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First Principles Molecular Dynamics Simulations of High-Pressure Melting of Diamond

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Abstract. Although the high-pressure phase diagram of carbon at extreme temperatures and pressures is in focus of theoretical and experimental dynamic compression studies, there still exist outstanding problems including disagreement between theoretical predictions and experiments. Using first-principles molecular dynamics simulations at high temperatures and pressures and employing large unit cells, we construct an accurate phase diagram of carbon using two-phase and Z-methods. In accord with previous simulations, a large positive slope of the melting line is observed for pressures from 0 to 200 GPa, whereas at pressures above 500 GPa a very small negative slope exists, which is in contrast to most of previous simulations and experiment. Our accurate results demonstrate the necessity for future dynamic compression experiments to clarify behavior of carbon at extreme conditions including its melting line.

INTRODUCTION

Phase diagram of carbon at extreme pressures and temperatures is urgently sought for the development of interior models of carbon-rich rocky exoplanets [1, 2, 3, 4] as well as for design of inertial confinement fusion (ICF) implosion capsules [5]. At ambient conditions, the most stable phase of carbon is graphite, while metastable diamond becomes thermodynamically stable above 2 GPa [6]. Although diamond has been predicted stable in a wide range of pressures, at 1 TPa it transforms to bc8, another high pressure phase of carbon [7], the reproducible experimental observation of the metallic bc8 phase is still to be achieved [8, 9, 10]. The only indirect observation of bc8 phase has been made Kundson *et al.* [8] in shock experiments involving transitions through the diamond-liquid-bc8 triple point, which demonstrates the importance of precise location of diamond/liquid phase boundary.

Previous theoretical calculations of diamond melting line are contradictory [11, 12, 13, 14] as they predict negative slopes varying by substantial amounts. The disagreement seems to be related to insufficient accuracy of some of the calculations due to employment of a small size of simulation cell. Therefore, more accurate first-principles calculations of carbon phase diagram including diamond melting line are warranted to support current and future dynamic compression experiments.

In this work, we aim to obtain the most accurate melting line of diamond up to 1000 GPa by performing first-principles density functional theory (DFT) simulations utilizing the largest simulation cells employed so far. The calculated chemical bonding and electronic properties of liquid phase of carbon allow us to analyze the source of disagreements with prior calculations. Our work provides reliable data to guide future dynamic compression experiments at National Ignition Facility (NIF) and Z-machine.

COMPUTATIONAL METHODS

First-principles calculations are performed using Vienna Ab initio Simulation Package (VASP) [15, 16] employing Perdew, Burke, Ernzerhof (PBE) generalized gradient approximation (GGA) functional, and projector augmented wave potentials (PAW). The plane wave basis set cutoff 400 eV and Γ -point only sampling of the k-space. The parameters were determined in test calculations of the diamond equation of state at 0 K at pressures 0 to 1 TPa. To simulate melting line of diamond, we use two complimentary methods: Z-method [17] and 2-phase method [18]. In Z-method, the threshold of thermal stability is determined by running a series of microcanonical NVE simulations with increasing amount of initial thermal energy supplied to the system. As the total energy is kept constant in each simulation, at some point the temperature of the system drops to melting temperature and the connected $P - T$ points of isochore form a characteristic shape of Z-shape [19]. The two-phase method involves a series of NPT simulations of a system consisting of liquid and solid halves, the melting temperature being determined by a condition that both

liquid and solid phases coexist at T_m [18]. Although Z-method is the most economical in terms of computational resources, its semi-empirical nature requires additional validation using two-phase method. In this work 216-atom simulation cells ($3 \times 3 \times 3$ supercell of diamond conventional cell) are used in Z-method calculations and 432 atom simulation cells (twice the size of Z-method cell) are used in two-phase method.

RESULTS AND DISCUSSION

The Z-method simulation of diamond melting curve involves a series of NVE MD simulations at several volumes corresponding to cold pressures 100, 200, 400, 600 and 800 GPa. Each series involves individual MD runs with elevated temperatures to locate the point when overheated solid transforms to liquid state. Upon melting, a drop of temperature with subsequent increase of the temperature of the liquid state displayed as a series of (P,T) points connected by line for a characteristic Z-shape. However, the results of Z simulations, see Fig. 1, show substantial error in predicting melting curve of diamond compared to that obtained from more accurate 2-phase method, discussed below. The problem seems to be attributed to simultaneous onset of solid-liquid and insulator-metal transitions resulting in anomalous densification of the liquid carbon compared to solid diamond phase, resulting in the inverted Z- line, e.g. near 800 GPa.

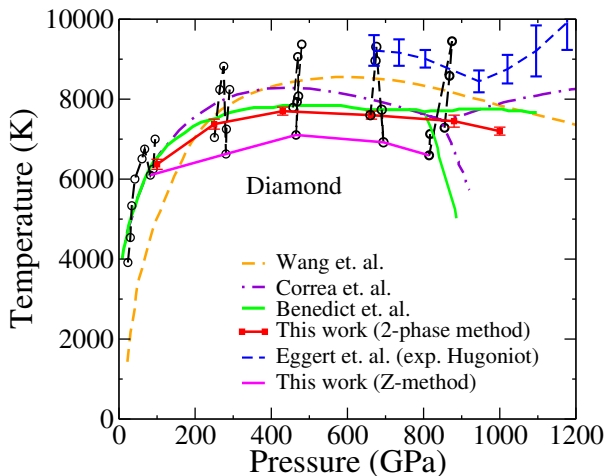


FIGURE 1. Melting line of carbon for pressures up to 1000 GPa calculated with both Z- and two-phase methods and compared with previous simulations and experiment.

To obtain a reliable melting curve of diamond, we proceed with two-phase method calculations. The simulation cells for two-phase method are constructed by utilizing 216-atom unit cells for solid and liquid phases which are then brought together to form a combined 432-atom cell. An additional step is undertaken to prepare a system with realistic solid-liquid interface by running canonical ensemble (NVT) simulations of the combined cell with the solid part is frozen. In the second step, a series of NPT simulations are performed at different temperatures. At a given temperature, the system evolves either to completely melted or solidified state depending whether the temperature is above or below of unknown T_m at a given pressure. Through a series of such simulations with varying temperature, but fixed pressure, T_m is determined as the one at which the both two phases survive and co-exist in equilibrium in the simulation cell. Due to computational limitations, the melting temperature is determined with uncertainty of 200 K.

The melting line of diamond calculated using two-phase method at pressures up to 1000 GPa is shown in Fig. 1. As mentioned above, the solid-liquid phase transition is accompanied by insulator-metal transition: diamond has a finite band gap at any temperature even in metastable superheated region above the melting temperature accessed in Z-method simulations. In contrast, the carbon liquid is metallic, i.e. has a finite density of states at the Fermi level.

We compare our results with previous calculations of melting line using 2-phase-method Correa *et. al.* [13], and using free-energy calculation by Wang *et. al.* [11] and Benedict *et. al.* [14]. Our melting line is significantly lower than that of Wang *et. al.* [11] and Correa *et. al.* [13], whereas it is in an overall agreement (but slightly lower) with the melting line obtained by Benedict *et. al.* [14]. In accord with all prior simulations, the melting temperature increases dramatically at pressures from 0 GPa to 200 GPa. However, the melting curves by Wang *et. al.* [11], and Correa

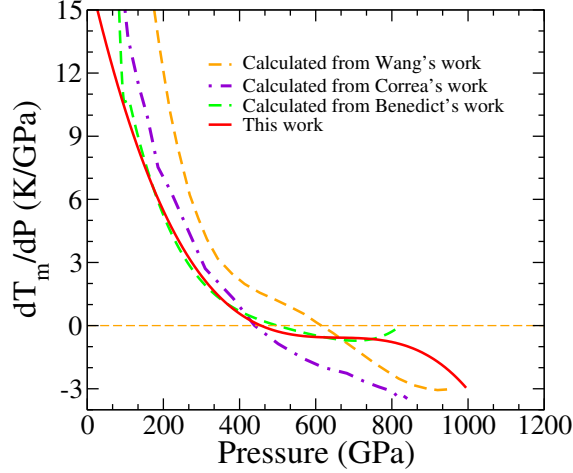


FIGURE 2. The slope of melting lines calculated from $T_m(P)$ presented in Fig. 1.

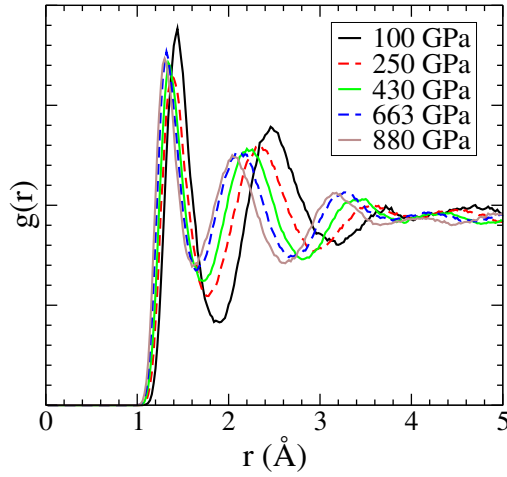


FIGURE 3. Radial distribution function of liquid phase at 8000 K and at different pressures.

et. al. [13] exhibit rather significant negative slope after the maxima of 8600 K at 600 GPa, and 8300 K at 450 GPa respectively, see Figs. 1 and 2. In addition, the experimental results by Eggert *et. al.* [9] display even higher melting temperatures, e.g. 9200 K at 660 GPa. In contrast, both our two-phase simulations and free-energy calculations of Benedict *et. al.* [14] are in very good agreement, while displaying a smaller negative melting curve slope as well as lower melting temperatures around its maximum. As our work and that of Benedict *et. al.* employ complimentary methods for calculation of melt temperatures, the agreement validates the accuracy of both calculations and raises an important issue of disagreement between theory and experiment, see Fig. 1, the resolution of which would require new more accurate experimental measurements of melting curve of diamond.

We investigate the properties of the liquid phase at 8000 K at range of pressures 100-900 GPa and calculate the radial distribution function (RDF) and distribution of coordination numbers of carbon atoms in the liquid phase, see Fig. 3 and Fig. 4. Interestingly, the average first nearest neighbor distance as identified by the position of the first maximum of RDF, changes substantially (from 1.45 Å to 1.35 Å) as pressure changes from 100 to 250 GPa, and then exhibits much smaller reduction with pressure to 1.30 Å at 850 GPa. The pressure-dependent distribution of coordination numbers, shown in Fig. 4, indicates that the liquid carbon at lower pressures around 100 GPa consists mostly of sp^2 (3-fold) and sp^3 (4-fold) carbon atoms, whereas at high pressures the liquid structure exhibits increased fraction of 5-fold and 6-fold C atoms. Our RDF and coordination number results at high pressures (around 900 GPa) are significantly different from those obtained by Correa *et. al.* [13], which reflects a substantial differences in our and their melting curves. We believe our results (which are consistent with those of Benedict *et. al.* [14] from an

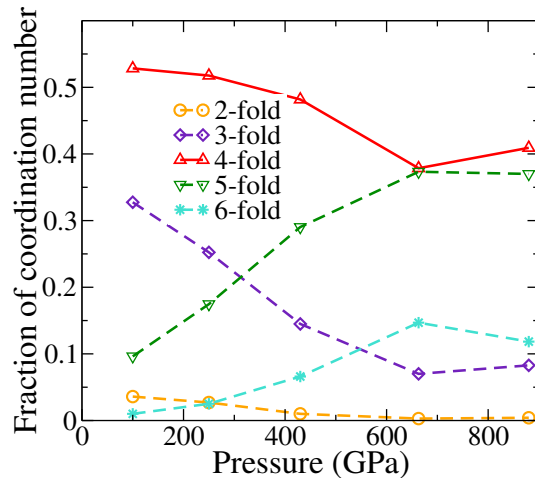


FIGURE 4. Coordination numbers of carbon atoms in liquid carbon at 8000 K as a function of pressure.

approximation model) are more accurate than that of Correa *et. al.* [13] as we use much larger simulation cells, which is critical to properly resolve the long-range correlations in both liquid and solid phases.

CONCLUSIONS

The melting line of diamond up to 1000 GPa was investigated using Z-method and two-phase-method based on first-principles DFT molecular dynamics simulations in order to resolve inconsistencies between previous simulations as well as experiment. Compared to previous works, our results from two-phase simulations are the most accurate obtained so far due to substantially larger simulation cells employed. The differences between our and Benedict *et. al.* [14] melting lines and that measured in shock experiments by Eggert *et. al.* [9] warrants new experiments aimed at improving temperature measurements during dynamic compression of carbon.

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