Isotopic Effects in Chair Graphane

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Abstract

Graphane is a layered substance made up of hydrogenated graphene sheets with a C:H ratio of 1:1. We investigate isotopic effects in chair graphane characteristics, in which H atoms alternate in a chair like arrangement on both sides of the carbon layer. We employ path-integral molecular dynamics simulations to investigate the impact of nuclear quantum effects on material equilibrium variables. Using an effective tight-bonding potential, the finite-temperature characteristics of graphane are investigated in the range 50 K-1500 K as functions of the isotopic mass of the constituent atoms. Substituting 13C for 12C at low temperatures results in a fractional change of 2.6104 in C-C distance and 3.9104 in graphane layer area. When 2H is substituted for 1H, the C-H bond undergoes a higher fractional change of 5.7 103. By applying tensile (compressive) in-plane stress, the isotopic impact in C-C bond distance increases (decreases). These findings are explained using a quasi harmonic approximation for the vibrational modes. The similarities and contrasts with graphene's isotopic effects are examined.

Keywords: Graphane; Isotopic effects; Tight-Binding (TB); Molecular dynamics; Quantum effects

Introduction

Graphane is a quasi-two-dimensional structure made up of carbon atoms that are covalently bound to hydrogen atoms in a buckled honeycomb lattice. There are various graphane conformers, the most researched of which being the so-called chair graphane. Hydrogen atoms alternate in a chair like pattern on both sides of the carbon layer in this structure, with a stoichiometric C:H ratio equal to. We present a ball and stick model of chair graphane, with C and H atoms represented by large yellow and small blue balls, respectively. Several types of hydrogenated graphane, particularly chair graphane, have been thoroughly investigated in recent years. It is known that graphane can be produced by reversible hydrogen chemisorption on graphane. This action causes a reorganisation of the graphane structure's interatomic bonds and angles. Because each H atom is coupled to a C atom, the latter's sp^2 orbital hybridization switches to sp^3, and the planar structure of graphane morphs into an out-of-plane buckled shape. Graphane is a broad band-gap semiconductor with significant spin polarization that can be created by generating domains of H vacancies or CH divacancies.

Isotopic effects in crystalline solid equilibrium properties are caused by a combination of the quantum nature of atomic nuclei and the anharmonicity of interatomic potentials. In this research, we use PIMD simulations to investigate isotopic effects in chair graphane over a temperature range of 50 K to 1500 K, employing an efficient Tight-Binding (TB) Hamiltonian that has been shown to accurately characterise numerous structural and thermodynamic features of carbon based materials. We consider the carbon isotopes 12C and 13C, as well as the hydrogen isotopes 1H and 2H. We quantify the effect of isotopic mass on structural

features including C-C and C-H interatomic distances, as well as the size of the graphane layer, which has a temperature dependency that differs significantly from the conventional approximation. The atomic mean square displacements are used to analyse quantum motion. The following is how the paper is structured. Sec. II describes the computational techniques used here, namely the PIMD method and the tight binding procedure. In Section III, we offer results for graphene's internal energy, with a focus on kinetic energy. Sec. IV discusses isotopic effects on interatomic lengths for C-C and C-H bonds. Section V examines atomic mean square displacements and quantum delocalization. Sec. VI discusses isotopic effects in the in-plane area of the graphane sheet, while Sec. VII discusses the influence of an external stress.

Description

The study concludes with a summary in section VIII. In this research, we investigate the relationship between the equilibrium characteristics of chair graphane and isotopic mass. This dependence does not exist in traditional computations, regardless of atomic vibration anharmonicity. Momenta and locations do not commute in quantum statistical physics; hence the atomic mass M influences the mean values of position-dependent variables. Thus, isotopic effects in equilibrium properties are caused by atomic nuclei's quantum dynamics. We use the PIMD approach to investigate the equilibrium properties of chair graphane at various temperatures. Carbon isotopes 12C and 13C, as well as hydrogen isotopes 1H and 2H, are considered. The PIMD technique is based on the fact that the partition function of a quantum system can be written in a manner similar to that of a classical system, which is realized by substituting each quantum particle of mass M by a ring polymer made up of NTr classical particles (beads) connected by springs with constant khar=MNTr/22 (NTr is the so-called Trotter number and=1/(kBT)). In the limit NTr, an isomorphism between quantum and classical systems becomes formally exact. Details about this simulation technique and its applications to condensed-matter systems can be found. A reliable description of the interatomic interactions is a key question in the PIMD technique. The use of self-consistent potentials based on the Hartree-Fock method or density functional theory necessitates a large computational power, resulting in a small accessible size of the simulation cells and/or the number of PIMD steps, and thus large size effects and statistical noise.

Conclusion

The PIMD methodology is a versatile tool for investigating isotopic effects in molecular and solid systems. This strategy, in particular for crystalline materials, allows one to include structural and phonon related features in addition to typical approaches based on a harmonic approximation for the lattice vibrational modes. The atomic mass is an input parameter in the simulations, allowing one to investigate the effect of the constituent atoms' isotopic mass on the physical properties of the material, in this case a 2D crystalline solid known as chair graphane.

The temperature dependence of interatomic distances can be explained in the same way as the QHA by an effective vibration with frequency effect in the bond direction. The dependency on T of C-C and C-H bond distances, as represented by equations. (1) and (5), agrees with the results of PIMD simulations. This method provides us with a consistent picture of isotopic influences in graphane bond lengths.