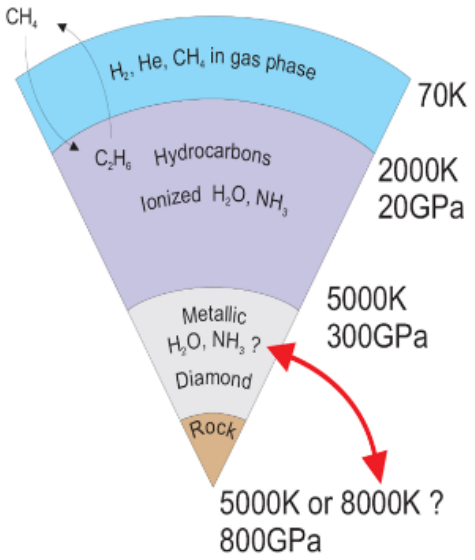
8 High-pressure transitions to plastic and superionic ammonia ices

Ammonia, NH_3, is a prototypical hydrogen-bond molecular system that crystallizes in a cubic form at ambient pressure. It is a major component of the interiors of giant planets such as Neptune and Uranus, where extreme conditions of temperature (up to thousands of ^oC) and pressure (up to several millions of atmospheres) are present. The physical properties of ammonia are profoundly modified at such conditions, but their knowledge is indispensable for a correct modellisation of the planets' interiors. We will focus on its phases III and IV, characterized, at high pressures and temperatures, by molecular plasticity (free rotations of ammonia molecules around their crystallographic site) and superionicity (liquid-like proton diffusion within the crystal). The present project is inspired by the research described in Ninet et al, *Phys. Rev. Lett.* 108, 165702 (2012).



1. Build up the elementary cell of the cubic phase via the symmetry rules of the crystallographic phase, knowing that the coordinates for N correspond to $4a$, while those of H correspond to $12b$, and that the respective values of x, y, z are, in crystal units, as follows:
   N
   $x = y = z = 0.2110$
   H
   $x = 0.390 \quad y = 0.243 \quad z = 0.124$
   Knowing that the ambient pressure lattice parameter is 5.035 Å , create a file `phasecubique.xyz` containing the full coordinates in Å units, ordered as follows :

   ```
   total number of atoms
   (blank line)
   N x_N1 y_N1 z_N1
   N x_N2 y_N2 z_N2
   ...
   H x_H1 y_H1 z_H1
   H x_H2 y_H2 z_H2
   ...
   ```

   Visualise the system by reading this file with the `xcrysden` command, as follows:
   `xcrysden --xyz phasecubique.xyz`
   and check the system looks reasonable, for example by checking a few distances (hint: typical intramolecular N-H distance ≈ 1.0 Å; typical H-bond N-H distance ≈ 1.4 -1.7 Å).

2. Build up the Quantum-ESPRESSO input file `ammonia.in`, according to instructions, inserting the `phaseIII.xyz` coordinates at the right place. Choose a starting cutoff (keyword: `ecutwfc`) and a Brillouin-zone sampling grid `nk1,nk2,nk3`, and run a test `scf` electronic minimisation calculation using the `pw.x` executable. Optimise then the internal position and the atomic coordinates by running the corresponding calculation (keyword: `calculation = 'relax'`). Include at the end of the run the optimised positions in your input file, and then check the convergence of the total energy of the system with respect to the energy cutoff to within 1 mRy, by running other `relax` calculations with increasing values of `ecutwfc`. Do then the same analysis of convergence of the total optimised energy to within 1 mRy with respect to the k-point grid `nk1,nk2,nk3`.

3. Calculate, via the `calculation = 'relax'` mode, the pressure-volume equation of state of the system, by fitting your results with the Murnaghan equation (procedure: page 8, eq. 2). Compare the fitted equilibrium lattice parameter and bulk modulus at two different cutoffs of your choice.

4. Select the lattice parameter corresponding to a pressure of about 40 GPa (= 400 kbar), as calculated in output by the `calculation = 'relax'` mode. Take the corresponding internal positions, and build up a supercell equal to a 2×2×2 multiple of the elementary cell, thus contaning 32 ammonia molecules. Verify by `xcrysden` that this supercell is correct, and recalculate its zero temperature `calculation = 'relax'` configuration.

5. Start a finite temperature (ab initio) molecular dynamics simulation (keyword: `calculation = 'md'`), by testing, at room temperature (300 K), the choice of a timestep. Trace on gnuplot some relevant quantities (Kinetic energy, potential energy, temperature, pressure).

6. Once the best timestep established, evaluate (and justify) the length of the equilibration time. From that moment, calculate the average distance of H atoms from its intramolecular N atom. Then calculate the corresponding distribution function (histogram of all the calculated distances).

7. Calculate the orientational correlation function, *i.e.* the following quantity:

$$C(t) =< \mathbf{u}(0) \cdot \mathbf{u}(t) >, \tag{3}$$

   where $\mathbf{u}(t)$ is the unit vector of the molecular axis, in Cartesian coordinates, at time t.

8. Increase progressively the temperature of the system (keywords: `ion_temperature='rescale-T', delta_t=1.0001 ou 1.0002`), and record on three columns:
   t $T(t)$ $C(t)$.
   Plot $C(t)$ as function of $T(t)$, and try to detect the plasticity transition.