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2002 J. Phys.: Condens. Matter 14 10901

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Crystal structure of solid molecular hydrogen under high pressures

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Received 10 June 2002

Published 25 October 2002

Online at stacks.iop.org/JPhysCM/14/10901

Abstract

In an effort to achieve a comprehensive understanding of the structure of dense H₂, we have performed path-integral Monte Carlo simulations for three combinations of pressures and temperatures corresponding to three phases of solid hydrogen. Our results suggest three kinds of distribution of molecules: orientationally disordered hexagonal close packed (hcp), orientationally ordered hcp with *Pa3*-type local orientation order and orientationally ordered orthorhombic structure of *Cmca* symmetry, for the three phases.

1. Introduction

The phase diagram of solid hydrogen in the pressure (P) and temperature (T) plane has been studied for many years. For P up to about 200 GPa, it is well established that the solid hydrogen shows at least three relevant molecular phases (phases I–III), on the basis of static compression experiments [1–6].

- (1) Phase I, at $P < 110$ GPa: an orientationally disordered hexagonal close-packed (hcp) phase.
- (2) Phase II or the broken-symmetry phase, at P between 110 and 150 GPa: an orientationally ordered phase.
- (3) Phase III or the $H-A$ phase: expected to be another kind of orientationally ordered phase.

Even though the structures of these phases have been extensively investigated both in experimental and theoretical studies, some detailed structural information is still in dispute. In an effort to achieve an understanding of the dense H₂ phases theoretically, several methods have been used for different levels of approximation to the *ab initio* Hamiltonian representing the coupled system of N_a protons and N_a electrons, including the local density approximation (LDA)—and its refinements—to the density-functional theory [7–16], *ab initio* molecular dynamics treating protons as classical particles [17–19], first-principles path-integral molecular dynamics [20] and quantum Monte Carlo (QMC) simulation [21–23]. In this paper, we treat the hydrogen molecules as a basic ingredient in simulations, rather than the proton–electron mixture; the system is reduced to a quantum-mechanical problem of

N ($=2N_a$) molecules interacting with each other through an effective intermolecular potential. The QMC calculation is implemented only for the nuclear degrees of freedom [24–30], while the electronic degrees of freedom are implicitly taken into account in the choice of the potential. We employ the finite-temperature path-integral Monte Carlo method to investigate both lattice and orientational structures in the molecular phase with zero-point motions incorporated rigorously.

2. Theoretical model

Within the approximation that a molecule can be regarded as a basic ingredient, a quantum solid with translational and rotational degrees of freedom can be described by the Hamiltonian

$$\begin{aligned} H &= T + V, \\ T &= -\frac{\hbar^2}{2m} \sum_i^N \nabla_{\mathbf{R}_i}^2 + \frac{\hbar^2}{2I} \sum_i^N \mathbf{L}_i^2, \\ V &= \frac{1}{2} \sum_{i \neq j}^N V(\mathbf{R}_{ij}, \boldsymbol{\Omega}_i, \boldsymbol{\Omega}_j), \end{aligned} \quad (1)$$

where \mathbf{R}_i is the centre-of-mass position vector of the i th molecule, $\boldsymbol{\Omega}_i$ its orientation vector, \mathbf{L}_i its angular momentum operator and $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$ is the intermolecular separation vector. M and I denote the molecular mass and moment of inertia, respectively.

The intermolecular interaction potential employed here consists of an isotropic part (the Silvera and Goldman potential V_{SG} with an additional *ad hoc* correction V_{SR} proposed by Hemley *et al* [31]) and an anisotropic part (the Schaefer potential $V_{Schaefer}$ with a scaling factor χ proposed by Runge *et al* [25]), as follows:

$$\begin{aligned} V &= V_{SG} + V_{SR} + V_{ani}, \\ V_{SG}(R) &= e^{\alpha - \beta R - \lambda R^2} - f(R) \left\{ \frac{C_6}{R^6} + \frac{C_8}{R^8} + \frac{C_{10}}{R^{10}} - \frac{C_9}{R^9} \right\}, \\ f(R) &= \begin{cases} e^{-(1.28R_m/R-1)^2}, & \text{if } R \leq 1.28R_m, \\ 1, & \text{otherwise,} \end{cases} \\ V_{SR}(R) &= \begin{cases} a_1(R - R_C)^2 + a_2(R - R_C)^6, & \text{if } R \leq R_C, \\ 0, & \text{otherwise,} \end{cases} \\ V_{ani} &= \chi V_{Schaefer}, \\ \chi &= 0.61 + 0.31(R_{NN}/R_{NN}^0 - 0.5) \end{aligned} \quad (2)$$

where R_{NN} is the nearest-neighbour spacing, and $R_{NN}^0 = 3.789 \text{ \AA}$. Additional details about the potential can be found in [29, 30]. The potential has been proved reliable for solid H_2 and D_2 up to 150 GPa [6]. The potential does not contain any dependence on the intramolecular bond length, so each molecule in the solid is considered as a movable, orientable rigid rotor.

The extended solid is modelled by a simulation cell of finite size, which is periodically duplicated in all three spatial dimensions to minimize surface and finite-size errors. The N molecules are initially placed according to a given crystal structure in the cell. The interactions are evaluated making use of the periodicity and the ‘minimum imaging’ method. A cut-off correction to the potential energy is included by assuming that beyond the cut-off length the solid is a continuous and uniform medium, with the same density as inside the cell. This allows integration over the exterior density. The cut-off length is chosen to be equal to half of the smallest cell dimension.

The initial size and geometry of the simulation cell are chosen to accommodate a particular density ($N = 64$) and hcp structure. A simulation cell is determined by two basis vectors (\mathbf{a}_p and \mathbf{b}_p) forming a 60° angle and the third one (\mathbf{c}_p) perpendicular to both \mathbf{a}_p and \mathbf{b}_p with the appropriate length ratio:

$$a_p:b_p:c_p = 1:1:\sqrt{6}/3.$$

The packing pattern is ABAB \cdots , forming the hcp lattice structure. There are four layers in the \mathbf{c}_p -direction and 4×4 molecules in each layer.

In order to avoid the bias of a restrictive cell geometry with a predetermined crystal structure, the path-integral Monte Carlo (PIMC) method with a constant-pressure (NPT) ensemble is used, instead of the simpler constant-volume (NVT) ensemble where the simulation cell remains fixed. The implementation of the NPT ensemble is achieved by an extra Metropolis move of the cell size and geometry, which generates a Markov chain of states having a limiting distribution proportional to

$$\exp[-\beta PV - \beta E(s) + N \ln V]. \quad (3)$$

Here P is the given pressure, V the cell volume, $E(s)$ is the energy (H) of the configuration s , s represents a set of scaled coordinates. This enables us to monitor volume changes and therefore to observe any possible first-order phase transition directly. The technique is documented in [29], so we omit the details here.

3. Results

The study is confined to a solid system of *para*-H₂, to avoid the ‘minus-sign problem’ encountered in QMC studies associated with fermions. About 5000 Monte Carlo steps are used for equilibration. Statistical averages are collected from every second step after equilibrium is reached, to a total of about 10 000 data points. The partition number $M = 80$ is used. The lattice structure of the solid is monitored by the pair distribution function $g(R)$:

$$g(R) = \frac{1}{4\pi R^2 \rho} \left\langle \sum_{i<j} \delta(R_{ij} - R) \right\rangle \quad (4)$$

where ρ is the density of system. This function has well-defined peaks indicating the neighbour shells.

The correlations in the molecular orientations are monitored by a two-body correlation function $O(R)$ defined in [29]:

$$O(R) = \left\langle \frac{\sum_{i<j} P_2(\cos \theta) \delta(R_{ij} - R)}{\sum_{i<j} \delta(R_{ij} - R)} \right\rangle$$

where θ is the polar angle between the orientation vectors of the molecules located at \mathbf{R}_j and \mathbf{R}_i . This function measures the two-body orientation correlation at the intermolecular distance R , normalized by the number of molecules at that distance.

Figure 1 shows our PIMC results for both $O(R)$ and $g(R)$ at 100 K and 30 GPa, in phase I. The fact that $O(R)$ averages to approximately zero shows that the molecular orientation is disordered in the solid. The lattice stays in the hcp structure, described by an $g(R)$ curve. This result is consistent with the structure suggested by single-crystal x-ray diffraction data [1].

The simulation results for both $O(R)$ and $g(R)$ at 100 K and 120 GPa, corresponding to phase II, are shown in figure 2. At this temperature and pressure point, a well-defined structure in $O(R)$ can be found, revealing that the molecular orientation is ordered. The ordering signature, i.e. the detailed structure of $O(R)$ curve, is similar to that for $Pa3$ [29]. But $g(R)$

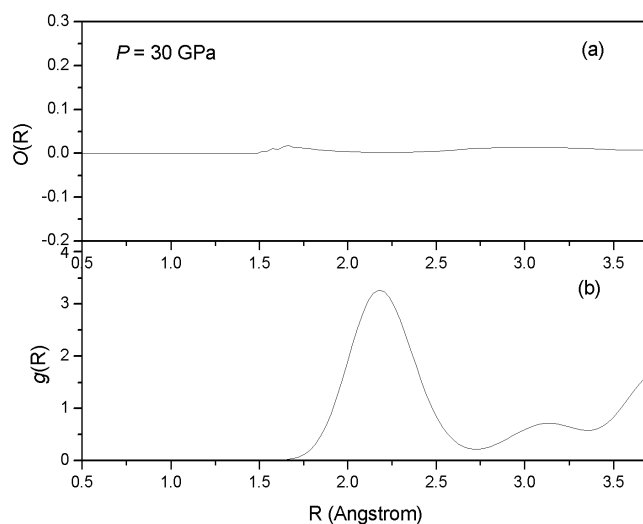


Figure 1. The orientational correlation function $O(R)$ and the pair distribution function $g(R)$ at 100 K and 30 GPa.

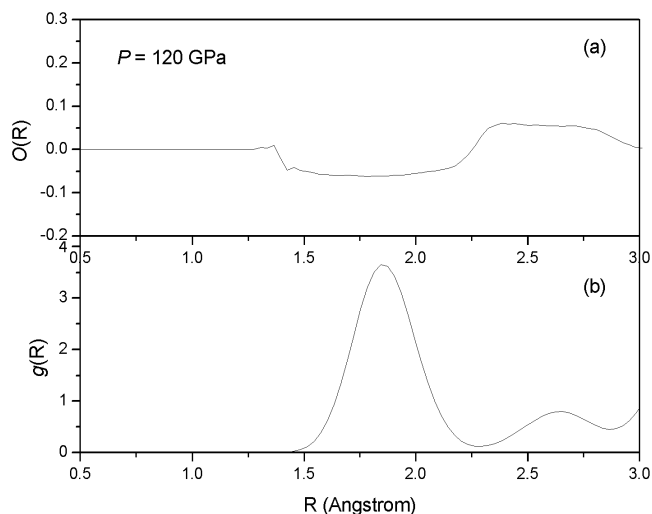


Figure 2. The orientational correlation function $O(R)$ and the pair distribution function $g(R)$ at 100 K and 120 GPa.

retains the characteristics of hcp structure. Snapshots of the average equilibrium distribution of molecules in real space (not shown here) confirm the lattice information. Therefore, it is concluded that phase II is an orientationally ordered hcp phase with $Pa\bar{3}$ -type local orientation order.

Figure 3 gives $O(R)$ and $g(R)$ at 100 K and 180 GPa corresponding to phase III. The detailed structure of $O(R)$ also shows that the phase is orientationally ordered. But the $g(R)$ gives different information from the hcp one, suggesting that phase III has different lattice structure to phase II. So, phase III is another kind of orientationally ordered phase with different lattice structure.

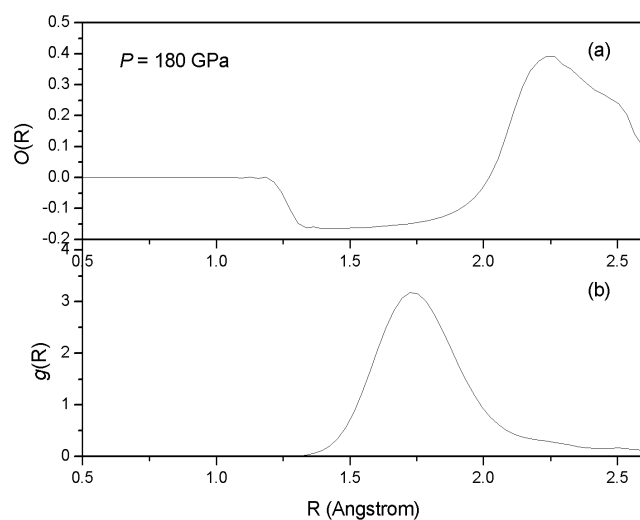


Figure 3. The orientational correlation function $O(R)$ and the pair distribution function $g(R)$ at 100 K and 180 GPa.

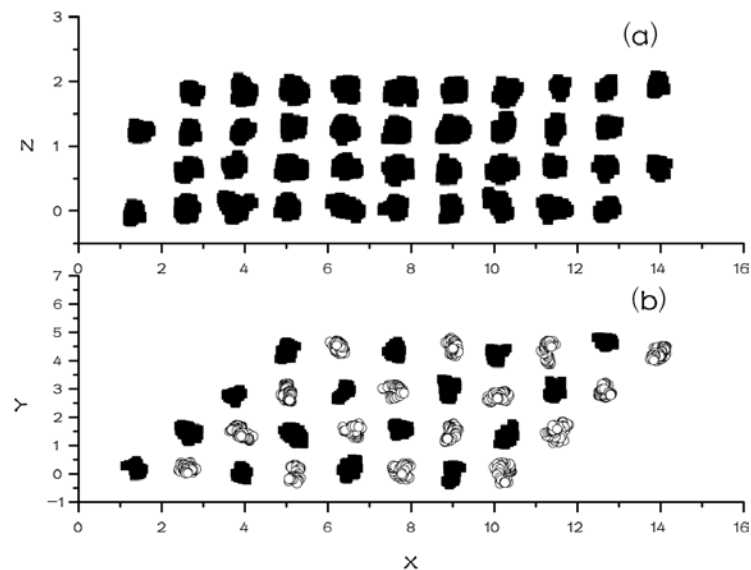


Figure 4. Snapshots of the equilibrium distributions of molecules at 100 K and 180 GPa in real space projected on (a) the XZ-plane and (b) the YZ-plane. Fluctuations are also shown here. In (b) filled and open symbols show the molecules for layer A and layer B, respectively.

To help one to understand the structure of phase III more clearly, the equilibrium distributions of 64 ($=4 \times 4 \times 4$) molecules in real space projected on XZ- and YZ-planes are shown in figure 4. Figure 4(a) tells us that the structure is still layered, and figure 4(b) shows that each molecule occupies the lattice site of an orthorhombic $Cmca$ structure. So our result suggests that phase III is an orientationally ordered phase based on $Cmca$ symmetry, which is similar to that suggested by Kitamura *et al* [20].

In summary, from a model treating a hydrogen molecule as a movable, orientable rigid rotor, three kinds of structure corresponding to the three phases of solid hydrogen have been found systematically. Further work is needed to explore in more depth the reasons for the stabilities and properties of the three phases.

Acknowledgment

This work was supported by the Chinese National Foundation for Doctoral Education, No 98018309.

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