CHIN. PHYS. LETT. Vol. 34, No. 12 (2017) 123401

An Isotropic Empirical Intermolecular Potential for Solid H_2 and D_2: A Classical Molecular Calculation *

Li Yang(杨莉)[1**], Hui Liu(刘慧)[1], Hui-Ling Zhou(周慧玲)[1], Qing-Qiang Sun(孙庆强)[1,2], Shu-Ming Peng(彭述明)[3], Xing-Gui Long(龙兴贵)[3], Xiao-Song Zhou(周晓松)[3], Xiao-Tao Zu(祖小涛)[1], Fei Gao(高飞)[4]

[1]*School of Physical Electronics, University of Electronic Science and Technology of China, Chengdu 610054*
[2]*School of Science, Huaihai Institute of Technology, Lianyungang 222005*
[3]*Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang 621900*
[4]*Department of Nuclear Engineering and Radiological Sciences, University of Michigan, Ann Arbor, MI 48109 USA*

(Received 3 August 2017)

We develop an isotropic empirical potential for molecular hydrogen (H_2) and deuterium (D_2) by fitting to solid-state data, which is appropriate for classical molecular dynamics (CMD) approach. Based on the prior isotropic intermolecular potential used in self-consistent phonon approximation, a zero-point energy term and an embedded energy term are introduced to describe the H_2–H_2 and D_2–D_2 interactions in CMD simulations. The structure, cohesive energy and elastic properties of solid H_2 (D_2) are used as the fitting database. The present method is tested by calculating the melting point of solid H_2, and the pressure and bulk elastic modulus as a function of volume. The developed potentials well reproduce many properties of solid H_2 and D_2.

PACS: 34.20.Gj, 02.70.Ns, 62.20.de, 61.50.Lt

DOI: 10.1088/0256-307X/34/12/123401

The quality of deuterium-tritium fuel target is a critical aspect in the fusion fuel gains of inertial confinement fusion.[1] The structural and mechanical behaviors of solid molecular hydrogens (H_2) have been studied for a long time, including the recent calculations based on density functional theory (DFT).[2–4] However, the DFT calculations significantly underestimate the lattice constant of solid H_2 at 0 K and 0 bar. Furthermore, it is known that the DFT calculations are limited to study relatively small systems. The Monte-Carlo[5] and the self-consistent phonon approximation[6] were performed to calculate the structural and static mechanical properties of solid hydrogen, which have also been carried out with a small fcc lattice system. The classical molecular dynamics (CMD) method is an important tool to simulate the kinetic process of deuterium-tritium layers at nanometer and larger scale. The central problem in CMD simulations is to develop an effective intermolecular potential of solid hydrogen. This work focuses on the isotropic interaction potentials between spherical para-hydrogen or ortho-deuterium at low pressure. Many different semi-empirical isotropic potentials have been proposed to describe the intermolecular interactions of hydrogen.[6,7] The potential derived by Silvera and Goldman (SG potential for short)[6] is an effective isotropic potential because it is able to reproduce the experimental pressure–volume relationship of solid hydrogen for pressures up to about 25 kbar. However, the lattice constant and the cohesive energy of fcc solid H_2 obtained by the CMD with the SG potential are 4.73 Å and 22.03 meV, which deviate significantly from the experimental values of 5.29±0.05 Å[8] and 7.74 meV.[6] Obviously, the SG potential is unsuitable to directly use in CMD simulations. We modify the SG potential to adapt the CMD simulations based on the properties of solid H_2 (D_2).

The unsuitability of the SG potential in CMD is attributed to the fact that the normal CMD does not consider the zero point energy (ZPE) effect of quantum crystals at 0 K. As a quantum crystal, the ZPE of solid H_2 cannot be ignored. Based on the SG potentials of H_2 and D_2, the contribution of the ZPE was added in this work. An embedding function term was introduced to help describe the elastic properties at relatively high pressure. The total energy of solid hydrogen is

$$E = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \Phi(r_{ij}) + \sum_{i=1}^{N} b\sqrt{\rho_i}, \tag{1}$$

where $\Phi(r)$ is the modified SG potential

$$\Phi(r) = \exp(\alpha - \beta r - \gamma r^2) - \left(\frac{C_6}{r^6} + \frac{C_8}{r^8} + \frac{C_{10}}{r^{10}} - \frac{C_7}{r^7} - \frac{C_9}{r^9}\right) f_c(r), \tag{2}$$

with $f_c(r)$ being the same as that in the SG potential.[6] The second term in Eq. (1) is the embedded energy of many-body effect, where ρ represents the density of s-band electrons[9]

$$\rho = \sum_j N \times \exp(-\xi r). \tag{3}$$

The 1s-type Slater-function of helium is chosen to describe H_2 (D_2), thus $\xi = 3.375$/atomic units (a.u.). According to the calculations of Bruce based on a Monte-Carlo integration scheme,[5] the main part of the average kinetic energy at 0 K is approximately

*Supported by the National Natural Science Foundation of China under Grant No U1430109.
**Corresponding author. Email: yanglildk@uestc.edu.cn
© 2017 Chinese Physical Society and IOP Publishing Ltd

proportional to $1/r^7$. Therefore, in Eq. (2), a term of C_7/r^7, representing the ZPE, is added. The interactions between hydrogen atoms are calculated by the potential of Brenner,[10] and the modified molecular dynamics code MOLDY[11] is employed in this work. The initial parameters of α, β, γ, C_6, C_8, C_9 and C_{10} in Eq. (1) are obtained from Ref. [6] while the initial C_7 and b in Eq. (1), and N in Eq. (3) are educated guesses. Starting from an initial guess, the potential parameters are optimized by adjusting the properties predicted by the potential. We consider lattice constants, cohesive energy and elastic constants of fcc and hcp H_2 (D_2) at 0 K and 0 bar in the basic fitting database, as determined from the experimental and DFT results. The parameters derived for the intermolecular potential of solid H_2 and D_2 are listed in Table 1. In Eqs. (1)–(3), the units of the energy and distance r are Hartree and Bohr, respectively. The cutoff distance of the interactions between molecules is located between the third and fourth neighbors. It should be noted that all parameters but C_7 for H_2 and D_2 are identical. H_2 and D_2 have the same electron structures, but different masses. The value of C_7, reflecting the zero motion, depends on the molecular mass. Therefore, the parameters of C_7 are different for H_2 and D_2.

Table 1. Potential parameters of H_2–H_2 and D_2–D_2 in a solid phase.

	α	β	γ	C_6	C_7	C_8	C_9	C_{10}	N	b
H_2–H_2	1.7241	1.5727	0.0100	12.04	46.087	210.94	143.13	4813.9	4.0	0.4566
D_2–D_2	1.7241	1.5727	0.0100	12.04	26.089	210.94	143.13	4813.9	4.0	0.4566

Table 2. Properties of H_2 and D_2 crystals, including lattice parameters of a (Å) and c/a, the cohesive energy E_c (meV), the elastic constants C_{ij} and bulk modulus B (kbar), the formation energy of a vacancy E_{vac} (meV), melting point T_m (K) and energy difference between fcc and hcp structures $E_{fcc-hcp}$ (meV).

		Present	DFT[2]	Calc[12]	Calc[13]	Expt[14]	Expt[15]	Expt and Calc
hcp H_2	a	3.79	3.62					3.73±0.05[8], 3.783[4]
	c/a	1.64	1.60					1.63[8]
	E_c	7.19	17.00					
	C_{11}	4.56	7.48	3.72	3.70	4.2±0.1	3.62±0.09	
	C_{12}	1.51	3.19	1.37	1.41	1.8±0.1	1.19±0.09	
	C_{13}	1.08	1.80	0.57	1.02	0.5±0.1	0.41±0.09	
	C_{33}	4.87	8.50	4.51	4.08	5.1±0.1	4.4±0.35	
	C_{44}	1.09	1.75	1.15	1.02	1.1±0.1	0.83±0.04	
	B	2.37	4.15	1.89	2.04	2.1±0.1	1.74±0.1	
	E_{vac}	7.31	7.30					9.65[16]
	T_m	18						14[17]
fcc H_2	a	5.35	5.02					5.29±0.05[8]
	E_c	7.31	20					7.74[6], 7.37[6]
	$E_{fcc-hcp}$	0.12						0.14[18]
hcp D_2	a	3.61						3.60±0.006[19]
	c/a	1.64						1.63[19]
	E_c	11.32		11.39				11.44[7]
	C_{11}	8.07		6.24		8.2	6.68±0.2	
	C_{12}	2.68		2.52		2.9	2.32±0.2	
	C_{13}	1.91		1.25		0.9	1.11±0.2	
	C_{33}	8.66		7.50		10.2	7.88±0.5	
	C_{44}	1.92		1.79		2.3	1.64±0.1	
	B	4.20		3.33		4.0	3.37±0.2	
	E_{vac}	11.63						11.37[16]
fcc D_2	a	5.10						5.081±0.006[19]
	$E_{fcc-hcp}$	2.11						

In the present work, we consider the most stable fcc H_2 (D_2) crystal with a $Pa3$ structure and the most stable hcp H_2 (D_2) crystal with a disordered hydrogen molecule structure,[2] whose unit cells are shown in Fig. 1. Using the parameters in Table 1, the cohesive energy, the lattice constants and mechanical properties at 0 K and 0 bar are calculated and listed in Table 2 for H_2 and D_2 crystals, together with the experimental data and other calculations. As listed in Table 2, the lattice constants $a = 3.79$ Å and $c/a = 1.64$ of hcp H_2 in the present work are in good agreement with the experiment due to the introduction of ZPE in the current potential, but significantly larger than the DFT data.[2] The present cohesive energy of hcp H_2 is 7.19 meV, which is lower than the DFT data (17.00 meV). The experimental cohesive energy of hcp H_2 is hard to obtain in available literature, therefore the cohesive energy is benchmarked to that of fcc H_2, which will be discussed in the following. Five independent elastic constants, representing the mechanical properties of hcp H_2, are calculated and listed in Table 2. The values of C_{ij} of hcp H_2 are close to the experimental and theoretical results, except for C_{13}, while C_{13} is similar to the result of harmonic theory.[13] The

bulk modulus B in this work approaches to that of neutron scattering.[14] However, C_{ij} and B of DFT for hcp H_2 are significantly larger than all the other values. The present potential almost reproduces the elastic constants and the bulk modulus of hcp H_2. The formation energy of a vacancy in hcp H_2 crystal (7.31 meV) is lower than the experimental value of 9.65 meV, but excellently agrees with the average DFT data (7.30 meV). We further test the present potential by calculating the melting point of hcp H_2, which is estimated to be 18 K by a two-phase method,[20] 4 K higher than the experiment.[17] Previous studies show that solid hydrogen exists in hcp or fcc phases, depending on the preparation conditions. Therefore, we also calculate the lattice constant and the cohesive energy of fcc H_2. The lattice constant of fcc H_2 is determined to be 5.35 Å, which agrees well with the experimental value,[8] but contrast to the DFT result.[2] The present cohesive energy of fcc H_2 is 7.31 meV, which is slightly lower than the experimental value (7.74 meV) and Goldman's calculation (7.37 meV). The value of E_c of fcc H_2 is 0.12 meV/molecule higher than hcp H_2, which suggests that the fcc structure is more favorable than the hcp at 0 K and 0 bar, and the result is similar to the previous classical calculation (0.14 meV/molecule).[18,21] For hcp D_2, the lattice $a = 3.61$ Å and $c/a = 1.64$ in the present work are also consistent with the experimental data.[19] The difference in the cohesive energies of hcp D_2 between our results and others is within 1%. The elastic constants and bulk modulus of hcp D_2 in this work are similar to the results of neutron scattering except for C_{13}.[14] Compared with the experimental value (11.37 meV), the present potential of D_2 reproduces well the formation energy of a vacancy (11.63 meV). The lattice constant of fcc D_2 is 5.10 Å, which is close to the experimental value of 5.081±0.006 Å. The fcc structure of solid D_2 has higher energy than an hcp structure at 0 K and 0 bar, the same as solid H_2, which is also consistent with the experimental observation.[7] The good reproduction of the cohesive energies of H_2 and D_2 at 0 K and 0 bar in the present work is also attributed to the correction of ZPE effect.

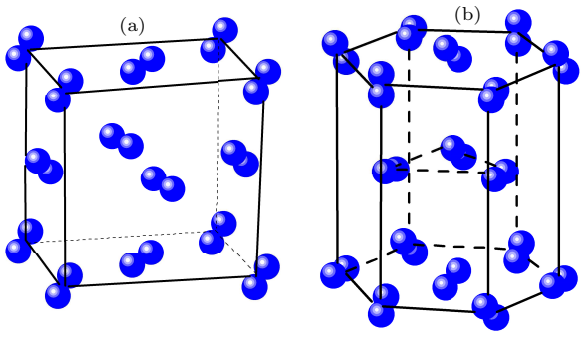

Fig. 1. Unit cell of the most stable H_2 (D_2) crystal for (a) fcc and (b) hcp structures, where the spheres represent hydrogen or deuterium atoms.

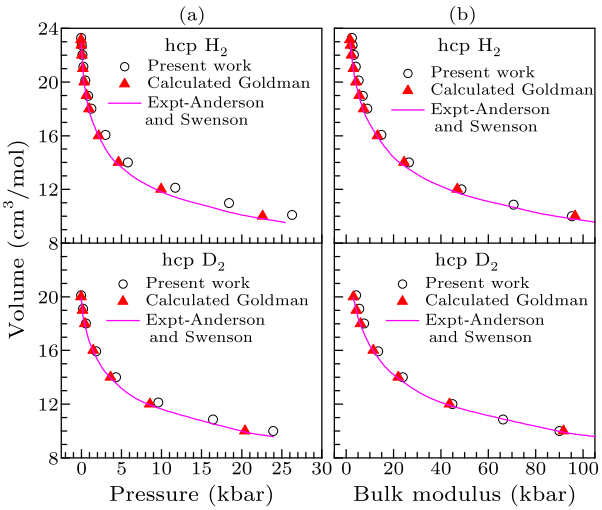

Fig. 2. (a) Pressure–volume relation and (b) bulk modulus–volume relation at 0 K for hcp H_2 and D_2 crystals.

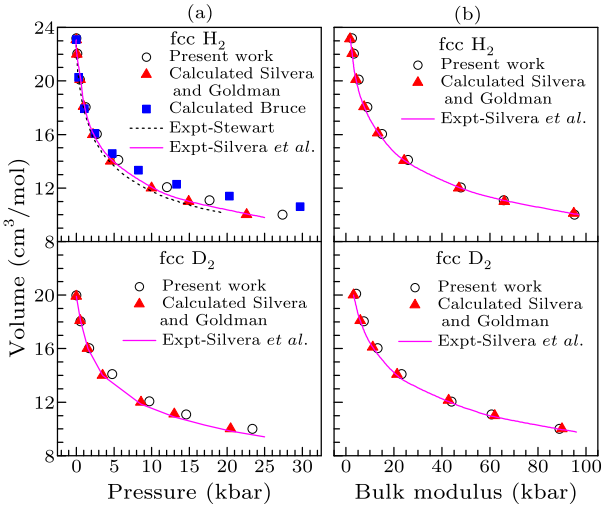

Fig. 3. (a) Pressure–volume relation and (b) bulk modulus–volume relation at 0 K for fcc H_2 and D_2 crystals.

To evaluate the reliability of the present potentials, we calculate the pressure and elastic modulus of H_2 and D_2 crystals at different volumes. Figure 2 shows the pressure–volume relation and bulk modulus–volume relation at 0 K for hcp H_2 and D_2. The present results are compared with the calculated results of Goldman[22] and the experiments of Anderson and Swenson (AS) for n-D_2 and n-H_2 at 4.2 K.[23] It is clear that at low pressure, the volumes of hcp H_2 and D_2 are similar to the results of Goldman and AS. With increasing the pressure, the volume difference of our results from the others increases. However, the volume difference for hcp H_2 is less than 7%, and less than 5% for hcp D_2 in comparison with the experiments. Contrary to the pressure, the bulk modulus at small volumes obtained by the present potentials agrees well with the experiments and other calculations, especially for hcp D_2. With increasing the volume, our calculations moderately overes-

timate the bulk modulus. Moreover, our potentials and fitting parameters are tested by calculating the pressure and the elastic properties at different volumes of fcc H_2 and D_2 crystals, and the results are shown in Fig. 3. The present results are in excellent agreement with the experimental data and other calculations at large volumes. At smaller volumes, the present work is close to the experimental values of Silvera *et al.*,[24] while slightly higher than the experimental values of Stewart[25] and the calculated results of Silvera–Goldman.[6] However, it is clear that our results are more accurate than the calculated values of Bruce,[5] especially at small volumes. For fcc D_2, the present pressure–volume relation is almost the same as other results. Figure 3(b) illustrates that our results agree well with the experimental values of Silvera *et al.*, and the calculations of Silvera–Goldman for both fcc H_2 and D_2 structures. In general, the CMD method with the present empirical potential is reliable to describe the pressure and elastic properties as a function of volume for both H_2 and D_2 crystals within the volume range considered. The correction of the molecular interactions at short distance brings about the good behavior of H_2 and D_2 at relatively high pressure at 0 K. In the future work, we will carry out more tests for the potentials of H_2 and D_2, for example, the elastic constants at high pressure and room temperature.

In summary, the CMD method with isotropic empirical intermolecular potentials has been performed to describe the properties of solid H_2 and D_2 by including the zero point energy. It can well reproduce the structural, mechanical and some thermal properties of H_2 and D_2. The pressure–volume and pressure–bulk modulus relations for the pressure up to 25 kbar are well described by the present potentials. Therefore, the CMD with the present potentials can be used to describe the behavior of solid H_2 and D_2 in a wide range of pressures (<25 kbar). We focus on the properties of solid H_2 and D_2 at low temperature and low pressure in this work, therefore the present potentials are not suitable to describe the behavior of metallic hydrogen at extreme pressure.

References

[1] Hurricane O A, Callahan D A and Casey D T 2014 *Nature* **506** 343
[2] Ye Y T, Yang L, Yang T L, Nie J L, Peng S M, Long X G, Zu X T and Du J C 2015 *Eur. Phys. J.* B **88** 161
[3] Sun Q Q, Ye Y T, Yang T L, Yang L, Peng S M, Long X G, Zhou X S, Zu X T and Du J C 2015 *Eur. Phys. J.* B **88** 332
[4] Guerrero C, Cuesta-Lopez S and Perlado J M 2013 *EPJ. Web Conf.* **59** 16004
[5] Bruce T A 1972 *Phys. Rev.* B **5** 4170
[6] Silvera I F and Goldman V V 1978 *J. Chem. Phys.* **69** 4209
[7] Silvera I F 1980 *Rev. Mod. Phys.* **52** 393
[8] Curzon A E and Mascall A J 1965 *Brit. J. Appl. Phys.* **16** 1301
[9] Gao F, Deng H Q, Heinisch H L and Kurtz R J 2011 *J. Nucl. Mater.* **418** 115
[10] Brenner D W 1990 *Phys. Rev.* B **42** 9458
Matsubara K, Sugihara K and Tsuzuku T 1992 *Phys. Rev.* B **46** 1948
[11] Gao F, Bacon D J, Flewitt P E J and Lewis T A 1997 *J. Nucl. Mater.* **249** 77
[12] Goldman V V 1977 *J. Low Temp. Phys.* **26** 203
[13] Morn M and Huang K 1954 *Dynamical Theory of Crystal Lattices* (Oxford: Clarendon Press)
[14] Nielsen M 1973 *Phys. Rev.* B **7** 1626
[15] Wanner R and Meyer H 1973 *J. Low Temp. Phys.* **11** 715
[16] Ebner C and Sung C C1972 *Phys. Rev.* A **5** 2625
[17] https://www.webelements.com/hydrogen/
[18] Felsteiner J 1965 *Phys. Rev. Lett.* **15** 1025
[19] Schuch A F and Mills R L 1966 *Phys. Rev. Lett.* **16** 616
[20] Li X C, Shu X L, Liu Y N, Gao F and Lu G H 2011 *J. Nucl. Mater.* **408** 12
[21] Zu X T, Yang L, Gao F, Peng S M, Heinisch H L, Long X G and Kurtz R J 2009 *Phys. Rev.* B **80** 054104
[22] Goldman V V 1979 *J. Low Temp. Phys.* **36** 521
[23] Anderson M S and Swenson C A 1974 *Phys. Rev.* B **10** 5184
[24] Silvera I F, Driessen A and De Waal J A 1978 *Phys. Lett.* A **68** 207
[25] Stewart J W 1956 *J. Chem. Phys. Solids* **1** 146