Calculating bulk modulus and studying compressibility in MD simulations

Written by Luke M Edwards, 140185050, In affiliation with Queen Mary's University of London- School of physics and astronomy, Wednesday 15th November 2017.

Abstract: DLPOLY program simulated silica glass at 0, 3, 6, and 10 GPa at 10 Kelvin giving an average volume of 10107.71056Å³, 8763.515687Å³, 7796.231988Å³ and 6893.508528Å³ respectively, Giving a bulk modulus of 31.78336±, Fluctuations at 0 GPa and 10 GPa give a standard deviation of ±18.8Å³ and ±28.19874Å³ which accounts for the percentage error of 13.4%

Introduction

The purpose of this practical is to calculate the bulk modulus of silica glass using DLPOLY.Z which uses a high pressure Berendsen barostat algorithm. This works by scaling the unit cell size and the coordinates by a scale factor μ. This Berendsen thermostat and barostat is applied to ensure that the scaled values remain at their correct values.

$$\mu = 1 - \frac{\kappa_T \Delta t}{3\tau_P}(P_0 - P) \qquad \left.\frac{dP}{dt}\right|_{\text{bath}} = \frac{P_0 - P}{\tau_P} \quad [1]$$

Where κ_T is the isothermal compressibility, DLPOLY uses the value of the compressibility of water at 1 atm and 300K which is equal to $4.6\ x\ 10^{-5}\ bar^{-1}$

The bulk modulus (B) is the proportionality coefficient between applied pressure and the change in volume (ΔV/V), the bulk modulus is calculated via: $\mathrm{P} = -\mathrm{B}\cdot\Delta\mathrm{V}/\mathrm{V}$

Method, Results, Analysis and error calculation

In order to obtain the values for average volume and pressure the following parameters are set up within the CONTROL file of the DLPOLY program. This sets the initial system pressure, compressing the material from its initial configuration which is refined by the CONFIG file. The compression occurs during equilibrium steps. The run cannot provide accurate data during compression as equilibrium must be complete before the system reaches the predefined pressure set in the CONFIG file and thus you need to wait at least several picoseconds before you can start recording result relating to the high-pressure system. The CONTROL fine contacts the following parameters: cut-off distance= 7.5Å, 3,000 steps, 2,000 equilibrium steps for each of the required pressures: 0, 30,60,100 kbars which corresponds to the 0, 3, 6, and 10 GPa stated above. An example of this is given below:

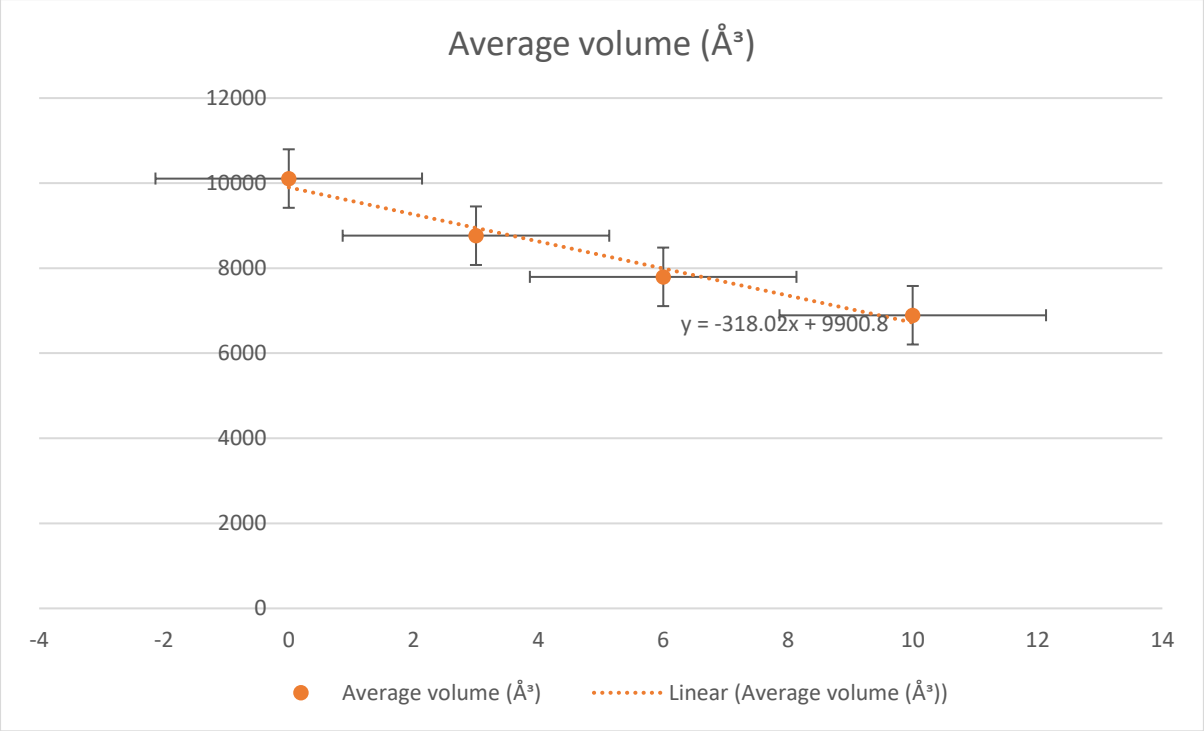
```
DL_POLY : Glass 216 tetrahedra
temperature            10
pressure               100
steps                  3000
equilibration steps    2000
scale every 1
timestep               0.001 ps
ensemble npt ber 1.0 1.0
cutoff                 7.5 angstrom
rvdw                   7.5 angstrom
delr                   1.0 angstrom
ewald precision 0.00001
print every 10 steps
job time  28800 seconds
close time     100 seconds
finish
```

(CONTROL file)

The "npt ber 1.0 1.0" is the directive for constant pressure. After each fun a STATIS file is created and is saved as its correlating pressure. The STATIS file gives the particles location and energy after each step. After each pressure run the OUTPUT fine is viewed and a record of the average volume over the past 1000 MD time steps;

Which have given the following results:

Pressure (GPa)	Average volume (Å³)
0	10107.71056
3	8763.515687
6	7796.231988
10	6893.508528



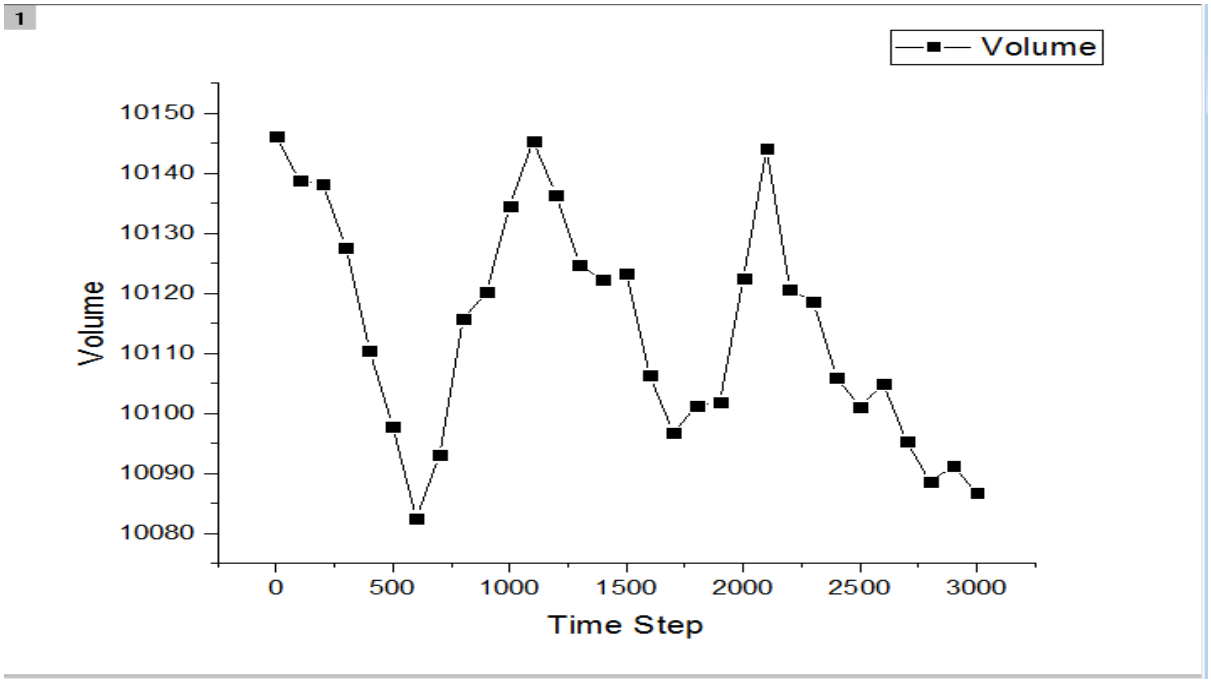
The Graph gives a slight curve, This is due to Intermolecular forces which become more prominent at higher pressures as the particles become pressed together, the intermolecular forces resist the compression and result in a small increase in the average volume at these higher pressures. An additional reason is the shortened cutoff distance within DLPOLY FIELD file, This reduced the time at which DLPOLY would run but at the expense of some long range forces been missed, thus lowering the calculated bulk modulus.

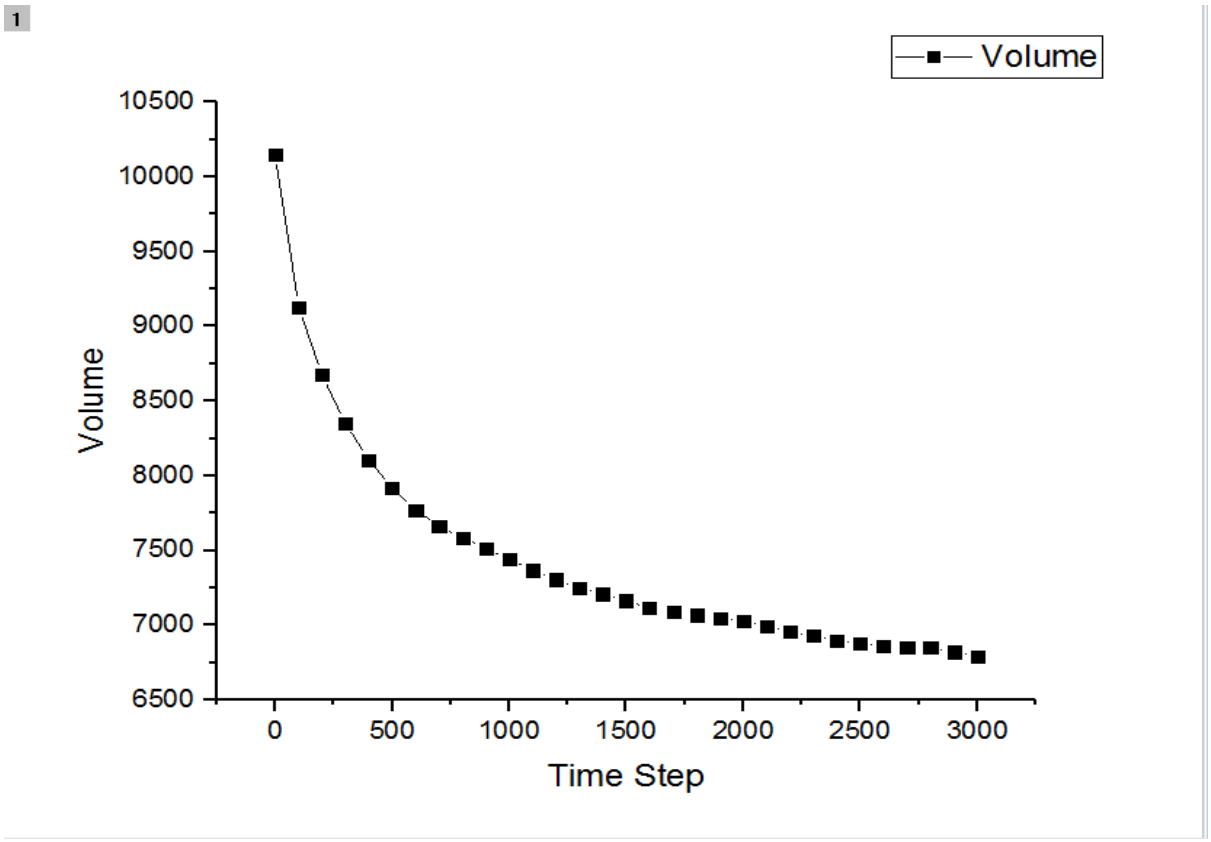
Using a straight line fit the gradient is calculated at -318.02, dividing this value by the average volume at 0 pressure (10107.71056Å³) gives a value of -0.31463. This is the $(\Delta V/V)$ part of the original formula that was given to calculate the bulk modulus at 10 GPa. Giving a resulting Bulk modulus of:

$$\frac{-P}{(\frac{\Delta V}{V})} = B \qquad \frac{-10}{-0.31463} = 31.78336\ GPa$$

Comparing this to the actual bulk modulus of 36.7 GPa [2] This gives a percentage error value of 13.4%

In order to calculate the true error of these results, including the error of average volumes of 0 GPa and 10 GPa 2 additional runs at these pressures is conducted to measure the fluctuations of volume:





These two graphs shown display the volume of the simulated system in a time frame of 3000 seconds at 0 GPa and 10 GPa respectively, In the first graph the fluctuations are much more prominent where the second appears to give a smooth exponential decay. However this is a function of the volume scale: both systems show similar fluctuations but is much more

noticeable on the first (0GPa) graph. The maximum change of volume is 77Å^3 which is hidden by 3600Å^3 change due to compression of the system

To find the accuracy of these volumes at given pressures the standard deviations: ±18.81581Å^3 for 0 GPa and ±28.19874Å^3 which correspond to variations of ±0.186% and ±0.409% respectively within a standard deviation

Conclusion

The bulk modulus was calculated using 3,000 pico seconds value of 2 DLPOLY runs at 0 GPa and 10 GPa. Both these values suffer from fluctuations as a direct result of intermolecular forces and temperature (giving it kinetic energy) which is displayed in the last two graphs. The error is calculated using the volume values after the system has gone through its equilibrium steps to find the standard deviation which are ±18.81581Å^3 for 0 GPa and ±28.19874Å^3 for 10 GPa. These values correspond to variations of ±0.186% and ±0.409% respectively. The Bulk modulus is calculated to be 31.78336 GPa and gives a percentage error value of 13.4%, accurate within 1 standard deviation.

References

[1] Berendsen barostat algorithm: http://www.sklogwiki.org/SklogWiki/index.php/Berendsen_barostat

[2] actual bulk modulus of silica glass: https://www.crystran.co.uk/optical-materials/silica-glass-sio2