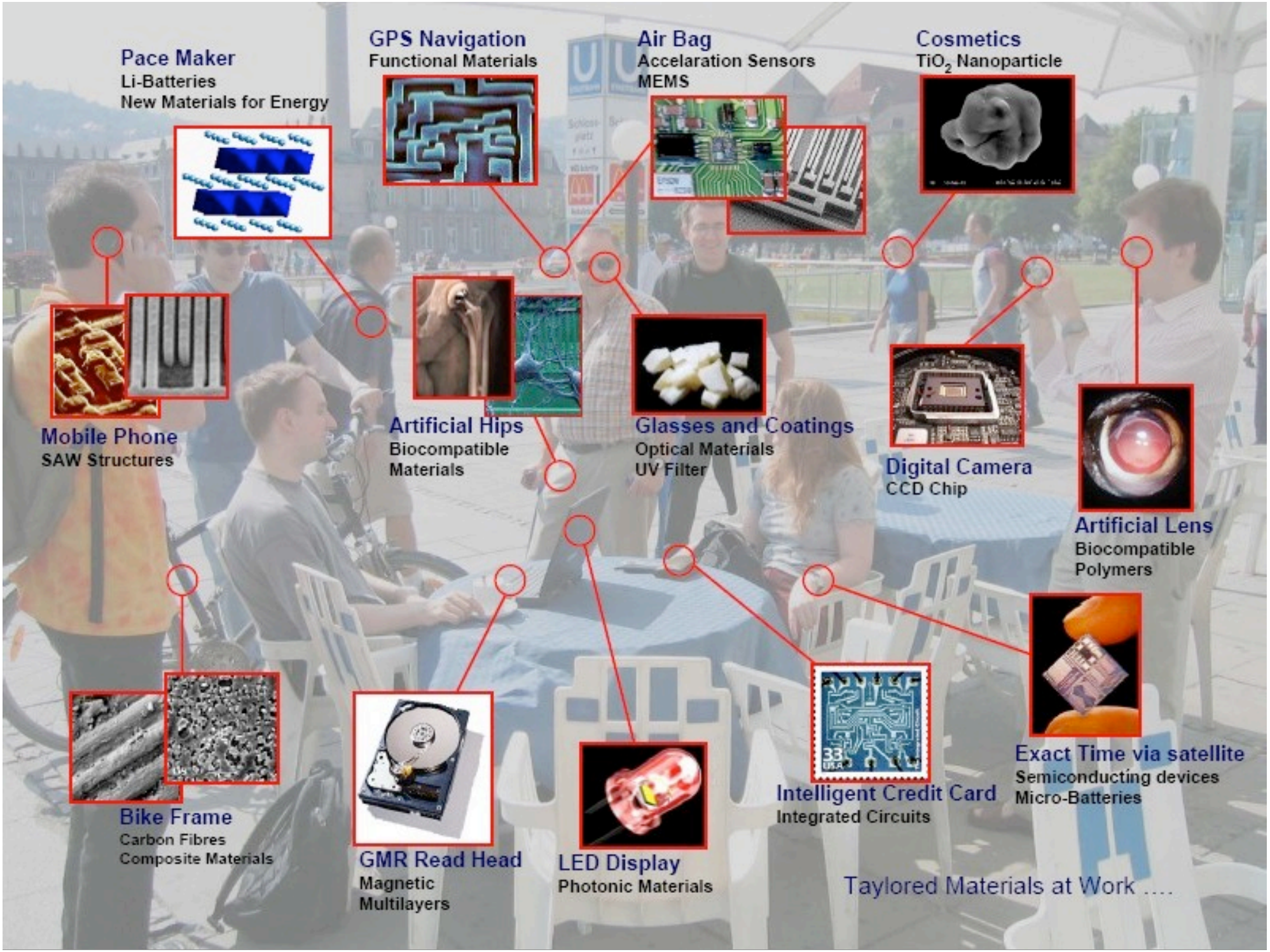
Computación en Materia Condensada

Pablo Ordejón
Theory and Simulation Group


On a typical day in Stuttgart .....
Courtesy of Prof. Helmut Dosch
Max Planck Institute for Metal Research
Stuttgart (Germany)


Pace Maker
Li-Batteries
New Materials for Energy
GPS Navigation
Functional Materials
Air Bag
Accelaration Sensors
MEMS
Cosmetics
TiO_2 Nanoparticle
Mobile Phone
SAW Structures
Artificial Hips
Biocompatible
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Glasses and Coatings
Optical Materials
UV Filter
Digital Camera
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Artificial Lens
Biocompatible
Polymers
Bike Frame
Carbon Fibres
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GMR Read Head
Magnetic
Multilayers
LED Display
Photonic Materials
Intelligent Credit Card
Integrated Circuits
Exact Time via satellite
Semiconducting devices
Micro-Batteries
Taylored Materials at Work ....

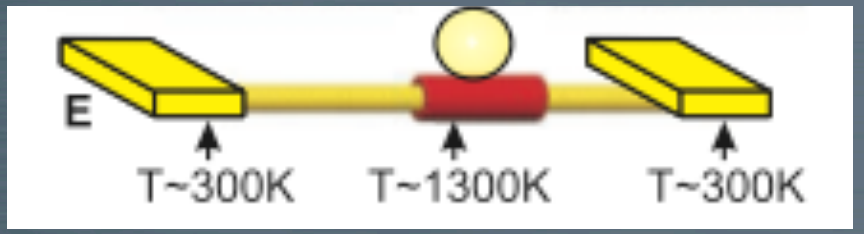
SIMULATION AND EXPERIMENT …
… IN NANOSCIENCE

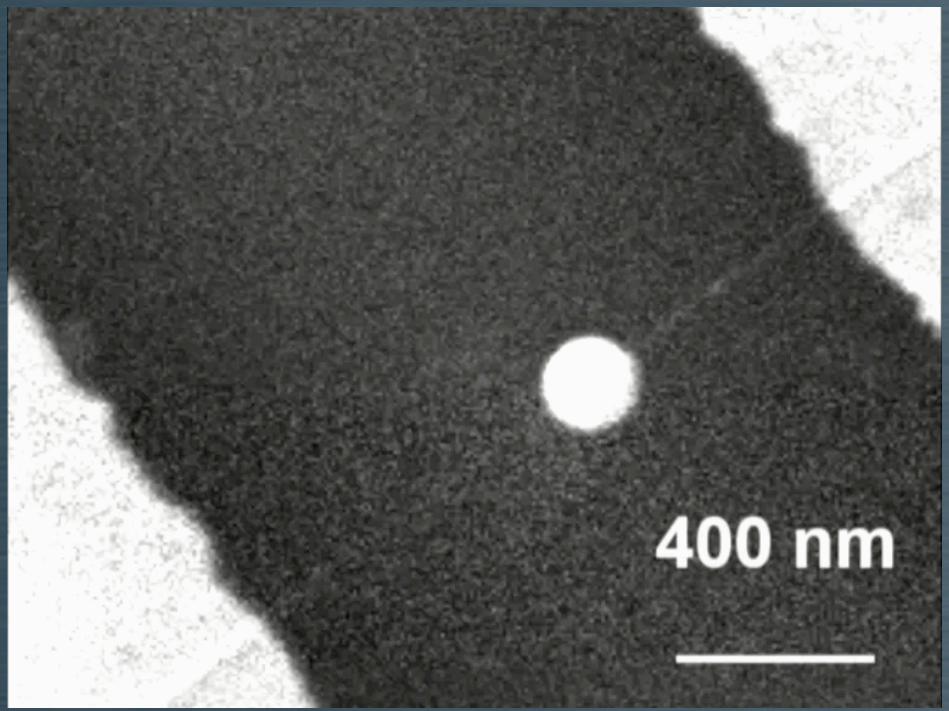
CIN2

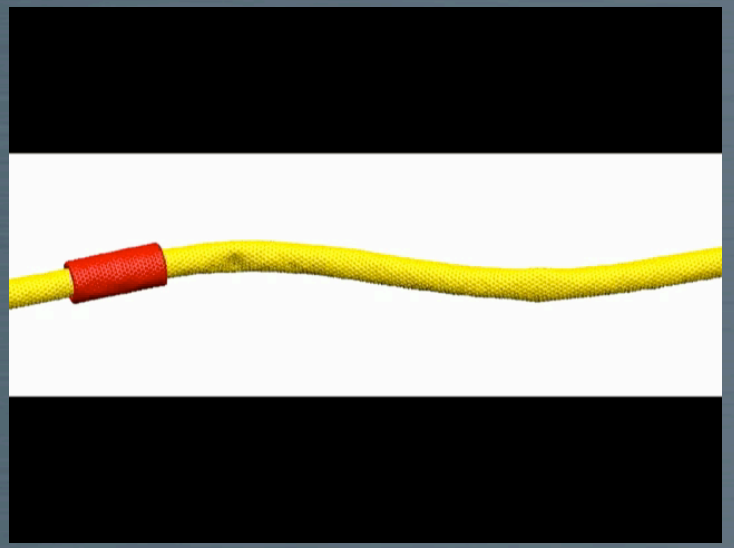
Motion of nano-objects driven by thermal gradients

Barreiro, Rurali, Hernandez, Moser, Pichler, Forro, and Bachtold

Science **320**, 775 (2008)







COMPUTER SIMULATIONS

Why do computer simulations? (instead of good-old ‘pen and paper’ theory)?

- Solve complex (i.e., realistic) models without approximations

The advantages of Simulations (the “virtual lab”)

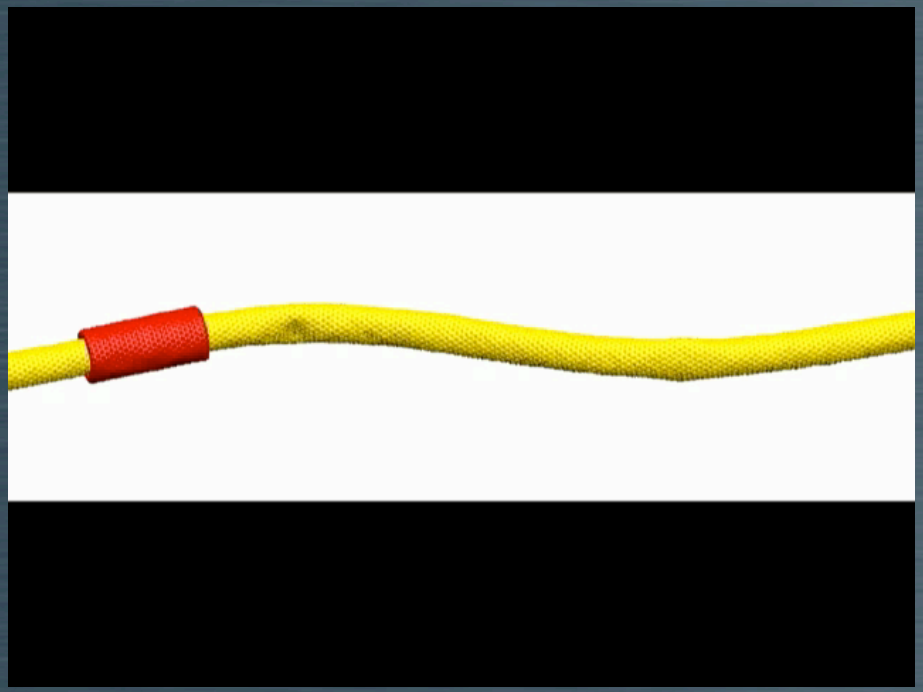
- Basic understanding
- Focus on specific details
- Systems and conditions not feasible in experiments
- Specify external conditions

These give us:

- Predictive power
- Aid in the interpretation of experiments

WHAT IS A SIMULATION?

Simulation in condensed matter: Study the way in which the "blocks" that build matter interact with one another and with the environment, and determine the internal structure, the dynamic processes and the response to external factors (pressure, temperature, radiation, etc…).



1. A **model of the interactions** between the "blocks" that build the material.

   For instance: interatomic interactions in atomistic models.

2. A **simulation algorithm**: the numerical solution to the equations that describe the model.

3. A set of **tools for the analysis** of the results of the simulation.

“Complexity” of a Simulation

The relation between computing time T (CPU)
and degrees of freedom N (number of atoms, electrons, length…)
(either due to the model or to the solution algorithm)

$T \propto O(N)$	in the best (simplest) cases - linear scaling (classical force fields)
$T \propto O(N^3)$	quantum mechanics - DFT (Matrix diagonalisation and inversion)
$T \propto e^N$ (or worse!)	complex problems (Quantum chemistry; multiple minima problems, etc)

Estimate of accessible time and size scales

- Supercomputer with performance: F Flops (floating point operations per second)
- One week of CPU of the whole computer: $T_{CPU} \sim 6 \times 10^5$ seconds
- Number of operations in one week: $N_{ops} \sim 6 \times 10^5 \times F$
- Operations in a simulation: $\#ops \propto C \times (N_{at})^s \times n_t$
  (Typicall, C ~ 10^3 --10^6 floating point operation per MD step)
- $N_{at} \propto$ Volume $\propto L^D$ (L = typical length scale, in units of atomic distances)

  D = dimension of the system (1,2,3).
- Time (n_t) scales as L (for information to propagate across the system) $n_t \sim 100\ L$

$$N_{at} \sim F^{D/(sD+1)}$$

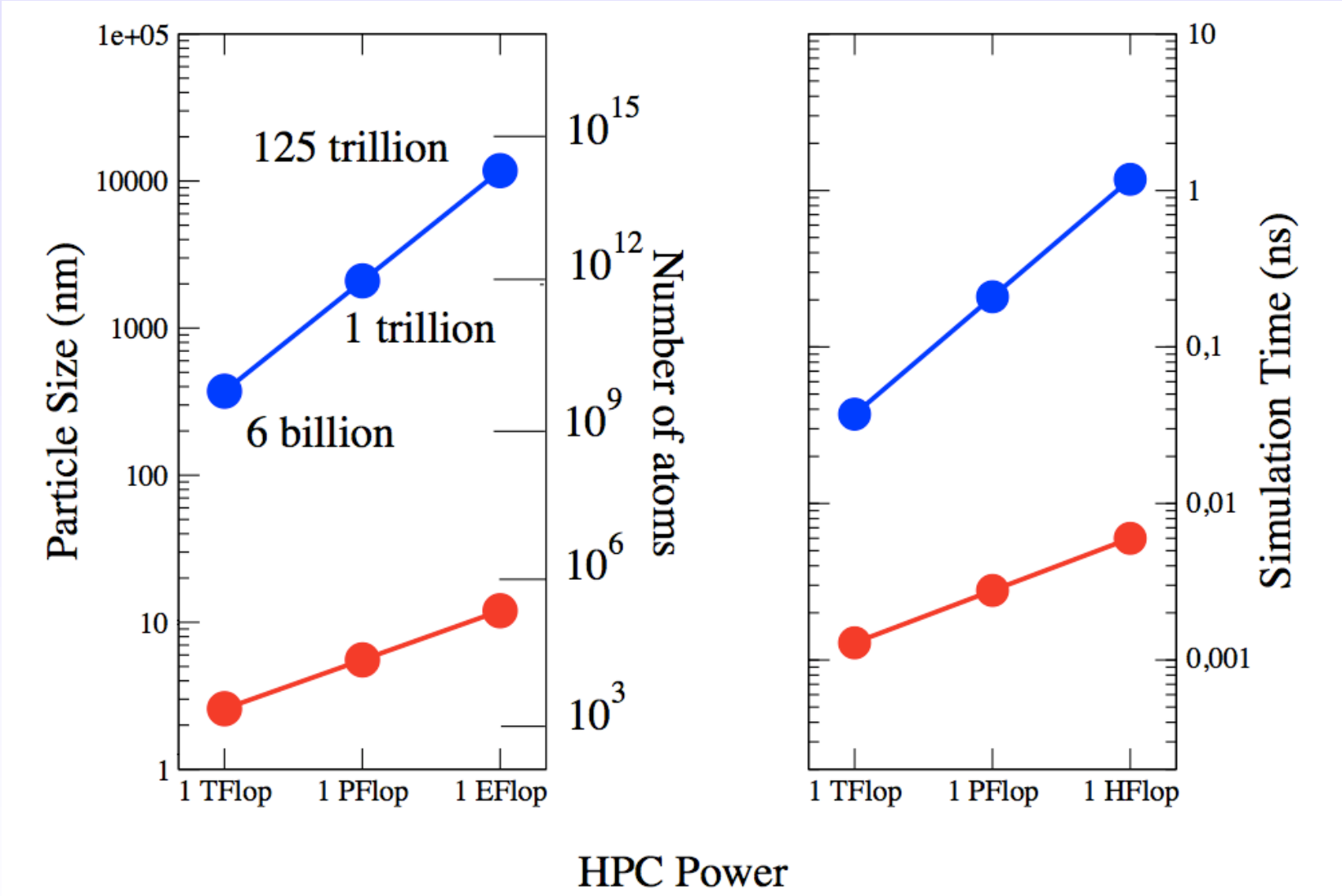
$$n_t \sim L \sim F^{1/(sD+1)}$$

For D=3:

s=1: $N_{at} \sim F^{3/4}$ $n_t \sim L \sim F^{1/4}$

s=3: $N_{at} \sim F^{3/10}$ $n_t \sim L \sim F^{1/10}$

Example in 3D system
(one week of full usage)



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TRILLION-ATOM MOLECULAR DYNAMICS BECOMES A REALITY

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By utilizing the molecular dynamics code *SPaSM* on Livermore's BlueGene/L architecture, consisting of 212 992 IBM PowerPC440 700 MHz processors, a molecular dynamics simulation was run with one trillion atoms. To demonstrate the practicality and future potential of such ultra large-scale simulations, the onset of the mechanical shear instability occurring in a system of Lennard-Jones particles arranged in a simple cubic lattice was simulated. The evolution of the instability was analyzed on-the-fly using the in-house developed massively parallel graphical object-rendering code *MD_render*.

Keywords: Molecular dynamics; BlueGene/L; high performance computing; SPaSM; large-scale; trillion-atom; visualization.

MODELS :

*"The general theory of **quantum mechanics** is now almost complete. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble."*

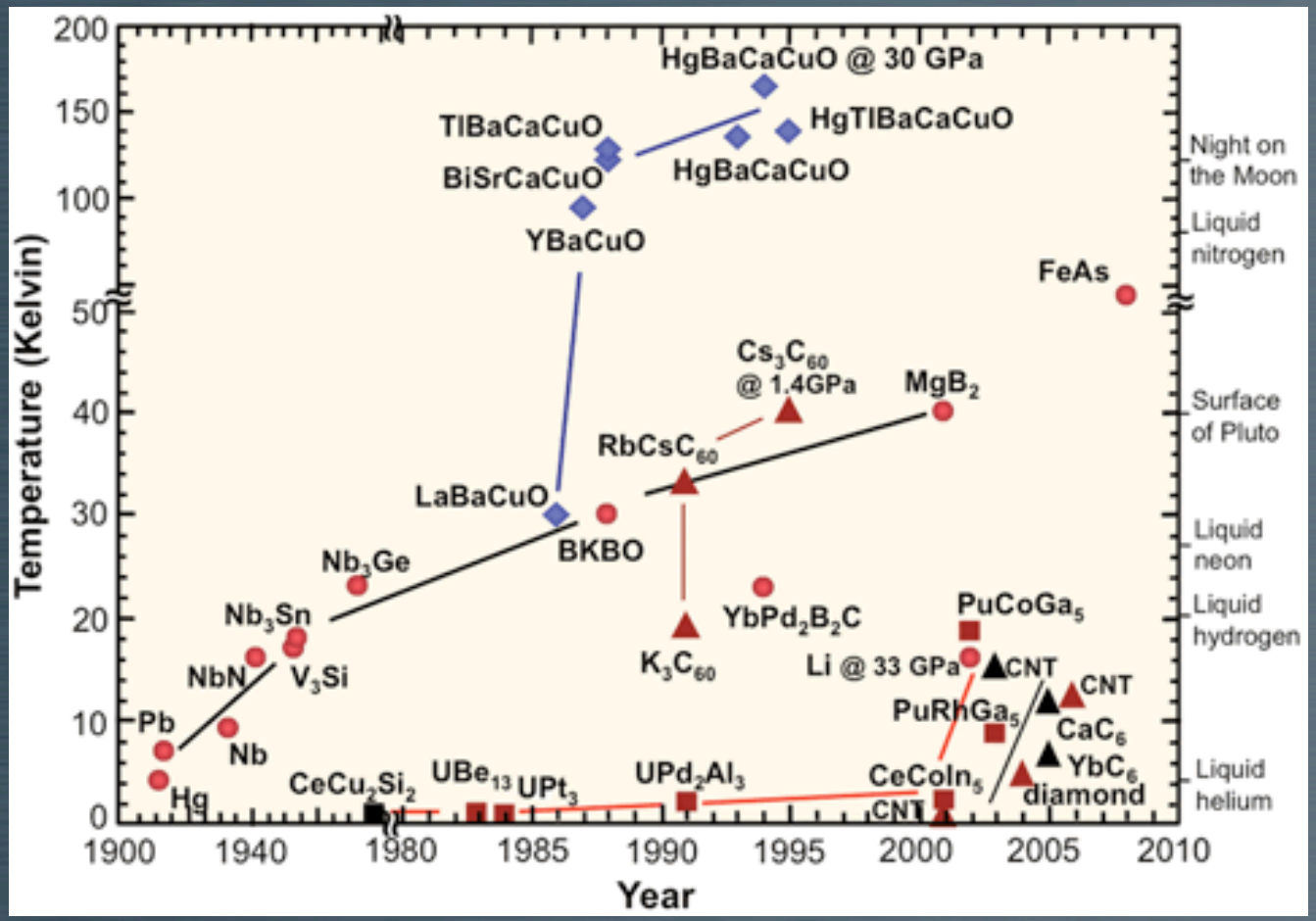
Dirac, 1929

$$i\hbar \frac{d\Psi(\{\mathbf{r}_i, \mathbf{R}_I\}; t)}{dt} = \hat{H}\Psi(\{\mathbf{r}_i, \mathbf{R}_I\}; t)$$

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + V(\{\mathbf{r}_i, \mathbf{R}_I\})$$

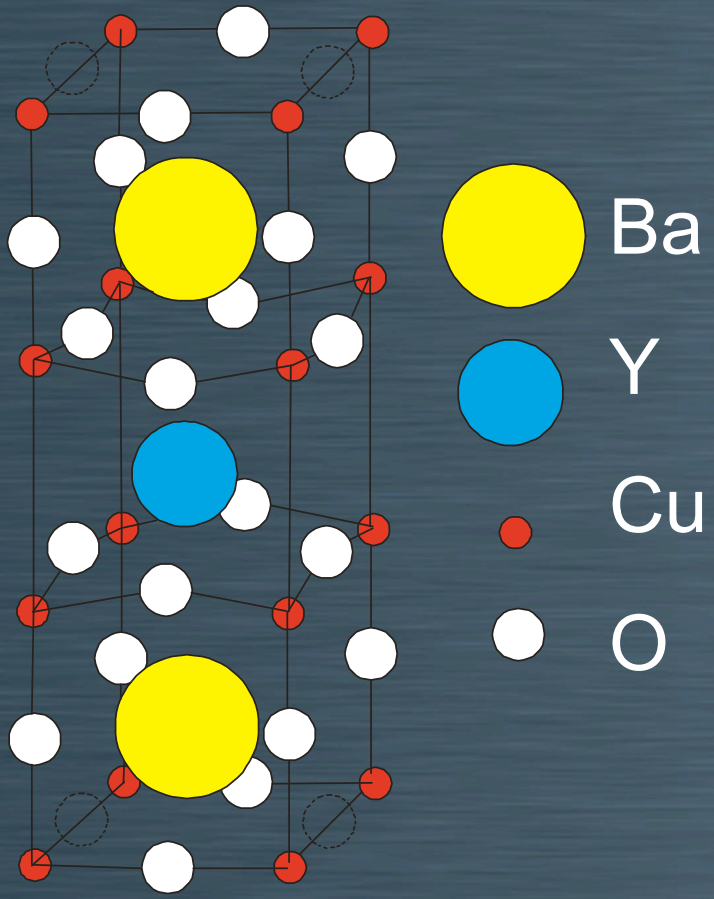
In practice, this can only be done for a small set of problems. For most of the cases, we need to look for the relevant physics and derive appropriate models which can be solved.
(NOTE: Quantum Chemistry is devoted to solving these eqs.!)

MODELS:
High-Tc SUPERCONDUCTORS



Wikipedia High-Tc Superconductivity

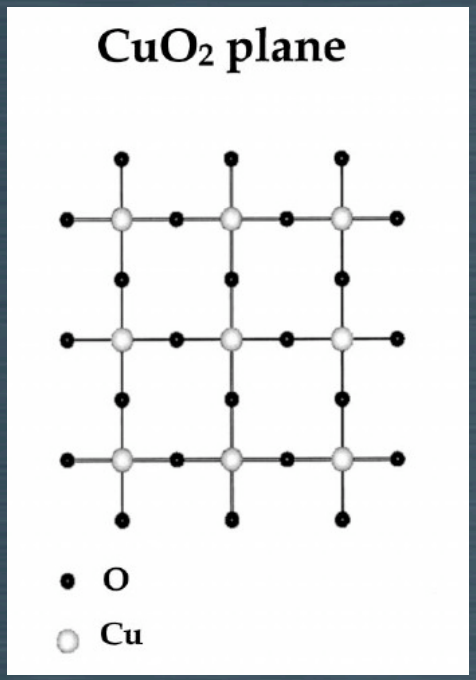
High-Tc SUPERCONDUCTORS

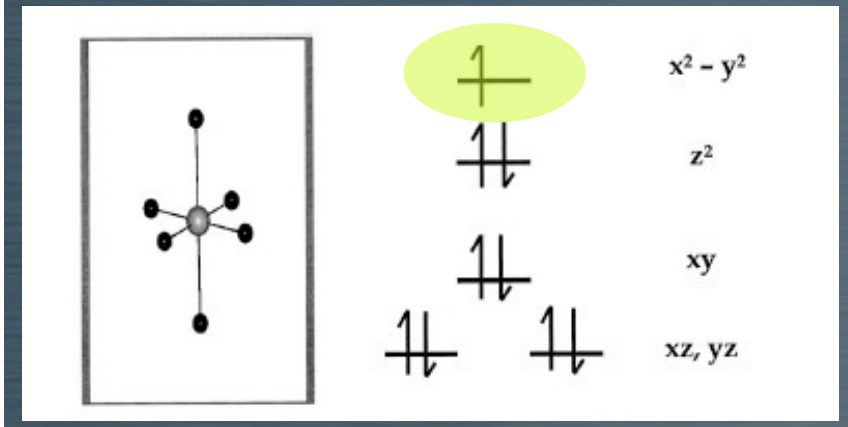


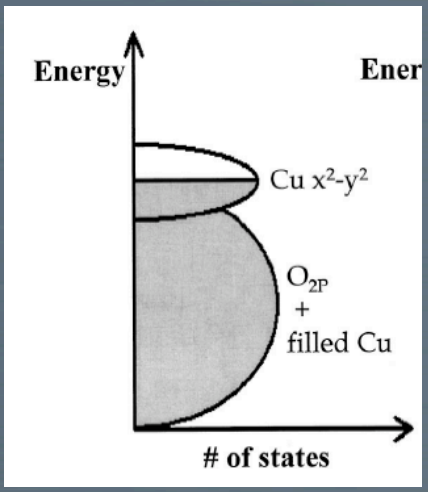
$YBa_2Cu_3O_6$

- Bednorz y Müller (1986): 30 K
  La-Ba-Cu-O pervskite
- Univ. Alabama (1987): 92 K
  Y-Ba-Cu-O
- Record actual: alrededor de 140 K
- Perovskitas con planos CuO_2
- ‘Doping’: Falta de Oxígeno, o substituciones de los aniones (Ba, Y) o el metal (Cu)

The action is in the CuO_2 planes!

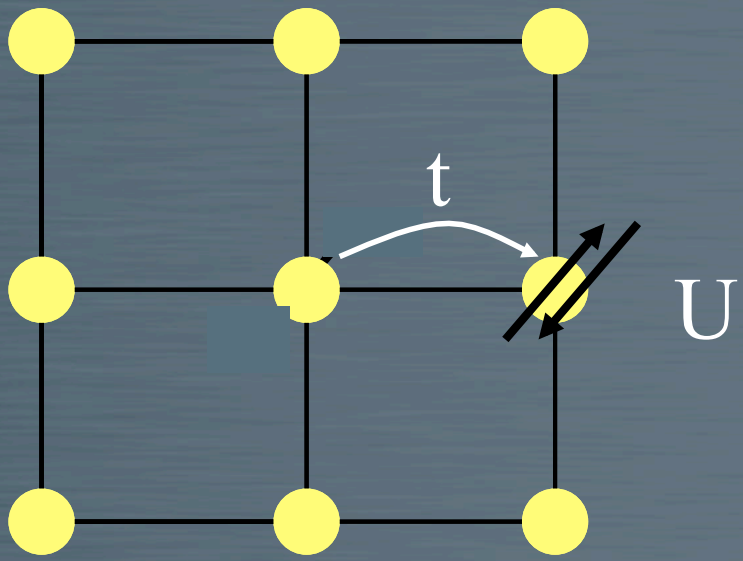






Cu^{2+} - d^9 shell

Simplified model: square lattice with one orbital (Cu d_{x2-y2}) per site ('one band model')

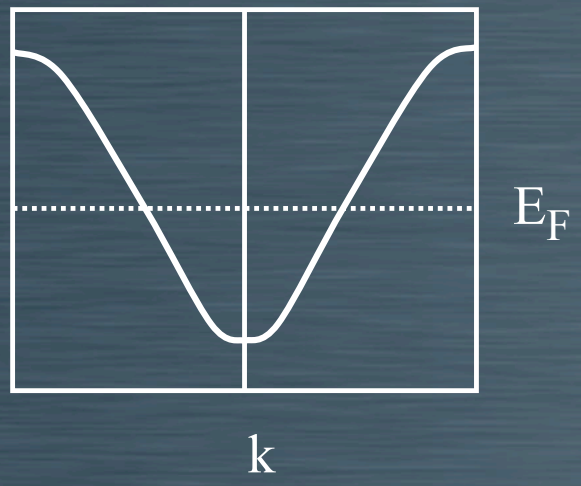


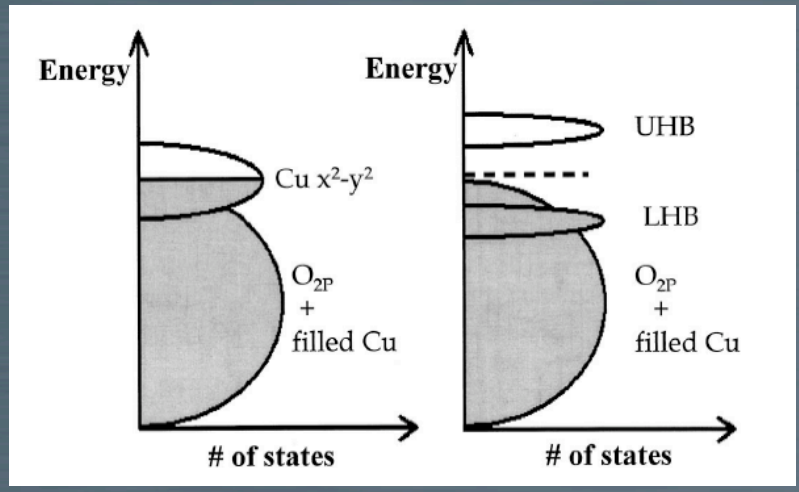
Hubbard Model

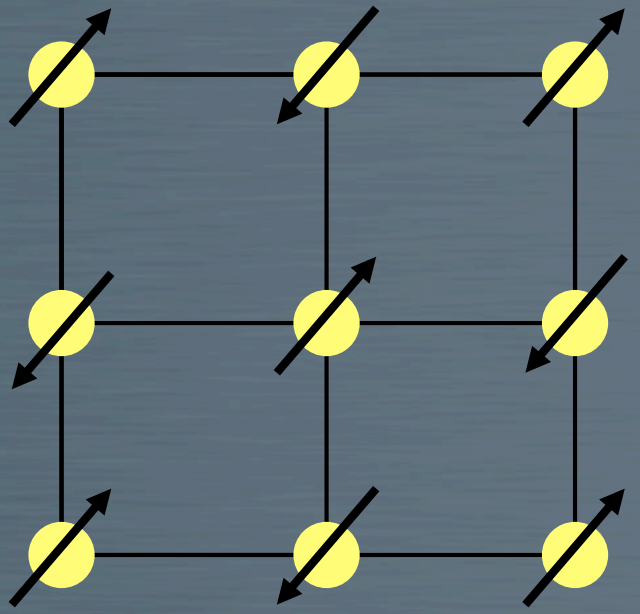
$$H = -t \sum_{<i,j>,\sigma} c^{+}_{i\sigma} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

The action is in the CuO_2 planes!

- Undoped systems: 1 electron per site
- Half filling
- Band theory: metallic planes (U<t)



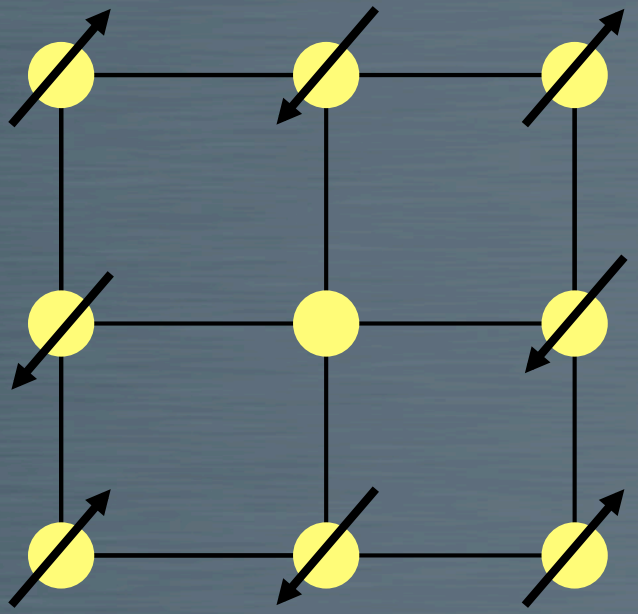


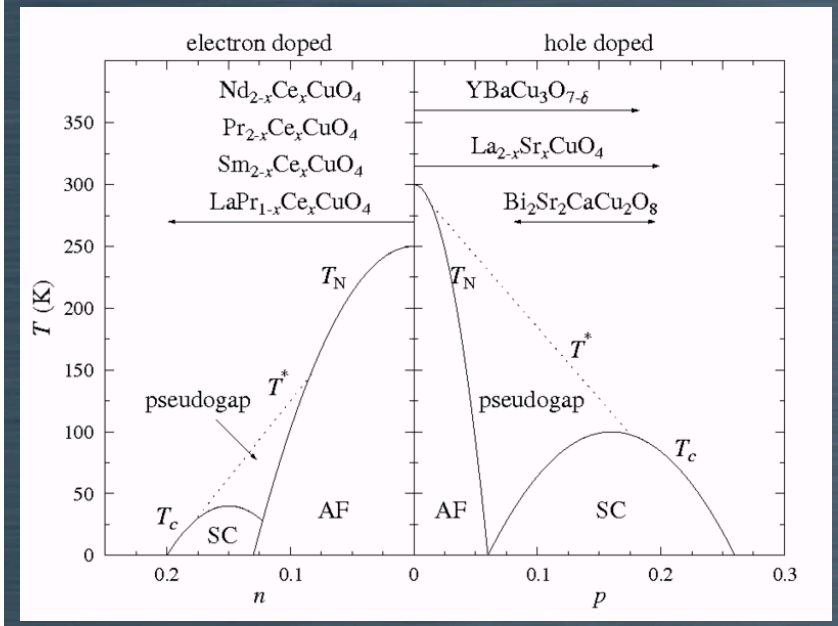


- However, for U > t: 'Mott insulator'
- Antiferromagnetic order ($J = t^2/U$)

Doping of CuO_2 planes

- Competition between J and t.
- Carrier (e, h) mobility implies AF frustration!
- Appearance of exotic phases
- Very complex phase diagram





- Multiple theories, both for normal and SC phases
- Many partial advances, but the problem is still open!
- Numerical calculations are essential to understand and solve the problem!

Numerical Calculations: an example

Dynamical Cluster Approximation

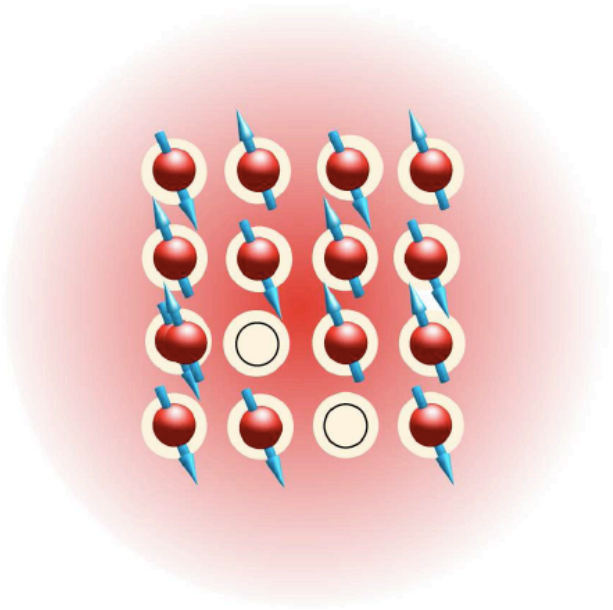
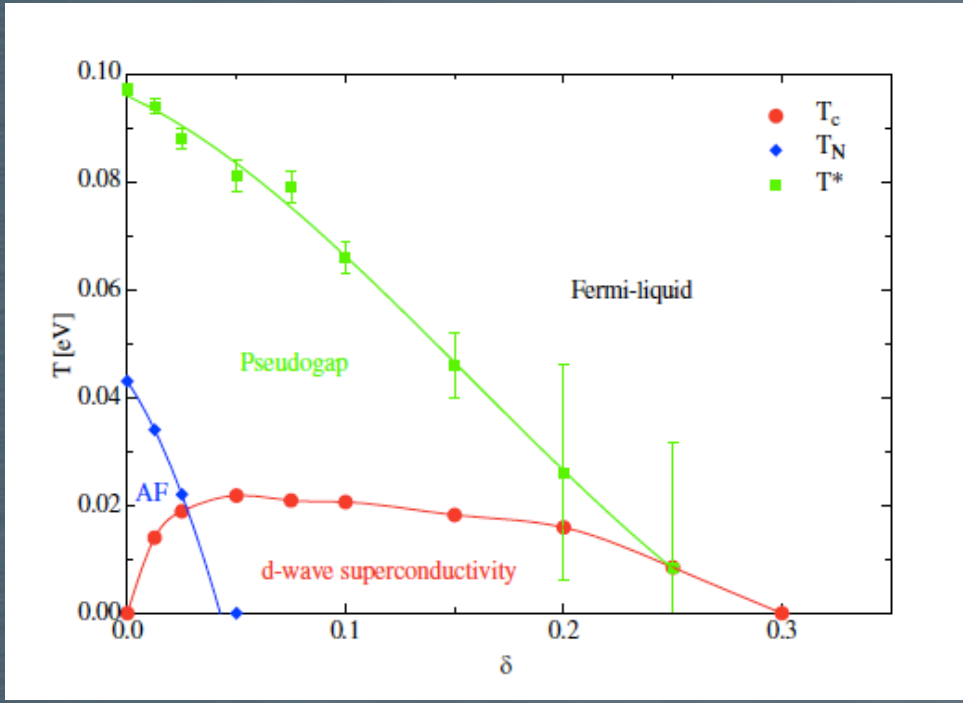


Figure 2: Schematic illustration of the DCA formalism. The model is mapped onto a finite-size cluster self-consistently coupled to a mean-field host. Correlations within the cluster are treated accurately while the physics on length scales beyond the cluster size is described on the mean-field level.

- Numerical solution of the Hubbard model
- Finite cluster coupled to a 'mean field' host
- Correlations in the cluster solved accurately (QMC)
- Interaction with host at the mean field level



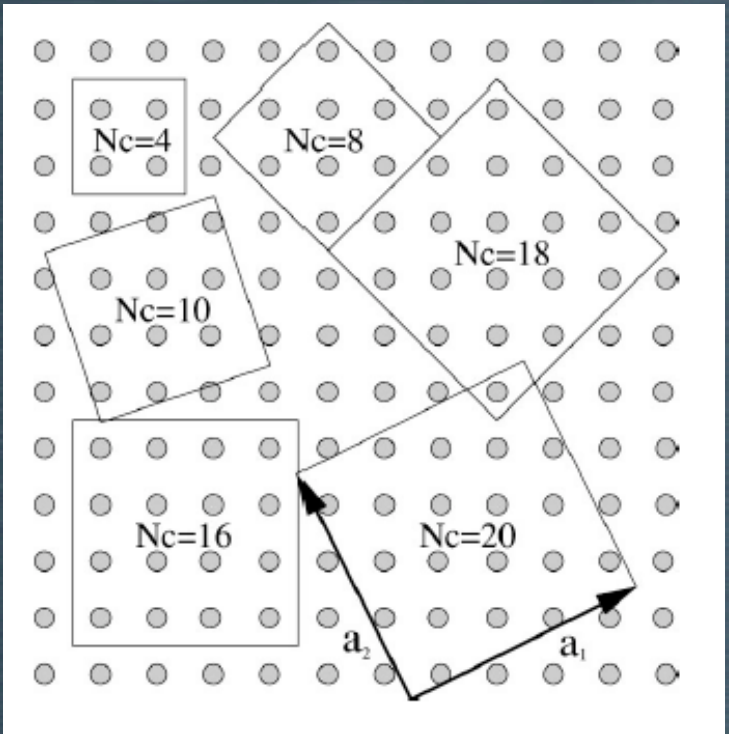
Jarrell et al., EPL 56, 563 (2001)

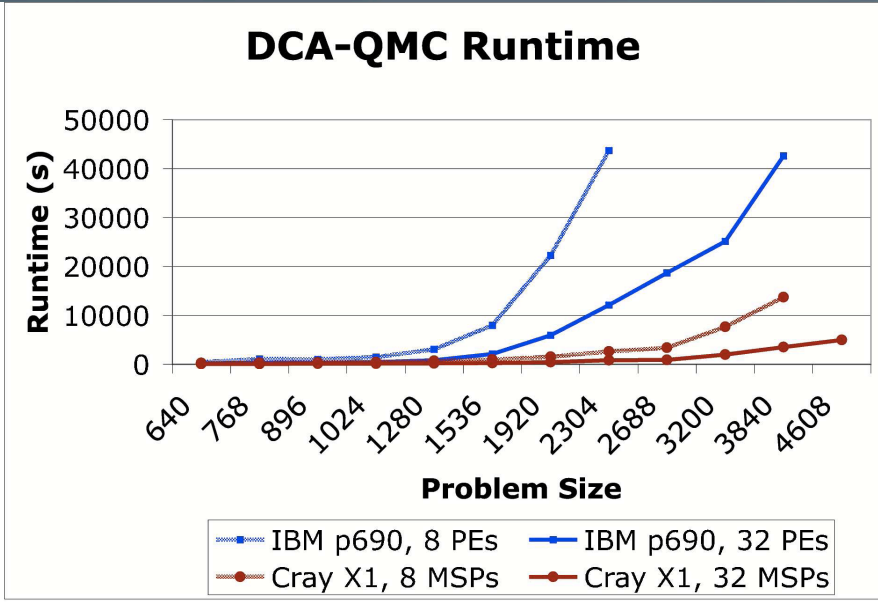
Numerical Calculations: an example

Dynamical Cluster Approximation

- QMC Scaling: $O(N^3)$ $N = N_c \times N_t$ N_c = cluster size

N_t = number of time slices in QMC





Jarrell et al., EPL 56, 563 (2001)

Current Activity

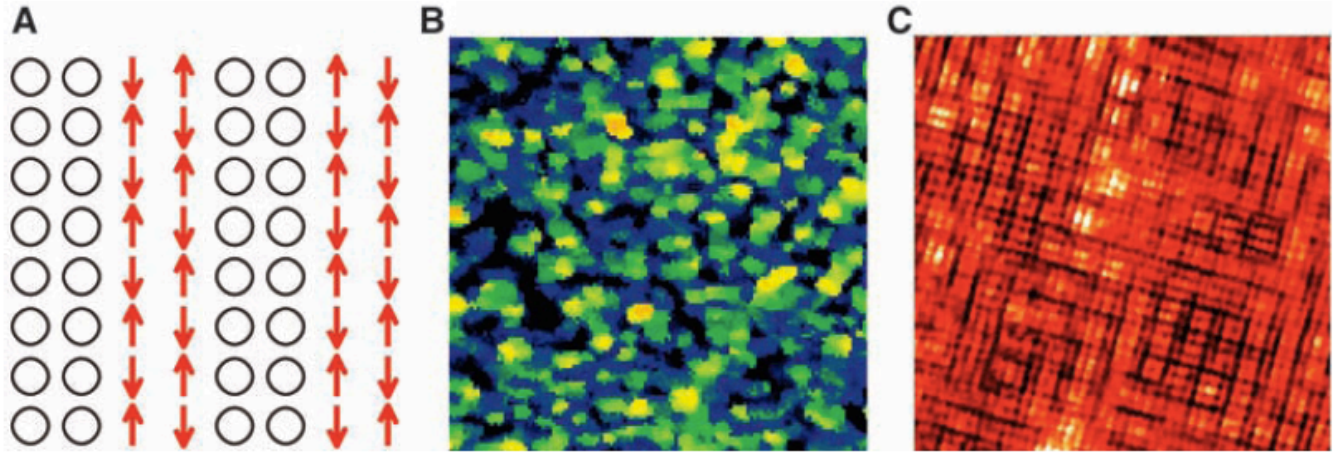


Fig. 3. Examples of inhomogeneous states in HTSC materials. (A) Schematic perfect stripes (*35*) (circles are holes; arrows, spins). Real systems may present more dynamical stripes (*29*). (B) *d*-wave SC gap real-space distribution obtained by using STM techniques (*37*). Inhomogeneities at the nanoscale are observed (patches). The entire frame is 560 Å by 560 Å. (C) Recently unveiled charge-order state (checkerboard) in Na-doped cuprates (*40*, *41*).

"Stripe phases"

Present in many other systems (Manganites, Transition Metal Oxides...)

See review by Dagotto, Science 309, 257 (2005)

- Multiplicity of competing quasi-degenerate phases
- Very large susceptibility to external changes
- Complexity of quantum origin

Atomistic Simulation: Spectrum of Methods

J. Neaton, LBNL

Fewer Approximations
Quantum Effects
Fewer Adjustable Params.

More Approximations
Classical Dynamics
Many Empirical Params.

Level of Theory

Many-Electron Excited-States

Density Functional Theory

Tight-Binding

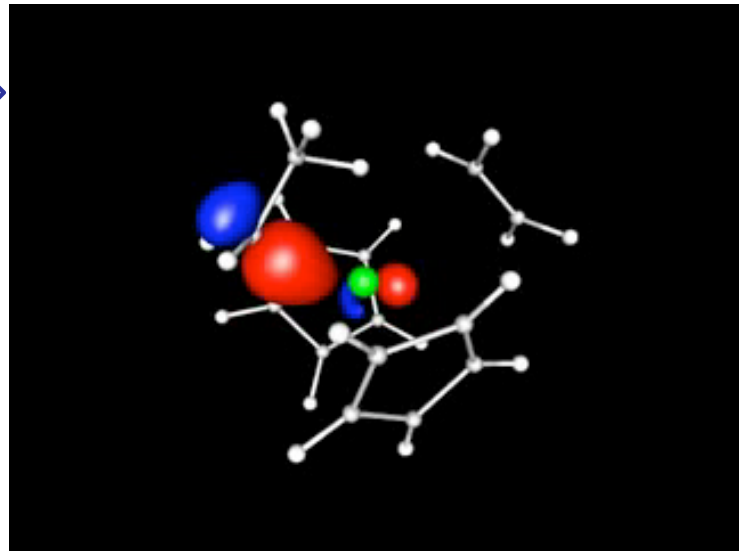
Empirical Potentials

Coarse Graining Methods

Continuum Models

Computational Cost and L tions

High Cost
Small Length Sca
Short Time Scales



Low Cost
Large Length Scales
Long Time Scales

Rowley, C.N., Woo, T.K.
Organometallics. 27(24), 6405-6407, 2008

K. Schulten et al., U. of Illinois

Atomistic Models

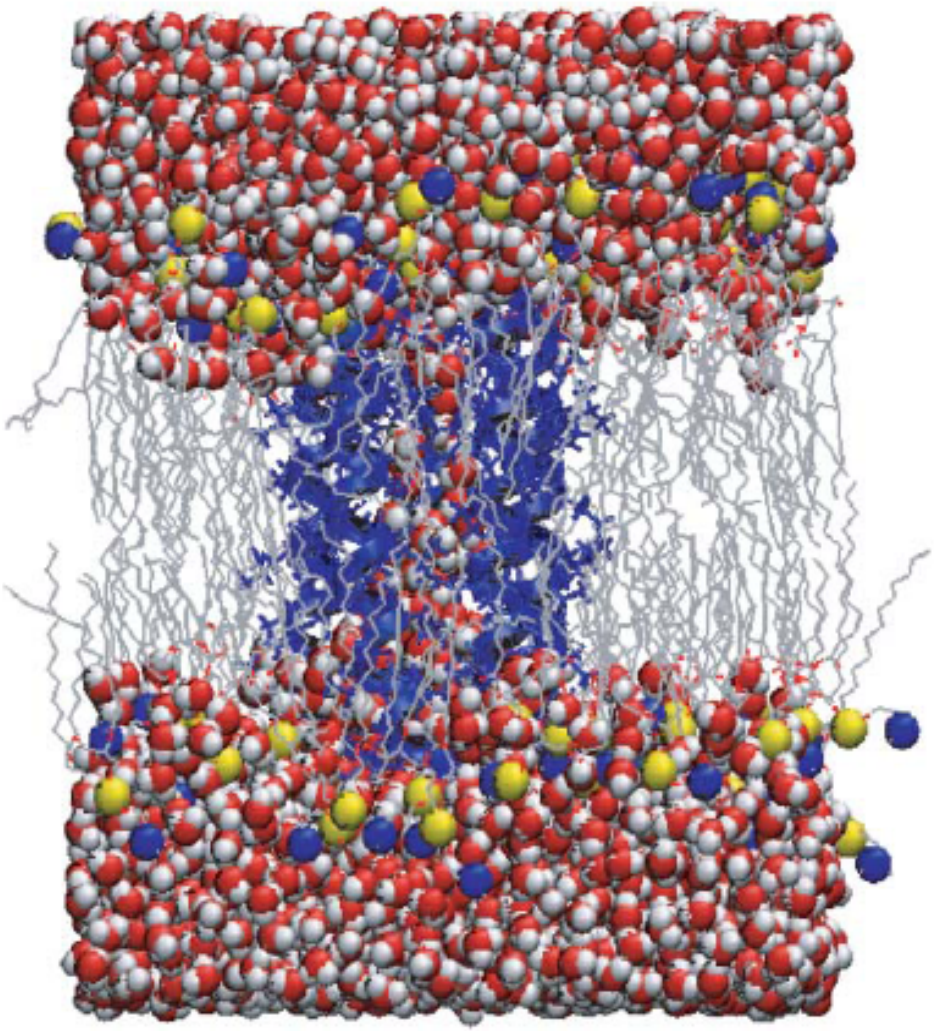
(I) Interatomic Potentials

- Only atoms are considered (e.g. Lennard-Jones)

$$v(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^{6}]$$

- Parameters determined from experimental information or from *ab-initio* calculations

- Easy/fast to compute. Allow calculations in very large systems (10,000+ atoms)



Transport across membranes

L. Saiz & M.L. Klein,
Biophysical Journal (2005)

~ 130 lipids, ~ 3500 H_2O

~ 10 ns dynamics

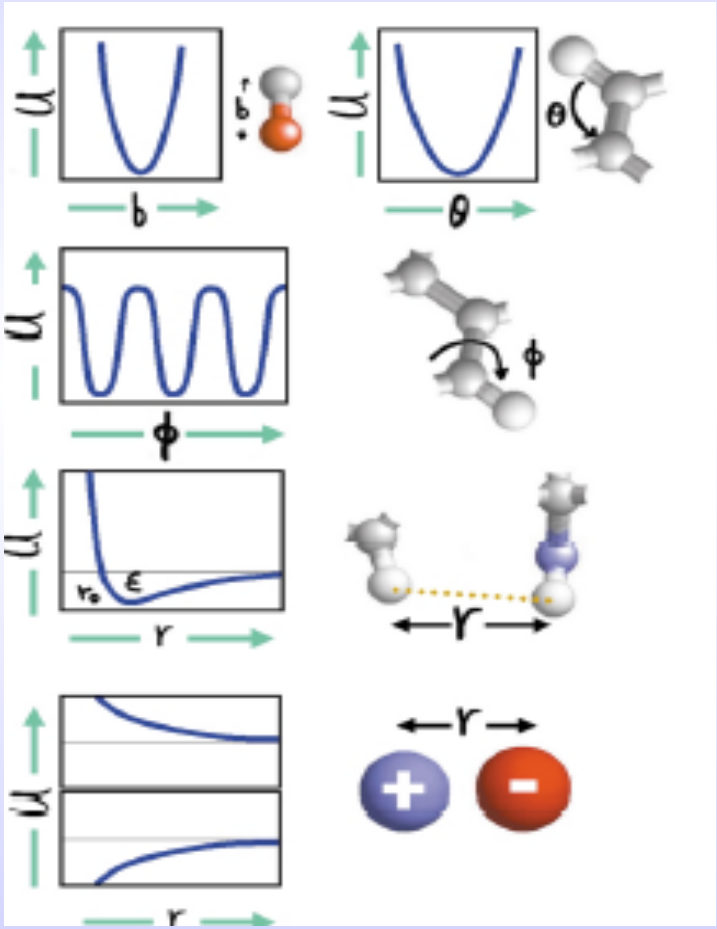
Example: AMBER Force Field
(widely used for simulation of biomolecules)

$$U = \sum_{\text{All Bonds}} \tfrac{1}{2} K_b (b - b_o)^2 + \sum_{\text{All Angles}} \tfrac{1}{2} K_\theta (\theta - \theta_o)^2$$

$$+ \sum_{\text{All Torsion Angles}} K_\phi [1 - \cos(n\phi + \delta)]$$

$$+ \sum_{\text{All nonbonded pairs}} \epsilon \left[\left(r_o/r\right)^{12} - 2\left(r_o/r\right)^{6} \right]$$

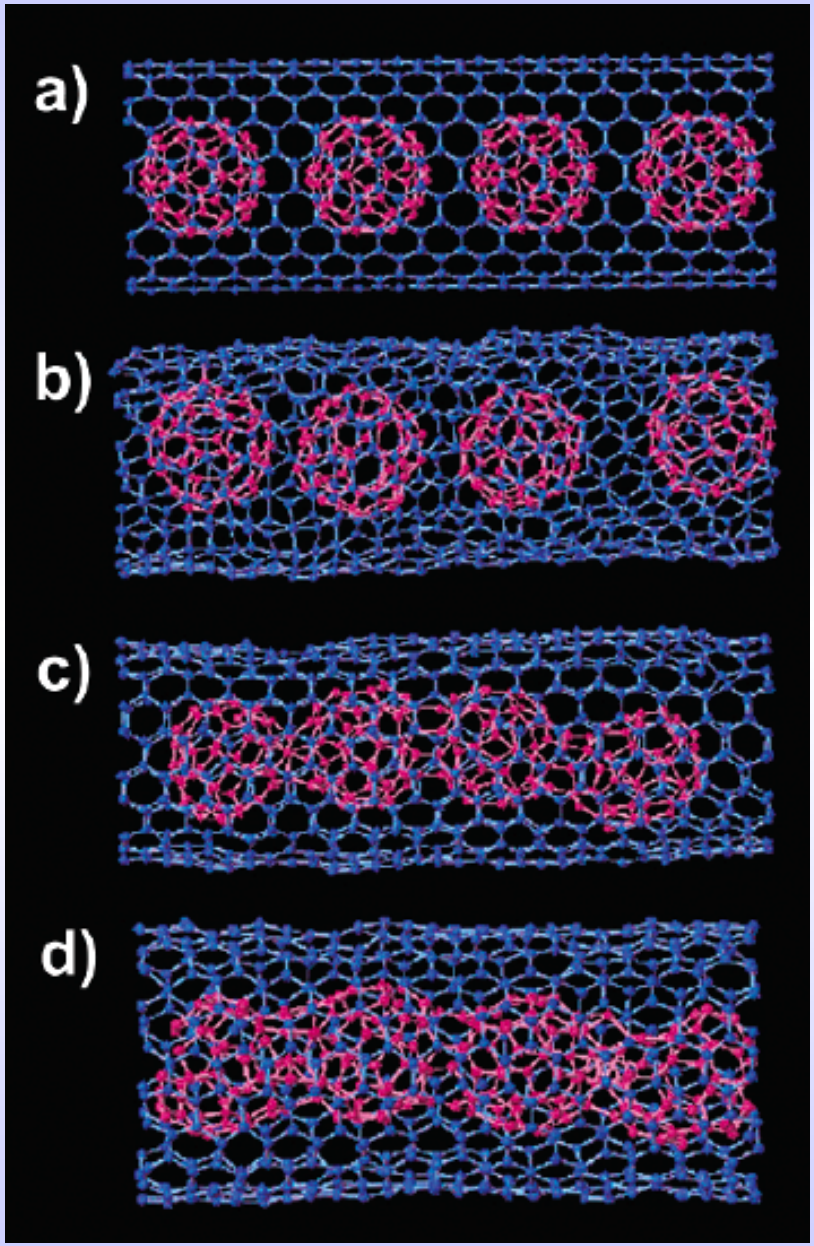
$$+ \sum_{\text{All partial charges}} 332 q_i q_j / r$$



Atomistic Models

(II) Semi-empirical methods ("tight binding")

- Electrons considered explicitly, in a simplified way (electron potential fitted)
- Electronic properties (bands, transport, bond breaking and formation
- Parameters determined from experimental information or from *ab-initio* calculations
- Easy/fast to evaluate, allow large systems (1,000+ atoms)

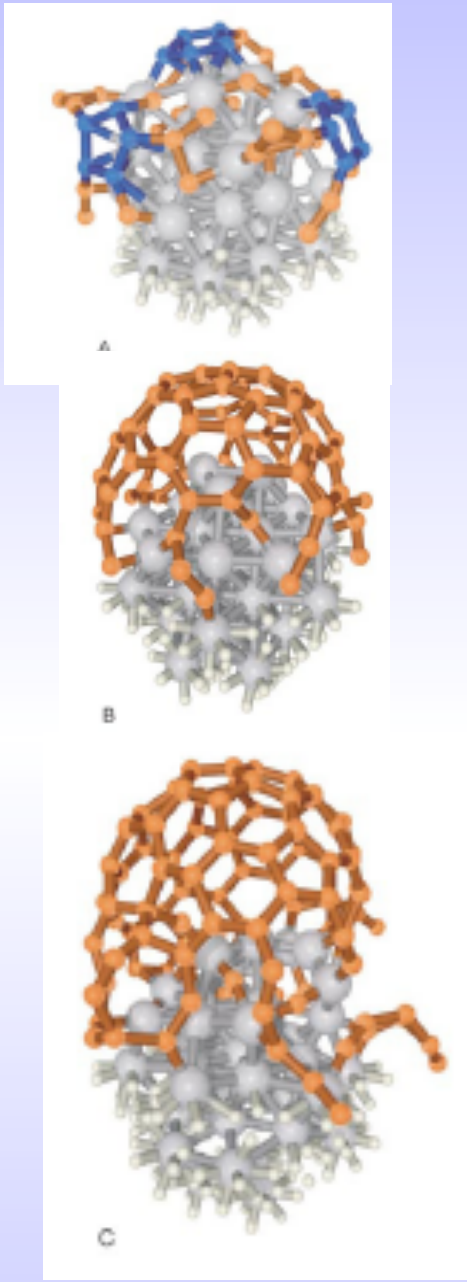


Fullerenes coalescence
Hernández et al., Nanoletters (2003)

Atomistic Models

(III) *ab initio* or "First-Principles" methods

- Explicit fundamental interactions between electrons and ions
- No parameters to fit!
- Computationally expensive, possible for only relatively small systems (100+ atoms)
- Full electronic structure is available!



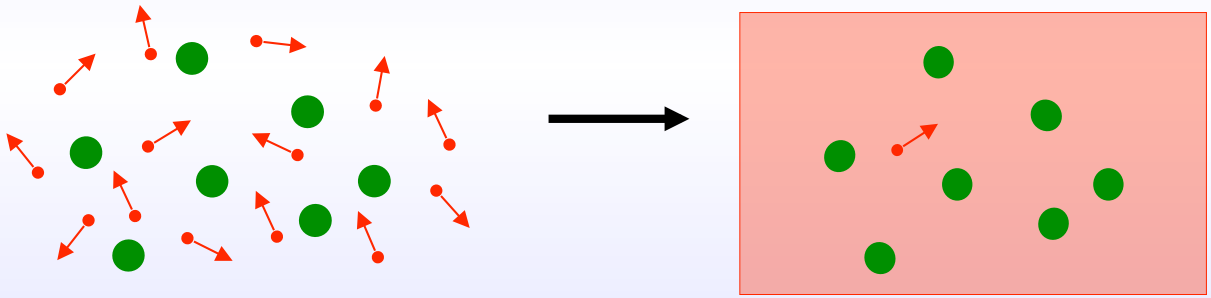
Nanotube growth on metallic catalytic nanoparticles
Raty, Galli *et al*. (PRL'05)

Density Functional Theory

1. $\Psi(\{\vec{r}_i\}) \rightarrow \rho(\vec{r})$ *particle density* (Hohenberg-Kohn Theorems)

2. Interacting electrons: As if *non-interacting* electrons in an *effective potential* (Kohn-Sham Ansatz)

$$\hat{h}\psi_n(\vec{r}) = \varepsilon_n \psi_n(\vec{r})$$



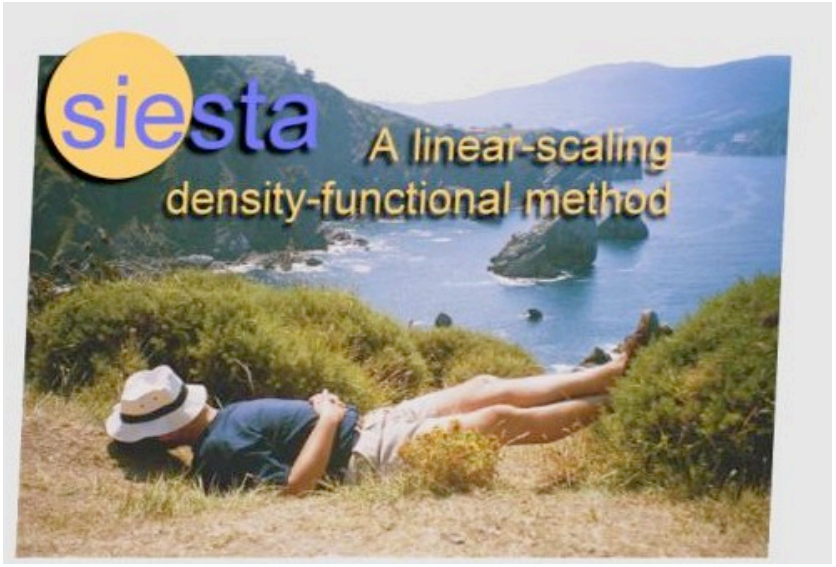
$$\hat{h} = -\frac{1}{2}\nabla^2 + V_{eff}[\rho]$$

$$\rho(\vec{r}) = \sum_n^{occ} |\psi_n(\vec{r})|^2$$

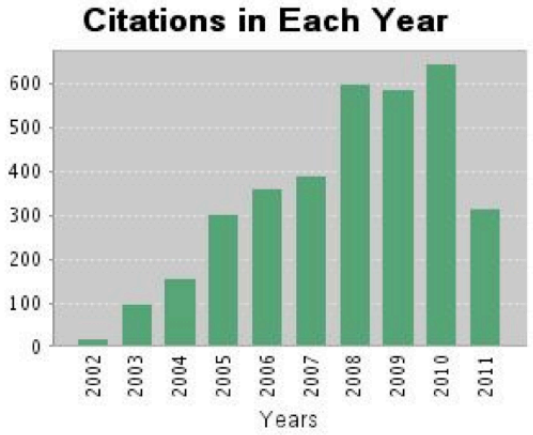
3. Approximation: the effective XC potential - Local and Quasilocal

LDA $V_{XC}(\vec{r}) = V_{XC}[\rho(\vec{r})]$

GGA $V_{XC}(\vec{r}) = V_{XC}[\rho(\vec{r}), \nabla\rho(\vec{r})]$



http://www.uam.es/siesta



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1. Title: The SIESTA method for ab initio order-N materials simulation Author(s): Soler JM, Artacho E, Gale JD, et al. Source: **JOURNAL OF PHYSICS-CONDENSED MATTER** Volume: **14** Issue: **11** Pages: **2745-2779** Published: **MAR 25 2002**	2,578	257.80
2. Title: Density-functional method for nonequilibrium electron transport Author(s): Brandbyge M, Mozos JL, Ordejon P, et al. Source: **PHYSICAL REVIEW B** Volume: **65** Issue: **16** Article Number: **165401** Published: **APR 15 2002**	899	89.90

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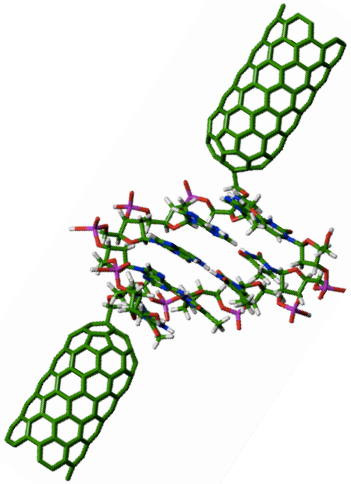
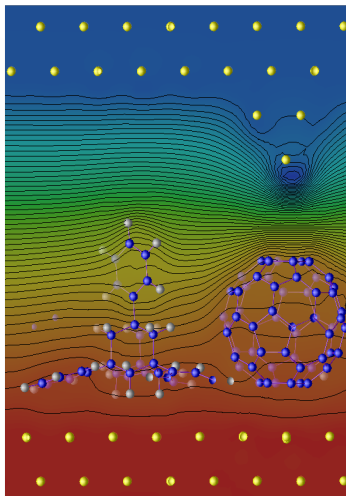
  (Motorola, Sumitomo Chem., Samsung, Air Products, Fujitsu,...)





Algorithms

Structural Optimization

- minimum energy configurations
- T = 0

- no information on real dynamics
- no temperature
- local minima

Monte Carlo

- T > 0
- thermodynamics: statistical averages
- several ensambles
- long time scales (equilibrium)

- no information on dynamics
- no real time (kMC)
- only at equilibrium

Molecular Dynamics

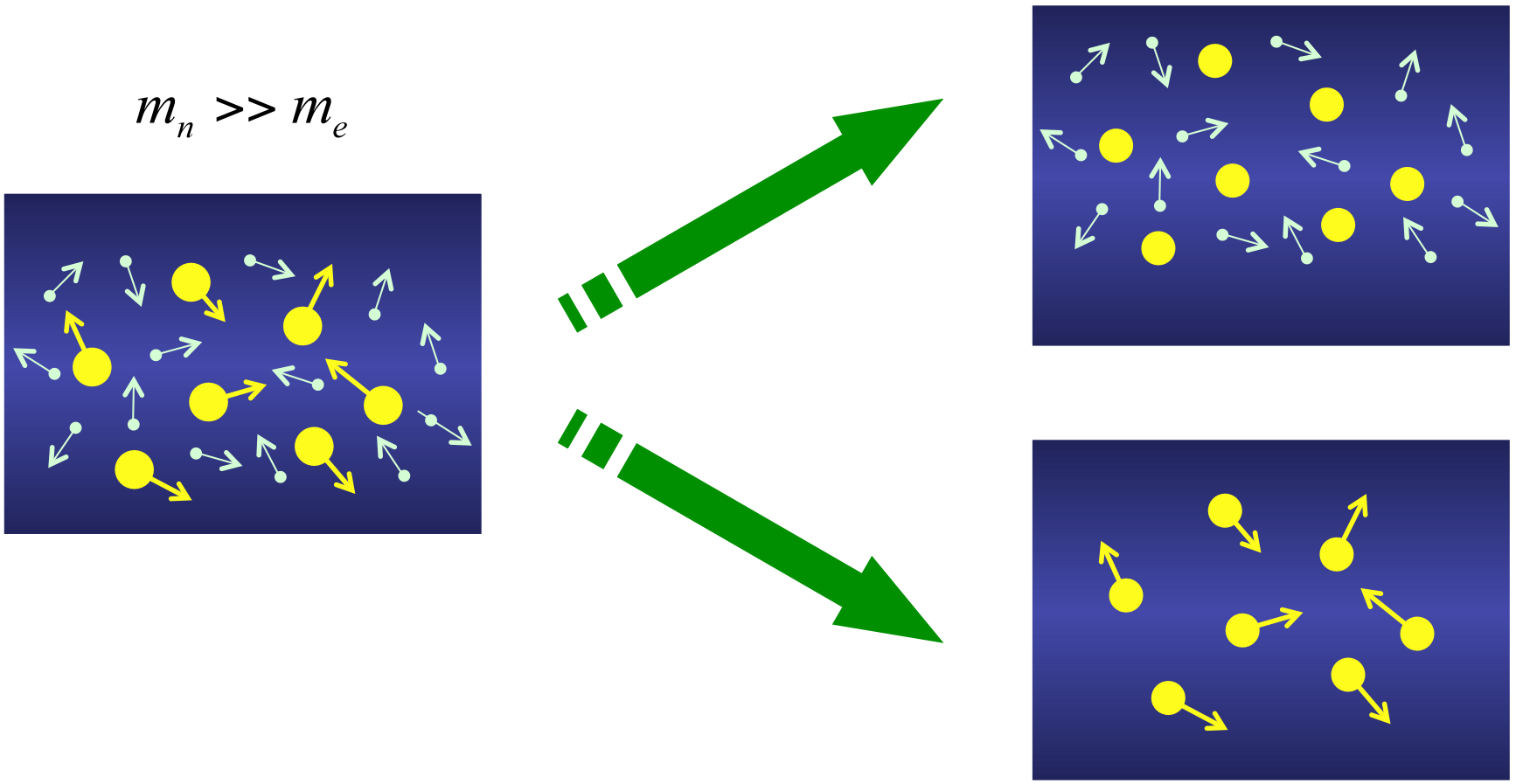
- T > 0
- thermodynamics: statistical averages
- several ensambles
- información on real dynamics (non-equil)

- large computational cost
- limited time scale (accelerated dyn.)
- ergodicity problems

Born-Oppenheimer dynamics

Nuclei are much slower than electrons

$m_n >> m_e$



Classical Nuclear Dynamics

Molecular Dynamics

- Follows the time evolution of a system
- Solve Newton's equations of motion:

$$\vec{F}(t) = -\frac{dE}{d\vec{x}} = m\vec{a}(t) = m\frac{d^2\vec{x}(t)}{dt^2}$$

- Treats nuclei *classically*
  - Hydrogen may raise issues: tunneling, zero point E...

- Allows study of dynamic processes
- Annealing of complex materials
- Influence of temperature and pressure

- Simulations for Macroscopic Systems (liquids, solids):
  Time averages vs Statistical averages

Ergodicity

- In MD we want to replace a full sampling on the appropriate statistical ensemble by a SINGLE, long trajectory. We want to represent a Macroscopic system with a (very small, but periodic) Microscopic sample.

- This is OK only if system is ergodic.

- *Ergodic Hypothesis: a phase point for any isolated system passes in succession through every point compatible with the energy of the system before finally returning to its original position in phase space. This journey takes a Poincare cycle.*

- *In other words, Ergodic hypothesis*: each state consistent with our knowledge is equally "likely".

  - Implies the average value does not depend on initial conditions.
  - $\langle A \rangle_{time} = \langle A \rangle_{ensemble}$, so $\langle A_{time} \rangle = (1/N_{MD}) = \sum_{t=1,N} A_t$ is good estimator.

- Are systems in nature really ergodic? Not always!
  - Non-ergodic examples are glasses, folding proteins (in practice) and perfectly harmonic crystals (in principle).

Different aspects of ergodicity

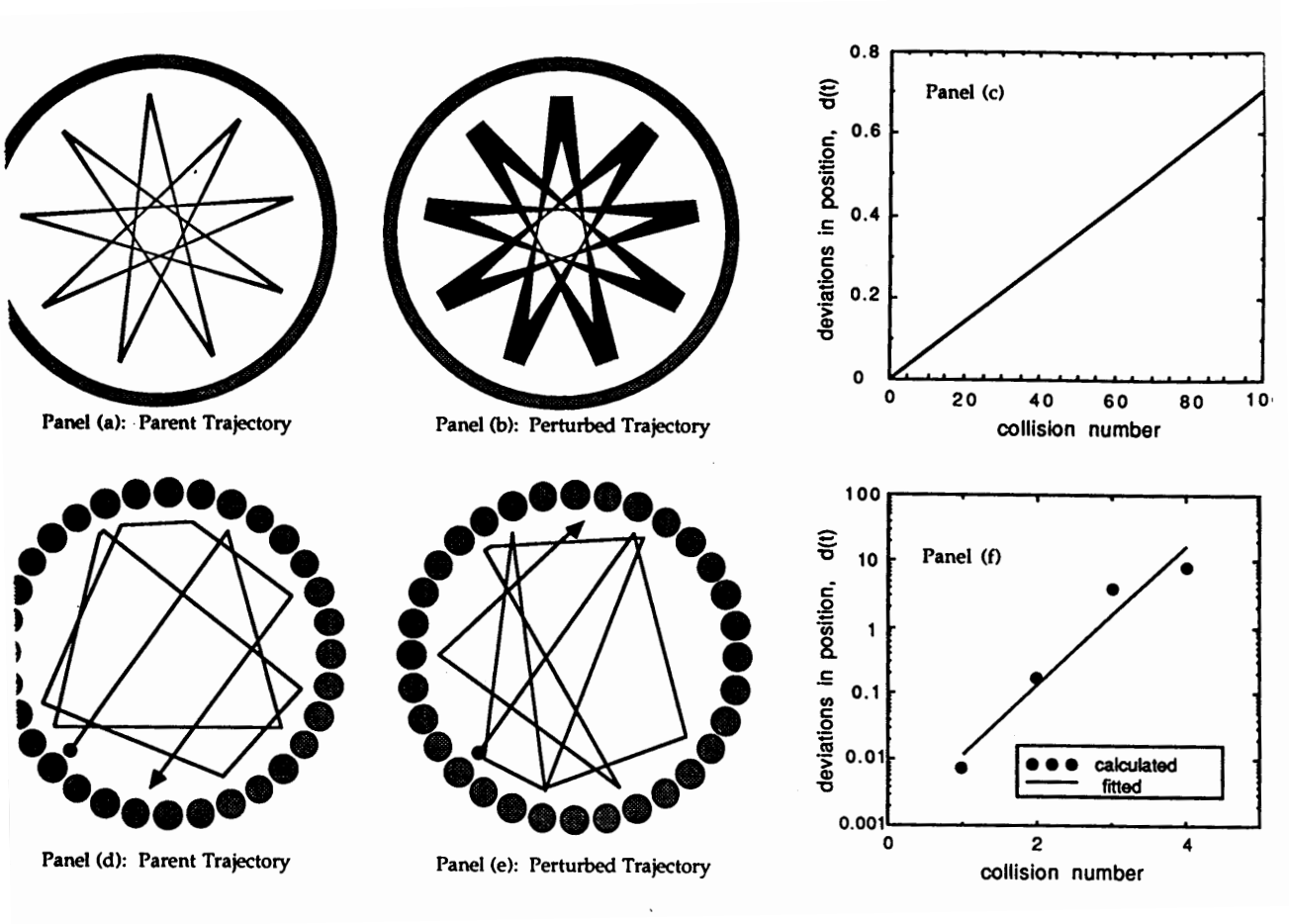
- **The system relaxes on a “reasonable” time scale towards a unique equilibrium state (microcanonical state)**
- **Trajectories wander irregularly through the energy surface eventually sampling all of accesible phase space.**
- **Trajectories initially close together separate rapidily (Sensitivity to initial conditions).**

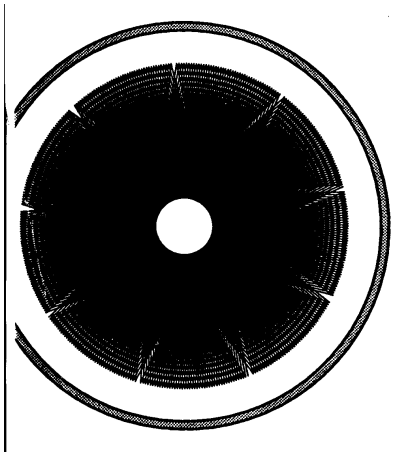
Ergodic behavior makes possible the use of statistical methods on MD of small systems.

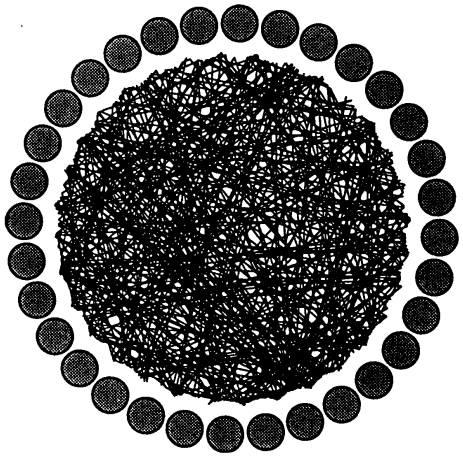
Small round-off errors and other mathematical approximations should not matter.

Particle in a smooth/rough circle

From J.M. Haile: MD Simulations







Molecular Dynamics (I)

In Molecular Dynamics simulations, one computes the evolution of the positions and velocities with time, solving Newton's equations.

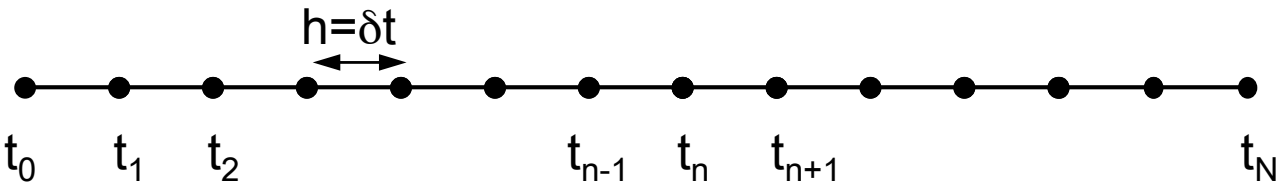
$$\vec{F}(t) = -\frac{dE}{d\vec{x}} = m\vec{a}(t) = m\frac{d^2\vec{x}(t)}{dt^2} \quad \Rightarrow$$

$$\vec{x}(t) = \vec{x}(t_0) + \vec{v}(t_0)(t - t_0) + \int_{t_0}^{t} dt' \int_{t_0}^{t'} \frac{1}{m}\vec{F}(t'')dt''$$

- **Algorithm to integrate Newton's equations: "Verlet"**
- **Initial conditions in space and time.**

Molecular Dynamics (II)

- Initialize positions and momenta at t=0 (initial conditions in space and time)
- Solve F = ma to determine r(t), v(t). (integrator)
  - We need to make time discrete, instead of continuous!!!



$x(t+h) = x(t) + v(t)\,h + 1/2\,a(t)\,h^2 + b(t)\,h^3 + O(h^4)$ (Taylor series expansion)
$x(t-h) = x(t) - v(t)\,h + 1/2\,a(t)\,h^2 - b(t)\,h^3 + O(h^4)$

$x(t+h) = 2\,x(t) - x(t-h) + a(t)\,h^2 + O(h^4)$ Sum

$v(t) = (r(t+h) - r(t-h))/(2h) + O(h^2)$ Difference (*estimated velocity)*

$a(t) = F(t) / m$ Newton!

Molecular Dynamics III

- Timestep must be small enough to accurately sample highest frequency motion
- Typical timestep is 1 fs (1×10^{-15} s)
- Typical simulation length: Depends on the system of study!!
  (the more complex the PES the longer the simulation time)
- *Is this timescale relevant to your process?*
- Simulation has two parts
  - equilibration – when properties do not depend on time
  - production (record data)
- Results:
  - diffusion coefficients
  - Structural information (RDF's,)
  - Free energies / phase transformations (very hard!)
- *Is your result statistically significant?*

Different ensembles: conserved magnitudes

- **NVE (Verlet): Microcanonical.**
- **Integrates Newtons equations of motion, for N particles, in a fixed volume V.**
- **Natural time evolution of the system: E is a constant of motion**

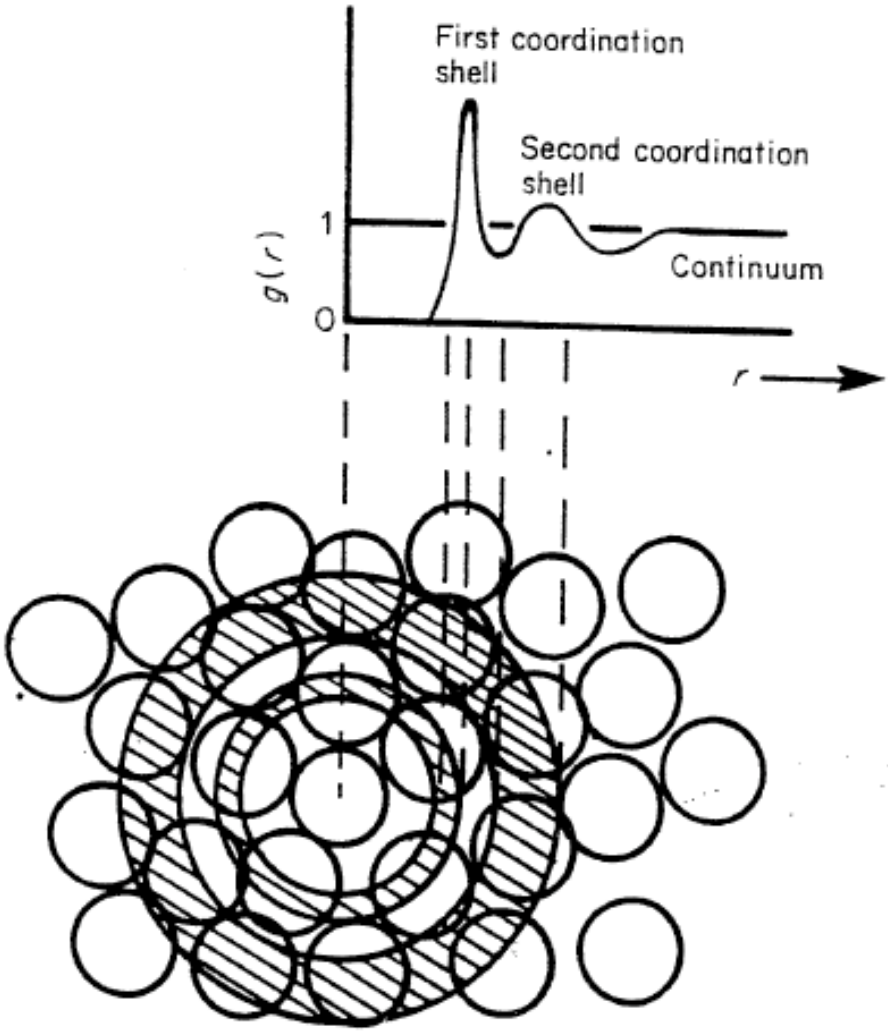
Same sampling (thermodynamic limit)

- **NVT (Nose): Canonical**
- **System in thermal contact with a heat bath.**
- **Extended Lagrangian:**
- **N particles + Thermostat, mass Q.**

- **NPE (Parrinello-Rahman) (isobaric)**
- **Extended Lagrangian**
- **Cell vectors are dynamical variables with an associated mass.**

- **NPT (Nose-Parrinello-Rahman)**
- **2 Extended Lagrangians**
- **NVT+NPE.**

Analysis of MD results

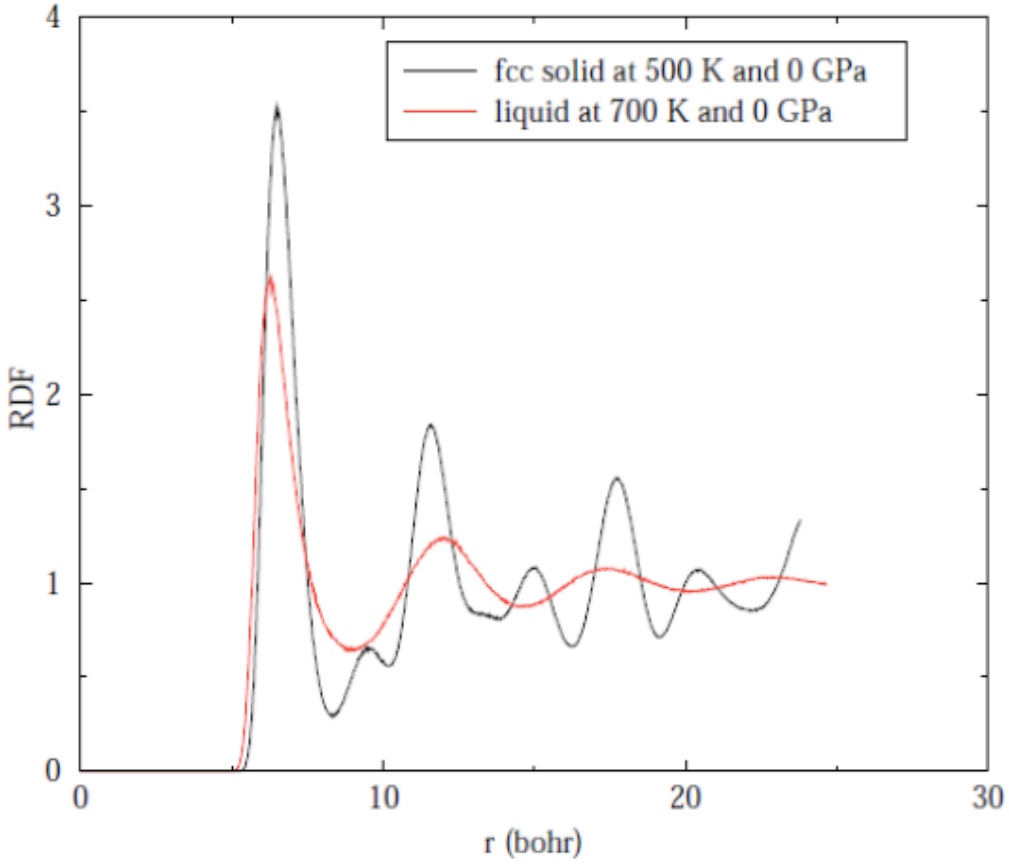


Radial Distribution Function

- For an ideal gas (unstructured, uncorrelated): g=1
- For real gases and liquids: g(r) → 1 for large r
- For solids: Peak structure (coordination shells), even at large distances.

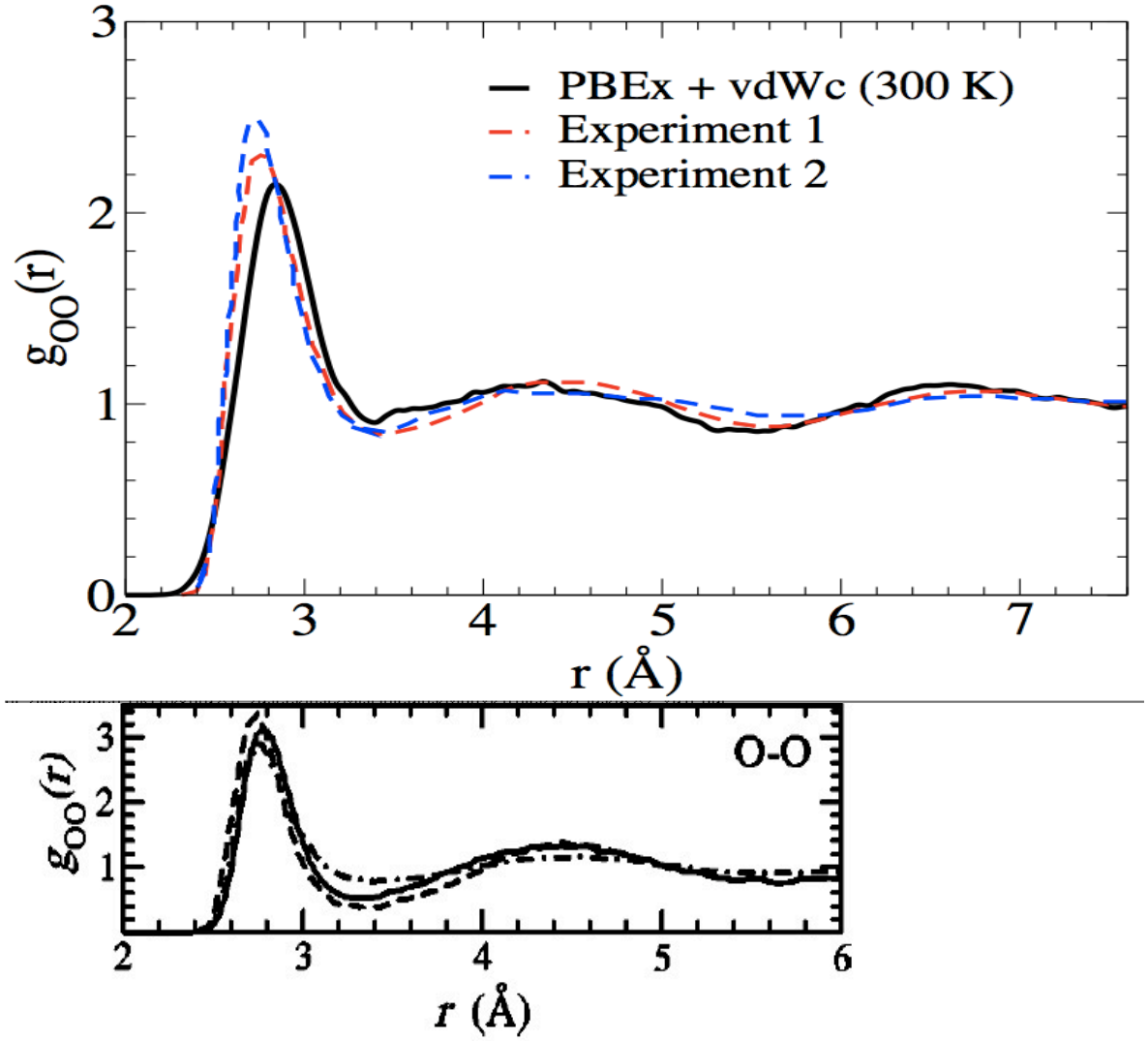
Analysis of MD results

Radial distribution function of Pb (solid and liquid)



From E. Hernández, ICMM-CSIC

The structure of H_2O



Liquid Water, 300 K

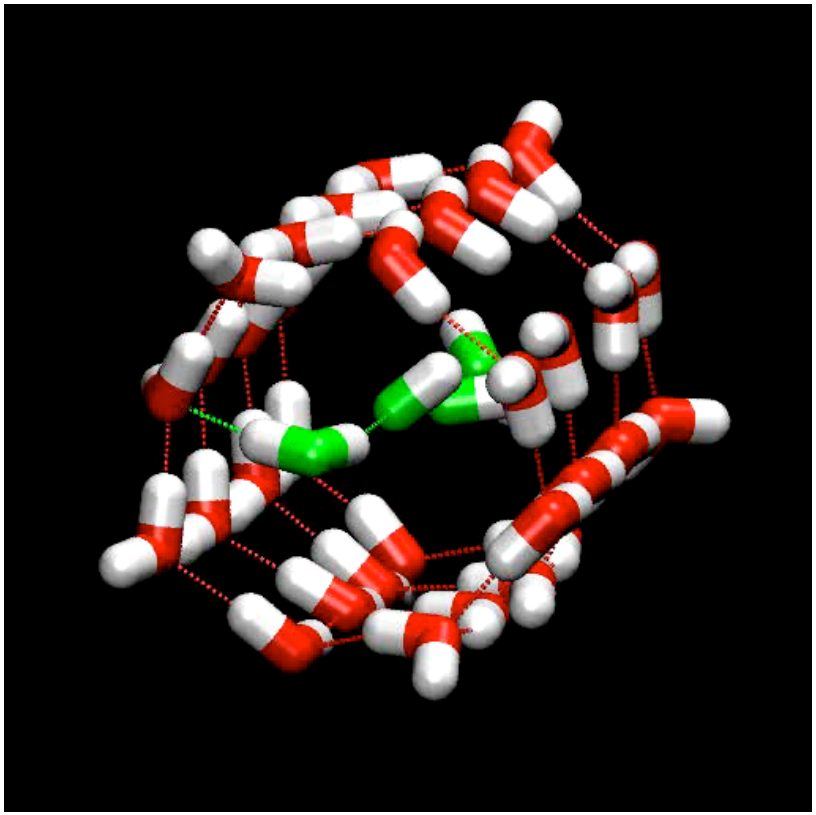
- Many empirical potentials (none perfect!!)
- First-Principles (DFT):
  too much structure
  density too low
  diffusion coefficient too low
- Too small cells and too short times
- Better potentials and better DFT functionals needed!!

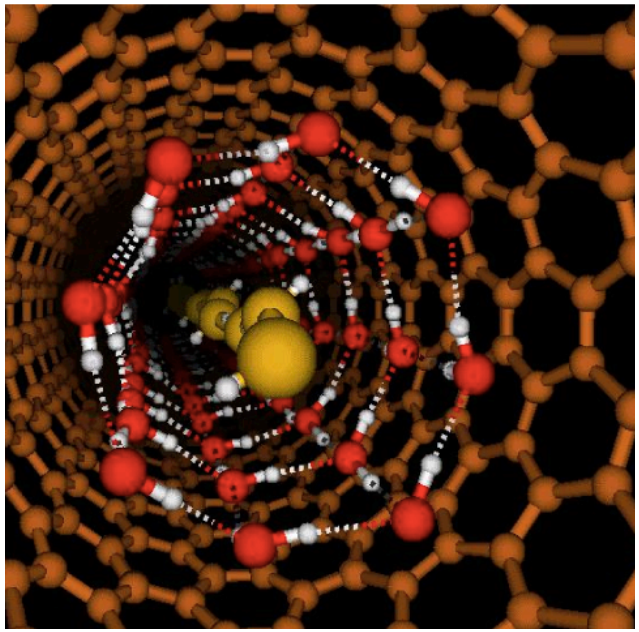
DFT Simulations: Fernández-Serra & Artacho, JCP**121** (2004)
Soler, Artacho et al., JCP **132**, 024516 (2011)

H_2O in Constrained Conditions

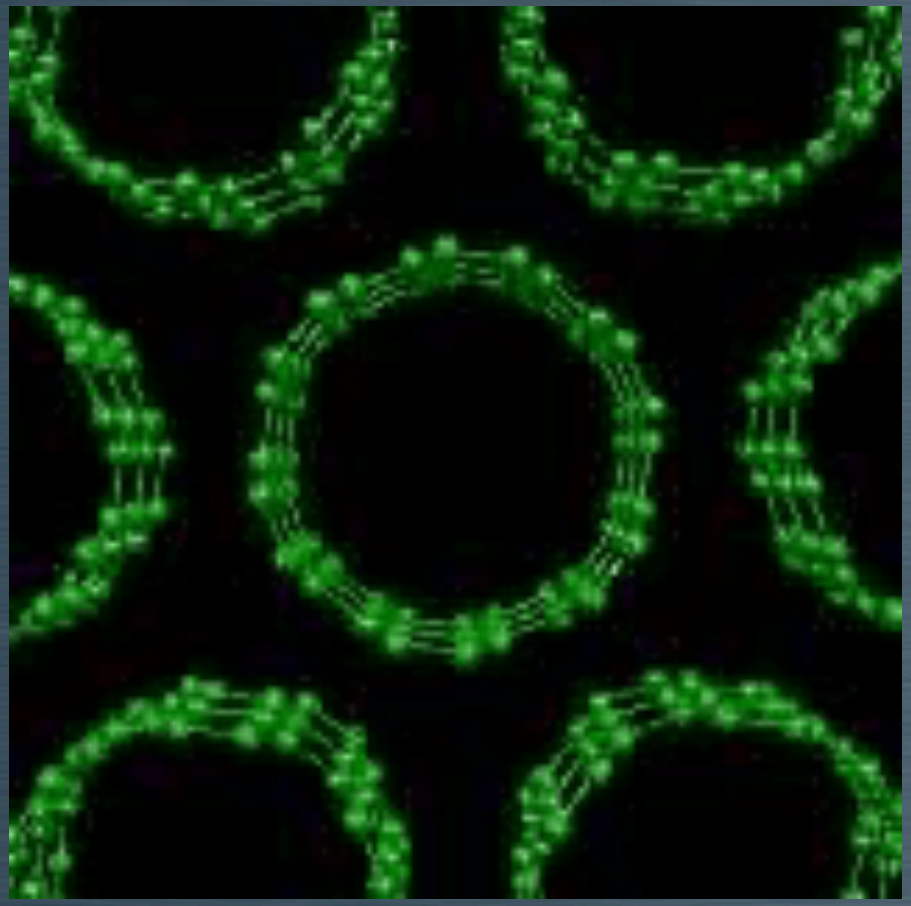
Water inside a Carbon Nanotube

- ‘layer’ structure (walls and chain)
- 2D ice at walls
- Highly diffusive chain
- Soft dynamics to very low temperature (disruption of H-bond network)

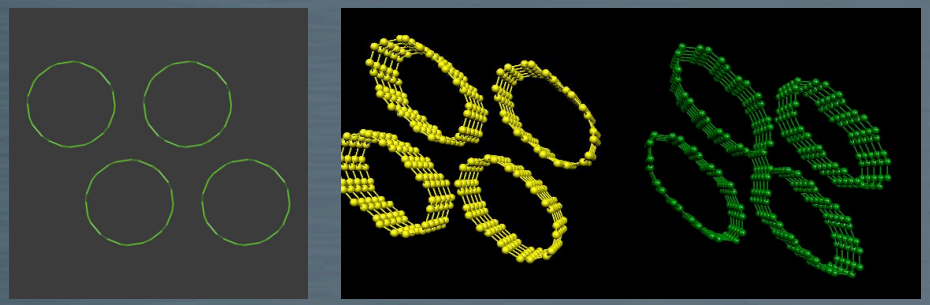




EXAMPLE:
from NANOTUBES to DIAMOND



Transformation of nanotubes bundles under pressure

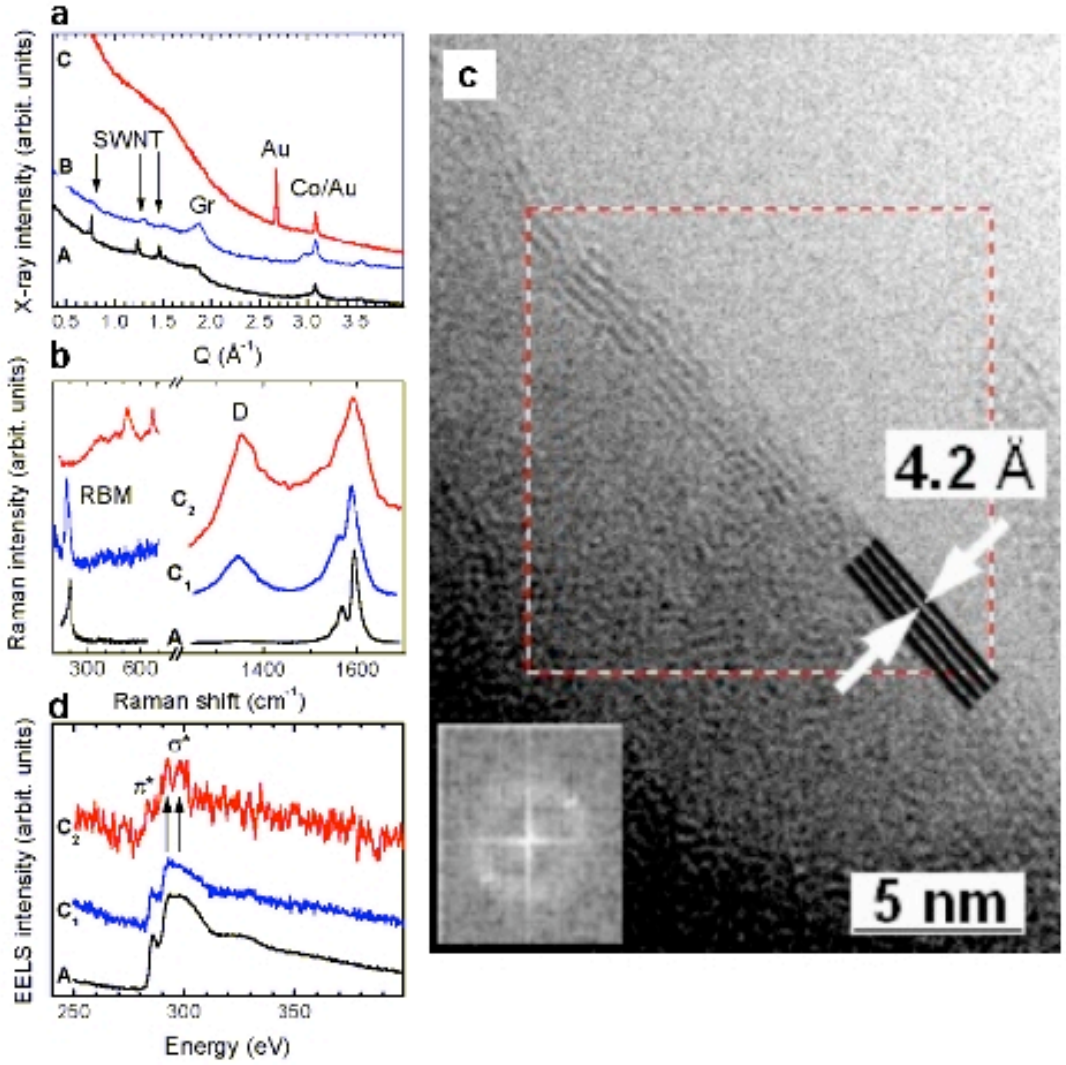


P = 0 ⟶ P = 9 GPa ⟶ P = 10 GPa

1 GPa = 10000 atm

S. Reich, C. Thomsen and P. Ordejón,
phys. stat. sol. (b) **235,** 354 (2003)

EXAMPLE:
from NANOTUBES to DIAMOND



P = 7 GPa

T = 700 °C

- Optical microscope

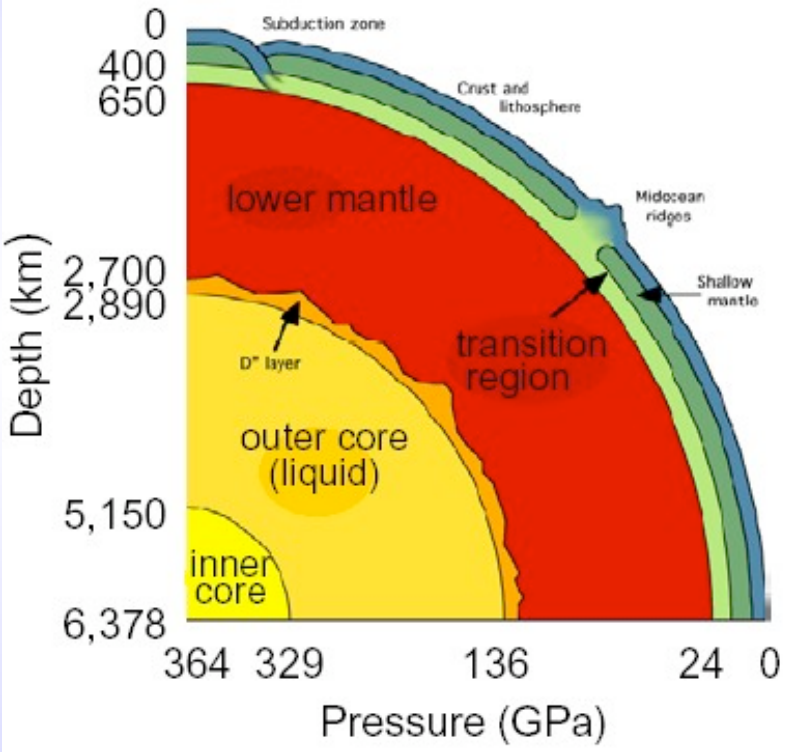
  Transparent μm crystallites

- TEM:

  Particles covered by h-d crystallites

Melting curve (P vs T) of Fe

D.Alfè, M.J.Gillan y G.D.Price, Nature 401, 462 (1999)



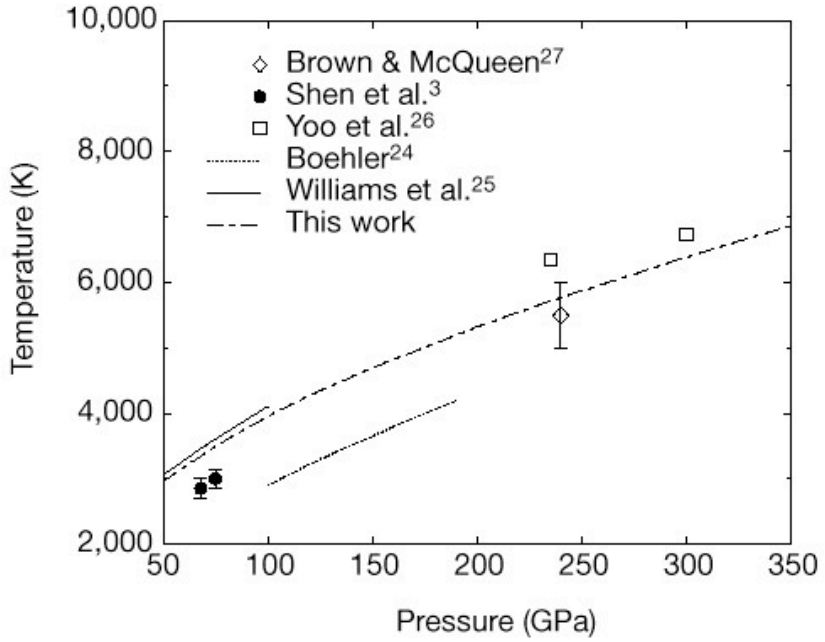


Figure 1 The *ab initio* melting curve of iron compared with experimental results. The dashed curve shows *ab initio* results; solid and dotted curves are interpolations of DAC measurements made by Williams *et al.*[25] and Boehler[24] respectively; the data points due to Shen *et al.*[3] represent a lower bound rather than the melting curve itself; the squares and diamond with error bar are shock data from refs 26 and 27.

DAC experiments: up to 200 GPa

Shock experiments: scatter of 2000 K

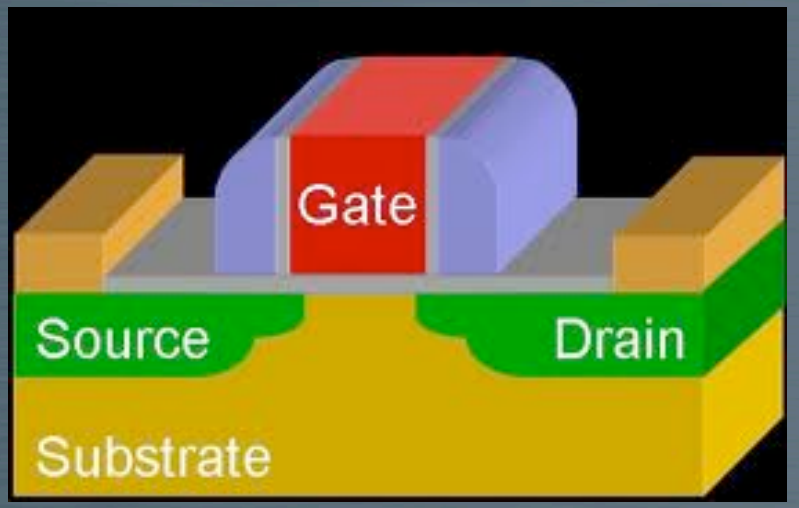
EXAMPLE OF MD SIMULATIONS: An Industrial Problem

Metallic gates: Cu

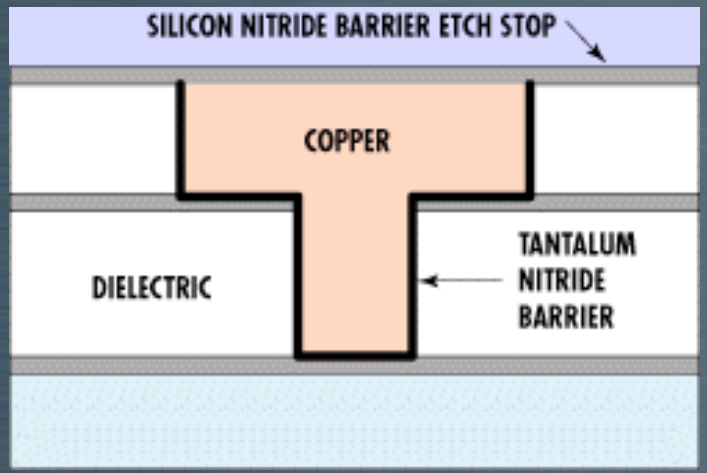
Cu:

- very good conductor

- ... but: it diffuses into Silicon



'Diffusion Barriers' between Cu and Silicon: Ta, TaN, W, Ti,...

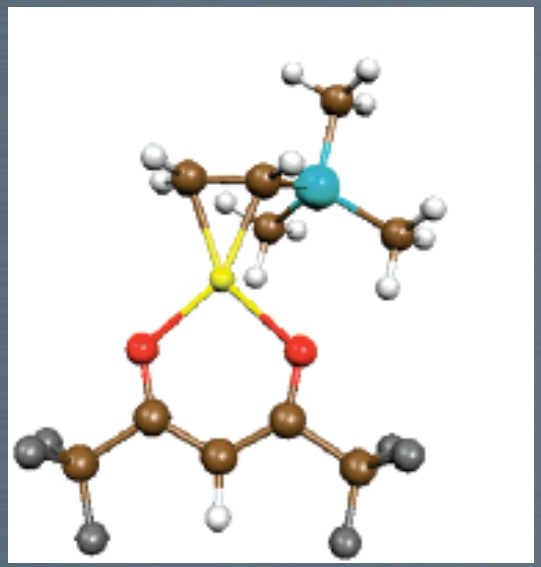


EXAMPLE:
An Industrial Problem

CIN2

Air Products and Chemicals (USA): “CupraSelect (TM)”

A chemical for the growth of thin Cu films



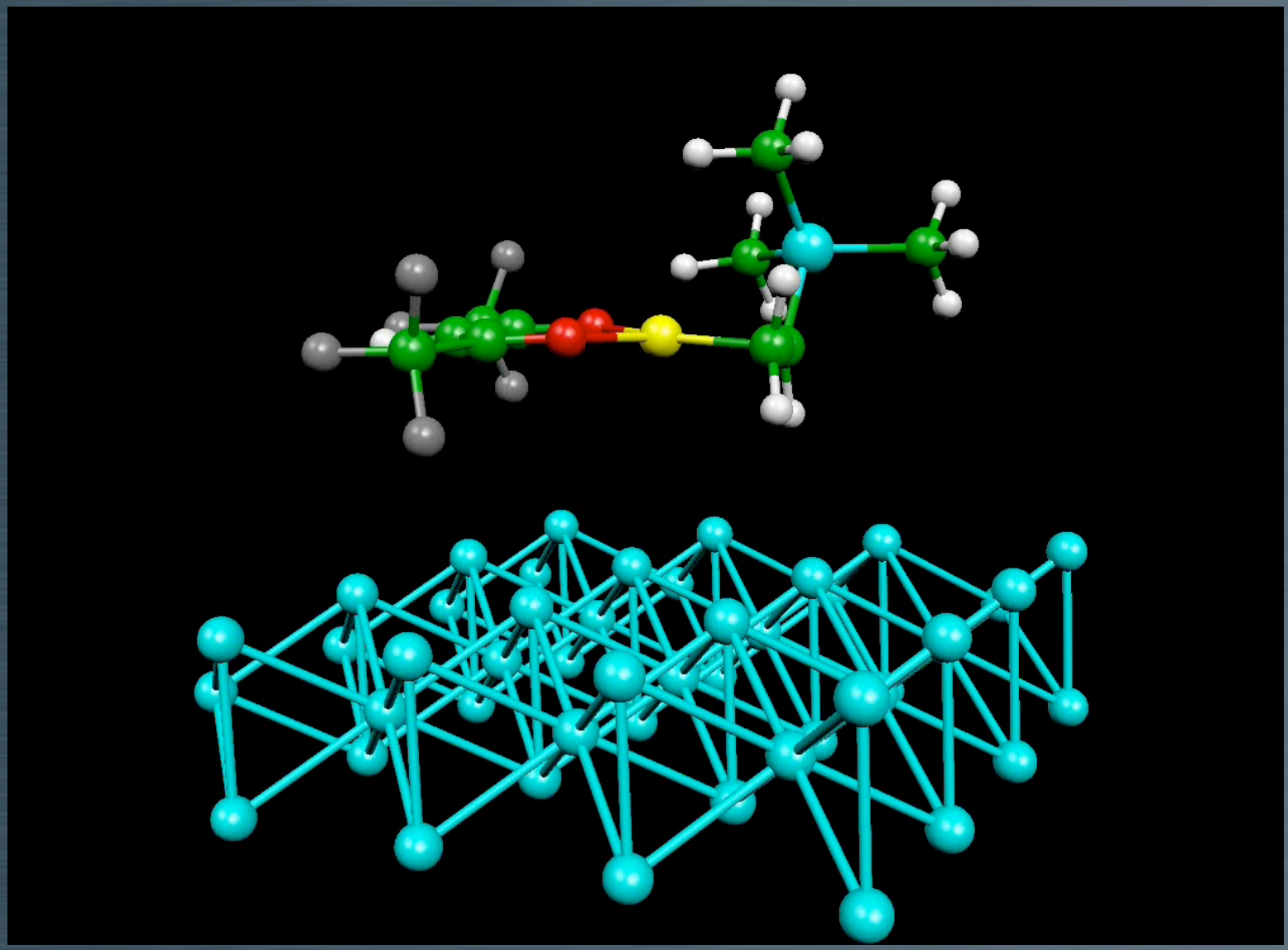
The problem:

CupraSelect produces thin Cu films on Ta, W, Ti which with very low adherence -- they ‘peel-off’ very easily

WHY, AND HOW TO FIX THE PROBLEM??

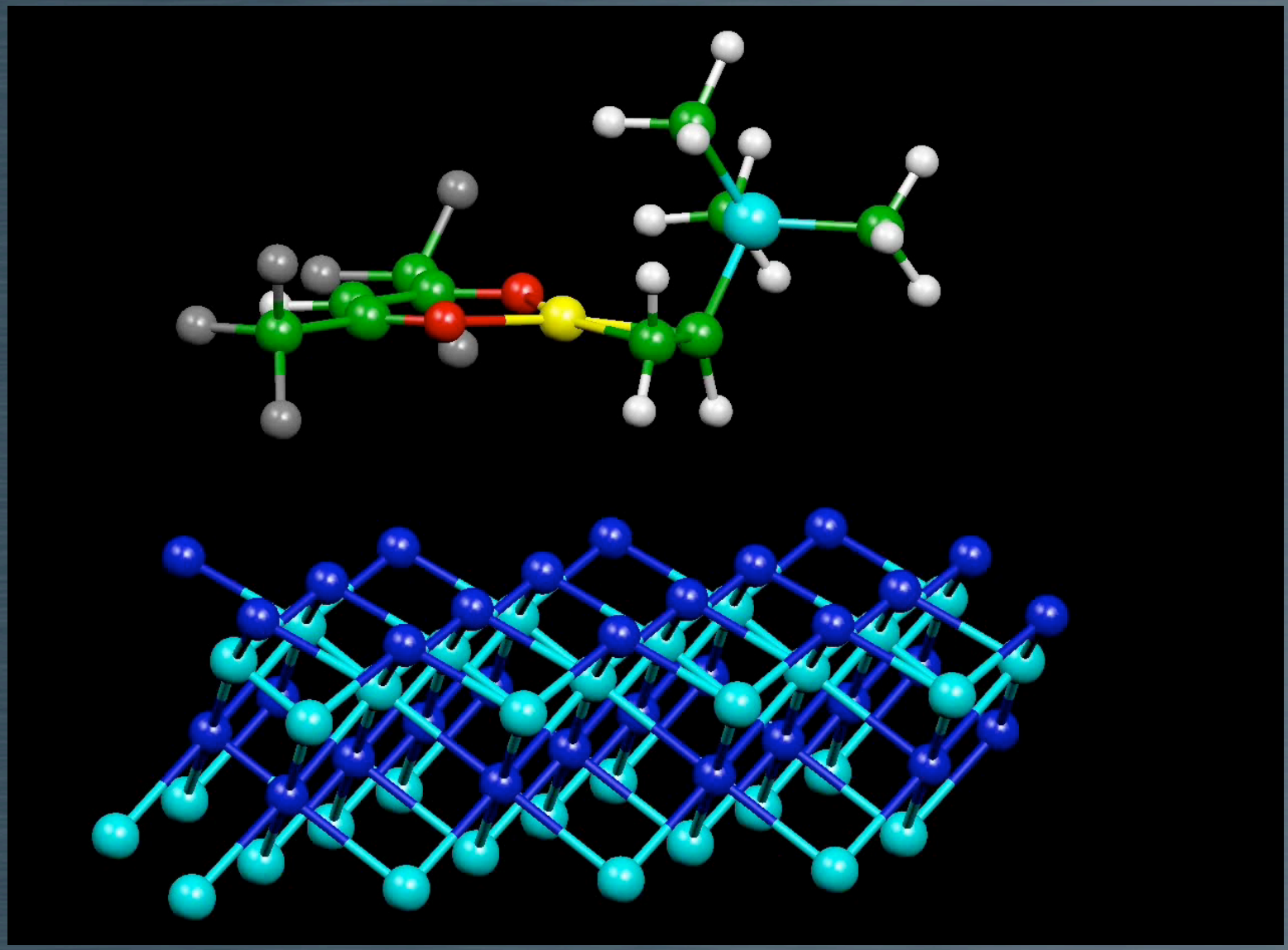
EXAMPLE:
An Industrial Problem

CIN2



EXAMPLE:
An Industrial Problem

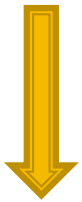
CIN2



Monte Carlo Methods
(statistical mechanics of classical particles)

- Suppose we want to compute a statistical average of a certain observable A:

$$\langle A \rangle = \frac{1}{N!} \frac{\sum_{\text{all } X} A(X) e^{-E(X)/k_B T}}{\sum_{\text{all } X} e^{-E(X)/k_B T}} \equiv \frac{1}{Z} \sum_{\text{all } X} A(X) e^{-E(X)/k_B T}$$



SAMPLE **all** WITH JUST **M** AT RANDOM

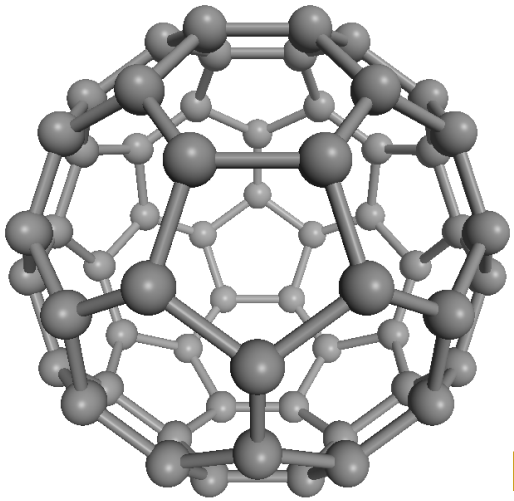
$$\langle A \rangle = \frac{1}{N!} \frac{\sum_{m=1}^{M} A(X_m) e^{-E(X_m)/k_B T}}{\sum_{m=1}^{M} e^{-E(X_m)/k_B T}}$$

WHY IS THIS NOT GOOD ENOUGH?

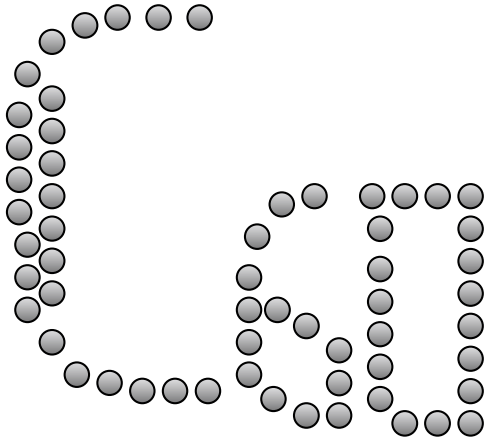
Monte Carlo Methods

$$\langle A \rangle = \frac{1}{N!} \frac{\sum_{m=1}^{M} A(X_m) e^{-E(X_m)/k_B T}}{\sum_{m=1}^{M} e^{-E(X_m)/k_B T}}$$

WHY IS THIS PURE RANDOM SAMPLING NOT GOOD ENOUGH?



SAMPLED WITH SAME PROBABILITY!



Importance Sampling:

$$\langle A \rangle = \sum_{\text{all } X} w(X) A(X), \quad w(X) = \frac{e^{-E(X)/k_B T}}{Z}$$

- The lower the energy $E(X_m)$ the more X_m contributes
- Our random sampling should concentrate on those X_m with low energy (this is what is called *importance sampling*)
- How to achieve that?

- Metropolis Method: an algorithm to produce a sequence of configurations $X_1, X_2, \ldots, X_M$ (Markov chain) such that

$$\lim_{M \to \infty} \frac{M_X}{M} = w(X)$$

Metropolis Algorithm:

- These are the steps of the Metropolis algorithm:

1) Pick any initial configuration X_m

2) Pick a trial configuration X_t (usually not far from X_m)

   Compute: $r = w(X_t)/w(X_m)$

   Draw a uniform deviate p between 0 and 1

   Set: $X_{m+1} = X_t \quad \text{if} \;\; p \leq r$

   $X_{m+1} = X_m \quad \text{if} \;\; p > r$

3) Go back to step 2 using X_{m+1} instead of X_m

4) When finished, compute average: $\langle A \rangle \approx \frac{1}{M} \sum_{m=1}^{M} w(X_m) A(X_m)$

Metropolis Algorithm:

- The new configurations are accepted or not following:

$$r = w(X_t)/w(X_m) = e^{-(E(X_t)-E(X_m))/k_B T} \qquad p \sim U(0,1)$$

$$\Longrightarrow \quad \begin{aligned} X_{m+1} &= X_t \quad \text{if} \;\; p \leq r \\ X_{m+1} &= X_m \quad \text{if} \;\; p > r \end{aligned}$$

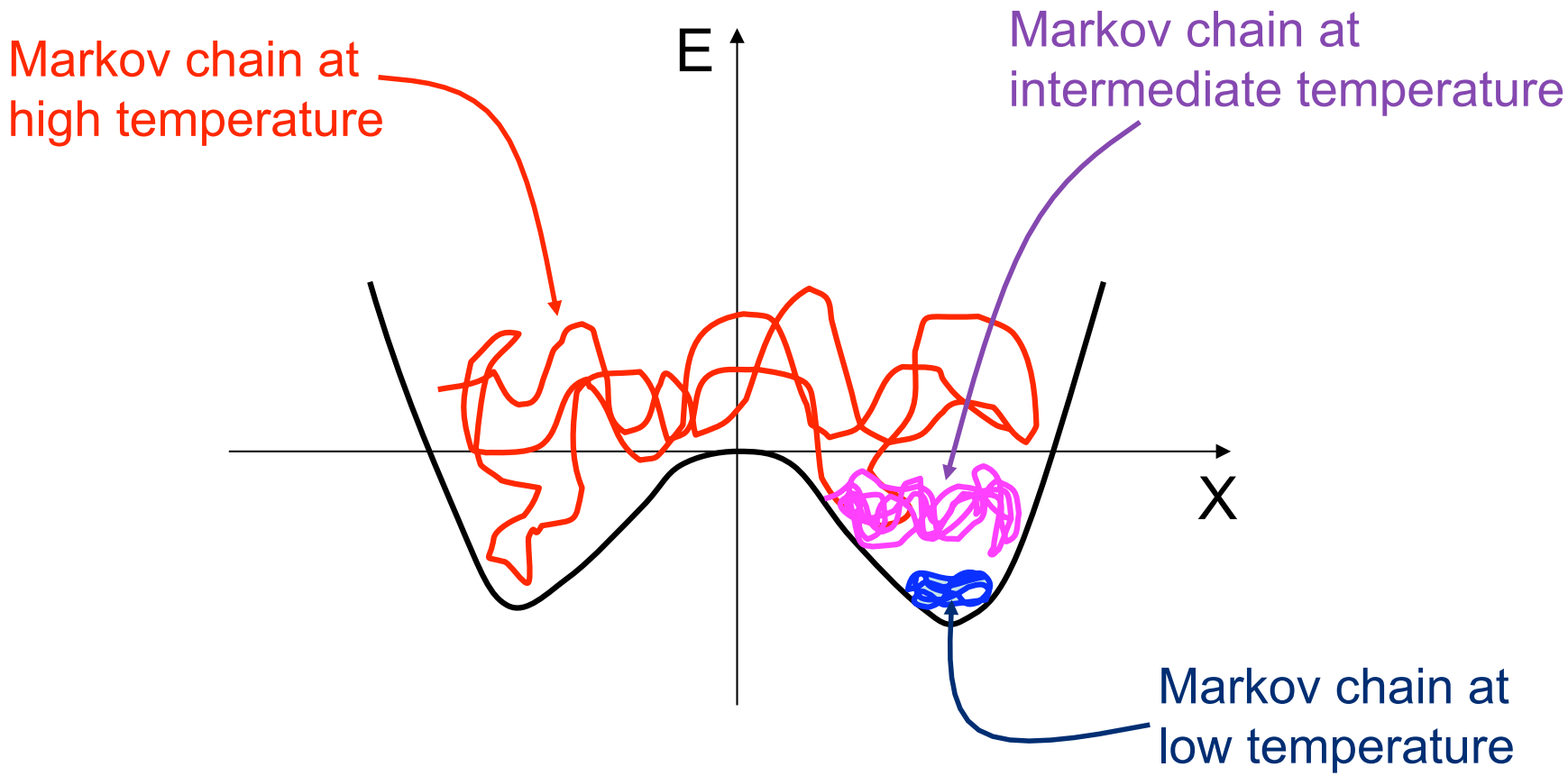
- Role of energy:

$$E(X_t) < E(X_m) \Rightarrow X_t \text{ ALWAYS accepted}$$
$$E(X_t) > E(X_m) \Rightarrow X_t \text{ SOMETIMES accepted}$$

- Role of temperature

$$T \to 0 \Rightarrow \text{ higher energies ALWAYS rejected}$$
$$T \to \infty \Rightarrow \text{ higher energies SOMETIMES accepted}$$

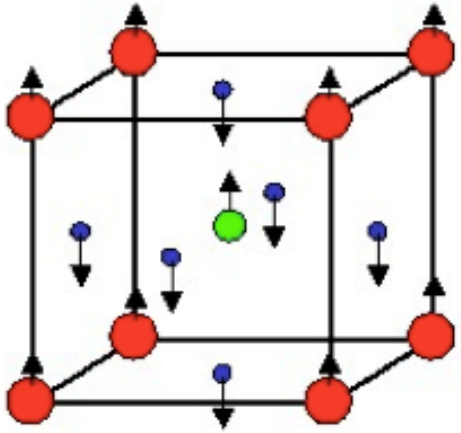
Monte Carlo and Phase Transitions



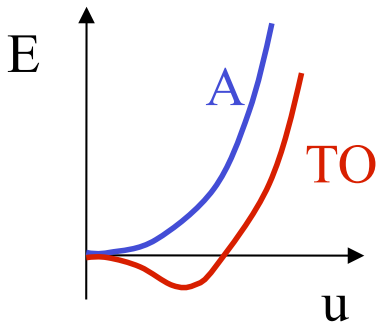
FERROELECTRIC TRANSITION: $BaTiO_3$

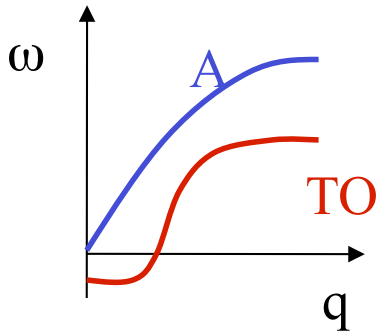
Zhong, Vanderbilt & Rabe, PRL **73**, 1861 (94)

- Free Energy: $F = -kT \ln \sum_j e^{-E_j / kT}$
- Monte-Carlo simulation $P \propto e^{-E_j / kT}$
  (Supercell: 12 × 12 × 12)
- Low energy modes:
  - Soft modes
  - Acoustic modes



(computed from first-principles calculations, and used in a simplified model Hamiltonian)





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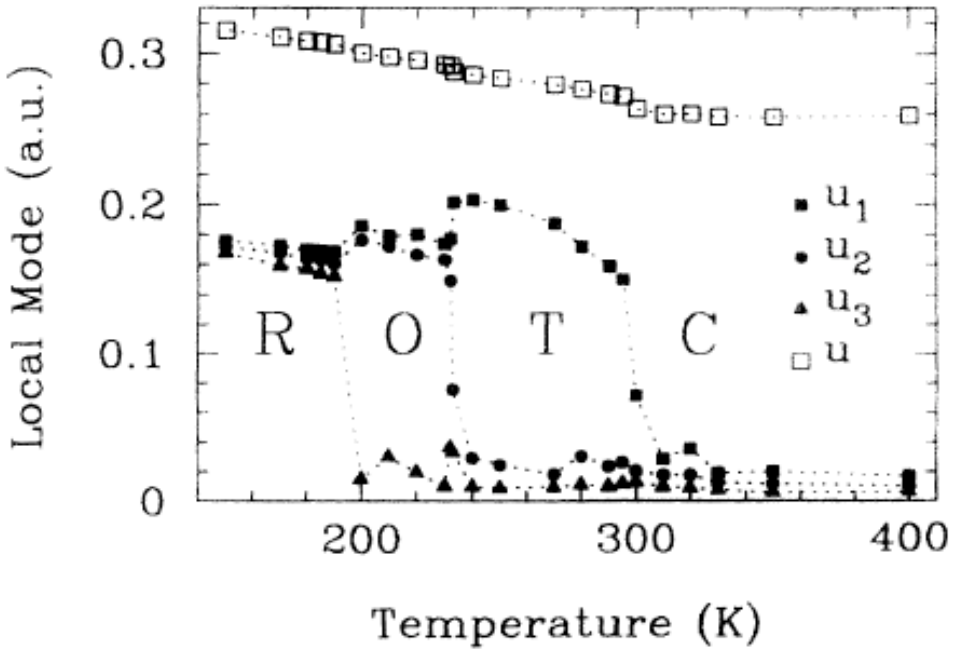


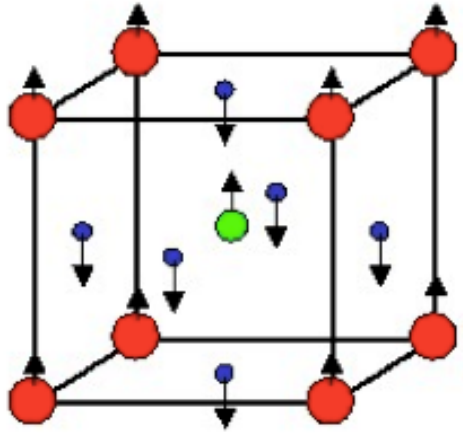


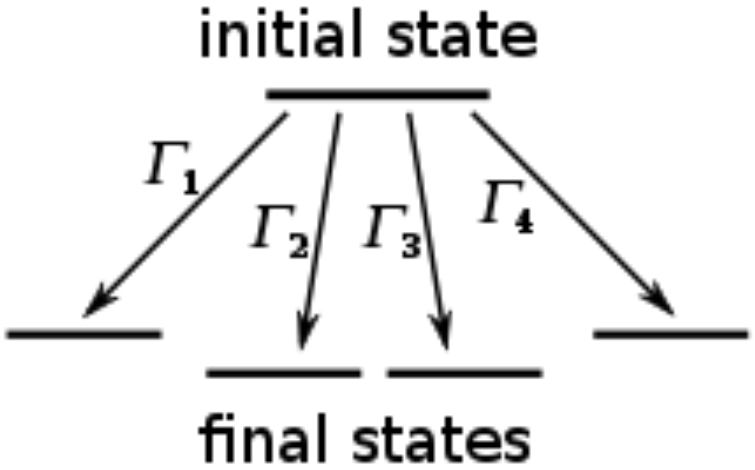
TABLE I. Calculated transition temperatures T_c, saturated spontaneous polarization P_s, and estimated latent heat l, as a function of simulation cell size.

	Phase	$L = 10$	$L = 14$	Expt.[a]
T_c (K)	*O-T*	197 ± 3	200 ± 5	183
	T-O	230 ± 10	230 ± 10	278
	C-T	~ 290	297 ± 1	403
P_s (C/m^2)	*R*	0.43	0.43	0.33
	O	0.35	0.35	0.36
	T	0.28	0.28	0.27
l (J / mol)	*O-R*	50	60	33-60
	T-O	90	100	65-92
	C-T	···	150	196-209

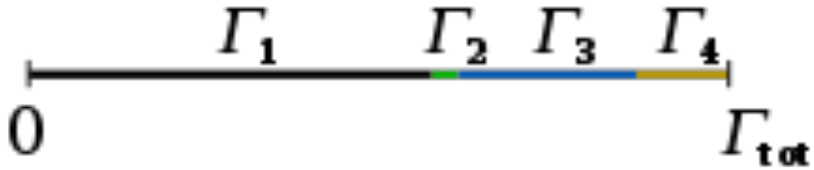
[a]T. Mitsui *et al.*, *Landolt-Bornstein Numerical Data and Functional Relationships in Science and Technology (Springer-Verlag, 1981)*, NS, III/**16**.

Time evolution: Kinetic Monte Carlo

- If we know the relevant processes and their rate, we can use Kinetic Monte Carlo to study the time evolution.
- The processes and their rates are INPUT to the KMC solver (they must be known a-priori)
- The processes must be Poissonian and uncorrelated to each other



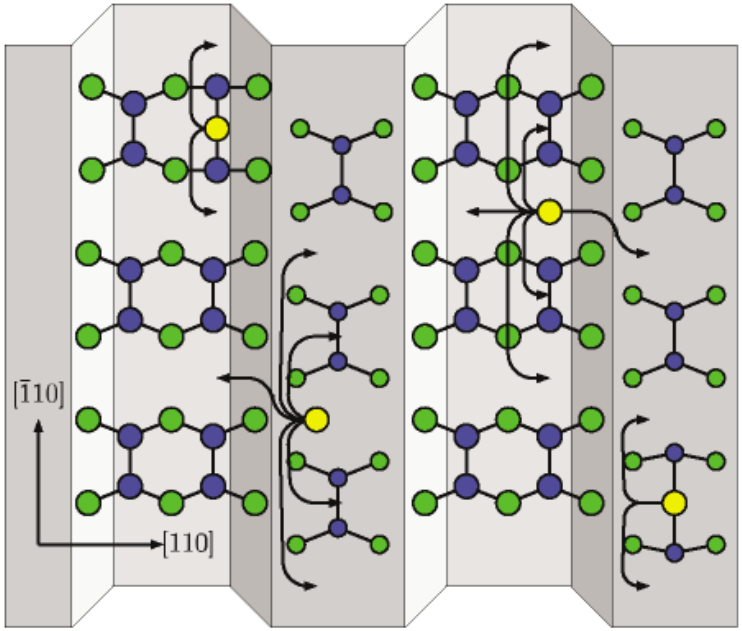
Random variable drawn from 0 to Γ_{tot} to choose which jump i to make (probability proportional to Γ_i)

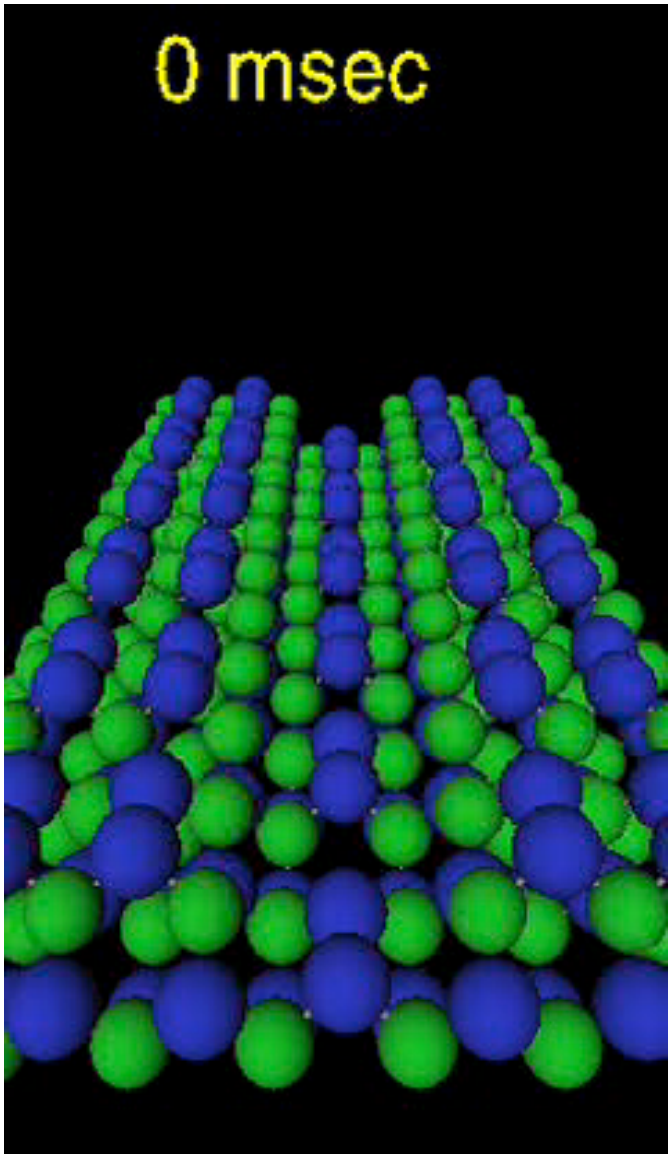


Kinetic Monte Carlo for crystal growth

P. Kratzner and M. Scheffler,
PRL 88, 036102 (2002)

Growth of GaAs (001) surface
many processes considered (adsorption, desorption, diffusion, incorporation...)





Monte Carlo Methods

to solve quantum problems...

Ground state properties:

- Variational Monte Carlo
- Diffusion Monte Carlo

Methods for finite temperatures are also available

VARIATIONAL MONTE CARLO

Use explicitly the Monte Carlo integration method to compute the energy of a given 'trial' many body wave function:

$$\psi_T(R) \quad (R = \{r_1,\ldots,r_N\})$$

$$E = \frac{\int \psi_T^* \hat{H} \psi_T \, dR}{\int \psi_T^* \psi_T \, dR} = \frac{\int |\psi_T|^2 \frac{\hat{H}\psi_T}{\psi_T} \, dR}{\int |\psi_T|^2 \, dR} = \sum_i \frac{\hat{H}\psi_T(R_i)}{\psi_T(R_i)} = \sum_i E_L(R_i)$$

Metropolis algorithm: sampling configurations from $|\psi_T|^2$

- The solution is only as good as the trial wave function!
- Allows optimizing somewhat the trial wf. (parametric)
- Reasonable computational cost - large systems (~100 atoms)

VARIATIONAL MONTE CARLO

C[N2

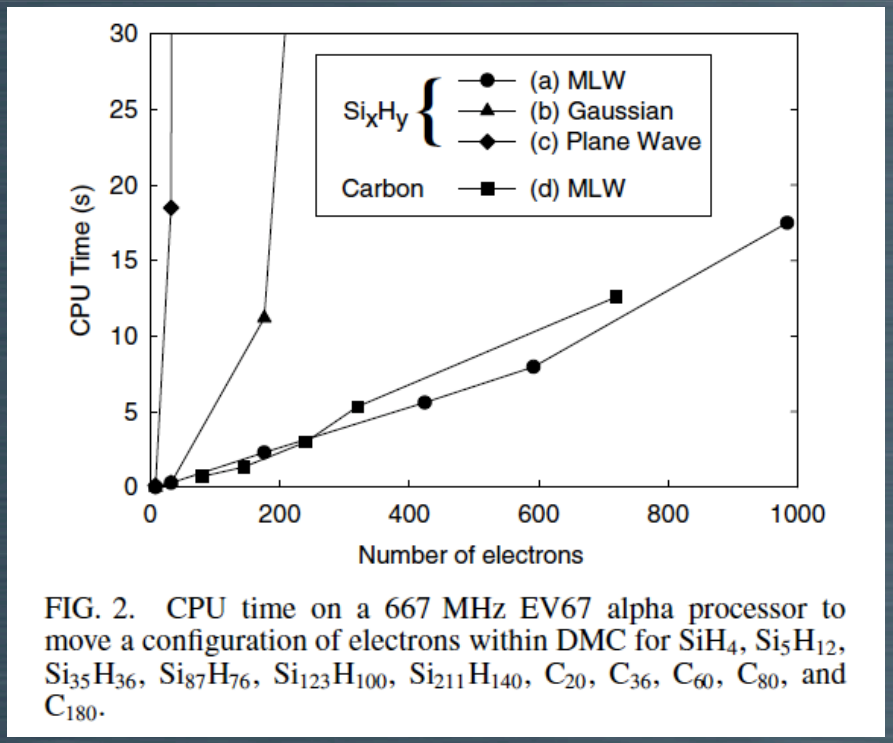
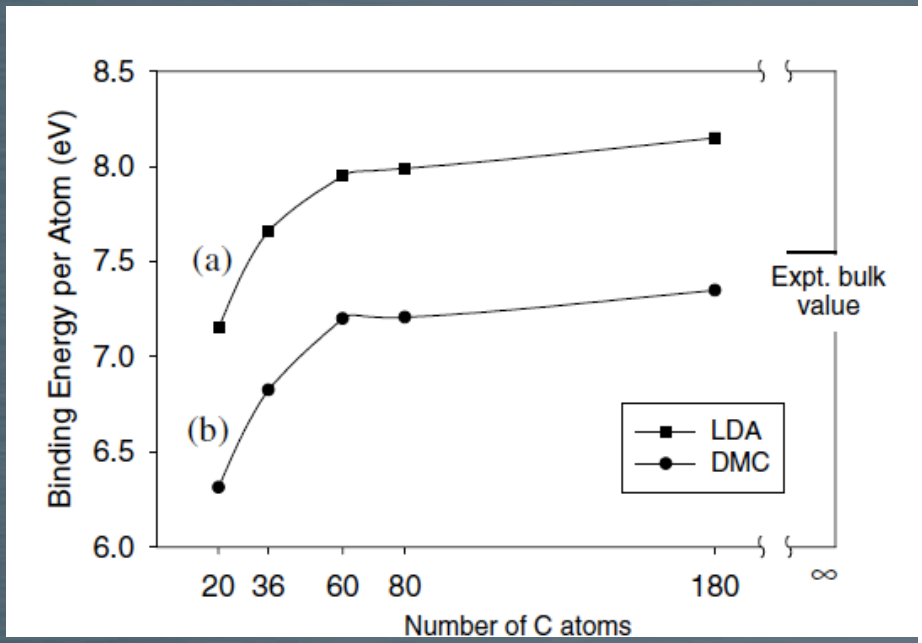
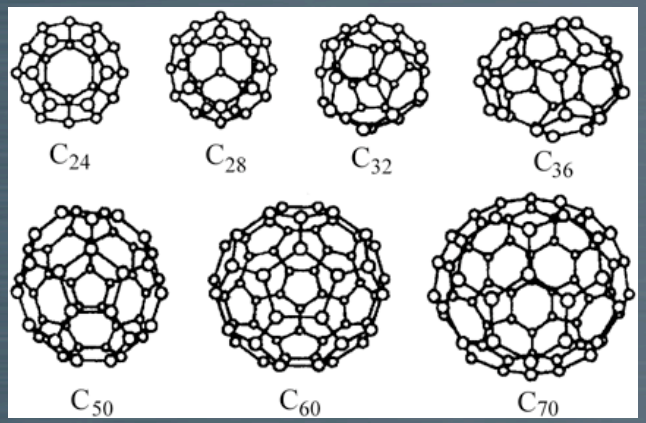
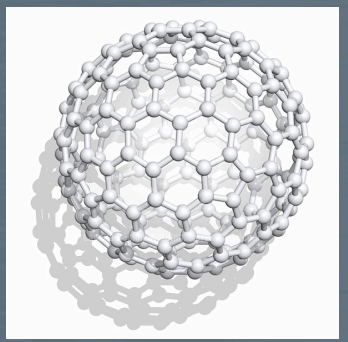


FIG. 2. CPU time on a 667 MHz EV67 alpha processor to move a configuration of electrons within DMC for SiH_4, Si_5H_{12}, $Si_{35}H_{36}$, $Si_{87}H_{76}$, $Si_{123}H_{100}$, $Si_{211}H_{140}$, C_{20}, C_{36}, C_{60}, C_{80}, and C_{180}.



Grossman et al., PRL (2001)





DIFFUSION MONTE CARLO

A method to calculate the EXACT ground state of a many-body system, starting from a trial wave function $\psi_T(R)$:

- Evolution in imaginary time:

$$e^{-\beta H}\psi_T = \sum_i e^{-\beta\varepsilon_i}\Phi_i\langle\Phi_i|\psi_T\rangle$$

- For large β: only GS survives!

$$\lim_{\beta\to\infty} e^{-\beta H}\psi_T = \Phi_0 e^{-\beta\varepsilon_0}\langle\Phi_0|\psi_T\rangle$$

Equations for time evolution of ψ_T can be put in the form of a diffusion equation

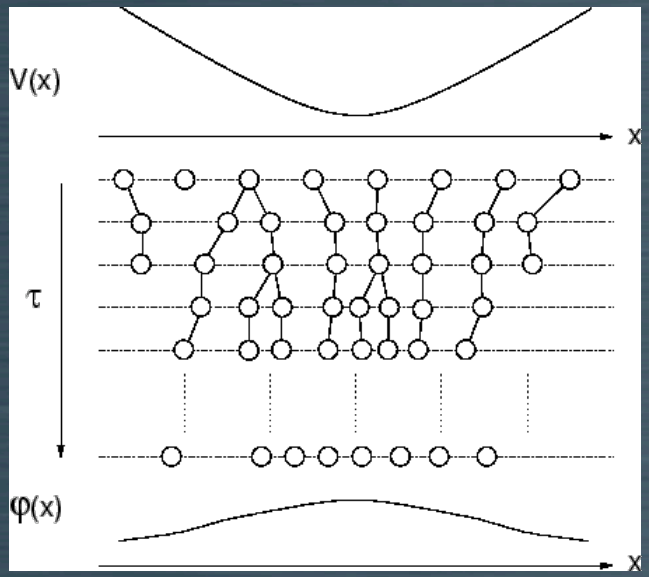
$$-\frac{\partial\psi(\mathbf{R},\tau)}{\partial\tau} = \left[\sum_{i=1}^{N} -\frac{1}{2}\nabla_i^2\psi(\mathbf{R},\tau)\right] + (V(\mathbf{R}) - E_T)\psi(\mathbf{R},\tau) \quad .$$

DIFFUSION MONTE CARLO

Monte Carlo solution of the Diffusion Equation:

$$-\frac{\partial \psi(\mathbf{R},\tau)}{\partial \tau} = \left[\sum_{i=1}^{N} -\frac{1}{2}\nabla_i^2 \psi(\mathbf{R},\tau)\right] + (V(\mathbf{R}) - E_T)\psi(\mathbf{R},\tau) \quad .$$

- $\psi_T(R)$ is interpreted as a density of diffusive particles (walkers)
- $(V(R)\text{-}E_T)$ is a rate term the increase or decrease of particle density



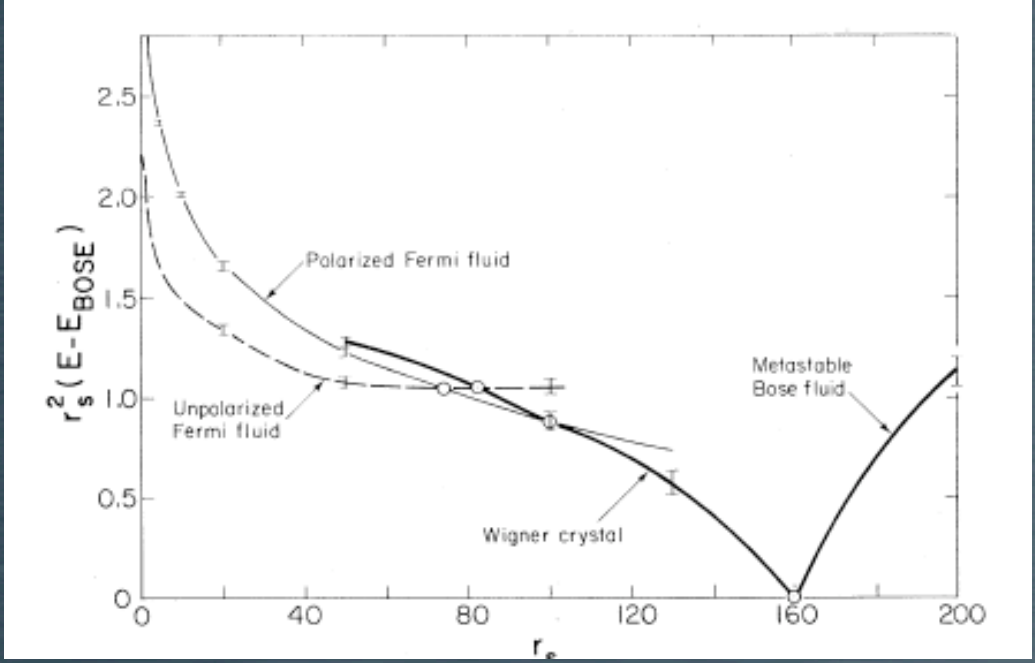
- More costly than VMC
- Essentially exact for Bosons (within statistical noise)
- Problems for Fermions: sign of the wavefunction can be negative (Pauli)
- 'Fixed sign' approximation (assume that the ground state wavefunction has the same nodes as the trial wavefunction).

DIFFUSION MONTE CARLO

VOLUME 45, NUMBER 7 PHYSICAL REVIEW LETTERS 18 AUGUST 1980

Ground State of the Electron Gas by a Stochastic Method

D. M. Ceperley
National Resource for Computation in Chemistry, Lawrence Berkeley Laboratory, Berkeley, California 94720
and
B. J. Alder
Lawrence Livermore Laboratory, University of California, Livermore, California 94550

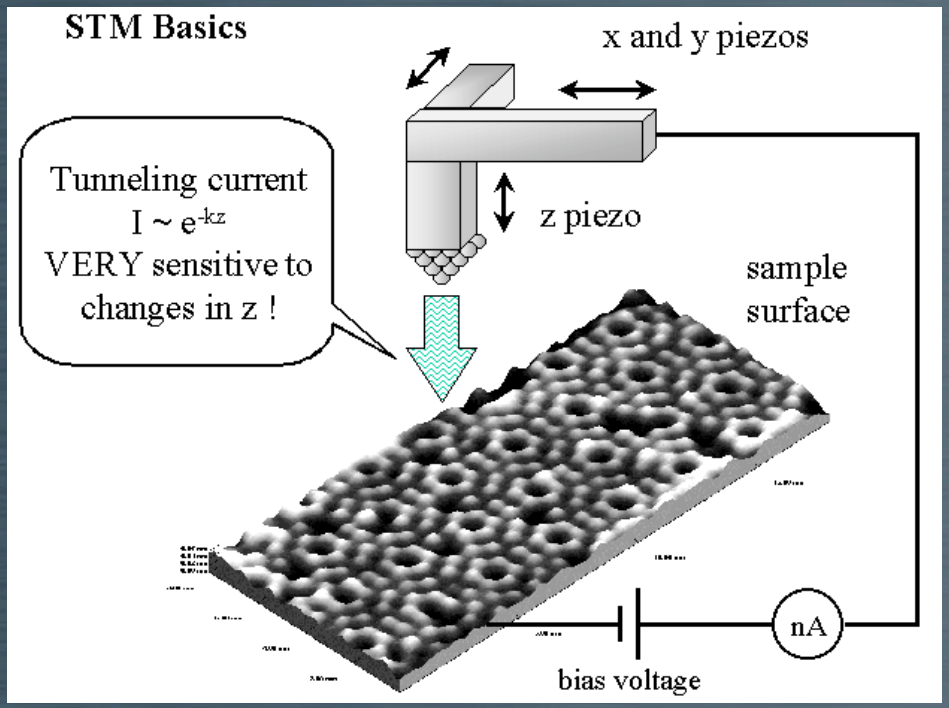


- Results used to obtain DFT functionals $\varepsilon_{xc}(n)$
- ~7000 citations!!

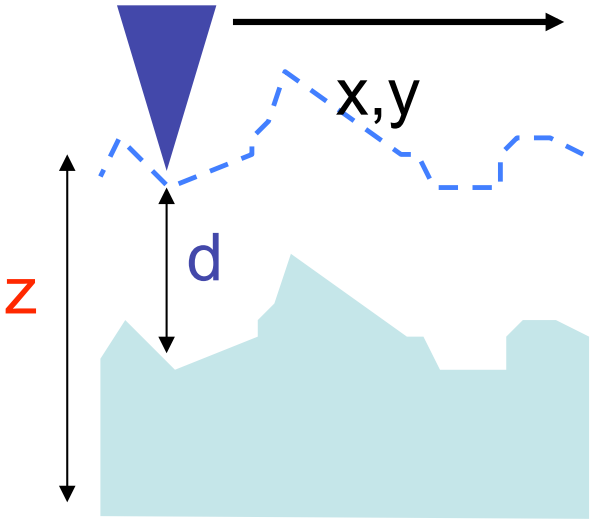
SIMULATIONS OF ELECTRONIC PROPERTIES: STM

Scanning Tunneling Microscopy:

- Invented in the 80's by Binning and Rohrer
- Characterization AND manipulation of surfaces at the atomic level
- A tool that revolutionized surface physics and brought Nanoscience!!



SIMULATIONS OF ELECTRONIC PROPERTIES: STM

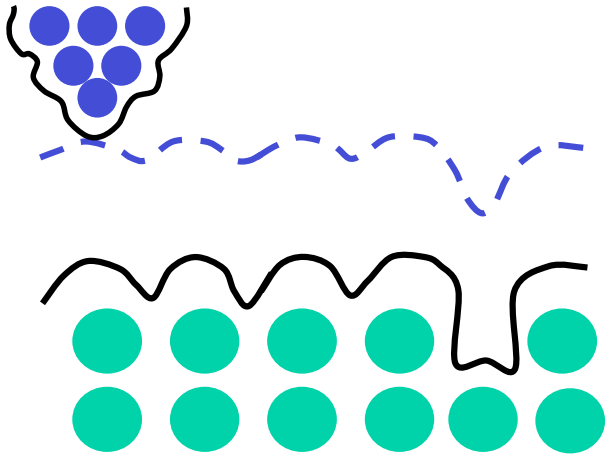


Constant current mode

I = fixed constant ➔ d = constant

z = z(x,y) measured (VERY sensitively)

- Atomic resolution (for atomically sharp tips)
- Convolution between surface and tip



SIMULATIONS OF ELECTRONIC PROPERTIES: STM

Tunneling current depends on

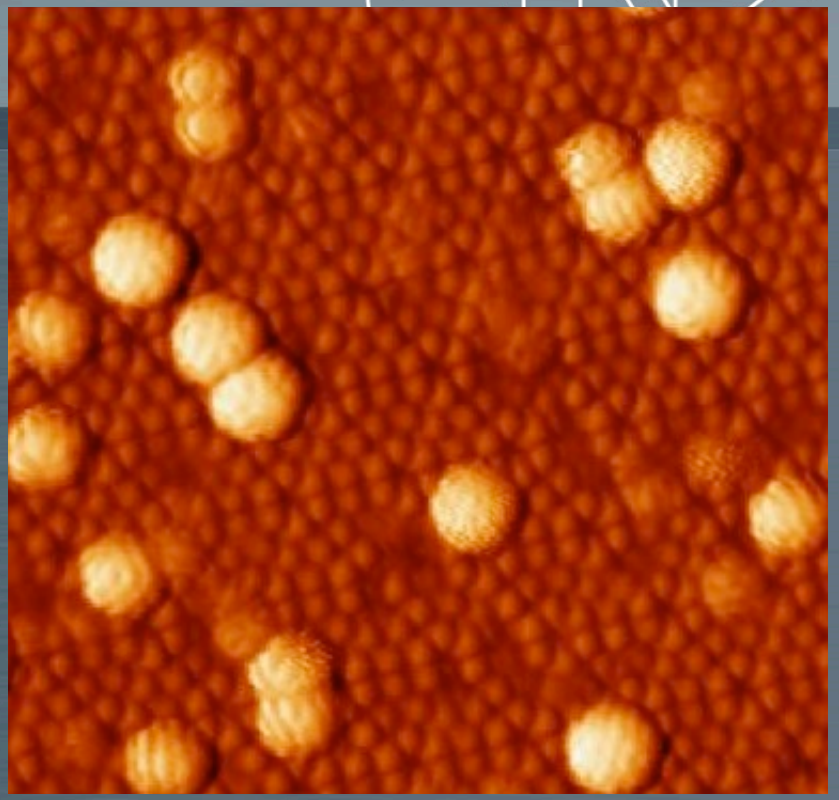
- distance between surface and tip
- materials (both sample and tip)
- atomic AND electronic structure of surface AND tip
- voltage ....

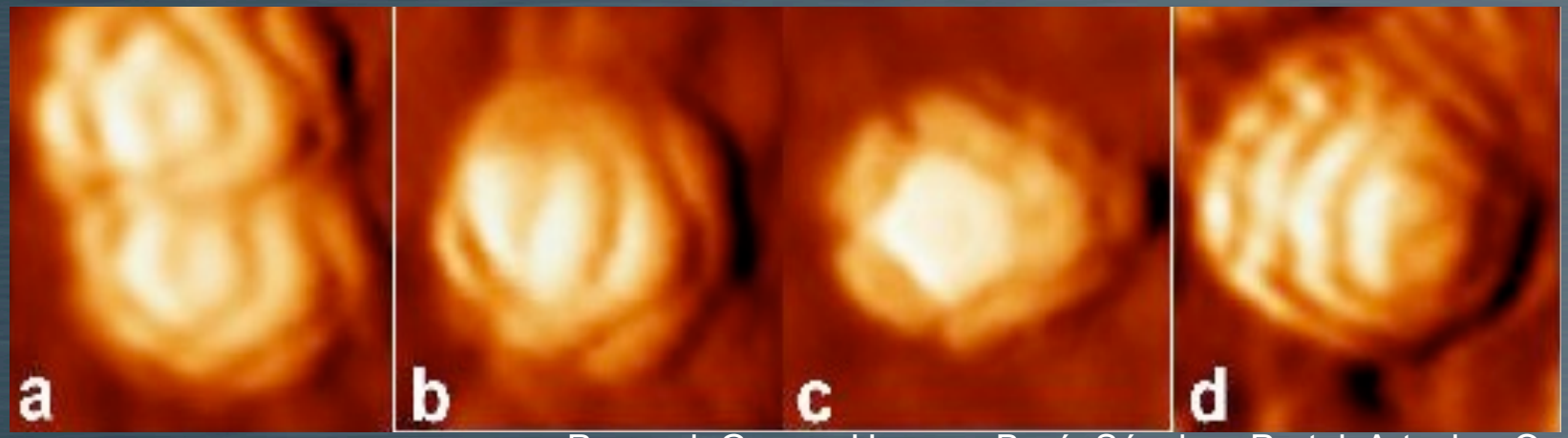
STM does not see the ‘atoms’; it sees the electronic states!

Theory and Simulation are essential to interpret the experimental images.

SIMULATION AND EXPERIMENT…
… IN NANOSCIENCE

C_{60} on Si(111) 7x7





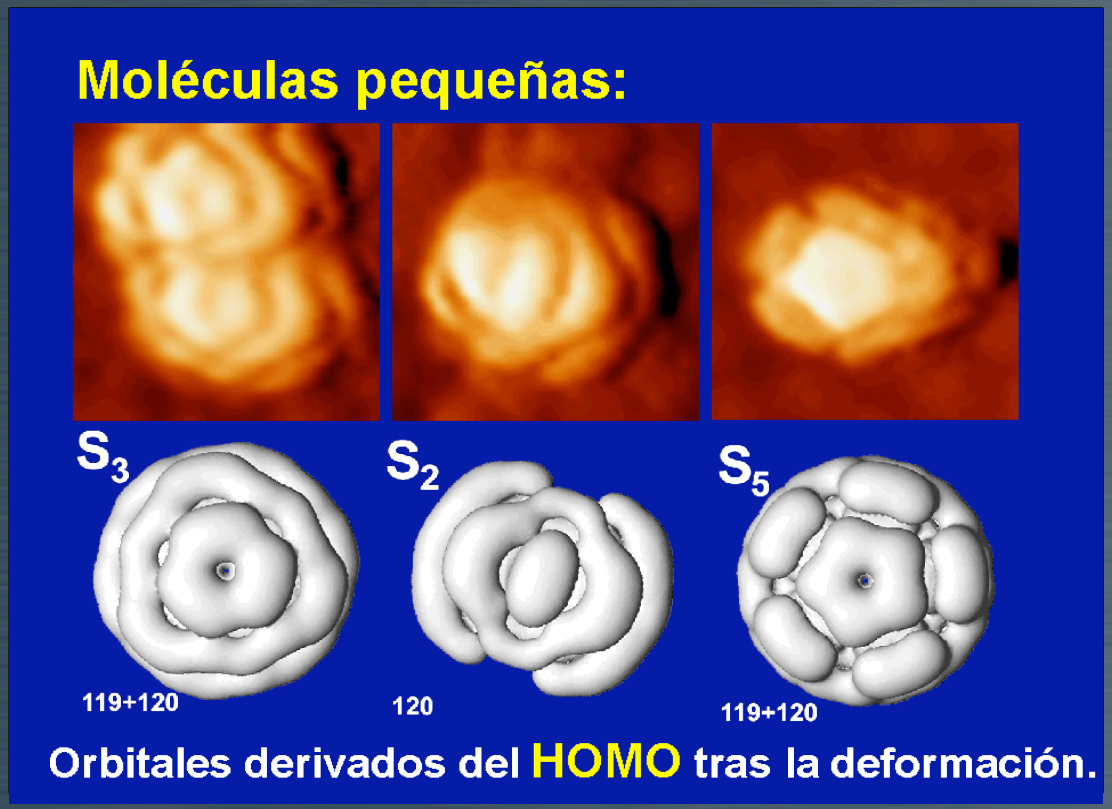
Pascual, Gomez-Herrero, Baró, Sánchez-Portal, Artacho, Ordejón and Soler,

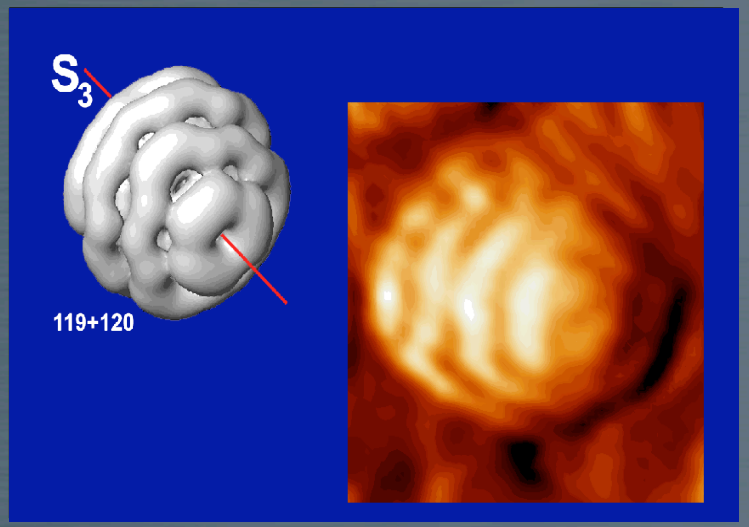
Phys. Rev. Lett. **85**, 2653 (2000)

SIMULATION AND EXPERIMENT…
… IN NANOSCIENCE

CIN2

C_{60} on Si(111) 7x7





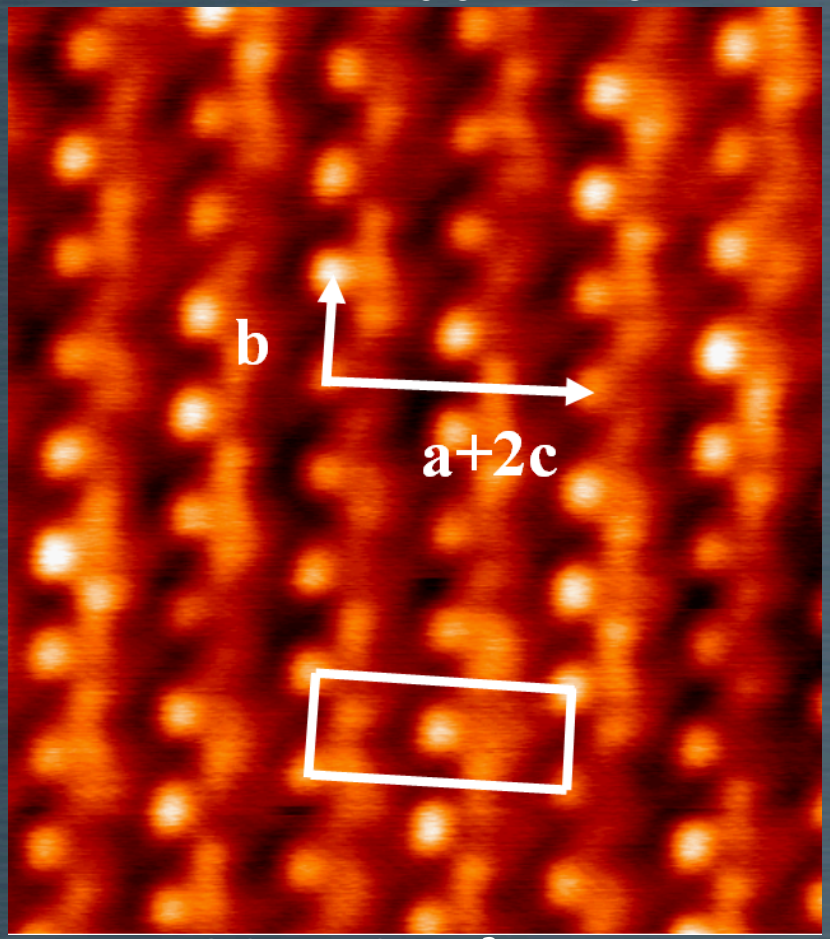
Pascual, Gomez-Herrero, Baró, Sánchez-Portal, Artacho, Ordejón and Soler,

Phys. Rev. Lett. **85**, 2653 (2000)

SIMULATION AND EXPERIMENT…
… IN NANOSCIENCE

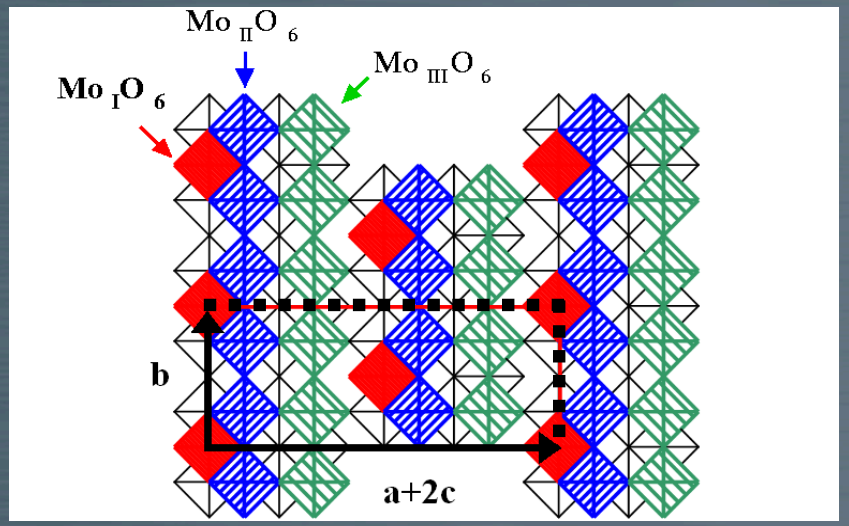
CIN2

Blue bronze: $Rb_{0.3}MoO_3$ ‘CHARGE DENSITY WAVES’



6.2 x 7.0 nm²

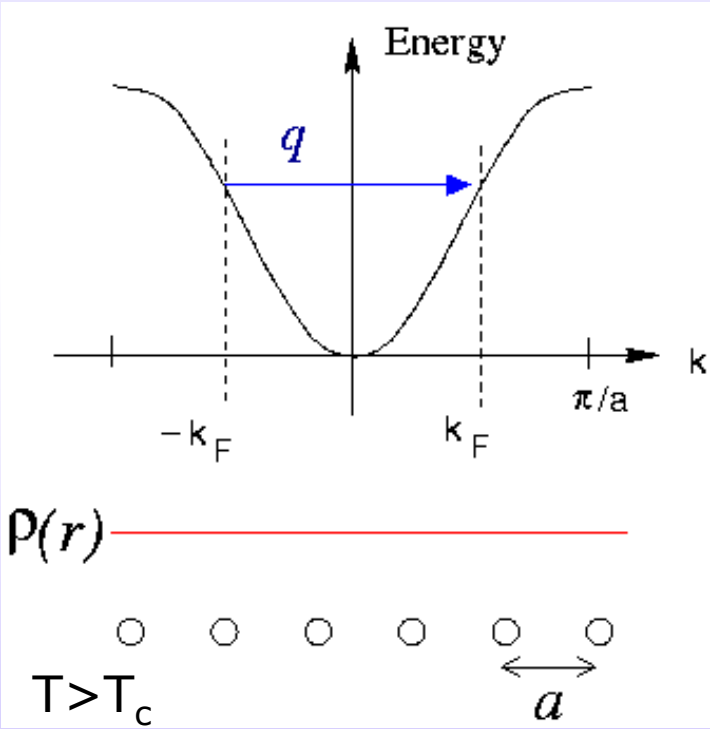
STM image at 63 K.



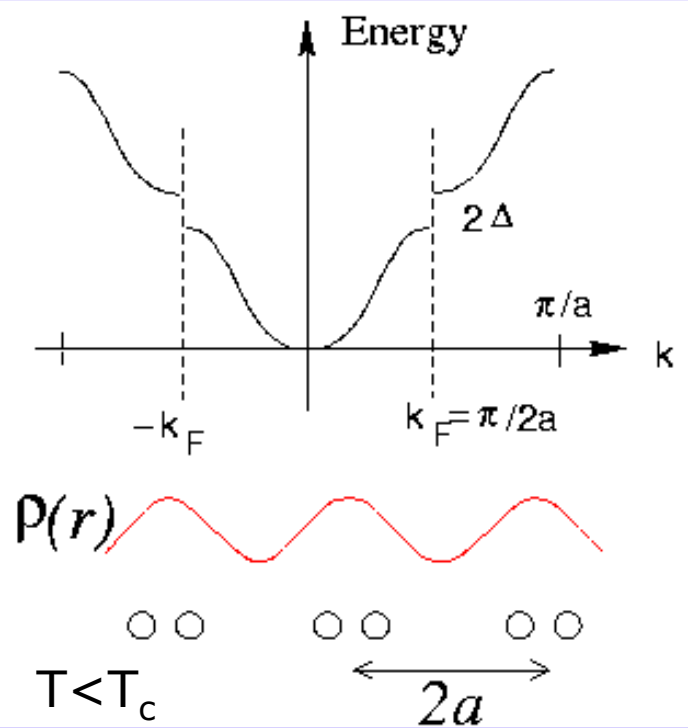
Brun.et al. *PRB* **72**, 235119 (2005)

Charge Density Modulation (waves)

In systems with1D bands: existence of 'Peierls Instabilities'



Periodic electron density

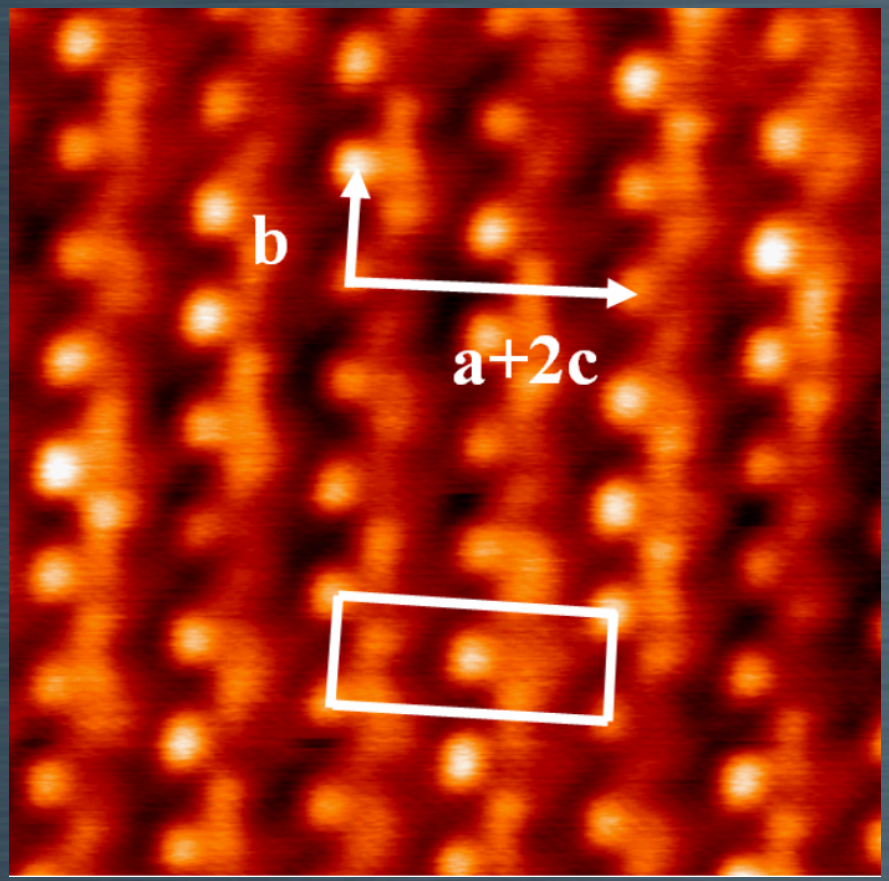


Modulated Electron density
(*Charge Density Wave*)

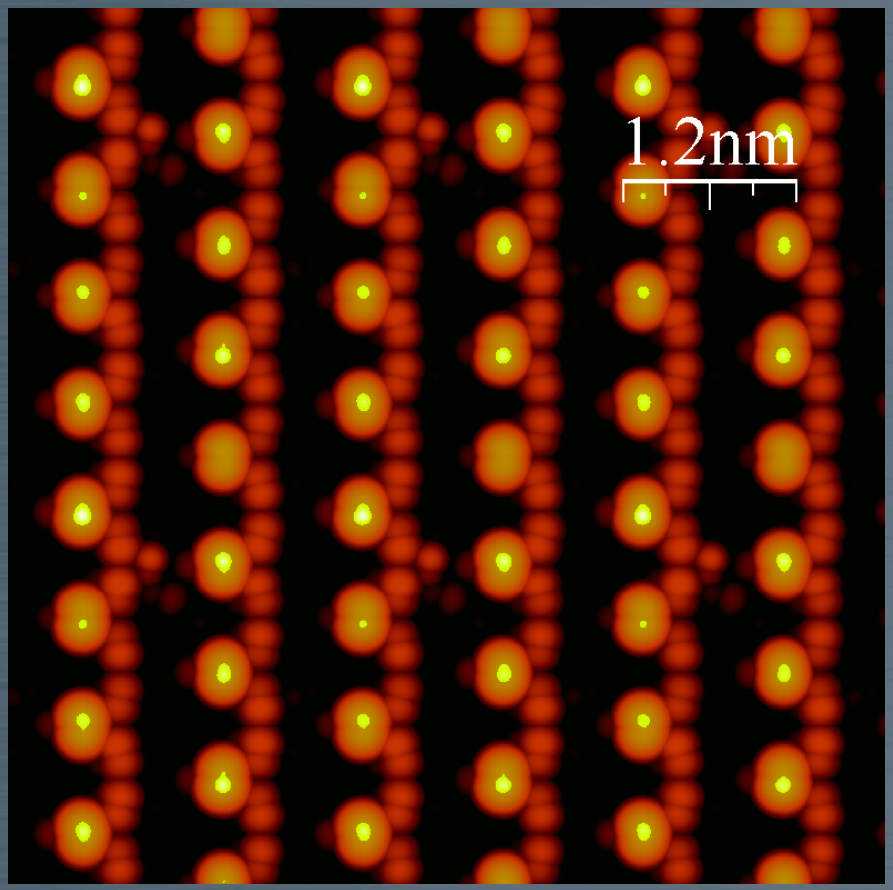
SIMULATION AND EXPERIMENT…
… IN NANOSCIENCE

CIN2

Experiment



Simulation

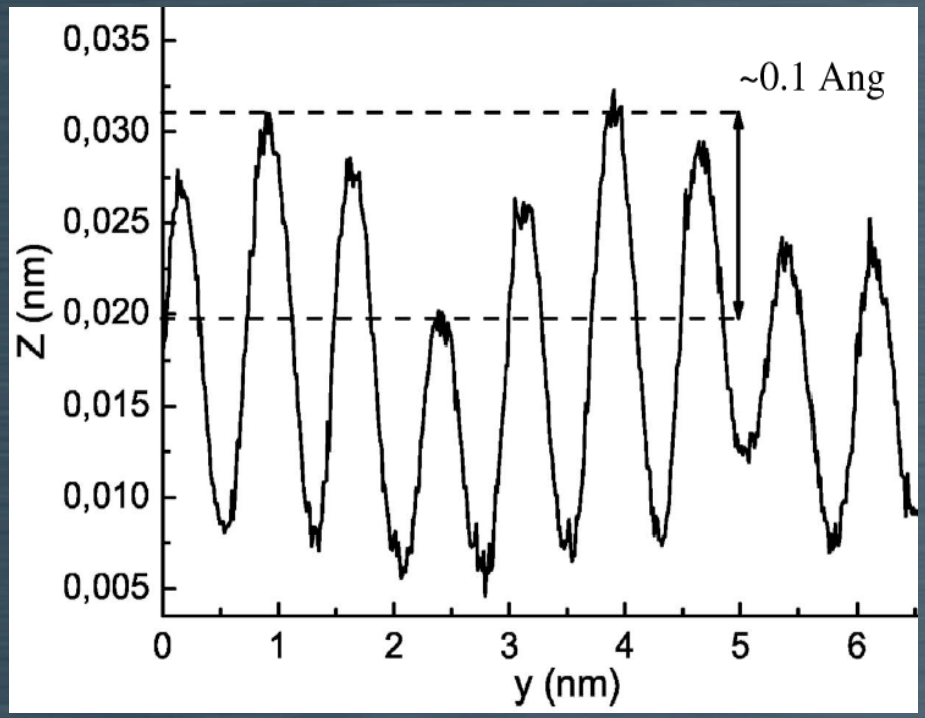


Machado-Charry, Ordejón, Canadell, Brun, Wang., *PRB* **74**, 155123 (2006)

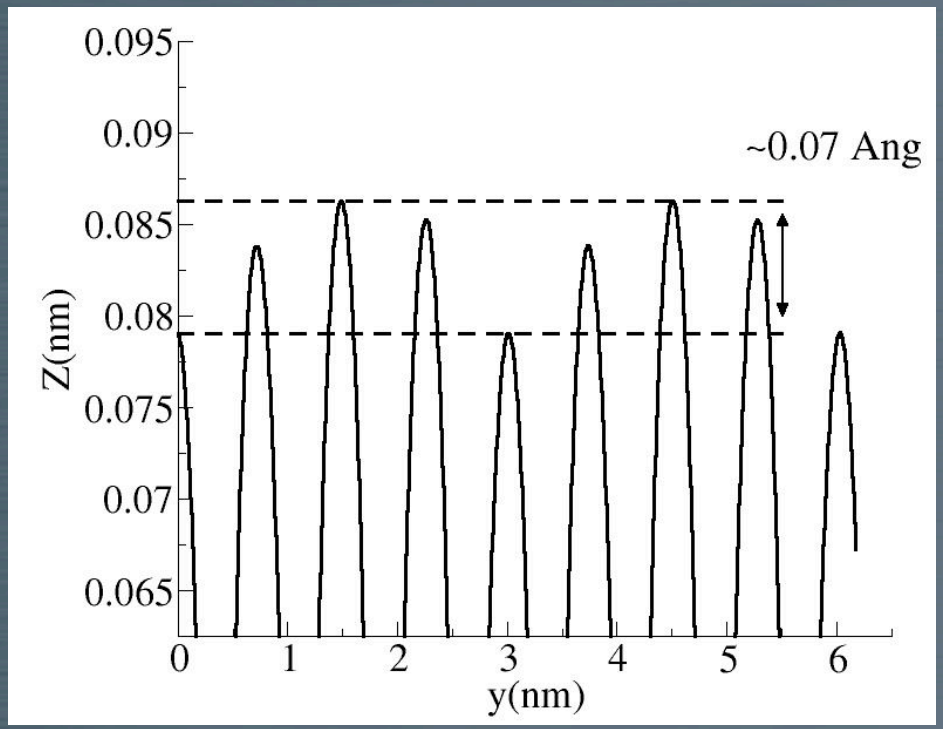
SIMULATION AND EXPERIMENT…
… IN NANOSCIENCE

Profiles: Measured corrugation shows charge profile, rather than atomic profile.

Experiment



Simulation



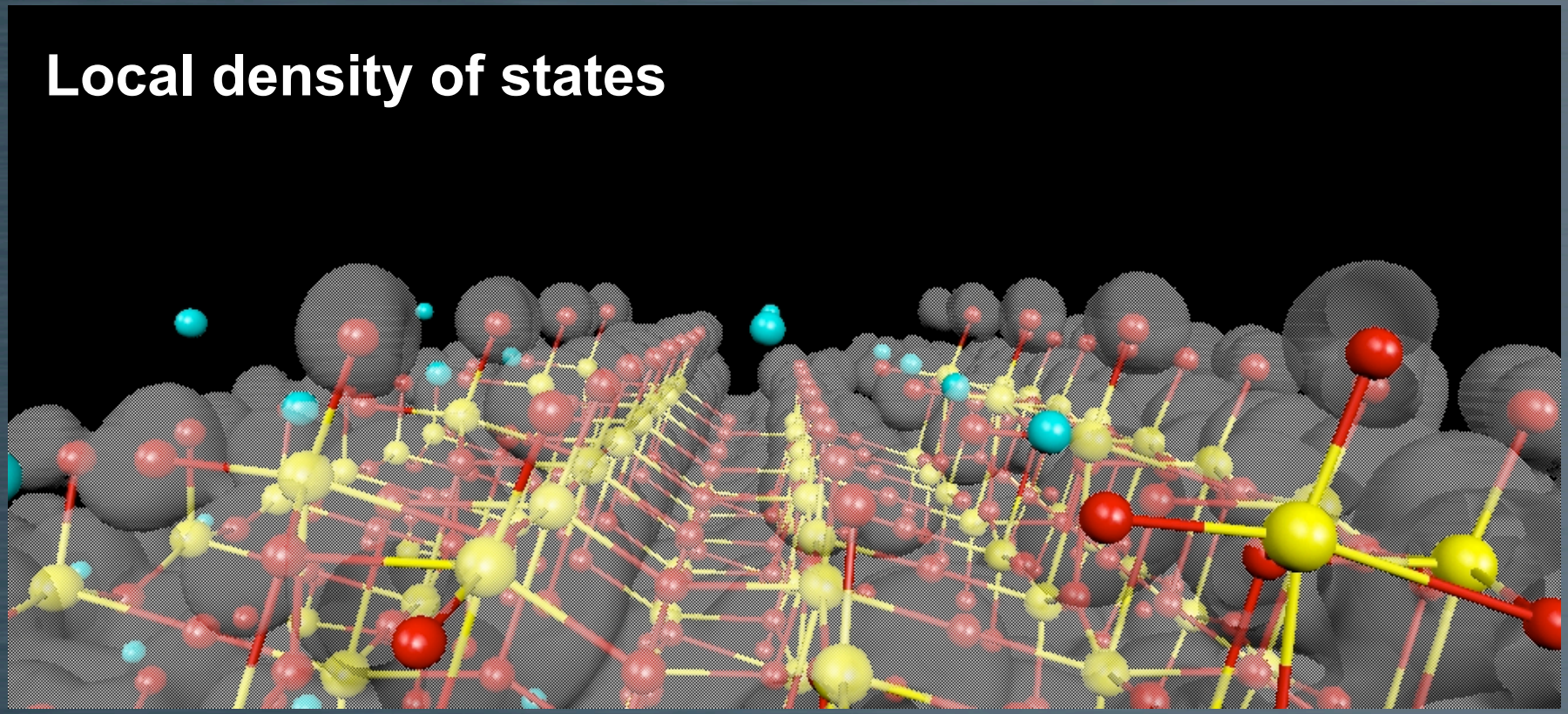
Atomic corrugation (bulk, from X-Rays): 0.018 Ang

similar in surface, as shown in our simulations.

SIMULATION AND EXPERIMENT…
… IN NANOSCIENCE

CIN2

Local density of states



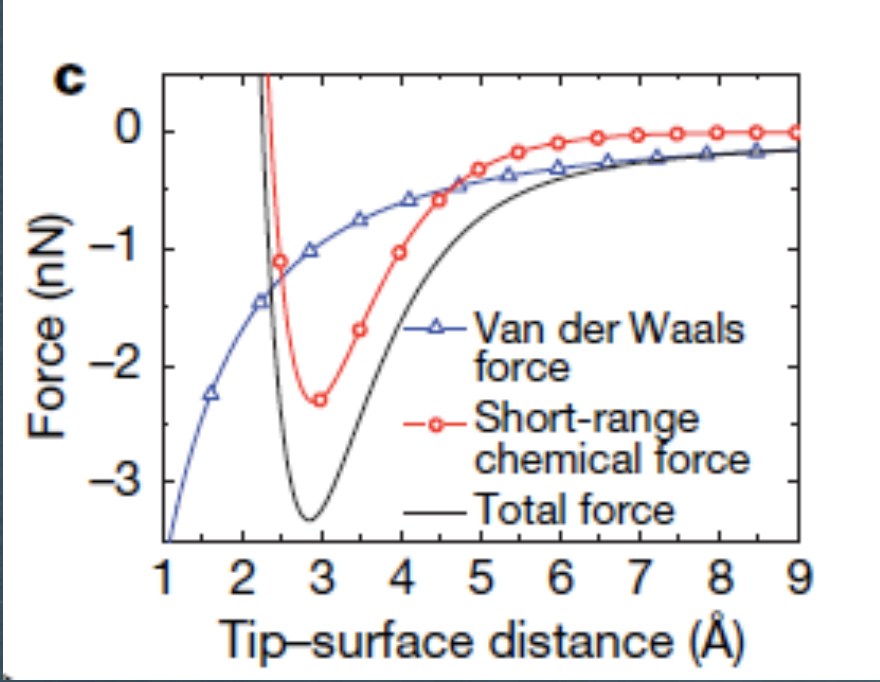
Tunneling current ~ LDOS (E_F , V_{bias})

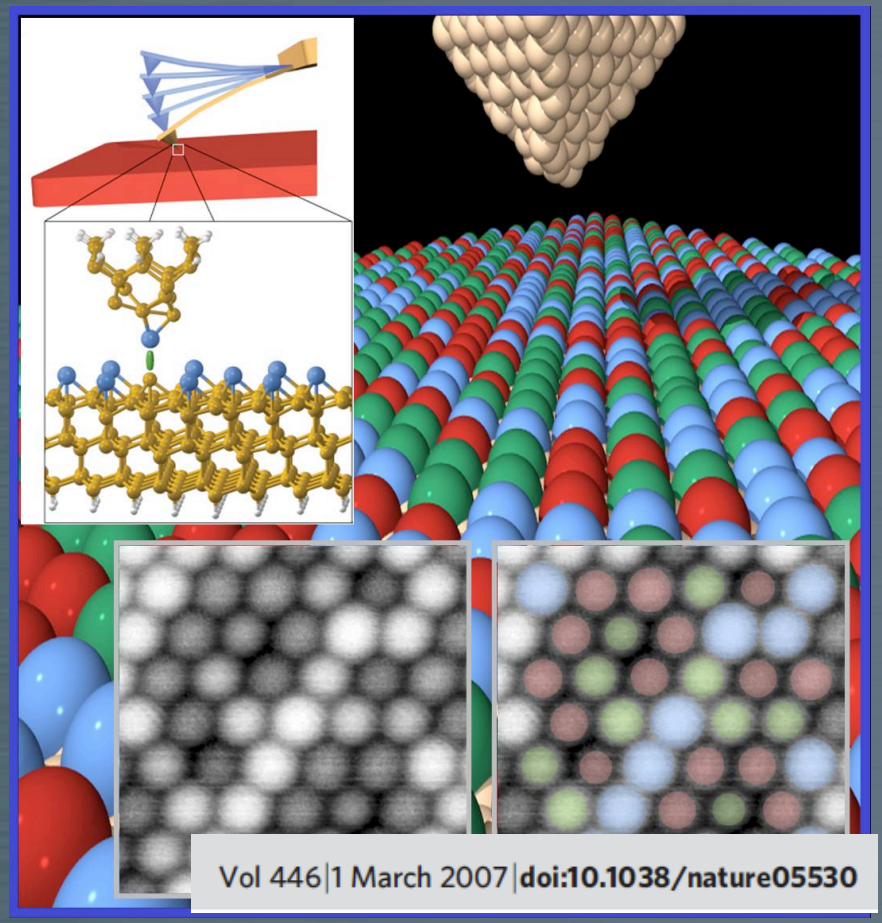
- Mo_I 1.9 %
- Mo_{II} 42.5 %
- Mo_{III} 22.1 %
- Highest Oxygen **1.2**%

OTHER SCANNING PROBE MICROSCOPIES: AFM

Atomic Force Microscopy

(Ruben Perez, UAM)





Si / Sb / Pb on Si(111)

.... Thank you!

Pablo Ordejón
pablo.ordejon@cin2.es
Theory and Simulation Group

CSIC

ICN2 Institut Català de Nanotecnologia

CIN2

CENTRE D'INVESTIGACIÓ
EN NANOCIÈNCIA
I NANOTECNOLOGIA

CAMPUS UAB. BELLATERRA. BARCELONA

Challenges of Simulation of Materials

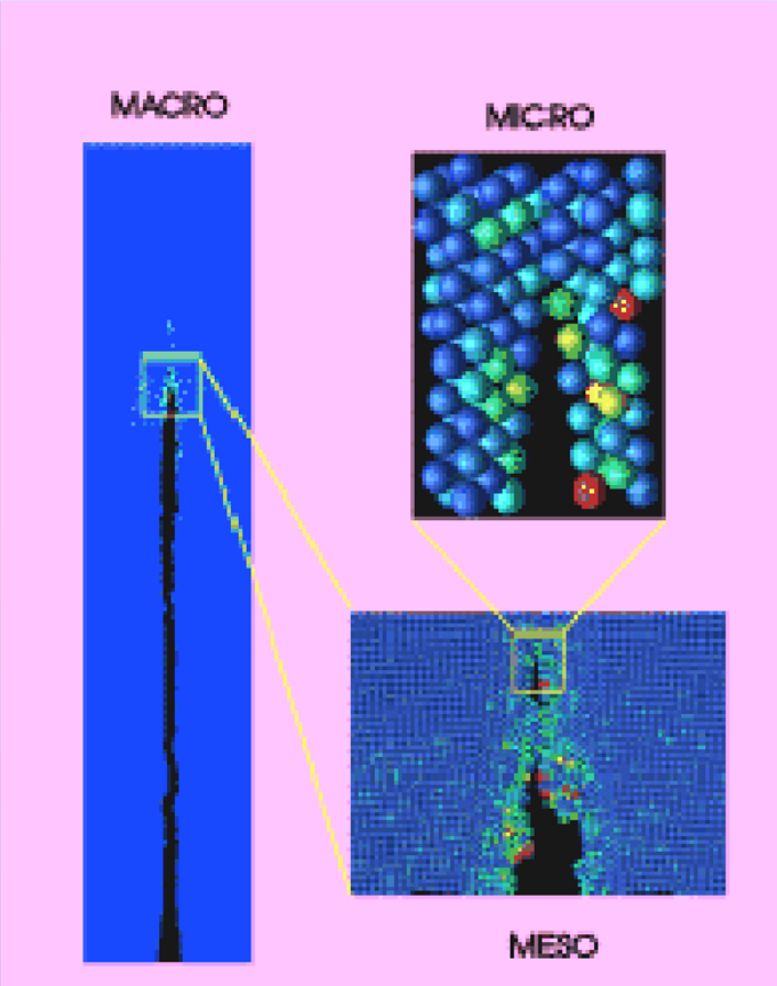
Multiples scales:

lengths

1 cm --- 1 Å (10^{-10} m)

times:

years --- fs (10^{-15} s)



Challenges of Simulation of Materials

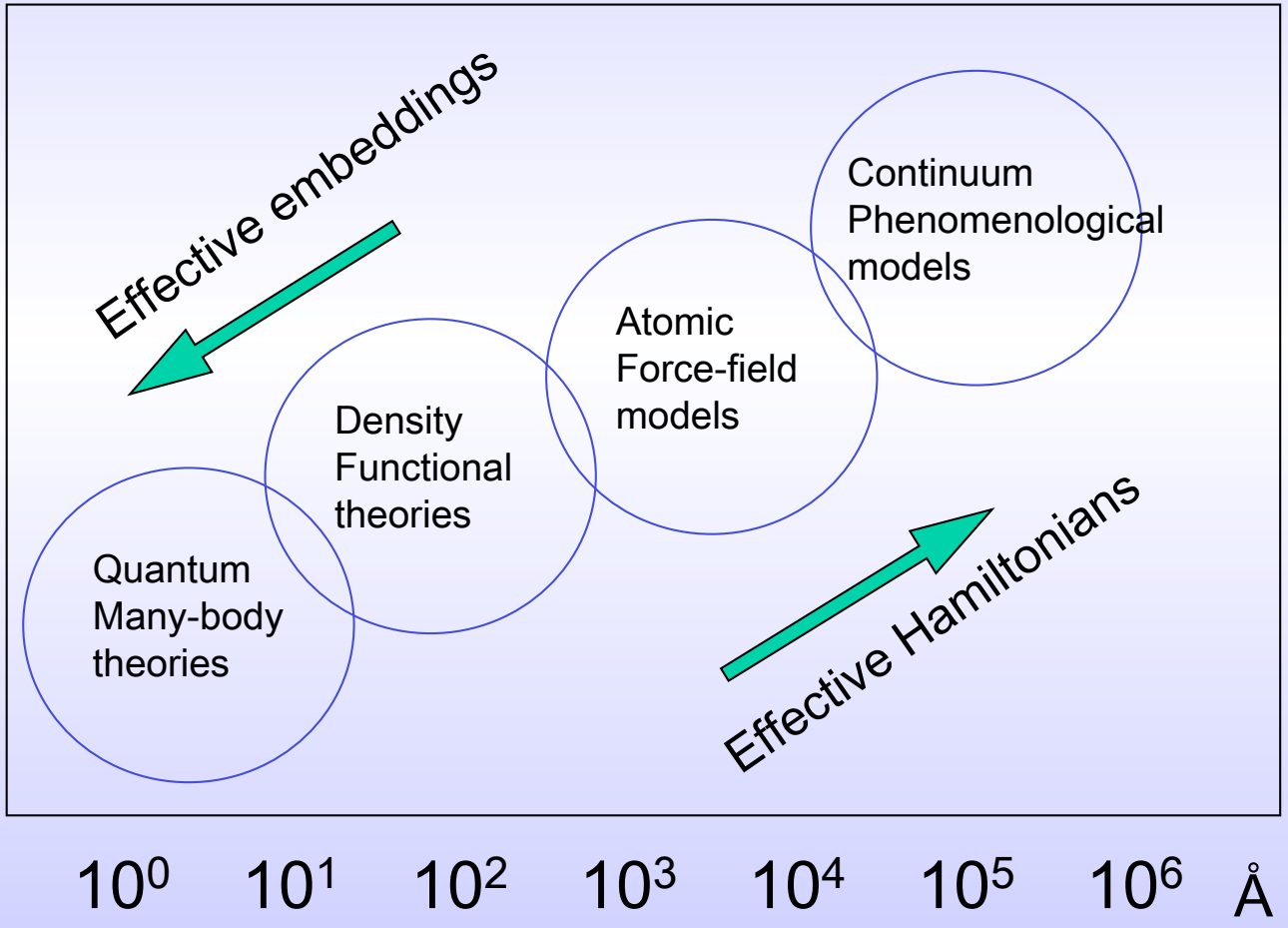
Multiple scales

Macro – and *mesoscopic* phenomena; Thermodynamics

Atomic structure and dynamics

Electronic states Chemical bonds and reactions, excitations …

Taken from: Ceperley/Johnson UIUC



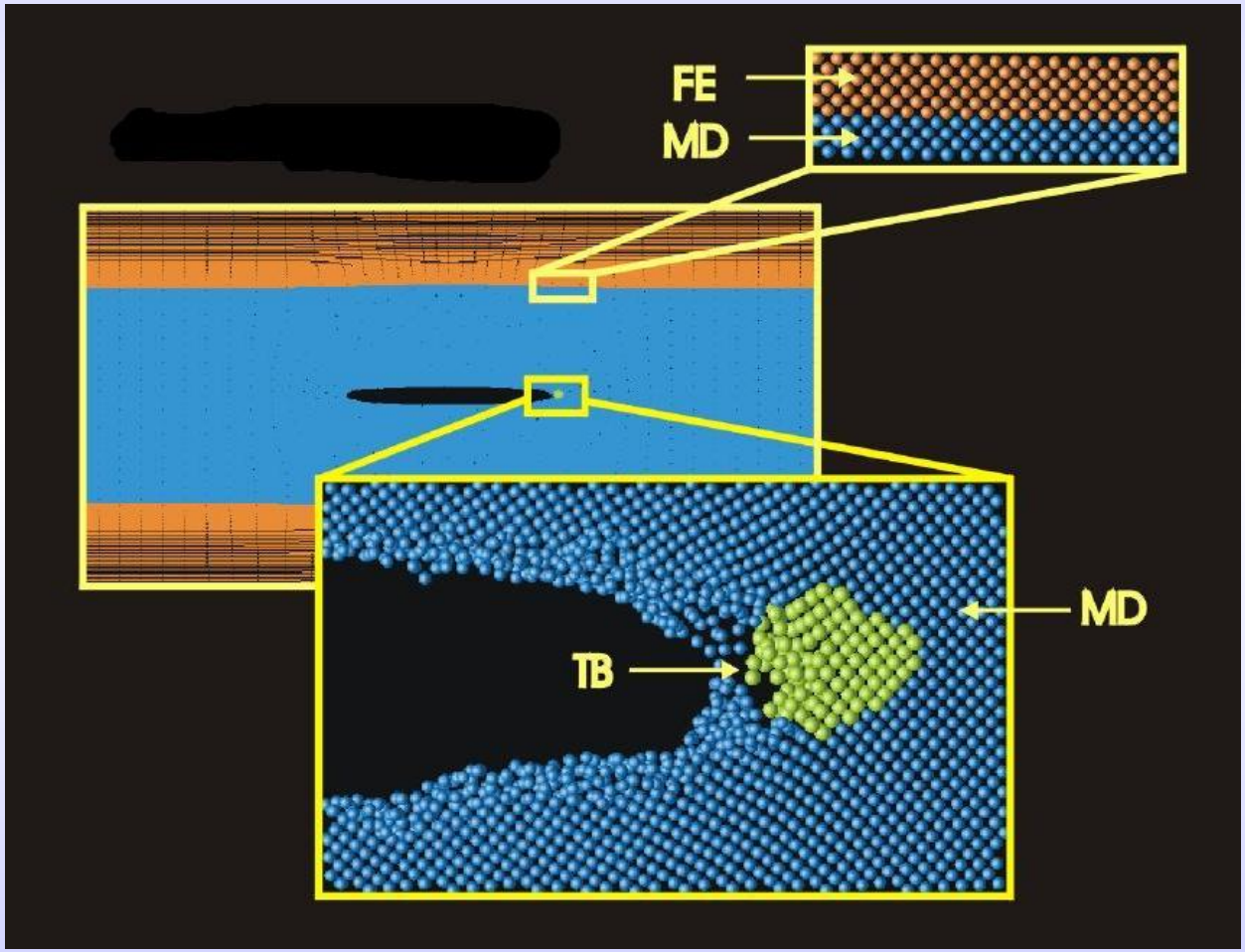
Challenges of Simulation of Materials

Multi-scale methods

FE: Finite Elements

MD: with
Interatomic
Potentials

TB: Tight Binding



Crack propagation in Silicon (Prof. E. Kaxiras, Harvard)