Chair of Condensed Matter Physics
Institute of Theoretical Physics
Faculty of Physics, Universityof Warsaw

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Lecture

Modeling of Nanostructures and Materials

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Modeling of Nanostructures and Materials

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Lecture 5 – *March 24, 2014*

Molecular Dynamics

- **Classical vs. ab initio molecular dynamics**
- **Born-Openheimer MD**
- **Car-Parrinello Method**
- **Thermostats**
- **Time evolution of atomic positions in MD**

Molecular Dynamics

✓ **Classical vs. *ab initio***

✓ **Ehrenfest vs. Born Oppenheimer**

✓ **Car-Parrinello MD**

Molecular Dynamics – What is it ?

- **Classical dynamics (given by Newton equations) of atoms in the system**

$$M_I \ddot{\vec{R}}_I = \vec{F}_I$$
$$\vec{F}_I = -\nabla_I V_{eff}(\{\vec{R}_I\})$$

- **Goal** – **to determine classical trajectories of all atoms in the system** $\{R_I(t)\}$

- At the very heart of any molecular dynamics scheme is the question of how to describe - that is in practice how to approximate - the *interatomic interactions*.

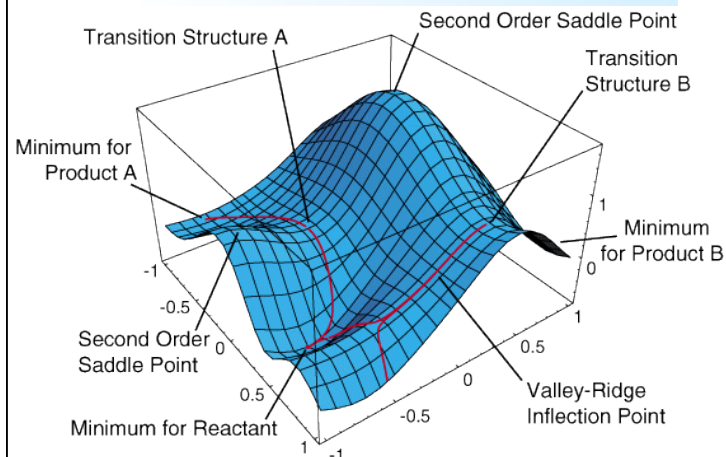- **Where to get forces on atoms from ?**

Classical vs. *Ab initio* Molecular Dynamics

$$M_I \ddot{\vec{R}}_I = -\nabla_I V_{eff}(\{\vec{R}_I(t)\})$$

Potential energy surface

- *Classical* – based on **predefined potentials**
  - either obtained from empirical data, or
  - obtained from independent electronic structure calculations

- *Ab initio* – based on fully **quantum mechanical calculations**

Potential Energy Surface

Classical Molecular Dynamics

- Typically, the full *interaction potential* is broken up into two-body, three-body and many-body contributions, long-range and short-range terms etc., which have to be represented by suitable functional forms.

$$V_e^E \approx V_e^{approx}(\{\mathbf{R}_I\}) = \sum_{I=1}^{N} v_1(\mathbf{R}_I) + \sum_{I<J}^{N} v_2(\mathbf{R}_I, \mathbf{R}_J) + \sum_{I<J<K}^{N} v_3(\mathbf{R}_I, \mathbf{R}_J, \mathbf{R}_K) + \cdots$$

- The electronic degrees of freedom are replaced by interaction potentials v_1, v_2, etc. and are not featured as explicit degrees of freedom in the equations of motion.

Classical Molecular Dynamics

- Very often, the interactions can faithfully be described by additive two-body terms

$$V_e^{approx}(\{\mathbf{R}_I\}) \approx \sum_{I<J}^{N} v_2(|\mathbf{R}_I - \mathbf{R}_J|)$$

  For example, Argon in liquid phase

  E. Ermakova, J. Solca, H. Huber, and D. Marx, Chem. Phys. Lett. **246**, 204 (1995).

- Well established tool to investigate many-body condensed matter systems

- A lot of monographs, e.g.,
  - M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon Press, Oxford, 1987; reprinted 1990).
  - D. Frenkel and B. Smit, *Understanding Molecular Simulation - From Algorithms to Applications* (Academic Press, San Diego, 1996).

Classical Molecular Dynamics - Drawbacks

🙂 Moderate computation time and possibility to deal with large systems.

world's record – about 19 billion atoms

😐 **Limitations in applicable phenomena**

☹ **Restricted predictive power,**
specifically in *simulating bond breaking and forming*

☹ Very difficult fitting procedure of *ab initio* results to a suitable functional form of interaction potential.
- It can be done only for extremely small systems.
- It is difficult to design a well-behaved fitting function.

➡ *Ab initio* **Molecular Dynamics**

Ab initio Molecular Dynamics (AIMD)

● The fitting step can be bypassed
and the dynamics performed directly by **calculating the inter-atomic forces** (obtained from the electronic structure calculated *on-the-fly*)
at each time-step of an MD simulation

● The methods are widely applicable and possess potential to predict new phenomena and novel materials.

➡ **New Area in Materials Science – Materials Design**

● The methods may cost huge computation time, however
- Progress in Computational Techniques
(new solvers, new optimization techniques, etc.)
- Progress in high-performance computers

Ab initio Molecular Dynamics (AIMD)
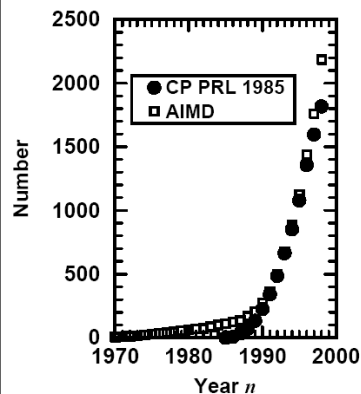
Squares: number of publications which appeared up to the year *n* that contain the keyword "ab initio molecular dynamics" (or synonyms such as "first principles MD", "Car-Parrinello simulations" etc.) in title, abstract or keyword list.

Circles: number of publications which appeared up to the year *n* that cite the 1985 paper by Car and Parrinello

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Ab initio Molecular Dynamics (AIMD) - Theory

$$\frac{d\mathbf{P}_I}{dt} = -\nabla_I \int d\mathbf{r}\, \Psi^\star \mathcal{H}_e \Psi \quad \text{or}$$

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \int d\mathbf{r}\, \Psi^\star \mathcal{H}_e \Psi$$
$$= -\nabla_I V_e^{\mathrm{E}}(\{\mathbf{R}_I(t)\})$$

● Thus, the nuclei move according to classical mechanics in an effective potential V_e^E due to the electrons.

● This potential is a function of only the nuclear positions at time t as a result of averaging H_e over the electronic degrees of freedom, i.e. computing its quantum expectation value $<\psi|\hat{H}_e|\psi>$, while keeping the nuclear positions fixed at their instantaneous values $\{\vec{R}_I(t)\}$.

Ab initio Molecular Dynamics (AIMD) - Theory

Time-dependent wave equation for the electrons

■ ■
$$i\hbar\frac{\partial\Psi}{\partial t} = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2\Psi + V_{n-e}(\{\mathbf{r}_i\},\{\mathbf{R}_I(t)\})\Psi$$
$$= \mathcal{H}_e(\{\mathbf{r}_i\},\{\mathbf{R}_I(t)\})\ \Psi(\{\mathbf{r}_i\},\{\mathbf{R}_I\};t)$$

- Hamiltonian and wave-function are parametrically dependent on the classical nuclear positions $\{\vec{R}_I(t)\}$

- Procedure of solving simultaneously Eqs. ■ and ■ ■ is very often called *"Ehrenfest molecular dynamics"*.

- It was never in widespread use for systems with many active degrees of freedom typical for condensed matter problems

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Ehrenfest molecular dynamics

In practical calculations only ground state considered

$$M_I\ddot{\mathbf{R}}_I(t) = -\nabla_I\langle\Psi_0|\mathcal{H}_e|\Psi_0\rangle$$
$$i\hbar\frac{\partial\Psi_0}{\partial t} = \mathcal{H}_e\Psi_0$$

- Electronic Hamiltonian is time-dependent via the nuclear coordinates

- The propagation of the wavefunction is unitary, i.e. the wavefunction preserves its norm and the set of orbitals used to build up the wavefunction will stay orthonormal

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Born-Oppenheimer AIMD

An alternative approach to include the electronic structure in molecular dynamics simulations

- Straightforwardly solve the static electronic structure problem in each molecular dynamics step given the set of fixed nuclear positions at that instance of time.

- $E_0(\{\vec{R}_I\}) = min <\Psi_0|\hat{H}_e(\{\vec{R}_I\})|\Psi_0>$

- $M_I\ddot{\vec{R}}_I = -\nabla_I E_0(\{\vec{R}_I\})$ $\hat{H}_e(\{\vec{R}_I\})\Psi_0 = E_0(\{\vec{R}_I\})\Psi_0$

- $E_0(\{\vec{R}_I\})$ -- *ground state energy* of electrons for instantaneous ionic positions $\{\vec{R}_I(t)\}$
  may be calculated using DFT (Kohn –Sham)
  [or Hartree-Fock method]

Density Functional Theory (DFT)

- **One particle density determines the ground state energy of the system for arbitrary external potential**

$$E[\rho] = \int d^3\vec{r}\rho(\vec{r})v_{ext}(\vec{r}) + F[\rho]$$

$$E[\rho_0] = E_0 \quad \text{ground state energy}$$

ground state density

Total energy functional		Kinetic energy	Exchange energy	Correlation energy

- $E[\rho] = \int d\vec{r}v_{ext}(\vec{r})\rho(\vec{r}) + T_S[\rho] + U[\rho] + E_x[\rho] + E_c[\rho]$

External energy	Classic Coulomb energy	**unknown!!!**

Born-Oppenheimer AIMD (cnt.)

- The electronic structure part is reduced to solving a *time-independent quantum problem*

- The time-dependence of the electronic structure is a consequence of nuclear motion, and not intrinsic as in Ehrenfest molecular dynamics.

Ehrenfest vs. Born-Oppenheimer MD

- In **Ehrenfest dynamics** the *time scale is dictated by the intrinsic dynamics of the electrons*.

- Since electronic motion is much faster than nuclear motion, the largest possible time step is that which allows to integrate the electronic equations of motion.

- There is no electron dynamics whatsoever involved in solving the **Born-Oppenheimer dynamics**, i.e. they can be integrated on the *time scale given by nuclear motion*.

- However, this means that the electronic structure problem has to be solved self-consistently at each molecular dynamics step.

Car- Parrinello Method - Motivation

R. Car and M. Parrinello, Phys. Rev. Lett 55, 2471 (1985)

- A non-obvious approach to cut down the computational expenses of molecular dynamics

- It can be seen as an attempt to combine the advantages of both Ehrenfest and Born-Oppenheimer molecular dynamics.

- From an algorithmic point of view the main task achieved in ground-state Ehrenfest dynamics is simply to keep the wavefunction automatically minimized as the nuclei are propagated.

- This, however, might be achieved -- in principle – by another sort of deterministic dynamics than first-order Schrödinger dynamics.

Car- Parrinello Method - Motivation

The "Best of all Worlds Method" should
(i) integrate the equations of motion on the (long) time scale set by the nuclear motion but nevertheless
(ii) take intrinsically advantage of the smooth time-evolution of the dynamically evolving electronic subsystem as much as possible.

The second point allows to circumvent explicit diagonalization or minimization to solve the electronic structure problem for the next molecular dynamics step.

- *Car-Parrinello molecular dynamics* is an efficient method to satisfy requirement (ii) in a numerically stable fashion and makes an acceptable compromise concerning the length of the time step (i).

Car- Parrinello Method – Lagrangian

Lagrangian
Kohn-Sham Energy Functional
Ionic positions

$$L = \sum_i \mu \int_\Omega d^3r \, |\dot{\psi}_i|^2 + \sum_I \frac{1}{2} M_I \dot{R}_I^2 - E[\{\psi_i\},\{R_I\}] + \sum_{i,j} \Lambda_{ij} \left(\int_\Omega d^3r \psi_i^*(\vec{r}) \psi_j(\vec{r}) - \delta_{ij} \right)$$

Ficticious 'masses' of the wavefunctions
Ionic masses
One particle orbitals
Lagrange multipliers to ensure the orthonormality of the orbitals

The corresponding Newtonian equations of motion are obtained from the associated Euler-Lagrange equations

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_I} = \frac{\partial \mathcal{L}}{\partial \mathbf{R}_I}$$

$$\frac{d}{dt}\frac{\delta \mathcal{L}}{\delta \dot{\psi}_i^\star} = \frac{\delta \mathcal{L}}{\delta \psi_i^\star}$$

Car- Parrinello Method – Equations of Motion

Equations of motion

$$\mu\ddot{\psi}(\vec{r}) = -\frac{\delta E}{\delta \psi_i^*(\vec{r},t)} + \sum_j \Lambda_{ij} \psi_j(\vec{r},t)$$

$$M_I \ddot{R}_I = -\nabla_{\vec{R}_I} E$$

(+) Coupling to some external reservoir in order to maintain the ionic temperature, the so-called 'Nose's thermostat'

● Born-Oppenheimer surface $\Phi(\{\vec{R}_I\}) = \min_{\{\psi_i\}} E[\{\psi_i\},\{\vec{R}_I\}]$

*R. Car & M. Parrinello, PRL **55**, 2471 (1985)*

Car- Parrinello Method – Two temperatures

● According to the Car-Parrinello equations of motion, the nuclei evolve in time at a certain (instantaneous) physical temperature $\propto \sum_I M_I \dot{\vec{R}}_I^2$

● A 'fictitious temperature' associated to the electronic degrees of freedom $\propto \sum_i \mu_i < \dot{\psi}_i | \dot{\psi}_i >$

● "*Low electronic temperature*" or "*cold electrons*" means that the electronic subsystem is close to its instantaneous minimum energy $min_{\{\psi_i\}} < \Psi_0 | \hat{H}_e(\{\vec{R}_I\}) | \Psi_0 >$
i.e. close to the exact Born-Oppenheimer surface.

● **It must be achieved during the simulation process**

Car- Parrinello Method vs. Born-Oppenheimer MD
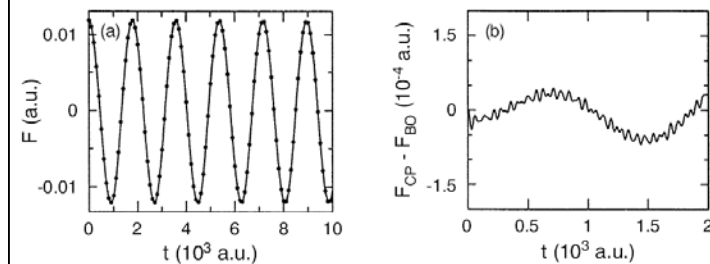
Comparison of the x-component of the force acting on one atom of a model system obtained from Car-Parrinello (solid line) and well-converged Born-Oppenheimer (dots) molecular dynamics.

Ab initio Molecula Dynamics: Applications –
From Materials Science to Biochemistry

- **Solids, Polymers, and Materials**
  - Thermal expansion of solids
- **Surfaces, Interfaces, and Adsorbates**
- **Liquids and Solutions**
  - Liquid phases of solids
  - Phase transitions liquid → solid
- **Glasses and Amorphous Systems**
- **Matter at Extreme Conditions**
- **Clusters, Fullerenes, and Nanotubes**
- **Chemical Reactions and Transformations**
- **Biophysics and Biochemistry**

CPMD
consortium
page

http://www.cpmd.org

John von Neumann Institute for Computing

NIC

Ab initio molecular dynamics: Theory and Implementation

Dominik Marx and Jürg Hutter

published in

Modern Methods and Algorithms of Quantum Chemistry,
J. Grotendorst (Ed.), John von Neumann Institute for Computing, Jülich, NIC Series, Vol. 1, ISBN 3-00-005618-1, pp. 301-449, 2000.

http://www.fz-juelich.de/nic-series/

(150 pages, 708 references)

AIMD – computer codes

CPMD Version 3.3:
developed by J. Hutter, A. Alavi, T. Deutsch,
M. Bernasconi, St. Goedecker, D. Marx, M. Tuckerman, and M. Parrinello, Max-Planck-Institut für Festkörperforschung and IBM Zurich Research Laboratory (1995-1999).

CASTEP   Accelrys

CP-PAW   P. E. Blöchl

fhi98md   Fritz-Haber-Institut, Berlin

NWChem   developed and distributed by
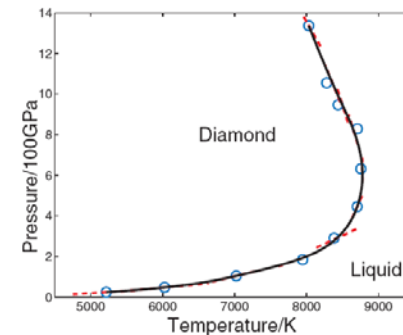Pacic Northwest National Laboratory, USA.

VASP   University of Vienna

Extensive review (708 references): D. Marx and Jürg Hutter
http://www.fz-juelich.de/nic-series/

Ab Initio Molecular Dynamics

Applications

Car- Parrinello Method - Application

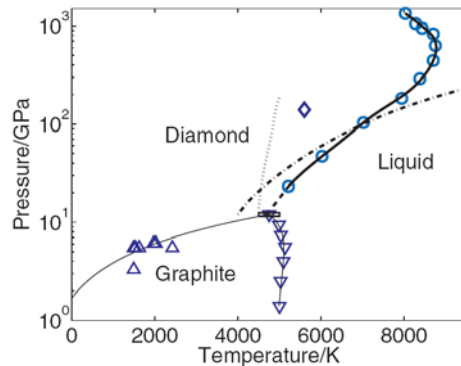**Carbon Phase Diagram - Diamond melting line**

AIMD with modern thermodynamic integration techniques was used to compute the **free energy of solid and liquid carbon** in an extended range of pressures and temperatures.

X. Wang, S. Scandolo, and R. Car, Phys. Rev. Lett. **95,** 185701 (2005)

Car- Parrinello Method - Application

Carbon Phase Diagram

X. Wang, S. Scandolo, and R. Car, Phys. Rev. Lett. **95,** 185701 (2005)

Car- Parrinello Method - Application
The dissociation of a water molecule

- **Under ambient conditions**, **water molecules** rarely **dissociate** (come apart) — **just once every 11 hours**. When dissociation does occur, two water (H_2O) molecules become hydroxide (OH^-) and hydronium (H_3O^+), with one proton hopping to the other H_2O molecule.

- How increased pressure does affect dissociation ? (a long debated problem)

- In AIMD simulations of static pressure conditions ranging up to 30 giga-pascals, it has been found that the dissociation process begins in earnest at 14 giga-pascals. **By 30 giga-pascals, dissociation is occurring once every billionth of a second**.
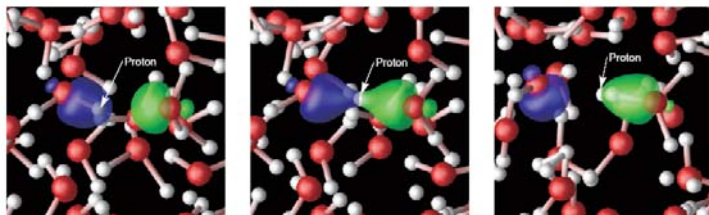
The lifetime of H_3O^+ is 10^{-12} sec

Car- Parrinello Method - Application
The dissociation of a water molecule

Mechanisms of water dissociation under ambient and high pressure are identical

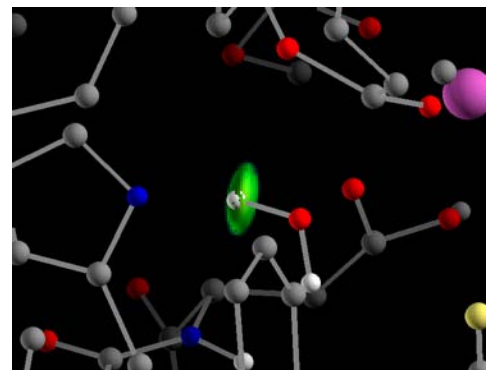Snapshots of the dissociation of a water molecule
at high pressure.

| As the water molecules dissociate, | a proton is transferred to a neighboring water molecule | a hydroxide **OH⁻** and a hydronium ion H_3O^+ are formed |

Ab initio MD Simulations of Chemical Reaction

Dissociation of water molecule

Atomistic Fabrication Technology
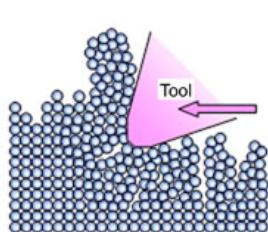
Center of AFT at Osaka University, Japan

Fig. 1: Example of mechanical machining

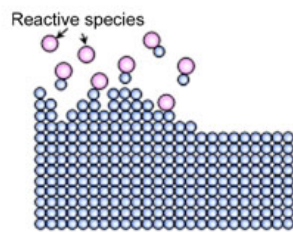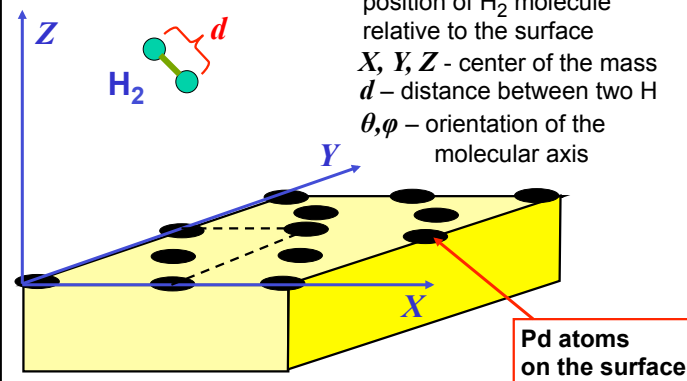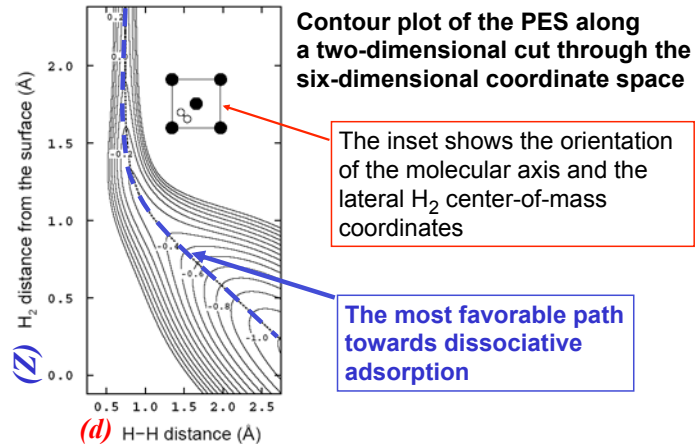Fig. 2. Example of "Atomistic Fabrication Technology"

AIMD used for design of modern tools

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

Z
H₂
d
Y
X

Pd atoms on the surface

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

(d)

H₂ distance from the surface (Å)
(Z)
H–H distance (Å)

Molecular Dynamics &

Thermodynamical Properties

MD and Thermodynamical Properties

- **From MD simulations, one gets**

  $\{\vec{R}_I(t)\}$ $\{\vec{v}_I(t)\}$ $\{E_{kin,I}(t)\}$ $E_{pot}(t)$

  trajectories   **velocities**   **kinetic energies**   **potential energy**

- These quantities may be used for performing time averages

- **Time averages replace the ensemble average required to calculate the thermodynamic properties of a system.**

- The simulation time should be large enough, that one
  - reaches the thermodynamic equilibrium,
  - and has enough data after the equilibrium point to compute averages

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MD and Thermodynamical Properties

- If one is interested in *equilibrium properties*, some extensive or intensive parameter of the simulation must be fixed.

- In the statistical thermodynamics there are several possible ensembles: **NVE**, **NTV**, **NHP**, **NTP**, **µTV**, and **µTP**.

  N – the number of particles
  E – the total energy
  V – the volume
  T – the temperature
  P – the pressure
  H – the enthalpy
  µ – the chemical potential

MD and Thermodynamical Properties

- **NVE – the microcanonical ensemble**

- **NTV – the canonical ensemble**

- **µTV – the grand canonical ensemble**
  - T. Cagin and B. M. Pettitt, Molecular Simulations **6,** 5 (1991)

- The elaborate molecular-dynamics techniques has been elaborated for all ensembles.

- **Non-equilibrium molecular-dynamics simulation also possible**
  - D. J. Evans and G. P. Morriss, *Statistical Mechanics of Nonequilibrium Liquids* (Academic Press, London, 1990)

MD and Canonical (NVT) Ensemble

- **In NVE** (microcanonical) ensemble the total energy is conserved quantity.

- **More realistic situations, T or P kept fixed.**
  In such cases, integrating Newton's equations is not enough.
  One needs to add the effect of a thermostat interacting with system

- **For canonical simulations** the total energy is allowed to fluctuate, but its conjugate intensive parameter, the temperature T, is kept fixed.

  ⟹ Two possibilities**:**
  - simple one – rescaling velocities
  - more sophisticated – Nose's thermostat

MD and Canonical (NVT) Ensemble

The easiest way to keep T constant

- Use the equipartition theorem and equate the kinetic energy to $\frac{3}{2}Nk_BT$

- Rescale the velocities at each time step (every few time steps) so that the total kinetic energy satisfies $\sum_I \frac{1}{2}M_I v_I^2 = \frac{3}{2}Nk_BT$

- For simulation of polyatomic molecules, one should take into account the
  - rotational,
  - vibrational,
  - translational kinetic energies separately.

- From these kinetic energies,
  - deduce the respective temperatures,
  - perform velocity scaling in such a way as to equilibrate three temperatures

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MD and Canonical (NVT) Ensemble – Nosé's Thermostat

S. Nosé, J. Chem. Phys. **81,** 511 (1984).

- One adds a thermostat with a degree of freedom s, and conjugate momentum p_s, and an inertia Q

- **The system + thermostat treated in the microcanonical ensemble (total energy conserved)**

- **The kinetic & potential energies of the thermostat**

$$KE = \frac{1}{2}Q\left(\frac{ds}{dt}\right)^2 = \frac{p_s^2}{2Q}$$

$$PE = (1+f)k_B \ln s$$

f - the number of degrees of freedom

$$f = 3N - 3$$

if the center of mass is fixed

MD and Canonical (NVT) Ensemble – Nosé's Thermostat

- **The coupling to the system with the thermostat takes place through the equation**

$$\vec{v}_I = s\frac{d\vec{R}_I}{dt} = s\frac{\vec{p}_I}{M_I} \quad \forall I \in \{1,2,\ldots,N\}$$

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

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

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

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

MD and NTP Ensemble

Similar scheme

- **Add another "pressure thermostat"** to the composite system

- **Introduce coupling to the system's degrees of freedom**

Molecular Dynamics

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

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

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

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

- $\vec{F}_I = -\nabla_I V_{eff}(\{\vec{R}_I\})$

  - **Classical MD**
  - *Ab initio* **MD (AIMD)**

MD and Time Averages

- **From MD simulations, one gets**

  $\{R_I(t)\}$ $\{\vec{v}_I(t)\}$ $\{E_{kin,I}(t)\}$ $E_{pot}(t)$

  trajectories   **velocities**   **kinetic energies**   **potential energy**

- These quantities maybe used for performing time averages

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

MD and Structural Quantities

- MD provides us with structural quantities such as the **pair correlation function**, which gives the distribution of distances between pairs of atoms

- **The structure factor** $S(k) = \dfrac{1}{N} < \rho(k)\rho(-k) >$

  can be measured in neutron-scattering experiments

- **The Time Correlation Functions** between two quantities
  $$C_{AB}(t) = < \delta A(t)\delta B(0) >$$
  ⟹ **Response Functions,** such as
  - diffusion coefficient,
  - viscosity,
  - compressibility,
  - electrical and heat conductivities,
  - dynamical structure factor.

Time evolution

Time Evolution of Atomic Positions

- Integration of the Newton's equations using
  finite difference methods

  L. Verlet, Phys. Rev. **159**, 98 (1967)

  Expansion of the atomic positions at two times $t + \Delta t$ and $t - \Delta t$

  (i) $\quad \vec{R}_I(t + \Delta t) = \vec{R}_I(t) + \Delta t \vec{v}_I(t) + \dfrac{(\Delta t)^2}{2}\vec{a}_I(t) + \ldots$

  (ii) $\quad \vec{R}_I(t - \Delta t) = \vec{R}_I(t) - \Delta t \vec{v}_I(t) + \dfrac{(\Delta t)^2}{2}\vec{a}_I(t) - \ldots$

  $$\vec{a}_I(t) = \vec{F}_I(t) / M_I$$

Time Evolution of Atomic Positions

- Adding (i) to (ii)
  $$\vec{R}_I(t + \Delta t) + \vec{R}_I(t - \Delta t) - 2\vec{R}_I(t) = (\Delta t)^2 \dfrac{\vec{F}_I(t)}{M_I}$$

  Finite-difference expression for the second derivative

  Errors of the order $(\Delta t)^4$

- Subtracting (ii) from (i)
  $$\vec{v}_I(t) = \dfrac{\vec{R}_I(t + \Delta t) - \vec{R}_I(t - \Delta t)}{2\Delta t}$$

  Velocity

  Errors of the order $(\Delta t)^3$

Time Evolution of Atomic Positions

$$\vec{R}_I(t+\Delta t) = 2\vec{R}_I(t) - \vec{R}_I(t-\Delta t) + (\Delta t)^2 \frac{\vec{F}_I(t)}{M_I}$$

Calculation of atomic positions using this formula is numerically ineffective

- The addition of large values and very small ones introduces a numerical error
  - ⇒ **Better algorithms needed**
    - **leapfrog method**
      R. W. Hockney, Methods Comput. Phys. **9**, 136 (1970)
    - **Gear predictor-corrector algorithm**
      C. W. Gear, *Numerical Initial Value Problems in Ordinary Differential Equations* (1971)
    - **The velocity Verlet method**
      W.C. Swope, H.C. Andersen, P.H. Berens, and K. R. Wilson, J. Chem. Phys. **76**, 637 (1982)

The velocity Verlet method

$$\vec{R}_I(t+\Delta t) = \vec{R}_I(t) + \Delta t \vec{v}_I(t) + \frac{1}{2m}\vec{F}_I(t)(\Delta t)^2$$

$$\vec{v}_I(t+\Delta t) = \vec{v}_I(t) + \frac{1}{2m}[\vec{F}_I(t+\Delta t) + \vec{F}_I(t)](\Delta t)^2$$

- **Algorithm requires the storage of coordinates, velocities, and forces at every time step**

- **It minimizes round-off errors**

- **In terms of stability and accuracy, it is the best of the proposed methods**

MD and Long Range Forces

- **Calculation of short range forces**
  $O(N)$ **procedure**

- **Calculation of long range forces (Coulomb forces)**
  $O(N^2)$ **procedure**

  Ewald Method - requires to evaluate a sum of order 10^2
  for each ion
  Very heavy task in large systems !

  ⇒ **New efficient methods**
    - **Particle-Mesh Method**
      E. Bertschinger & J. M Gelb, Computers in Phys. Mar/Apr 164 (1991)
    - **The fast multipole method**
      L. Greengard & V.I. Rokhlin, J. Comput. Phys. **73**, 325 (1987)

Treatment of long-range forces

MD and Long Range Forces – The Multipole Method
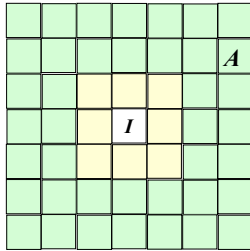
- One discretizes the volume (unit cell) of the system into many subcells

- The potential acting on atom I can be decomposed into two parts:
  - direct interaction caused by the adjacent (yellow) cells
  - Multipole interactions caused by the atoms in the green cells

$$V(\vec{R}_I) = \sum_{J \in near} \frac{q_J}{|\vec{R}_I - \vec{R}_J|^p} + \sum_{A \in far} V_A^{pole}(\vec{R}_I - \vec{R}_A)$$

p = 1 for Coulomb potential
6 for Van der Waals potential

center of cell A

The Multipole Method

$$V(\vec{R}_I) = \sum_{J \in near} \frac{q_J}{|\vec{R}_I - \vec{R}_J|^p} + \sum_{A \in far} V_A^{pole}(\vec{R}_I - \vec{R}_A)$$

$$V_A^{pole}(\vec{R}_I - \vec{R}_A) = \frac{Z_A}{R^p} + \frac{\mu_\alpha R_\alpha}{R^{p+2}} + \frac{Q_{\alpha\beta} R_\alpha R_\beta}{R^{p+4}} + \frac{Q_{\alpha\beta\gamma} R_\alpha R_\beta R_\gamma}{R^{p+6}} + \ldots$$

$\vec{R} = \vec{R}_I - \vec{R}_A$ $R = |\vec{R}|$ α, β, γ - Cartesian coordinates

$Z_A = \sum_i q_i$ **charge**

$\mu_\alpha = p \sum_i q_i r_{i\alpha}$ **dipole**

$Q_{\alpha\beta} = p \sum_i q_i [(p+2) r_{i\alpha} r_{i\beta} - \delta_{\alpha\beta} r_i^2] / 2$ **quadrupole of the cell A**

The Multipole Method vs. Fast Multipole Method

- The multipole algorithm accelerates the calculation of forces typically by a factor of several tens, when one discretizes the whole space into subcells of the same size

- Greengard & Rochlin showed that the computation of forces can be accelerated further by grouping small cells hierarchically into larger cells

  ⟹ *Fast Multipole Method*

- Ding et al. [J. Chem. Phys. **97**, 4309 (1992)] applied the FMM to macromolecular system (1.2 milion atoms) and showed that the computation becomes faster by *2400 times*

MD – limitations
system size and time scales

Ab initio (Car-Parrinello) MD

size: **100 – 200 atoms** (workstations)
100 000 atoms (multiprocessor supercomputers)

time: **10 ps**

Classical MD

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

time: **10 ns**

- **Both methods – atomistic scale methods**

- **Advantage of AIMD – bond formation and bond breaking**

- **Simulation of materials properties – larger scales needed**

AIMD – simulation of chemical reactions

Example: Alcohol (CH$_3$OH) Oxidation by CrCl$_2$O$_2$

- 1st stage -- CH$_3$OH $\rightarrow$ CH$_3$O
- 2nd stage -- CH$_3$O $\rightarrow$ CH$_2$O

Time scale ps, time steps 1-2 fs

MOVIE

Thank you!