Faculty of Physics,
University of Warsaw

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Lecture

Modeling of Nanostructures and Materials

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Monte Carlo Methods

Monte Carlo Methods – Basics

- Hierarchy of theoretical approaches
- Monte Carlo vs. deterministic philosophy
- Stochastic processes
- Markov process
- Algorithms for Monte Carlo Simulations
- Metropolis Algorithm
- Example of Monte-Carlo calculations
- Simulation of epitaxial crystal growth – Kinetic Monte Carlo Method

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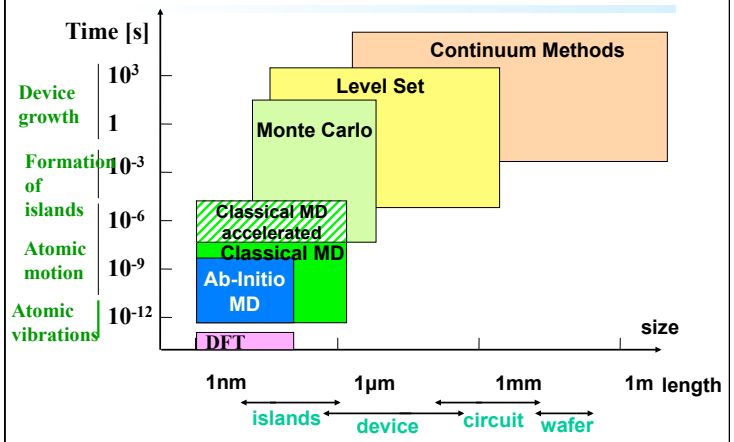
Hierarchy of Theoretical Approaches



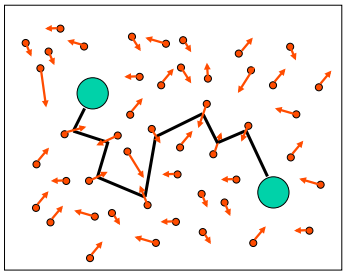
Basics of the Monte Carlo Method

- 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

Brownian Motion

A typical example of Monte Carlo method



The bigger colloidal particle (Brownian particle) moves randomly, colliding with small solvent particles.

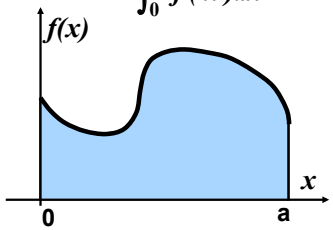
When one observes it through a microscope, one identifies the position (or velocity) of the Brownian particle only.

Applying coarse-graining procedure, the other degrees of freedom (e.g., the motion of small solvent particles) are removed and, finally they can be regarded as a **random force acting on the Brownian particle.**

Monte Carlo vs. Deterministic Philosophy

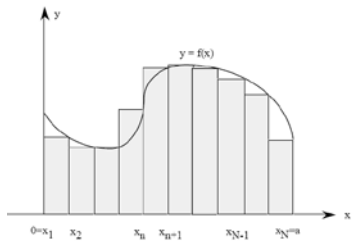
Problem:
evaluate an integral

$$I = \int_0^a f(x)dx$$



Clearly:
I **= area under the curve**

Deterministic (calculus based) approach

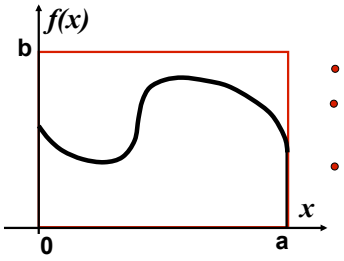


spatial grid: $x_n = \frac{n}{N}a \quad , \quad 0 \le n \le N$

$$I \approx \sum_{n=1}^{N} f(x_n)\Delta x_n = \frac{a}{N}\sum_{n=1}^{N} f\left(\frac{a}{N}n\right)$$

Monte Carlo vs. Deterministic Philosophy

Monte Carlo-Based Approach



Probabilistic interpretation

- Throw N random darts at the rectangle.
- M = the number of times the dart lands under the curve.
- P = probability that a random point lies under the curve

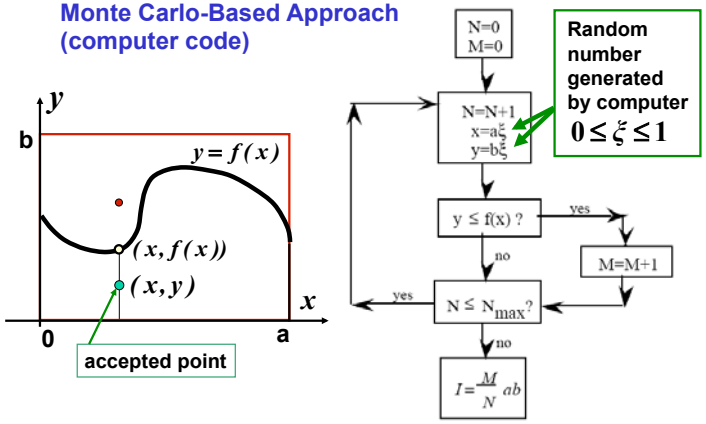
$$P = \frac{I}{ab} \approx \frac{M}{N}$$

- **No spatial grid, no discretization error**
- **Statistical error -** $\propto \frac{\sigma}{\sqrt{N}}$

$$I \approx \frac{M}{N}ab$$

Monte Carlo vs. Deterministic Philosophy

Monte Carlo-Based Approach (computer code)



Stochastic Processes – Dynamical Variables

A set of all variables that characterizes the internal state of a **dynamical system** – ***dynamical variables*** $\vec{q}$

Examples:

- **An assembly of N molecules in the gas phase**
  a set of atomic positions and momenta
  $(\vec{X}_1, \vec{X}_2, \ldots, \vec{X}_N)$ $(\vec{P}_1, \vec{P}_2, \ldots, \vec{P}_N)$
- **A system of weakly interacting harmonic oscillators**
  e.g., for studies of thermal motion of atoms in a solid
  A set of energies of the oscillators $(\varepsilon_1, \varepsilon_2, \mathrm{K}\ , \varepsilon_N)$
- **A magnetic spin system**
  A set of spin variables

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

Stochastic Processes – Dynamical Variables

Studies of the time evolution of the dynamic variables

- Suppose we have obtained successive data for the dynamical variables $\vec{q}_1, \vec{q}_2, \ldots, \vec{q}_L$
  by observing the system L times at different time steps $t_1, t_2, \ldots, t_L$
- If these successive data seem to change stochastically with time step, we may call this a ***stochastic process.***
- In the Monte Carlo methods which are used to the dynamics of a many-body system,
  - the time evolution is considered as a stochastic process,
  - the dynamical variables at each time step are updated by using ***random numbers.***
- A sample obtained in one simulation $\vec{q}_1, \vec{q}_2, \ldots, \vec{q}_L$

The real Monte Carlo - simulations repeated many times and analyzed using standards of statistical physics

Stochastic Processes – Distribution Function

- ***Transition probability*** that the system with a dynamic variable q_i at time t_i moves to the state between $q_j + \delta q_j$ and q_j at a later time t_j

$$\Phi(q_i,t_i \mid q_j,t_j)\delta q_j$$

- ***Distribution function of q*** - probability $p(q,t)$ that the system is in the state defined by q at time t

$$p(q,t) = \int dq_0\, p(q_0,t_0)\Phi(q_0,t_0 \mid q,t)$$

- **Transition probability should be normalized**

$$\int \Phi(q_i,t_i \mid q_j,t_j)\, dq_j = 1$$

for any state q_i at time $t_i < t_j$

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

- The transition probability $\Phi(q_0,t_0 \mid q_1,t_1;q,t)\delta q_1 \delta q$

q_0 at $t_0 \rightarrow (q_1, q_1+\delta q_1)$ at $t_1 \rightarrow (q, q+\delta q)$ at t

- $\Phi(q_0,t_0 \mid q_1,t_1;q,t) = \Phi(q_0,t_0 \mid q_1,t_1)\Phi(q_1,t_1 \mid q,t)$

- $\Phi(q_0,t_0 \mid q,t) = \int dq_1\, \Phi(q_0,t_0 \mid q_1,t_1)\Phi(q_1,t_1 \mid q,t)$

Chapman-Kolmogorov equation

- **The stochastic process satisfying these two equations is called in general *Markov process* or *Markov chain***

- The stochastic process depending on the history is called a "***non-Markov process***"

Markov Process

- By introducing a kind of random updating of the dynamical variable in compensation for neglecting the microscopic details of the real system, one may arrive at a Markov process.

- Replacement of the neglected details with a random updating process is identical to the introduction of a ***heat bath***

- **Detailed motion of atoms on the microscopic scale can be seen as heat on the macroscopic scale.**

- The form and amount of the updating probability are directly related to the temperature of the equilibrium state.

Markov Process

Time evolution of a system obeying a Markov Process

new variables $\Gamma(q)$ and $W(q_1;q)$

- **Transition amplitude**

$$\Phi(q_1,t\,|\,q,t+\Delta t)=[1-\Gamma(q)]\delta(q-q_1)+W(q_1;q)+O(\Delta t^2)$$

- **Change of the Transition amplitude**

$$\Phi(q_0,t_0\,|\,q,t+\Delta t)-\Phi(q_0,t_0\,|\,q,t)=$$
$$=\int dq_1\ \Phi(q_0,t_0\,|\,q_1,t)W(q_1;q)-\Phi(q_0,t_0\,|\,q,t)\Gamma(q)+O(\Delta t^2)$$

- **Change of the distribution function**

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

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) $W(q_1;q)=\frac{v}{2d}\sum_i^{2d}\delta(q-q_1+a\vec{e}_i)$

v -- diffusion velocity

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

a -- lattice constant

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

$D=\frac{va^2}{2d\Delta t}$ 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**

Algoritms for Monte Carlo Simulations

Simple Sampling Technique

Handling a thermodynamic ensemble based on a stochastic model by the simple sampling technique

$$\bar{A} \approx \frac{\sum_{l=1}^{N} A(q_l) exp[-E(q)/k_B T]}{\sum_{l=1}^{N} exp[-E(q)/k_B T]}$$

Note, all samples *l* are selected here completely randomly, irrespective of the Boltzmann weight

Now assume $A(q_l) = E(q_l)$

The relative width of the energy fluctuations decreases with the number of particles N, in the system

$$\frac{< E^2 > - < E >^2}{< E^2 >} \propto \frac{1}{N}$$

Algoritms for Monte Carlo Simulations

Simple Sampling Technique for thermodynamic ensamble

The one-particle energy distribution function $p(\varepsilon)$ shows a peak of height $\sqrt{N}$ and width $1/\sqrt{N}$ around its expectation value $< E > / N$

$$p(\varepsilon) \propto exp\left[-\frac{(\varepsilon - < E > / N)^2}{2Ck_B T^2} N \right]$$

Note, Gaussian form for large N

Probability to generate states with one particle energy close to $< E > / N$ becomes exponentially small for large N

Simple Sampling Algorithm becomes very inefficient

Algoritms for Monte Carlo Simulations
Importance Sampling Technique

- **Simple Sampling Technique** offers an efficient algorithm to evaluate the average of a physical quantity $A(q)$, only if the distribution function $p(q)$ resembles a more or less uniform distribution
- In contrast, if the distribution function has a big value only at an isolated point, it becomes more efficient to choose the integration points with the same probability as that given by the distribution function $p(q)$.
- Such a biased sampling with a probabilistic weight is called ***Importance Sampling Technique***

  N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A. M. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).

  - **Commonly called Metropolis Algorithm**

Algoritms for Monte Carlo Simulations
Importance Sampling Technique

- If the sample integration points are chosen with the same probability as the distribution function $p(q)$, the expression for the expectation value can be replaced simply by $\bar{A} = \frac{1}{N}\sum_{l=1}^{N} A(q_l)$
- **Metropolis et al.** considered a Markov process that generates a descendant sample l' from the present sample l according to the transition rate $W(q_l, q_{l'})$

  They showed that by suitable choice of the transition rate, it is possible to bring the distribution of the dynamic variable to the expected (prescribed) distribution $p(q)$ in the limit $N \to \infty$

Algoritms for Monte Carlo Simulations
Importance Sampling Technique

- **Markov chain**

  We consider one particle in the multidimensional space of the dynamic variable q and move it step by step according to random numbers. $q \to q'$
- **The movement obeys following rule**
  - Calculate the value of the distribution function $p(q')$
  - Compare $p(q')$ to the present value of the distribution function $p(q)$
  - *If* $p(q') > p(q)$ **move the particle to the new position**
  - *If* $p(q') < p(q)$ generate random number $\xi \in [0,1]$
  - *If* $\xi < \frac{p(q')}{p(q)}$ **move the particle to the new position**
  - *If* $\xi \geq \frac{p(q')}{p(q)}$ **leave the particle at the same position**

Algoritms for Monte Carlo Simulations
Importance Sampling Technique

- In IST one updates the particle position with the probability min[x,1] $x = \frac{p(q')}{p(q)}$
- **After repeating this process enough times, the distribution of this random walker approaches** $p(q)$

Algoritms for Monte Carlo Simulations
Importance Sampling Technique

Back to the specific problem of the thermodynamic ensembles

- We assume that the samples are chosen with the same probability as the distribution function $p(q_l)$

$$\bar{A} \approx \frac{\sum_{l=1}^{N} A(q_l)\exp[-E(q)/k_BT]/p(q_l)}{\sum_{l=1}^{N} \exp[-E(q)/k_BT]/p(q_l)}$$

- **How to choose the distribution function $p(q_l)$?**
- **The simplest and most natural choice is the Boltzmann distribution $p(q_l) \propto \exp[-E(q)/k_BT]$**

Algoritms for Monte Carlo Simulations
Importance Sampling Technique

- **Using Metropolis's idea of importance sampling, one may bring the distribution function $p(q_l)$ close to the thermal-equilibrium distribution**

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

- **A sufficient condition to achieve the equilibrium distribution is to impose**
  the principle of detailed balance

$$p^{eq}(q_l)W(q_l,q_{l'}) = p^{eq}(q_{l'})W(q_{l'},q_l)$$

However, the principle of detailed balance does not uniquely determine the transition rate $W(q_l,q_{l'})$

Algoritms for Monte Carlo Simulations
Importance Sampling Technique

Two often used choices of transition rate

- **Heat bath method (Glauber algorithm)**

  R. J. Glauber, J. Math. Phys. **4,** 294 (1963)

$$W(q_l,q_{l'}) = \frac{1}{\tau}\left(1 - \tanh\left(\frac{\delta E}{2k_BT}\right)\right) = \frac{1}{\tau}\frac{\exp(-\delta E/k_BT)}{[1+\exp(-\delta E/k_BT)]}$$

$$\delta E = E(q_{l'}) - E(q_l)$$

- **Metropolis Algorithm**

$$W(q_l,q_{l'}) = \begin{cases} \frac{1}{\tau}\exp(-\delta E/k_BT) & \delta E > 0 \\ \frac{1}{\tau} & \text{otherwise} \end{cases}$$

Metropolis Monte Carlo Simulation

Standard, very important sampling technique to realize the canonical ensemble

By using random numbers, produce a new state from the present one

↓

Calculate the energy difference δE of the new state relative to the present one

↓

If $\delta E \le 0$, update to the new state.

If $\delta E > 0$, then generate a random number $\eta \in [0,1]$, and

if $\exp(-\delta E/k_BT) > \eta$

update to the new state

else

leave the state as it is.

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

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

Monte Carlo Simulations – Systems of Classical Particles

A system of N classical interacting particles

- **Hamiltonian**

$$H = \sum_{I=1}^{N} \frac{\hat{\vec{p}}_I^{\,2}}{2M_I} + U(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$$

- **Partition function**

$$Z = \frac{1}{h^{3N} N!} \int exp[-H / k_B T] \prod_{I=1}^{N} d\vec{r}_I d\vec{p}_I = \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} Q(T,V)$$

$$Q(T,V) = \frac{1}{N!} \int d\vec{r}_1 \ldots d\vec{r}_N \, exp[-U(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) / k_B T]$$

- ***The distribution function*** for the coordinates of the N particles

$$p(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) = \frac{1}{N! Q(T,V)} exp[-U(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) / k_B T]$$

Monte Carlo Simulations – Systems of Classical Particles

Procedure

- One chooses one particle among N particles randomly (or one may select them one by one from 1 to N)
- Move the position $\vec{r}_i$ of the selected particle to the new position $\vec{r}_i + \Delta\vec{r}_i$ $\qquad \vec{r}_i \rightarrow \vec{r}_i + \Delta\vec{r}$

  $\Delta\vec{r}_i$: **a random vector**
- ***Metropolis algorithm***
  Check whether the new configuration is energetically more stable than the original configuration
  - If ***YES*** ⇒ **allow this movement**
  - If ***NO*** ⇒ **further procedure**

Monte Carlo Simulations – Systems of Classical Particles

Procedure (ctn.)

- Calculate the ratio of the distribution function before and after this movement $\dfrac{p(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_i + \Delta\vec{r}_i, \ldots \vec{r}_N)}{p(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_i, \ldots \vec{r}_N)}$
- **Allow this movement** if this ratio is larger than a uniform random number $\in [0,1]$

- The random vector $\Delta\vec{r}$ is chosen so that the allowance rate of the movement is roughly several tens of per cent
- **The Monte Carlo procedure is usually performed with a fixed particle number N, temperature T, and volume V**

NTV ensemble

Monte Carlo Simulations – Systems of Classical Particles

Form of potential U ?

- **The simplest one - "Hard sphere system"**

  liquid – solid phase transition

  B. J. Alder & T. E. Wainwright, J. Chem. Phys. **27**, 1208 (1957)

  Molecular dynamics

  W.W. Wood & J.D. Jacobson, J. Chem. Phys. **27,** 1207 (1957)

  Monte Carlo Simulations

- **Soft-core, pair potentials** $V(r)=\frac{1}{\varepsilon}\left(\frac{\sigma}{r}\right)^n$
- **Lennard-Jones potential** $V_{ij}(R_{ij})=U_0\left[\left(\frac{R_0}{R_{ij}}\right)^{12}-2\left(\frac{R_0}{R_{ij}}\right)^{6}\right]$

Monte Carlo Simulations – Systems of Classical Particles

System of charged particles ?

- **Long-range Coulomb potential** $V(r)=\frac{1}{\varepsilon}\left(\frac{\sigma}{r}\right)$
- ***One should pay attention***
- Usually, charge neutrality should be preserved
- Periodic boundary conditions usually imposed

  ➡ Even if the number of N of particles is small, one has to evaluate an infinite sum of Coulomb interact.

  - The Ewald sum

  ➡ **Fast multipole method**

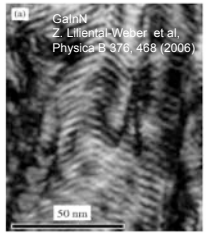
Monte Carlo Studies of Ordering in InGaN, AlInN, and AlGaN ternary alloys

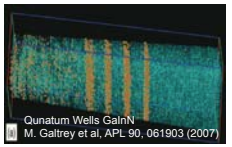
M. Lopuszynski & J. A. Majewski

*Phys. Rev. B **85***, 035211 (2012)

Ordering in Nitrides

- Various ordering patterns reported in experiments
  - Clustering
  - Compositional modulation (LRO)
  - Uniform alloy, maybe with some SRO
- Ordering is important
  - LRO/SRO influences band structure
  - Indium clusters are believed to impact luminescence
  - Many modeling methods (e.g. VCA, CPA, SQS) assumes random uncorrelated alloy (SRO=0, LRO=0). Is that right?





Indium Clustering Controversy

CLUSTERING	NO CLUSTERING
• HRTEM pictures show ordering • It is possible to minimize radiative damage	• This is an artifact due to radiative damage of the sample, 3DAP does not show it
• Thermodynamics predicts phase separation and forbids uniform alloys	• It depends on the employed model, inclusion of strains etc. • Epitaxial methods are at least partially non-equilibrium
• Clustering explains high luminescence	• Other mechanisms could also explain it
• ...	

Three thermodynamic states for semiconductor alloys $A_xB_{1-x}N$

- **Bulk-incoherent thermodynamics**
  - thick film (> h_c) without lattice coherence (binary alloys AN & BN have different lattice constants)
  - phase separation AN + BN
  - in real systems dislocations & defects
- **Bulk-coherent thermodynamics**
  thick film (> h_c) with lattice coherence
- **Substrate-coherent epitaxial thermodynamics**
  thin film (< h_c)

THIS example: cubic GaInN, AlInN, AlGaN

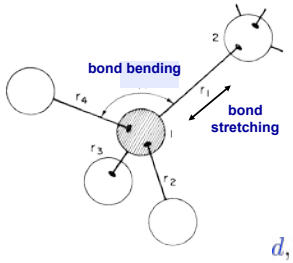
Computational Approach

- Keating Model
- Monte Carlo Metropolis Method with cationic exchange and atomic shifts
- Cubic supercell with periodic boundary cond. (typical cell with 1728 atoms)
- Lattice coherent thermodynamics

  Chan, Liu & Zunger PRB 82 045112 (2010)

Multibody Potential - Keating VFF

$$V = \sum_i \sum_{j \in NN(i)} \frac{3\alpha}{8d^2} \left(\Delta R_{ij}^2 - d^2\right)^2$$



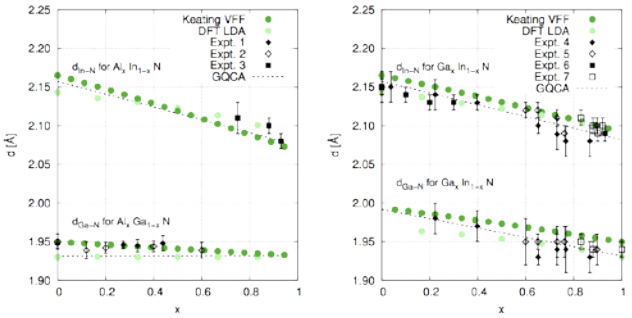
$V^{(2)}$ - bond stretching term

$$+ \sum_i \sum_{\substack{j,k \in NN(i) \\ j \neq k}} \frac{3\beta}{16d^2} \left(\Delta R_{ij} \cdot \Delta R_{ik} + \frac{d^2}{3}\right)^2$$

$V^{(3)}$ - bond bending term

d, α, β - **interaction parameters, determined on the basis of DFT calculations**

Bond Length - Theory vs Experiment

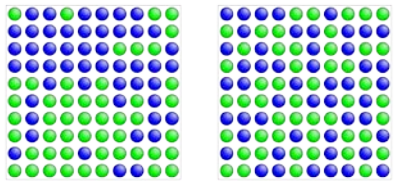


Good agreement with experimental data

How to Quantify Ordering?

Short Range Order

$\Gamma_{AB}^{(1)} = 0.3$



$\Gamma_{AB}^{(1)} = -0.3$

- Warren-Cowley Short Range Order (SRO) parameter:

$$\Gamma_{\mathrm{AB}}^{(i)} = 1 - \frac{P_{\mathrm{AB}}^{(i)}}{c_B}$$

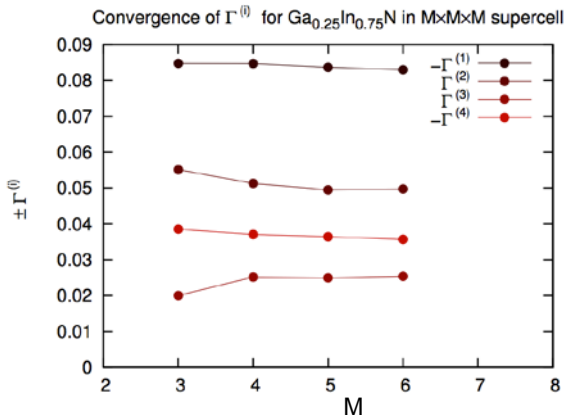
Probability to find B as i^{th} nearest neighbor of A

Concentration of B

- Interpretetation:

$\Gamma_{AB} > 0$ - B avoids A
$\Gamma_{AB} < 0$ - B likes A
$\Gamma_{AB} = 0$ - A neutral for B

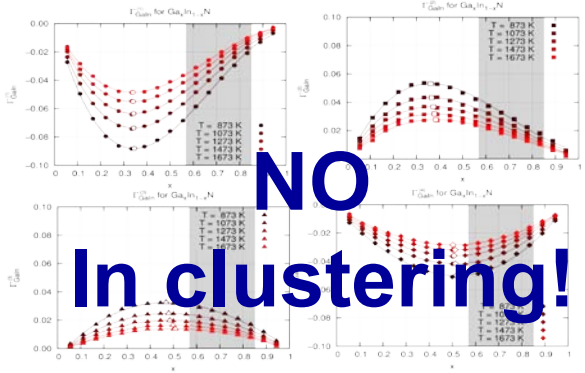
Convergence of $\Gamma^{(i)}$ With Cell Size



RESULTS:
Bulk-coherent structures

Results for Bulk Ternaries - GaInN

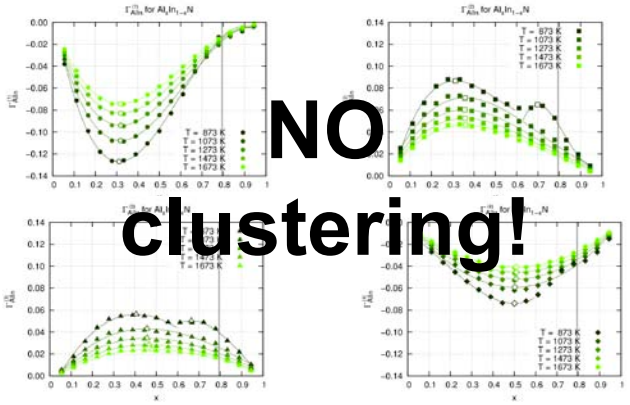
- GaInN - exhibits considerable SRO, no LRO



NO In clustering!

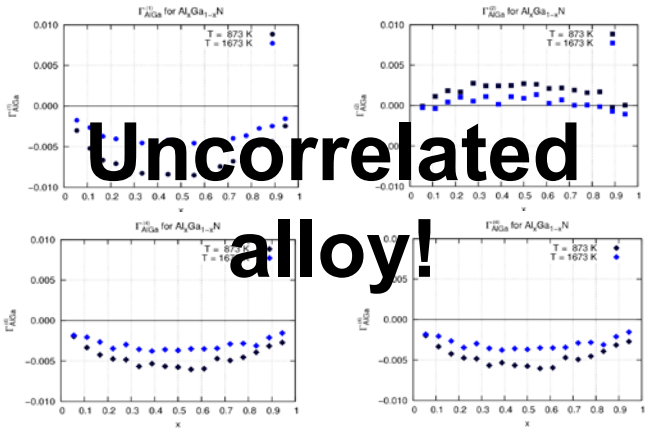
Results for Bulk AlInN

AlInN (as GaInN) **- exhibits considerable SRO, no LRO**



NO clustering!

Results For Bulk AlGaN



Uncorrelated alloy!

Kinetic Monte Carlo Methods

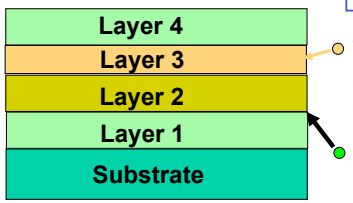
Kinetic Monte Carlo Simulations – An approach to perform epitaxial growth simulations

- ***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)



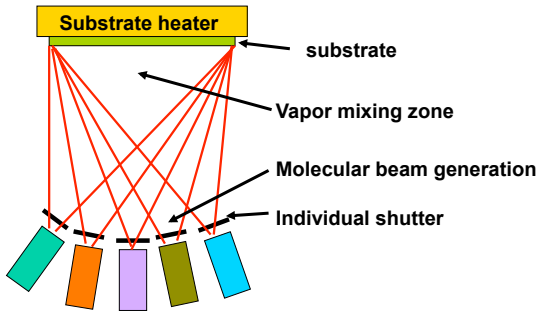
To employ quantum effects some of these structures are only a few atomic layers thick.

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

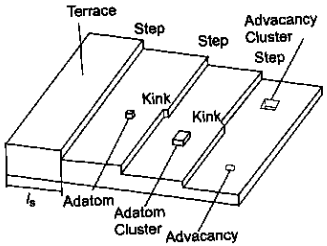


Effusion cells for constituent elements and dopants

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

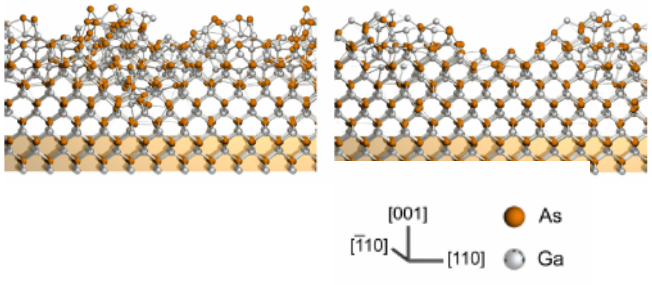
- In MD simulations as input no *a priori* information is needed
- They provide detailed insight into microscopic processes of deposition.
- Due to limitations in computational power, ***MD*** method is mostly restricted to very short simulation ***times of the order of picoseconds*** and ***small simulation 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

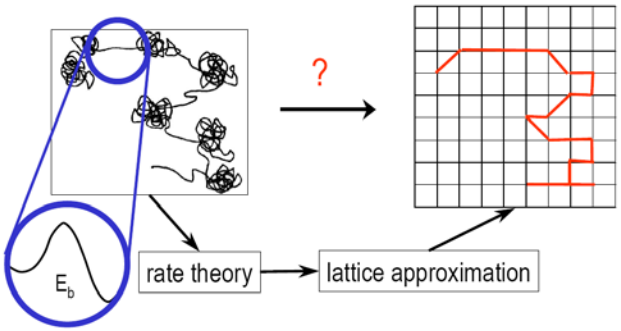
D. A. Murdick et al.

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**

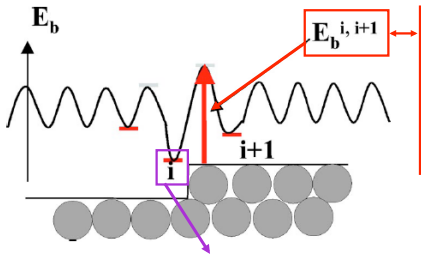
  Realistic means here that the surface has various structural features such as surface steps, kinks, and facets.

- **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

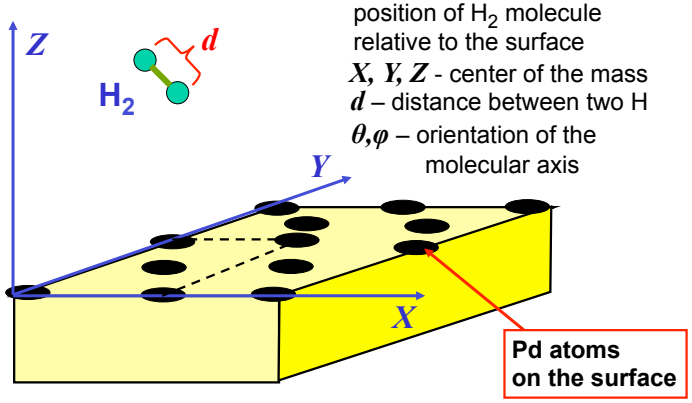


The energy barrier that one ***adatom*** has to overcome to hop from site i to site $i+1$.

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

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



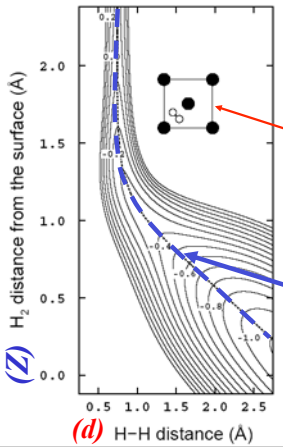
6 coordinates determines position of H_2 molecule relative to the surface

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

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

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

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

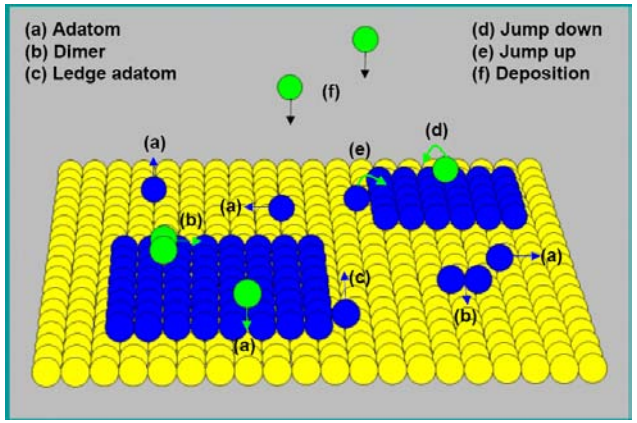
$P_n(t)$ - the probability of finding the system at time *t* in configuration *n*,

$w_{n' \to n}$ - 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

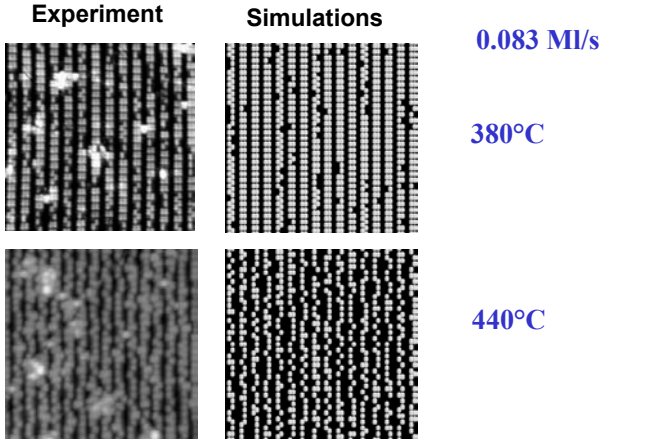
With increasing growth temperature KMC becomes more expensive

Why?

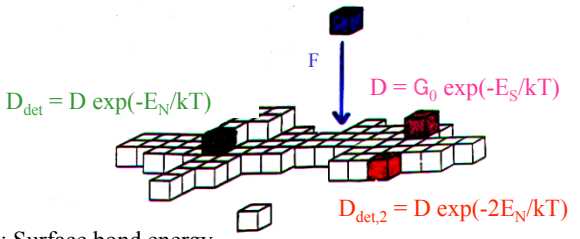
- The transition probability increases exponentially with temperature T
- The transition probability is inversely proportional to the time step

⇒ **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

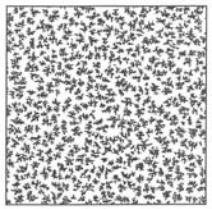


E_S: Surface bond energy
E_N: Nearest neighbor bond energy
G_0: Prefactor $[O(10^{13} s^{-1})]$

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

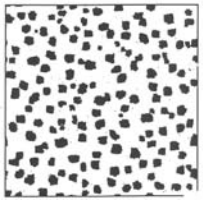
KMC Simulations: Effect of Nearest Neighbor Bond Energy E_N

KMC Simulations



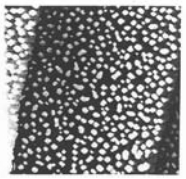
Large E_N:
Irreversible Growth

Small E_N:
Compact Islands



Experimental Data

Au/Ru(100)



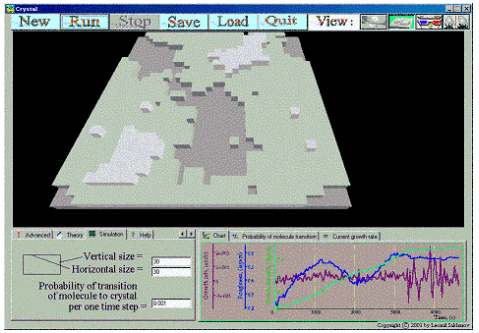
Ni/Ni(100)

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.

Thank you !