1. Overview

We aim to accurately study the behaviour of pure hydrogen, including the equation of state and the conditions under which phase transitions occur, by using Monte Carlo (MC) methods.

2. The CEIMC Approach

The central idea of CEIMC is to couple:
- A quantum Monte Carlo (QMC) simulation for the electrons at wavefunction for QMC energy differences.
- A classical or quantum MC simulation for the nuclei at finite temperature.

This approximation is good for low T since the thermal excitation of electrons is small for T \(\lesssim T_\text{F} \approx 136 \text{ K} \) for densities of interest. The CEIMC method is in contrast with the PIMC approach which treats the entire system at finite temperature but becomes inefficient for low T. For classical nuclei, we sample the Boltzmann distribution of configurations using MC with a Metropolis acceptance:

\[
A = \min[1, \exp(-\Delta E(s,s'))]
\]

where \(\Delta E(s,s')\) is the Born-Oppenheimer (BO) total energy difference of nuclear configurations \(s\) and \(s'\).

3. Noisy B.O. Energy Differences

In practice, \(\Delta E(s,s')\) is approximated with a noisy estimate computed with a stochastic method (VMC or RQMC). We can proceed in a number of ways:
- Reduce noise by sampling the QMC for longer.
- Reduce noise through correlated sampling methods.
- Tolerate noise with a modified acceptance criterion.

We use a combination of all three.

4. Comparison with CPMD

- Molecular Dynamics (MD) has the advantage that it samples dynamics, but longer simulations are required.
- Conversely, MC offers fast exploration of configuration space since it is not bound by physical dynamics. There is no time-step error in the nuclear MC simulation.
- DFT-LDA offers faster simulations, but hydrogen fluid pair-correlation functions (PCFs) are less structured than those from CEIMC. LDA matches CEIMC simulations at 2T (see Fig. 2 and Ref. 93, 146402 (2004)).
- CEIMC matches accurate PIMC simulations at higher temperatures (T = 5000 K).
- DFT with LDA/GGAAs predict the wrong melting pressure of hydrogen at T = 0 K.

5. Trial Wavefunction

We require a fast and transferable wavefunction for QMC energy differences. Single-particle orbitals, for a Slater-Jastrow wavefunction, are generated with a fast band-structure calculation using a single-particle Hamiltonian with a bare electron-ion potential. Figure 3 demonstrates that this is a good choice for a range of densities in hydrogen.

6. Hydrogen PPT

The Problem

The hydrogen Plasma Phase Transition (PPT) is the transition from a molecular fluid to a non-molecular fluid (see Eq. 1), assumed to be accompanied by a metallization of the system. We aim to study the nature of the transition and the possible presence of a critical point at or above, T = 2000 K.

Results

Figures 4 and 5 show nuclear PCFs for simulations in the NVT ensemble of hydrogen at T = 2000 K for a variety of volumes. The simulation cells contain 32 atoms and twist-averaged boundary conditions are used to reduce finite-size effects in the energy differences. Nuclear fluid is treated classically (Eq. 1). Simulations begin either with a molecular fluid (circles) or a non-molecular fluid (crosses). Molecules are stable at low pressure and dissociate at high pressure in what appears to be a first-order phase transition when using VMC and a continuous transition when using RQMC. We use an order parameter corresponding to the mixing ratio of molecular/non-molecular fluid to study the size of hysteresis (Fig. 6).

Finite-Size Error Assessment

Simulations of first-order phase-transitions are often subject to large finite-size errors in metastable states due to the size of the free-energy barrier separating the pure phases and the large cost of creating an interface for phase separation. Figure 7 shows PCFs for VMC and RQMC with simulation cells of 32 and 54 atoms. The VMC simulations show finite-size errors in the region of the transition, giving a further indication of first-order behaviour. Conversely, the RQMC simulations show no appreciable finite-size error.

7. Conclusions

- VMC predicts a first-order PPT at T = 2000 K.
- VMC simulations suffer from finite-size errors in localizing the transition pressure.
- RQMC (more accurate \(\Delta E(s,s')\)) predicts a continuous transition at the same temperature.
- Future Work:
  - Investigate metallization of fluid.
  - Investigate corrections for quantum nuclei using path integrals.