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PIMC simulations of solid parahydrogen

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We have evaluated the kinetic energy of the center of mass of solid parahydrogen at $T=18.9$ K, and four different densities, by means of path-integral Monte Carlo computer simulation, using the pairwise additive Lennard-Jones potential. The results have been compared with the available experimental neutron data of Herwig *et al.* [Phys. Rev. B **41**, 96 (1990)]. The agreement between experiment and simulation is excellent for the kinetic energy but not as good for the pressure. There are indications that the use of a more realistic pair potential would increase the agreement with the experimental pressure data without destroying that of the kinetic energy.

I. INTRODUCTION

The momentum distribution of atoms, in quantum solids and liquids, can be determined with good precision using deep inelastic neutron scattering.[1] This experimental technique, which is characterized by a large momentum transfer Q, has now become more widely available with the recent development of the intense spallation neutron sources at Argonne National Laboratory (USA) and at Rutherford Appleton Laboratory (UK). For instance, the momentum distribution of liquid helium has been determined experimentally by many authors at different temperatures and densities.[2]

Because of its large (incoherent) scattering cross section hydrogen is the ideal candidate, among quantum solids, for a deep-inelastic-neutron-scattering experiment. Due to its relatively high compressibility, it is also not difficult to determine its properties over a relatively large range of densities. Recently, Langel *et al.*[3] have performed a deep-inelastic-neutron-scattering experiment on solid molecular hydrogen (at 10 K and a pressure of 0.1 MPa). The experiment was then extended to a larger density range by Herwig *et al.*[4] who designed a sample cell allowing to reach pressures up to 200 MPa at a temperature of $T=18.9$ K. From the experiments the average translational kinetic energy of molecular, almost pure ($\cong 99.8\%$), parahydrogen was derived and reported as a function of density in the interval $\rho=25.96-35.42$ molecules/nm^3. The experimental results were compared with the variational calculation on solid hydrogen in the ground state by Bruce,[5] and fair overall agreement was found.

Bruce's aim had been to give an equation of state for compressed solid hydrogen, and therefore the explored density interval was quite large, covering an estimated pressure range extending from 0 to $\sim 10^{10}$ Pa at $T=0$ K. The calculation used a variational Monte Carlo (MC) technique, which is a very powerful approach to the problem but, in principle, can only give an upper bound to the total energy, with the accuracy of the results depending on the quality of trial function.[6] In order to keep the calculations manageable, Bruce also introduced a number of simplifying assumptions: intramolecular interactions were assumed to be pairwise additive and spherically symmetric, particles were assumed to be distinguishable, and the model systems studied were rather small ($N=256$). In addition, the crystal lattice was assumed to be fcc, whereas solid hydrogen is now known to be hcp,[7] and because of the uncertainty in the intermolecular potential only intermediate length MC runs were performed, resulting in rather large uncertainties of the numerical results. In fact, the computed kinetic energy shows quite appreciable fluctuations in the overall density range (cf. Fig. 2 of Ref. 5). Thus, Bruce's calculations, although impressive at the time, do not reflect the recent advances in computer technology and simulation techniques, which, at present, allow direct calculations of at least some properties of quantum systems even at finite temperatures.

It should also be pointed out that, while most of the hydrogen experiment[4] was performed at 18.9 K, the comparison was done with a calculation performed at $T=0$ K, since it is generally assumed that close enough to the ground state the temperature dependence of the kinetic energy of the solid is negligible for all practical reasons. This assumption was largely based on the high value of the Debye temperature (>100 K) of solid hydrogen in this density range.[4] However, a temperature of 18.9 K corresponds to about half the well depth of the intermolecular potential, and therefore the system cannot be assumed *a priori* to be very close to the ground state. Moreover, noting that the reported error bars are of the same order of magnitude as the *classical* kinetic energy of the center of mass at the experimental temperature, it appears desirable to compare the experiment with more refined calculations.

The availability of proper calculations would also be an incentive for improving the accuracy of the experiments (and vice versa) and, by allowing a truly quantitative comparison, contribute to a deeper understanding of the physics of condensed matter in this extreme temperature region where quantum behavior becomes dominant. As a matter of fact, from the lowest density result of Herwig *et al.*,[4] it seems to us that the accuracy of the experiment can be increased, and therefore we have decided to perform a series of path-integral Monte Carlo (PIMC) simulations,[8] to calculate the translational kinetic energy of solid parahydrogen at the same thermodynamic states where the experiment was done. Another motivation for performing these simulations was the desire to demonstrate that the primitive algorithm, which is fairly straightforward to implement and has been shown to be convenient and useful in simulations of almost classical fluids and solids,[9] is much more widely applicable and may even be used to study quite strongly quantum mechanical N-body systems, provided that suitable extrapolations can be made. It should be recognized, however, that in order to utilize the full power of PIMC, such as for the prediction of the λ anomaly in the specific heat of liquid helium by Ceperley and Pollock,[10] more sophisticated algorithms may be necessary.

II. SIMULATIONS

In our calculations, the intermolecular potential for solid parahydrogen was assumed to be pairwise additive and, in accordance with the available experimental information,[7] the crystal lattice was assumed to be hcp. For molecular hydrogen, several specific pair potentials obtained either from *ab initio* calculations and/or fitting the experimental data, have been suggested in the literature, but in order to be able to compare our results with Bruce's calculations we decided, for the time being, to work mainly with the same (6–12) Lennard-Jones (LJ) potential with $\varepsilon/k_B=36.7$ K and $\sigma=0.2959$ nm. As a check on the quantitative dependence of the results on the choice of the potential, one of the simulations was duplicated using a more realistic model, namely the pair potential given by Norman, Watts, and Buck.[11] Since the molecular wave function for parahydrogen in the ground level ($v=0$, $J=0$) is spherically symmetric and this feature seems to be conserved even in the condensed phase (at least at not too high density), only the spherical component of the Norman, Watts, and Buck potential was used in that simulation.

The number of particles was $N=180$ in all our simulations. Although relatively small, this number should be sufficient to describe single-particle properties such as the kinetic energy, which is our main concern here. The particles were assumed to obey Boltzmann statistics. The reason for this choice, apart from the desire to keep the PIMC program simple, was mainly based on the results of a calculation by Poll and Miller,[12] who solved the Schrödinger equation for a pair of hydrogen molecules and showed that the exchange contribution to the radial distribution function is negligible above 10 K, and less than 1% at 5 K.

The number of beads on the ring polymers (Trotter number), which are equivalent to the quantum particles in the classical isomorphism[13] was varied from $P=8$ to 32 (and in one instance up to $P=64$). Our program is a straightforward implementation of the primitive PIMC algorithm, except that the "intramolecular" coordinates of the polymer were sampled directly from a multivariate Gaussian distribution. Thus, each Monte Carlo move consisted of a trial set of "intramolecular" positions and a random displacement of the "center of mass," and was accepted or rejected according to the usual Metropolis criterion. The total energy was calculated using the

TABLE I. Simulation parameters for solid hcp LJ parahydrogen at $T=18.9$ K. The number of particles was always $N=180$. The numbers in parentheses are relative to the potential function of Ref. 11. Each run consisted of $5000\times N_M$ passes.

ρ (nm^{-3})	Box dimensions (nm)	Δ^a (nm)	$N_M{}^b$	P	$x_A{}^c$	R^d (nm)
28.27	$a=1.842$	0.03	5	8	0.1353	0.0462
	$b=1.915$			16	0.1336	0.0469
	$c=1.805$			32	0.1325	0.0470
					(0.1948)	(0.0476)
				64	0.1334	0.0470
30.88	$a=1.789$	0.02	10	8	0.0933	0.0439
	$b=1.859$			16	0.0877	0.0448
	$c=1.753$			32	0.0883	0.0449
33.09	$a=1.748$	0.01	10	8	0.0616	0.0419
	$b=1.817$			16	0.0562	0.0429
	$c=1.713$			32	0.0569	0.0431
35.42	$a=1.709$	0.01	30	8	0.0348	0.0397
	$b=1.776$			16	0.0308	0.0408
	$c=1.674$			32	0.0308	0.0411

[a] Maximum displacement cube edge length.

[b] Number of passes skipped between analyzed configurations (dilution factor).

[c] Average acceptance ratio.

[d] rms spread (radius of gyration) of ring polymers.

"crude" energy estimator.[9]

Initial configurations were created by stacking together $5\times3\times3$ copies (containing four particles each) of the nonprimitive orthogonal unit cell of the hcp lattice. This results in an almost cubical simulation box (cf. Table I) to which periodic boundary conditions were applied. All interactions were truncated spherically at a cutoff equal to half the minimum edge length of the box, and potential energies and pressures were corrected by integrating over a uniform density beyond the cutoff. We have verified that summing over an hcp lattice instead yields long-range corrections which differ only by a few J/mol and atm, respectively.

The thermodynamic conditions and the details of our PIMC simulations are summarized in Table I. All calculations were performed at a temperature of 18.9 K and the densities were chosen to match the experimental conditions of Ref. 4. Each simulation was started from a perfect hcp lattice and consisted of $5000\times N_M$ passes (=moves per particle), after a $1000\times N_M$ passes equilibration stage. N_M is the "dilution factor," i.e., the number of passes performed before analyzing the next configuration. Thus averages were accumulated using 5000 configurations out of each run. x_A is the acceptance ratio, i.e., the fraction of accepted trial moves. Its values in Table I are rather low and decrease rapidly with increasing density. This is so because our PIMC program was originally optimized for systems at fluid densities. In dense, strongly quantum mechanical systems, where the effective distribution of "intramolecular" coordinates is quite different from the free-particle form, our direct sampling becomes increasingly less efficient, and an algorithm based on single-bead moves might have been more economical. We have, therefore, chosen the dilution factor such that the product of x_A and N_M is roughly the same for all simulations, i.e., a comparable number of *accepted* moves have been performed.

The entry in the last column of Table I is the rms spread of the classical ring polymer. It is interesting to note that the size, or dispersion, of the quantum particle decreases slowly as density increases. To our knowledge, this is the first, direct, microscopic corroboration of a principle invoked by several authors:[4,5,14–16]". . . as the solid becomes more compressed at lower molecular volumes one would like to observe a region where the solid becomes more 'classical'. . .".[4]

III. RESULTS AND DISCUSSION

The results of our simulation are listed in Table II. In order to study the rate of convergence of the results from classical to quantum mechanical behavior, the number of intermediate states (beads) was varied from 8 to 32 for all thermodynamic states. Obviously, the results cannot be claimed to have fully converged even for $P=32$, but an extrapolation in $1/P$ is possible, and as a partial check on such a procedure we have also simulated the lowest density state using $P=64$. The dependence of the computed translational kinetic energy $\langle K_{\mathrm{tr}}\rangle$ on $1/P$ is shown in

TABLE II. PIMC results for energy and pressure of solid hcp LJ parahydrogen at $T=18.9$ K. The numbers marked "$P=\infty$" have been obtained by linear extrapolation as a function of $1/P$. The numbers in parentheses are relative to the potential function of Ref. 11.

ρ (nm^{-3})	P	28.27	30.88	33.09	35.42
Kinetic energy (K)	8	73.66	83.66	93.12	103.36
	16	84.40	97.93	110.92	125.60
	32	90.10	105.46	119.96	137.17
		(83.78)			
	64	92.17			
	∞	95.1	112.6	128.9	148.3
	Expt.[a]	101±8	122±14	131±14	146±11
Potential energy (kJ/mol)	8	−1.528	−1.663	−1.747	−1.805
	16	−1.504	−1.619	−1.688	−1.725
	32	−1.488	−1.601	−1.663	−1.688
		(−1.443)			
	64	−1.485			
	∞	−1.477	−1.579	−1.634	−1.648
Pressure (atm)	8	17.9	225.5	535.1	1014.2
	16	89.7	368.0	741.6	1309.3
	32	133.8	426.4	828.3	1442.5
		(185.4)			
	64	146.3			
	∞	167	498	932	1590
	Expt.[b]	238	576	983	1551

[a] From Ref. 4.

[b] From Ref. 18.

Fig. 1. As can be seen, the data fall nicely on straight lines and the extrapolation for $P \rightarrow \infty$ is readily performed. From these graphs we infer that the probable error margins on our extrapolated values can at most be a few degrees kelvin. The potential energies and pressures were treated in an analogous way, and the extrapolated values for translational kinetic energy, potential energy, and pressure are also included in Table II.

Figure 2 compares the kinetic energies with the experimental data[4] and with the ground-state calculations by Bruce.[5] Bearing in mind that the LJ potential was not fitted to the solid but to high-temperature gas-phase data (B_2),[17] the agreement between PIMC and experiment is surprisingly good: our extrapolated values are well within the error bars and perfectly consistent with the experimental data over the whole range of densities studied. The experimental results seem to increase just slightly less rapidly with density, but this is not significant at the present level of accuracy. The figure also demonstrates the necessity of actually performing the limit $P \rightarrow \infty$, as the values for finite P are systematically too low.

Our kinetic energies also represent a plausible interpolation through Bruce's (somewhat scattered) results for $T=0$ K. Thus, at $T=18.9$ K the kinetic energy is still basically that of the ground state, and Herwig *et al.* were justified (given the mutual uncertainties) in comparing their results with calculations at $T=0$ K. We have now shown that the experimental data may even be predicted quantitatively, by simulations pertaining to the correct temperature, using the simple Lennard-Jones potential for H_2.

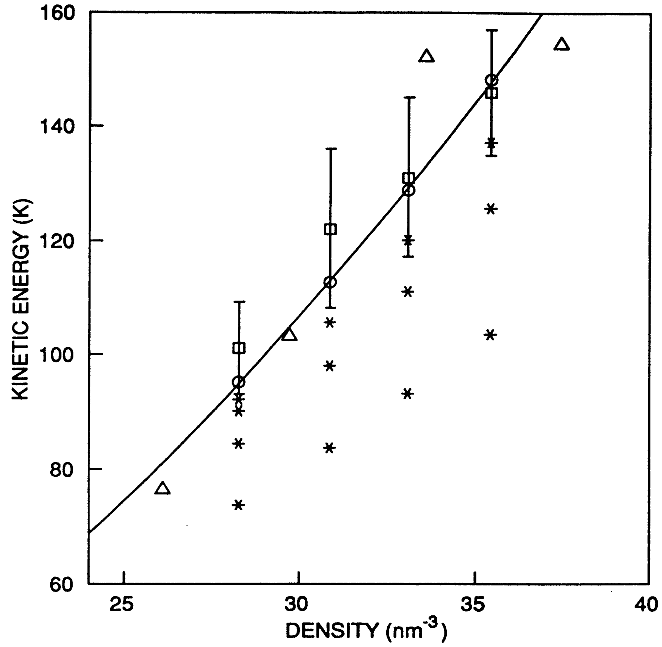

FIG. 2. Comparison between theoretical and experimental data for the kinetic energy of solid parahydrogen at $T=18.9$ K. The squares with error bars are the experimental data of Ref. 4; the stars represent the various PIMC results obtained for finite values of the Trotter number P; the circles are the extrapolated values for $P \rightarrow \infty$; and the triangles refer to the ground-state calculations of Bruce (Ref. 5). The full line is a quadratic fit to the extrapolated PIMC values.

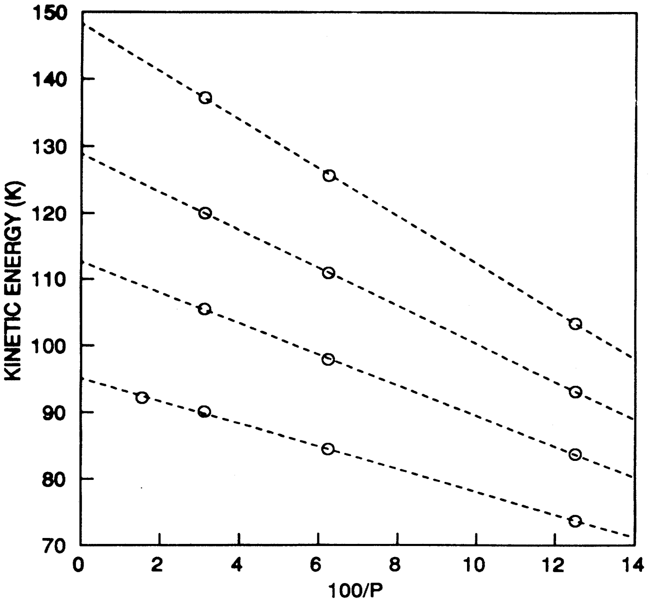

FIG. 1. Behavior of the computed kinetic energy, K_{tr}, for solid parahydrogen at 18.9 K, as a function of $1/P$, the reciprocal of the Trotter number. The densities are (from top to bottom) $\rho=35.42$, 33.09, 30.88, and 28.27 nm^{-3}. The dashed lines are linear extrapolations, and the values for $P \rightarrow \infty$ are given in Table II.

For the pressure, shown in Fig. 3, we again find substantial agreement between PIMC and Bruce's results, with our data being slightly higher, which is not unreasonable in view of the difference in temperature. The fact that we have used a slightly smaller system and a hcp lattice is probably not significant. When compared with the experimental equation of state for parahydrogen given by Driessen and Silvera,[18] the predictions of the LJ model are quite good, and in fact much better than what one is usually willing to accept from simulations: On the average, the pressure is almost quantitatively correct but rises too steeply at higher densities. This deficiency has been noted before[5] and attributed to the unrealistically harsh repulsion of the (6-12) LJ potential. Thus, for quantitative predictions of the equation of state a more sophisticated interaction may be necessary.

Since our primary goal was the kinetic energy, which is adequately reproduced by the LJ model, we limited the investigation of more realistic interactions to a single simulation with the spherical part of the pair potential proposed by Norman, Watts, and Buck.[11] This was a repetition of the lowest density run using $P=32$ beads. The results are given in parentheses in Table II, and the pressure is found to be somewhat higher, and the kinetic energy somewhat lower, than for the LJ model. If the ex-

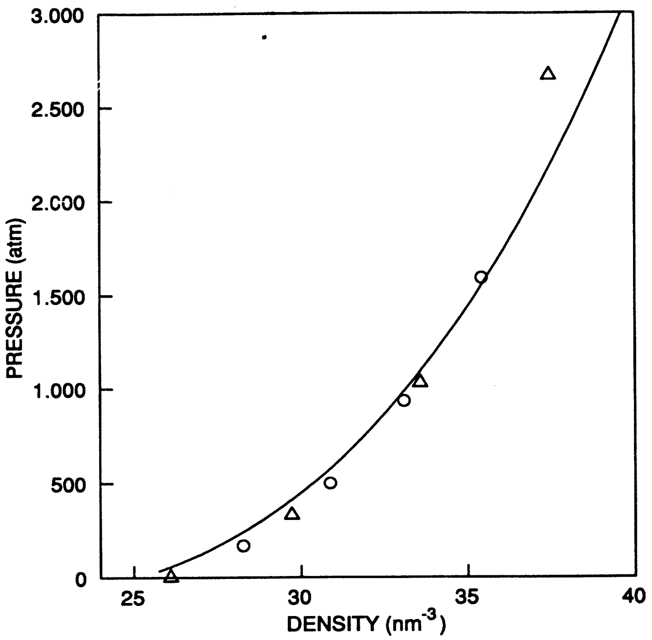

FIG. 3. Comparison between theoretical and experimental data for the pressure of solid parahydrogen at 18.9 K. The circles are the PIMC values extrapolated for $P \to \infty$. The triangles are the ground-state results by Bruce (Ref. 5). The solid line represents the experimental equation of state given by Driessen and Silvera (Ref. 18).

trapolated values may be assumed to undergo the same fractional changes as the 32-bead system, the pressure predicted by the Norman, Watts, and Buck potential for the lowest density state would be around 230 atm, which compares quite favorably with the experimental value of 238 atm, while the predicted kinetic energy would just be slightly outside the experimental error bars. Due to its softer repulsion we expect the pressure for the Norman, Watts, and Buck potential at very high densities to be below the LJ values. Thus a carefully tailored "realistic" potential might considerably improve the agreement with the experimental equation of state without spoiling the almost perfect results for the kinetic energy.

It would be very interesting to investigate the dependence of thermodynamic (and other) properties on the form of the intermolecular potential in more detail. In fact, in our calculations we have completely neglected irreducible many-body properties, which might be responsible for the small discrepancies between the simulations and the experiment. However, from translational light scattering experiments[19,20] we know that these many-body effects are usually associated with strongly polarizable systems[21] and can, therefore, be responsible for small corrections only. Thus, it is gratifying to note that even the use of a realistic *pair* potential already narrows the gap between experimental and theoretical physical-vapor-transport data. For a critical assessment of the kinetic energies more accurate experimental results, covering a wider temperature and density range, would be desirable.

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