Comparison of path integral Monte Carlo, coupled electron-ion Monte Carlo, and Kohn-Sham simulations for Hydrogen and Deuterium

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I. COMPARISON

Recently published work[1] presents a study of hydrogen for densities between 0.724 and 2.329 g/cm^3 and temperatures in the range 2-10 kK using the coupled electron-ion Monte Carlo (CEIMC) and standard Kohn-Sham (KS) density functional theory (DFT) methods. The KS calculations used ground-state exchange-correlation functionals.

In particular Table I of Ref. 1 gives the total pressure P_{tot} as a function of temperature T for H at $\rho_H = 0.983$ g/cm^3. The instantaneous pressure, P_{inst}, is defined as the pressure from the electron-electron, electron-ion, and ion-ion interactions. It can be obtained by subtracting the ideal gas dynamic (or kinetic) ionic contribution from P_{tot}. Values of P_{inst} obtained thusly from the data of Table I in Ref. 1 are shown in Figure 1. The upper panel shows the full temperature range, while the lower is shows the region $0 \leq T \leq 60$ kK at an expanded scale.

Similarly, Table I of Ref. 2 gives path integral Monte Carlo (PIMC) data for deuterium for at "equivalent" densities, $\rho_D = 1.96361$ g/cm^3 $\approx 2\rho_H$. The corresponding P_{inst} vales also are shown in Fig. 1.

Additionally, both panels of Fig. 1 show KS-DFT *ab initio* molecular dynamics (MD) results for H and D of the same densities. Note that the H calculations used PBE XC, while the H calculations used LDA.

At a fixed nuclear arrangements, the instantaneous pressures for H and D are exactly the same. During an MD simulation, the nuclear configurations for H and D will differ slightly, however, and, as a consequence, the average P_{inst} also may be slightly different for the two. Nevertheless, from the lower panel of Fig. 1, it is clear that the KS data for H and D can be "visually" interpolated quite well by a straight line. The small discrepancy is consistent with the difference in XC functionals.

In contrast, comparison of the CEIMC and PIMC data shows:

(i) these data cannot be interpolated by a physically sensible smooth curve;

(ii) the CEIMC P_{inst} is below the KS P_{inst}, while the PIMC curve lies above the KS values for T$\leq$ 95 kK;

(iii) the PIMC data extrapolate to what seems to be an incorrect $T \to 0$K limit;

(iv) if the three points of the PIMC data corresponding to the lowest three temperatures are excluded, then the CEIMC and PIMC data can be interpolated, at least roughly, by a smooth curve.

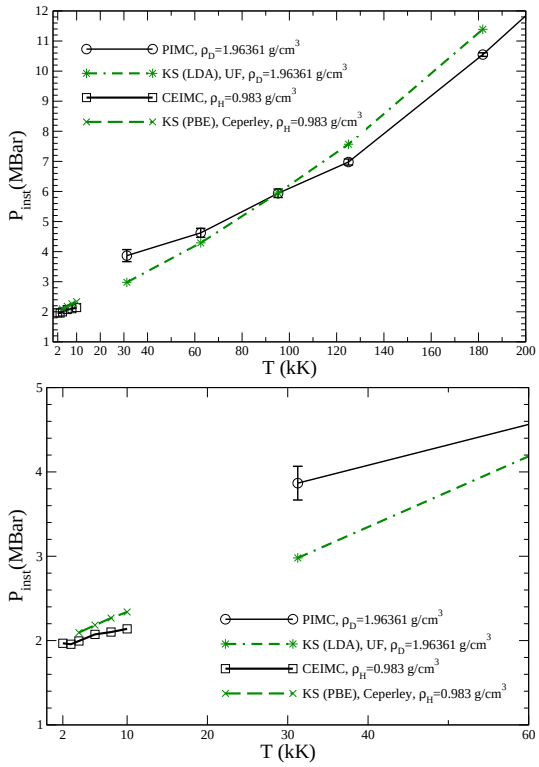

FIG. 1: Instantaneous pressure for hydrogen at $\rho_H = 0.983$ g/cm^3 (for T$\leq$ 10 kK) obtained by CEIMC and KS-DFT (with PBE XC) methods and for deuterium at approximately "equivalent" density $\rho_D = 1.96361$ g/cm^3 (for T *ge* 31.250 kK) from the PIMC and KS-DFT (with LDA XC).

As a conclusion, we suspect that three points of PIMC data corresponding to the lowest three temperatures may not be reliable or, perhaps, the error bars on those three points should be much larger.

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