

Equation of State of Solid ^3He

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We present results of diffusion Monte Carlo calculations for the bcc and hcp phases of solid ^3He , using a recent *ab initio* interatomic potential, including two- and three-body terms. This potential is found to yield an equation of state for condensed ^4He in excellent agreement with experiment, in a wide density range. For ^3He , we find a systematic discrepancy, worth 0.7 K, between our computed equation of state and a commonly accepted experimental one. We attribute such a discrepancy to an improper choice of reference energy in the determination of the experimental equation of state.

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Although solid helium is arguably the simplest realization of a quantum crystal, its phase diagram is surprisingly rich [1,2]. Obtaining a satisfactory theoretical equation of state (EOS) for this archetypal quantum solid is both a long standing problem and a worthwhile objective, not only for its intrinsic interest and its broad relevance to solid state physics, but also as a cogent test of the most accurate theoretical many-body techniques and interatomic potentials currently available.

Particularly interesting is the case of ^3He . Previous studies of the EOS of bcc and hcp ^3He , mostly based on variational calculations, have yielded only *qualitatively* accurate results [3,4]. Interestingly, theoretical predictions obtained with similar computational methods are much closer to experiment for the ^4He than the ^3He crystal (Fig. 1). This is undoubtedly surprising, considering the relatively small mass difference and the negligible energy contribution of quantum statistics in the solid phase. It is not clear to what extent this state of affairs may be attributed to the variational wave functions and/or the interatomic potentials utilized in the various studies. Therefore, a reliable calculation, based on a robust computational method and accurate interatomic forces, is a necessary step for making progress in this problem.

In this Letter, we present results of diffusion Monte Carlo (DMC) calculations for the ground state of solid ^3He . DMC projects the eigenstate with the lowest eigenvalue out of a trial wave function Ψ . It has been adopted to investigate ground state properties of a variety of quantum fluids and solids; results for the energy are usually very accurate and largely insensitive to the details of the trial wave function chosen [7]. We compute by DMC the solid ^3He EOS in both the bcc and hcp structures, at $T = 0$. We use an accurate *ab initio* interatomic potential, featuring a two-body [8] and a three-body [9] term; in order to assess its reliability, we also compute the EOS of condensed ^4He , both in the liquid and in the hcp phases, and compare with experiments. In all solid simulations described here,

quantum statistics is neglected; this is the only approximation, which is quite reasonable and commonly made, as exchange energies in helium solids are very small (of the order of a mK) [10].

Our main findings are the following: (a) The potential utilized, which has no adjustable parameters, yields a ^4He EOS in remarkable agreement with experiment [11,12], over a wide range of densities, for both the liquid and crystalline phases. (b) For solid ^3He there is a large discrepancy between our computed EOS and a generally accepted experimental one [1,13,14]. We argue, however, that such a discrepancy is merely due to an incorrect reference value for the energy used to obtain the experimental EOS from measured quantities [14]. A proper value of the reference energy brings agreement between theory and experiment

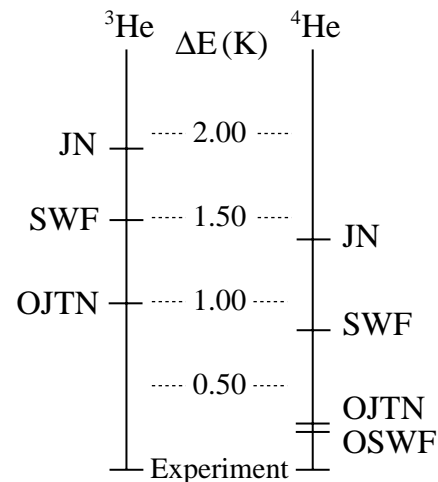


FIG. 1. Deviations of theoretical estimates of the ground state energy from the quoted experimental values in solid He close to the melting point. For ^4He : JN, Jastrow-Nosonow results from Ref. [3]; SWF, shadow wave function results from Ref. [5]; OJTN and OSWF, optimized JN + triplet and SWF from Ref. [6]. For ^3He : JN as for ^4He ; SWF results from Ref. [4]; OJTN, optimized JN+triplet result obtained in this work.

to the same level as for ^4He . We note that such a value for the reference energy had already been suggested some time ago [15], but has never been adopted in subsequent work on this subject.

We model a system of N helium atoms by means of the following microscopic Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i<j} v_2(r_{ij}) + \sum_{i<j<k} v_3(\mathbf{r}_{ij}, \mathbf{r}_{ik}, \mathbf{r}_{jk}). \quad (1)$$

The two-body interaction v_2 used here is the *ab initio* SAPT potential recently proposed by Korona *et al.* [8]. Although there is still some controversy about some of its fine details [16], the two-body part of the helium potential is one of the most intensely studied and best known interactions. A much greater source of uncertainty is the three-body term. The well-known Bruch-McGee (BM) potential, extensively discussed in the literature [17], features an attractive term, whose strength A has been typically adjusted to enforce agreement with experimental information, the optimal choice of A being strongly density dependent [18,19]. The three-body term v_3 adopted in this work is an analytical expression given by Cohen and Murrell (CM) [9], which extrapolates from energies computed fully *ab initio* for helium trimers in the isosceles geometry. We assume that the contribution to the energy from further many-body terms can be neglected. Our DMC simulations, for both helium isotopes in the various phases, have been carried out using an optimized trial wave function of the Jastrow-triplet-Nosanow (OJTN) form

$$\Psi(R) = e^{-\sum_{i<j} u(r_{ij}) - \sum_{i<j<k} u_3(\mathbf{r}_{ij}, \mathbf{r}_{ik}, \mathbf{r}_{jk}) - \sum_i C(\mathbf{r}_i - \mathbf{a}_i)^2}, \quad (2)$$

where $R = \{\mathbf{r}_1, \dots, \mathbf{r}_N\}$ are the coordinates of the N atoms. The $\{\mathbf{a}_i\}$ are the coordinates of a lattice of the proper symmetry (bcc or hcp) and density. For liquid simulations, $C = 0$. The two- and three-body pseudopotentials $u(r)$ and $u_3(r)$ have been taken of the form proposed in Ref. [20], and have been optimized, together with the parameter C , for each thermodynamic point considered.

We performed calculations for ^3He in the range of molar volumes between 12 and 25 cc/mol, for the bcc and the hcp phases of the crystal, and for ^4He between 17 and 31 cc/mol, for the hcp crystal and the liquid. The variational estimate of the ground state energy per atom for solid ^3He at the melting point ($T = 0$), given by the trial wave function (2) with the Hamiltonian (1), is shown in Fig. 1. The DMC calculation performed here is standard (see, for instance, [7]). In our simulations the energy contribution ϵ_3 due to the three-body potential v_3 was computed perturbatively, as illustrated in Ref. [21]. This improves considerably the computational efficiency, with no significant

loss of accuracy, at least in the density range considered here; we explicitly verified this point by repeating a few calculations at the highest densities using the full Hamiltonian (1).

The results presented here pertain to simulations with a number of atoms equal to $N = 128$, for the liquid and solid bcc phase, and $N = 180$, for the solid hcp phase. Besides the energy per atom ϵ as a function of the molar volume v , we have also computed the kinetic energy per atom k , using the standard DMC extrapolated estimators [7]. This quantity is of particular interest, as it can be measured by neutron scattering experiments. Path integral Monte Carlo calculations for high-pressure helium have shown that k is mainly sensitive to the repulsive core of the two-body part of the interatomic potential [19]. The reported values for the total and kinetic energies have been extrapolated to zero time step [7].

We now examine our results in detail. In order to assess the accuracy of the interatomic potential utilized, we compare in Fig. 2 the DMC results for the $T = 0$ ^4He EOS (also listed in Table I) with experiment [11,12]. The agreement is remarkable, considering the extended density interval for which it holds, as well as the fact that the potential has no adjustable parameters. The largest deviation between our theoretically computed and the experimental curve occurs in the liquid phase, and even there it is quite small. For example, we find a value of the energy per atom at the equilibrium density at saturated vapor pressure (0.02186 \AA^{-3}) equal to -7.21 K , to be compared to the experimental -7.17 K [12]. One might argue that a similar agreement with experiment could already be obtained, at least for the liquid phase, by using a two-body potential such as, for example, an earlier version of the well-known Aziz potential [22] (see, for instance, Ref. 18)).

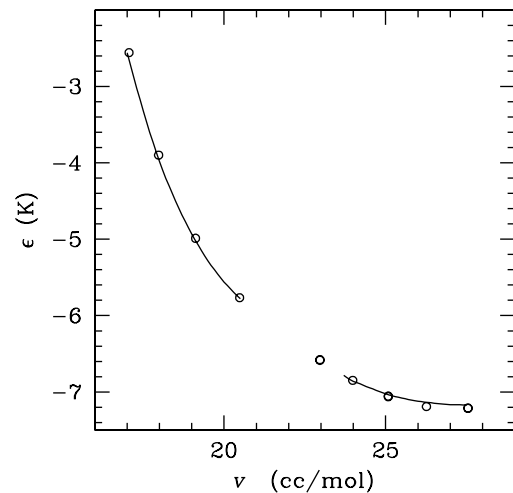


FIG. 2. DMC energy per ^4He atom (circles). Statistical errors are smaller than the symbol size. Solid lines are spline fits to experimental data (from Ref. [11] for the hcp region and Ref. [12] for the liquid region). Solid lines end at the coexistence zone, whose limits are taken from Ref. [15].

TABLE I. DMC energy per atom ϵ (in K) for ^4He in the liquid and hcp phases. Also shown is the single-particle kinetic energy k . Statistical errors (in parentheses) are on the last digits; when not explicitly indicated, the error is less than 1 on the last digit. Molar volumes (first column) are in cc/mol.

v	Liquid		v	hcp	
	ϵ	k		ϵ	k
30.66	-7.0866(15)	11.7	20.48	-5.7655(59)	25.1
27.55	-7.2100(22)	14.0	19.12	-4.9881(42)	28.4
25.08	-7.0615(36)	16.5	17.98	-3.8993(34)	31.4
22.97	-6.5769(59)	19.3	17.06	-2.558(12)	34.6

We note two points: the first is that the agreement with experiment obtained in this work extends over a much wider density range than that afforded by a two-body potential alone, well into the solid phase. Second, the inclusion of a realistic model for the three-body forces improves upon the predictions offered by the two-body potential, at *all* densities considered here. This is in marked contrast with earlier attempts to improve upon the physical description given by the two-body potential by including *phenomenological* three-body forces, which typically led to *poorer* agreement with experiment [18]. Within the molar volume range considered in this work, the CM three-body contribution to the total energy ϵ_3 is dominated by the repulsive triple-dipole Axilrod-Teller interaction, with only a tiny attractive exchange term showing up at the highest densities.

This is shown in Fig. 3 for the case of hcp ^3He , with similar trends being observed for bcc ^3He , as well as for liquid and hcp ^4He . The three-body repulsion compensates the overbinding given by the pair potential alone, resulting in the final agreement between the experimental and computed EOS of Fig. 2. For comparison we also show in Fig. 3 the BM three-body contribution, with the value of the parameter A given in Ref. [19]. The BM potential has a strongly attractive exchange term, which is clearly inconsistent with the experimental EOS. The results obtained for ^4He give us confidence in the reliability of the SAPT-CM interaction for a quantitative description of the physical properties of helium isotopes. We now turn to the main focus of our work, namely, the ^3He EOS. The results of the DMC calculations for ^3He are given in Table II and shown in Fig. 4. Although there is a clear improvement over previous calculations (since we used a virtually exact algorithm and a more sophisticated potential), a significant disagreement remains between our results and the EOS of Ref. [14], generally held as the reference experimental data.

Because a DMC simulation can occasionally get “stuck” in a metastable phase, induced by the trial function utilized, we have also performed a few numerical simulations based on path integral Monte Carlo (PIMC), an unbiased technique which does not rely on any *a priori* input, such as

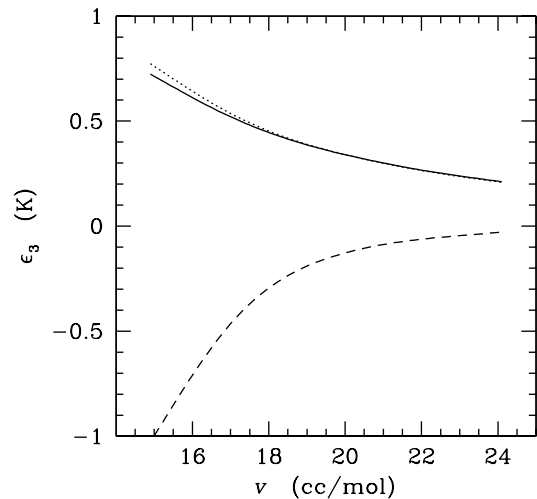


FIG. 3. Three-body contribution ϵ_3 to the ground state energy of ^3He according to three different models of the interaction potential v_3 . Dotted line, Axilrod-Teller; solid line, Cohen-Murrell; dashed line, Bruch-McGee.

Ψ [24]. PIMC results for $\epsilon(v)$ are in agreement with the DMC results, within the statistical uncertainties.

We have therefore undertaken a critical examination of the EOS of Ref. [14], which was produced by integrating the experimental constant- T pressure vs volume curve extrapolated at $T = 0$, $\epsilon(v) = \epsilon_0(v_0) + \int_{v_0}^v dv' p(v')$. Here $\epsilon_0(v_0) = -0.83$ K is the ground state energy at $v_0 = 23.5$ cc/mol, the melting molar volume of the bcc phase at $T = 1$ K. This value for $\epsilon_0(v_0)$ was found by taking the ^3He gas at zero pressure and $T = 1$ K as a reference state [14]. A similar procedure, using the liquid at zero pressure and zero temperature as a reference state, was carried out in Ref. [15]. The result, which we reproduced independently, is $\epsilon_0 = -0.13$ K, as opposed to -0.83 K of Ref. [14]. The corresponding EOS of solid ^3He , obtained with this different value of ϵ_0 , is shown by the dashed line in Fig. 4, and, as can be seen, it agrees remarkably well with our DMC results in the range of existence of the bcc crystal.

TABLE II. DMC energy per atom $\epsilon(v)$ (in K) for the bcc and hcp solid phases of ^3He . Also shown are the energy contribution ϵ_3 from the three-body potential and the single-particle kinetic energy k . Statistical errors are as in Table I. Molar volumes (first column) are in cc/mol.

bcc v	bcc			hcp		
	ϵ	ϵ_3	k	ϵ	ϵ_3	k
24.00	-0.3565(58)	0.211	23.6	-0.2548(83)	0.214	23.8
23.00	0.1685(51)	0.238	25.3	0.248(10)	0.239	25.4
22.00	0.8015(60)	0.265	27.2	0.8748(44)	0.267	27.4
21.00	1.5922(98)	0.299	29.4	1.653(11)	0.301	29.7
20.00	2.6897(59)	0.340	31.8	2.7217(97)	0.340	32.2
17.00	8.6289(67)	0.520	—	8.4833(52)	0.520	42.6
15.00	—	—	—	16.6106(96)	0.714	52.8

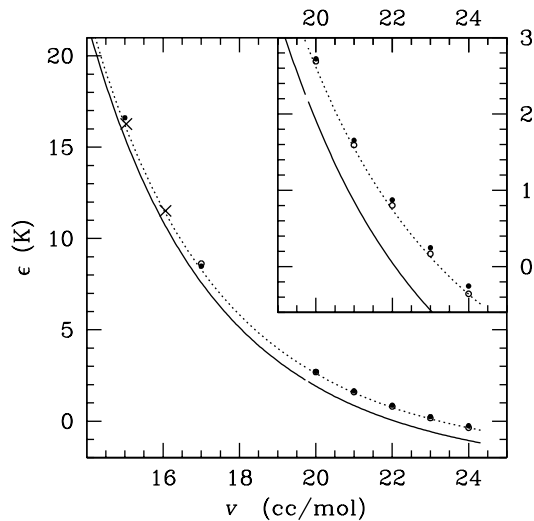


FIG. 4. DMC energy per ${}^3\text{He}$ atom, for a hcp (filled symbols) and for a bcc (open symbols) crystal. Statistical errors are smaller than symbol sizes. Solid (dashed) lines are experimental EOSs in the Murnaghan form, with parameters taken from Ref. [13], using different values for the reference energy $\epsilon_0(v_0)$. Crosses are experimental data for the hcp phase, from Ref. [23]. The inset shows an expanded view of the stability region of the bcc phase.

In Table I and Fig. 4, we also report on the results obtained for the hcp phase. A double tangent construction using cubic fits to the DMC energies gives a coexistence phase between $v_{\text{hcp}} = 19.13$ cc/mol and $v_{\text{bcc}} = 19.23$ cc/mol. Since the energies of the bcc and hcp phases are very close in the range of molar volumes between 17 and 22 cc/mol, v_{hcp} and v_{bcc} are very sensitive to any source of bias: For instance, they would change by ~ 0.3 upon a relative shift of the bcc and hcp energies of only 10^{-2} K, and by a similar amount upon use of quartic fits; additional biases could arise from finite size effects, although the simulated systems are relatively large, as well as from details of the interaction potential. Therefore, the comparison between the computed phase transition and the experimental values [13], $v_{\text{hcp}} = 19.73$ cc/mol and $v_{\text{bcc}} = 19.80$, should be considered quite satisfactory.

In conclusion, we have presented results of DMC calculations for ${}^4\text{He}$ and solid ${}^3\text{He}$ using an interaction potential based on the two-body SAPT potential plus the CM three-body potential. This entirely *ab initio* interparticle interaction provides an EOS for ${}^4\text{He}$ in very good agreement with available experimental data.

The computed EOS for solid ${}^3\text{He}$ is also in remarkable agreement with the experimental EOS, provided that the ground state energy per atom at $v = 23.50$ cc/mol be taken to be -0.13 K. This value (not a fitting parameter) is obtained by direct integration of the measured constant- T pressure vs volume curve, taking as a reference state the liquid at equilibrium density and zero temperature [15]. It should supersede the value -0.83 K [14] that has been commonly used to derive the experimental EOS for solid ${}^3\text{He}$.

Finally, we find that the bcc-hcp phase transition in the ${}^3\text{He}$ crystal is well described quantitatively by the interparticle interaction employed in this calculation. In our view, as more and more accurate pair potentials become available, correspondingly accurate three-body terms should be included in the interaction potential for accurate calculations of low-temperature properties of helium.

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