High Pressure Hydrocarbons Revisited: From Van Der Waals Compounds to Diamond

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Methane and other hydrocarbons are major components of the mantle regions of icy planets. Several recent computational studies have investigated the high-pressure behaviour of specific hydrocarbons [1-5] - but tend not to take into account all of the literature work. As a consequence, hydrocarbon phase diagrams in the literature are incomplete. To develop a global picture of hydrocarbon stability, to identify relevant decomposition reactions, and probe eventual formation of diamond, a complete study of all hydrocarbons is needed.

Using density functional theory calculations we consider here all known C-H crystal structures, augmented by targeted crystal structure searches [6] to build hydrocarbon phase diagrams in the ground state and at elevated temperatures.

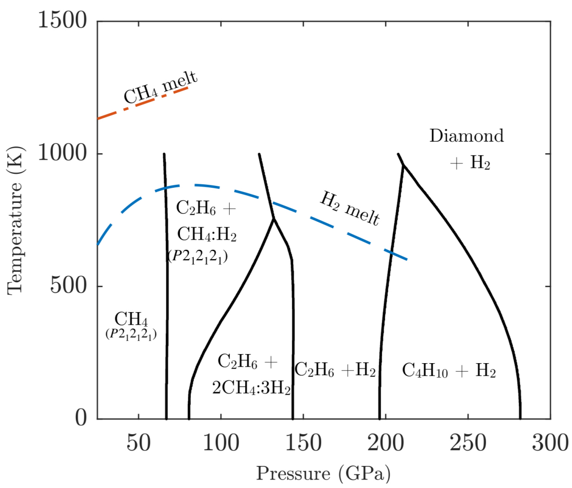

Figure 1. Updated pressure - temperature phase diagram for methane, CH_4.

We find that an updated pressure-temperature phase diagram for methane as seen in Figure 1 is dominated at intermediate pressures by CH_4:H_2 van der Waals inclusion compounds. The presence of these compounds implies that the onset of methane decomposition happens at *lower* pressures than envisaged initially; on the other hand, a proportion of methane molecules remains to *higher* pressures in these compounds.

We discuss the P-T phase diagrams for CH (i.e. polystyrene) and CH_2 (i.e. polyethylene) to illustrate that

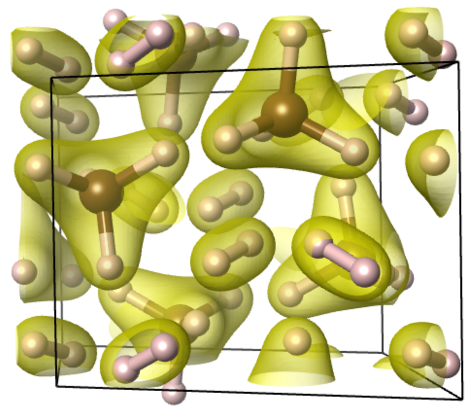

Figure 2. Crystal structure and charge density of $CH_4(H_2)_2$ at 200 GPa.

diamond formation conditions such as those created in recent dynamic compression experiments [7,8] are strongly composition dependent.

Finally, crystal structure searches uncover a new $CH_4(H_2)_2$ van der Waals compound (see Figure 2), the most hydrogen-rich hydrocarbon with a releasable hydrogen content of 20 wt-%, to be stable between 170 and 220 GPa [9].

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