

Self-consistent phonon calculations and equations of state of solid hydrogen and deuterium*†

A. B. Anderson‡

Colorado State University, Fort Collins, Colorado 80521

and Theoretical Division, University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87545

J. C. Raich and R. D. Etters

Colorado State University, Fort Collins, Colorado 80521

(Received 20 October 1975)

A numerical computation of the ground-state energies and zero-temperature pressure-volume relations of fcc para-H₂ and ortho-D₂ was carried out within the framework of the self-consistent phonon approximation. The calculations employed two recently proposed pair potentials and are expected to be valid up to several hundred kilobars. The effect of the hard core in the intermolecular interaction was treated with a short-range correlation function. The pressure dependence of the phonon density of states, sound velocities, and bulk moduli were determined and comparison with experimental data was made where possible.

I. INTRODUCTION

Recent years have witnessed a resurgence of interest in the high-pressure properties of hydrogen and its isotopes. The promise of a high-density metallic phase¹ has brought about a wealth of theoretical calculations concerning predictions of the transition pressure.²⁻¹² Additional motivation can be ascribed to the belief that the planets Jupiter and Saturn are composed mainly of hydrogen isotopes.^{13,14} The possible role of deuterium in laser-controlled fusion¹⁵ provides additional incentive for further study of the high-pressure properties of the hydrogen isotopes.

Most recent research has been directed towards an ultimate goal of predicting the pressure at which the molecular phase transforms into the metallic phase. At this time the greatest uncertainty concerning the transition pressure lies in the description of the molecular phase. The equation of state for the metal has been known reasonably accurately for some time.^{3,5-7} Although this paper does not attempt to predict the transition pressure, for reasons given below, we feel that an increased understanding of the molecular phase is an important contribution towards this goal.

It is well known that the lattice dynamics of solid molecular H₂ and D₂, as well as other quantum crystals at low densities, cannot be treated by the conventional harmonic approximation.¹⁶⁻²⁰ This method does not adequately treat the large contribution of the zero-point motion of the molecules in the solid. Indeed, the harmonic approximation yields imaginary frequencies for these crystals at low pressure.²¹ For this reason we have chosen the self-consistent phonon approximation (SCPA) to calculate the pressure dependence of the lattice dynamics of molecular H₂ and D₂ at zero temperature. Klein and Koehler²² have recently used the

SCPA to predict the lattice dynamics of hexagonal close-packed *o*-D₂ at zero pressure. Using a Lennard-Jones potential, $\phi(r)$, in conjunction with a Jastrow function of the form $\exp[-\frac{1}{2}c\phi(r)]$ they calculated the phonon dispersion curves in the (0001) direction. Although their results were not in excellent agreement with the experimental results of Nielsen and Moller,²³ possibly owing to their choice of potential and short-range correlation function, their results as well as other calculations²⁴⁻²⁷ using the SCPA to explain the behavior of other quantum crystals as well as rare-gas crystals, justify the use of the SCPA as a valid tool for investigation of quantum crystal lattice dynamics at temperatures well below melting.

II. H₂-H₂ PAIR POTENTIALS

The results of any lattice-dynamical calculation depend strongly on the form assumed for the intermolecular potential.²⁸ For this reason, we have chosen two recently proposed potentials differing greatly in their origin.

The potential recently proposed by England, Etters, Raich, and Danilowicz²⁹ (EERD) was obtained by fitting *ab initio* calculations of the short-range repulsive part of the H₂-H₂ interaction potential containing the valence and the quadrupolar interaction terms. The potential is conventionally separated into four parts

$$V = V_{QQ} + V_{DD} + V_{QD} + V_V.$$

Here V_{DD} and V_{QD} are the induced dipole-dipole and quadrupole induced dipole terms. V_{QQ} are the quadrupole-quadrupole and V_V the valence terms. All terms are dependent on the relative orientations of the two H₂ molecules. For the present work we are mainly interested in the intermolecular interactions between molecules in solid para-

hydrogen and orthodeuterium. At low pressure the rotational wave functions for both para- H_2 and ortho- D_2 are characterized by $J=0$, where J is the orbital angular momentum quantum number. It is expected^{30,31} that J remains a good quantum number up to pressures of several hundred kilobars. Molecules with $J=0$ have a spherically symmetric rotational wave function and can be considered to be rotating uniformly. At higher pressures the admixture of the higher rotational states becomes significant and the molecules will be ordered as is the case for ortho- H_2 and para- D_2 . For a uniformly rotating molecule, the anisotropic contribution to the interaction potential due to V_{QD} averages to zero. Spherically averaging the Van der Waals energy, V_{DD} , one obtains

$$V_{DD} = -1.18479 \times 10^{-59} / r^6,$$

and the spherically averaged induced dipole-quadrupole energy V_{QD} is given as

$$V_{QD} = -3.1081 \times 10^{-75} / r^8.$$

The spherically averaged valence energy V_V , obtained from atomic orbital calculations is given as²⁹

$$V_V = [83.69171 \times 10^{-11} - (24.58269/r) \times 10^{-19}] \\ \times \exp[-(3.53397 \times 10^8)r].$$

Here all energy units are in ergs and all distances r are in cm. The above potential plunges to an unphysical value of $-\infty$ as $r \rightarrow 0$. It starts to go negative at approximately $r = 1.5 \text{ \AA}$. It is desirable to modify the potential in a manner similar to that suggested by Trubitsyn¹¹

$$V = V_V + V_f(V_{DD} + V_{QD}),$$

where

$$V_f = \{\exp[-(7.561 \times 10^8)(r - 1.8515 \times 10^{-8})] + 1\}^{-1}.$$

This form for V_f was found to smoothly extend the potential nearly to $r=0$, although the unphysical behavior is still present for r less than 0.5 \AA . This presents no problems as values of the intermolecular distance this small are not considered here. It should be pointed out that this potential is only strictly valid for para- H_2 and ortho- D_2 at sufficiently low pressures so that all molecules are rotating freely. However, orientational corrections for ortho- H_2 and para- D_2 , as well as para- H_2 and ortho- D_2 at very high pressures are expected to be small.²⁸

The other potential investigated is one among several proposed by Ross.² Using the liquid perturbation theory of Mansoori and Canfield,³² Ross calculated Hugoniot for a family of potentials that satisfy existing shock data. The large error bars

of the shock data made it less meaningful to pick a single potential than to find a range of potentials satisfying experiment. The 0-K isotherms using his family of potentials were then calculated using a Lennard-Jones-Devonshire cell model. Ross reports that the potential which seems to fit both the shock data and the experimental results of Stewart³³ is given as

$$V(r) = 3.268 \times 10^{-10} \exp(-3.195 \times 10^8 r) \\ - \left(\frac{1.2414 \times 10^{-59}}{r^6} + \frac{3.0998 \times 10^{-75}}{r^8} \right) \\ \times \exp\left(-\frac{8.766 \times 10^{-48}}{r^6}\right),$$

where energy units are ergs and r is in cm. Again this potential is spherically symmetric and thus cannot describe orientation-dependent properties of the solid hydrogen isotopes.

III. CALCULATIONS

When grown under normal conditions at ambient pressure, the crystal structure of p - H_2 and o - D_2 at zero temperature is known to be hexagonal close packed³⁴ (hcp). Recently, Durana and McTague³⁵ have observed a phase transition to face-centered cubic (fcc) structure at pressures on the order of 0.8 kbar. Recent x-ray evidence³⁶ has shown that when grown on special substrates o - D_2 and p - H_2 form in the fcc structure. This indicates that the hcp structure at zero pressure may be only metastable with the fcc structure being kinetically inaccessible under normal growth conditions. For these reasons we have chosen the fcc structure in our calculations.

The self-consistent phonon approximation (SCPA) as a method of treating the anharmonicity of quantum crystals has been reviewed by Werthamer¹⁷ and we shall therefore present only a brief outline of the theory as it applies to the present problem.

The SCPA frequencies $\omega_{\vec{k}\lambda}$ and polarization vectors $\hat{\epsilon}_{\vec{k}\lambda}$ are given by the eigenvalue equation

$$\omega_{\vec{k}\lambda}^2 \hat{\epsilon}_{\vec{k}\lambda} = \frac{1}{M} \sum_{\vec{\tau}} (1 - e^{-i\vec{k}\cdot\vec{\tau}}) \vec{\Phi}(\vec{\tau}) \cdot \hat{\epsilon}_{\vec{k}\lambda}, \quad (1)$$

where M is the molecular mass, \vec{k} is a wave vector in the first Brillouin zone, and λ is a branch index running from one to three. The vector $\vec{\tau}$ is equal to $\vec{R}_l - \vec{R}_l'$ where \vec{R}_l' and \vec{R}_l are position vectors of lattice sites l' and l , respectively, with the lattice site at l chosen as the origin.

To account for the hard core of the molecular interaction we have included a short-range correlation function. With the addition of a short-range correlation function, f , the force constants $\vec{\Phi}(\vec{\tau})$ are given as

$$\bar{\Phi}(\vec{\tau}) = \langle \nabla \nabla W(\vec{\tau} + \vec{u}) \rangle - \langle W(\vec{\tau} + \vec{u}) \rangle \langle \nabla \nabla f^2(\vec{\tau} + \vec{u}) \rangle, \quad (2)$$

where $\vec{u} = \vec{u}_l - \vec{u}_l$ and \vec{u}_l is the displacement of molecule l from equilibrium. The effective potential, $W(r)$, is obtained from the true intermolecular potential $V(r)$ by

$$W(r) = f^2(r) [V(r) - (\hbar^2/2M)\nabla^2 \ln f(r)],$$

where $r = |\vec{\tau} + \vec{u}|$.

The angular brackets in the above expression for $\bar{\Phi}(\vec{\tau})$ are a shorthand notation and are defined by

$$\langle g(\vec{\tau} + \vec{u}) \rangle = \frac{\int d^3u g(\vec{\tau} + \vec{u}) e^{-\vec{u} \cdot \bar{D}^{-1}(\vec{\tau}) \cdot \vec{u}/2}}{\int d^3u f^2(\vec{\tau} + \vec{u}) e^{-\vec{u} \cdot \bar{D}^{-1}(\vec{\tau}) \cdot \vec{u}/2}}.$$

The displacement-displacement correlation function $\bar{D}(\vec{\tau})$ is found from the self-consistent frequencies $\omega_{\vec{k}\lambda}$ and polarization vectors $\hat{\epsilon}_{\vec{k}\lambda}$.

$$\bar{D}(\vec{\tau}) = \frac{1}{NM} \sum_{\vec{k}\lambda} \frac{\hbar}{\omega_{\vec{k}\lambda}} (1 - e^{i\vec{k} \cdot \vec{\tau}}) \hat{\epsilon}_{\vec{k}\lambda} \hat{\epsilon}_{\vec{k}\lambda}. \quad (3)$$

With frequencies and polarization vectors obtained from an initial guess (in this case a harmonic approximation with potential parameters adjusted to give real frequencies) $\bar{D}(\vec{\tau})$ is obtained from Eq. (3). The force constants are then calculated from Eq. (2). Frequencies and polarization vectors are calculated using Eq. (1). Equations (1)–(3) are then iterated until self-consistency is obtained.

For the short-range correlation function, f , we have chosen a form recently proposed by Horner³⁷ for use at low temperatures,

$$f(r) = f_0(r) [A_0 + A_1(r - \tau) + A_2(r - \tau)^2]^{1/2},$$

where $f_0(r) = e^{-(\sigma b/r)^{5/2}}$. The constant σ corresponds to the Lennard-Jones value 2.958 Å. In the present work the constant b is treated as a variational parameter. The constants A_0 , A_1 , and A_2 are determined by the following set of equations:

$$\langle f^2(r) \rangle = 1, \quad (4)$$

$$\langle f^2(r) \vec{u} \rangle = 0, \quad (5)$$

$$\langle f^2(r) \vec{u} \vec{u} \rangle = \bar{D}. \quad (6)$$

Equation (4) is the normalization condition. Equations (5) and (6) ensure that the short-range correlations do not alter the average distance between molecules and the width of the distribution of any pair of molecules. Following Horner, we have used the longitudinal components of Eqs. (5) and (6) to determine the constants A_0 , A_1 , and A_2 for each lattice shell. The dimensionless parameter b was found, for each molar volume, to an accuracy of better than one part in 10^4 by minimization of the ground-state energy with respect to b .

The r dependence of $f_0(r)$ is strictly valid only

for potentials exhibiting a $1/r^{12}$ repulsion. Since the potentials are not known accurately in the core region, the variational form was chosen as a means of approximating the form appropriate to each potential.

The ground-state energy of the crystal is then given as

$$E = \sum_{\vec{k}\lambda} \frac{\hbar \omega_{\vec{k}\lambda}}{4} + \frac{N}{2} \sum_{\vec{\tau}} \langle W(\vec{\tau} + \vec{u}) \rangle. \quad (7)$$

The condition that the Gibbs free energy be stationary with respect to any change in the unit cell gives the equation for the pressure P . For an fcc crystal the pressure is given as

$$P = -\frac{2}{3a^3} \sum_{\vec{\tau}} \vec{\tau} \cdot [\langle \nabla W(\vec{\tau} + \vec{u}) \rangle - \langle W \rangle \langle \nabla f^2(\vec{\tau} + \vec{u}) \rangle], \quad (8)$$

where a is the lattice constant.

Five shells of nearest neighbors were treated self-consistently in the determination of the force constants $\bar{\Phi}$, frequencies $\omega_{\vec{k}\lambda}$, and polarization vectors $\hat{\epsilon}_{\vec{k}\lambda}$. A total of 96 shells of nearest neighbors were included in the lattice sums appearing in the expressions for the energy and pressure, Eqs. (7) and (8), respectively, with shells 6–96 being treated harmonically. The calculations were repeated at several molar volumes treating ten shells self-consistently. Since no significant difference was found, we assume a SCPA treatment of five shells and a harmonic treatment of the remainder to be sufficient.

In the evaluation of the reciprocal-lattice sums appearing in Eqs. (3) and (7) we have employed ten special reciprocal-lattice vectors in $\frac{1}{48}$ of the Brillouin zone. The ten special vectors along with their appropriate weights, proposed by Chadi and Cohen,³⁸ were found to give more accurate Brillouin zone sums than several hundreds of points and weights chosen using the conventional grid method.³⁹ The use of the special reciprocal-lattice vectors allows for considerable savings in computer time with virtually no loss in accuracy. For further reduction in computation time we have exploited the symmetry of both the real lattice as well as the reciprocal lattice in Eqs. (1), (3), (7), and (8). The details of the symmetry considerations are given in Ref. 40 as well as references contained therein.

Normally, inclusion of a short-range correlation function in the self-consistent theory also has the effect that the calculated frequencies are not the true frequencies for the crystal. The true frequencies, $\Omega_{\vec{k}\lambda}$, and polarization vectors, $\hat{e}_{\vec{k}\lambda}$, are to be identified with the poles of the displacement-displacement correlation, \bar{D} , and are given by the equation

$$\Omega_{\vec{k}\lambda}^{-1} \hat{e}_{\vec{k}\lambda} = \left(\sum_{\vec{k}'} \omega_{\vec{k}\lambda}^{-1} \hat{e}_{\vec{k}\lambda'} \hat{e}_{\vec{k}\lambda'} \right) - M \sum_{\vec{r}} e^{-i\vec{k}\cdot\vec{r}} \vec{D}(\vec{r}) \cdot \langle \nabla \nabla f^2(\vec{r} + \vec{u}) \rangle \cdot \vec{D}(\vec{r}) \cdot \hat{e}_{\vec{k}\lambda}.$$

However, if all components of Horner's second and third conditions [Eqs. (5) and (6)] are used to determine the constants A_0 , A_1 , and A_2 , the self-consistent frequencies $\omega_{\vec{k}\lambda}$, and polarization vectors $\hat{e}_{\vec{k}\lambda}$, will in fact be identical to the true values $\Omega_{\vec{k}\lambda}$ and $\hat{e}_{\vec{k}\lambda}$. The use of the longitudinal components of Eqs. (5) and (6) in our calculations does in fact induce a slight error. We have calculated the zero-temperature dispersion curves in three symmetry directions as a function of pressure for both the self-consistent frequencies and the real frequencies. At pressures greater than 0.6 kbar we have found no difference between the self-consistent frequencies $\omega_{\vec{k}\lambda}$, and the actual frequencies $\Omega_{\vec{k}\lambda}$. Below 0.6 kbar the longitudinal frequencies differ slightly at the zone edge with the self-consistent frequencies being negligibly higher.

Assuming the self-consistent frequencies to be identical to the real frequencies we have calculated the phonon density of states as a function of molar volume. The method used in this calculation was that of Raubenheimer and Gilat.⁴¹ All density of state curves generated had the typical fcc form shown in Fig. 1. The effect of pressure on the density of states is shown in Figs. 2-5 where we have plotted the logarithm of each Van Hove singularity as well as the maximum fre-

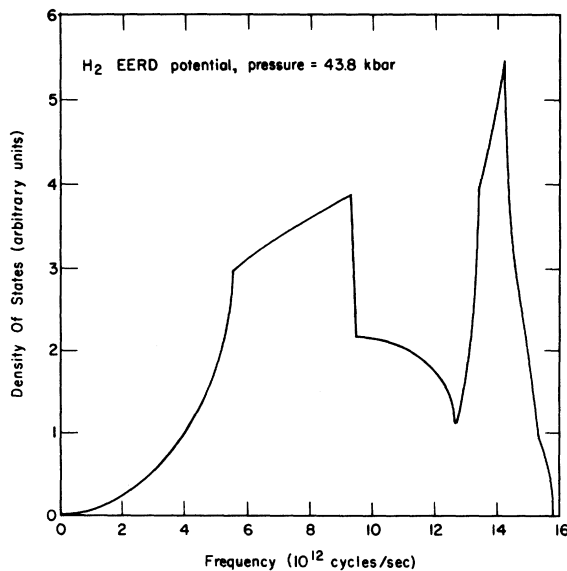


FIG. 1. Typical parahydrogen phonon density of states calculated from the EERD potential.

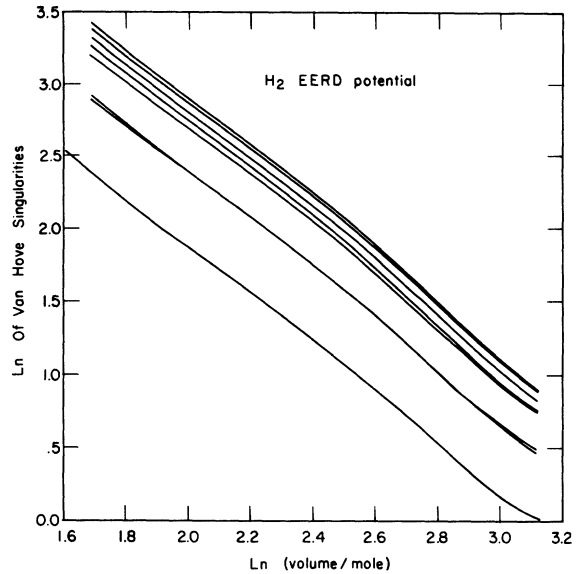


FIG. 2. Volume dependence of the singularities and maximum frequency in the parahydrogen phonon density-of-states curve as calculated with the EERD potential.

quency as a function of the logarithm of molar volume.

Our pressure-volume results were fit smoothly to the functional form

$$P = \sum_{i=0}^n e^{C_i V^i}, \tag{9}$$

where V is the molar volume. The $n+1$ constants,

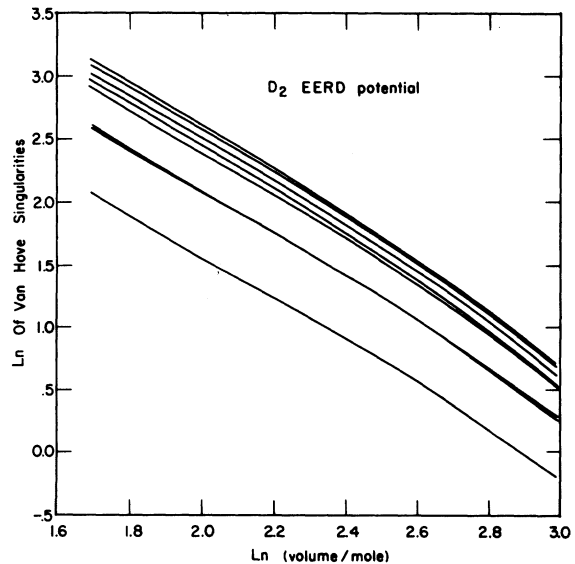


FIG. 3. Volume dependence of the singularities and maximum frequency in the orthodeuterium phonon density-of-states curve as calculated with the EERD potential.

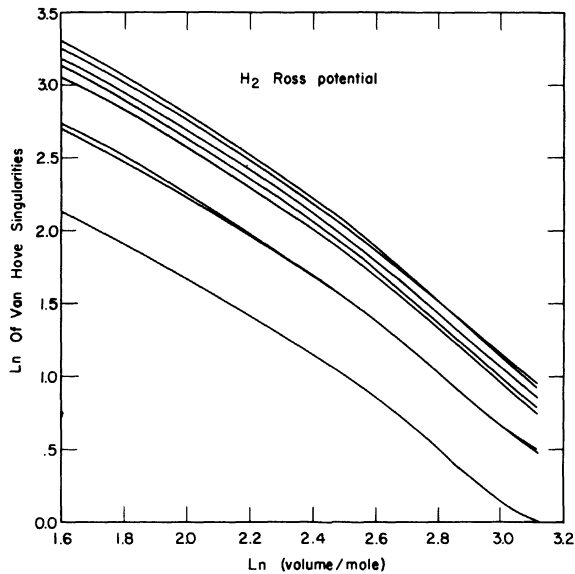


FIG. 4. Volume dependence of the singularities and maximum frequency in the parahydrogen phonon density-of-states curve as calculated with the Ross potential.

C_i , were evaluated numerically for both potentials for p - H_2 and o - D_2 . The number of terms needed for best-fit conditions varied from 8 to 15 depending upon the potential and the isotope considered. Bulk moduli, B , were then calculated as a function of volume, where

$$B = -V \left(\frac{\partial P}{\partial V} \right).$$

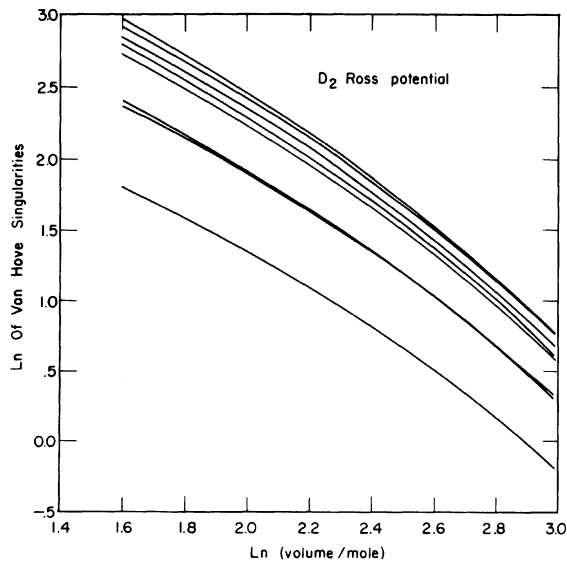


FIG. 5. Volume dependence of the singularities and maximum frequency in the orthodeuterium phonon density-of-states curve as calculated with the Ross potential.

Figures 6 and 7 show the calculated bulk moduli as a function of molar volume.

The velocity of sound

$$v_s = \lim_{k \rightarrow 0} \frac{\partial \omega_{\vec{k}}}{\partial k}$$

was calculated for the three symmetry directions [100], [110], and [111]. The pressure dependence of the sound velocities is shown in Figs. 8 and 9.

IV. DISCUSSION

Figures 10 and 11 show the zero-degree isotherms for both the EERD and Ross potentials. We have assumed the zero-pressure volume, V_0 , of 22.65 cm³/mole for parahydrogen as suggested by Roder *et al.*⁴² For orthodeuterium we have used the value $V_0 = 19.998$ cm³/mole which is consistent with the neutron-diffraction experiments of Yarnell, Mills, and Schuch.⁴³ The bulk moduli calculated from Eq. (9) are displayed in Figs. 6 and 7. The zero-pressure volumes used to convert the V/V_0 values of Anderson and Swenson⁴⁴ to the molecular volumes shown are 22.90 cm³/mole for normal H_2 and 19.94 cm³/mole for normal D_2 as reported in Ref. 44.

The EERD potential gives excellent agreement with the experimental pressures and bulk moduli of Anderson and Swenson for hydrogen. The deuterium pressure-volume results obtained with the EERD potential follow more closely the results of Stewart than those of Anderson and Swenson.

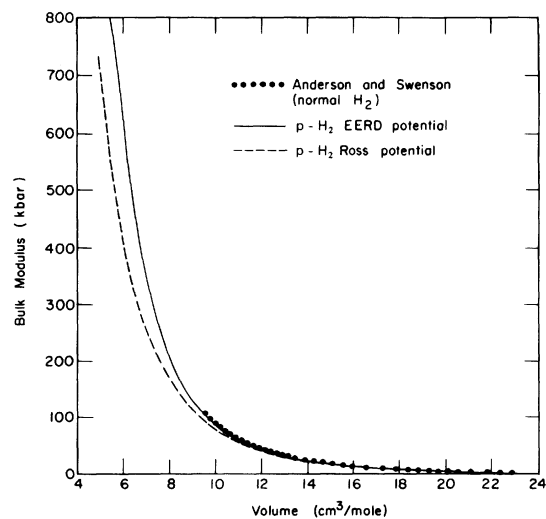


FIG. 6. Hydrogen bulk modulus as a function of molar volume. Dots represent experimental bulk moduli (Ref. 44) for normal hydrogen. Solid and dashed lines are bulk moduli calculated with the EERD potential and Ross potential, respectively.

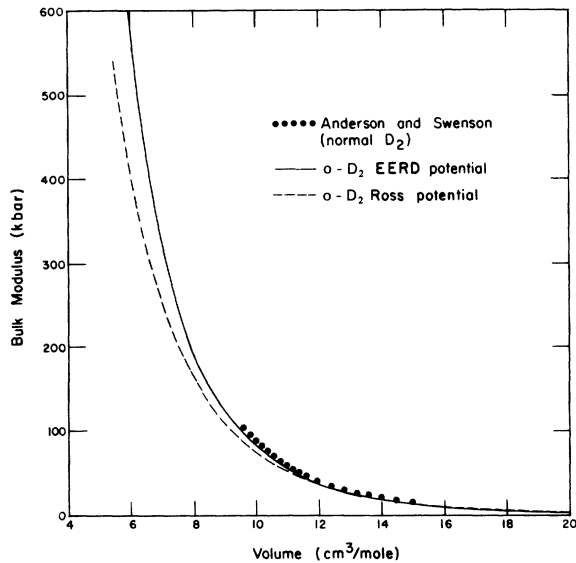


FIG. 7. Deuterium bulk modulus as a function of molar volume. Dots represent experimental bulk moduli (Ref. 44) for normal deuterium. Solid and dashed lines are bulk moduli calculated with the EERD potential and Ross potential, respectively.

The deuterium bulk moduli derived from calculations using the EERD potential are in good agreement with the results of Anderson and Swenson; however, the results for hydrogen are clearly superior. The EERD potential predicts zero-pressure volumes which are in good agreement with the values $22.65 \text{ cm}^3/\text{mole}$ and $19.998 \text{ cm}^3/\text{mole}$ for $p\text{-H}_2$ and $o\text{-D}_2$, respectively.

It is not surprising that the Ross potential does not predict accurately the zero-pressure volumes

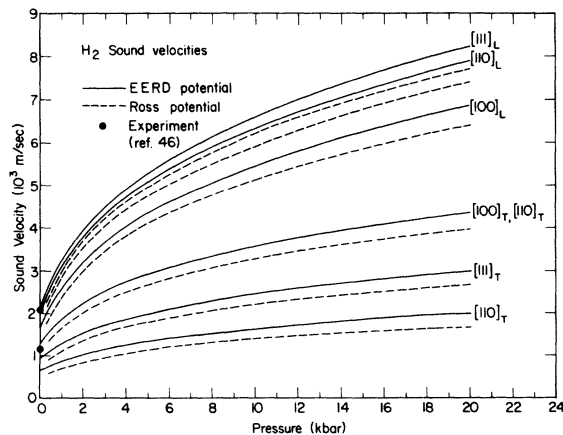


FIG. 8. Parahydrogen sound speeds in the [111], [110], and [100] directions. Solid lines were calculated with the EERD potential and the dashed lines were calculated with the Ross potential. Experimental points are from Ref. 46 and represent polycrystalline parahydrogen sound velocities.

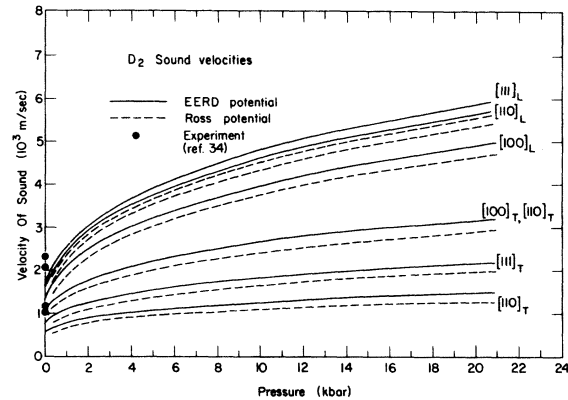


FIG. 9. Orthodeuterium sound speeds in the [111], [110], and [100] directions. Solid lines were calculated with the EERD potential and the dashed lines were calculated with the Ross potential. Experimental points are from Ref. 34 and represent hcp orthodeuterium sound velocities at $5.4 \text{ }^\circ\text{K}$.

for parahydrogen and orthodeuterium. The potential was in fact designed for investigation of the very high-pressure properties of the hydrogen isotopes, in the neighborhood of the metal-insulator transition pressure. Figure 11 shows that the pressures calculated at $V = V_0$ using the Ross potential are approximately 0.33 kbar for both H_2 and D_2 . At pressures above 15 kbar Ross's potential predicts pressures in as good agreement

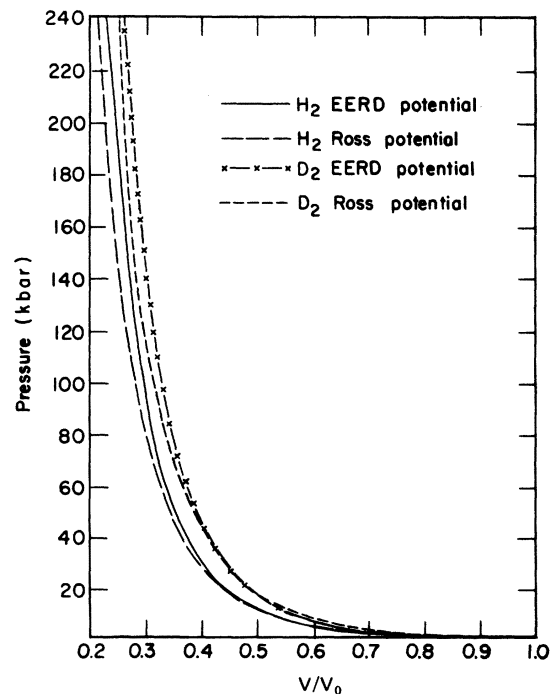


FIG. 10. Calculated pressure vs reduced volume for both parahydrogen and orthodeuterium.

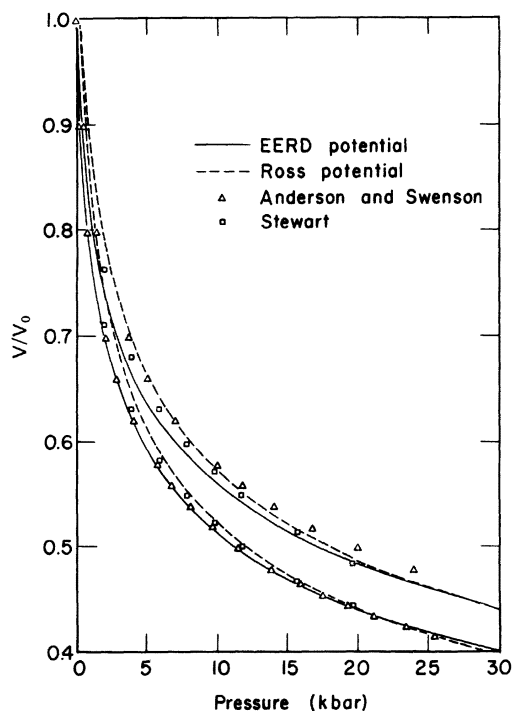


FIG. 11. Reduced volume vs pressure in the range $0 \leq P < 30$ kbar. Upper curves represent the deuterium results and the lower curves give the hydrogen results. Dashed and the solid lines were calculated with the Ross potential and the EERD potential, respectively. Triangles give the experimental results of Anderson and Swenson (Ref. 44). Squares are Stewart's data (Ref. 33).

with H_2 experiment as does the EERD potential. Between the pressures of 3 and 20 kbar Ross's potential predicts better pressure-volume results for D_2 than does the EERD potential. However, the bulk modulus results of Figs. 6 and 7 indicate that the Ross potential is too "soft." Therefore, in Fig. 10 the results calculated from the EERD potential are expected to provide a more realistic description of H_2 and D_2 than the results calculated from the Ross potential.

The two-body intermolecular potentials are commonly taken to be identical for parahydrogen and orthodeuterium. If this were the case, the EERD potential would be expected to yield better agreement than is actually observed with the deuterium results of Anderson and Swenson, since the agreement with their hydrogen results is excellent. The fact that Ross's potential gives best agreement with experiment for deuterium precisely in the region where its hydrogen predictions are the poorest leads us to agree with Anderson and Swenson that the two-body intermolecular potentials might be slightly different for these two solids.

England, Raich, and Etters³¹ have shown that

sudden transitions from spherically symmetric rotational states to orientationally dependent librational states occur in orthodeuterium and parahydrogen at pressures above several hundred kbar. At these high pressures the molecules cannot be accurately treated as free rotators and the spherically symmetric potentials we have used are no longer appropriate. For this reason we do not make any predictions of the metal-insulator transition pressure.

Figures 12 and 13 show the calculated ground-state energies for parahydrogen. The low-pressure weakness of the Ross potential is again seen in Fig. 12 where the binding energy/molecule for hydrogen at the zero-pressure volume is $-65^\circ K$. Experimental values range from -93.47 to $-101^\circ K$.⁴⁵ The EERD potential predicts a value of $-98.6^\circ K$ at $V = V_0$ in good agreement with experimental hydrogen results.

Sound velocities in the three symmetry directions [111], [110], and [100] are shown in Figs. 8 and 9 for parahydrogen and orthodeuterium, respectively. The EERD potential predicts somewhat larger sound velocities than does Ross's potential. Unfortunately, there is very little experimental data available for comparative purposes.

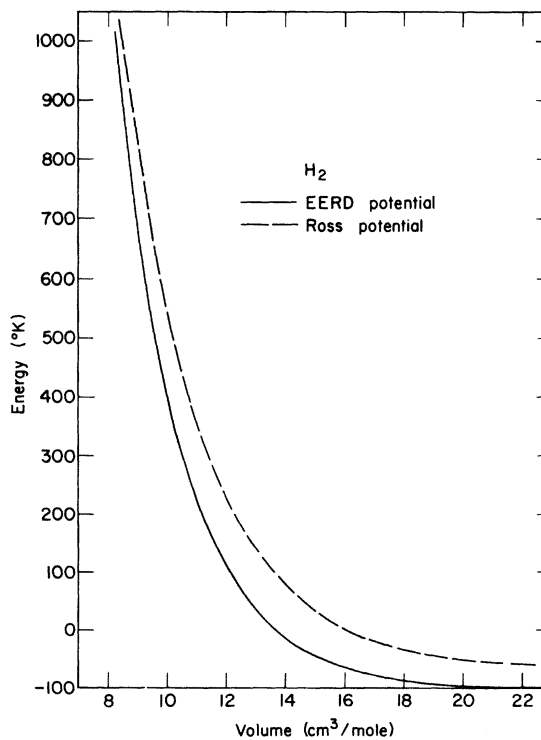


FIG. 12. Parahydrogen ground-state energy vs molar volume for $8 < V < 22.65$ $cm^3/mole$. Dashed and solid lines were calculated using the Ross potential and EERD potential, respectively.

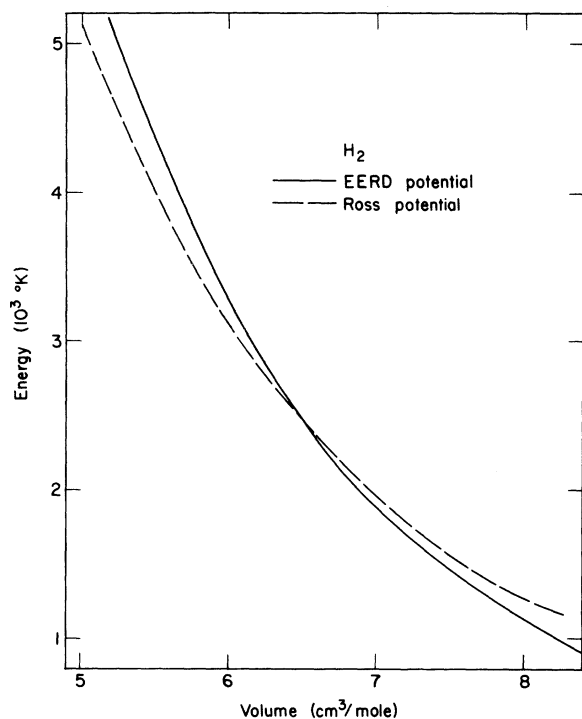


FIG. 13. Parahydrogen ground-state energy vs molar volume for $8.5 > V > 5$ cm^3/mole . Dashed and solid lines were calculated using the Ross potential and EERD potential, respectively.

The zero-pressure experimental results are shown in the figures. The sound velocities of Bezuglyi, Plakhotin, and Tarasenko⁴⁶ were measured with ultrasonic waves in polycrystalline parahydrogen and are therefore average velocities. Nielsen³⁴ measured the phonon dispersion curves with coherent neutron scattering in single crystals of hcp parahydrogen and orthodeuterium at 5.4 °K. Using a third-nearest-neighbor force model he then calculated the sound velocities shown in the figures. No experimental sound velocities appear to be available at the present time in the region the face-centered cubic structure is expected.

Previous authors have used the harmonic approximation to compute the zero-degree isotherm⁴⁷ and recently⁴⁸ to compute sets of parameters for the Lennard-Jones and Buckingham potentials that would satisfy Stewart's data. To test the validity of this approach we calculated the trace of the nearest-neighbor displacement-displacement correlation both self-consistently and harmonically for H_2 using the EERD potential. The square root of the trace of the displacement-displacement correlation divided by the nearest-neighbor distance was found to decrease with increasing density. At

zero pressure this ratio in the self-consistent approximation is approximately 25%, while in the harmonic approximation it is infinite. The harmonic approximation gives higher values of this ratio than the self-consistent approximation over all pressures considered; however, at pressures greater than 10 kbar the difference is nearly zero. This leads us to agree with the authors of Ref. 47, at least for pressures greater than 10 kbar, that the short-range correlations may be adequately accounted for in the harmonic approximation.

V. CONCLUSIONS

We have calculated the zero-degree isotherms for parahydrogen and orthodeuterium, as well as various lattice-dynamical quantities such as sound velocities, phonon density of states, and ground-state energies for solid para- H_2 and ortho- D_2 . We have also determined the bulk moduli. Our pressure-volume results appear to be in better agreement with experiment than several other recent calculations.^{47, 49-52} The most important contribution to the improved results is no doubt due to the forms of the intermolecular potentials studied. The potential due to England *et al.* was found to give better agreement with experimental static pressure volume results for parahydrogen than the potential suggested by Ross. Ross's potential appears to fit more closely the results for orthodeuterium although the potential does exhibit some weaknesses at densities corresponding to zero pressure, as well as predicting less accurate bulk moduli. A comparison of the hydrogen and deuterium results for the two potentials investigated suggests that the two-body intermolecular potentials might be somewhat different for these two solids.

By examining the rms displacements of the molecules we have verified that the classical harmonic approximation may be used at pressures greater than about 10 kbar to calculate lattice-dynamical properties of parahydrogen.

It is hoped that this work will stimulate further experimental work on solid molecular hydrogen.⁵³ In particular, more accurate values of the sound velocities or a determination of the dispersion relations for the fcc phase would be very helpful in the determination of intermolecular potentials for hydrogen and deuterium.

ACKNOWLEDGMENT

The authors wish to thank Dr. T. R. Koehler for suggesting the use of Horner's short-range correlation function.

- *Work supported by the National Science Foundation.
 †Supported by Associated Western Universities, Inc.
 ‡Work performed under the auspices of the U.S. Energy Development and Research Administration.
- ¹N. W. Ashcroft, *Phys. Rev. Lett.* **21**, 1748 (1968).
 - ²M. Ross, *J. Chem. Phys.* **60**, 3634 (1974).
 - ³E. Wigner and H. B. Huntington, *J. Chem. Phys.* **3**, 764 (1935).
 - ⁴B. L. Holian, thesis (University of California/Livermore (1972) (unpublished); University Microfilm, 3009 N. Zebe Rd., Ann Arbor, Michigan. Also Lawrence Livermore Laboratory report UCRL-51286 (unpublished).
 - ⁵R. Kronig, J. DeBoer, and J. Korringa, *Physica (Utr.)* **12**, 243 (1946).
 - ⁶W. J. Carr, *Phys. Rev.* **129**, 219 (1962).
 - ⁷G. A. Neece, F. J. Rogers, and W. G. Hoover, *J. Comput. Phys.* **7**, 621 (1971).
 - ⁸M. VanThiel, M. Ross, L. B. Hord, A. C. Mitchell, W. H. Gust, M. D'Addario, R. N. Keeler, and K. Bontwell, *Phys. Rev. Lett.* **31**, 979 (1973).
 - ⁹M. VanThiel, L. B. Hord, W. H. Gust, A. C. Mitchell, M. D'Addario, K. Bontwell, E. Wilbarger, and B. Barrett, *Phys. Earth Planet Inter.* **9**, 57 (1974).
 - ¹⁰A. A. Abrikosov, *Astron. Z.* **31**, 112 (1954).
 - ¹¹V. P. Trubitsyn, *Fiz. Tverd. Tela* **8**, 862 (1966) [*Sov. Phys.-Solid State* **8**, 688 (1966)].
 - ¹²B. J. Davydov, *Trudy Geofiz. Inst. Akad. Nauk SSSR* **26**, 86 (1953).
 - ¹³W. C. DeMarcus, *Astrophys. J.* **63**, 2 (1958).
 - ¹⁴W. B. Hubbard and R. Smoluchowski, *Space Sci. Rev.* **14**, 599 (1973).
 - ¹⁵J. Nuckols, J. Emmett, and L. Wood, *Phys. Today* **26**, 46 (1973).
 - ¹⁶F. W. DeWette, L. H. Nosanow, and N. R. Werthamer, *Phys. Rev.* **162**, 824 (1967).
 - ¹⁷N. R. Werthamer, *Ann. J. Phys.* **37**, 763 (1969); *Phys. Rev. B* **1**, 572 (1970).
 - ¹⁸L. H. Nosanow and N. R. Werthamer, *Phys. Rev. Lett.* **15**, 618 (1965).
 - ¹⁹L. H. Nosanow, *Phys. Rev.* **146**, 120 (1966).
 - ²⁰M. L. Klein and G. H. Horton, *J. Low Temp. Phys.* **9**, 151 (1972).
 - ²¹F. W. DeWette and B. R. A. Nijboer, *Phys. Lett.* **18**, 19 (1965).
 - ²²M. L. Klein and T. R. Koehler, *Phys. Lett. A* **33**, 253 (1970).
 - ²³M. Nielsen and H. B. Moller, *Phys. Rev. B* **3**, 4383 (1971).
 - ²⁴N. S. Gillis, T. R. Koehler, and N. R. Werthamer, *Phys. Rev.* **175**, 1110 (1968).
 - ²⁵N. S. Gillis, N. R. Werthamer, and T. R. Koehler, *Phys. Rev.* **165**, 951 (1968).
 - ²⁶M. L. Klein and T. R. Koehler, *J. Phys. C* **3**, L102 (1970).
 - ²⁷T. R. Koehler, *Phys. Rev. Lett.* **18**, 654 (1967).
 - ²⁸A. K. McMahan, H. Beck, and J. A. Krumhansl, *Phys. Rev. A* **9**, 1852 (1974).
 - ²⁹W. England, R. Etters, J. Raich, and R. Danilowicz, *Phys. Rev. Lett.* **32**, 758 (1974).
 - ³⁰J. C. Raich and R. D. Etters, *J. Low Temp. Phys.* **6**, 229 (1972).
 - ³¹W. England, J. C. Raich, and R. D. Etters (unpublished).
 - ³²G. A. Mansoori and F. B. Canfield, *J. Chem. Phys.* **51**, 4958 (1969).
 - ³³J. W. Stewart, *J. Phys. Chem. Solids* **1**, 146 (1956).
 - ³⁴M. Nielsen, *Phys. Rev. B* **7**, 1626 (1973).
 - ³⁵S. C. Durana and J. P. McTague, *Phys. Rev. Lett.* **31**, 990 (1973).
 - ³⁶C. Barrett, L. Meyer, and J. Wasserman, *J. Chem. Phys.* **45**, 824 (1966).
 - ³⁷H. Horner, *Z. Phys.* **242**, 432 (1971).
 - ³⁸D. J. Chadi and M. L. Cohen, *Phys. Rev. B* **8**, 5747 (1973).
 - ³⁹D. C. Wallace, *Thermodynamics of Crystals* (Wiley, New York, 1972).
 - ⁴⁰J. C. Raich, N. S. Gillis, and A. B. Anderson, *J. Chem. Phys.* **61**, 1399 (1974).
 - ⁴¹G. Gilat and L. J. Raubenheimer, *Phys. Rev.* **144**, 390 (1966).
 - ⁴²H. M. Roder, G. E. Childs, R. D. McCarty, and P. E. Angerhofer, NBS Technical Note 641, available as Catalogue No. C13.46:641 from the Superintendent of Documents, U.S. Government Printing Office, Washington, D. C.
 - ⁴³J. L. Yarnell, R. L. Mills, and A. F. Schuch (unpublished).
 - ⁴⁴M. S. Anderson and C. A. Swenson, *Phys. Rev. B* **10**, 5184 (1974).
 - ⁴⁵A. W. Wolley, R. R. Scott, and F. G. Brickwedde, *J. Res. Natl. Bur. Stand. (U.S.)* **41**, 379 (1948).
 - ⁴⁶P. A. Bezuglyi, R. O. Plakhotin, and L. M. Tarasenko, *Fiz. Tverd. Tela* **13**, 309 (1971) [*Sov. Phys.-Solid State* **13**, 250 (1971)].
 - ⁴⁷E. L. Pollock, T. A. Bruce, G. V. Chester, and J. A. Krumhansl, *Phys. Rev. B* **5**, 4180 (1972).
 - ⁴⁸L. V. Meisel and J. F. Cox, *Phys. Rev. B* **11**, 1762 (1975).
 - ⁴⁹J. A. Krumhansl and S. Y. Wu, *Phys. Rev. B* **5**, 4155 (1972).
 - ⁵⁰T. A. Bruce, *Phys. Rev. B* **5**, 4170 (1972).
 - ⁵¹R. D. Etters, J. C. Raich, and P. Chand, *J. Low Temp. Phys.* **5**, 711 (1971).
 - ⁵²R. D. Etters and R. L. Danilowicz, *Phys. Rev. A* **9**, 1698 (1974).
 - ⁵³R. L. Mills, D. H. Liebenberg, and J. C. Bronson, *J. Chem. Phys.* **63**, 1198 (1975).