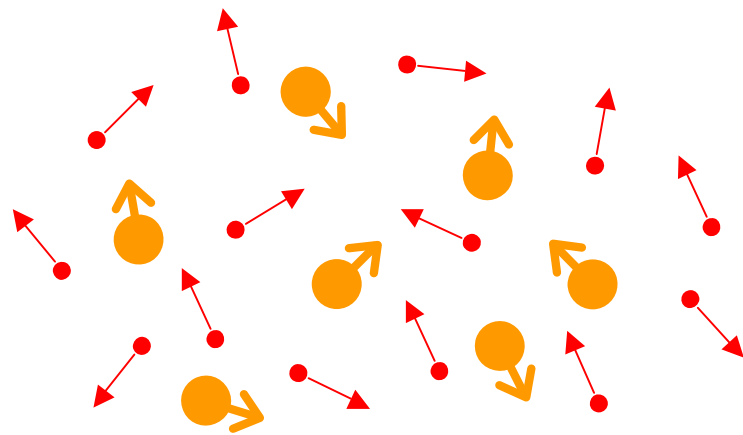# *Molecular dynamics*
(based on talk by MV Fernandez-Serra)

Emilio Artacho

Nanogune, Ikerbasque & DIPC, San Sebastian, Spain
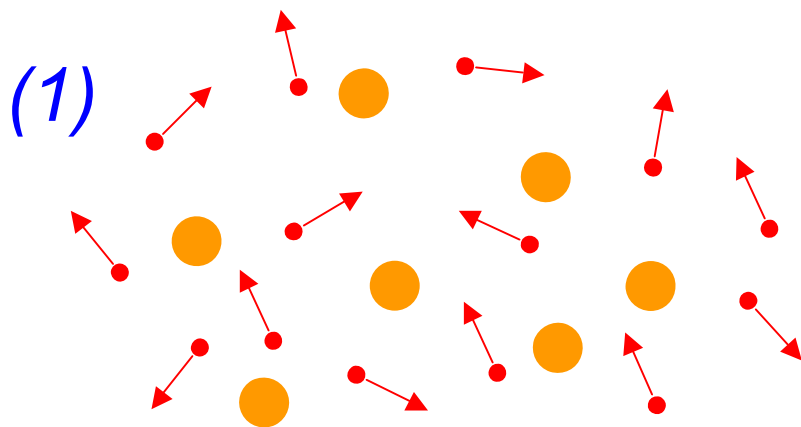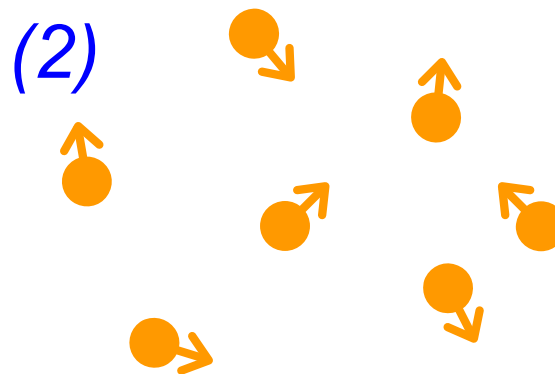*Cavendish Laboratory, University of Cambridge*

Adiabatic decoupling

$$\frac{m_n}{m_e} >> 1$$

$\Rightarrow$ *Nuclei are much*

slower than electrons

(1)

(2)

Quantum mechanics
Many electron problem:
Density Functional Theory

F = m a, *evolution in*
(discretised) time:
Molecular 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 electrons quantum mechanically
- Treats nuclei **classically**
  - Hydrogen may raise issues:
    - tunnelling   (overestimating Energy barriers)
- Allows study of dynamic processes
- Annealing of complex materials
- Examines the influence of temperature
- *Time averages Vs Statistical averages*

Ergodicity

- *In MD we want to replace a full sampling on the appropriate statistical ensemble by a SINGLE very long trajectory.*

- *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.*
  - $<A>_{time} = <A>_{ensemble}$,
    so $<A_{time}> = (1/N_{MD}) = \sum_{t=1,N} A_t$ *is good estimator.*

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

When do we use MD?

Dynamical systems in general, e.g.

- *Liquid and Amorphous systems:*
  - *Molecular Liquids (H_2O, CO_2)*
  - *Glasses (Si, SiO_2)*
- *Displacive Phase transitions (P and T relevant).*
- *Study of kinetic effects.*
  - *Diffusion at surfaces*
  - *Thermal stability*
- *Finite-temperature effects in non-harmonic systems*

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)

- *Choosing particles, masses and interatomic forces (model of interactions)*

- *Initialize positions and momenta at t=0 (initial conditions in space and time)*

- *Solve F = m a to determine r(t), v(t). (integrator)*
  - *time discrete, instead of continuous*

$h = \delta t$

$t_0 \quad t_1 \quad t_2 \qquad\qquad t_{n-1} \quad t_n \quad t_{n+1} \qquad\qquad t_N$
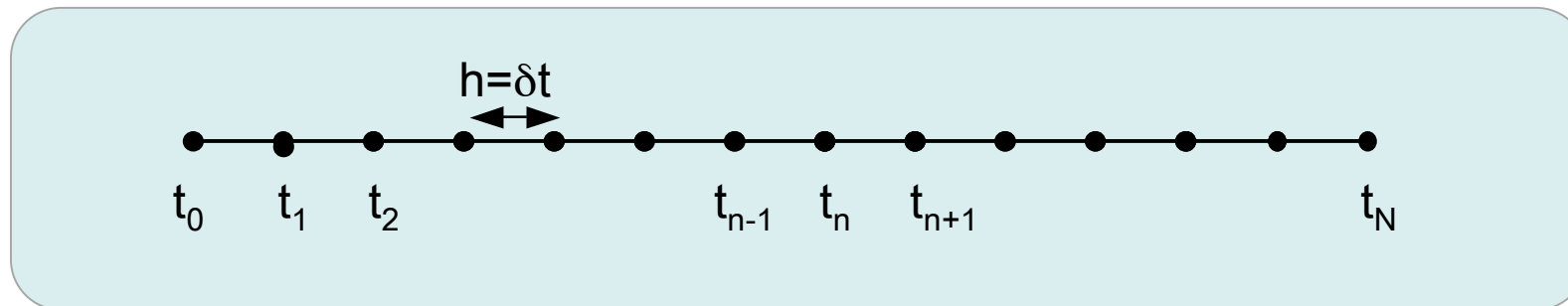
- *Calculate the properties of interest along the trajectory*

- *Estimate errors*

- *Use the results of the simulation to answer physical questions*

Molecular Dynamics III

- *Timestep must be small enough to accurately sample highest frequency motion*
- *Typical timestep is 1 fs (1 x 10^{-15} s)*
- *Typical simulation length = Depends on the system of study!!*

    (the more complex the PES the longer the simulation time)

- *Simulation has two parts:*
    - *equilibration (redistribute energy)*

        System is equilibrated if averages of dynamical and structural quantities do not change with time.

    - *production (record data)*
- *Results:*
    - *diffusion coefficients*
    - *Structural information (RDF's,)*
    - *free energies / phase transformations (very hard!)*
- *Is your result statistically significant?*

Choosing the integrator

- *Small errors or minimal differences in initial conditions -> different trajectories (Ergodicity!).*

- *Statistical averages are relevant quantities; do not depend on details of trajectories (IF simulation is long enough).*

- *Conservation of energy is important.*
  Error in energy conservation < 0.01 kT.

- *CPU time dominated by calculation of forces. Preferable algorithms requiring few evaluations of the forces, and do not need higher derivatives of the potential.*

Verlet algorithm

The most commonly used algorithm:

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

$r(t+h) = 2 r(t) - r(t-h) + a(t) h^2 + O(h^4)$ *Sum*

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

- *Trajectories are obtained from the first equation. Velocities are not necessary.*
- *Errors in trajectory: $O(h^4)$*
- *Preserves time reversal symmetry.*
- *Excellent energy conservation.*
- *Modifications and alternative schemes exist (leapfrog, velocity Verlet), always within the second order approximation*
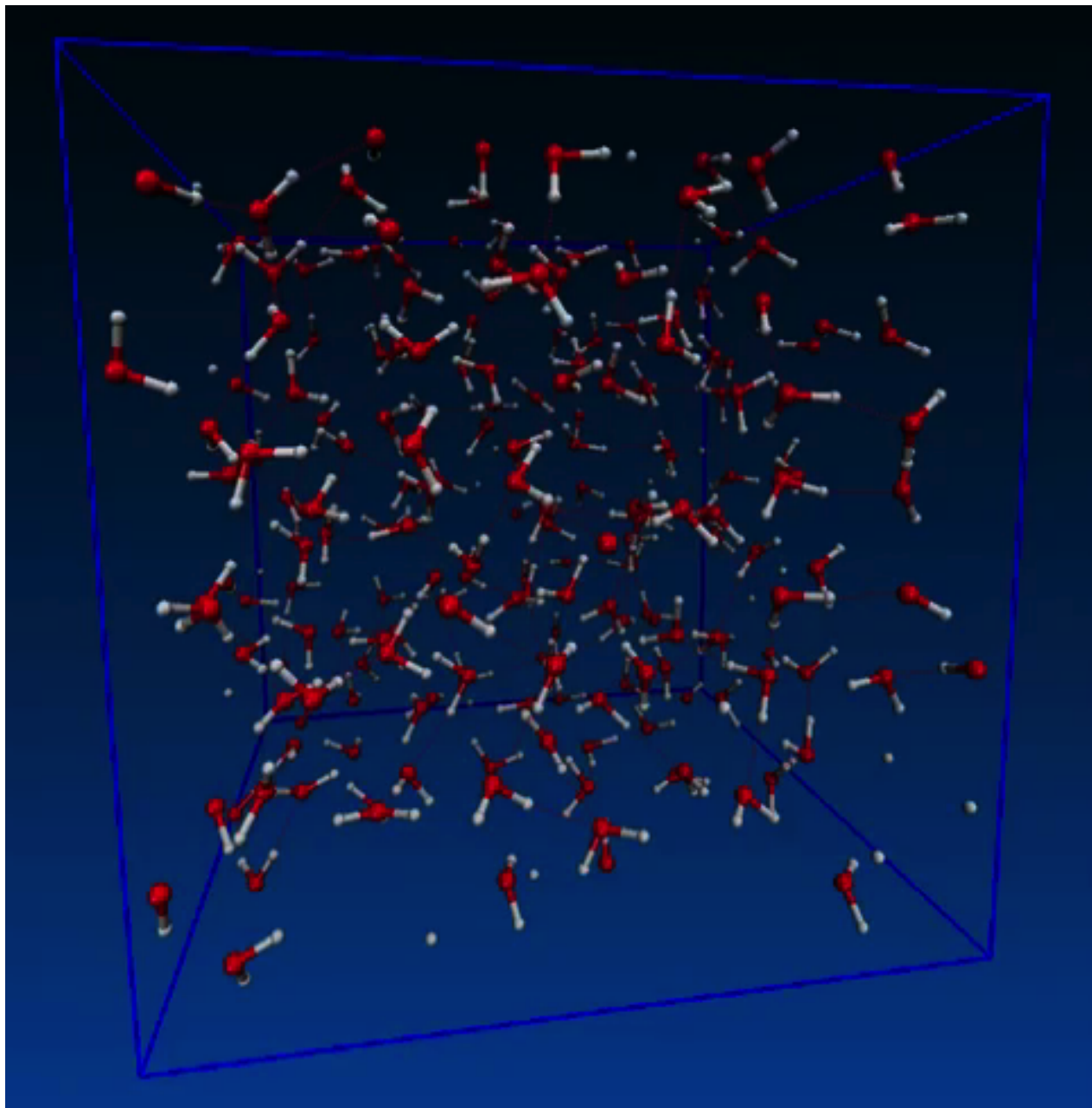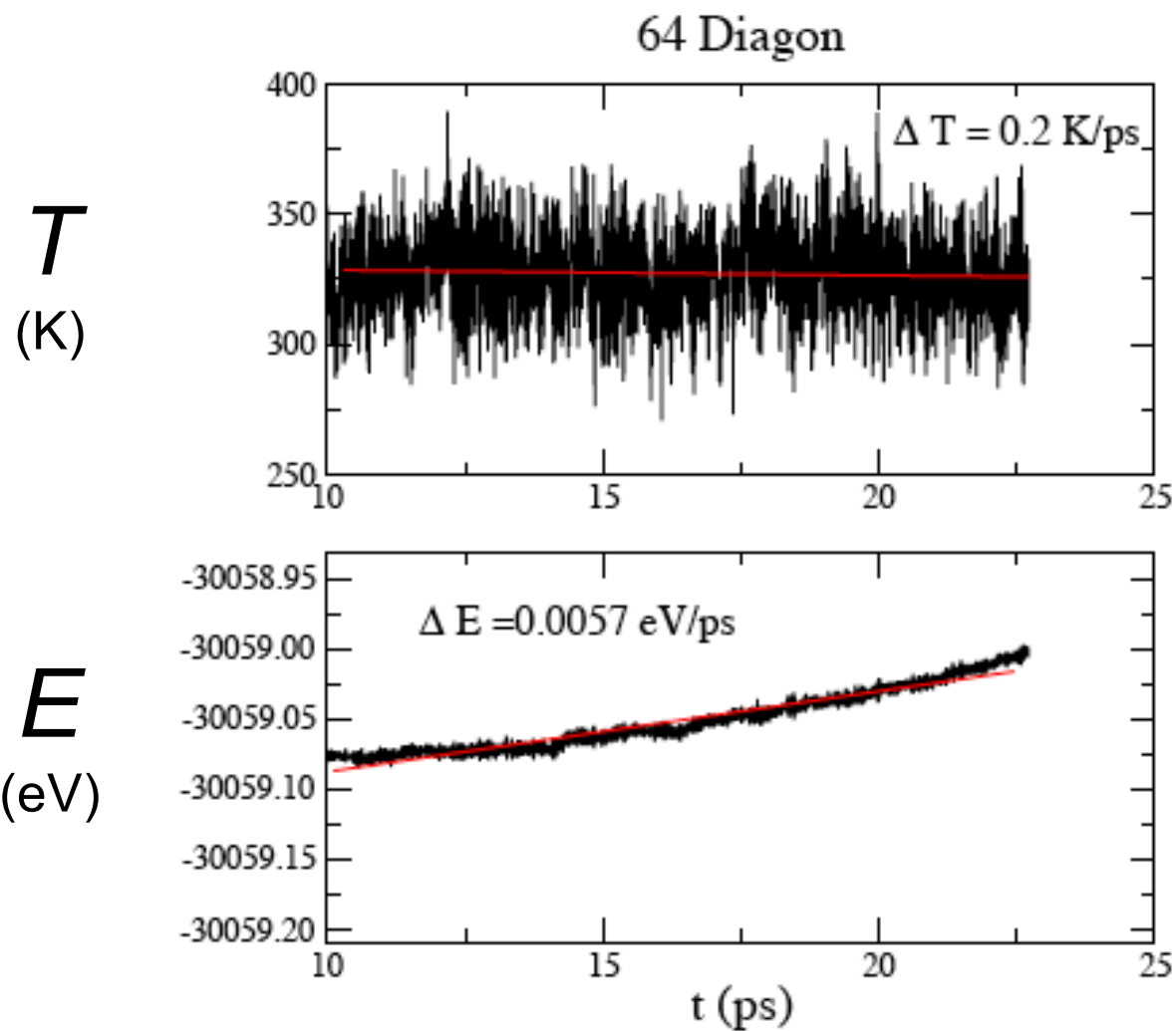
Liquid water

MD simulations from first principles

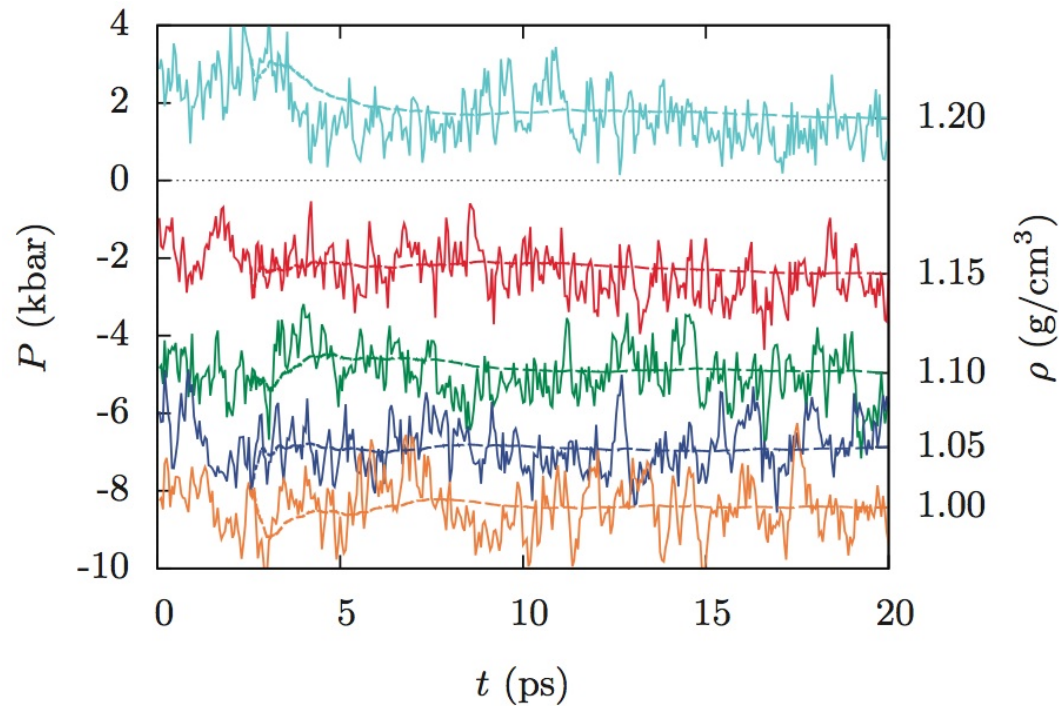*200 water molecules in a box periodically repeated;*

30 ps in 0.5 fs timesteps

F Corsetti

First-principles molecular dynamics of liquid water

Equation of state of liquid water
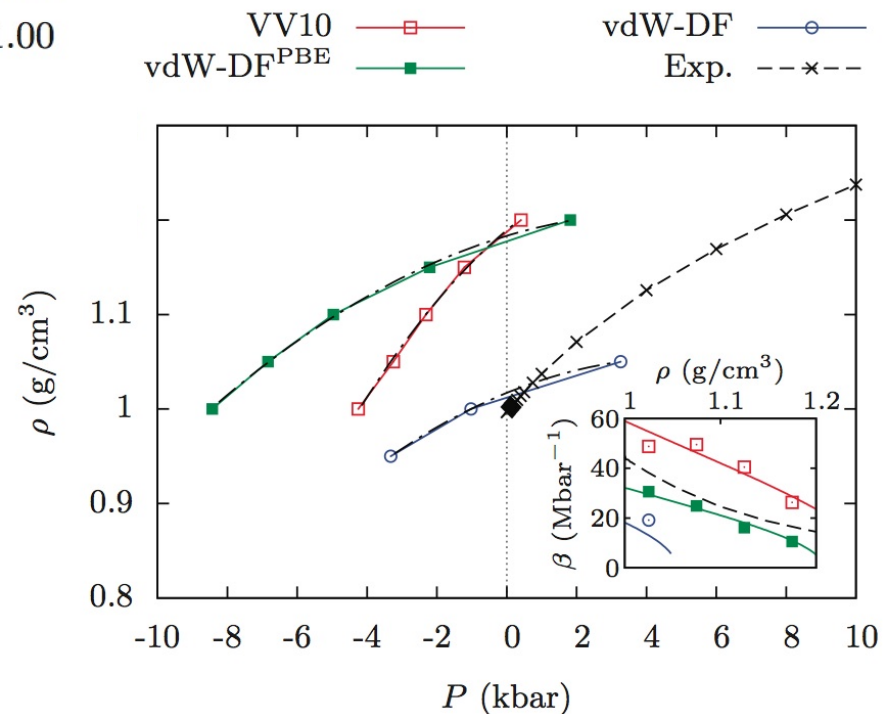

Follow pressure vs time
for different densities
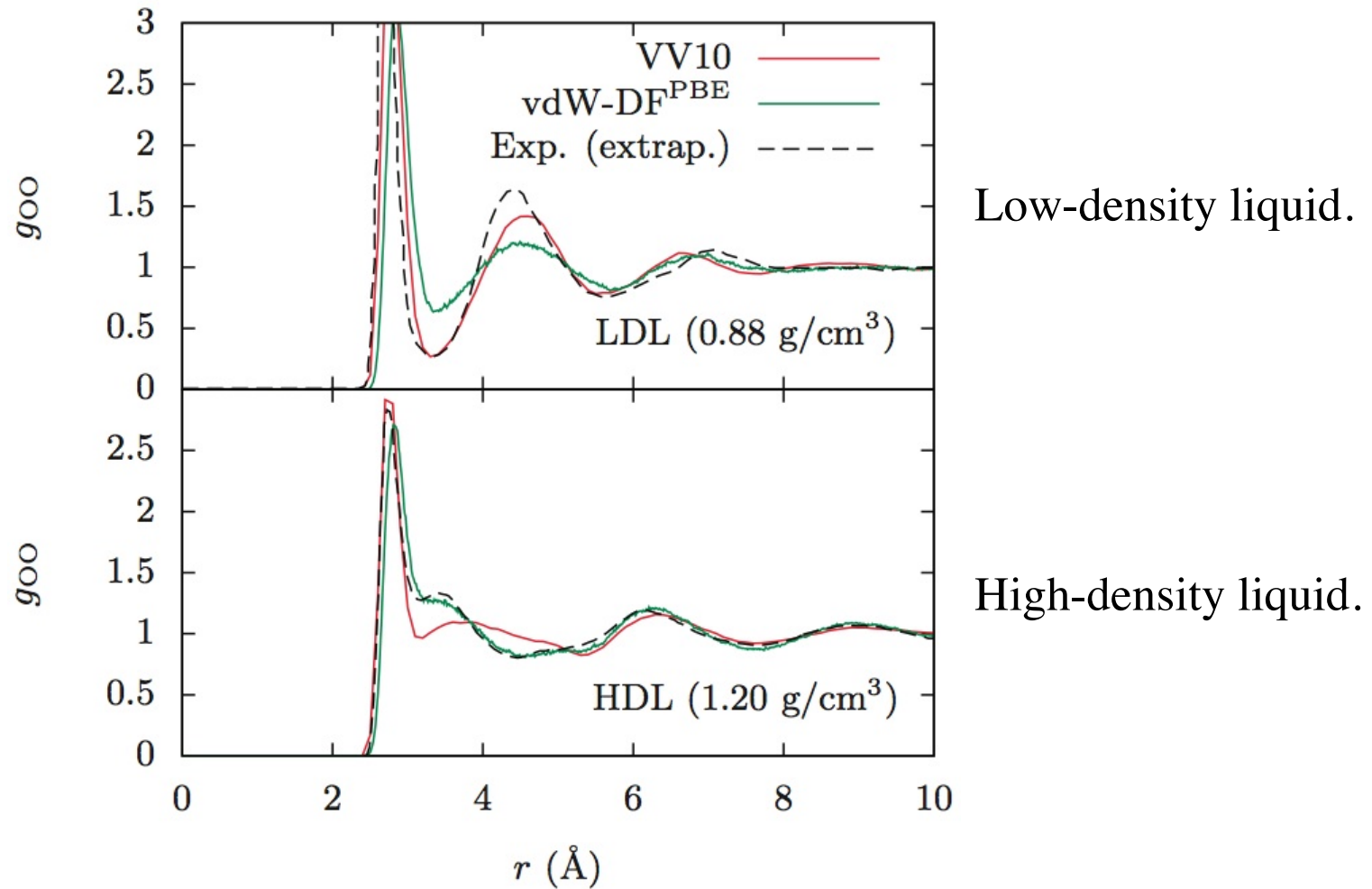
Then average

Average P vs density

Different density
functionals

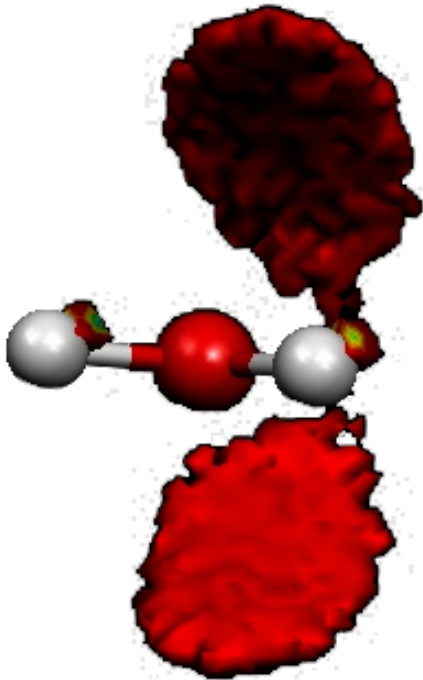F Corsetti et al, J. Chem. Phys. 2013

Radial distribution functions
O-O

Low-density liquid.

High-density liquid.

F Corsetti, E Artacho, J M Soler, S S Alexandre and M.-V.Fernandez-Serra, J. Chem. Phys. (2013).
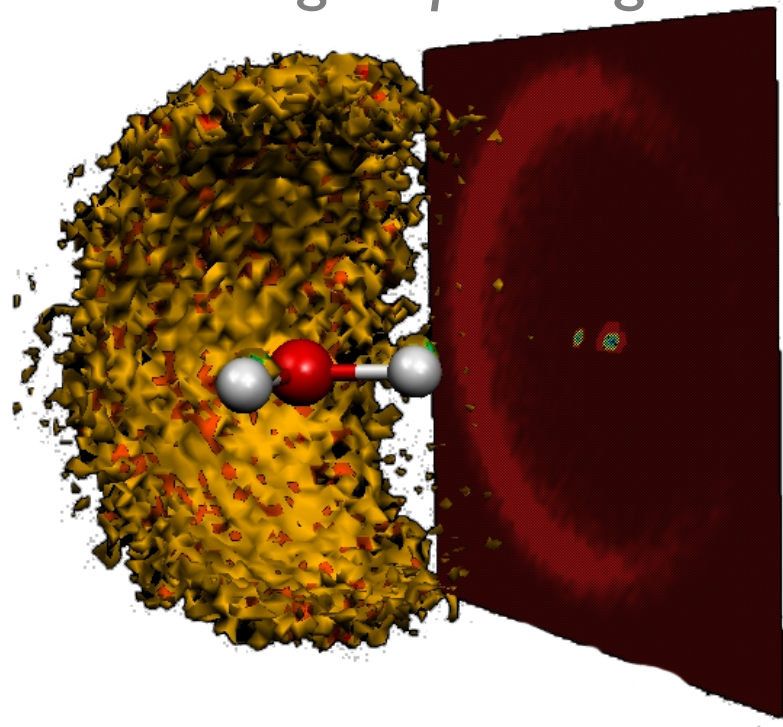
Understanding the coordination

On electrons and hydrogen-bond connectivity in liquid water
M. V. Fernandez-Serra & E. Artacho, PRL 2006

*Strong bonds,
no pre-edge*
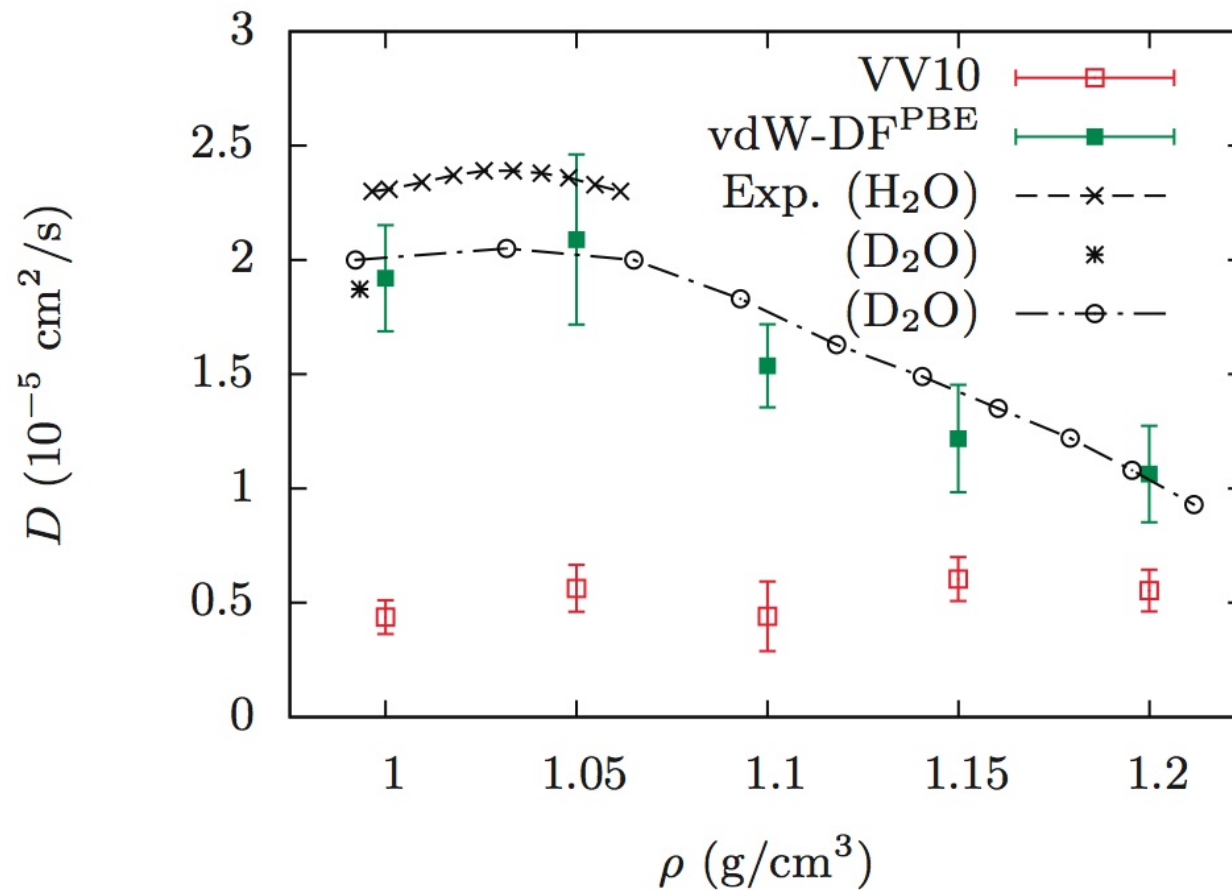
*Weak bonds
could give pre-edge*

*Electronic effect associated to intermolecular vibrations
Now understood and exploited for wet surfaces (Stanford & Berkeley)*

Dynamics: Diffusion
Diffusivity maximum vs Pressure

F Corsetti et al, J. Chem. Phys. 2013

Different ensembles, different Lagrangians, different 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*

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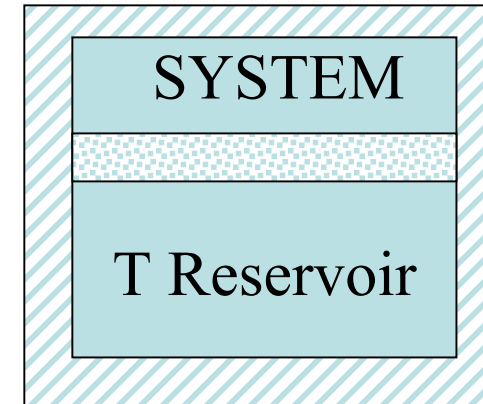 - *N particles + Thermostat, mass Q.*

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

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

Nose-Hoover *thermostat*

- *MD in canonical distribution (TVN)*
- *Introduce a friction force $\zeta(t)$*

SYSTEM

T Reservoir

$$\frac{dp}{dt} = F(q,t) - \zeta(t)\, p(t)$$

Dynamics of friction coefficient to get canonical ensemble

$$Q\frac{d\zeta}{dt} = \sum \frac{1}{2}m_i v_i^2 - \frac{3N}{2}k_B T$$

Feedback makes K.E.=3/2kT

Q= fictitious "heat bath mass". Large Q is weak coupling

Hints

- *Nose Mass:*

  Match a vibrational frequency of the system, better high energy frequency

$$Q \approx \frac{KT}{\omega^2}$$

Which Ensemble should we use?

- **NVE (Verlet): Microcanonical**

  - *Good trajectories.*
  - *Time reversible (up to numerical error)*
  - *Dynamical variables are well defined.*
  - *Initial X and V are relevant: necessity of equilibration.*

Same sampling in thermodynamic limit

- **NVT (Nose): Canonical**

  - *Good T control*
  - *Equilibrates the system.*
  - *Choice for Structural sampling.*
  - *Sensitive to Nose mass.*

- **NPE (Parrinello-Rahman)**

  - *Phase transitions systems under pressure.*
  - *1 mass parameter (barostat)*

- **NPT (Nose-Parrinello-Rahman)**

  - *Phase transitions under P and T*
 - *2 mass parameters, barostat and thermostat. (Fluctuations!!*

Molecular Dynamics in SIESTA(1)

- MD.TypeOfRun Verlet
  NVE ensemble dynamics

- MD.TypeOfRun Nose
  NVT dynamics with Nose thermostat

- MD.TypeOfRun ParrinelloRahman
  NPE dynamics with P-R barostat

- MD.TypeOfRun NoseParrinelloRahman
  NPT dynamics with thermostat/barostat

- MD.TypeOfRun Anneal
  Anneals to specified p and T

Variable cell

Molecular Dynamics in SIESTA(2)

- *Setting the length of the run:*
  MD.InitialTimeStep 1
  MD.FinalTimeStep 2000

- *Setting the timestep:*
  MD.LengthTimeStep 1.0 fs

- *Setting the temperature:*
  MD.InitialTemperature 298 K
  MD.TargetTemperature 298 K

- *Setting the pressure:*
  MD.TargetPressure 3.0 Gpa

- *Thermostat / barostat parameters:*
  MD.NoseMass / MD.ParrinelloRahmanMass
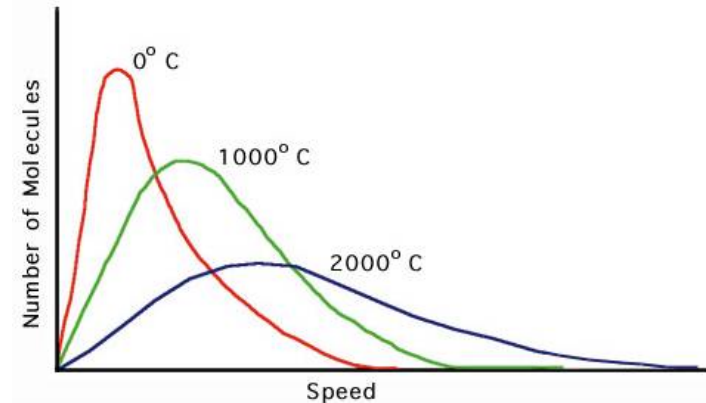
Maxwell-Boltzmann

Annealing in SIESTA

- *MD can be used to optimize structures:*
  MD.Quench true
  (zeros velocity when opposite to force)

- *MD annealing:*
  MD.AnnealOption Pressure
  MD.AnnealOption Temperature
  MD.AnnealOption TemperatureAndPressure

- *Timescale for achieving target*
  MD.TauRelax 100.0 f

Vibrational spectrum: Phonons

- *Calculating Dynamical Matrix: Mass weighted Hessian Matrix (Harmonic approximation).*

$$H_{i,j}^{\alpha,\beta} = \frac{\delta^2 E}{\delta x_i^\alpha \delta x_j^\beta} = \frac{\delta F_i^\alpha}{\delta x_j^\beta}$$

Harmonic Approx.

- *Frozen Phonon approximation:*
  - *Numerical evaluation of the second derivatives. (finite differences).*

- *Density Functional Perturbation Theory (Linear Response):*
  - *Perturbation theory used to obtain analytically the Energy second derivatives within a self consistent procedure.*

Beyond Harmonic

- *Molecular dynamics: Green-Kubo linear response.*
  - *Link between time correlation functions and the response of the system to weak perturbations.*

Phonons and MD

1. *MD simulations (NVE)*
2. *Fourier transform of*
   Velocity-Velocity autocorrelation function.

1. *Anharmonic effects: $\omega(T)$*
2. *Expensive, but information available for MD simulations.*

$$Ph(\omega) = \int_0^\infty dt \, e^{2\pi i \omega t} \frac{\langle \vec{v}(0)\vec{v}(t) \rangle}{\langle \vec{v}(0)^2 \rangle}$$

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). Lyapunov exponent.

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

Small round-off errors and other mathematical approximations may not matter.
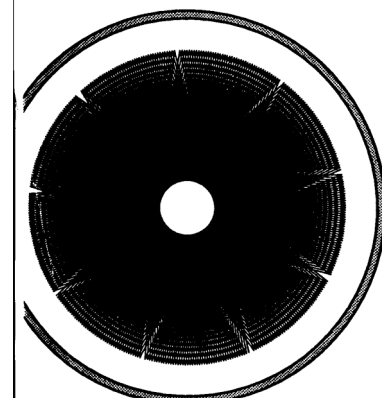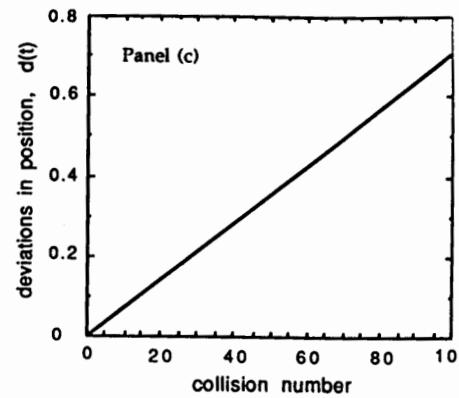
Particle in a smooth/rough circle
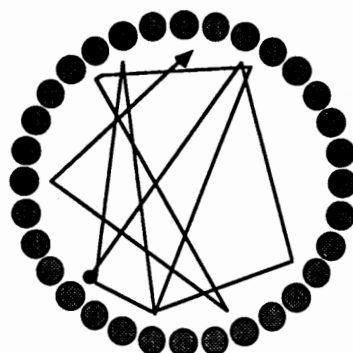
From J.M. Haile: MD Simulations