process of transition into state q (probability increases)

describes the process of transition out of the state q (probability decreases)

- In order to get $p(q,t)$ normalized

$$\Gamma(q)=\int dq_1 W(q;q_1)$$

$W(q_1;q)$ **stochastic operator** represents transition rate

Markov Process – Random Walk

Example of master equation – a random walk on a d-dim. hypercubic lattice

The kernel (transition rate) $W(q_1;q)=\frac{\upsilon}{2d}\sum_i^{2d}\delta(q-q_1+a\vec{e}_i)$

υ -- diffusion velocity

$\vec{e}_i$ -- one of the 2d neighbors

a -- lattice constant

$$p(q,t+\Delta t)-p(q,t)=\upsilon\left[\frac{1}{2d}\sum_i^{2d}p(q+a\vec{e}_i,t)-p(q,t)\right]+O(\Delta t^2)$$

$D=\frac{\upsilon a^2}{2d\Delta t}$ diffusion constant $\quad a,\Delta t\to 0$ with constant D

⇒ **Master equation = a finite-difference version of diffusion equation**

$$\frac{\partial}{\partial t}p(q,t)=D\nabla^2 p(q,t)$$

Ergodicity

- If there is a unique equilibrium state without any periodic motion, this Markov process is called ***ergodic***.
- ***Egodicity*** -- property of approaching a ***unique final state from an arbitrary initial state***
- In many thermodynamic systems, the final state after enough time has past is the ***thermal equilibrium state***
- **A system at thermal equilibrium obeys the Boltzmann distribution**

$$p^{eq}(q)=\frac{1}{Z}exp[-E(q)/k_BT]$$

Partition function $Z=\sum_q exp[-E(q)/k_BT]$

Algoritms for Monte Carlo Simulations

The most basic algorithm of the Monte Carlo method:

- **(1) Generate a random number**
- **(2) Take or do not take a new random step, depending on the generated random number**
- **(3) Repeat trial**

Random numbers

- The "random numbers" generated on a computer are not mathematically ideal random numbers
- **pseudo-random numbers –** uniformly distributed numbers in the interval [0,1] having long but finite period
- For 32-bit processor, the **period** is $M = 2^{31} - 1 = 2\ 147\ 483\ 647$

Algoritms for Monte Carlo Simulations

Simple Sampling Techniques

The evaluation of an expectation value of a physical quantity

$$\bar{A} = \int dq A(q) p(q)$$

an important theme in the field of Monte Carlo methods

$$\bar{A} \approx \frac{\sum_{l=1}^{N} A(q_l) p(q_l)}{\sum_{l=1}^{N} p(q_l)}$$

- Monte Carlo method is introduced to extract samples of the system in a completely random way.
- This method actually offers a well–defined stochastic process

Such a method of Monte Carlo sampling is called a **Simple Sampling Technique**

Applications of Monte Carlo Simulations in the field of condensed-matter & materials science

- **Classical particles**
- **Percolation**
- **Polymers**
- **Classical Spins**
- **Crystal Growth**

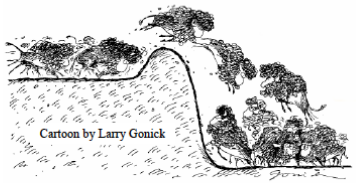
Kinetic Monte Carlo Methods

Summary: MD, Metropolis MC and kinetic MC

With MD we can only reproduce the dynamics of the system for ≤ 100 ns. Slow thermally-activated processes, such as diffusion, cannot be modeled. An alternative computational techniques for slow processes are Monte Carlo methods.

Monte Carlo method is a common name for a wide variety of stochastic techniques. These techniques are based on the use of random numbers and probability statistics to investigate problems in areas as diverse as economics, nuclear physics, and flow of traffic. There are many variations of Monte Carlo methods. In this lecture we will briefly discuss two methods that are often used in materials science - classical Metropolis Monte Carlo and kinetic Monte Carlo.

Metropolis Monte Carlo – generates configurations according to the desired statistical-mechanics distribution. There is no time, the method cannot be used to study evolution of the system. Equilibrium properties can be studied.



Kinetic Monte Carlo – can address kinetics. The main idea behind KMC is to use transition rates that depend on the energy barrier between the states, with time increments formulated so that they relate to the microscopic kinetics of the system.

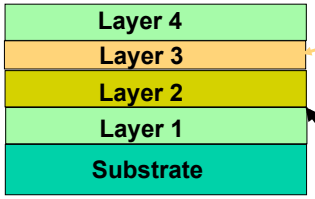
University of Virginia, MSE 4270/6270: Introduction to Atomistic Simulations, Leonid Zhigilei

Kinetic Monte Carlo Simulations – An approach to perform epitaxial growth simulations

- ***Epitaxial growth*** is a key technique in fabricating semiconductor-based electronic and optoelectronic devices such as
  - light-emitting diodes (LED's),
  - laser diodes (LDs), or
  - high electron mobility transistors.
- These devices consist of vertically stacked thin films that differ by the material, alloy composition, or doping.

Epitaxial growth of materials

Vertically stacked layers of various materials



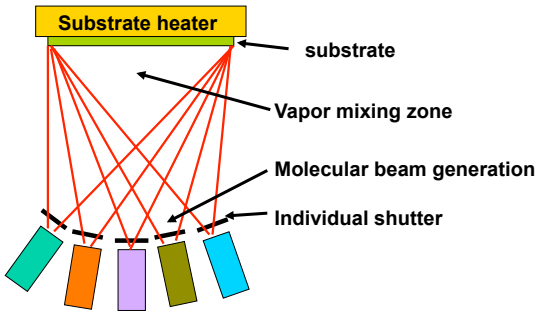
Epitaxy (from Greek ***epi*** = upon; ***taxis*** = ordered)

- To employ quantum effects some of these structures are only a few atomic layers thick.
- For the performance/efficiency of such devices the quality of the interfaces between the different layers is crucial.

Realistic growth simulations could help to understand mechanisms affecting the interface quality but also to identify optimum growth conditions or suitable material combinations.

Molecular Beam Epitaxy (MBE)

Schematic view of a MBE system for the growth of multi-element films

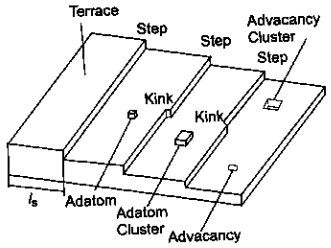


Effusion cells for constituent elements and dopants

MBE – real maschine

Film Growth Modes

- **Nucleation and growth of a film proceeds from energetically favorable places on a substrate surface**



Schematic view of the elements of surface morphology

- **If the surface diffusion is fast enough, a randomly deposited adatom will diffuse to the energetically most favorable places like steps and especially kinks.**
- **If at lower temperatures the diffusion is slower, several mobile addatoms may encounter each other within a terrace and may form additional immobile adatom cluster within terraces**

Simulation of growth processes

- **A challenge to perform such growth simulations is the large range of relevant length and time scales.**
- The features interesting for device design (interface morphology, formation of nanostructures) are of the order of 100–1000 nm and the time to grow these structures is of the order of seconds.
- ***The origin of these effects***, however, lies in the atomic processes on the surface (adatom adsorption, desorption, nucleation,etc.).
  This requires a resolution in the ***length scale*** **0.1 nm** and in the ***time scale*** of $\mathbf{10^{-13}}$ **s**.

Simulation of growth processes – Various approaches

Methods to perform growth simulations can be classified in three main categories:

- ***rate equations*** (giving only global information such as island density or adatom coverage) without spatial resolution,
- ***continuum equations***, which describe the surface morphology on a mesoscopic scale,
- ***computer simulations***, describing the full atomistic structure of the growing surface, such as molecular dynamics (MD) or the kinetic Monte Carlo (KMC) simulation.

The first two approaches do not really bridge the large range of length and time scales but work exclusively on a mesoscopic scale by using effective parameters.
A problem - the effective parameters cannot be directly related to the actual atomic parameters

Simulation of growth processes – Molecular Dynamic Simulations

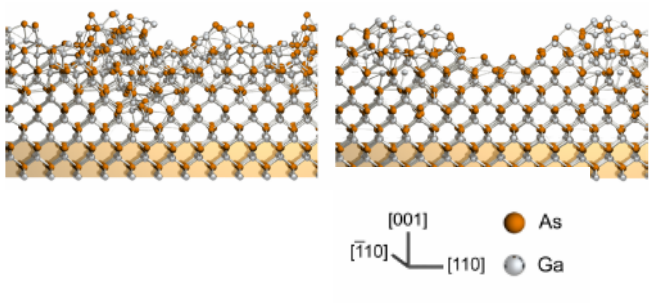
- In MD simulations as input no *a priori* information is needed
- They provide detailed insight into microscopic processes of deposition.
- Due to limitations in computational power, ***MD*** method is mostly restricted to very short simulation ***times of the order of picoseconds*** and ***small simulation areas***.
- **The Molecular Dynamics approaches are important tools to identify all relevant diffusion processes *a priori* and calculate their diffusion rates**.

Molecular Dynamics Simulations of GaAs MBE

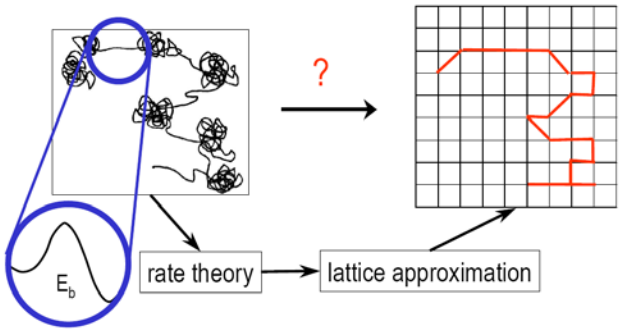
D. A. Murdick et al.

The effect of substrate temperature on film morphology

$T_{sub} = 473\ K$ $T_{sub} = 673\ K$



From Molecular Dynamics to Kinetic Monte Carlo



Simulation of growth processes – Kinetic Monte Carlo (KMC)

- Modeling crystal growth with the KMC method allows one to cover experimentally relevant growth times and system sizes, since each event on the surface is just described by a single quantity—the transition rate—rather than by modeling the full reaction path including atomic geometries and energies

➡ **Bridging of length and time scales**

Simulation of growth processes – Kinetic Monte Carlo (KMC)

- In order **to describe growth** we must in principle **follow the trajectory of each individual atom** starting from the adsorption on the surface over the motion on the surface until it eventually gets incorporated or desorbed.
- In general, all information necessary to get this information can be obtained by calculating the ***potential energy surface (PES)*** an atom experiences on a **realistic surface**

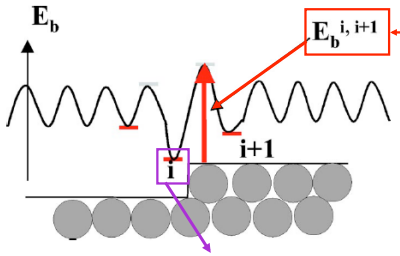
  Realistic means here that the surface has various structural features such as surface steps, kinks, and facets.

- **Such a *potential energy surface (PES)* can be calculated based on first-principles total energy calculations**

  J. Neugebauer, T. Zywietz, M. Scheffler, and J. Northrup, Appl. Surf. Sci. 159, 355 (2000).

One-dimensional potential energy surface (PES)

can be obtained from *ab initio* calculations

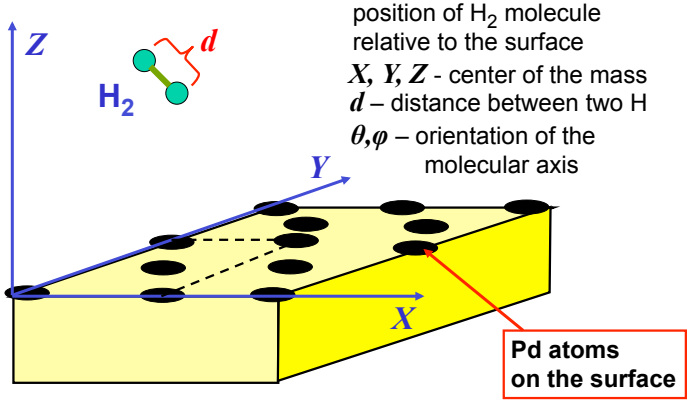


The energy barrier that one ***adatom*** has to overcome to hop from site i to site $i+1$.

$$E_b^{i,i+1} > k_B T$$

The ***site in front of the step*** has a higher coordination (the atom can form more bonds with the surface) and is thus energetically more favorable than the adsorption sites (local minima in the PES) on the flat surface.

AIMD Simulations of H_2 Molecule Adsorption on the (100) surface of Pd



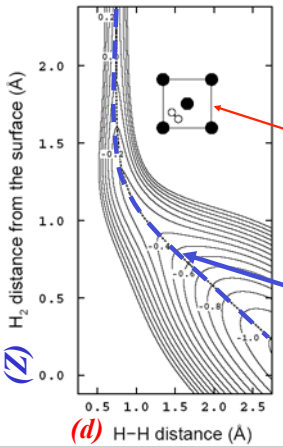
6 coordinates determines position of H_2 molecule relative to the surface

X, Y, Z - center of the mass

d – distance between two H

θ, φ – orientation of the molecular axis

AIMD Potential Energy Surface (PES) for H_2 / Pd(100) system



Contour plot of the PES along a two-dimensional cut through the six-dimensional coordinate space

The inset shows the orientation of the molecular axis and the lateral H_2 center-of-mass coordinates

The most favorable path towards dissociative adsorption

Simulation of growth processes – Kinetic Monte Carlo (KMC)

Condition $E_{diff}^{i,i+1} > k_B T$ **well fulfilled in semiconductors**

diffusion barriers on semiconductor surfaces are of the order of a few tenths of an eV up to a few eV

Transition rate for an adatom jump from site i to $i+1$

$$w_{i \to i+1} = \Gamma_{i,i+1} \exp\left(- \frac{E_{\mathrm{diff}}^{i,i+1}}{k_B T} \right)$$

called ***attempt frequency*** and can be directly calculated from total energy calculations

Simulation of growth processes – Kinetic Monte Carlo (KMC)

- **To describe surface growth we have not only to follow a *single atom* but an *ensemble of atoms*.**
- Let certain configuration in this ensemble be n
- As for the individual adatom each possible configuration is given by a minimum in the total energy surface and neighboring minima are separated by a barrier $E_{diff}^{n,n'}$

Simulation of growth processes – Kinetic Monte Carlo (KMC)

Master Equation

$$\frac{\partial P_n(t)}{\partial t} = \sum_{\{n'\}} \left[w_{n' \to n} P_{n'}(t) - w_{n \to n'} P_n(t) \right]$$

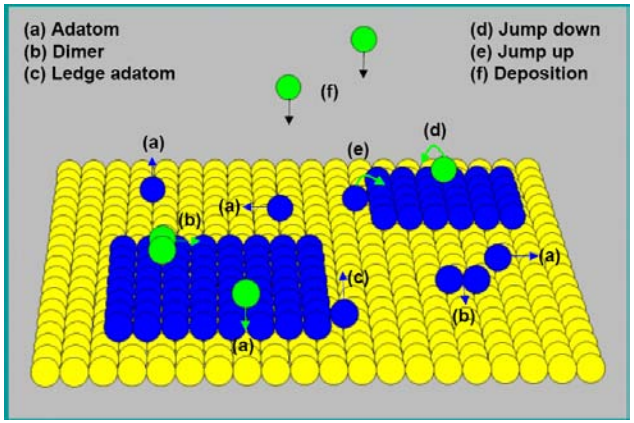
$P_n(t)$ - the probability of finding the system at time t in configuration n,

$w_{n' \to n}$ - the transition rate to go from configuration n to n'.

For a typical growth simulation these transitions involve

- **adsorption,**
- **desorption,**
- **diffusion**, and
- **nucleation**

Possible events during film growth



Simulation of growth processes – Kinetic Monte Carlo Method

Procedure

- start from a configuration n_0
- calculate the transition probability $w_{n_0 \to n'}$ for all possible events
- select a new configuration by using a random number r_{rand} in the interval between 0 and 1
- the time for this event can be calculated by

$$\Delta t = -\frac{\ln(r_{rand})}{\sum_{n'} w_{n_0 \to n'}}$$

n' runs over all neighbor configurations of n_0

The above procedure is subsequently repeated and one directly obtains how the growing surface evolves in time $n(t)$

Simulation of growth processes – Kinetic Monte Carlo Method

Problem

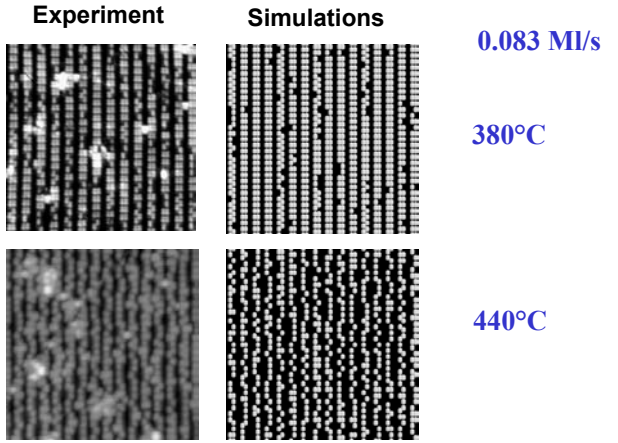
With increasing growth temperature KMC becomes more expensive

Why?

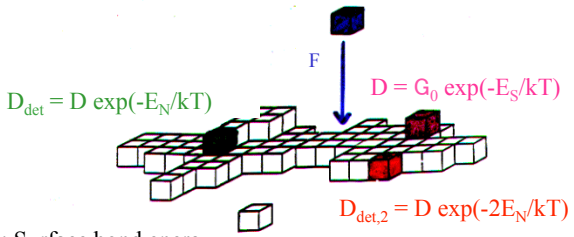
- The transition probability increases exponentially with temperature *T*
- The transition probability is inversely proportional to the time step

➡ **The number of time steps and thus the computational effort to follow the system over a fixed time *t* increases exponentially**

KMC Simulation for Equilibrium Structures at Various Temperatures



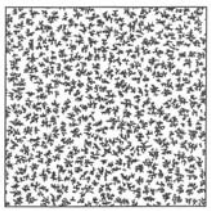
KMC Simulations of a Cubic, Solid-on-Solid Model



E_S: Surface bond energy
E_N: Nearest neighbor bond energy
G_0 : Prefactor $[O(10^{13}s^{-1})]$

- Parameters that can be calculated from first principles (e.g., DFT)
- Completely stochastic approach

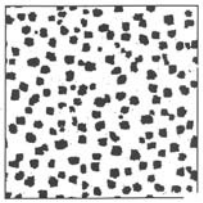
KMC Simulations: Effect of Nearest Neighbor Bond Energy E_N



KMC Simulations

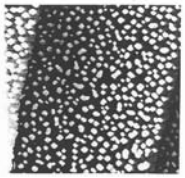
Large E_N: Irreversible Growth

Small E_N: Compact Islands



Experimental Data

Au/Ru(100)



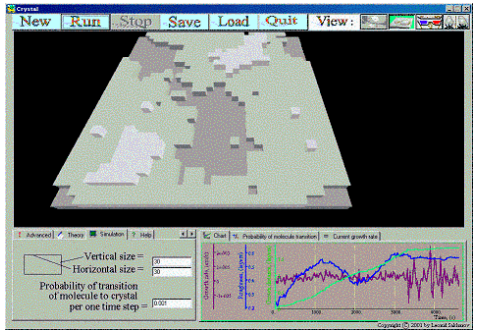
Ni/Ni(100)

Hwang et al., PRL 67 (1991)

Kopatzki et al., Surf.Sci. 284 (1993)

LeoCrystal – crystal growth simulation software

LeoCrystal is a program that performs modeling of reaction on the surface of crystal for educational and research purposes.



www.leokrut.com/store/leocrystal.html

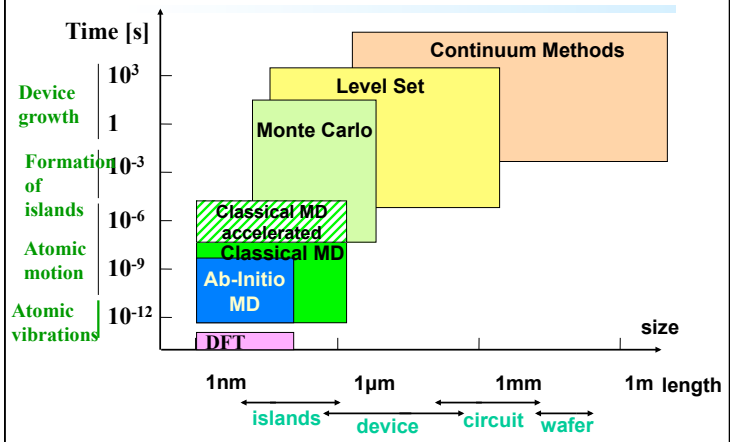
LeoCrystal – crystal growth simulation software

- With the help of this program you can estimate influence of different parameters of the structure elements of crystals on topology and kinetic of the crystallization.
- Process of crystal growth is present in practically all major technology processes.
- In depth understanding of complexity of this process is essential for professional research.
- The creative presentation of the surface including 3D perspective projection and stereo red/blue (corresponding glasses required) and separate for both eyes are available and make the performing of educational and research process a sort of fun.

Continuum Methods in Materials Science

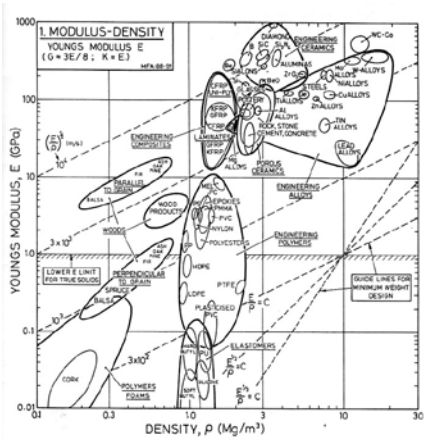
- Hierarchy of theoretical approaches
- Continuum models of carbon nanotubes composites
- Continuum Field Description of Crack Propagation
- Continuum models of crystal growth

Hierarchy of Theoretical Approaches



Elasticity of composite materials

The Young's Moduli of Engineering Materials



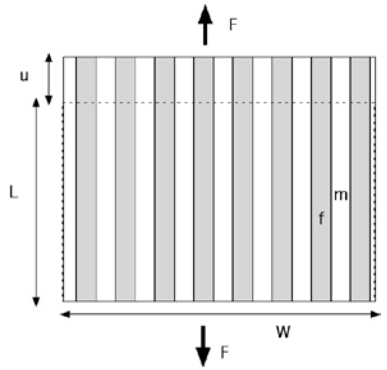
The different classes of material tend to cluster:

Metals have relatively high moduli and high densities.

Polymers have low moduli and densities.

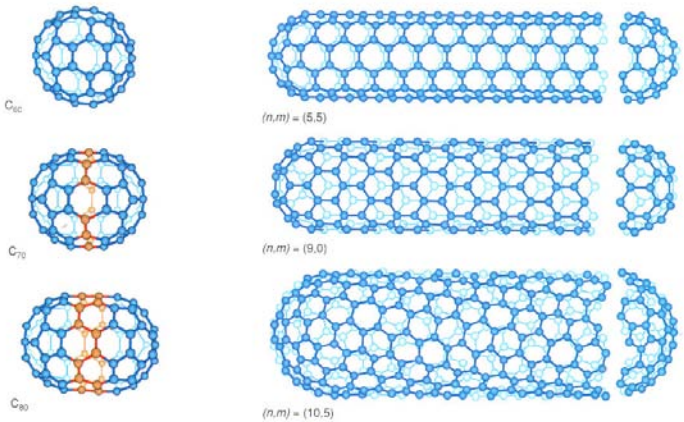
Elastic moduli of composites, anisotropic materials

CFRP – carbon fiber reinforced polymers



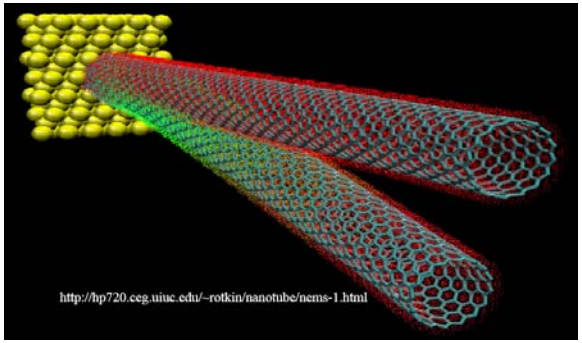
What happens if the composite is loaded by force F ?

Carbon nanotubes (CNTs)



*S. Iijima, Nature **354**, 56 (1991)*

CNTs – Mechanical Properties

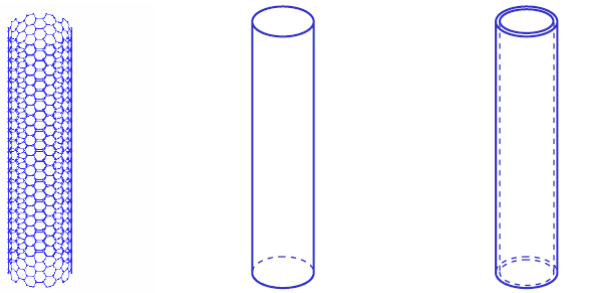


Mechanical strength – graphite-like strong bonds
-- no dangling bonds
-- no weakly bound sheets

CNTs – Mechanical Applications

- **very high Young's modulus** ~ 10^{12} N/m^2
  (5 times the value for steel)
  - deformations (bending, squeezing) are elastic, i.e., they disappear when the load is removed
- new composite materials with high strength and elasticity
- **futuristic applications???**
  - earthquake-resistant buildings;
  - cars which come to its undamaged form after a crash

Continuum Models of Carbon Nanotube-Based Composites



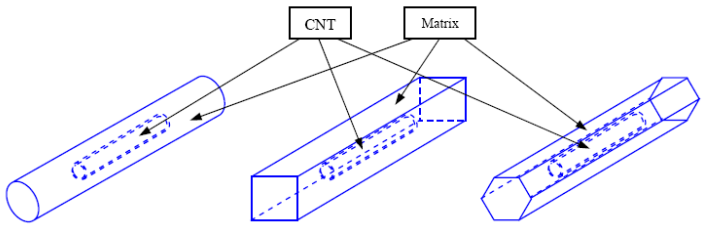
Discrete (MD) model

Continuum *shell* model

Continuum *solid* model

Continuum Models of Carbon Nanotube-Based Composites

Three possible representative volume elements (RVE) for the analysis of *CNT-based nanocomposites*



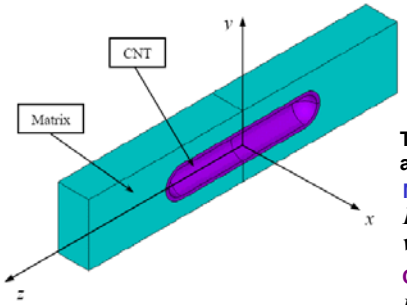
Circular (Cylindrical) RVE

Square RVE

Hexagonal RVE

Continuum Models of Carbon Nanotube-Based Composites

A short single-walled carbon nanotube (CNT) embedded in a matrix material



Matrix:
height = width = 10 nm,
length = 100 nm;

CNT: outer radius = 5 nm,
inner radius = 4.6 nm,
length = 50 nm

The Young's moduli and Poisson's ratios:

Matrix:

E_M = 100nN/nm^2 (=100GPa)

ν_M = 0. 3

CNT:

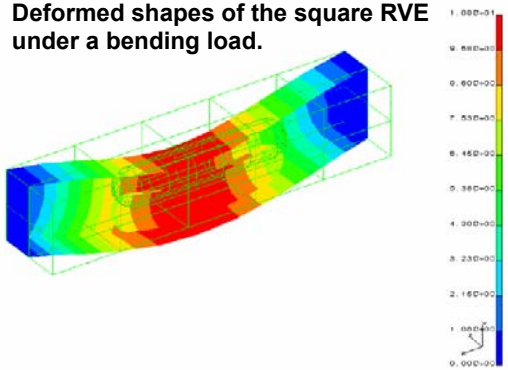
E_{CNT} = 1000nN/nm^2 (=1000GPa)

ν_{CNT} = 0. 3

Continuum Models of Carbon Nanotube-Based Composites

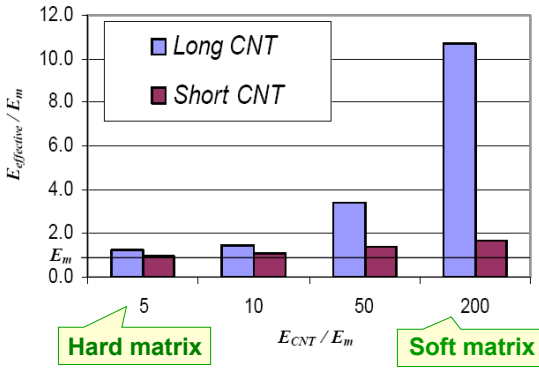
- **Simulations of CNT-based composites using the continuum mechanics approach**

⟹ **Deformed shapes of the square RVE under a bending load.**



Continuum Models of Carbon Nanotube-Based Composites

Effective Young's moduli in the CNT direction for CNT-based Composites with various matrices



CNT modulus 1000 GPa

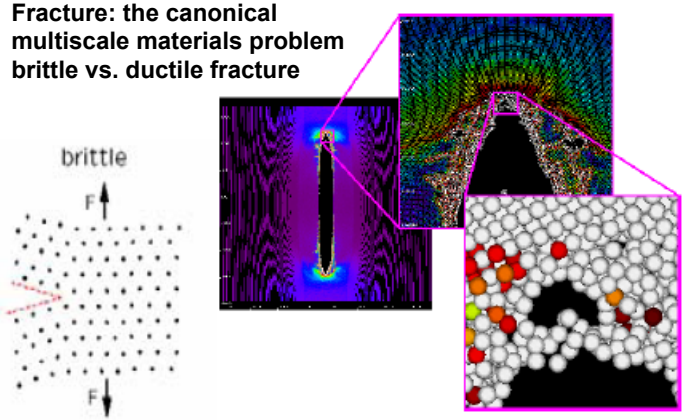
volume fraction = 0.05 **(long)**

volume fraction = 0.02 **(short)**

Crack spreading

Multiscale Simulations of Fracture

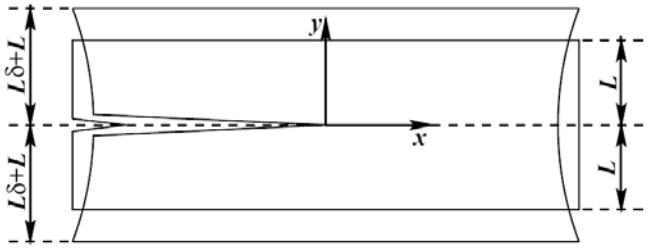
Fracture: the canonical multiscale materials problem brittle vs. ductile fracture



Continuum Field Description of Crack Propagation

I. S. Aranson et al., Phys. Rev. Lett. **85**, 118 (2000)

Schematic representation of fixed-grips loading



The two-dimensional geometry focusing on the so-called type-I crack mode

Continuum Field Description of Crack Propagation

- ***Model of the crack propagation*** - is a set of the elastodynamic equations coupled to the equation for the ***order parameter*** ρ
  - ρ is related to the relative concentration of point defects in the amorphous material (e.g., microvoids) and characterizes ***local order***
- We define $\rho = 1$ ***outside*** the crack (no defects) and $\rho = 0$ ***inside*** the crack (all the atomic bonds are broken).
- At the crack surface ρ varies from 0 to1 on the scale much larger than the interatomic distance, justifying the continuum description of the crack.
- Material fails to support tensile stress and breaks when ρ becomes below critical value ρ_c.

Continuum Field Description of Crack Propagation

Equations of motion for an elastic medium

the density of material

accounts for viscous damping, η is the viscosity coefficient

$$\rho_0 \ddot{u}_i = \eta \Delta \dot{u}_i + \frac{\partial \sigma_{ij}}{\partial x_j}, \qquad j = 1, 2.$$

u_i - **the components of displacements**

σ_{ij} -- ***the stress tensor*** is related to deformations

$$\sigma_{ij} = \frac{E}{1+\sigma}\left(u_{ij} + \frac{\sigma}{1-\sigma} u_{ll}\delta_{ij}\right) + \nu\dot{\rho}\delta_{ij}$$

Continuum Field Description of Crack Propagation

The stress tensor

$$\sigma_{ij} = \frac{E}{1+\sigma}\left(u_{ij} + \frac{\sigma}{1-\sigma}u_{ll}\delta_{ij}\right) + \nu\dot{\rho}\,\delta_{ij}$$

trace of the elastic strain tensor

- u_{ij} -- the elastic strain tensor
- E -- the Young's modulus
- σ -- the Poisson's ratio
- To take into account the effect of weakening of material with the decrease of ρ one assumes dependence of E upon ρ, $E = E_0\rho$
- $\nu\dot{\rho}$ -- accounts for the hydrostatic pressure created due to generation of new defects; ν is a constant

Continuum Field Description of Crack Propagation

Equations of motion for order parameter

- We assume that the order parameter ρ is governed by pure dissipative dynamics which can be derived from the "free-energy" type functional F
- Following Landau ideas on phase transitions, we adapt the simplest form for the free energy

$$F \propto \int dxdy\,[\,D\,|\nabla\rho|^2 + \varphi(\rho)]$$

"local potential energy" φ has minima at $\rho = 0$ and $\rho = 1$.

Polynomial form for $\varphi(\rho)$

Continuum Field Description of Crack Propagation

Equations of motion for order parameter

$$\dot{\rho} = D\Delta\rho - a\rho(1-\rho)F(\rho, u_{ll}) + f(\rho)\frac{\partial\rho}{\partial x_l}\dot{u}_l$$

Coupling of the order parameter to the displacement field enters through the position of the unstable fixed point defined by the function $F(\rho, u_{ll})$

Coupling of the order parameter to the velocity. It is responsible for the localized shrinkage of the crack due to material motion.

This term is crucial to maintain the sharp form of the crack tip.

Continuum Field Description of Crack Propagation

Constrains imposed on function F

- The constraint imposed on $F(\rho, u_{ll})$ is that it must have one zero in interval $1 > \rho > 0$
- $F(\rho_c, u_{ll}) = 0 \qquad 1 > \rho_c > 0$
- $\partial_\rho F(\rho, u_{ll})\big|_{\rho=\rho_c} < 0$
- The simplest form of F satisfying this constraint is

$$F(\rho, u_{ll}) = 1 - (b - \mu u_{ll})\rho$$

Material constants related to such properties as crack toughness and strain to failure

Continuum Field Description of Crack Propagation

Constrains imposed on function f

- The specific form of this function is irrelevant
- One takes $f(\rho)=c\rho(1-\rho)$

  a dimensionless material constant

to ensure that f vanishes at $\rho = 0$ and $\rho = 1$

Continuum Field Description of Crack Propagation

Static solutions

The static one-dimensional equations read $\frac{\partial \rho u_{yy}}{\partial y} = 0$

$$\frac{\partial^2 \rho}{\partial y^2} - \rho(1-\rho)[1-(b-\mu u_{yy})\rho] = 0$$

With the fixed-grips boundary conditions (BC)

- $u_y(y=\pm L)=\pm L\delta$
- $\rho(y=\pm L)=1$
- $\partial_y(\rho=0)=0$

Continuum Field Description of Crack Propagation

Static solution

- **The width of the crack** opening d defined as

$$\rho(d/2) = 1/2$$

$$d = \sqrt{\frac{8}{b}} \ln\left[\frac{\sqrt{8b}}{\pi} L\left(\frac{2\mu\delta}{b-2} - 1\right)\right]$$

- The solution exists only if δ exceeds some critical value

The strain to failure $\delta_c \approx (b/2 - 1)/\mu$

- The logarithmic, instead of linear, dependence of crack opening on system size L is a shortcoming of the model resulting from an oversimplified dependence of the function F on u_{ll}

Continuum Field Description of Crack Propagation

- To study the ***dynamics of cracks***, one has to perform numerical simulations.
- Usually, one uses an explicit second order scheme.

Discretization methods :
finite difference
finite element method (FEM)

- The number of grid points used in simulation of the model discussed here -- up to **4000 x 800** grid points.

Continuum Field Description of Crack Propagation

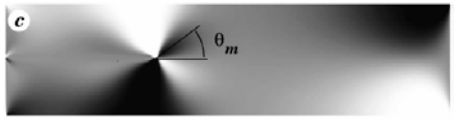
Results of the simulation

Quasistationary propagation

The crack produces the stress concentration near the tip, while the stress is relaxed behind the tip

Hydrostatic pressure
$p = -(\sigma_{xx} + \sigma_{yy})$

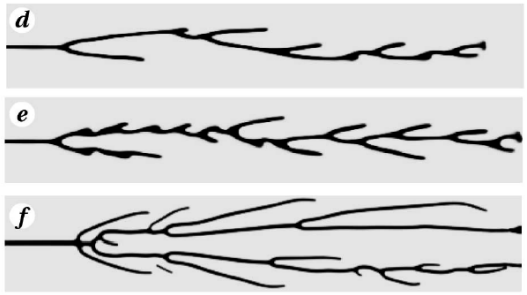
Shear σ_{xy}



Continuum Field Description of Crack Propagation

Results of the simulation -- *Instability of crack propagation*

Order parameter $\rho(x, y)$



propagation with fragmentation

Crystal Growth:

Continuum Methods

Growth science

- In recent times, the evolution processes have ultimately become a central object of scientific study in many fields.
- A vast variety of phenomena are studied by ***growth science***, ranging from
  - **the spread of a forest fire to**
  - **the sedimentation of sand on the bottom of a water basin**.
- These growth phenomena have been recently reviewed in beautiful articles and books
  - T. Halpin-Healy & Y.-C. Zhang, *Phys. Rep.* **254,** 215 (1995)
  - Evans, *Rev. Mod. Phys.* **65,** 1281 (1993)
  - A.L. Barab´asi & H. E. Stanley, *Fractal Concepts in Surface Growth* (Cambridge: Cambridge University Press, 1995)

Crystal growth and growth science

Crystal growth is special in that it was studied in detail, because of its practical importance, much before the present fashion

Hurle D T J (ed) *Handbook of Crystal Growth* (Amsterdam: North-Holland, 1993)

- Atomistic description of crystal growth

⟹ **Continuum models of crystal growth**

dependent on the physics of growth

Traditional concepts of crystal growth

Surface growth

- For stable growth the most widely considered geometry is that of a planar or quasi-planar surface, moving in the positive z-direction with (on average) constant velocity v.

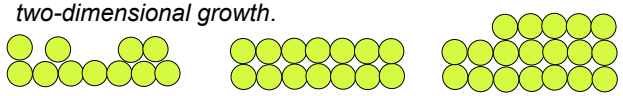
The chemical potential of the vapor μ

of the crystal μ_{eq}

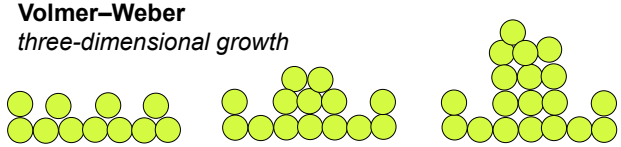
- **The driving force for crystal growth:** $\Delta\mu = \mu - \mu_{eq}$
- Two basic and related questions are:
  - what is the ***growth mode*** and
  - what is the ***growth kinetics***, i.e., how does the rate of growth G depends on the driving force

Growth modes

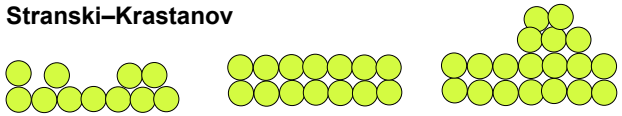
Frank–van der Merwe ***(layer-by-layer)*** *two-dimensional growth*.



Volmer–Weber *three-dimensional growth*



Stranski–Krastanov



Growth of rough surfaces

- Quantitatively, the surface roughness is described by the surface width w.
- Let us consider a surface in a d-dimensional space given by a single-valued function $h(\mathbf{x}; t)$ of a d'-dimensional ($d = d'+1$) substrate coordinate $\mathbf{x}$

$$w^2 = \langle N^{-1} \sum_i (h_i - \bar{h})^2 \rangle$$

The average height $\bar{h} = N^{-1} \sum_i h_i$ $\quad N = L^{d'}$

$h_i = h(x_i)$

is a linear size of the system,

Growth of rough surfaces – Stochastic differential equations

- The simplest time-dependent description of a stochastic surface is afforded by the ***Edwards–Wilkinson*** (EW) equation

Edwards S F and Wilkinson D R, *Proc. R. Soc.* A **381,** 17 (1982)

$$\frac{\partial h}{\partial t} = \nu \nabla^2 h + \eta$$

has the dimensions of a diffusion coefficient

a noise term

- The solutions of the EW equation give rise to a ***mean square height difference*** $g(x) = \langle [h(x) - h(0)]^2 \rangle$ behaving asymptotically as ln *r*

Growth of rough surfaces – Stochastic differential equations

- A non-linear perturbation of the EW equation is the ***Kardar–Parisi–Zhang (KPZ) equation***

Kardar M, Parisi G and Zhang Y, *Phys. Rev. Lett.* **56,** 889 (1986)

$$\frac{\partial h}{\partial t} = \nu \nabla^2 h + \lambda (\nabla h)^2 + \eta$$

- The KPZ equation generates surfaces whose roughness may be stronger than logarithmic, i.e. of *power-law* form.

Growth of rough surfaces – Stochastic differential equations

- If the EW equation is perturbed by a *periodic force* favoring the *integer levels* (i.e. if the crystal structure is taken into account) the ***Chui–Weeks*** (CW) equation is obtained

Chui S. and Weeks J., *Phys. Rev. Lett.* **40,** 733 (1978)

$$\frac{\partial h}{\partial t} = \nu \nabla^2 h + y_0 \sin 2\pi h + \eta$$

- and the surface tends to become *smoother.*
- Thus a surface obeying the CW equation either is smooth, or if it is rough cannot be more than logarithmically rough.

Growth of rough surfaces – Stochastic differential equations

An important class of equations are the *conserving* equations of the form $\frac{\partial h(\boldsymbol{x}, t)}{\partial t} = -\boldsymbol{\nabla} \cdot \boldsymbol{J}[\boldsymbol{\nabla} h(\boldsymbol{x}, t)] + \eta(\boldsymbol{x}, t)$

J is the surface current depending on the derivatives of *h* and possibly on *h* itself.

A linear diffusion equation is obtained for

$$\boldsymbol{J} = -K \, \boldsymbol{\nabla} \nabla^2 h(\boldsymbol{x}, t)$$

With the particular choice

$$\boldsymbol{J} = -K \, \boldsymbol{\nabla} \nabla^2 h(\boldsymbol{x}, t) + \lambda \, \boldsymbol{\nabla} (\nabla h)^2$$

where *J* is the gradient of the right-hand side of the KPZ equation, we obtain the so-called ***conserved KPZ equation***.

Thank you !