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Dynamic and thermodynamic behavior of carbeneous and hydrogen-bonding materials

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Dissociation behavior of carbeneous materials with or without fluorine atoms at pressures (P) of tens of gigapascal (GPa) and temperature (T) at several thousand Kelvin is not so well understood. The main issues are: (a) carbon condensation processes and (b) thermodynamics of hydrogen fluoride (HF) produced from dissociation. Item (a) requires information on (i) the melting line of carbon, (ii) liquid carbon, (iii) stability and energy barrier between graphite and diamond clusters, and (iv) kinetics of cluster growth. Item (b) requires knowledge of (v) intermolecular potentials involving HF and (vi) influence of fluorine chemistry on supercritical phase change. The details concerning these issues are described below.

Carbon

With regard to item (i), experimental determination of the diamond melting line remains elusive because of the strong covalent bonding, producing extreme stability of diamond. Theoretically, complex free energy calculations have prevented the determination of the phase diagram using first principle methods. We have used the Brenner bond order potential [1] to describe interatomic interactions and Monte Carlo and molecular dynamics (MD) simulations to calculate the free energies of graphite, diamond, and liquid carbon. The resulting melting line of diamond gives a positive slope consistent with the present understanding [2]. Its low-pressure location is also consistent with experiment.

With regard to item (ii), liquid carbon is one of the outstanding unsolved problems in high-pressure research field. Our computer simulations with the Brenner potential show a first-order phase change in liquid carbon [3]. This is the first non-empirical evidence of a liquid-liquid transition between thermodynamically stable fluid phases. It supports a recent flash-heating experiment by Togaya [4], showing a first-order phase change in liquid carbon.

The phase change is associated with density and local structural changes. The low-density liquid is predominantly sp -bonded with little sp^3 character. The high-density liquid is mostly sp^3 -bonded with little sp character. The simulation shows very little sp^2 -liquid, since its π -bond character has a large torsional energy barrier and forces the structure to be planar. Such low entropy of the sp^2 -liquid is not favored relative to the sp - or sp^3 - dominated liquid phase.

It is important to validate the predicted first-order phase change in liquid carbon. MD simulations using the non-empirical density functional theory is in progress for this purpose [5]. One can also perform a shock wave experiment with a low-density aerogel of carbon. Such a soft material under shock can attain an enormous compression, producing high shock heating at low shock pressure. Hence, it is an ideal sample to explore the relevant P - T range. Our calculations suggest 0.15 g/cm^3 to be the optimum initial density for principal Hugoniot experiments to detect the predicted phase change. [6].

In (iii) we made quantum chemical calculations [7] using up to 300 atoms with or without surface orbitals capping with H atoms. Small graphite and diamond clusters change their relative stability to their bulk-like behavior when clusters grow larger than 33,000 to 70,000 atoms. The graphite \rightarrow diamond barriers lie close to the bulk value ($\approx 0.4 \text{ eV}$) insensitive to cluster size and the level of approximations. If the diamond clusters is optimized without the capping atoms, many surface atoms form double bonds to reduce dangling bonds, hereby, producing onion-like clusters (OLC). We investigated the diamond \rightarrow OLC transformation kinetics by the MD simulation with the Brenner potential [8]. The simulation of a 1330-atom cluster at 1000 K at zero pressure shows the rate of bond conversion to OLC to be about 2.9% per ps. The fraction of sp^2 bonds increases with time as new inner sp^2 shells form. This is consistent with the inward conversion of diamond to OLC observed by Mal'Kov and Titiov [9].

Item (iv) describe modeling the diffusion processes during carbon cluster and effects of cluster sizes. A new high explosive (HE) burn model has been developed to capture the physics of diffusion limited carbon cluster kinetics. Comparison of results from hydrodynamic simulations indicates the new burn model helps improve agreement between theory and experiment [10].

HF

With regard to item (v), HE's with binder containing fluorine produces HF as a detonation product. Hence, the performance prediction of these HE's requires information on intermolecular potentials involving HF. However, because HF is highly corrosive, relevant experimental data (e.g., shock wave) are not available. Furthermore, HF is a strongly hydrogen bonding system, which, in spite of its simplicity, makes predicting its intermolecular potential difficult. We are carrying out first principles quantum MD simulations for HF at high P and high T to derive an effective HF-HF potential [11]. In meantime, we tested several semi-empirical HF-HF potentials derived from available information; i.e., bond strength, structures in the gas, liquid, crystal phases, and quantum mechanical calculations. So far, the best available potential was obtained by spherically averaging the ab initio data for an isolated pair potential, weighted with its Boltzmann factor.

With regard to item (vi), systems with C, H, N, O, F atoms produce mixtures of CO, CO₂, H₂O, N₂, etc. at high P and high T . We made thermochemical calculations with a reliable mixture model using the HF-HF potential derived above. The calculations without F atoms predict that these molecular species separate into N₂-rich and N₂-poor supercritical fluids. Addition of F atoms produces mostly HF in fluid phase α (poor in

N_2) up to a certain pressure, beyond which they form CF_4 in fluid phase β (rich in N_2). This shift, $HF(\alpha) \rightarrow CF_4(\beta)$, in fluorine chemistry can be abrupt or gradual in pressure and is sensitive to small variations in the unlike pair potentials involving HF. It can significantly affect detonation properties of some HEs. The change in fluorine chemistry can occur at pressure as low as 10 to 20 GPa at 1000 K, which is accessible by present-day experimental techniques.

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