

# The High Pressure Multiphase Equation of State of Carbon

Guicun Ma, Gongmu Zhang, Hongzhou Song and Qiong Li

*Institute of Applied Physics and Computational Mathematics, Beijing 100094, China*

**Abstract:** The high pressure equation of state for carbon is constructed by some simple physical models. For solid state, a multiphase equation of state is considered, which includes four solid states. For liquid state, the liquid perturbation theory of CRIS model is used. In the high temperature, the electronic contribution is obtained by the ionization equilibrium theory. The result of our calculation based on the above models is compared with the first principle density functional calculation and the other models. The Hugoniot and the phase diagram of carbon are also compared with the experiments. The results are satisfactory.

**Key words:** Carbon, high pressure equation of state, phase diagram, hugoniot.

## 1. Introduction

In the study of inertial confinement fusion (ICF), the equations of state (EOS) of materials at high pressure and temperature are demanded for capsule design. The compression efficiency and shock structure in fusion capsules critically depend on the EOS [1]. When materials have been loaded from ambient condition to high temperature and pressure state, they will go on some phase changes, such as from solid to liquid, from liquid to plasma state. The equation of state used in hydrodynamic simulations must be able to resolve this issue.

At high pressure, carbon has several solid phases [2], such as graphite, diamond, BC8 (body centered cubic with 8 atom per cell), simple cubic (sc), simple hexagonal (sh). When temperature becomes high, these solid phases will melt. The melting curve of carbon like is an interesting subject of past studies [2-7]. Because of the complex solid phase structures, the melting properties of carbon are different from the other materials (e.g., Si and Ge). For diamond its melting line has a maximum, i.e. the slope of the melting curve changes sign at some pressure, which

has been confirmed by the experiment [8]. In the early studies of the equation of state models, the melting line of diamond had a positive slope, which had been shown in the figure of Kerley's article [9]. Fried and Howard [10] got the negative slope by supposing that there are two fluids phases, also see Thiel and Ree's article [11] for graphite's melting line. Whether there is a fluid to fluid phase transition is an unresolved problem. Based on first principles' calculations, Correa et al. [3] and Benedict et al. [2] obtained the equation of state and the melting line of carbon. They use Wallace's [12, 13] monatomic fluid EOS model for carbon liquid state. Their results have been supported by the experiments [8, 14].

In this article we will give multiphase equation of state of carbon by using Kerley's fluid EOS model [15]. For solid phase Debye model plus anharmonic correction has been used. But for diamond, BC8 and sc phase double Debye model [4] had been used. For electronic excitations the ionization equilibrium theory (IEQ) [16] is used, this model can represent electronic contribution to the EOS properly for low atomic number materials. After giving the EOS for each phase, the phase diagram and the Hugoniot of carbon are calculated. The results are consistent with the ab-initio calculations and the experiments. In

---

**Corresponding author:** Guicun Ma, Ph.D., professor, research fields: high pressure physics, equation of state of materials at high temperature and pressure.

Section 2 a brief description of the model is given and in Section 3 the results and the discussion are shown.

## 2. Model of Equation of State

### 2.1 Solid Phases

For solid phase Debye model is a good approximation to atomic vibrations, the energy and pressure at temperature  $T$  and density  $\rho$  is

$$E_{ion}(\rho, T) = Nk_B \left[ \frac{9}{8} \Theta_D + 3TD(\Theta_D/T) \right] \quad (1)$$

$$P_{ion}(\rho, T) = \gamma_G \rho Nk_B \left[ \frac{9}{8} \Theta_D + 3TD(\Theta_D/T) \right] \quad (2)$$

where  $N$  is total number of atom,  $k_B$  is the Boltzmann's constant,  $\Theta_D$  is the Debye temperature,  $D(x)$  is Debye function,  $\gamma_G$  is the Gruneisen parameter. For diamond, BC8 and simple cubic phase the phonon spectrum is very complicated and double Debye model [4] should be taken into account.

When temperature is high or near melting, anharmonic effect must be considered. The correction to the ion thermal energy coming from anharmonicity is of the form,

$$E_{anh} = \alpha T^2 / 2 \quad (3)$$

where  $\alpha$  is a constant independent of volume. The parameters used for each solid phase are taken from Ref. [2].

### 2.2 Liquid Phase

For liquid carbon we use Kerley's CRIS model [15] to calculate thermodynamic functions, such as energy and pressure. The internal energy of the liquid is

$$E_{ion}(\rho, T) = E_{cr}(\rho, T) + E_{el}(\rho, T) \quad (4)$$

where  $E_{el}$  is the contribution of the excited electrons (see next subsection for this part).  $E_{cr}$  is defined by the CRIS model,

$$E_{cr} = \frac{3}{2} Nk_B T + N \langle \phi \rangle_0 + \Delta E_1 + \Delta E_2 \quad (5)$$

correspondingly the pressure is

$$P_{cr} = Nk_B T \rho + N \rho^2 \left[ \frac{\partial \langle \phi \rangle_0}{\partial \rho} \right]_{\eta, T} + \Delta P_1 + \Delta P_2 \quad (6)$$

In Eqs. (5) and (6),  $N \langle \phi \rangle_0$  is the first order correction term.  $\eta = \frac{1}{6} \rho \pi \sigma_0^3$  is the packing fraction of hard sphere system.  $\Delta E_1, \Delta E_2, \Delta P_1, \Delta P_2$  are the higher order correction terms [15].

### 2.3 Thermal Electronic Contributions

We use ionization equilibrium theory [16] to calculate thermal electronic contributions. Supposing at temperature  $T$  in volume  $V$ , there are  $N$  particles which include neutral and charged ions with atomic number  $Z$  and atomic weight  $W$ . The electronic configurations of atom or ion are determined by prescribing occupation numbers for each electronic orbital. The energy of electronic state is obtained by quantum mechanical principles. The macroscopic variables, such as energy, entropy are determined by statistical average. In describing the state of electrons, two different states should be considered, one is the bound state and the other is the itinerant state. The free energy of the system is [16]

$$A_e = - \frac{RT}{W} \ln q_e \quad (7)$$

$$q_e = \sum_{z=0}^Z q_z \exp[-\beta(\delta_z + u_z + z a_f^0(z))] \quad (8)$$

$$q_z = \sum_n g_z(n) \exp[-\beta \varepsilon_z(n)] \quad (9)$$

where  $R$  is the gas constant.  $\beta = 1/k_B T$ ,  $q_e$  is the partition function of the system, and  $q_z$  is the partition function of the ion with charge  $z$ . In Eq. (8) the summation is over all  $Z+1$  states of ionization, the charges of ionization are  $z = 0, 1, 2, 3, \dots, Z$ .  $u_z$  is the ground state energy of ion with charge  $z$ ,  $a_f^0(z)$  is the free energy (per electron) for an electron gas in which there are  $z$  free electrons per ion.  $\delta_z$  is the charge fluctuation of ion  $z$ . In Eq. (9) the sum is over levels of the ion.  $\varepsilon_z(n)$ ,  $g_z(n)$  are the energy and degeneracy. In order to accurately describe the electronic state of ion, the following three corrections should be considered: (1) continuum lowering effect should be taken into account, which comes from the

existence of free electrons ; (2) charge fluctuations, i.e. the charge of each ion fluctuates a little about the ion average charge  $z$ , which requires  $\delta_z \neq 0$  in Eq. (8); (3) volume fluctuations, i.e. the volume of each ion is not equal to the volume of atomic sphere, but has a small fluctuations about this.

#### 2.4 Cold Energy and Pressure

Although carbon has many solid phases (including liquid phase), its zero temperature energy and pressure can be expressed by the Vinet equation of state [17],

$$P_c(V) = 3B_0(1-X)/X^2 \exp[1.5(B'_0-1)(X-1)] \quad (10)$$

$$E_c(V) = \Phi_0 + 4B_0V_0/(B'_0-1)^2[1-(1+\eta)\exp(-\eta)] \quad (11)$$

$$\eta = \frac{3}{2}(B'_0-1)(X-1), \quad X = (V/V_0)^{1/3}$$

Here,  $B_0$  is the bulk modulus at the volume  $V_0$  and  $B'_0$  is the pressure derivative of the bulk modulus at the volume  $V_0$ ,  $\Phi_0$  is the internal energy at  $V_0$ . For solid state we use the parameter's values of Ref. [2]. According to CRIS model one should assign a cold energy and pressure for it [9]. In this work we use the form of Eqs. (10) and (11) in

CRIS model for the calculations of the liquid state of carbon. But the parameters take the following values,

$$\Phi_0 = -60.448 \text{ KJ/g}, \quad \rho_0 = 2.496 \text{ g/cm}^3,$$

$$B_0 = 52.0 \text{ GPa}, \quad B'_0 = 5.97$$

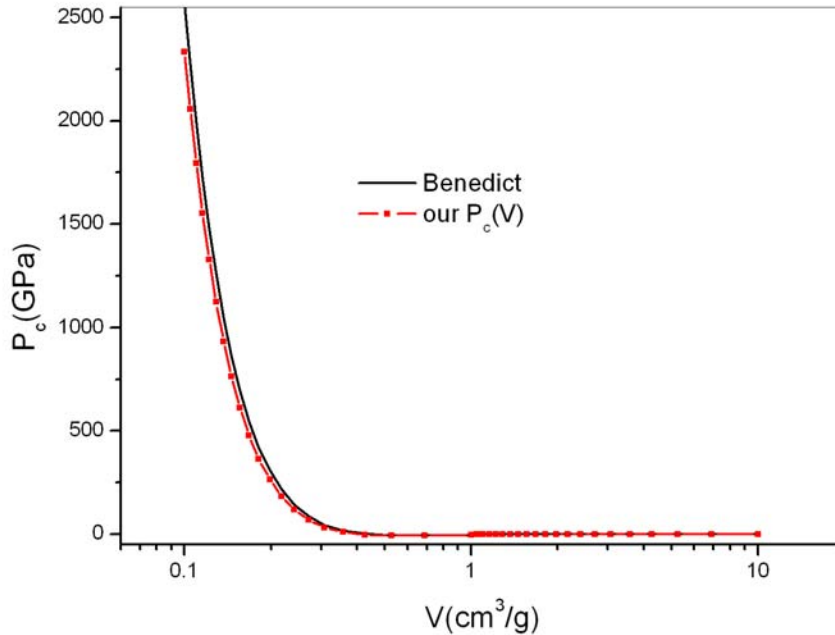
In Fig. 1 we show the cold curve for the pressure used in the liquid phase calculation. The dotted line is from Eq. (10), and the black line is from Ref. [2]. From the figure we can see that the two curves are very similar.

### 3. Results and Discussion

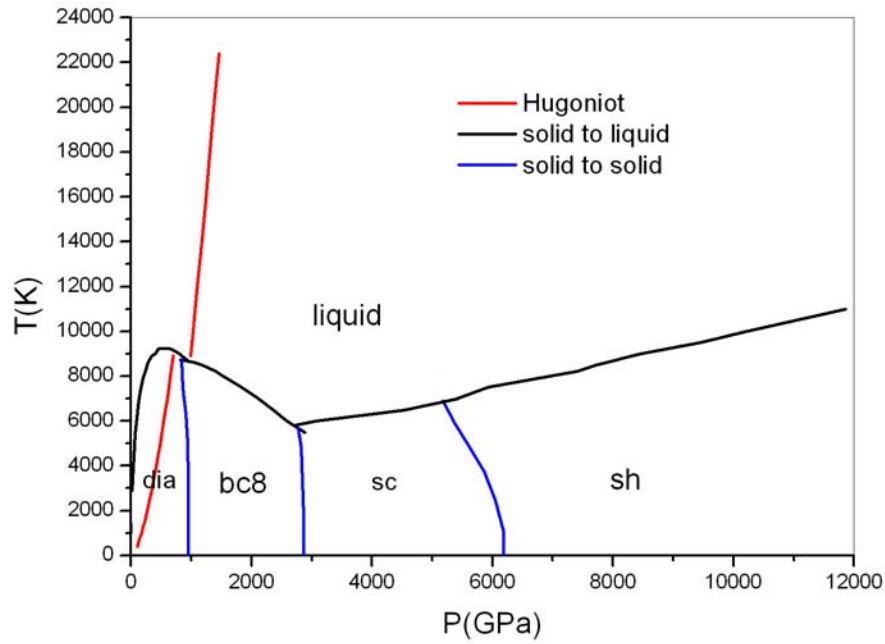
Based on the equation of state models described in Section 2, we have calculated the phase diagram of carbon, which is shown in Fig. 2. From the figure we can see that our phase diagram is very similar to that of Ref. [2], especially for diamond phase, the melting line has a maximum and negative slop, that is,

$$\left(\frac{dT}{dP}\right)_{\text{melting}} \text{ changes sign with pressure along the}$$

melting curve. This phenomenon manifests the volume (or density) changes upon melting, which had

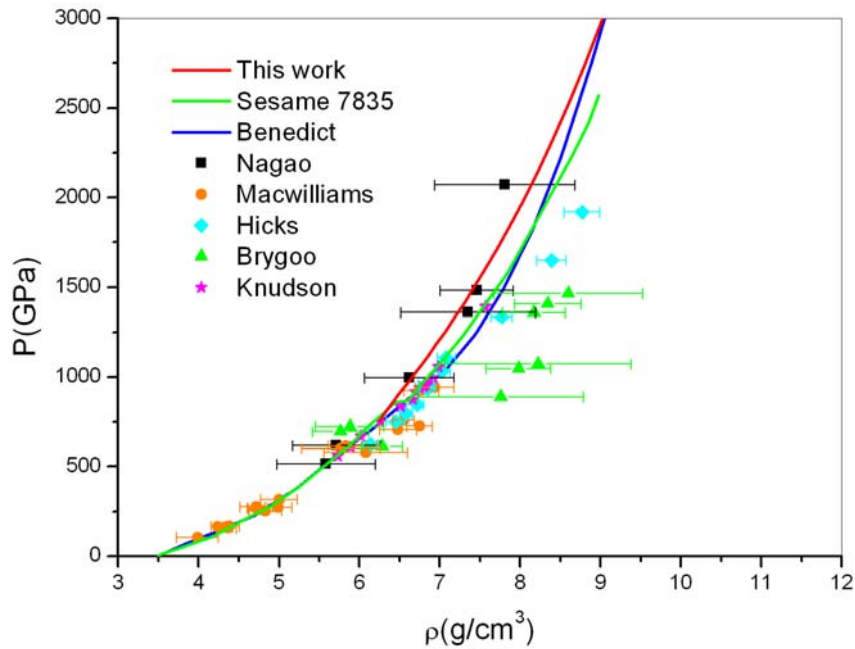


**Fig. 1 The cold pressure versus volume.**  
It has been used in liquid state calculation.



**Fig. 2 The phase diagram of carbon.**

Black lines are melting curves. Blue lines are the solid to solid phase transition lines. Red lines are Hugoniots of solid and liquid. dia, bc8, sc, sh are short notations of diamond, BC8, simple cubic and simple hexagonal respectively.



**Fig. 3 The Hugoniot of carbon.**

Our result is the red line. The blue and green line are the sesame 7835 [21] and Benedict's result [2] respectively. Dot points with error bar are experimental results of references [8, 14, 18-20].

been supported by the experiment [8] and the first principles calculations [3-4, 6-7]. Meanwhile in Fig. 2 we also give the melting lines of other solid phases, such as BC8, sc, sh phase. The results are also consistent with the ab-initio [3] and the model of reference [2]. In Fig. 3 we give the Hugoniot of carbon which is calculated from the above EOS. Here the solid line is the result of our calculation, the dot points with error bar are come from experiments [8, 14, 18-20], which were obtained by Laser shock and Z-pinch driven experiments. In Fig. 3 we also show the Hugoniot of Sesame 7835 [21] and the result of Benedict [2], who use Wallace's liquid EOS model in their calculations. From Fig. 3 we can see that the theory and the experiments nearly coincide. But at high pressure (about 1.5 TPa) the deviations between theory and experiments are very large. This means that the EOS model used in this work needs to be improved further. We expect that this will be solved in the near future.

#### 4. Conclusions

By using Debye model for solid phase, CRIS model for liquid phase, IEQ model for electronic ionization, we got the equation of state of carbon at wide range of temperatures and pressures. The phase diagram of carbon calculated by us is consistent with that of other EOS models, especially for the melting line of diamond phase which changes slope's sign with pressure. Although there is some difference, the theoretical Hugoniot of the liquid phase still approaches the results of the experiments. Our work indicates that if the parameters in the CRIS model are finely tuned, they can give the reasonable results for the carbon liquid state.

#### References

- [1] Lindl, J. D., Amendt, P., Berger, R. L., Glendinning, S. G., Glenzer, S. H., Haan, S. W., et al. 2004. "The Physics Basis for Ignition Using Indirect Drive Targets on National Ignition Facility." *Phys. Plasmas* 11 (February): 339-491.
- [2] Benedict, L. X., Driver, K. P., Hamel, S., Militzer, B. I., Qi, T., Correa, A. A., et al. 2014. "Multiphase Equation of State for Carbon Addressing High Pressure and Temperature." *Phys. Rev. B* 89 (June): 224109-1-19.
- [3] Correa, A. A., Bonev, S. A., and Galli, G. 2006. "Carbon under Extreme Conditions: Phase Boundaries and Electronic Properties from First Principles Theory." *Proc. Natl. Acad. Sci. USA* 103 (January): 1204-8.
- [4] Correa, A. A., Benedict, L. X., Schwegler, E., Bonev, S. A. 2008. "First-Principles Multiphase Equation of State of Carbon under Extreme Conditions." *Phys. Rev. B* 78 (July): 024101-1-13.
- [5] Bundy, F. P., Bassett, W. A., Weathers, M. S., Hemley, R. J., Mao, H. U., and Goncharov, A. F. 1996. "The Pressure Temperature Phase and Transformation Diagram for Carbon: Updated through 1994." *Carbon* 35 (September): 141-53.
- [6] Grumbach, M. P., and Martin, R. M. 1996. "Phase Diagram of Carbon at Pressures and temperatures." *Phys. Rev. B* 54 (February): 15730-41.
- [7] Wang, X., Scandolo, S., and Car, R. 2005. "Carbon Phase Diagram from Ab Initio Molecular Dynamics." *Phys. Rev. Lett.* 95 (October): 185701-1-4.
- [8] Bryoo, S., Henry, E., Loubeyre, P., Eggert, J. H., Koenig, M., Loupais, B., Benuzzi-Mounaix, A., Rabec Le Gloahec, M. 2007. "Laser Shock Compression of Diamond and Evidence of a Negative Slope-Melting Curve." *Nat. Mater.* 6 (March): 274-7.
- [9] Kerley, G. I., and Chhabildas, L. 2001. *Multicomponent Multiphase Equation of State for Carbon*. Sandia National Laboratories Report, No. SAND2001-2619.
- [10] Fried, L. E., and Howard, W. M. 2000. "Explicit Gibbs Free Energy Equation of State Applied to the Carbon Phase Diagram." *Phys. Rev. B* 61 (August): 8734-43.
- [11] Thiel, M., and Ree, F. H. 1993. "High Pressure Liquid-Liquid Phase Change in Carbon." *Phys. Rev. B* 45 (December): 3591-9.
- [12] Chisolm, E. D., and Wallace, D. C. 2001. "Dynamics of Monatomic Liquids." *J. Phys. Condens. Matter* 13 (August): R739-769.
- [13] Chisolm, E. D., Crockett, S. D., and Wallace, D. C. 2003. "Test of a Theoretical Equation of State for Elemental Solids and Liquids." *Phys. Rev. B* 68 (September): 104103-1-12.
- [14] Kundson, M. D., Desjarlais, M. P., Dolan, D. H. 2008. "Shock Wave Exploration of the High Pressure Phases of Carbon." *Science* 322 (December): 1822-5.
- [15] Kerley, G. I. 1980. "Perturbation Theory and Thermodynamic Properties of Fluids. II: The CRIS Model." *J. Chem. Phys.* 73 (July): 478-86.
- [16] Kerley, G. I. 1986. "Theory of Ionization Equilibrium: An Approximation for the Single Element Case." *J.*

- Chem. Phys.* 85 (November): 5228-31.
- [17] Vinet, P., Rose, J. H., Ferrante, J., and Smith, J. R. 1989. "Universal Features of the Equation of State for Solids." *J. Phys. Condens. Matter* 1 (September): 1941-63.
- [18] Hicks, D. G., Boehly, T. R., Celliers, P.M., Bradley, P.M., Eggert, J. H., McWilliams, R. S., et al. 2008. "High Precision Measurements of the Diamond Hugoniot in and above the Melt Region." *Phys. Rev. B* 78 (November): 174102-1-8.
- [19] McWilliams, R. S., Eggert, J. H., Hicks, D. G., Bradley, D. K., Celliers, P. M., Spaulding, D. K., et al. 2010. "Strength Effects in Diamond under Shock Compression from 0.1 to 1 TPa." *Phys. Rev. B* 81 (January): 014111-1-19.
- [20] Nagao, H., Nakamura, K. G., Kondo, K., Ozaki, N., Takamatsu, K., Ono, T., et al. 2006. "Hugoniot Measurement of Diamond under Laser Shock Compression Up to 2 TPa." *Phys. Plasmas* 13 (May): 052705-1-5.
- [21] Coe, J. D., and Gemmel, J. T. 2016. *A New 5-Phase Equation of State for Carbon*. Los Alamos National Laboratory Report, LA-UR-16-26877.