

Tutorial on Path Integral Monte Carlo Simulations of Atomic Hydrogen in Wigner Crystal Regime at High Pressure

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This tutorial uses classical and quantum simulations to study the melting behavior of solid hydrogen. At very high pressures, as they occur in neutron stars, hydrogen molecules are dissociated and the electronic charge is fully delocalized providing neutralizing background. At low enough temperature, the protons form a Wigner crystal. This quantum solid shares many similarities with the more commonly known Wigner crystal of electrons.

The units of *nuclear* Bohr radii, $a_0 = 4\pi\epsilon_0\hbar^2/m_p e^2 = 2.9 \times 10^{-14}$ m, and *nuclear* Hartrees, $\text{Ha} = e^2/(4\pi\epsilon_0 a_0) = 8.0 \times 10^{-15}$ J = 5.8×10^8 K k_b , which are a factor by $m_p/m_e = 1836$ less, or greater respectively, than the usual atomic units. However, for all purposes of this tutorial, one can think of the usual Wigner crystal of electrons and use the common atomic units.

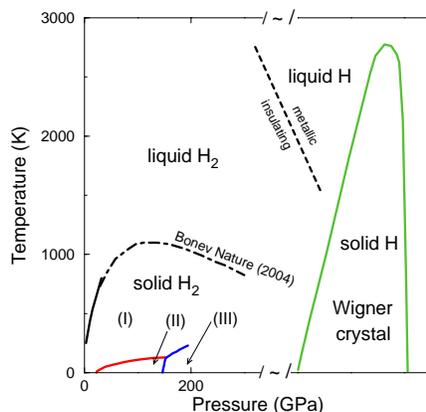


Fig. 1: Energy vs temperature.

The interactions in Wigner crystal are fairly simple. However, quantum effects of the nuclei are very large. This makes it a good candidate to study the effects of anharmonicity and zero-point motion.

Begin the tutorial with:

```
> bsub -Is -n1 -W 1:00 tcsh
> limit stacksize unlimited
> cd ~/scratch-global
> tar xzvf ~train08/tutorial.tar.gz
> cd tutorial
```

1 Classical Monte Carlo code for Coulomb systems (CMC)

Before running the CMC code, please write down the formulae for the energy per particle in the limits of very low and very high temperature. For simplicity, ignore the long-range effect and think of a pair potential $V(r_i - r_j)$:

For crystal with atoms at positions r_i the internal energy (kin.+pot.) per particle is,

$$E(T \rightarrow 0)/N = \quad \quad \quad + \quad \quad \quad (1)$$

In the limit of infinite temperature, the charge are randomly distributed (Why is that?). What is the internal energy then?

$$E(T \rightarrow \infty)/N = \quad \quad \quad + \quad \quad \quad (2)$$

CMC is require no input files but takes 4 command lines parameters:

- the number of particles (please use 54),
- the Wigner-Seitz radius r_s ($\frac{4\pi}{3}r_s^3 = V/N$) to specify the density,
- the temperature,
- and maximum displacement d in the Monte Carlo moves (enter d/r_s).

Now run the CMC code like:

```
> cmc
> cmc 54 200 0.01 1.0
> cmc 54 200 0.01 1.0 > log01
> cmc 54 200 1e-3 1.0 > log02
```

• Please run the CMC code for a grid of temperature, leaving the number of particle and density the same. Keep the output by choosing different file name like *log01*, *log02*, etc. The code reports the acceptance ratio, potential energy (here labeled “E”) and how far particles have moved (“DR”):

```
all moves=all          p tri=      5400 acc=      4928 ratio= 0.9126
E: Block: -0.00242203 +- 0.00000470   total: -0.00244794 +- 0.00000659
DR: Block: 87.51806630 +- 0.51041911   total: 86.32873562 +- 0.04096862
```

If the acceptance ratio drop below 5%, shorter moves but me moved (reduce d/r_s and rerun)! Please add your results to Figures 2 and 3.

• Now study the pair correlation function $g(r) = \frac{V}{N(N-1)} \sum_{i \neq j} \delta(r - r_{ij})$:

```
> grep gr log01 > gr01
> grep gr log02 > gr02
> gnuplot
gnuplot> plot "gr01" u 2:3,"gr02" u 2:3
```

At which temperature did the classical system melt? Study $g(r)$ and “DR”. Mark it im Figs. 2 and 3.

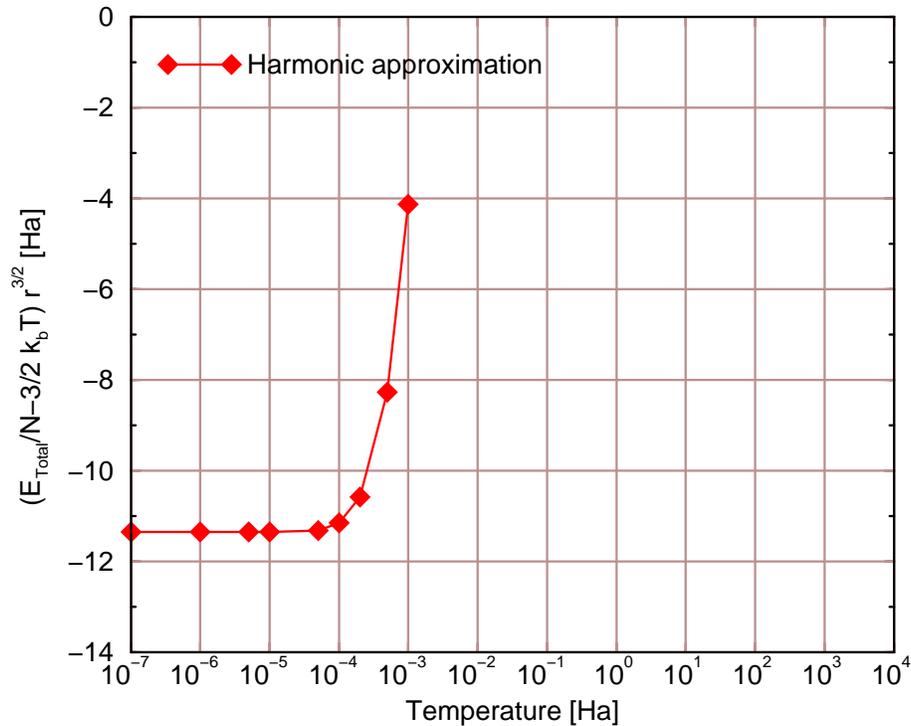


Fig. 2: Energy vs temperature.

2 Path integral Monte Carlo code CUPID

The focus of this exercise is to familiarized yourself with the C++ Universal Path Integral Daemon (CUPID) and the input files it requires.

```
> cupid
```

Starting CUPID without arguments provides a list of keywords it understands.

```
> cupid name
```

starts the simulation 'name'. It reads the input file 'name.sy' and writes the output file 'name.out'. The statistical averages are written (dumped) into 'name.dmp' in HDF5 (Hierarchical Data Format), which can be read by,

```
> h5trace name.dmp
> h5trace name.dmp root/obs/E_tot
> h5trace name.dmp root/obs/linde_e > name.linde_e.txt
> h5analysis name.dmp root/obs/E_tot
> h5analysis name.dmp root/obs/E_tot 2 0
> h5analysis name.dmp root/obs/g_ee 2 0 > name.gr.txt
> h5analysis name.dmp root/obs/s_ee 2 0 > name.sk.txt
```

'name' stands for different simulation runs names cc01, cc02, cc03,...

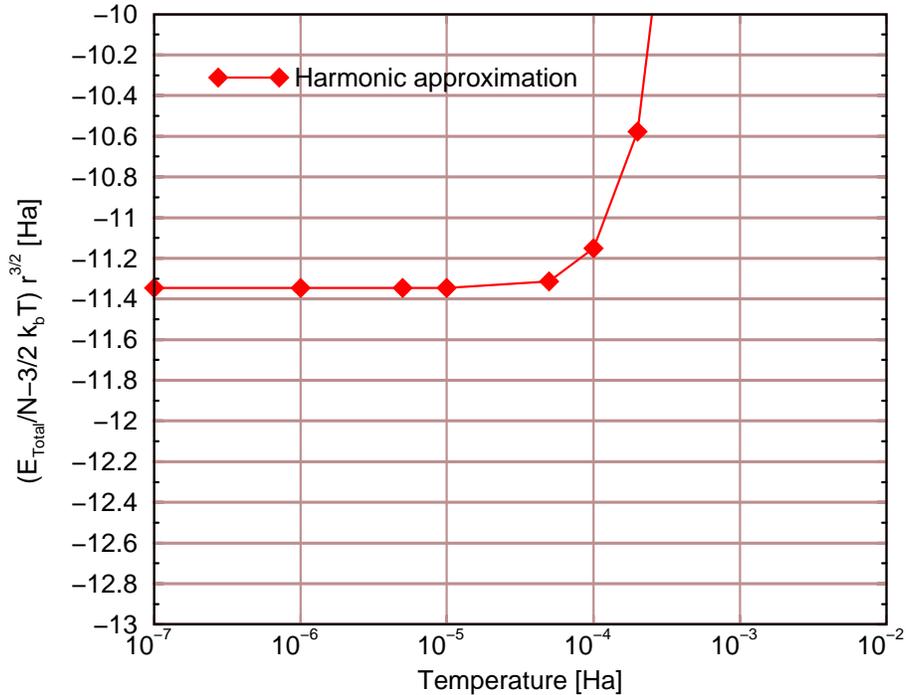


Fig. 3: Energy vs temperature.

3 A first cupid run

There is only one input file 'cc01.sy' provided. Please modify it as specified below and save under a new name each time (cc02, cc03 etc.)!

```
beta      50000.0
Specifies the temperature  $\beta = 1/k_B T$ .

nSlices   256
Here it Uses  $M=256$  time slices. In conjunction with  $\beta$ , this determines the time step  $\tau = \beta/M = 50000/256 = 195.312$ .  $\tau$  can only assume values, for which the pair density matrix table has been generated and stored in files 535.ee.dm and 535.ee.lr. Those are 24.4141, 48.8281, 97.6562, 195.312, 390.625, 781.25, 1562.5, and 3125.0

type      e  0.5  0  54  e.ic
Define particles: name (electron),  $\lambda = \hbar^2/2m_p$ , spin*2 (=0 make electron distinguishable particles), number of particles (here 54), file name to read the starting coordinates.

pot pair e e 535.ee.dm 535.ee.lr
Read the precomputed electron-proton pair-density matrix. It has been broken up in a long and a short-range part using the Ewald method.

units Ha a0
Use units of Hartrees and Bohr radii  $a_0$ .

enorm     1.
Divide all energy estimators by 54. Energy data in name.dmp will be per particle!

boxSize   1218.589557
The 3dimensional periodically repeated simulation cell with a length 1218.589557  $a_0$  in each direction.

displace e 0.2 30.0
Do only 20% classical moves as quantum moves. Displace maximally by 30.0  $a_0$ .
```

```

sofk 0.0312 20
Computes the structure factor  $S(k)$ .

lindemann
Lindemann ratio. Measure how far particles have move from initial positions.

RESTART
Restart the calculation if an old cc.rs file exists. (If this is commented out, all previous files
and results will be overwritten.)

SELECT 10 100 4 54
Parameters: #blocks, #steps per block, #level in bisection, #single particle moves per step
(before the code moves to a new window in imaginary time). #level specifies that  $2^{\#level} - 1$ 
beads will changed in one move.

```

Now run the PIMC simulation

```
> cupid cc01
```

and analyze the results in 'cc01.dmp'. The total energy can be looked by

```

> h5trace cc01.dmp root/obs/E_tot
> h5trace cc01.dmp root/obs/E_tot > E-vs-time.txt
> h5analysis cc01.dmp root/obs/E_tot
> h5analysis cc01.dmp root/obs/E_tot 2 0

```

The last command averages all blocks beginning with the second block. Use *gnuplot* with *plot "E-vs-time.txt"* to see how many blocks one has skip at the beginning, at least one!

4 Adjusting the time step τ

There is only one input file 'cc01.sy' provided. Please modify it as specified below and save under a new name each time (cc02, cc03 etc.)!

- Change the number of blocks to something between 20 and 50, and rerun 'cc01' to reduce the error bars.
- In 'cc01', a rather conservative time step of $\tau = 195.312$ was used. Please run new simulations with $1/2, 2, 4,$ and 8 times that time step. Give each a new name. Leave $\beta = 50000$ but keep adjusting the levels in the bisection (#levels) so that always the same length of path is modified.
- Analyze your results with *h5analysis*, maybe plot them. Based on this analysis choose an optimal time step and use it below. If you have question, check with an instructor.

5 Simulation a different T

Now that you have chosen a new time step, keep it constant for the following simulations. Now run a large number of PIMC simulations for different temperature in order to generate a $E(T)$ curves for Figs. 2 and 3. Derive the energy per particle with *h5analysis*, subtract $3/2k_bT$ and multiply by $r_s^{3/2}$.

- The only way to change the temperature, is to modify $\beta = 1/k_bT$. Only certain values are possible because we want to keep τ the same.
- Run the simulations, analyze the energies, and enter your results in Figs. 2 and 3. PIMC result should not agree with harmonic lattice approximation even at low T. What is the reason for the discrepancy?

- The thermal de Broglie wave, $\Lambda = \sqrt{4\pi\lambda\beta}$, determines roughly the spread of the paths. If the spread is less than the inter-particle spacing given by r_s then quantum and classical results should agree. Derive the temperature where this approximately happens. Check of the PIMC and CMC results indeed converge.

6 Further analysis

Use

```
> h5analysis name.dmp root/obs/g_ee 2 0 > name.gr.txt
```

and *gnuplot* with *plot "name.gr.txt"* to plot the $g(r)$ functions for the quantum case. Is it possible to see at which T the system has melted?

A liquid and a solid can better be distinguished use the structure factor. Analyze and plot with

```
> h5analysis name.dmp root/obs/s_ee 2 0 > name.sk.txt
```

Furthermore, one can analyze how particles have diffused during the course of the simulations. Plot using

```
> h5trace name.dmp root/obs/linde_e > name.linde_e.txt
```

For a quantum solid you should find approximately $0.3 * r_s$.

7 Questions

1. In our simulations, we have always started in the solid phase and then waited till the system melted spontaneously. This is *not a reliable* way to determine the melting temperature. Explain way!
2. You should have observed that the PIMC internal energy are below the harmonic value. What is the reason? Assuming that this difference comes mainly from the kinetic energy, what can be said about the degree of localization of the particles? How do the Lindemann ratio from PIMC and the harmonic lattice model compare?