Molecular dynamics: doing it by Car....

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... and Parrinello

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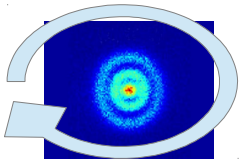
Born-Oppenheimer molecular dynamics

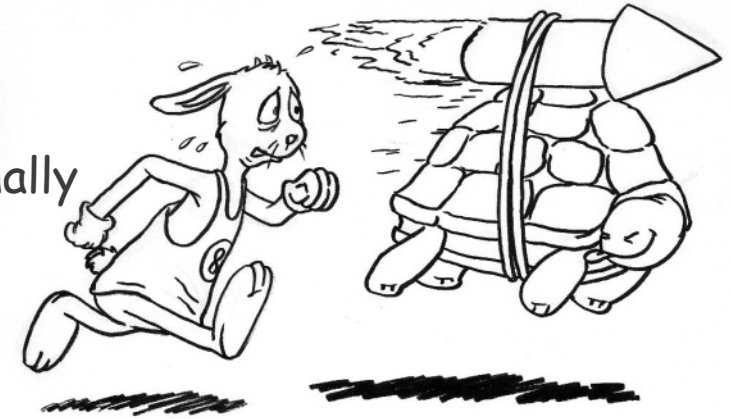
- Ions are treated classically
- Electrons are treated quantum mechanically
- Ionic mass >>>> Electronic mass: ion dynamics is decoupled from electron dynamics; i.e. ionic forces are determined by the ground-state electronic charge density for every ionic configuration

Relax electrons



Move ions

Ions: heavy, but computationally light



Electrons: light, but computationally heavy

Car-Parrinello molecular dynamics

- Ions are treated classically
- Electrons are treated quantum mechanically, but they are assigned a “fake”, unphysical, kinetic energy
- Ion dynamics and electron dynamics are more or less coupled, depending on ionic and (fake) electronic mass values (the fake electronic mass is not necessarily the physical one)

Move ions & electrons

Cheaper!

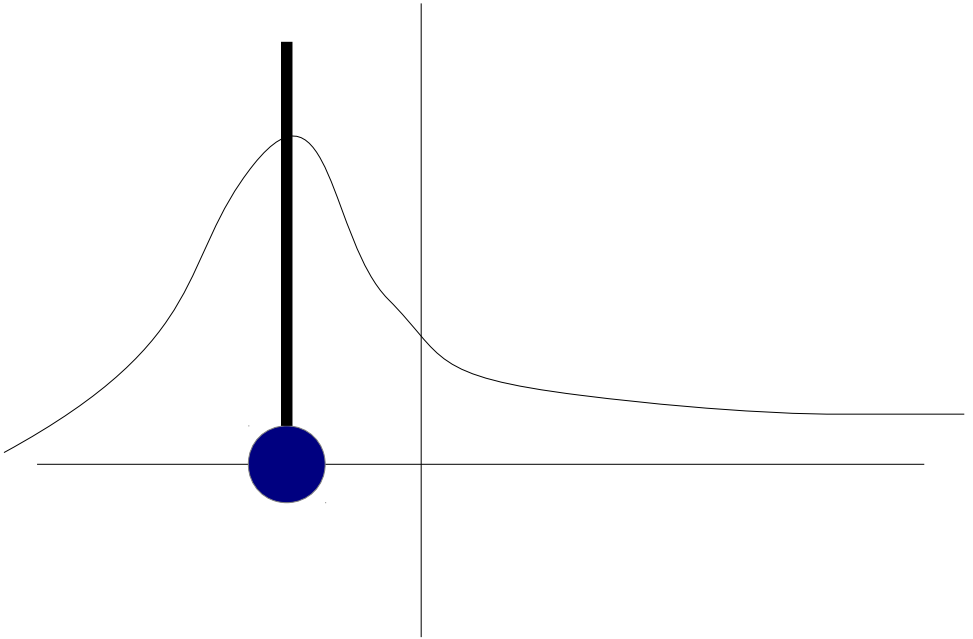
CP trick: fake Langevin dynamics

$$\bar{m} \cdot \frac{\partial^2 \bar{x}}{\partial t^2} = -\bar{\gamma} \cdot \frac{\partial \bar{x}}{\partial t} - \bar{\nabla} V(x)$$

Fake because electrons are quantum, they obey Schroedinger equation with a single time derivative, rather than a double one

$$\bar{m} = \begin{pmatrix} m_i \\ m_e \\ \vdots \\ m_e \end{pmatrix} \qquad \bar{x} = \begin{pmatrix} x_i \\ \psi_e(r_1) \\ \vdots \\ \psi_e(r_G) \end{pmatrix} \qquad \bar{\nabla} = \begin{pmatrix} \partial/\partial x_i \\ \partial/\partial \psi_e(r_1) \\ \vdots \\ \partial/\partial \psi_e(r_G) \end{pmatrix}$$

$$\bar{\gamma} = \begin{pmatrix} \gamma_i \\ \gamma_e \\ \vdots \\ \gamma_e \end{pmatrix}$$



The CP suite on my laptop

```
giovanni@peppone: ~/marzari/espresso_trunk/espresso
File  Edit  View  Search  Terminal  Help
giovanni@peppone:~/marzari/espresso_trunk/espresso$ ./configure &> /dev/null
giovanni@peppone:~/marzari/espresso_trunk/espresso$ make cp &> /dev/null
giovanni@peppone:~/marzari/espresso_trunk/espresso$
giovanni@peppone:~/marzari/espresso_trunk/espresso$
```

```
giovanni@peppone:~/marzari/espresso_trunk/espresso$ cd CPV
giovanni@peppone:~/marzari/espresso_trunk/espresso/CPV$ ls
Doc  examples  Makefile  src  tests
giovanni@peppone:~/marzari/espresso_trunk/espresso/CPV$ cd Doc
giovanni@peppone:~/marzari/espresso_trunk/espresso/CPV/Doc$ ls
html.sty        INPUT_WFDD          user_guide.aux  user_guide.tex
INPUT_CP.def    Makefile            user_guide.log  user_guide.toc
INPUT_CPPP.def  README.AUTOPILOT    user_guide.pdf
giovanni@peppone:~/marzari/espresso_trunk/espresso/CPV/Doc$ cd ../../
giovanni@peppone:~/marzari/espresso_trunk/espresso$ cd bin
giovanni@peppone:~/marzari/espresso_trunk/espresso/bin$ ls
cppp.x  cp.x  iotk  iotk_print_kinds.x  iotk.x  wfdd.x
giovanni@peppone:~/marzari/espresso_trunk/espresso/bin$
```

Online input description

http://www.quantum-espresso.org/wp-content/uploads/Doc/INPUT_CP.html

http://www.quantum-espresso.org/wp-content/uploads/Doc/INPUT_CPPP.html

Running CP!

```
espresso/bin$ ./cp.x < my_simulation.in > my_simulation.out
```

```
/espresso/bin$ mpirun -np 6 cp.x < my_simulation.in > my_simulation.out
```

CP postprocessing: CPPP!

```
/espresso/bin$ ./cppp.x < my_postproc.in > my_postproc.out
```

CP-MD run: what to do in practice

Set some ATOMC_POSITIONS

Relax electronic wavefunction:
(electron_dynamics='damp'
ion_dynamics='none')

dt=XXX
orthogonalization=
'Gram-Schmidt'

dt=XXX (larger number)
orthogonalization=
'ortho' (default)

If you want ions at
equilibrium positions:
(electron_dynamics='damp'
ion_dynamics='damp')

Perform MD run:
(electron_dynamics='verlet'
ion_dynamics='verlet')

Now initial positions are set!

ion_velocities='from_input'
('random', 'zero')

electron_velocities='default'
('zero')

Now initial velocities are set!

CP units: atomic units

Unless differently specified!!

$$\hbar = m_e = e = 4\pi\epsilon_0 = 1$$

$$\frac{Ze^2}{4\pi\epsilon_0 r^2} \longrightarrow \frac{Z}{r^2}, \qquad -\frac{\hbar^2}{2m_e}\nabla^2 \longrightarrow -\frac{1}{2}\nabla^2.$$

$$\hbar = 1.054\,571\,68 \cdot 10^{-34}\,\mathrm{J\ s} \qquad m_e = 0.910\,938\,26 \cdot 10^{-30}\,\mathrm{kg}$$
$$e = 1.602\,176\,53 \cdot 10^{-19}\,\mathrm{C} \qquad 4\pi\epsilon_0 = c^{-2} \cdot 10^{7}\,\mathrm{A^2\ N^{-1}}$$

Length: $a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = \frac{\hbar}{\alpha m_e c} = 5.291\,772\,06 \cdot 10^{-11}\,\mathrm{m}$

Velocity: $v_\mathrm{B} = \frac{e^2}{4\pi\epsilon_0\hbar} = \alpha c = 2.187\,691\,26 \cdot 10^{6}\,\mathrm{m\ s^{-1}}$

Time: $\tau_0 = \frac{(4\pi\epsilon_0)^2\hbar^3}{m_e e^4} = \frac{\hbar}{\alpha^2 m_e c^2} = 2.418\,884\,30 \cdot 10^{-17}\,\mathrm{s} = a_0/v_\mathrm{B}$

2.418 ... x 10^{-5} ps.

Energy: $E_\mathrm{h} = \frac{m_e e^4}{(4\pi\epsilon_0)^2\hbar^2} = \alpha^2 m_e c^2 = 4.359\,744\,2 \cdot 10^{-18}\,\mathrm{J} = m_e v_\mathrm{B}^2$

27.211.. eV

Temperature: 315770 °Kelvin

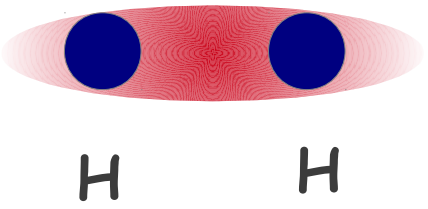
Let's look at some input files

Simple case: H2 molecule

```
/
&system
   ibrav=0,
   nat=2, ntyp=1, nbnd=1, nspin=1,
   ecutwfc=30.0, ecutrho=120.0,
```

```
ATOMIC_SPECIES
  H  1.00  H.pz-vbc.UPF
ATOMIC_POSITIONS angstrom
H -0.4 0. 0.
H 0.4 0. 0.
CELL_PARAMETERS angstrom
20.0 0. 0.
0.0 20.0 0.
0.0 0. 20.
```

Ionic mass



```
&control
   calculation='cp',
   restart_mode='from_scratch',
   nstep=40, iprint=60, isave=20,
   dt=5.0,
   ndr=90, ndw=91,
   pseudo_dir='/home/giovanni/marzari/espresso_trunk/espresso/pseudo/',
   outdir='./tmp/',
/
&system
   ibrav=0,
   nat=2, ntyp=1, nbnd=1, nspin=1,
   ecutwfc=30.0, ecutrho=120.0,
/
&electrons
   electron_dynamics='damp', electron_damping=0.2,
   startingwfc='random', ampre=0.01,
   emass=700., emass_cutoff=3.,
   orthogonalization='Gram-Schmidt',
/
&ions
   ion_dynamics='none',
   ion_radius(1)=1.0,
/
```

One first relaxes electronic degrees of freedom:
`dt` **small+**`'ortho'`
or `dt` **large+**`'Gram-Schmidt'`

Never use Gram-Schmidt in molecular (undamped) dynamics: it does not work!

```
&control
   calculation='cp',
   restart_mode='restart',
   nstep=40, iprint=50, isave=40,
   dt=15.0,
   ndr=91, ndw=94,
   pseudo_dir='/home/giovanni/marzari/espresso_trunk/espresso/pseudo/',
   outdir='./tmp/',
/
&system
   ibrav=0,
   nat=2, ntyp=1, nbnd=1, nspin=1,
   ecutwfc=30.0, ecutrho=120.0,
/
&electrons
   electron_dynamics='damp', electron_damping=0.2
   emass=700., emass_cutoff=3.,
   orthogonalization='ortho',
/
&ions
   ion_dynamics='none',
   ion_radius(1)=1.0,
/
```

Then:
larger `dt`, and `'ortho'`

`'ortho'` is the default orthogonalization

```
&control
   calculation='cp',
   restart_mode='reset_counters',
   nstep=2600, iprint=10, isave=20,
   dt=1.5,
   ndr=94, ndw=941,
   pseudo_dir='/home/giovanni/marzari/espresso_trunk/espresso/pseudo/',
   outdir='./tmp/',
   ekin_conv_thr=1.e-5,
   etot_conv_thr=1.e-7,
   forc_conv_thr=1.e-5,
/
&system
   ibrav=0,
   nat=2, ntyp=1, nbnd=1, nspin=1,
   ecutwfc=30.0, ecutrho=120.0,
/
&electrons
   electron_dynamics='damp', electron_damping=0.001,
   emass=500., emass_cutoff=3., electron_velocities='zero',
/
&ions
   ion_dynamics='damp',ion_velocities='zero',
   ion_radius(1)=1.0, ion_damping=0.02
```

Ionic+electronic relaxation: structural optimization

```
&control
   calculation='cp',
   restart_mode='reset_counters',
   nstep=400, iprint=10, isave=10,
   dt=1.5,
   ndr=94, ndw=942,
   pseudo_dir='/home/giovanni/marzari/espresso_trunk/espresso/pseudo/',
   outdir='./tmp/',
/
&system
   ibrav=0,
   nat=2, ntyp=1, nbnd=1, nspin=1,
   ecutwfc=30.0, ecutrho=120.0,
/
&electrons
   electron_dynamics='verlet', ortho_max=100,
   emass=100., emass_cutoff=3.,
/
&ions
   ion_dynamics='verlet',
   ion_radius(1)=1.0
/
```

MD run, no damping, 'verlet' dynamics

CP units: atomic units

Unless differently specified!!

In the input file:

Ecutwfc ---> Ry (0.5 E_H) Ecutrho ---> Ry (0.5 E_H)

Ionic mass ---> a.m.u (=1/12 of C12 mass, =1823 m_e)

ATOMIC_POSITIONS: (Bohr, angstrom, crystal)

Tempw --->°K fnosep --->THz (3 THz=100 cm^{-1})

In the output file:

Electronic eigenvalues ---> (eV), ion temperature (°K)

In 'prefix.evp':

Time---> picoseconds (ps)

Ionic temperature (tempp) ---> °K

Units should be specified either in input/output files, or in the online input description

What do we have as output?

```
&control
   outdir='outdir',
   prefix='prefix',
   ndr=$ndr, ndw=$ndw
   restart_mode= 'from_scratch'
       ('restart','reset_counters')
```

EVERY ... iprint_stdout, iprint, isave ... STEPS

Prints in standard output: my_simulation.out

Prints in:
'prefix'.pos (ion positions),
'prefix'.vel (ion velocities),
'prefix'.cel (cell parameters),
'prefix'.evp (energies, potentials),
'prefix'.eig (electronic eigenvalues),
...

Saves quantities inside 'outdir': 'prefix'_$ndr.save

```
            total energy =      -1.12571 Hartree a.u.
          kinetic energy =       1.00523 Hartree a.u.
electrostatic energy =      -0.70076 Hartree a.u.
                  esr =       0.08638 Hartree a.u.
               eself =       0.79788 Hartree a.u.
pseudopotential energy =      -0.79924 Hartree a.u.
n-l pseudopotential energy =       0.00000 Hartree a.u.
exchange-correlation energy =      -0.63095 Hartree a.u.
      average potential =       0.00000 Hartree a.u.


  Eigenvalues (eV), kp =   1 , spin =  1

  -9.94

  CELL_PARAMETERS
  37.79452266    0.00000000    0.00000000
   0.00000000   37.79452266    0.00000000
   0.00000000    0.00000000   37.79452266

  System Density [g/cm^3] :     0.0004

  Center of mass square displacement (a.u.):   0.000000

  ATOMIC_POSITIONS
  H   -0.755890E+00  0.000000E+00  0.000000E+00
  H    0.755890E+00  0.000000E+00  0.000000E+00

  ATOMIC_VELOCITIES
  H    0.000000E+00  0.000000E+00  0.000000E+00
  H    0.000000E+00  0.000000E+00  0.000000E+00
```

every iprint_output steps, we get a summary of energy, positions, velocities, cell parameters

Interesting file: 'prefix'.evp

```
!
IF( tfile ) WRITE( 33, 2948 ) nfi, ekinc, temphc, tempp, etot, enthal, &
                              econs, econt, volume, out_press, tps
```

nfi---> number of iterations

ekinc---> electron fake kinetic energy

temphc(°K)---> temperature due to "cell" kinetic energy

tempp(°K)---> temperature due to ionic displacements within the cell

etot---> dft total energy (without ionic and cell kinetic energy)

enthal---> etot+external_pressure*volume

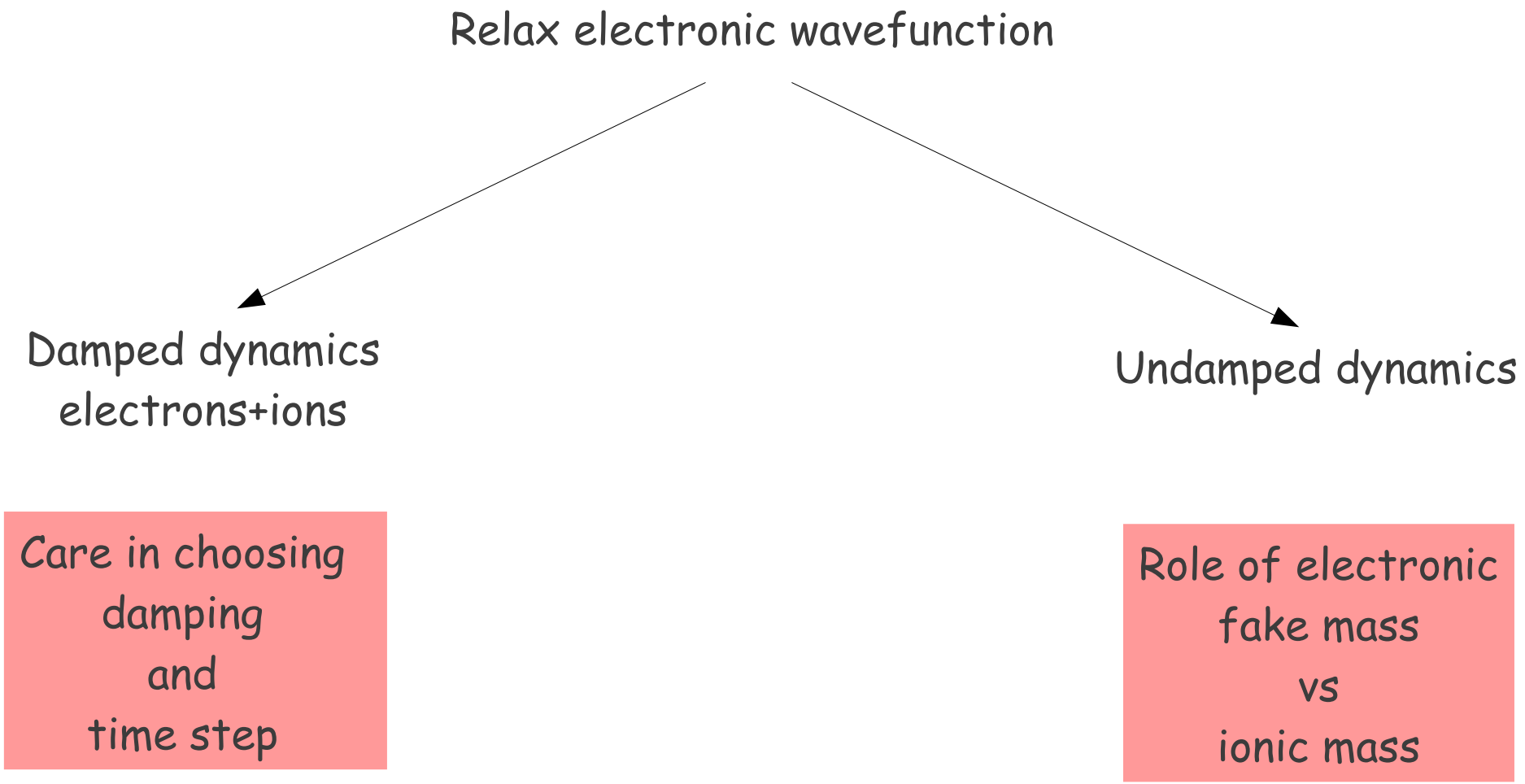
econs---> etot+kinetic_energy_due_to_ions_moving

econt---> econs+ekinc+(thermostat_total_energy)

tps(ps)---> time

```
  60   4.7354565559E-06   0.0000000000E+00   0.0000000000E+00  -1.1257015935E+00  -1.1257015935E+00  ......
  10   7.9581413250E-06   0.0000000000E+00   3.2452211964E+00  -1.1258211845E+00  -1.1258211845E+00
  20   2.0718314226E-06   0.0000000000E+00   7.0110755275E-01  -1.1258717932E+00  -1.1258717932E+00
  30   5.3214816448E-07   0.0000000000E+00   5.4578115660E-05  -1.1258720887E+00  -1.1258720887E+00  ......
  40   4.8452016544E-07   0.0000000000E+00   3.0606574237E-02  -1.1258729921E+00  -1.1258729921E+00
  50   4.8872573496E-07   0.0000000000E+00   1.1007216713E-02  -1.1258732872E+00  -1.1258732872E+00
  60   5.0924288049E-07   0.0000000000E+00   1.3445000727E-03  -1.1258733043E+00  -1.1258733043E+00  ......
  70   4.9161497324E-07   0.0000000000E+00   8.9105108844E-04  -1.1258733444E+00  -1.1258733444E+00
  80   4.3311216032E-07   0.0000000000E+00   6.6817336829E-04  -1.1258733330E+00  -1.1258733330E+00
  90   3.8907216922E-07   0.0000000000E+00   6.7517282961E-04  -1.1258733232E+00  -1.1258733232E+00  ......
 100   3.8526768053E-07   0.0000000000E+00   2.1955634295E-04  -1.1258733526E+00  -1.1258733526E+00
```

Hands on exercise 1: cp on H2


Relax electronic wavefunction
Damped dynamics
electrons+ions
Undamped dynamics
Care in choosing
damping
and
time step
Role of electronic
fake mass
vs
ionic mass

Sample input files : H.erelax.start.in

```
 &control
   calculation='cp',
   restart_mode='from_scratch',
   nstep=xxx, iprint=2, isave=20,
   dt=xxx,
   ndr=90, ndw=91,
   pseudo_dir='./pseudo/',
   outdir='./tmp/',
/
&system
   ibrav=0,
   nat=2, ntyp=1, nbnd=1, nspin=1,
   ecutwfc=30.0, ecutrho=120.0,
/
```

```
 &electrons
    electron_dynamics='xxx',
    electron_damping=xxx,
    startingwfc='random', ampre=0.01,
    emass=xxx, emass_cutoff=3.,
    orthogonalization='xxx',
 /
 &ions
    ion_dynamics='none',
    ion_radius(1)=1.0,
 /
ATOMIC_SPECIES
  H  1.00 H.pz-vbc.UPF
ATOMIC_POSITIONS angstrom
H -0.4 0. 0.
H 0.4 0. 0.
CELL_PARAMETERS angstrom
20.0 0. 0.
0.0 20.0 0.
0.0 0. 20.
```

Sample input files : H.erelax.restart.in

```
 &control
   calculation='cp',
   restart_mode='restart',
   nstep=xxx, iprint=2, isave=40,
   dt=xxx,
   ndr=91, ndw=92,
   pseudo_dir='./pseudo/',
   outdir='./tmp/',
   etot_conv_thr=1.e-7,
/
&system
   ibrav=0,
   nat=2, ntyp=1, nbnd=1, nspin=1,
   ecutwfc=30.0, ecutrho=120.0,
/
```

```
 &electrons
    electron_dynamics='xxx',
    electron_damping=xxx
    ortho_max=100,
    emass=xxx,
    emass_cutoff=3.,
 /
 &ions
    ion_dynamics='none',
    ion_radius(1)=1.0,
 /
ATOMIC_SPECIES
  H  1.00 H.pz-vbc.UPF
ATOMIC_POSITIONS angstrom
H -0.4 0. 0.
H 0.4 0. 0.
CELL_PARAMETERS angstrom
20.0 0. 0.
0.0 20.0 0.
0.0 0. 20.
```

Sample input files : H.ionrelax.in

```
&control
   calculation='cp',
   restart_mode='restart',
   nstep=xxx, iprint=2, isave=20,
   dt=xxx,
   ndr=94, ndw=941,
   pseudo_dir='./pseudo/',
   outdir='./tmp/',
   ekin_conv_thr=xxx,
   etot_conv_thr=xxx,
   forc_conv_thr=xxx,
/
&system
   ibrav=0,
   nat=2, ntyp=1, nbnd=1, nspin=1,
   ecutwfc=30.0, ecutrho=120.0,
/
```

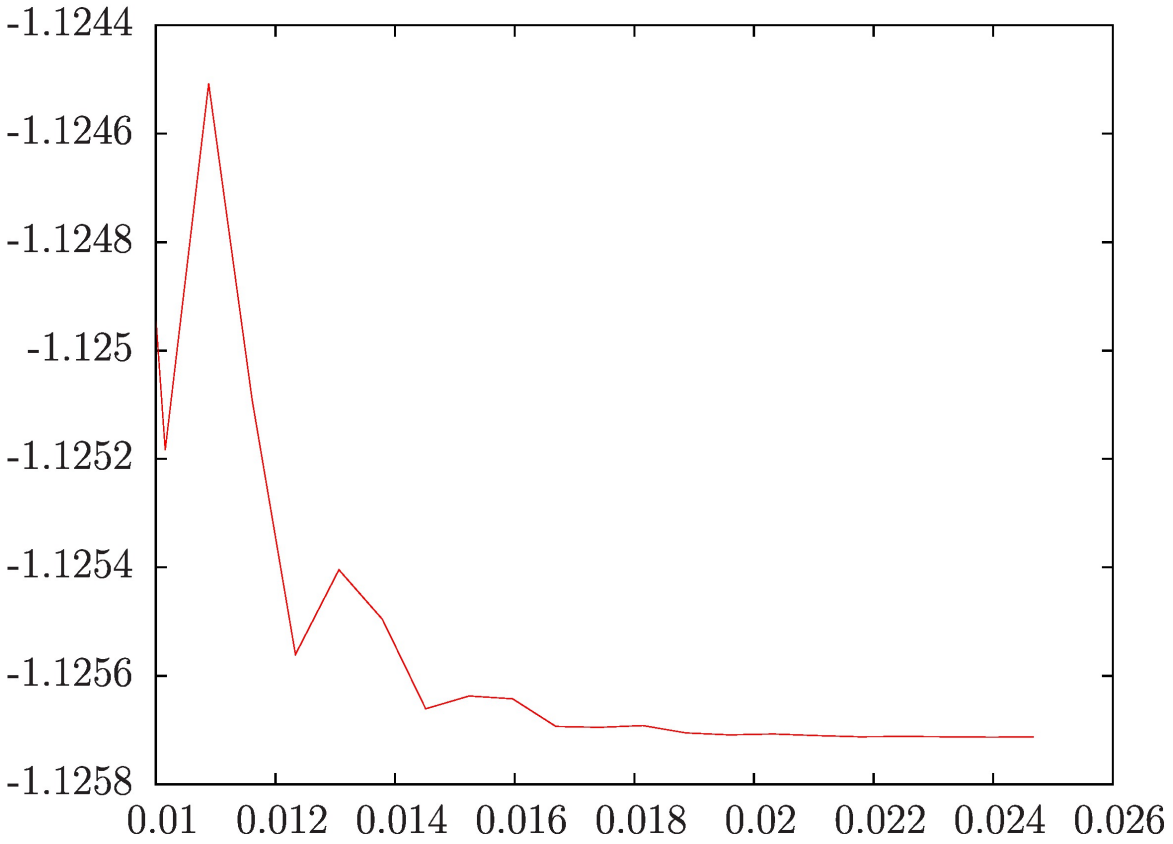
```
&electrons
   electron_dynamics='xxx',
   electron_damping=0.001,
   ortho_max=100,
   emass=500,
   emass_cutoff=3.,
   electron_velocities='zero',
/
&ions
   ion_dynamics='xxx',
   ion_velocities='zero',
   ion_radius(1)=1.0,
   ion_damping=0.01
/
ATOMIC_SPECIES
  H  1.00 H.pz-vbc.UPF
ATOMIC_POSITIONS angstrom
H -0.4 0. 0.
H 0.4 0. 0.
CELL_PARAMETERS angstrom
20.0 0. 0.
0.0 20.0 0.
0.0 0. 20.
```

Sample input files : H.md.in

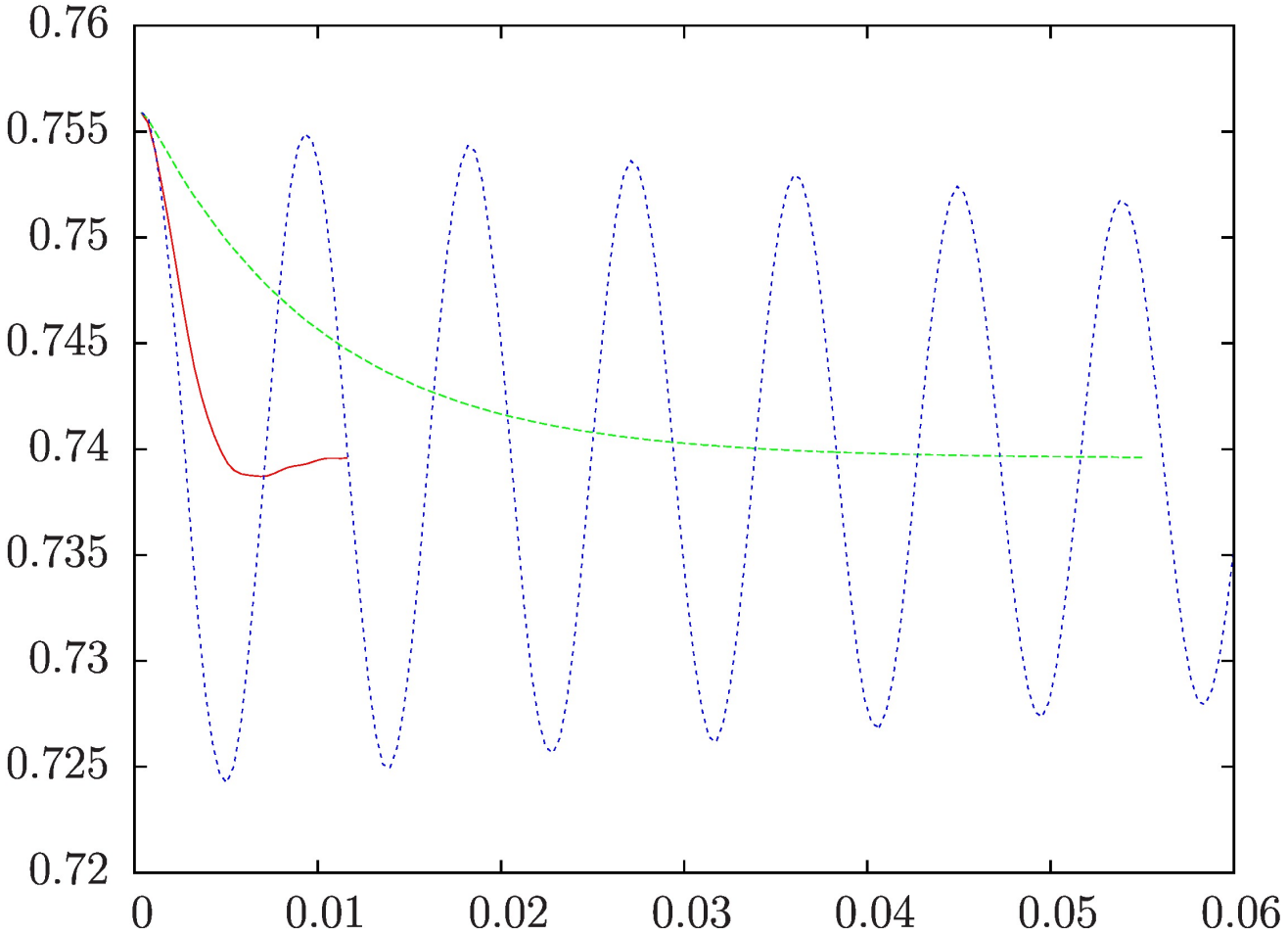
```
&control
   calculation='cp',
   restart_mode='reset_counters',
   nstep=100, iprint=1, isave=10,
   dt=8,
   ndr=92, ndw=932,
   pseudo_dir='./pseudo/',
   outdir='./tmp/',
/
&system
   ibrav=0,
   nat=2, ntyp=1, nbnd=1, nspin=1,
   ecutwfc=30.0, ecutrho=120.0,
/
```

```
 &electrons
    electron_dynamics='xxx',
    ortho_max=100,
    emass=500,
    emass_cutoff=3.,
 /
 &ions
    ion_dynamics='xxx',
    ion_radius(1)=1.0
 /
ATOMIC_SPECIES
  H  1.00 H.pz-vbc.UPF
ATOMIC_POSITIONS angstrom
H -0.4 0. 0.
H 0.4 0. 0.
CELL_PARAMETERS angstrom
20.0 0. 0.
0.0 20.0 0.
0.0 0. 20.
```

Some plots:
Adjusting the electronic damping for optimal convergence



Some plots:
Adjusting the ionic damping for optimal convergence



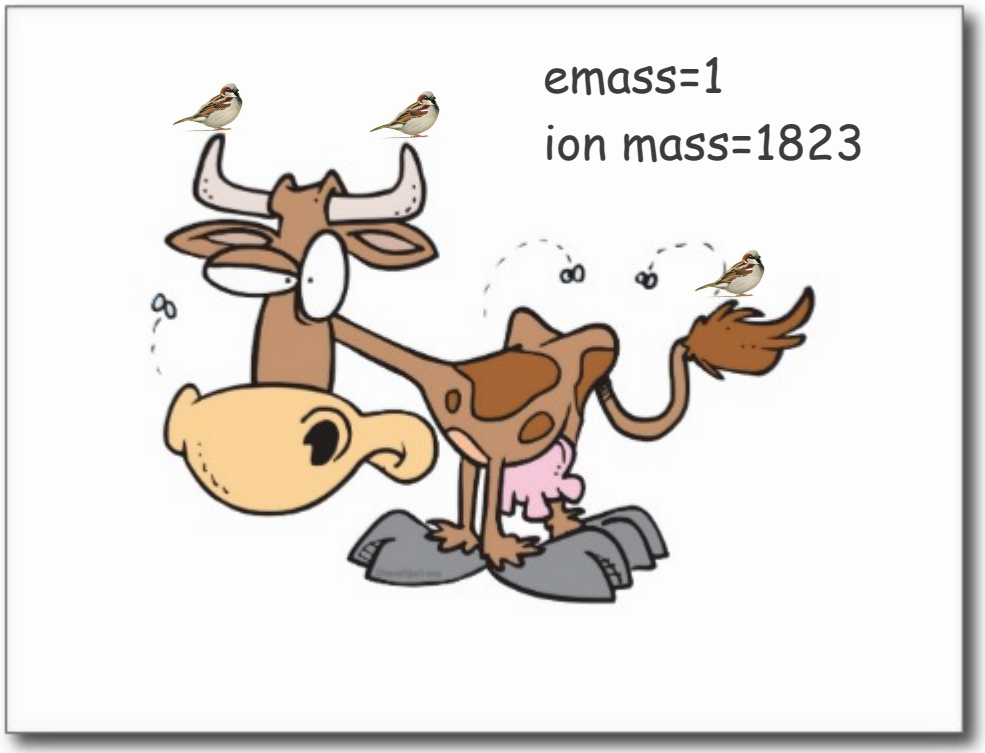
Electron & ion mass: their role

```
/
&electrons
  electron_dynamics='verlet', ortho_max=100,
  emass=100., emass_cutoff=3.,
```

1823

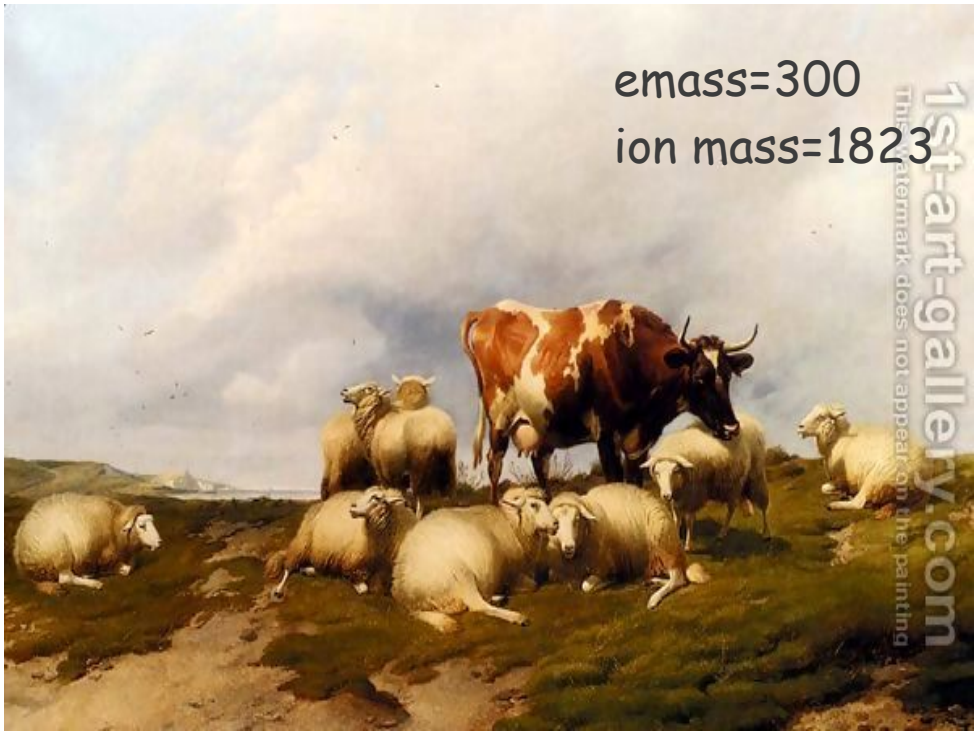
```
ATOMIC_SPECIES
  H  1.00  H.pz-vbc.UPF
```

This is the true picture



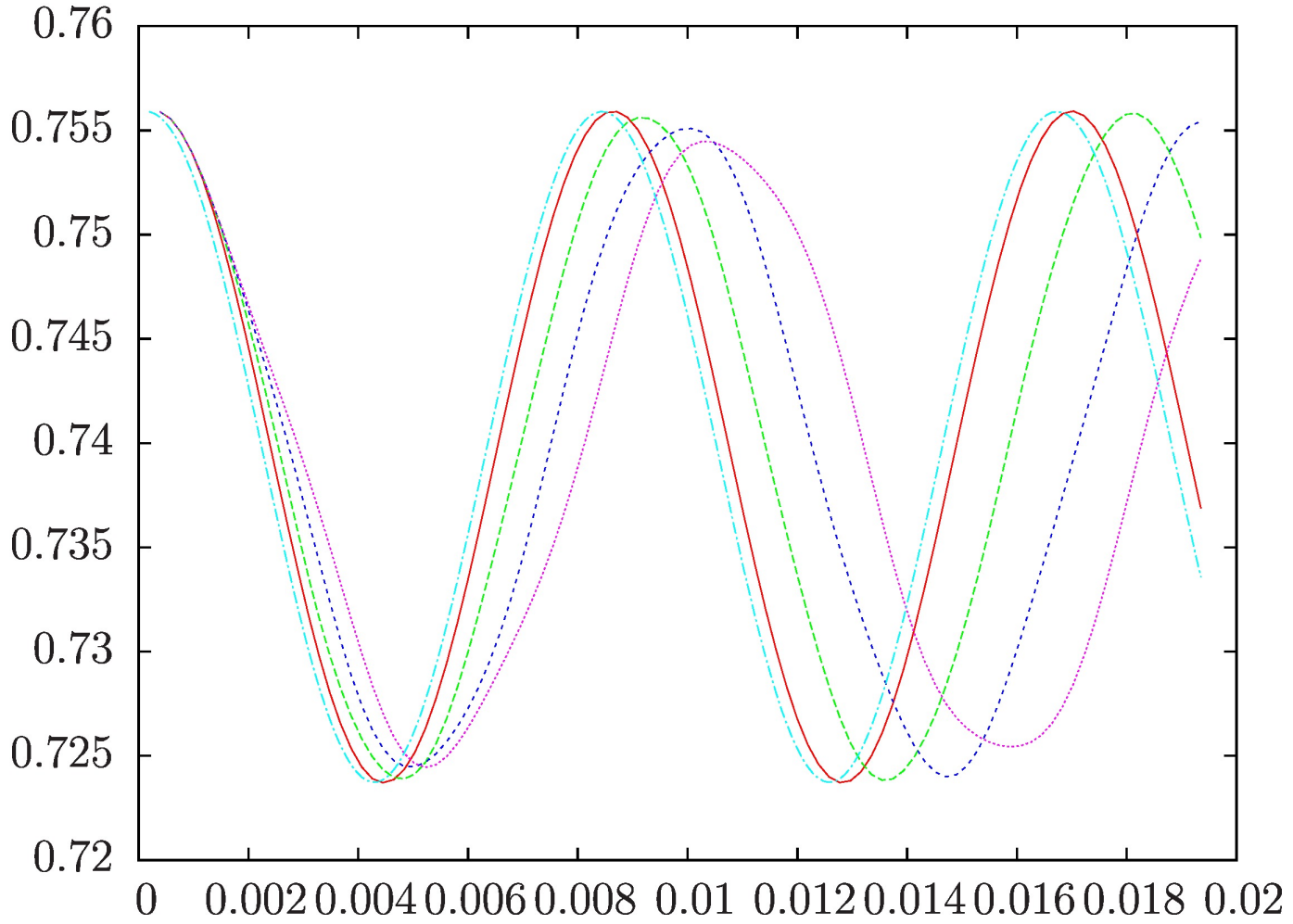
1 vs 1823

What happens if we increase emass?

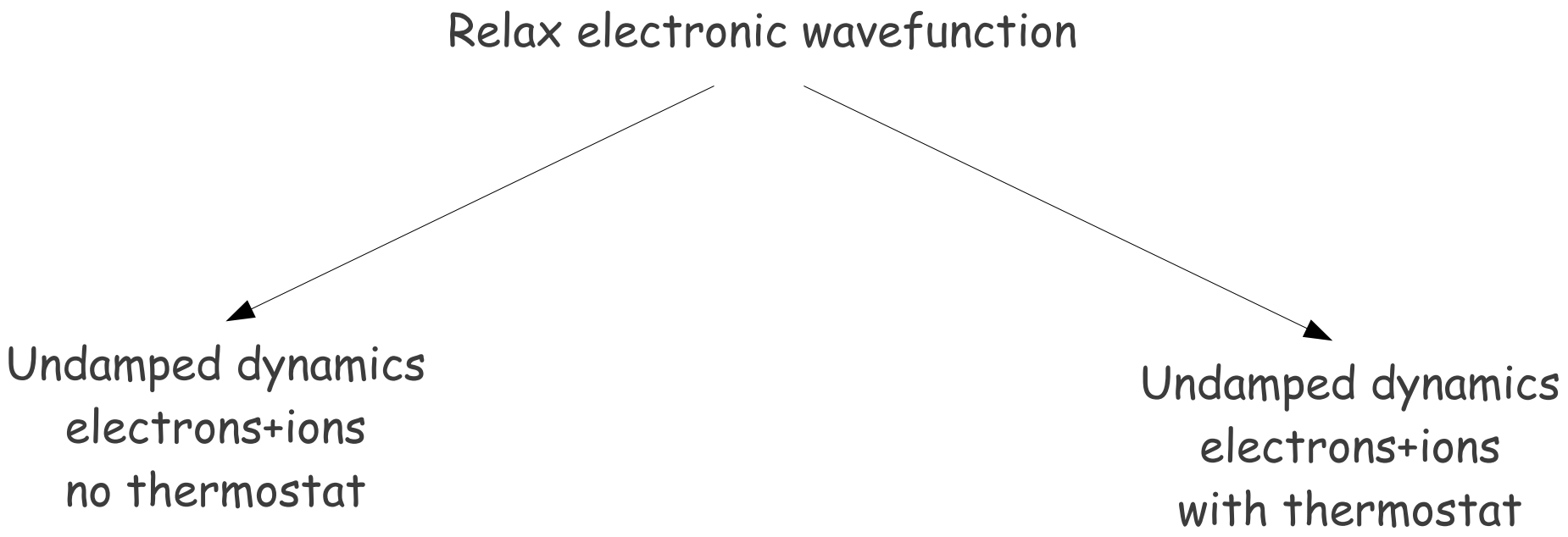


300 vs 1823

A large electron mass 'drags' the ions



Hands on exercise 2: silicon



How a Nose thermostat works.
Behavior of the different energy terms
in the output files of cp.

Sample input files : Si.erelax.start.in

```
 &control
   calculation='cp',
   restart_mode='from_scratch',
   nstep=xxx, iprint=20, isave=20,
   dt=xxx,
   ndr=90, ndw=91,
   pseudo_dir='./pseudo/',
   outdir='./tmp/',
/
&system
   ibrav=0,
   nat=xxx, ntyp=1, nbnd=xxx, nspin=1,
   ecutwfc=20.0, ecutrho=80.0,
/
```

```
&electrons
    electron_dynamics='xxx',
    electron_damping=0.1,
    startingwfc='random', ampre=0.01,
    orthogonalization='xxx',
    emass=xxx, emass_cutoff=3.,
 /
 &ions
    ion_dynamics='xxx',
    ion_radius(1)=1.0,
 /
ATOMIC_SPECIES
  Si  28.0855 Si.pz-vbc.UPF
ATOMIC_POSITIONS angstrom
....
```

Sample input files : Si.erelax.restart.in

```
 &control
   calculation='cp',
   restart_mode='restart',
   nstep=xxx, iprint=10, isave=50,
   dt=xxx,
   ndr=91, ndw=92,
   pseudo_dir='./pseudo/',
   outdir='./tmp/',
   etot_conv_thr=xxx
/
&system
   ibrav=0,
   nat=xxx, ntyp=1, nbnd=xxx, nspin=1,
   ecutwfc=20.0, ecutrho=80.0,
/
```

```
&electrons
    electron_dynamics='xxx',
    electron_damping=xxx,
    emass=700., emass_cutoff=3.,
 /
 &ions
    ion_dynamics='xxx',
    ion_radius(1)=1.0,
 /
ATOMIC_SPECIES
  Si  28.0855 Si.pz-vbc.UPF
ATOMIC_POSITIONS angstrom
```

Sample input files : Si.md.in

```
  &control
   calculation='cp',
   restart_mode='reset_counters',
   nstep=4000, iprint=10, isave=100,
   dt=4.0,
   ndr=92, ndw=931,
   pseudo_dir='./pseudo/',
   outdir='./tmp/',
/
&system
   ibrav=0,
   nat=16, ntyp=1, nbnd=32, nspin=1,
   ecutwfc=20.0, ecutrho=80.0,
/
```

```
 &electrons
    electron_dynamics='xxx',
    ortho_max=100,
    emass=100., emass_cutoff=3.,
 /
 &ions
    ion_dynamics='xxx',
    ion_radius(1)=1.0
 /
ATOMIC_SPECIES
  Si  28.0855 Si.pz-vbc.UPF
ATOMIC_POSITIONS angstrom
```

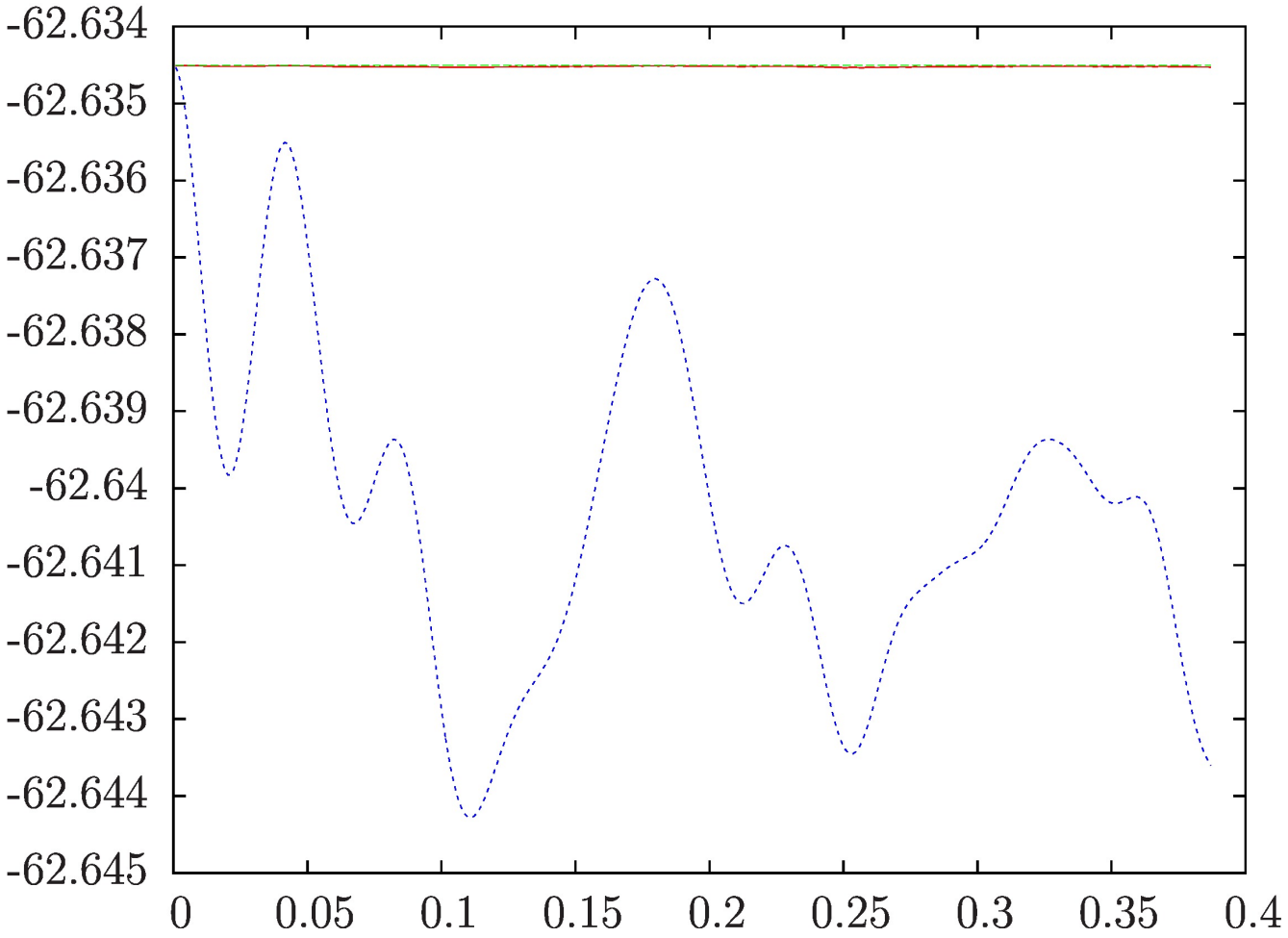
Sample input files : Si.md_th.in

```
&control
   calculation='cp',
   restart_mode='reset_counters',
   nstep=6000, iprint=10, isave=100,
   dt=4.0,
   ndr=92, ndw=932,
   pseudo_dir='./pseudo/',
   outdir='./tmp/',
/
&system
   ibrav=0,
   nat=xxx, ntyp=1, nbnd=xxx, nspin=1,
   ecutwfc=20.0, ecutrho=80.0,
/
```

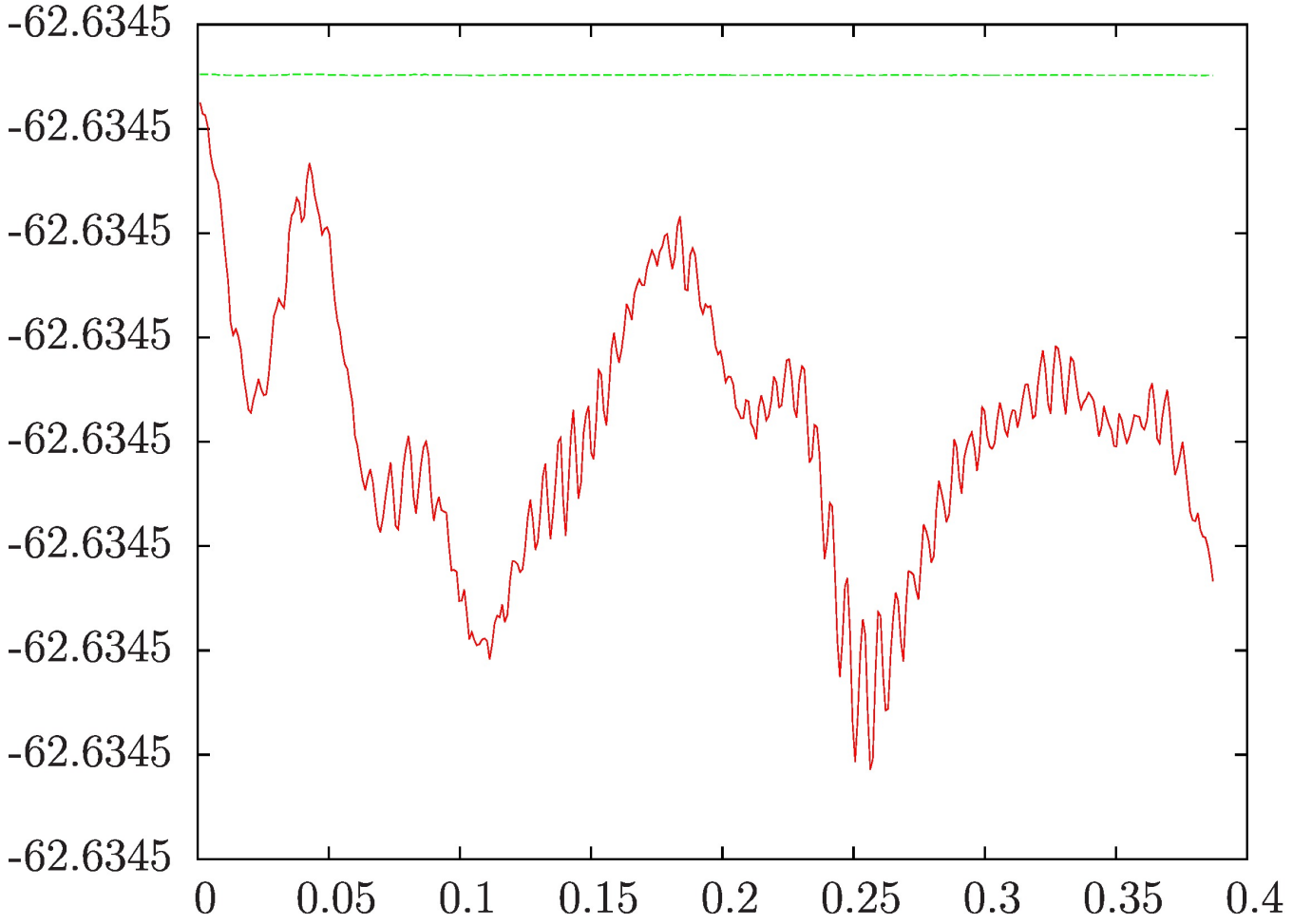
```
&electrons
   electron_dynamics='xxx',
   ortho_max=100,
   emass=100., emass_cutoff=3.,
/
&ions
   ion_dynamics='verlet',
   ion_temperature='nose',
   tempw=300, fnosep=xxx,
   ion_radius(1)=1.0,
/
ATOMIC_SPECIES
 Si  28.0855 Si.pz-vbc.UPF
```

Some plots

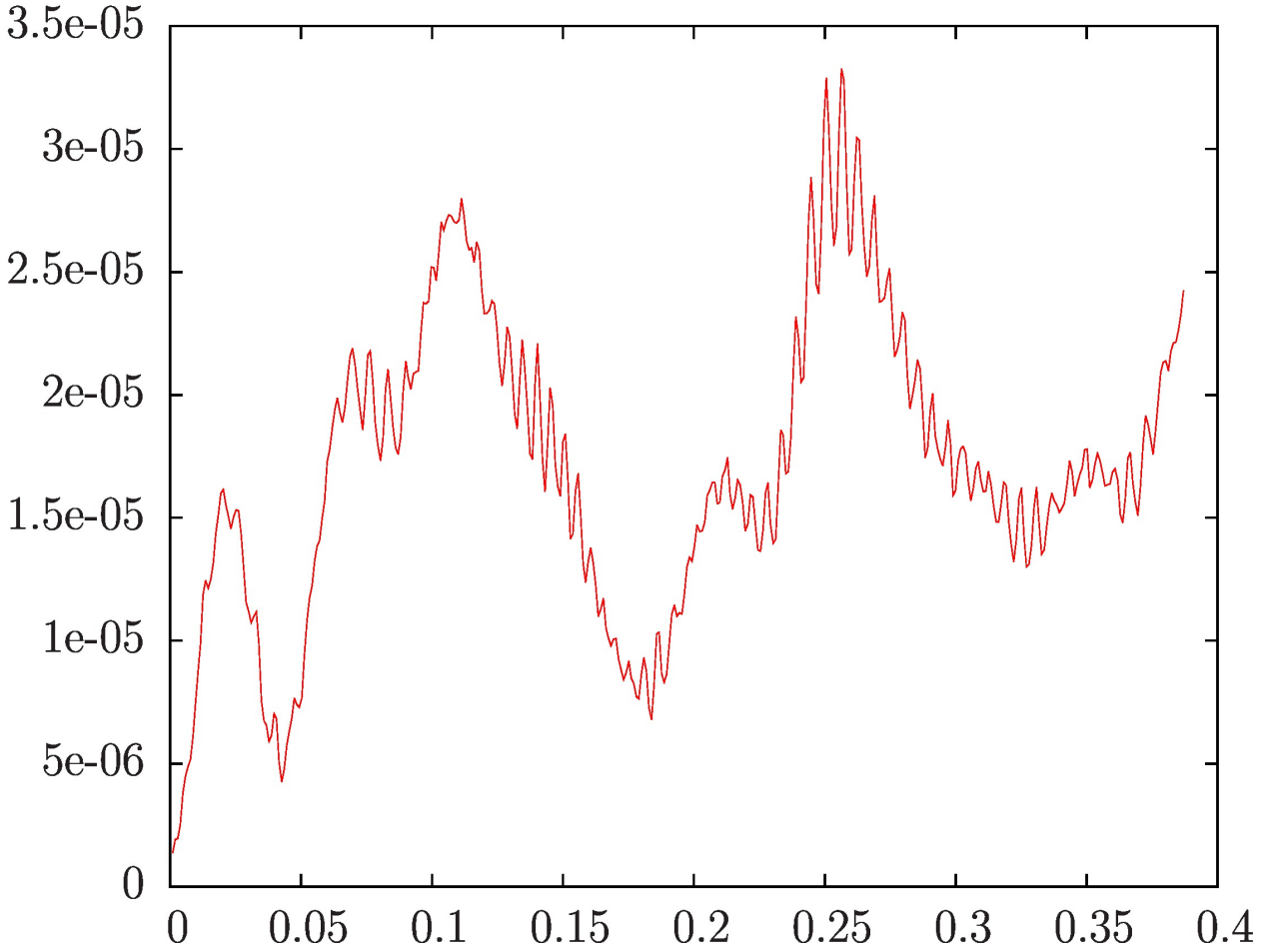
Etot, econs, econt (no-thermostat)



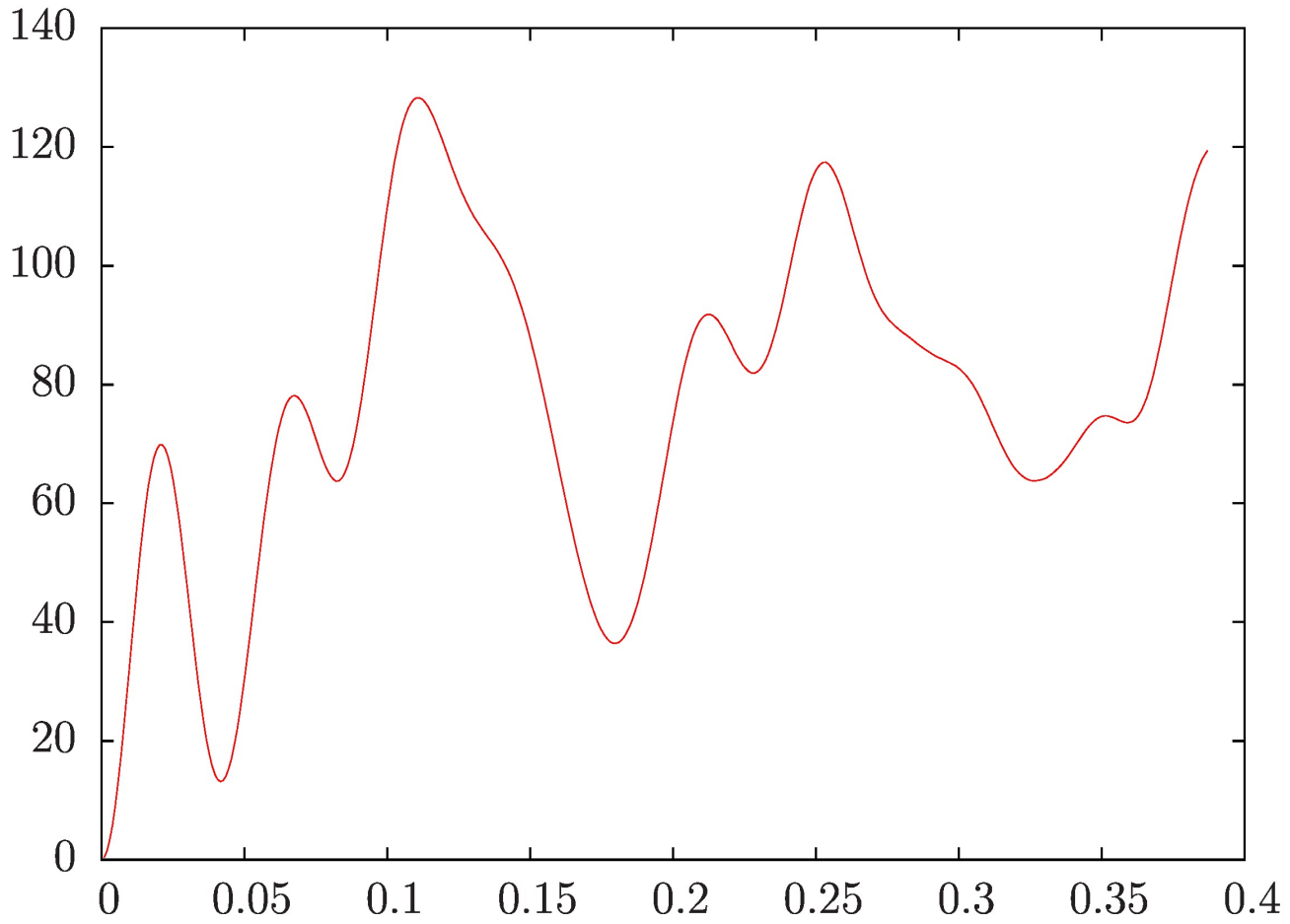
Econs, econt (no-thermostat)



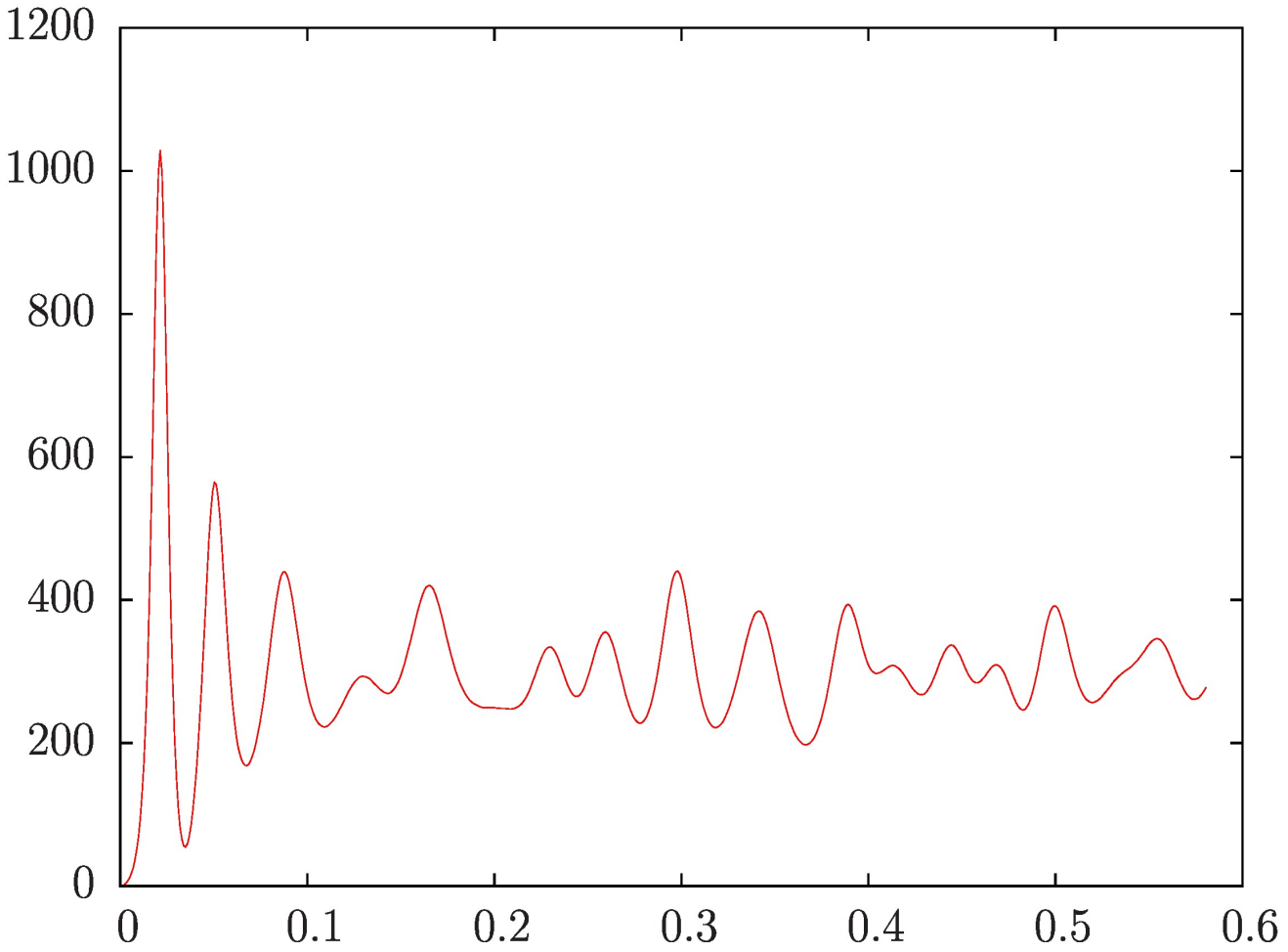
Ekinc (no-thermostat)



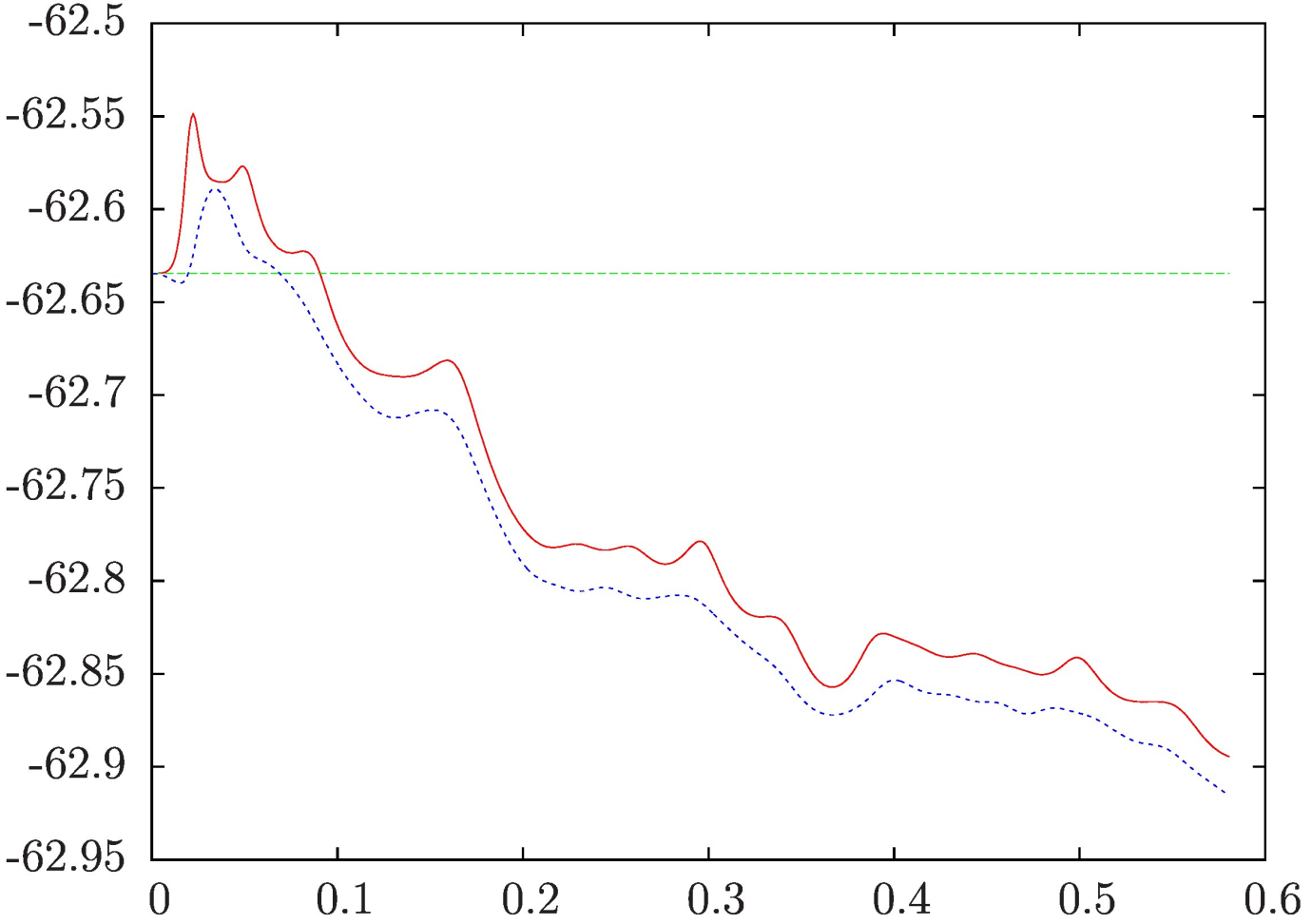
Temperature (no-thermostat)



Temperature (thermostat)

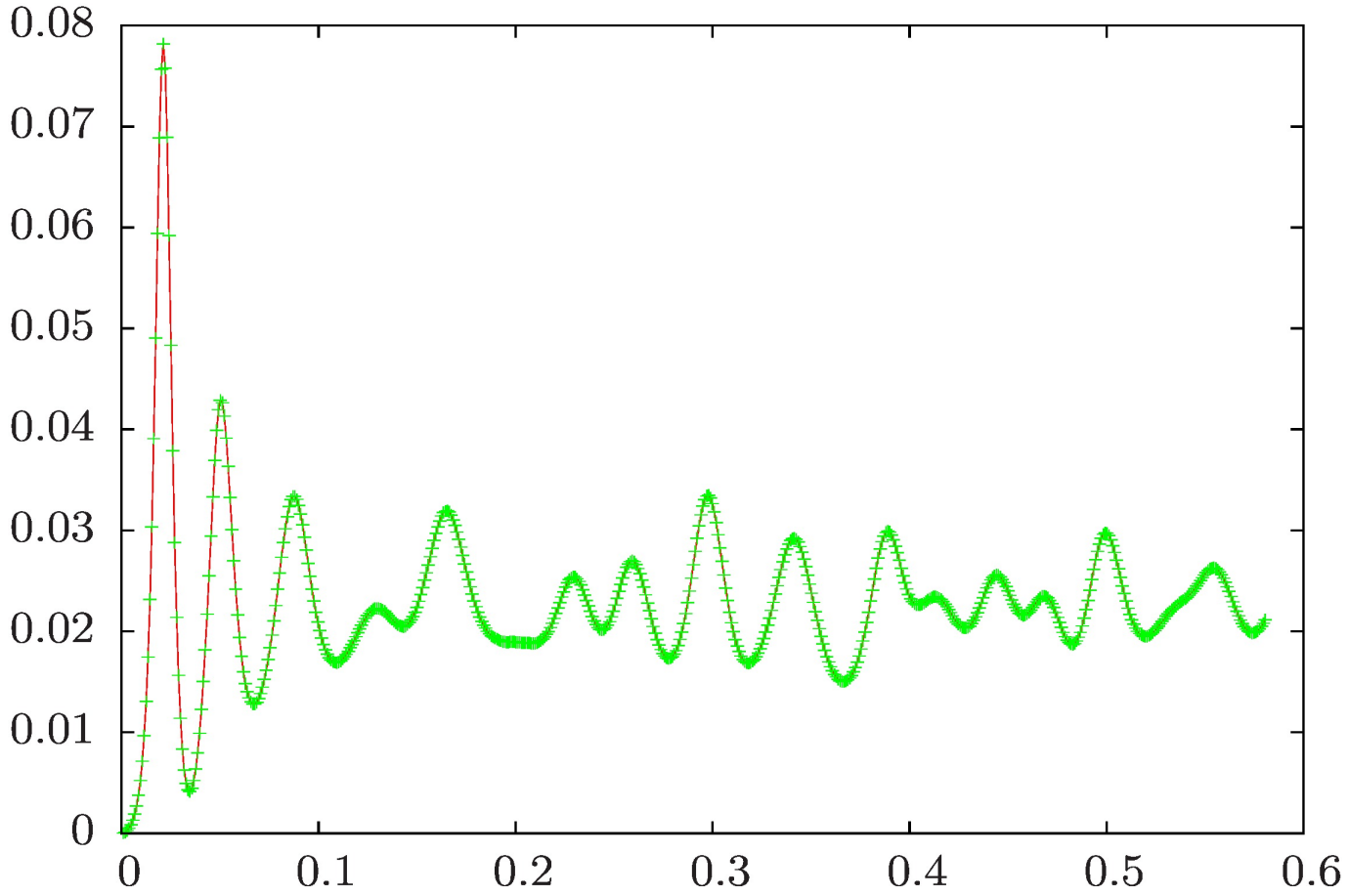


Etot, econs, econt (thermostat)



Econs-etot and temperature

Which is the proportionality coefficient?



cppp.x input file: movies

```
&INPUTPP
    prefix = 'cp' ,
    fileout = 'postproc' ,
    outdir = './tmp' ,
    output = 'xsf' ,
    ndr = 931 ,
    lcharge = .false. ,
    atomic_number(1)=1 ,
    ldynamics = .true. ,
    nframes = 200 ,
/
```

This produces a film .axsf
that you can open with
xcrysden