LECTURE 8 : PRACTICAL MD AND APPLICATIONS

- Packages
- Structure
- Post-treatment
- Applications

Given that most of the simulated liquids will form a glass at low temperature, one is free to investigate many systems

- Simple atomic systems, mixtures or unpolarisable point ions
  Ne, Ar, Kr, NaCl, KCl, etc.

- Polarisable point ions and molecules
  MgO, H_2O etc.

- Simple rigid molecules or rigid molecuar ions with charges
  CCl_4, Benzene, KNO_3, $(NH_4)_2SO_4$, etc.

- Polymers, proteins, macromolecules,

- Simple metals and alloys
  Al, Ni, Cu etc.

- Covalent systems
  C, Si, Ge, SiC, SiGe etc.

PRELIMINARY…

2 options

- Develop your own MD codes

  depending on you background, motivation, your time, money, pressure on your neck, time left during the course of your PhD, etc.

- Or use a package

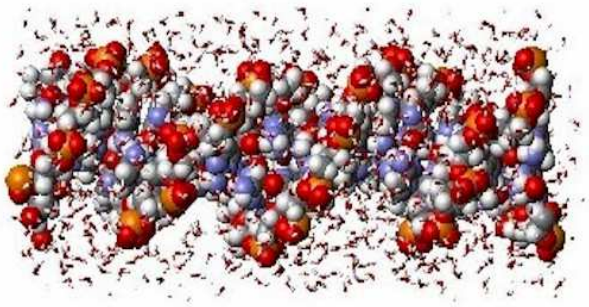
  bug reports, faqs, force field libraries, optimization, forum, manual, etc.

But in both cases…

- Work under UNIX environment !
- Minor alternative: under Windows with the CygWin UNIX shell

A. PACKAGES

1. DLPOLY



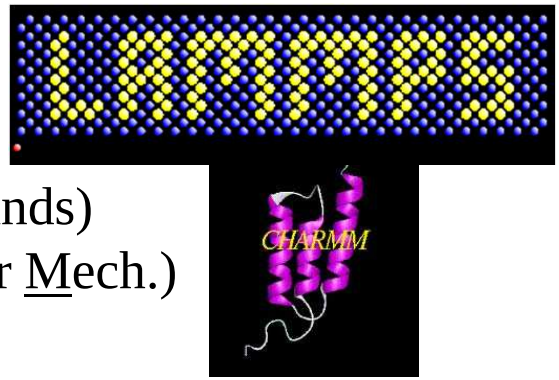
http://www.stfc.ac.uk/cse/25526.aspx

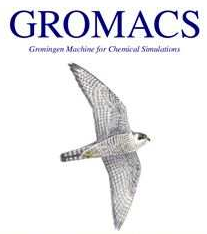
- Simulation package part of the british CCP5 research project developed at Daresbury Laboratory (conceived 1993, W. Smith, T.R. Forester).

- Fortran 90, serial (100s atoms, DLPOLY_2) and parallel (10^6, DLPOLY_4, under MPI software library) versions

- Free of charge for academia. Download from website or from open source sites (CCPForge, BSD,…)

- **Other packages**
  - LAMMPS (Sandia National Lab)
  - Gromacs (University of Groningen, Netherlands)
  - CHARMM (Chemistry at Harvard Molecular Mech.)





A. PACKAGES

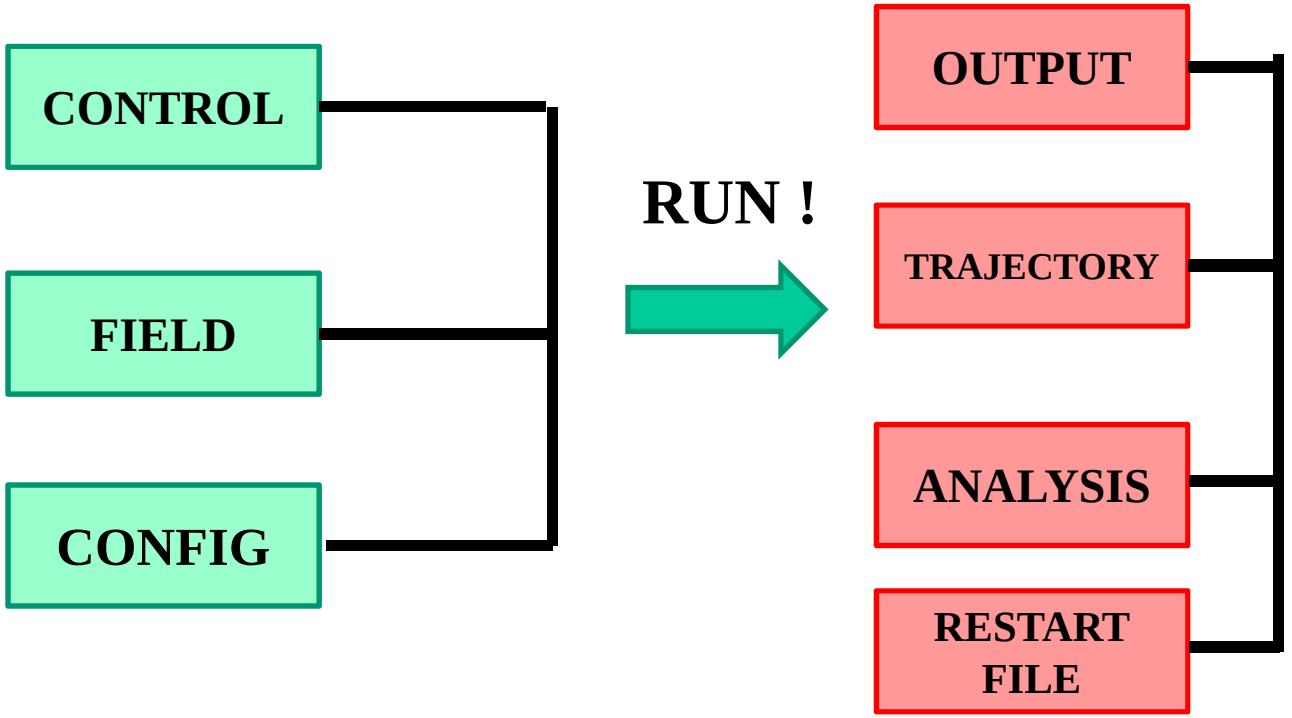
2. Structure (directories) of a package

- **Compiling directory** ***(build)*** *:* makefiles to assemble and compile the programs are located in:
- **Source directory** ***(srcf90)*** primary subroutines (*.f90 or *.c)
- **Utility directory** ***(utility)*** subroutines, programs and example data for all utilities
- **Example directory** ***(data)*** example input and output files
- **Users directory** (***public***) routines donated by users
- **Interface directories** ***(java)*** friendly interface dir. for runs and analysis

B. STRUCTURE OF A CODE

1. Input and Output files

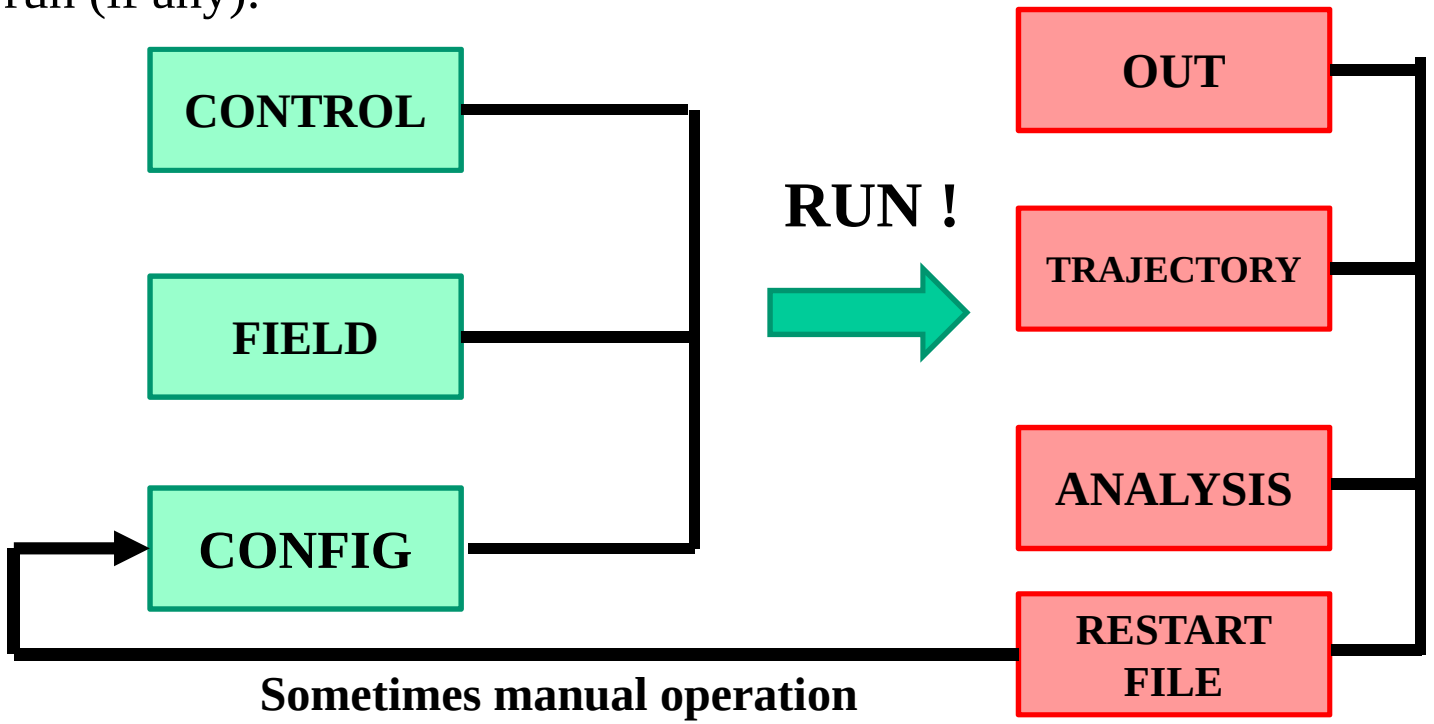
- The INPUT files provides all the information about the system, the interaction, the thermodynamic conditions. Some of the parameters do not change for the whole simulation. Others may be changed during the course of the run.



B. STRUCTURE OF A CODE

1. Input and Output files

- After or during the run, OUTPUT files are generated with information on energies, the trajectory (recorded x,v,… at different time steps), analysis files (rdf, msd, stress,…) and the last configuration which serves as input for the next run (if any).



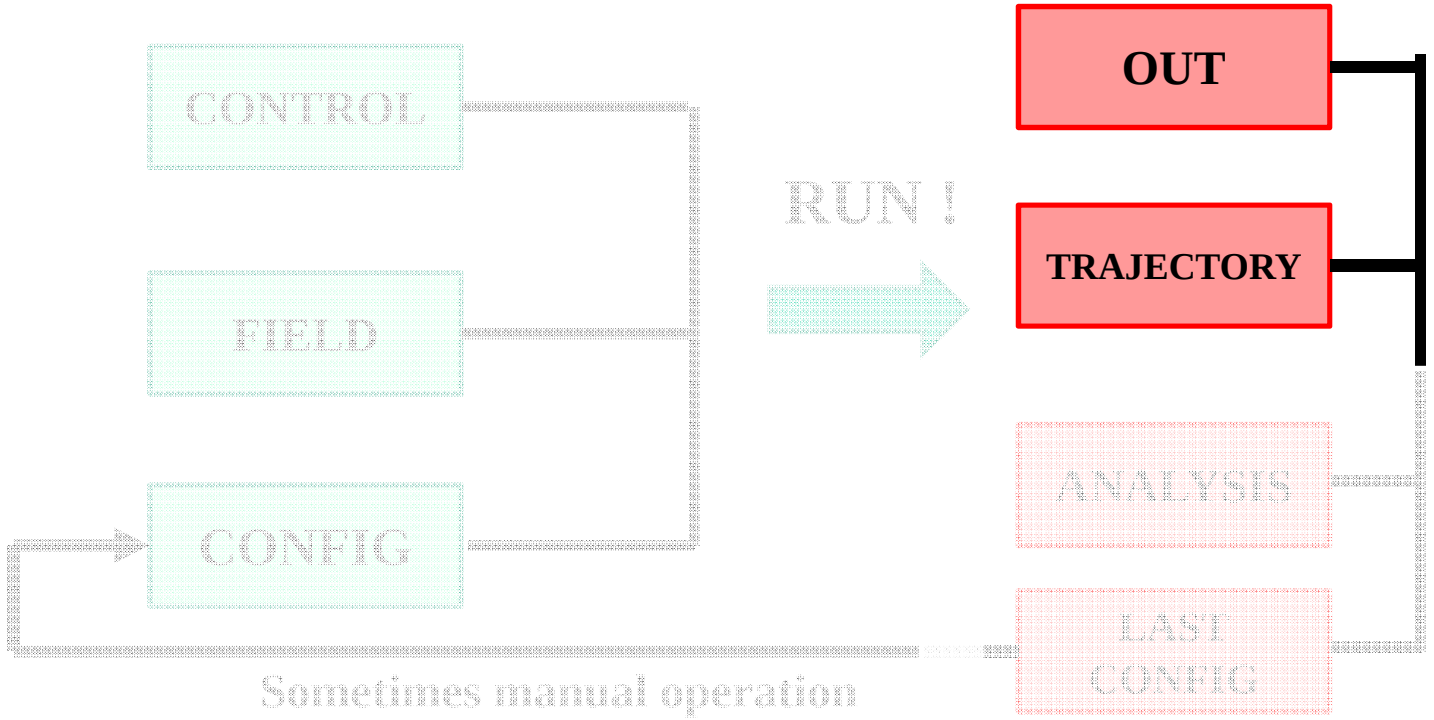
B. STRUCTURE OF A CODE

1. Among files…the important ones

- OUTPUT file with all informations about your run : recall of parameters, results (energy, temperature, pressure, …).

  if $T=10^{45}$ K, something must be wrong…

- TRAJECTORY or HISTORY file (i.e. x(t),y(t),z(t)) : **apple of your eye !**



B. STRUCTURE OF A CODE

1. Input files

❑ FIELD file:

- Will contain the infos about the parameters of the potential.
- Can sometimes be a tabulated (non-parametrized) potential
- Here, a simulation of 256 GeO_2 molecules

```
DL_POLY GeO2 :
units  kJ
MOLECULES 2
Oxygen
nummols 512
atoms 1
O2-        15.999      -0.47087
finish
Germanium
nummols 256
atoms 1
Ge4+       72.59        0.94174
finish
VDW 3
O2-      O2-      buck     292590.0   0.304404    4985.0
O2-      Ge4+     buck    7910800.0   0.163506    9000.0
Ge4+     Ge4+     buck        0.0      1.0000       0.0
CLOSE
```

Oeffner-Elliott potential
PRB 58, 14793 (1998).

Charges (partial)
$q_{Ge} = -2q_O$

Of Buckingham type

$$A_{ij}e^{-B_{ij}r} - \frac{C_{ij}}{r^6}$$

TABLE I. Potential parameters obtained from the *ab initio* energy surface.

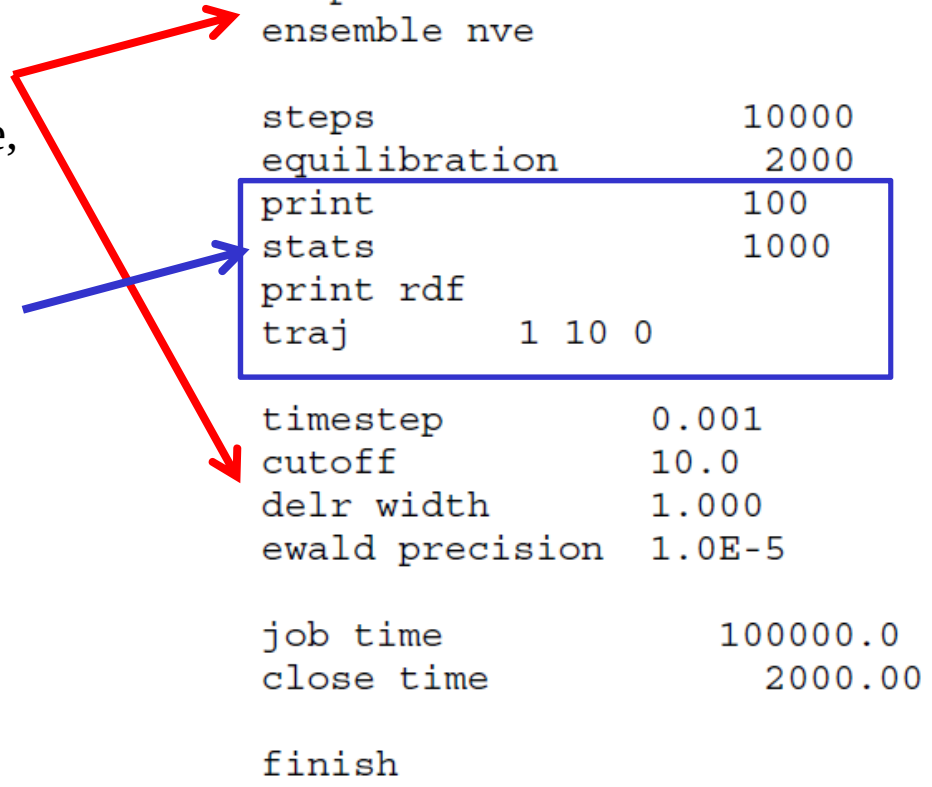
	A_{ij} in kJ/mol	ρ_{ij} in Å
Ge,O	7.9108×10^6	0.16315
O,O	2.9259×10^5	0.304404
$Z_{Ge} = -2Z_O = 0.94174e$		

B. STRUCTURE OF A CODE

1. Input files

❑ CONTROL file:

- ❑ Contains all the relevant informations about the run (temperature, Ensemble, pressure, volume, timestep).
- ❑ Also information about averages and data storage
- ❑ Information about Equilibration



```
DL_POLY : SODIUM SILICATE

temperature      2500.0
ensemble nve

steps                 10000
equilibration          2000
print                  100
stats                  1000
print rdf
traj        1 10 0

timestep          0.001
cutoff            10.0
delr width        1.000
ewald precision   1.0E-5

job time              100000.0
close time              2000.00

finish
```

B. STRUCTURE OF A CODE

1. Input files

❑ CONFIGURATION file:

- ❑ Gives information about cell size and shape
- ❑ Lists the atomic positions
- ❑ Eventually, velocities
- ❑ Or even forces

```
                DL_POLY : Ge02
         2          1     10000    0.1000000000E-02
     23.0440138240         0.0000000000         0.000000
      0.0000000000        23.0440138240         0.000000
      0.0000000000         0.0000000000        23.044013
O2-              1
      9.575384989       -0.3333484449E-01     -7.566015853
    -19.62699530          3.022118300        -9.117787331
    -5968.241819         -22344.52456         67985.64272
O2-              2
     -7.014286569          6.302978401        -6.267344504
   -0.9348542269           6.350904197         26.47499255
      1285.377514          129.9071936         11816.24969
O2-              3
      1.837895001          7.926648401        -9.520582060
      4.529815162         -19.26613748         5.992301313
     -33450.47991         -24299.50952         12017.78425
O2-              4
      2.140484951          3.390298875        -1.414346504
     -5.236491277         -25.19263439        -17.49959941
      1992.884668          14364.34056         963.7452061
O2-              5
      4.752606213         -0.3283280766         1.187770840
    0.2828851976           -3.460061373         7.955521511
    -4261.770977         -13630.47565        -9363.761205
O2-              6
    -11.50288249           1.748206550         5.981875396
    -3.717491593           11.14666488         6.685386221
    -8379.709686           7531.579832        -1719.198766
O2-              7
    -1.835347905          0.2120533574         9.962044012
     11.68661793         -4.400916350        -2.264003074
     6087.662910          2247.863123         27935.77775
O2-              8
     2.195643208          0.3564799296        -10.25664308
```

B. STRUCTURE OF A CODE

2. Output files

❑ OUTUT file:

```
**                                                                  ****************************************************************
**                                                                  ****************************************************************
******************************************************************************************************************************************
********************        DL_POLY SiO2 :                                                                              ********************
******************************************************************************************************************************************
******************************************************************************************************************************************
******************************************************************************************************************************************


SIMULATION CONTROL PARAMETERS


simulation temperature             4.0000E+01

selected number of timesteps          5000

equilibration period                     0

multiple timestep interval               1

temperature scaling on
temperature scaling interval             5

data printing interval                  10

data stacking interval               10000

statistics file interval             20000

trajectory file option on
trajectory file start                    1
trajectory file interval               100
trajectory file info key                 0

simulation timestep                1.0000E-03
```

❑ The OUTPUT file will first recall:

- the parameters of your run
- the thermodynamic conditions
- your potential, etc.

B. STRUCTURE OF A CODE

2. Output files

❑ OUTUT file:

```
    step      eng_tot    temp_tot     eng_cfg     eng_vdw     eng_cou     eng_bnd     eng_ang     eng_dih     eng_tet
time(ps)       eng_pv    temp_rot     vir_cfg     vir_vdw     vir_cou     vir_bnd     vir_ang     vir_con     vir_tet
cpu   (s)      volume    temp_shl     eng shl     vir shl       alpha        beta       gamma     vir pmf       press

-------------------------------- -----------------------------------------------------------------------------------
       1 -2.8692E+05  4.5220E+01 -                                                                  0.0000E+00
   0.001 -2.9053E+05  0.0000E+00                                                                  0.0000E+00
    0.04  1.2237E+04  0.0000E+00                                                                 -4.8337E+00

 rolling -2.8692E+05  4.5220E+01 -                                                                  0.0000E+00
averages -2.9053E+05  0.0000E+00                                                                  0.0000E+00
          1.2237E+04  0.0000E+00                                                                 -4.8337E+00
-------------------------------- -----------------------------------------------------------------------------------
      10 -2.8695E+05  9.5978E+02 -                                                                  0.0000E+00
   0.010 -3.1184E+05  0.0000E+00                                                                  0.0000E+00
    0.21  1.2237E+04  0.0000E+00                                                                 -3.3331E+01

 rolling -2.8694E+05  4.6900E+02 -                                                                  0.0000E+00
averages -3.0142E+05  0.0000E+00                                                                  0.0000E+00
          1.2237E+04  0.0000E+00                                                                 -1.9392E+01
-------------------------------- -----------------------------------------------------------------------------------
      20 -2.8695E+05  1.2753E+03 -                                                                  0.0000E+00
   0.020 -2.8868E+05  0.0000E+00                                                                  0.0000E+00
    0.40  1.2237E+04  0.0000E+00                                                                 -2.3180E+00

 rolling -2.8695E+05  8.3782E+02                                                                  0.0000E+00
averages -3.0196E+05  0.0000E+00                                                                  0.0000E+00
          1.2237E+04  0.0000E+00                                                                 -2.0101E+01
```

❑ Then, thermodynamic information about the run (time, elapsed time, etc):

- Total energy (must converge to an equilibrium value before performing production runs). Rolling averages and final averages.
- Various energetical contributions (if relevant), **pressure**, **temperature**,…
- Pair distribution function, msd

B. STRUCTURE OF A CODE

2. Output files

❑ TRAJECTORY file:

- ❑ Contains all the atomic positions over the run (or every n step of the run)
- ❑ Positions $x_i(t)$, $y_i(t)$, $z_i(t)$ and velocities $vx_i(t)$, $vy_i(t)$, $vz_i(t)$ with time.
- ❑ Serve for all further analysis of the system Structure, dynamics

```
                DL_POLY : Ge02
          0          1        768
timestep          1        768          0
    23.04        0.000        0.000
    0.000        23.04        0.000
    0.000        0.000        23.04
O2-                1   15.999000   -0.470870
  9.5941E+00 -2.9322E-02 -7.5730E+00
O2-                2   15.999000   -0.470870
 -7.0036E+00  6.3128E+00 -6.2872E+00
O2-                3   15.999000   -0.470870
  1.8503E+00  7.9323E+00 -9.5292E+00
O2-                4   15.999000   -0.470870

                    • • •

Ge4+             764   72.590000    0.941740
  7.6909E+00  8.4286E+00 -8.1524E+00
Ge4+             765   72.590000    0.941740
  3.0107E+00  7.0211E+00  1.1488E+01
Ge4+             766   72.590000    0.941740
 -7.7215E+00 -2.7583E+00  4.8200E+00
Ge4+             767   72.590000    0.941740
 -4.7277E+00  8.9125E+00 -9.3324E+00
Ge4+             768   72.590000    0.941740
  6.3287E+00  2.3355E+00  2.2326E+00
timestep         101        768          0
    23.04        0.000        0.000
    0.000        23.04        0.000
    0.000        0.000        23.04
O2-                1   15.999000   -0.470870
  8.8776E+00  1.0210E+00 -7.5912E+00
O2-                2   15.999000   -0.470870
 -7.3456E+00  6.1711E+00 -6.4655E+00
O2-                3   15.999000   -0.470870
  1.3416E+00  8.3284E+00 -8.8991E+00
O2-                4   15.999000   -0.470870
```

B. STRUCTURE OF A CODE

2. Output files

❑ RESTART file:

- ❑ Last configuration of the run
- ❑ Gives information about cell size
  may have changed if NPT
- ❑ Lists the atomic positions
  and velocities (target temperature)
- ❑ Sometimes also forces

```
                DL_POLY : Ge02
         2          1     10000    0.1000000000E-02
      23.0440138240        0.0000000000        0.000000
       0.0000000000       23.0440138240        0.000000
       0.0000000000        0.0000000000       23.044013
O2-              1
     9.575384989       -0.3333484449E-01    -7.566015853
   -19.62699530         3.022118300        -9.117787331
   -5968.241819        -22344.52456         67985.64272
O2-              2
    -7.014286569         6.302978401        -6.267344504
   -0.9348542269         6.350904197         26.47499255
    1285.377514          129.9071936         11816.24969
O2-              3
     1.837895001         7.926648401        -9.520582060
     4.529815162        -19.26613748         5.992301313
    -33450.47991        -24299.50952         12017.78425
O2-              4
     2.140484951         3.390298875        -1.414346504
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     1992.884668         14364.34056         963.7452061
O2-              5
     4.752606213        -0.3283280766        1.187770840
    0.2828851976        -3.460061373         7.955521511
    -4261.770977        -13630.47565        -9363.761205
O2-              6
    -11.50288249         1.748206550         5.981875396
    -3.717491593         11.14666488         6.685386221
    -8379.709686         7531.579832        -1719.198766
O2-              7
    -1.835347905         0.2120533574        9.962044012
     11.68661793        -4.400916350        -2.264003074
     6087.662910         2247.863123         27935.77775
O2-              8
     2.195643208         0.3564799296        -10.25664308
```
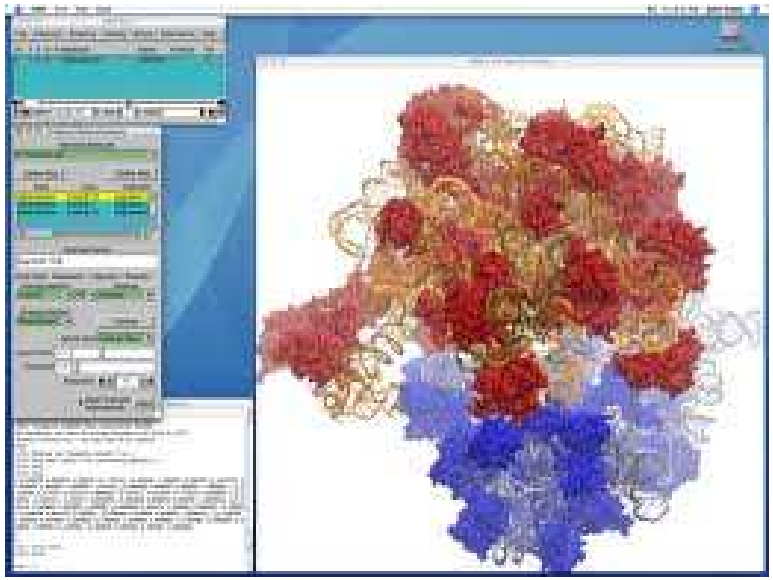
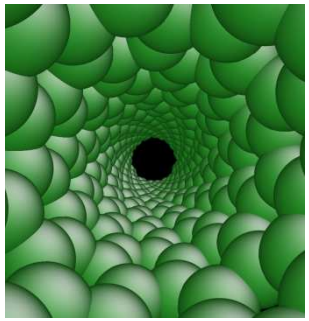

C. POST-TREATMENT

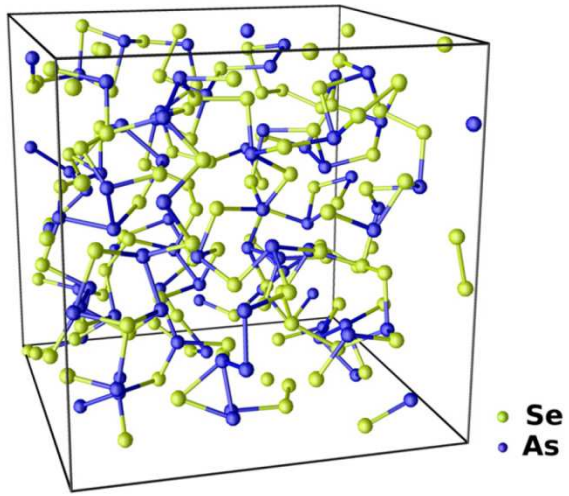
1. Visualizing



- **Beware of bloatwares (usines à gaz) !**
- **Graphical interfaces+analysis (see next slide)**
  - **VMD** (Visual Molecular Dynamics, Illinois at Urbana-Champaign) Very powerful…
  - **AtomEye** (MIT)



  - **RINGS** (Rigourous Investigation of Network Generated using Simulations, CNRS Strasbourg)



C. POST-TREATMENT

2. Analyzing

- **Write your own analyzing codes** (recommended)

  Pair correlation functions, bond angle and coordination distributions
  Structure factor, mean square displacement, scattering function, etc.

- **Use interfaces**
  - Java Interface in DLPOLY
  - **ISAACS** (Interactive Structure Analysis for Amorphous and Crystalline Systems, Central Michigan/CNRS Strasbourg)
  - **MDAnalysis** (John Hopkins, Baltimore)
  - **RINGS** (Rigourous Investigation of Network Generated using Simulations, CNRS Strasbourg)

D. APPLICATIONS

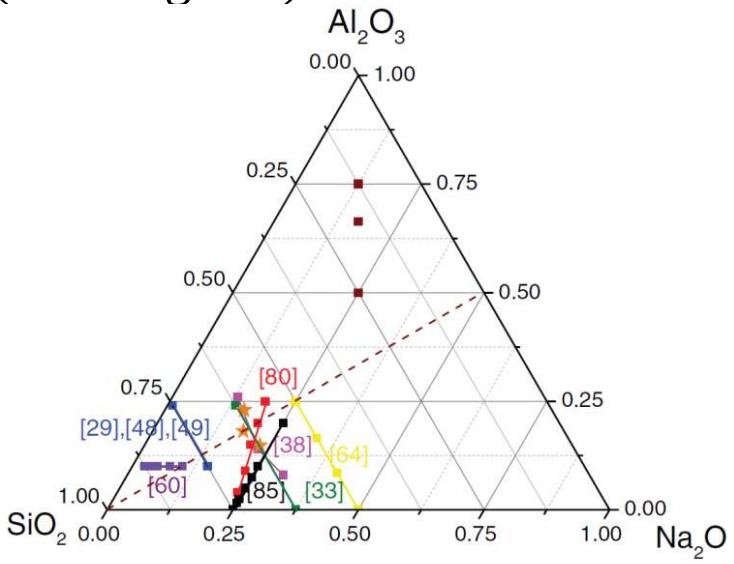
1. Structure of an aluminosilicate (~Gorilla©) glass (2013)
2. Irradiation in a nuclear waste glass (2011)
3. Atomistic response of silica under shear and pressure (2012)
4. Mechanical behavior of glass nanowires (2012)

D. APPLICATIONS

1. Structure of an aluminosilicate glass

Reference : J. Chem. Phys. 139, 044507 (2013)

- **System Na_2O-Al_2O_3-SiO_2** across the Al/Na join (Applications Gorilla Glass©) defining the paralkaline (Al/Na<1) and peraluminous (Al/Na>1) regions.
- **Comparison** between Born-Mayer-Huggins (Buckingham) and Morse-Pedone (see lecture 7) potential.



- **Whole analysis**

Structure, potential sensitivity, angles, coordination numbers, mechanical properties

D. APPLICATIONS

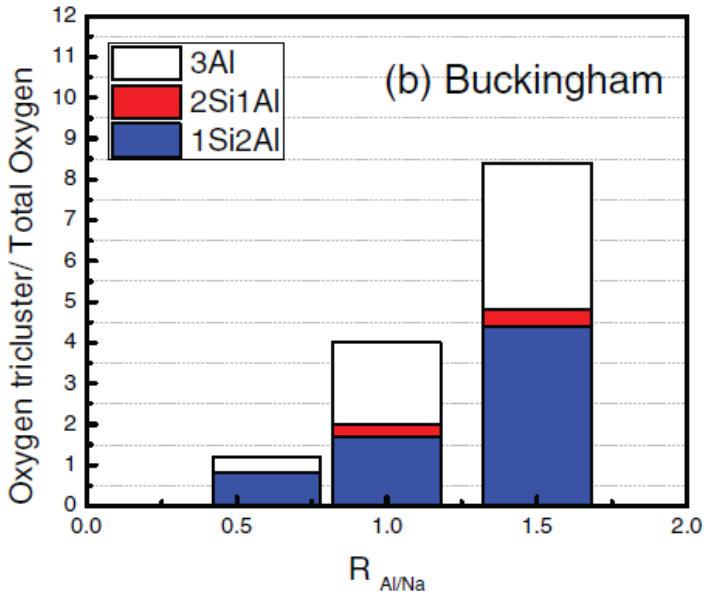
1. Structure of an aluminosilicate glass

TABLE III. The coordination distribution of O around Al.

	Buckingham (in %)				Morse (in %)			
$R_{Al/Na} = N_{Al}/N_{Na}$	3	4	5	6	3	4	5	6
1.5	1.0 ± 0.2	97.7 ± 0.7	1.3 ± 0.6	0	0	94.2 ± 0.9	5.5 ± 0.9	0.3 ± 0.3
1.0	0.6 ± 0.2	98.7 ± 0.1	0.7 ± 0.2	0	0.1 ± 0.1	95.7 ± 1.3	3.9 ± 1.3	0.3 ± 0.2
0.6	0.1 ± 0.1	99.5 ± 0.5	0.4 ± 0.3	0	0	98.0 ± 0.6	1.9 ± 0.6	0.1 ± 0.1

- Aluminum ions are mainly four-fold coordinated in peralkaline compositions (Al/Na < 1).

- In peraluminous compositions (Al/Na > 1), small amounts of five-fold coordinated aluminum ions, and oxygen triclusters.



D. APPLICATIONS

1. Structure of an aluminosilicate glass

- Si is mostly in Q^4 and Q^3, while Al is only Q^4.
- Increase of Q^3 units for peralkaline compositions (Al/Na < 1).
- BO bond angle distribution involving Al is strongly influenced by the Al/Na ratio.

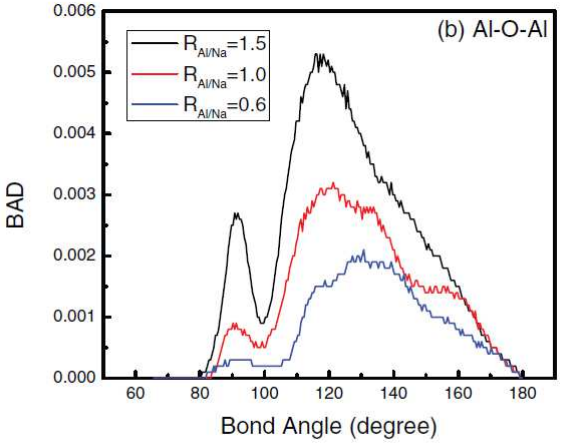
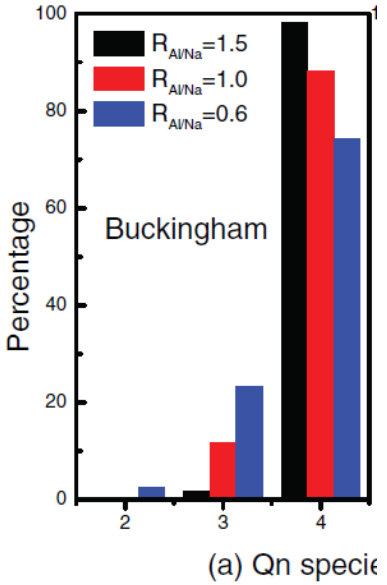
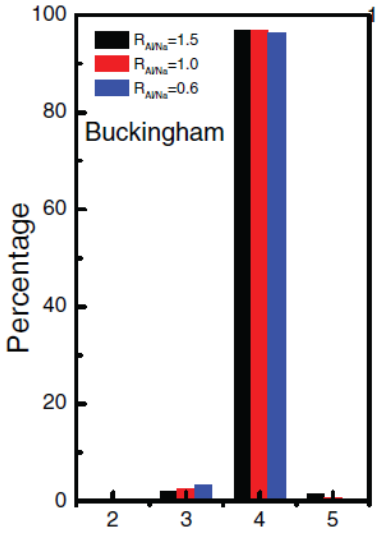


FIG. 8. Inter-polyhedron bond angle distribution (a) Al–O–Si and (b) Al–O–Al in the model simulated under Buckingham potential.

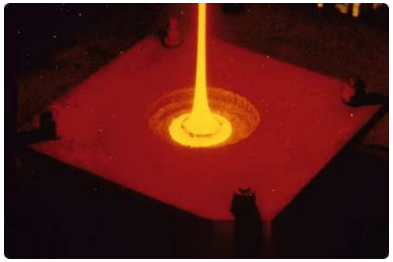




Q^n speciation n

D. APPLICATIONS

2. Irradiation on a nuclear waste glass



Context: Conditioning processes such as vitrification are used to convert nuclear waste into a stable solid form that is insoluble and will prevent dispersion to the surrounding environment. Technique developed by CEA and AREVA in France.

System: **$45SiO_2$**-$5Al_2O_3$-**$14B_2O_3$**-**$10Na_2O$**-4CaO
+ZnO+Li_2O+Fe_2O_3+P_2O_5+ZrO_2+Cs_2O+MoO_3+K_2O+SrO+…
typical of an AREVA NP glass

Physics:

- Nuclear glasses indicate the predominance of ballistic effects in accounting for the macroscopic changes at doses up to 10^{19} α/g.

- Under irradiation, glass density and hardness diminish, while fracture toughness increases. **What modification at the atomic scale ?**

Reference: J.-M. Delaye et al. JNCS 357, 2753 (2011); JNCS 358, 3427 (2012)

D. APPLICATIONS

2. Effect of the irradiation on a nuclear waste glass

- Model of 56 SiO_2-17 B_2O_3-12 Na_2O- 6 Al_2O_3-3.5 ZrO_2 +ppm UO_2 using a Born-Mayer potential with a 3-body term to account for boron-4 atoms.

  θ_0=109°

$$\phi_2(r_{ij}) = A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) + \frac{z_i z_j}{r_{ij}},$$

$$\phi_3(r_{ij}, r_{ik}, \theta_{jik}) = \lambda_i \exp\left(\frac{\gamma_i}{r_{ij} - r_{ci}} + \frac{\gamma_i}{r_{ik} - r_{ci}}\right) \times (\cos\theta_{jik} - \cos\theta_0)^2,$$

- Structural modification induced by a ballistic α particle with different energies ranging from 400 eV to 7keV.
- Decrease of time step to 0.01 fs (usually 2fs) to account for the energy change due to the particle
- Cascades of changes analyzed.

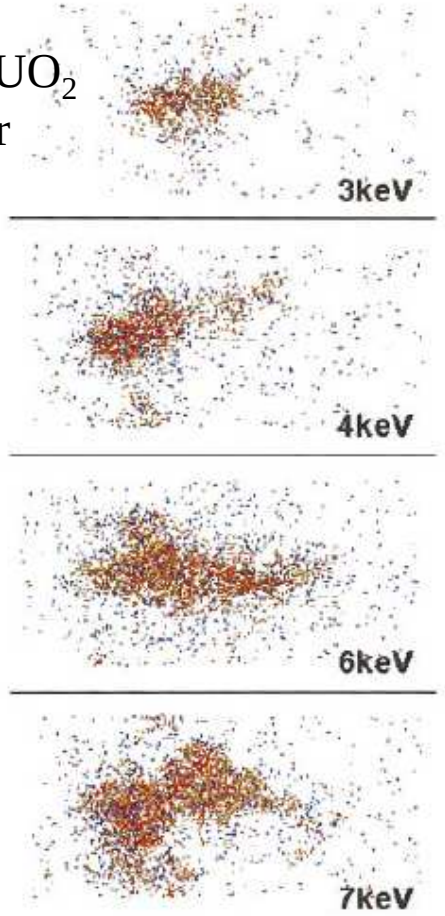


FIG. 3. (Color) Morphology (displaced atom positions) of four cascades in a 82944-atom alkali glass (see composition in Table I). These cascades are initiated by U atoms. Si(yellow), O(red), B(green), Na(blue), Zr(brown), and Al(gray).

D. APPLICATIONS

2. Effect of the irradiation on a nuclear waste glass

- Glass structure is being reconstructed by local rearrangements in presence of alkalis.
- Large majority of atomic displacement occur during the first instants of the cascade (thermal peak).
- Jumps and collective displacements, atomic nature changed (Boron-3, NBOs, rings with nb of cascades or energy dose)

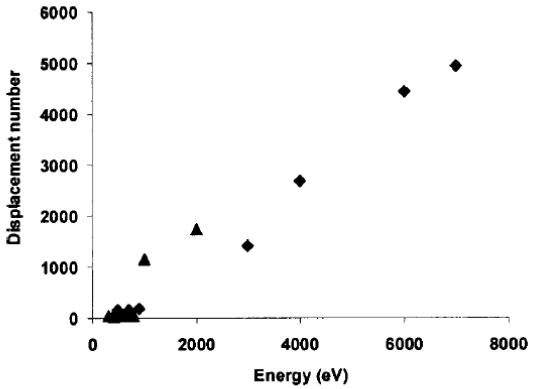


FIG. 4. Number of atom displacements versus cascade energy. Cascades initiated by (♦) U atoms and (▲) O atoms.

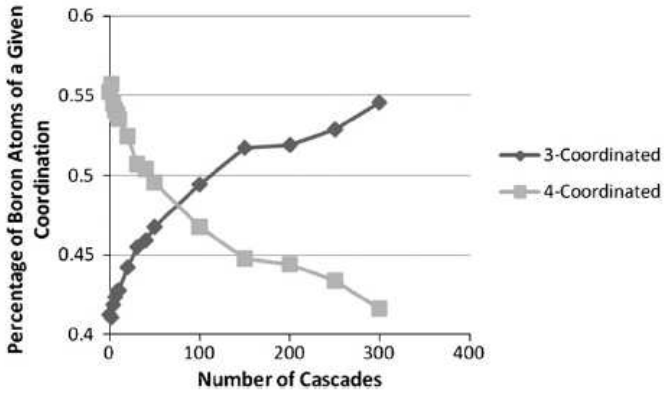
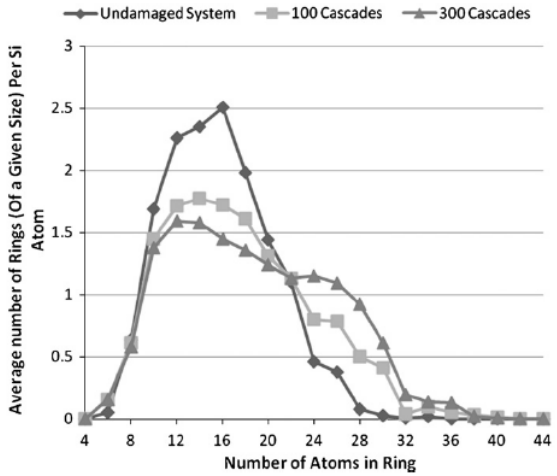


Fig. 3. Changes in boron coordination under ballistic collision-cascade self-irradiation.



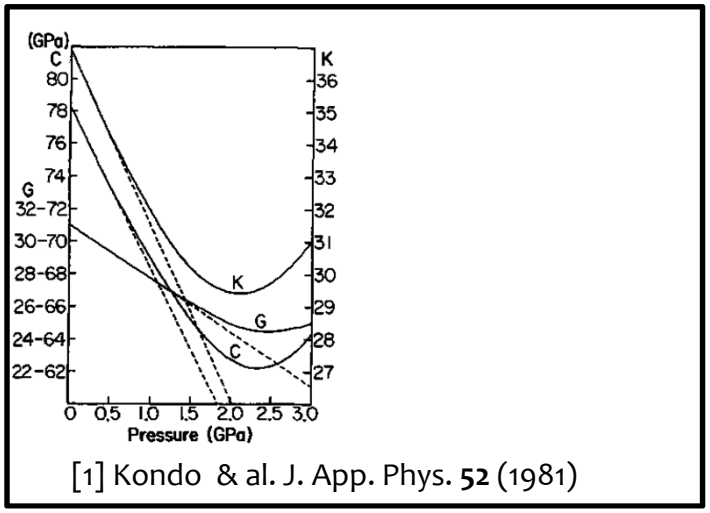
D. APPLICATIONS

3. Atomistic response of silica under pressure and shear

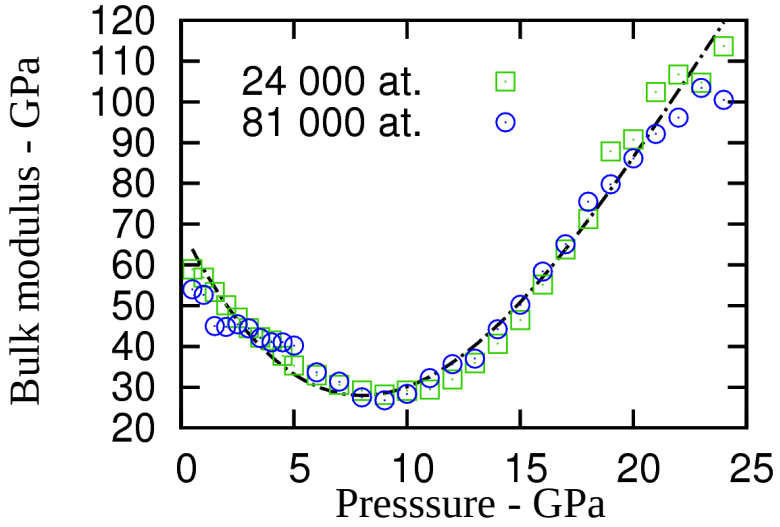
Context: understanding the mechanical response of a glass from MD simulation under hydrostatic pressure and shear deformation. In connection with the well-documented **compressibility anomaly** at 2.5 GPa in densified silica

Reference : B. Mantisi et al. , Eur. Phys. J. B 85, 304 (2012).

Model: BKS silica with addititve repulsion terms (collapse at high pressure, see lecture 7)

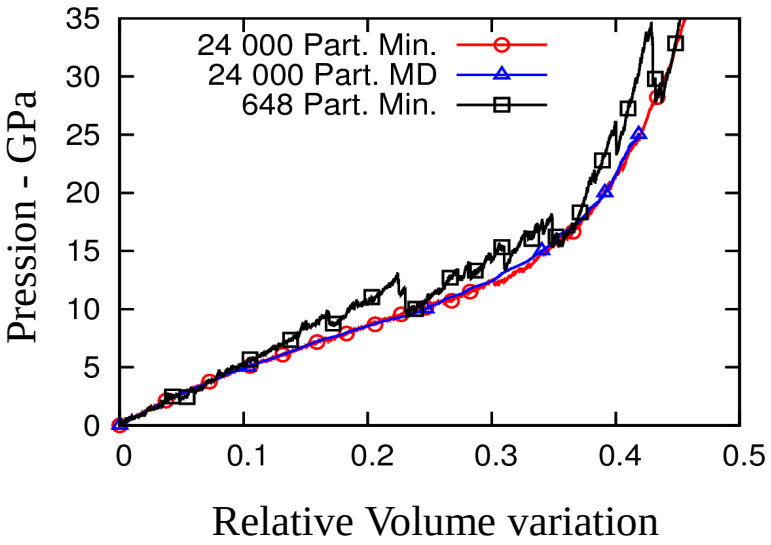


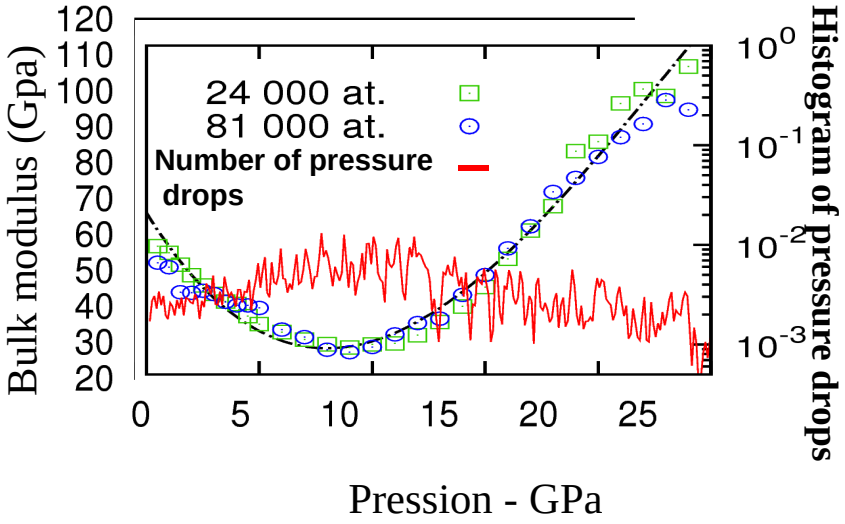
[1] Kondo & al. J. App. Phys. **52** (1981)



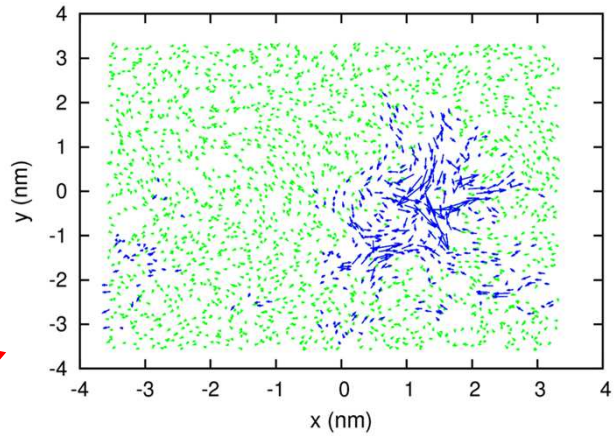
D. APPLICATIONS

3. Atomistic response of silica under pressure and shear





- Important role played by **pressure drops** upon compression
- Drops correlated with the anomalies
- Pressure drop = microplasticity (irreversible local deformations)

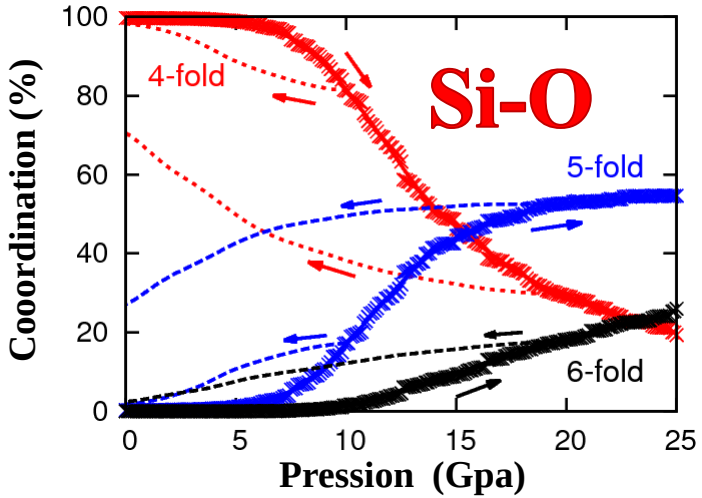


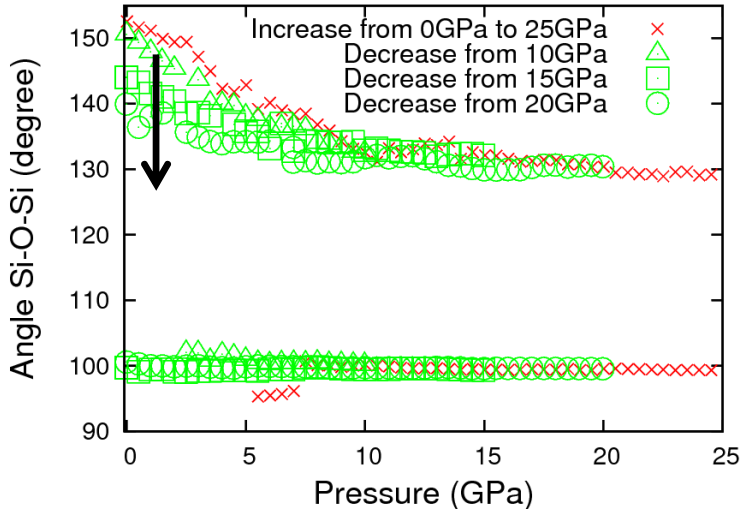
D. APPLICATIONS

3. Atomistic response of silica under pressure and shear

- Increase of pressure leads to irreversible structural changes when pressure is released (18 GPa).

- Reduction of the Si-O-Si angle depends on the max pressure before decompression.



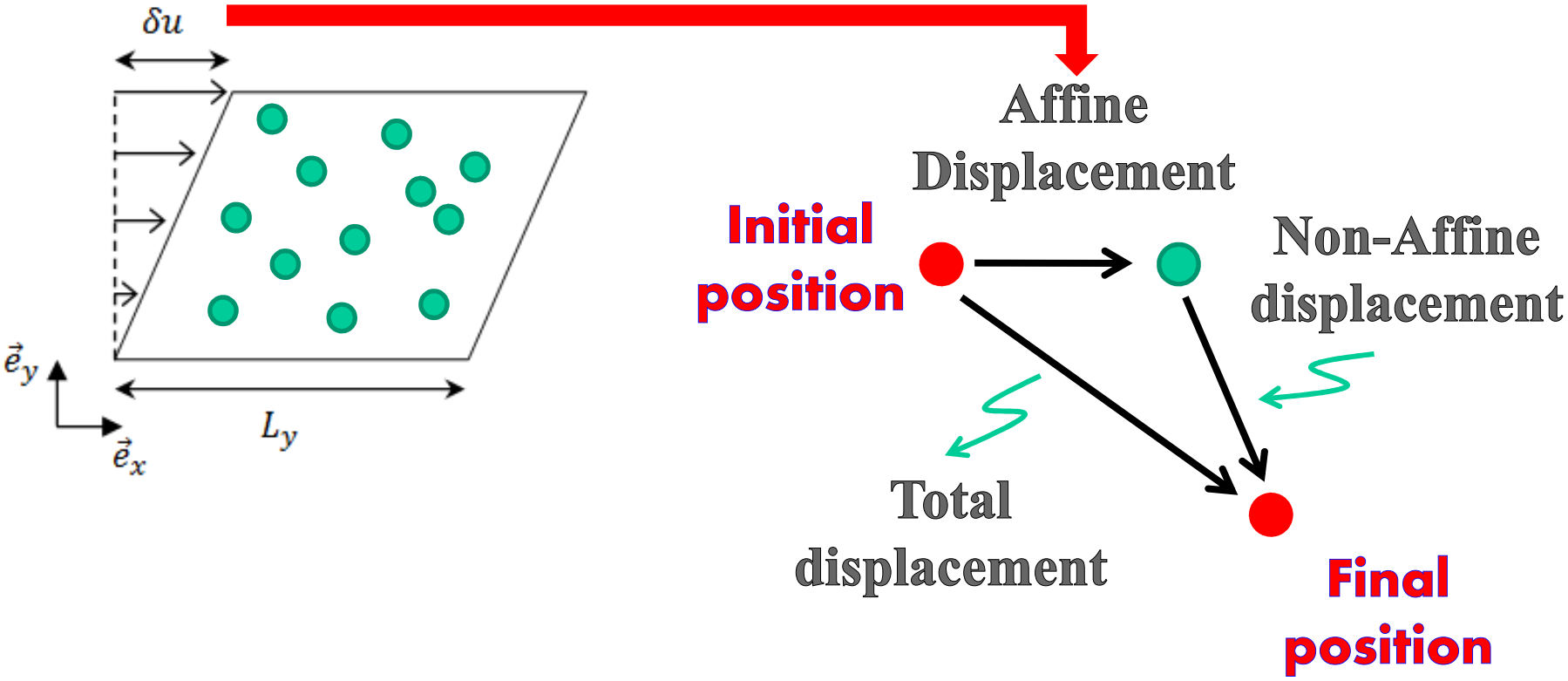


D. APPLICATIONS

3. Atomistic response of silica under pressure and shear

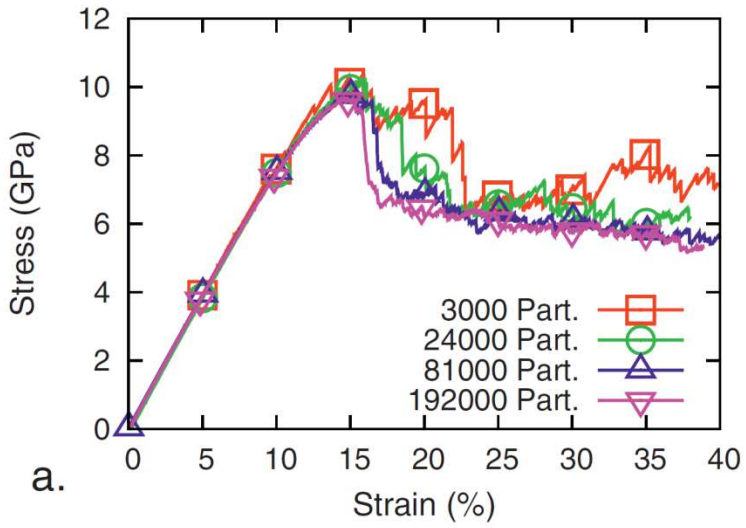
- Under shear, correlation between non-affine displacement field and micro-plastic events.

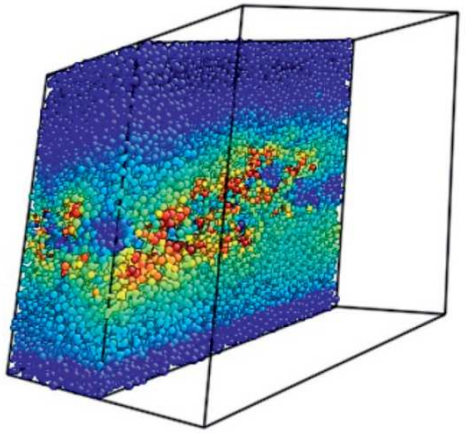
$$\vec{u}_{tot}(x,y,z) = \vec{u}_{aff}(x,y,z) + \vec{u}_{naff}(x,y,z)$$



D. APPLICATIONS

3. Atomistic response of silica under pressure and shear



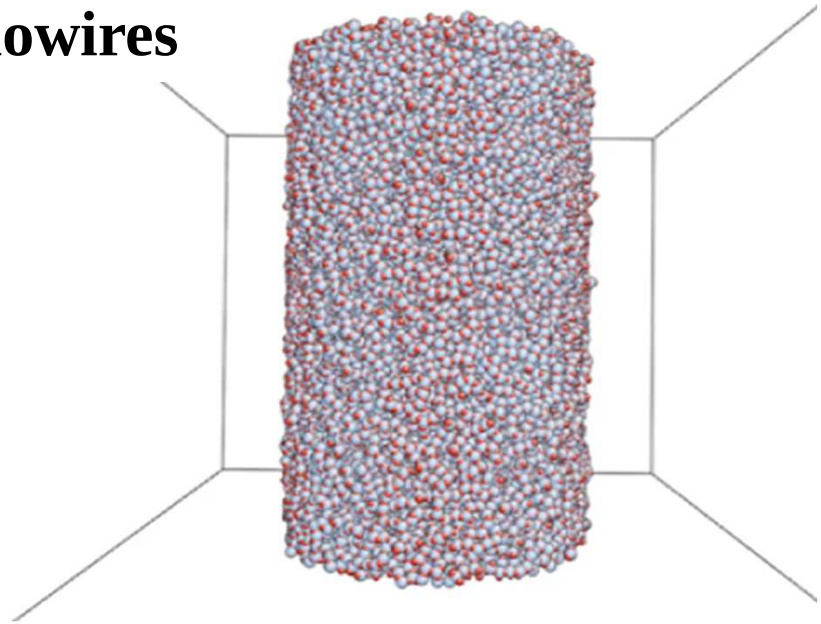


Distribution of non-affine displacement

- Plastic régime is a series of elastic events and stress drops
- Non-affine displacement fields lead to shear bands in the plastic régime. General behavior (a-Si, granular materials,…)
- See: http://www-lpmcn.univ-lyon1.fr/~atanguy

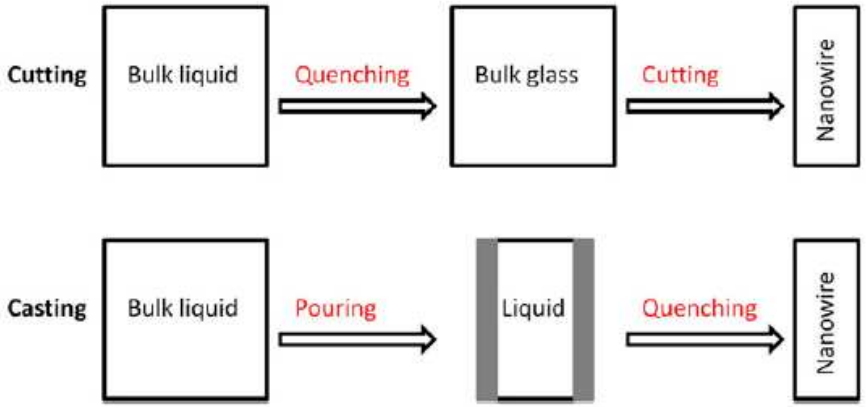
D. APPLICATIONS

4. Mechanical behavior of glass nanowires



Context: investigation of mechanical properties of nm sized silica under uniaxial tension test.

- Potential: BKS potential
- Preparation of nanowires: Cut and cast of bulk silica. Effect of the initial structure.
- Mechanical response (stress-strain)
- Reference: F. Yuan, L. Huang, JNC 358, 3481 (2012).



D. APPLICATIONS

4. Mechanical behavior of glass nanowires

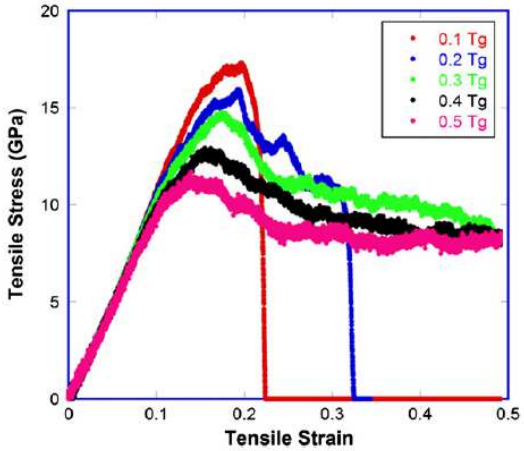
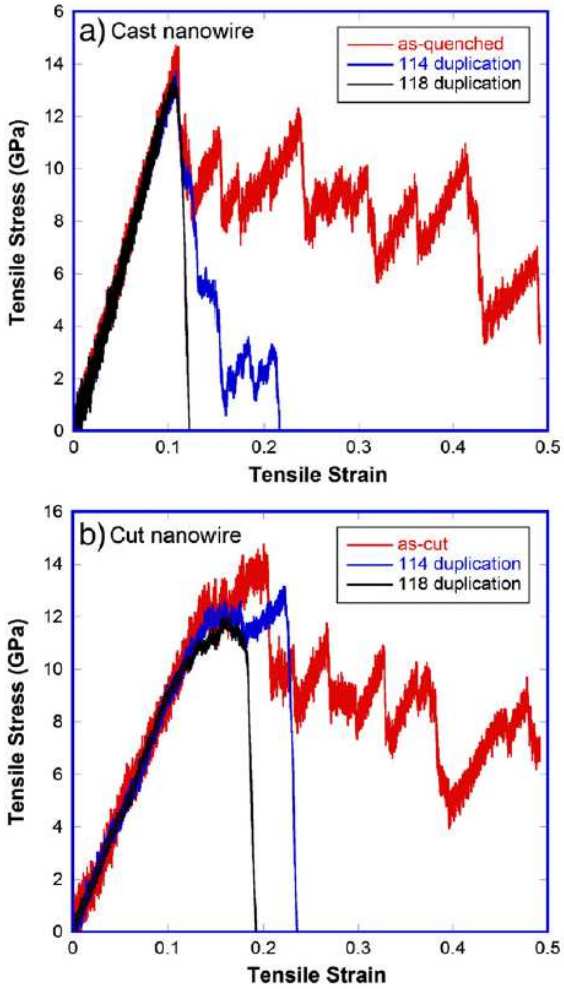


Fig. 9. Stress–strain curves of NPT uniaxial tension test in BKS silica glass at different homologous temperatures (113 duplication, 10 K/ps cooling rate, 10^9 strain rate).

- Mechanical deformation under tension
- Brittle to ductile transition under T increase in bulk silica (bond reformation increases with T). At T=0.1Tg fully brittle silica
- Effect of the preparation in nanowires: cut nanowires sustain strain more longer



g. 10. Stress–strain curves of uniaxial tension test in cast (a) and cut (b) BKS amorphous lica nanowires with a radius of ~1 nm (10 K/ps cooling rate, 0.1 Tg working temperature, $)^9$ strain rate).

Conclusion:

- You are (in principle) ready to go !
- Rely on MD packages.
- Many different applications can be considered from atomic scale description (mechanical properties, structure, dynamics, glass nano-engineering,…)

Next lecture: Topological engineering

D. APPLICATIONS

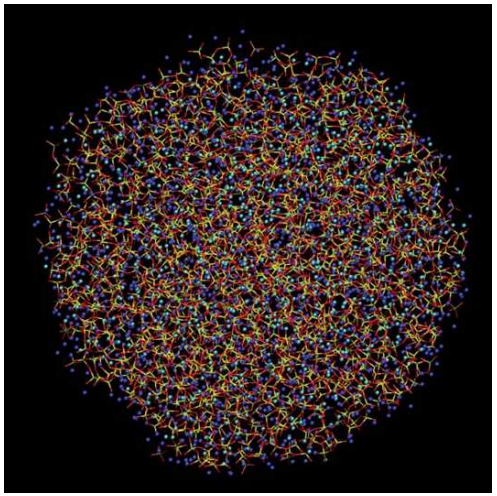
5. Bioactive glass nanoparticle

Context: active research field with important medical/clinical/orthopedic applications. Glass microparticles are used as fillers to treat bone or soft tissues and/or defects.

- Ion solubility promotes tissue regeneration (e.g. 45S5 Bioglass© : 46.1SiO_2 - 24.4 Na_2O; 26.9 CaO - 2.6 P_2O_5

- A key factor to control and tissue-regeneration activity is the size of the glass particles. Reducing the particle size should lead to an enhancement in the bioreactivity

System : Simulation of the a spherical (6 nm diameter) 45S5 Bioglass©) using a mixture harmonic O interactions and a Buckingham potentials.



Reference: A. Tilocca, J. Mater. Chem., 2011, 21, 12660