



Research paper

Thermodynamic properties of solid molecular hydrogen by path integral Monte Carlo simulations

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ABSTRACT

The solid molecular hydrogen under hydrostatic pressure varying from 0 up to 2.2 GPa at low temperatures is studied by path-integral Monte Carlo simulations in the isothermal-isobaric ensemble. The quantum contribution to the vibrational energy lies between 40% and 90% of their total values. The zero-point energy increases with increasing pressure and the anharmonicity is more pronounced at low temperature and pressure. A satisfactory agreement between our simulation results and available experimental measurements has been achieved. At very low temperatures, the quantum effects are responsible for softening the molecular crystal in about 1 GPa in the studied range of pressure.

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1. Introduction

Over the last few decades, there has been a continuous growth of the experimental and theoretical studies of condensed state hydrogen [1–4]. Perhaps, the main motivation is that over the years this system has been challenging the theorists and experimentalists in many ways. Solid molecular hydrogen is the simplest molecular quantum crystal in the nature. It has a high compressibility, a sizable zero-point energy, and a larger isotopic mass difference [5]. From the theoretical point of view, its simplicity is attractive but its intrinsic features make the calculations very cumbersome. The transition of the solid hydrogen from the molecular to the atomic metallic phase by means of compressing it at high pressures has revealed a rich phase diagram with several phases detected [6–9]. Bonev et al. [10], and more recently, Chen et al. [11] have reported that the melting curve is established only from 44 GPa up to about 200 GPa, and the slope of the melting curve is negative which means that a new phase might exist at high pressure and lower temperature. However, in the experiment it is always a challenge to achieve higher pressures. From the technological point of view, there have been speculations on possible future applications mainly as fuel for rockets [12,13].

As mentioned above, the solid hydrogen is very compressible. A pressure of 200 MPa can reduce the molar volume from 23.2 cm³ to about 17 cm³. Thus, this system is very interesting since it allows us to study its ground state in detail at moderate den-

sities [14]. In this work we use the path integral Monte Carlo (PIMC) technique in the isothermal-isobaric ensemble to study the thermodynamic and structural properties of the solid molecular hydrogen at pressures ranging from 0 GPa to 2.2 GPa. The PIMC is more advantageous than other quantum methods because it is able to provide the properties of a quantum system at finite temperatures without the need of expertise in the system's wave function [15].

One of the goals of this work is to make inferences about the impact of the zero-point energy (ZPE) and of the anharmonic effects on the total vibrational energy for pressures ranging from 0 GPa to 2.2 GPa. Beyond the many-body aspects of intermolecular interaction these issues should also be interesting for those doped solid molecular hydrogen systems which are of scientific importance in understanding the behavior of energetic species in cryogenic environments. Another goal is to verify if the kinetic energy shows some temperature effect at such moderate pressures since most of the experiments on hydrogen solid are performed at temperatures around 18.9 K. An agreement between theoretical results obtained for 0 K and experiments at 18.9 K could indicate that the kinetic energy at this latter temperature has already reached the ground-state value. Moreover, we shall extend this analysis to calculate the mean square displacement and the bulk modulus. Finally, we estimate the impact of the quantum effects on these quantities. We neglect the nuclear spin effects in the present work, since the exchange effects are almost negligible in the range of pressure and temperature under study.

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2. Numerical approaches and computational details

We perform both PIMC and classical Monte Carlo (MC) simulations for a solid molecular hydrogen in the isothermal-isobaric ensemble at pressures ranging from 0 GPa to 2.2 GPa. In this regime of pressures, the H_2 molecules can be well modeled by treating the whole molecule as a particle, since its charge distribution is nearly spherical. In this approach, the rotational degree of freedom of the molecule is not considered. Thus, in the present PIMC simulations, each hydrogen molecule is considered as a quantum particle of mass 2.016 amu and is modeled by a set of M beads forming a cyclic chain or a polymer. Several H_2 – H_2 pairwise interaction potentials have been proposed for the theoretical study of the solid molecular hydrogen [16–20]. The most commonly used pairwise potential for the study of the molecular hydrogen in condensed phase was developed by Silvera and Goldman (SG) [16]. However, the SG potential is suitable for hydrogen under ambient pressure. More recently, Hemley et al. [17] proposed a correction for the SG potential to study the solid hydrogen under high pressures. The correction softens the potential yielding the description of the enhanced many-body contribution in the short-range region. This modification makes the SG potential proper to describe the equation of state of solid molecular hydrogen for pressures up to 42 GPa [17,19].

The PIMC method [21] is based on the evaluation of the quantum density matrix

$$\rho(\mathbf{R}_0, \mathbf{R}_M; \beta) = \int d\mathbf{R}_1 \dots d\mathbf{R}_{M-1} \exp \left[-\sum_{m=1}^M S^m \right] \quad (1)$$

by sampling the set of paths, $\{\mathbf{R}_0, \mathbf{R}_1, \dots, \mathbf{R}_{M-1}, \mathbf{R}_M\}$, \mathbf{R}_k being the set of beads $\{\mathbf{r}_{1,k}, \dots, \mathbf{r}_{n,k}\}$, and $\mathbf{r}_{i,k}$ a bead that is the position of the i th particle in the k th time slice, $\beta = 1/k_B T$ where k_B is the Boltzmann constant and T the absolute temperature. The time step is defined as $\tau = \beta/M$ with M the number of beads of the path. The action $S^m \equiv S(\mathbf{R}_{M-1}, \mathbf{R}_M) \equiv -\ln[\rho(\mathbf{R}_{M-1}, \mathbf{R}_M)]$ is handled in the primitive approximation. To evaluate the $3NM$ -dimensional integrals (N being the number of atoms) in Eq. (1), we employ the Metropolis bisection sampling technique [15].

The PIMC simulations are performed in a three-dimensional (3D) box using an hexagonal close packing (HCP) unit cell with periodic boundary conditions in the three directions. Most of the calculations are performed within a simulation box containing 512 spinless hydrogen molecules. A “time step” $\tau = (1/2400) \text{K}^{-1}$ (corresponding to $M = 120$ at $T = 20 \text{K}$) is used for the discretized imaginary time path integrals. The extrapolation to the $\tau = 0$ limit shows that this approximation induces an error of about 0.1% in the obtained total energy. Checks for larger systems containing 1000 particles show that the obtained results do not change within the statistical error when compared to a system with 512 atoms. For the averages, we use 40.000 PIMC time steps.

3. Results and discussions

The total energy of the solid hydrogen can be decomposed into three terms:

$$E(V, T) = E_0 + E_{el}(V) + E_{vib}(V, T), \quad (2)$$

where E_0 is the minimum potential energy for the classical crystal at $T = 0 \text{K}$, $E_{el}(V)$ is the elastic energy, and $E_{vib}(V, T)$ is the vibrational energy. The elastic energy $E_{el}(V)$ for a given volume V is obtained as the value of increment of the classical energy at $T = 0$ with respect to the minimum energy E_0 as was defined in Ref. [22]. Notice that in the isothermal-isobaric ensemble, the volume is implicitly determined by the pressure and temperature. The vibrational energy $E_{vib}(V, T)$ depends explicitly on both V and T

and can be obtained by subtracting E_0 and $E_{el}(V)$ from the total energy $E(V, T)$ for a certain density at fixed temperature and pressure (see Eq. (2)). Fig. 1(a) shows the vibrational energy E_{vib} (the red circles) and elastic energy E_{el} (the black squares) for solid molecular hydrogen as a function of pressure at two different temperatures, $T = 20 \text{K}$ and 77K . In general, E_{vib} and E_{el} increase with increasing pressure, but E_{el} increases faster than E_{vib} , as shown by their difference (the blue triangles). With further increasing pressure, the vibrational energy E_{vib} may possibly be overwhelmed by E_{el} . We also notice that E_{vib} and E_{el} are, respectively, proportional and inversely proportional to the temperature. Such a behavior was also observed for rare-gas solids [22].

We have also performed classical MC calculations for the vibrational energy and obtained $E_{vib} \simeq 60 \text{K}$ for $T = 20 \text{K}$ and 236K for $T = 77 \text{K}$ being independent of the applied pressure. At $T = 20 \text{K}$ and a pressure of 0.6 GPa, the quantum contribution is about 80% of E_{vib} . However, at the higher temperature $T = 77 \text{K}$ and the same pressure, the quantum contribution is reduced to less than half E_{vib} . In the pressure and temperature range under investigation, we obtain the quantum contribution lying roughly from 40% up to 90% of the E_{vib} total values. We obtain the zero-point energy (ZPE) as the difference in energy between the extrapolated

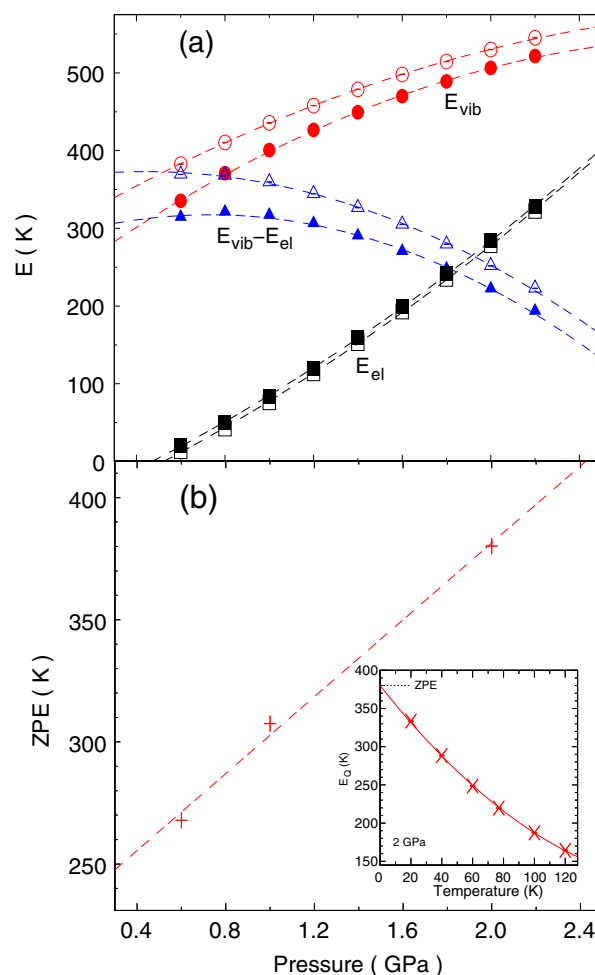


Fig. 1. (a) Pressure dependence of the vibrational energy E_{vib} (circles) and elastic energy E_{el} (squares) of H_2 solid hydrogen at $T = 20 \text{K}$ (the solid symbols) and $T = 77 \text{K}$ (the open symbols). The solid and open blue triangles are the differences between the corresponding E_{vib} and E_{el} . (b) The zero-point energy as a function of pressure. The inset shows the pure quantum contribution to the total energy, E_0 , as a function of temperature, the extrapolation to $T = 0 \text{K}$ (solid line) gives the ZPE. The dashed lines are guides to the eye.

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