20:30-21:30
https://meet.google.com/ahy-qupv-wyn

Atomistic structure of low-density liquid carbon

Stanislav Dereka[1,2] Nikita Orekhov[1,2]

[1] Joint Institute for High Temperatures (JIHT RAS)

[2] Moscow Institute of Physics and Technology

Introduction

Experimental data on the melting line of graphite and thermodynamic properties of liquid carbon still remain controversial despite the long history of investigation [1]. The results of several dozen experimental works cover the wide span from 3800 to 5000 K for the graphite melting temperature that is an essentially larger uncertainty than the errors of individual experiments. Liquid carbon remains the source of several unsolved questions related to its structure [5], pressure-temperature regions of stability and possibility of the existence of liquid-liquid phase transitions [6]. Recent experimental results [2] demonstrate one more intriguing property of liquid carbon -- its anomalously high heat capacity.

Extending our previous results on the melting kinetics and parameters of graphite melting line [3], we study properties of liquid carbon on the basis of molecular dynamics with machine learning based Gaussian Approximation Potential (GAP) for carbon [4] and Density Functional Theory. We calculate structural properties, atom hybridization and heat capacity of liquid carbon at T=5000-6000K and P=1-3 GPa.

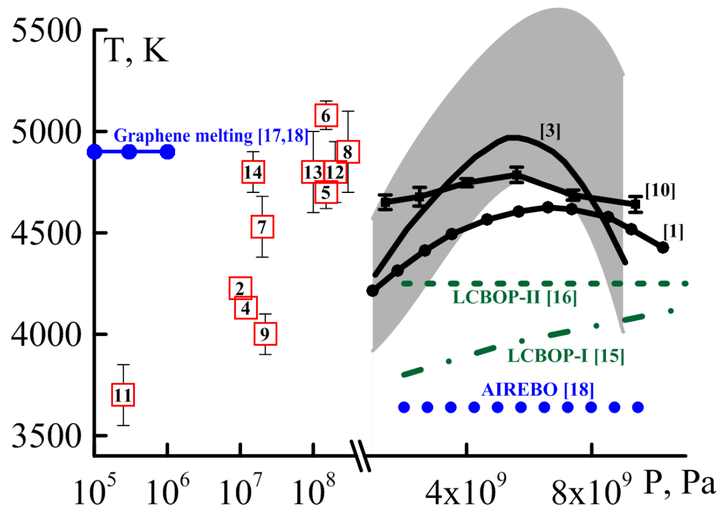

Figure 1. Experimental results on the graphite melting temperature [1-14] (numbers match the corresponding citations in the reference list below). Data from [3] is shown as an average line as well as the upper and lower envelope curves that show the scatter of the individual measurement results. Green lines represent results of atomistic calculation for LCBOP [15] and LCBOP-II [16] models, blue lines – for AIREBO [18].

[1] *F. P. Bundy,* **J. Chem. Phys.** 38, 618 **(1963)**.
[2] *G. J. Schoessow,* **Phys. Rev. Lett.** 21, 738 **(1968)**.
[3] *N. S. Fateeva and L. F. Vereshchagin,* **JETP Lett.** 13, 110 **(1971)**.
[4] *N. A. Gokcen, E. T. Chang, T. M. Poston, and D. J. Spencer,* **High. Temp. Sci.** 8, 81 **(1976)**.
[5] *M. A. Sheindlin and V. N. Senchenko,* **Sov. Phys. Dokl.** 298, 1383 **(1988)**.
[6] *A. V. Baitin, A. A. Lebedev, S. V. Romanenko, V. N. Senchenko, and M. A. Sheindlin,* **High Temp. High Pres.** 22, 157 **(1990)**.
[7] *A. Cezairliyan and A. P. Miiller,* **Int. J. Thermophys.** 11, 643 **(1990)**.
[8] *G. Pottlacher, R. S. Hixson, S. Melnitzky, E. Kaschnitz, M. A. Winkler, and H. Jager,* **Thermochim. Acta** 218, 183 **(1993)**.
[9] *E. I. Asinovskij, A. V. Kirillin, and A. V. Kostanovskij,* **High. Temp.** 35, 716 **(1997)**.
[10] *M. Togaya*, **Phys. Rev. Lett.** 79, 2474 **(1997)**.
[11] *E. I. Asinovskii, A. V. Kirillin, A. V. Kostanovskii, and V. E. Fortov*, **High. Temp.** 36, 716 **(1998)**.
[12] *M. Musella, C. Ronchi, M. V. Brykin, and M. A. Sheindlin*, **J. Appl. Phys.** 84, 2530 **(1998)**.
[13] *A. I. Savvatimskii*, **Physics-Uspekhi** 46, 1295 **(2003)**.
[14] *A. Y. Basharin, M. V. Brykin, M. Y. Marin, I. S. Pakhomov, and S. F. Sitnikov*, **High. Temp**. 42, 60 **(2004)**.
[15] *L. M. Ghiringhelli, J. H. Los, E. J. Meijer, A. Fasolino, and D. Frenkel,* **Phys. Rev. Lett.** 94, 145701 **(2005)**.
[16] *F. Colonna, J. H. Los, A. Fasolino, and E. J. Meijer,* **Phys. Rev. B** 80, 1 **(2009)**.
[17] K. V Zakharchenko, A. Fasolino, J. H. Los, M. I. Katsnelson, ***J. Phys.: Cond. Matter***, 2011, **23**, 202202
[18] N.D. Orekhov, V.V. Stegailov, **Carbon,** 2015, **87,** pp. 358-364.

Structure and hybridization of liquid carbon

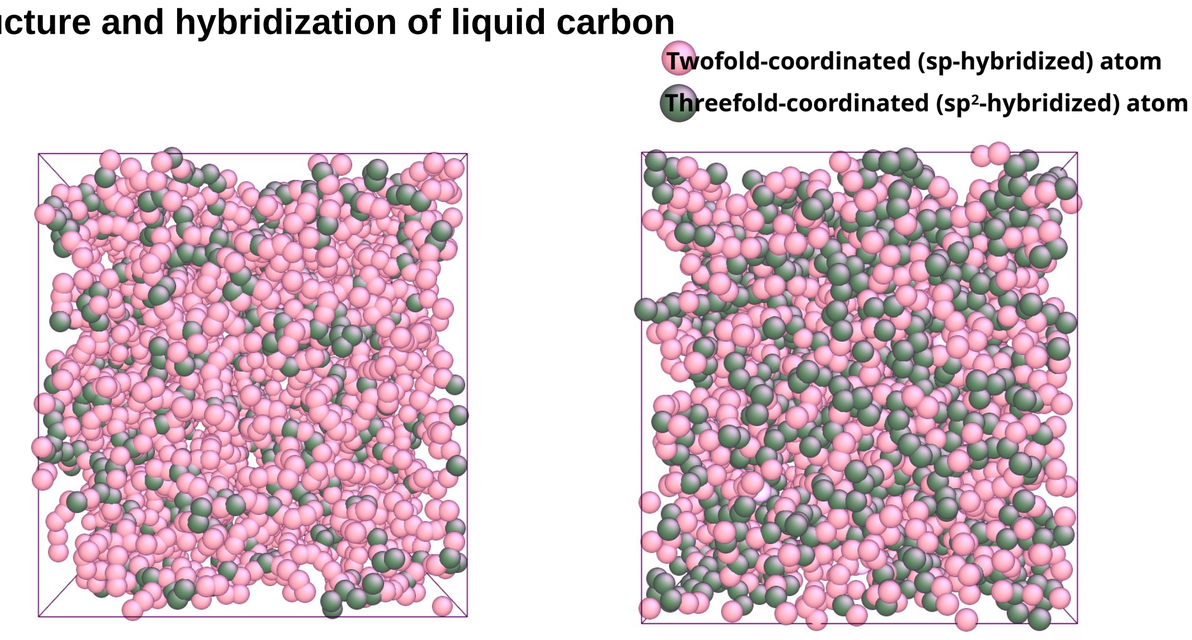

Figure 2. Atomic structure of liquid carbon at T=6000K and P=1GPa (left), P=3GPa (right). MD results with GAP potential for computational cell containing 4096 atoms.

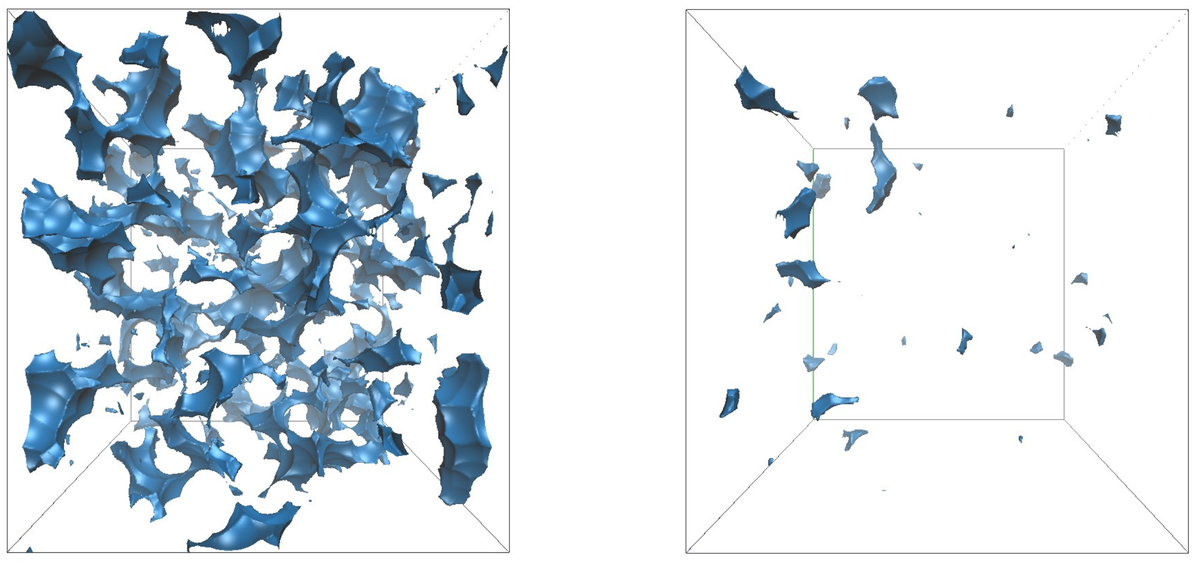

Figure 3. Corresponding distributions of voids simulation cell for liquid carbon at T=6000 K and pressures:
1 GPa (left), 3 GPa (right)

Despite the long history of research, there are still lots of speculations on the parameters of vapour-liquid-solid triple point for carbon, especially the aspect regarding its pressure: its estimations vary in a surprisingly wide range to from 0.1 to 100 MPa [1].

Figure 2 shows an atomistic structure of liquid carbon obtained with GAP potential at T=6000 K for two examined pressures: 1 and 3 GPa. Pink spheres represent sp-hybridized and green ones — sp2-hybridized. Here we defined the number of atoms with particular hybridization by counting coordination numbers for all atoms. The coordination number is calculated on the basis of the consideration that the two atoms form a covalent bond if the distance between them is less than or equal to 1.73 Å.

Analysis of structural properties and atom hybridization reveals that liquid carbon tends to form a net of long one-dimensional sp-hybridized carbon chains.

Comparison with DFT

DFT calculations were performed using VASP package in the pseudopotential approximation and the plane-wave basis. We used a supercell containing 96 atoms and the PAW potential with four outer-shell electrons for carbon and the GGA PBE exchange- correlation functional.

To verify the GAP-20 potential within our system we performed DFT calculations of liquid carbon with a much smaller unit cell containing 128 atoms and compare density and atom hybridization in an examined pressure range. Additionally we compare these dependencies with the results of AIREBO potential [14]—one of the most sophisticated and popular reactive empirical many-body potentials for carbon. One can see that contrary to AIREBO, GAP-20 demonstrates a perfect agreement with DFT data at considered pressures (figure 4).

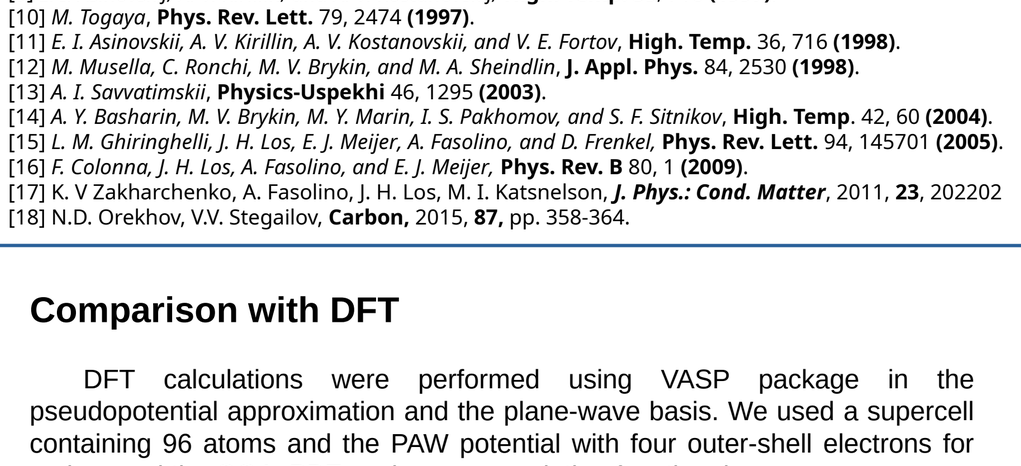

Figure 4. Figure 2. Density (a) and hybridization (b) of liquid carbon at T=6000K

Structural properties study

GAP-20 is probably the first MD potential allowing to perform calculation of liquid carbon in a relatively large unit cells containing several thousand atoms with a DFT level of precision. For all considered unit cells we choose all sp-hybridized atoms and apply clasterization algorithm to extract sp-chains and compute their lengths. Figure 5 demonstrates the probability distribution for the length of sp-hybridized one-dimensional chain at considered pressures and T = 6000 K. These curves represent the probability (vertical axis) of randomly chosen sp-hybridized atom to be in a chain of given length (horizontal axis). The average length of sp-chains rises with a decrease in pressure (and density).

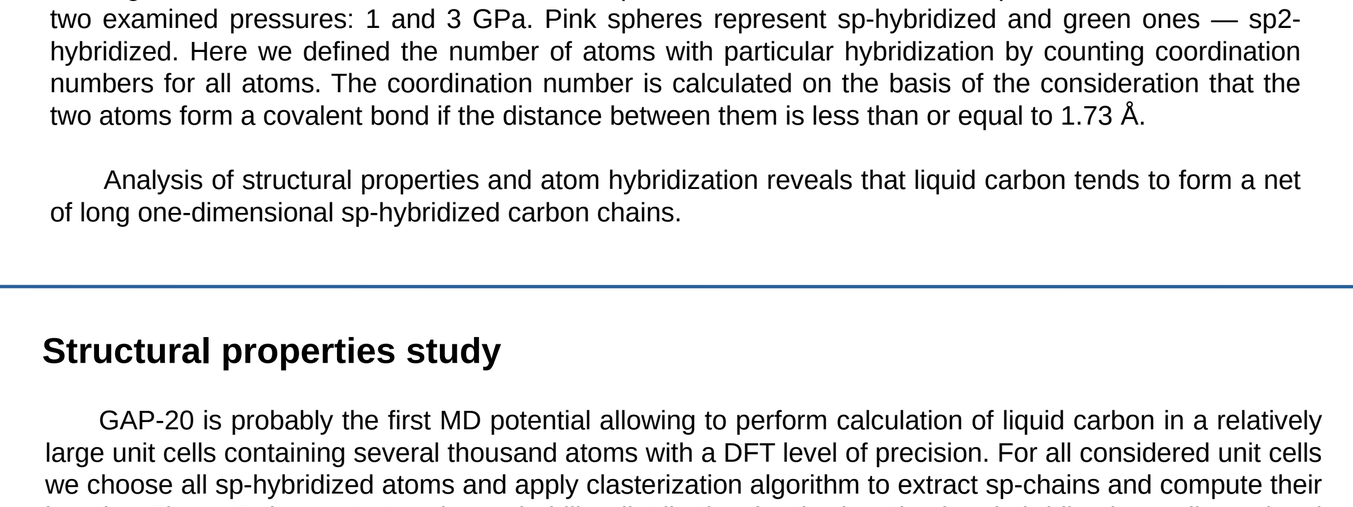

Figure 5. Sp-hybridized chain (b) length probability distribution (a) at T = 6000 K

Conclusions

Using classical molecular dynamics with a modern machine learning based Gaussian Approximation Potential (GAP) for carbon we calculated structural properties of liquid carbon at T = 5500–6000 K and P = 1–3 GPa. Structure of liquid carbon at P = 1–3 GPa demonstrates a distinct tendency to form a long one-dimensional carbon chains. While high fraction of sp-hybridized atoms in liquid carbon has been repeatedly discussed in literature, the form in which these atoms exist was not analyzed previously.

[1] Savvatimskiy, A.I. // *Carbon* 2005, *43*, 1115.
[2] Kondratyev, A.M.; Rakhel, A.D. // *Phys. Rev. Lett* 2019, *122*,175702.
[3] Orekhov, N.D.; Stegailov, V.V. // *Carbon* 2015, *87*, 358.
[4] Deringer, V.L.; Csányi, G. // *Phys. Rev. B* 2017, *95*, 094203.
[5] G. Galli, M. Martin, R. Car and M. Parrinello // PRL 1989, 63, 988
[6] C.J. Wu, J.N. Glosli, G. Galli, and F. H. Ree // PRL 2002, 89, 135701