A Brief Introduction to *Ab Initio* Molecular Dynamics

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http://www.cmt.york.ac.uk/cmd  
http://www.castep.org
Overview of Talk

• In this talk I hope to give you some ideas as to why you might want to do MD and what it can tell you.

• I hope to pass on some practical tips and advice, and answer some of your questions, particular w.r.t. CASTEP

• I shall illustrate with examples where possible. Time is short …
Why MD?

• Atoms move!
  – We may be interested in studying time dependent phenomena, such as molecular vibrations, phonons, diffusion, etc.
  – We may be interested in studying temperature dependant phenomena, such as free energies, anharmonic effects, etc.

• Ergodic Hypothesis
  – One of the key principles behind the usefulness of MD for statistical mechanics studies
  – Iff our MD trajectory is “good enough” then a time average over the trajectory is equivalent to an ensemble average – hence MD averages are useful.
Alternatives

• Monte Carlo
  – can do thermal averages
  – hard to do time dependant things

• Hybrid MD/MC
  – bad MD as good MC
  – generate configurations using poor/cheap/fast MD but then evaluate contribution to ensemble average using MC
Types of *ab initio* MD

- **Classical Motion**
  - We use classical mechanics to move the atoms
    - Born-Oppenheimer approximation decouples nucleus and electrons
  - But using forces and stresses derived from the electronic wavefunction
  - No quantum fluctuations, tunneling, zero point motion, etc.

- **Quantum Motion**
  - Can include ZPM etc using *ab initio* Path Integral MD

- **Damped MD as a geometry optimizer**
Choice of Ensemble

• **NVE**
  – Micro-canonical ensemble
  – Constant Number of atoms, Volume and Energy
  – Corresponds to Newtonian mechanics
  – Good for non-equilibrium situations, e.g. watching a bond vibrate or doing impact movies

• **NVT**
  – Canonical ensemble – constant Temperature
  – More physical as it allows energy exchange with a heat bath
  – Good for simulating thermal equilibrium
  – Choice of thermostating algorithms
Choice of Ensemble

• NPH
  – constant pressure $P$ and enthalpy $H$
  – Choice of barostats to handle pressure:
  – Andersen can allow cell to change size isotropically (liquids) whilst Parrinello-Rahman can allow changes in size and shape (solids)
  – External pressure can be isotropic (hydrostatic) or anisotropic (shear stress etc).

• NPT
  – Most physically relevant as system is now connected to a piston and a heatbath.
  – Again, choice of thermostats and barostats

• $\mu VT$ - constant chemical potential $\mu$
How do you do it? NVE …

• Integrate classical equations of motion
  – discretize time → time step
  – different integration algorithms, e.g. Velocity Verlet:
    \[
    r(t + \delta t) = r(t) + v(t) \delta t + \frac{f(t)}{2m} \delta t^2 + O(\delta t^3)
    \]
    \[
    v(t + \delta t) = v(t) + \frac{f(t) + f(t + \delta t)}{2m} \delta t + O(\delta t^2)
    \]
  – trade-off time step vs. stability vs. accuracy
  – need accurate forces (high cutoff energies and good k-point sampling)
Other Ensembles

- Other ensembles can be simulated by using appropriate equations of motion
  - Usually derived from an extended Lagrangian (e.g. Nosé-Hoover, Parrinello-Rahman)
  - Recent developments in Liouvillian formulation have been very successful in deriving new symplectic integration schemes

- Langevin schemes need to be derived differently as non-Hamiltonian!
  - Need Focker-Planck & Liouville equation
  - see Quigley & Probert, J. Chem. Phys. 120, 11432 (2004) or my last talk at the FHI Berlin!
Simple Example: N2

• Naïve Materials Studio approach:
  – put 2 N atoms in a 5 Å box at (0.4,0.5,0.5) and (0.6,0.5,0.5)
  – Use Gamma point for BZ sampling (it is an isolated molecule after all!)
  – Use default settings, e.g. “medium” Ecut.
  – Run NVT dynamics at default T=273 K using Langevin thermostat with default “Langevin time” of 0.1 ps and default time step of 1.0 fs
  – What do you see?
Simple N2 Movie
Temperature ???

![Graph showing temperature over time](image)
Constant of Motion ???

![Graph showing the change in Eham (eV) over time (ps)]
What is Going On?

• Why is the temperature not constant if it is supposed to be NVT?
• The initial conditions were a long way from equilibrium. Doing a simple fixed-cell geometry optimisation relaxed > 2 eV.
• This excess PE is turned into KE by the MD – hence the huge initial temperatures before the thermostat is able to control it.
• The 2 eV excess PE shows up in the change in “constant of motion”
What is this “constant of motion”?

• It certainly does not seem very constant!
  – It depends on the ensemble but is essentially the closest thing to the “value of the Hamiltonian” which should be a conserved quantity:

\[
\begin{align*}
NVE &: \quad E_{\text{Ham}} = E_{\text{electrons}} + KE_{\text{ions}} \\
NVT &: \quad E_{\text{Ham}} = E_{\text{electrons}} + KE_{\text{ions}} + PE_{\text{NHC}} + KE_{\text{NHC}} \\
NPH &: \quad E_{\text{Ham}} = E_{\text{electrons}} + KE_{\text{ions}} + p_{\text{ext}}V + KE_{\text{cell}} \\
NPT &: \quad E_{\text{Ham}} = E_{\text{electrons}} + KE_{\text{ions}} + p_{\text{ext}}V + KE_{\text{cell}} + PE_{\text{NHC}} + KE_{\text{NHC}}
\end{align*}
\]

May fluctuate on short times but no long-term drift!
Ignoring initial $T$ transient
Ignoring initial T transient
So …

- Better but still some wobble in $T$ – why?
- $T$ is only strictly defined as a *macroscopic* quantity – what you are seeing is the *instantaneous* KE of a 2-particle system!
- Hence it is the *average* $T$ that is important and should be conserved: $<T> = 217 \pm 140$ K
- And that will have a stat. mech. finite size variation given by

$$\frac{\delta T}{T} \approx \frac{2}{3\sqrt{N_{\text{ions}}}}$$

- $T^* = 273 \pm 129$ K
CASTEP MD keywords

Most set in the param file:

- `task=Molecular Dynamics`
- `md_num_iter=10000`
- `md_delta_t=1.0 fs`
- `md_ensemble=NVE or NVT or NPH or NPT`
- `md_temperature=300 K`
- `md_thermostat=Langevin or Nose-Hoover`
- `md_barostat=Andersen-Hoover or Parrinello-Rahman`

should be obvious but what about `md_ion_t` or `md_extrap`? What do they do?
Nosé-Hoover keywords

- Nosé-Hoover chains are a standard deterministic way of thermostating system
  - Add an extra degree of freedom to the Lagrangian, to represent heat-bath with coupling depending on the instantaneous and target temperatures
  - But is not guaranteed to be ergodic

- One way to improve this is to add a thermostat to the thermostat etc ... resulting in a Nosé-Hoover chain
  - `md_nhc_length=5` sets the length of this chain
  - `md_ion_t = 100 fs` sets the characteristic time for the feedback – for most efficient thermostating you want to set this time to resonate with dominant period of your system
Langevin keywords

- Langevin dynamics are an alternative and stochastic way of thermostating system
  - Implements a heat bath via Fluctuation-Dissipation theorem
  - $md_{ion\_t} = 100$ fs sets the characteristic time for the feedback - set this to be longer than the dominant period of your system
  - Typically $5*md_{ion\_t}$ is sufficient to lose all trace of initial conditions and be in equilibrium
  - Guaranteed to be ergodic if run long enough
Barostat keywords

• What about the barostat? How is that controlled?

• In all MD schemes, the barostat is implemented by giving something a fictitious “mass”
  – Andersen-Hoover uses $\frac{1}{3}\log(V/V_0)$ whilst Parrinello-Rahman uses the cell $\mathbf{h}$-matrix

• In both cases, this “mass” is set by $\text{md\_cell\_t}$ which sets the time scale for relaxations of the cell motion. Should be slow …
Extrapolation Explained

**Background**

- With *ab initio* MD, the forces and stresses are derived from the wavefunction $\varphi$
  - Hence need a converged $\varphi$ at each time step
- With CPMD, this is achieved by integrating the wavefunction and the ionic positions together
- CASTEP uses BOMD and hence must re-minimise $\varphi$ each time, which is costly
- Wavefunction extrapolation is a useful speedup:
  - instead of using $\varphi(t)$ as the initial guess at the new $\varphi(t+\delta t)$ we extrapolate forwards in time using the MD integrator as a framework
Extrapolation keywords

• BUT we do not know the acceleration of $\phi$
  – Approximate it using *known change in $\phi$ over previous time steps*
• If we use the current value of $\phi$ and that at the previous time step, then we have a 1st order extrapolation scheme:
  \[ \text{md\_extrap} = \text{first} \]
• Using the pre-previous time as well leads to a 2nd order scheme: \[ \text{md\_extrap} = \text{second} \]
• We can also switch between 1st and 2nd on alternate steps as a compromise: \[ \text{md\_extrap} = \text{mixed} \]
• The extrapolation can be done using coefficients fitted to the instantaneous behaviour of the ionic MD \( \text{md\_extrap\_fit=true} \) or using constant coefficients \( \text{md\_extrap\_fit=false} \)
Go-faster Stripes

• CASTEP uses convergence window to determine SCF convergence
  – default is for `elec_convergence_win=3`
  SCF iterations to be within `elec_energy_tol`
  (default $10^{-5}$ eV/atom)

• With well-behaved MD this can be over-kill
  – The extrapolation saves many SCF cycles
  – Hence can use `md_elec_energy_tol` and
    `md_elec_convergence_win` to slacken
tolerances if all is well.
Doing N2 “properly”

1) Do a proper convergence test for cut-off energy at fixed k-sampling $\rightarrow 400$ eV

2) Check for finite size interactions

5x5x5 Å, 0.01 charge isosurface

7x5x5 Å, 0.001 charge isosurface
Doing N2 “properly”

- Now do geometry optimisation:
  \( \delta E \sim 0.1 \text{ meV} \), final freq. est. = 2387.5 cm\(^{-1} \)
  (this is automatic from BFGS analysis)
  \( \tau = 1/(100.c.\nu) \sim 15 \text{ fsec} \) so \( \delta t=1 \text{ fsec} \) OK?

- Can change units of CASTEP input/output
  - e.g. `energy_unit = kcal/mol`
  - e.g. `frequency_unit = THz`, etc

- Now do NVE run – best for testing quality of MD – using default \( T=273 \text{ K} \):
Doing N2 “properly”
Doing N2 “properly”
Now what?

- Problem is in the velocity initialisation:
  - assigning a temperature means a random velocity to each degree of freedom
  - this leads to motion in arbitrary directions
  - hence molecule rotates
  - hence falls foul of small size in y & z

Solution is to use a 7x7x7 box or control the initial velocities
Default Nosé-Hoover in 7Å³ box

\[
\langle T_{150-300} \rangle = 299 \pm 256 \text{ K}
\]

\[
\langle E_{\text{ham}} \rangle = -543.40 \pm 0.02 \text{ eV}
\]
Velocity Control

- If doing NVE or NPH then can set T=0 K
  - But not if doing NVT or NPT!
  - So any initial velocity comes from the initial strain w.r.t. equilibrium, or by user input
- Can set up any condition by editing the .cell file, e.g.

```plaintext
%block IONIC VELOCITIES
ang/ps
12.7 12.7 12.7
0.0 0.0 0.0
0.0 0.0 0.0
0.0 0.0 0.0
<etc>
%endblock IONIC VELOCITIES
```

NB $\sqrt{3 \times 12.7}$ Ang/ps ~ speed of sound in silicon
Hence can simulate high velocity shock, non-equilibrium MD, etc
Non-Equilibrium MD

- Movie generated in FHI using PyMol and MovieMaker
- Bottom-most atom given initial velocity, others at rest …
NPT Statistical Mechanics

- *Phosphorus (II) iodide*
- soft molecular crystal with triclinic cell
- $E_{\text{cut-off}} = 300$ eV, 3x2x2 k-points
- $T=250$ K, $P=50$ MPa
- Highly flexible cell - $\beta_T = 5.4 \pm 0.1$ GPa
Path Integral MD

• Hydrogen defect in silicon
  – Important defect with strong coupling of quantum ZPM to surrounding silicon lattice
    md_use_pathint=true
    md_num_beads=16
    md_pathint_staging=true
    num_farms=16

• Movie generated from .md file using PovRay to render each timestep
Path Integral MD
Computational Steering

• … is trendy
• But it has been in CASTEP for ages!
• The .param file is re-read every time step
  – Many parameters can be changed “on-the-fly” to steer the calculation, e.g. md_temperature or md_num_iter or md_delta_t
  – and even more parameters can be changed upon a continuation
• But not the .cell file!
Analysis

• Materials Studio will give you elementary data and analysis
• The .castep file gives a brief summary of what is happening in the user units ...

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<td>Hamilt Energy</td>
<td>-543.397578 eV</td>
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</table>

The University of York
CMD Group
Department of Physics
Analysis

- More advanced analysis requires more data, for which we use the .md file.
- This contains a LOT of information, for each time step, always using atomic units:

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</table>
More Analysis of MD?

• Using the .md file as input you can easily write your own analysis codes
  – e.g. MDTEP on www.castep.org

• MDTEP can calculate
  – radial distribution function, velocity autocorrelation function, mean-squared displacement, heat capacity, thermal expansion coefficient, bulk modulus, temperature and volume distributions
  – and generate .xmol and .axsf files for standard Linux visualisation programs
Miscellaneous Tips

• The choice of time step should reflect the physics not the algorithm
  – e.g. smallest phonon period/10
  – effects the conservation properties of system and long-time stability
  – Langevin: \( \text{md\_ion\_t} \sim 10^*\text{period} \)
  – Nosé-Hoover: \( \text{md\_ion\_t} \sim \text{period} \)
  – NPH or NPT: \( \text{md\_cell\_t} \sim 100^*\text{period} \)
  – equilibration time \( \sim 5^*\text{max(md\_ion\_t, md\_cell\_t)} \)

• Can use constraints to increase time step
  – freeze motions that are not of interest
Use of Constraints

• Based upon an extended Lagrangian
• Can do any number of linear constraints
  – e.g. Fix atom, centre of mass, relative positions, plane, etc.
• Non-linear constraints requires extra coding for each different constraint
  – e.g. to fix relative separation
  – bond-length constraints written but not yet fully tested and ready for general release
• Can increase time step if freeze unimportant motions, e.g. C-H bond vibrations etc.
Choice of Electronic Minimizer?

- All-bands/EDFT
  - self consistent $\varphi$ and $\rho$
  - Variational $E \sim O(h^2)$, $F \sim O(h)$
  - Best for high-quality MD but slow

- Density-Mixing
  - Non-variational minimisation and non-self consistent $\varphi$ and $\rho$ => need high accuracy $\varphi$
  - Harris-Foulkes functional has $E \sim O(h^3)$
  - Energy-based convergence criteria deceiving!
Practical Tips

• Beware Equilibration
  – sensitivity to initial conditions
  – depends on the quantity of interest

• Not all configurations are equal
  – sampling and correlation
  – statistical inefficiency

• Apply basic physics to the results
  – conservation laws, equipartition, etc
Conclusions

• MD is a useful general-purpose tool for computer experiments
  – Widely applicable
  – e.g. to study finite temperature or time dependant or non-equilibrium phenomena
  – Much more than shown here!

• This has been a brief overview
  – see references for details
References

• “Molecular Dynamics Simulations”
• “Computer Simulation of Liquids”
• “Understanding Molecular Simulation 2nd Ed.”

• www.castep.org web site
  – Useful MD and geometry optimisation tutorials, plus FAQs, on-line keyword listing, MDTEP download, etc.