

High Temperature Thermodynamic Modelling of Graphite

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Abstract

We present the high-temperature thermodynamic properties of graphite from anharmonic first-principles theory. The ab initio electronic structure results from density functional theory combined with lattice dynamics methods used to model anharmonic lattice vibrations. This combined approach produces graphite free energies and specific heats that compare well with results from available experiments and models empirically representing experimental data such as: B.CALPHAD. We show that the anharmonic theory of phonons is essential for accurate thermodynamic quantities above about 1000K.

Keywords: Thermodynamic; (SCAILD);(DFT)

Introduction

Carbon atoms can form three types of materials: graphite, diamond and fullerene. Chemically, the carbon bonds of these grades are different, including sp² (graphite) and sp³ (diamond) orbital bonding, while fullerenes are mostly sp², with a small mixture of sp³. As a result, carbon polymorphs exhibit contrasting material properties that lend themselves to applications in a variety of fields, from foundry and molding to electronics and biotechnology. Graphite, the main focus of this work, consists of layers of carbon sheets (graphene sheets), which are only weakly bonded, giving rise to a large anisotropy in the material. Therefore, thermal and electronic conductivity, strength, and chemical reactivity are highly orientation-dependent properties of materials. Important anisotropic properties are rather unusual for elemental solids and, in the case of graphite, are available in electronic components, lubricants, pins, and mold materials [1]. Thermodynamically, graphite has a high melting point, moderate thermal expansion, and high specific heat, making it relevant for composites and structural materials, and as a heat shield for certain applications, including nuclear reactors. Of course, from an academic point of view, carbon is a very important element and one of the most abundant elements with the basic properties of life and biochemistry. Planetary science involves high-pressure morphologies such as diamonds. However, it targets the graphite phase, which may be present at high temperatures but only at moderate pressures. I am particularly interested in high temperature thermodynamics, but this research is limited to atmospheric pressure. Our research is based on first-principles theory methods combined with anharmonic lattice mechanics approaches. This method provides an abinitio model that describes the strong anharmonic phonon-phonon interactions that are often important at high temperatures. Density functional theory (DFT) has certainly been applied to the electronic structure of carbon and graphite in the past. But no studies have been found that point to high-temperature thermodynamics in a way that involves significant lattice anharmonicity. A lot has been written about the carbon system and it is not possible to give a complete overview here. Instead, we recommend a comprehensive review of carbon and graphene as a good starting point [2].

Method

It addresses high temperature unharmonic phonons in graphite by combining the DFT electron principle structure with a self-consistent lattice kinetics that can capture unharmonic phonon-phonon interactions. Our results are compared with approximate quasi-harmonic theories and thermodynamic models constrained by experimental data in a thermodynamically consistent manner.

As expected, graphite raises temperatures by thousands of degrees, indicating that anharmonicity cannot be ignored [3].

When trying to model graphite at high temperatures, the potential importance of anharmonic atomic vibrations must be considered. Although very convenient, quasi-harmonic (QH) modelling tends to break at temperatures above about 1000K, depending on the material in question. Our goal here is to use the parameter-free ab initio theory to calculate the free energy and heat capacity of Gibbs up to 4000 K and investigate the need to include in harmonic contributions to lattice mechanics. The traditional way to study the temperature effects of materials from the beginning is to perform quantum molecular dynamics (QMD) simulations. As a rule, QMD answers all thermodynamic questions, but computer simulations are usually so expensive that it is difficult to deal with larger parts of the material's topological space. Alternatively, we chose an efficient grid dynamics (SCAILD) method this has recently been applied to several actinide carbides and nitrides with very promising results. Initially, this approach focused on treating cold and dynamically unstable phonons, but has recently been applied to free energy calculations. SCAILD is efficient because it confines the phonons along the normal mode direction of the corresponding vibration and its amplitude is a mean-square shift governed by temperature. On the other hand, QMD calculations are much more computationally intensive as they are unconstrained [4, 5].

Weak bonds between graphene layers increase the c/a axial ratio of graphite, but are less accurately handled by conventional DFT approaches. This is because van der Waals interactions are known to play a role in these bonds and are not included in the DFT. In principle, these interactions can be computed with considerable computational effort and complexity. Fortunately, a reasonable and highly efficient workaround is available that alleviates the need to include the van der Waals contribution in the graphite DFT. The method consists of applying the local density approximation (LDA) of the DFT electron

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exchange and correlation functions in combination with freezing the c/a axial ratio of the graphite structure to the experimental value. This strategy is also consistent with the SCAILD methodology as the SCAILD super cell boxes are assumed to be rigid and have a frozen c/a axial ratio [6, 7].

Discussion and Conclusion

By combining the calculated electron mechanics and lattice mechanics contributions, we were able to construct the Gibbs free energy (or the Helmholtz free energy at zero pressure). This free energy is a basic quantity of thermodynamics, but it is usually not measured directly. Therefore, instead of explicitly verifying the *ab initio* free energy in the experiment, we compared the results with other theories and models developed for graphite. Our first-principles free energy, along with the quasi-harmonic theory (QH), CALPHAD and the EOS model. The quasi-harmonic free energy was calculated from the GIBBS2 package using the energy determined by the FPLMTO calculation of graphite. The same approximation was performed to keep the axial c/a ratio constant at the experimental value for all FPLMTO calculations and QH modelling. QH modelling of graphite has been studied, but no free energy data were found in the literature. Surprisingly, the CALPHAD and EOS models are in excellent agreement. This is expected given that both are thermodynamically consistent representations of the experimental data. Furthermore, the figure shows good agreement between the anharmonic theory of the underlying principle and the two empirical models. We therefore conclude that the anharmonic approximation is sufficient even at very high graphite temperatures. QH processing, on the other hand, is meaningful up to about 1000 K, but becomes increasingly inaccurate after that. This is certainly not unexpected. Similar behaviour was observed in thermodynamic studies

of actinide monocarbohydrides and mononitrides. We then focused on the specific heat at constant pressure. Similar to the free energy, we obtained C_p as the sum of the electronic and lattice contributions. In contrast to the actinide system, where the density of actinide 5f states is very high at the excitation energy, the electronic contribution of graphite is actually very small because there are very few energy states available for electronic excitation. See discussion of electronic density of states in graphite. Although small, the C_{pe} is still included in the total specific heat, but the contribution is not clearly visible.

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