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www.ictp.it

***School on Numerical Methods
for Materials Science Related to
Renewable Energy Applications***

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Hands-on : Model Potential Molecular Dynamics

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0. DL_POLY code introduction

0.a Input files

DL_POLY code is a general purpose parallel molecular dynamics simulation package developed at Daresbury Laboratory by W. Smith and I.T. Todorov. It can be freely downloaded at (<http://www.stfc.ac.uk/cse/25526.aspx>) upon registration, and its manual can be found at http://www.ccp5.ac.uk/DL_POLY/MANUALS/USRMAN4.pdf

Copy the executable (DLPOLY.Z) from \$WORKSHOP/dl_poly_4.04/execute/ into your working directory, and the manual (USRMAN4.04.pdf) from \$WORKSHOP/dl_poly_4.04/manual.

We need three files to start a DL_POLY MD simulation, named as CONFIG, CONTROL and FIELD:

CONFIG contains the informations on the system geometry and the simulation cell

FIELD contains the parameters of the force field which describes the molecular interactions (bond stretching, Van der Waals interactions, atomic partial charges etc.)

CONTROL contains the simulation parameters (e.g. temperature, pressure, number of timesteps...)

CONFIG – typical file structure

Periodic boundary conditions key (see manual)

Config file key (see manual)

n. of atoms

Simulation cell

Title

Atom name

Atom index

x,y,z coordinates

IceI	0	2	276	
<div>26.988000000000000 0.000000000000000 0.000000000000000 0.000000000000000 23.372293600000000 0.000000000000000 0.000000000000000 0.000000000000000 44.028000000000000</div>				
OW	1			
-2.505228382		-1.484234330		-7.274585343
HW	2			
-1.622622646		-1.972916834		-7.340573742
HW	3			
-3.258494716		-2.125627191		-7.491549620
OW	4			
0.9720599243E-01		-2.503798635		-3.732081894
⋮		⋮		⋮

FIELD – typical file structure (2)

If there are more than 1 molecular species, the FIELD file will look like this:

details on the first
molecular species

details on the second
molecular species

details on the third
molecular species

nonbonded interactions – unique
section for all the molecular species

p3ht,nanotube,thf

UNITS kcal

MOLECULES

3

p3ht

NUMMOL 4

ATOMS 202

bonds 400

angles 950

dihedrals 1480

FINISH

nanotube

NUMMOL 1

ATOMS 804

bonds 1500

angles 2450

dihedrals 8600

FINISH

thf

NUMMOL 1

ATOMS 13

bonds 13

angles 13

dihedrals 41

FINISH

vdw 18.0000000

C C lj 0.1094 3.3997

C H lj 0.0414 2.9355

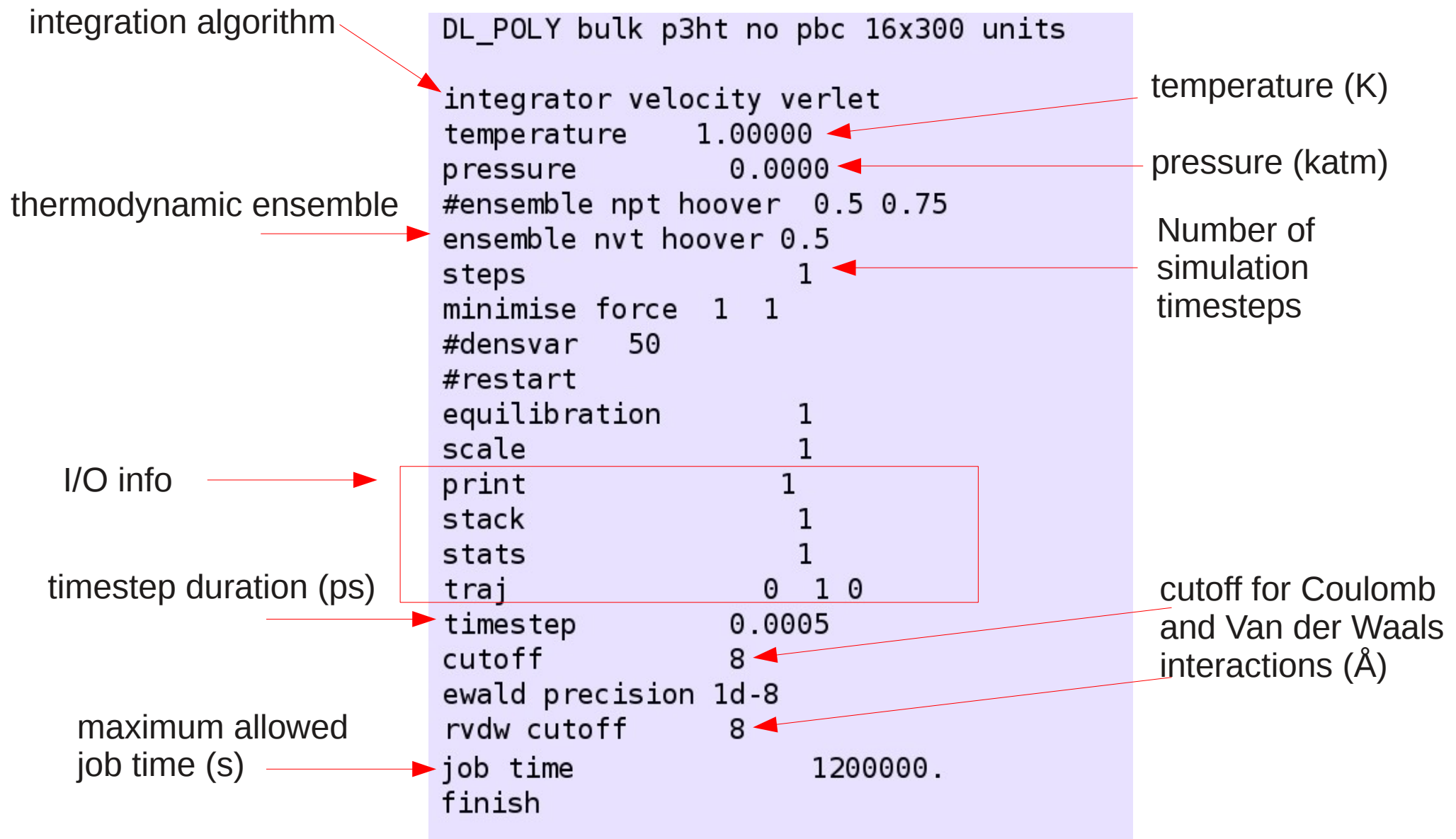
.

.

.

close

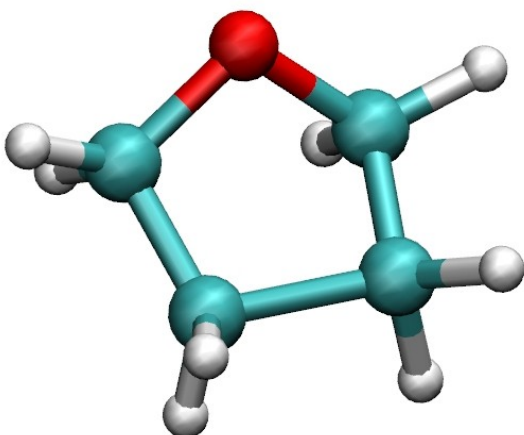
CONTROL – typical file structure



1. THF solvent molecule

1.a Geometry optimization

1.b NVE/NVT dynamics



"minimise force n f"

tells the code to perform a local optimization of the molecule every n step by minimizing the intramolecular forces with respect to the tolerance f , using conjugate gradient method.

The minimization can be performed also on the *energy* or *maximum displacement*.

Edit CONTROL file by adding the highlighted row

```
DL_POLY thf

integrator velocity verlet
temperature      1.00000
pressure         0.0000
ensemble nve
steps            1
minimise force 1 1
print            1
stack            1
stats            1
traj             0 1 0
timestep         0.0005
cutoff           8
ewald precision 1d-8
rvdw cutoff      8
job time         1200000.
finish
```


1. THF solvent molecule

1.a Geometry optimization

1.b NVE/NVT dynamics

Run the calculation by executing DLPOLY.Z (it should be very fast)



After the calculation, some new files have been created by the program:

OUTPUT contains a summary of the simulation details, force field, system configuration at different timesteps etc.

HISTORY contains the atomic coordinates at every timestep

REVCON contains the final atomic coordinates, velocities and forces. It is used mainly as restart file.

REVIVE binary file which is used as restart file

STATIS contains a collection of statistical data, useful for post-processing, such as system temperature, energy, volume etc.

1. THF solvent molecule

1.a Geometry optimization

1.b NVE/NVT dynamics

We can now perform a dynamic simulation, and we will verify that the theoretical assumptions on the NVE ensemble are correct.

We can use the REVCN file generated from the geometry optimization as a restart file (rename this file as CONFIG), or use the CONFIG file in the folder.

Edit the CONTROL file:

choose the number of steps
(5000 steps will take about 20 sec)

comment the minimise line

choose how often you want to collect data
(in this example, all data are collected
every 100 steps. See manual for details)

RUN!!!



```
DL_POLY thf

integrator velocity verlet
temperature      1.00000
pressure         0.0000
ensemble nve
steps            10000
#minimise force  1 1
print            100
stack            100
stats            100
traj              0 100 0
timestep         0.0005
cutoff            8
ewald precision  1d-8
rvdw cutoff       8
job time          1200000.
finish
```

We have performed an NVE run, i.e. we should have constant number of particles, volume and energy. We can use the STATIS file to verify that everything is OK:

potential energy

total energy system temperature system volume

thf

ENERGY UNITS = kcal/mol

0	0.000000E+00	40		
2.464903E+01	1.000000E+00	2.461326E+01	-5.701781E-02	-8.101568E-03
6.124452E+00	1.166301E+01	6.890921E+00	0.000000E+00	6.233710E+00
0.000000E+00	5.531750E+01	-1.926958E-01	5.732141E-03	5.550447E+01
0.000000E+00	0.000000E+00	0.000000E+00	2.700000E+04	0.000000E+00
0.000000E+00	0.000000E+00	9.000000E+01	9.000000E+01	9.000000E+01
0.000000E+00	-4.676705E-02	0.000000E+00	0.000000E+00	0.000000E+00
0.000000E+00	-1.379266E-01	5.789624E-02	1.591232E-01	5.789624E-02
3.486365E-02	-1.725527E-02	1.591232E-01	-1.725527E-02	-3.723816E-02
100	5.000000E-02	40		
2.462572E+01	2.096710E+02	1.712581E+01	-7.141238E-02	-7.778553E-03
3.258490E+00	7.496057E+00	6.450457E+00	0.000000E+00	5.906820E+00
0.000000E+00	7.115652E+01	1.222577E-01	5.087618E-03	7.102918E+01
0.000000E+00	0.000000E+00	0.000000E+00	2.700000E+04	0.000000E+00

this file contains also other useful data, we invite you to read the manual for details

TASKS

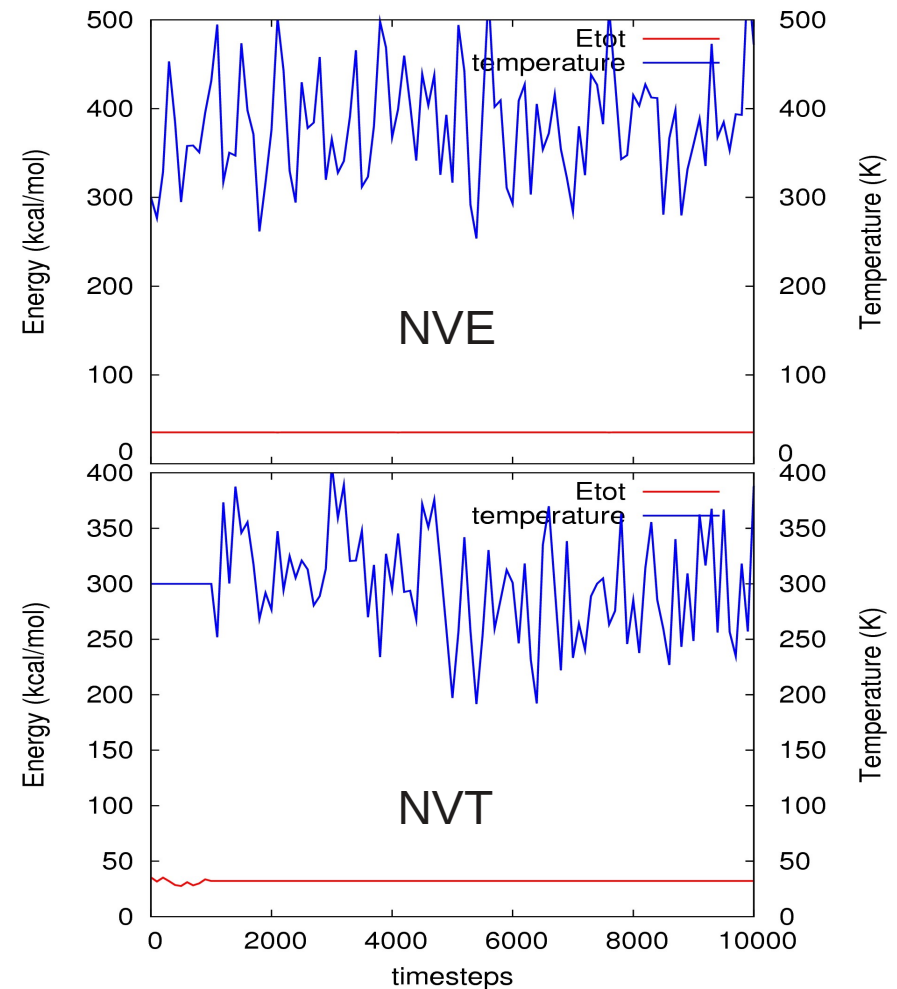
- ➡ Write a simple tool to extract the relevant data from the STATIS file
- ➡ Plot total energy, system temperature and system volume vs time
- ➡ Is average total energy conserved? What happens to temperature and volume?

If we want the system temperature to be conserved, we need to perform an NVT simulation. To do so, slightly modify the CONTROL file: change ensemble, choose the temperature, and rerun. You will also have to add two new keywords. These indicate that the code will scale the temperature every *scale* timesteps during the first *equilibration* steps (choose it to be about 10% of the total simulation time). Verify that the average system temperature is conserved now:

```
DL_POLY thf

integrator velocity verlet
temperature 300.00000
pressure 0.0000
ensemble nvt hoover 0.5
steps 10000
equilibration 1000
scale 1
#minimise force 1 1
#restart

print 100
stack 100
stats 100
traj 0 100 0
timestep 0.0005
cutoff 8
ewald precision 1d-8
rvdw cutoff 8
job time 1200000.
finish
```



Perform a NVT simulation at T=300K for both the systems of one and two THF molecules (nvt/1mol/ and nvt/2mol/). Observe the trajectories with vmd (*vmd -dlpoly3hist HISTORY*).

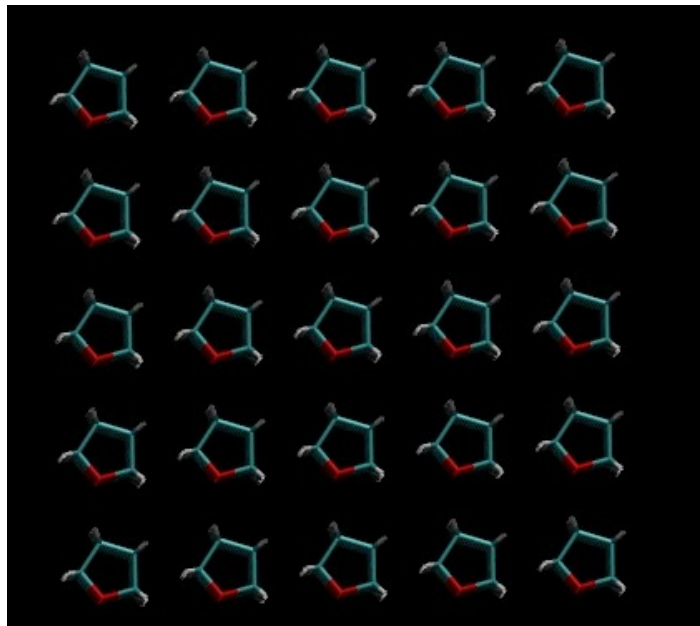
2. Liquid THF


2.a Equilibration – NPT

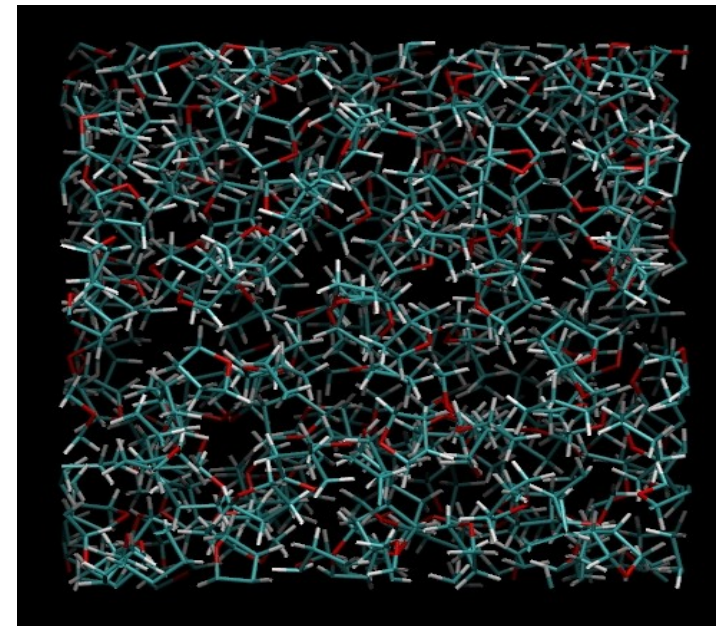
2.b Dipole moment calculation

2.c Static dielectric constant calculation

Since a liquid has no crystalline structure, i.e. it is disordered, we do not know where to put the molecules. We can start from any configuration (for example, a cubic crystal of arbitrary lattice constant), and then anneal the system to get a disordered, liquid-like structure.




Annealing



2. Liquid THF

2.a Equilibration - NPT

2.b Dipole moment calculation

2.c Static dielectric constant calculation

Any liquid has its own density at room temperature (g/cm^3), we must reproduce it to have a good simulated liquid.

The standard way to obtain it is to perform a constant pressure simulation (ensemble NPT): in this ensemble the volume is free to change in order to achieve the correct density.

Ambient conditions: $T=300\text{ K}$, $p=1\text{ atm}$

ensemble NPT

Allows the cell density to vary during the equilibration

Run the calculation and plot the volume and the potential energy.

NB: this run will take about 1min for 1000 steps!

```
DL_POLY thf

integrator velocity verlet
temperature 300.00000
pressure 0.00100
ensemble npt hoover 0.5 0.5
steps 10000
equilibration 1000
scale 1
densvar 60
#minimise force 1 1
print 100
stack 100
stats 100
traj 0 100 0
timestep 0.0005
cutoff 8
ewald precision 1d-8
rvdw cutoff 8
job time 1200000.
finish
```


2. Liquid THF

2.a Equilibration - NPT

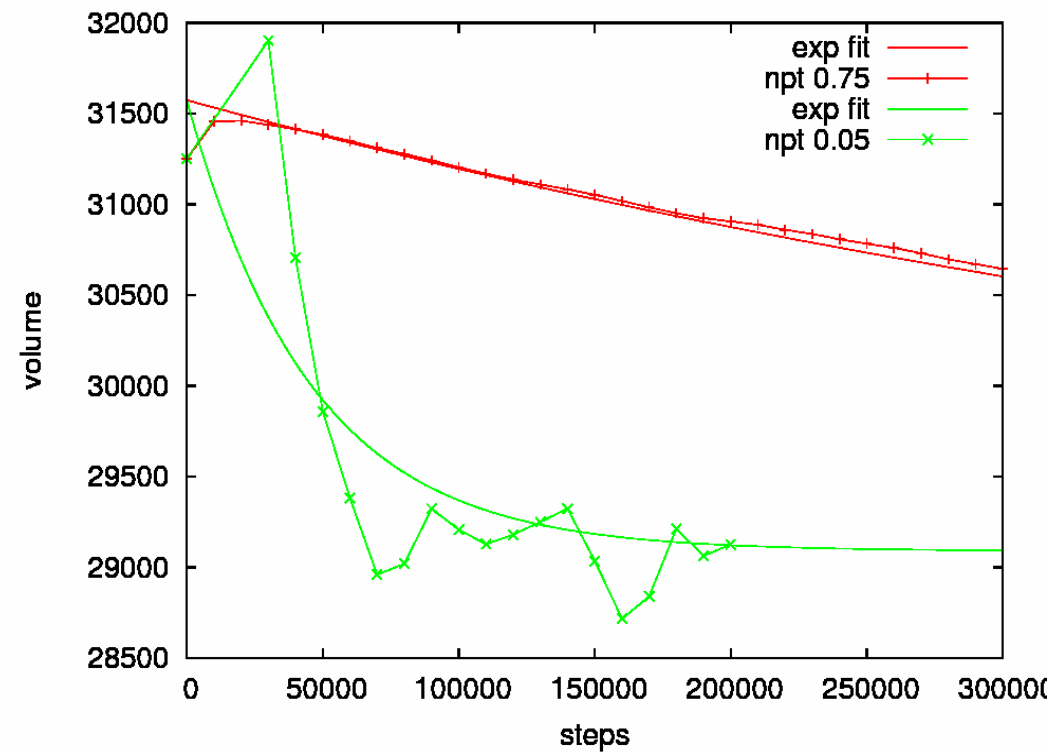
2.b Dipole moment calculation

2.c Static dielectric constant calculation

If the volume converges too slowly or it oscillates too much, you may consider changing the relaxation constant of the barostat: high values provide smaller oscillations but slow convergence, and vice versa.

```
DL_POLY thf

integrator velocity verlet
temperature      300.00000
pressure         0.00100
ensemble npt hoover 0.5 0.5
steps            10000
equilibration    1000
scale            1
densvar 60
#minimise force  1 1
print            100
stack            100
stats            100
traj             0 100 0
timestep         0.0005
cutoff           8
ewald precision  1d-8
rvdw cutoff      8
job time         1200000.
finish
```



2. Liquid THF

2.a Equilibration – NPT

2.b Dipole moment calculation

2.c Static dielectric constant calculation

Once your volume and potential energy have reasonably converged, we can calculate the liquid density ρ and other thermodynamic properties, e.g. the vaporization enthalpy ΔH_v

$$\rho = \frac{N_{mol} \cdot M_{mol}}{V}$$

$$\Delta H_v = RT - \frac{(E_{NB})_{liq}}{N_{mol}}$$

N_{mol}	number of molecules
M_{mol}	molecular mass (72.104 g/mol for THF)
V	system volume
RT	gas constant times temperature (0.5957 kcal at 300 K)
$(E_{NB})_{liq}$	nonbonding energy of the system (i.e. electrostatic+ VdW)

experimental values	
ρ	ΔH_v
0.889 g/cm ³	7.65 kcal/mol

NB: Very long simulations are required to obtain correct thermodynamic properties!
Use the STATIS.ref file to extract the data

2. Liquid THF

2.a Equilibration – NPT

2.b Dipole moment calculation

2.c Static dielectric constant calculation

Let's now calculate the molecular dipole moment for the solvent THF. This will be useful to calculate the static dielectric permittivity of the liquid

$$\vec{\mu} = \sum_{i=1}^{N_a} q_i \vec{r}$$

Where q_i is the atom's charge and \vec{r} is the atom-atom distance

Since we have the atoms' coordinates (in HISTORY file) and charges (in FIELD file), we can easily compute the value of the molecular dipole moment.

 Edit the dipole.f90 code in codes/step1/ to calculate the molecular dipole moment for THF, and compare it to the experimental value of 1.75 D.

(NB: since charges are given in units of electron charge and the positions in Å, you will have to multiply the calculated value by 4.803 to get the value in Debyes)

Calculate the dipole moment for the system of 1 and 2 molecules (use the STATIS files in folders nvt/1mol/ and nvt/2mol/ and edit the codes in codes/step2/).
Do you get the same results? Why?

2. Liquid THF

2.a Equilibration - NPT

2.b Static dielectric constant calculation

The relative static dielectric permittivity can be calculated from the total dipole moment fluctuations (fluctuation-dissipation theorem) in a NPT equilibrium simulation

$$\epsilon_r = 1 + 4 \frac{\pi}{(3k_B T \langle V \rangle)} (\langle \vec{M}^2 \rangle - \langle \vec{M} \rangle^2) \quad (M. Neumann, Mol.Phys. 1983)$$

$$\vec{M} = \sum_{i=1}^{N_{mol}} \vec{\mu}_i \quad \text{sum of all the molecular dipoles in the liquid}$$

$\langle V \rangle$ average system volume



Modify the code for the single molecule dipole (as a function of time) to calculate the total dipole moment and hence the dielectric permittivity. Edit the code in codes/step3 and use the liquid/HISTORY.ref and liquid/STATIS.ref to extract the data.

2. Liquid THF

2.a Equilibration - NPT

2.b Static dielectric constant calculation

$$\epsilon_r = 1 + 4 \frac{\pi}{(3k_B T \langle V \rangle)} (\langle \vec{M}^2 \rangle - \langle \vec{M} \rangle^2)$$

NB: this formula is valid with \vec{M} in Debyes

$$1 D = 10^{-18} \text{ statC} \cdot \text{cm} = \frac{10^{-27}}{2.99 \sqrt{4\pi \epsilon_0}} \text{ C} \cdot \text{cm}$$

$$\vec{M} = \sum_{i=1}^{N_{mol}} \vec{\mu}_i$$

$$\langle \vec{M}^2 \rangle = \langle M_x^2 \rangle + \langle M_y^2 \rangle + \langle M_z^2 \rangle$$

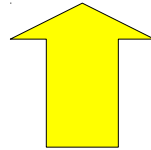
$$\langle \vec{M} \rangle^2 = \langle M_x \rangle^2 + \langle M_y \rangle^2 + \langle M_z \rangle^2$$

Compare the calculated value with the experimental one $\epsilon_r=7.52$

Does the two values compare well? Why?

A GENERAL RULE

In Model Potential Molecular Dynamics the calculated properties strongly depend upon the choice of the parameters, such as bond strength, atomic charges etc.



Furthermore, properties (such as the dielectric constant) which are related to electronic charge displacement cannot be properly taken into account with a simple fixed-charge model. Polarizable models have been developed and are available in Literature. Sec. 2.5 of the DL_POLY manual illustrates the ones which are implemented in this code.

Thanks for your attention!