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Ground-State Properties of Solid Helium-4 and -3[†]

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Previous Monte Carlo computations of ground-state properties of solid helium using a correlated trial wave function are extended in several directions. A generalized wave function which includes a simple model for "phonon" correlations is tested; no significant lowering of ground-state energies is obtained. Detailed results for bcc He³ and hcp He⁴ are tabulated in the low-density region. The extension of the variational computations to considerably higher densities (10 cm³/mole) stresses the need for inclusion of short-range correlations over a wide density range and clearly reveals the inadequacy of the commonly used Lennard-Jones 12-6 potential with the de Boer parameters. Various other recently proposed interaction potentials are investigated in conjunction with known three-body forces. Reasonable agreement with experimental energies, pressures, and compressibilities follows from the use of a potential due to Beck. The relation between the melting properties of helium and two "hard-core" models is discussed and the possibility of Bose-Einstein condensation in the solid is investigated in conjunction with a theorem due to Reatto.

I. INTRODUCTION

The low-temperature properties of solid helium, the most characteristic of quantum crystals, have received a considerable amount of attention both from theorists and experimentalists, mostly during the last decade. The ground-state problem especially has been thoroughly studied by an apparently wide variety of theoretical approaches. However most published calculations are essentially variational and generally make use of a "correlated" trial wave function, the product of a Jastrow function¹ by a "phonon" wave function, as first suggested by Nosanow.² In such a trial function the Jastrow

factors take into account the short-range correlations which are a consequence of the large zero-point motion of helium atoms and the strongly repulsive interactions for small separations, and the phonon part describes the long-range order of the solid. In order to compute matrix elements between correlated states, Nosanow was led to use a cluster expansion introduced earlier by Van Kampen.³ This expansion has since been widely used both in the ground-state calculations of Nosanow and co-workers⁴ and in the so-called "self-consistent phonon theory" (SCP) of Koehler and collaborators,⁵ which explicitly includes long-range (or phonon) correlations in the trial wave function.

Similar cluster expansions have been proposed by Brueckner and collaborators⁶ and more recently by Massey and Woo.⁷ A slightly different expansion, based on the treatment of a hierarchy of quasiharmonic model Hamiltonians, has been introduced by Guyer⁸ who has also written a review paper covering most of the above-mentioned work.⁹ Recently a perturbation theory of quantum crystals has been formulated by Horner,¹⁰ resulting in a Bethe-Goldstone equation for the short-range correlation function, similar to Guyer's two-body equation. Both Horner's theory and the various cluster-expansion approaches are essentially two-body approximations with respect to the short-range correlations, although occasionally three-body correlations have been considered.⁴ Nevertheless binding energies and pressures in reasonable agreement with experimental data have been calculated in this approximation, at least for molar volumes close to the melting volume, which is unusually large for solid helium. However, a major drawback of the cluster-expansion technique lies in the fact that it seems to converge rapidly only for a rather limited set of Jastrow trial functions, and even within this set the fast convergence breaks down when solid helium is compressed, i. e., when the nearest-neighbor distance contracts.

One way of treating the short-range correlations more accurately is to compute the matrix elements between correlated states "exactly" by a Monte Carlo method introduced first in the theory of classical fluids by Metropolis *et al.*¹¹ This technique was successfully applied to the study of liquid He⁴ by MacMillan,¹² liquid He⁴ and He³ by Schiff and Verlet,¹³ and solid He⁴ and He³ by Hansen and Levesque¹⁴ (this paper will hereafter be referred to as I) for an fcc lattice. Subsequent work by Hansen¹⁵ was extended to hcp and bcc lattices which are the actual symmetries observed for solid helium at low temperatures (this work will later be referred to as II). The previous work used a simple two-parameter variational function described by Eqs. (1)–(3) in Sec. II, and because no further approximations were made in the computation of the energy expectation value except the use of a finite system in the Monte Carlo work (of the order of 1000 atoms), the results quoted in I and II can be considered an upper bound to the ground-state energies computed with a given two-body potential. The agreement with experimental data obtained in I and II is the best obtained so far by any ground-state theory of solid helium, although the density dependence of the energy and pressure both for solid He³ and He⁴ is unsatisfactory. The major success of these variational results was the very reasonable "prediction" of melting properties and the bcc-hcp transition in solid He³. Moreover one of us has recently pointed

out¹⁶ that the bad variation of ground-state properties with density might be due essentially to the use of an inadequate interatomic potential which, in practically all the previously mentioned calculations, was the Lennard-Jones 12-6 potential:

$$v(r) = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6], \quad (1)$$

with parameters $\epsilon = 10.22^\circ\text{K}$ and $\sigma = 2.556 \text{ \AA}$ as determined by de Boer and Michels.¹⁷

The purpose of the present work is to extend the results of I and II in various directions. In Sec. II we investigate the effect on the variational results when a more general phonon wave function is used, introducing a simplified picture of "phonon correlations." The main conclusion of that section is that no significant improvement is obtained by using the more complicated trial wave function. Section III gives a detailed account of the variational results for hcp He⁴ quoted only briefly in the earlier work (II). An apparently new formula for the compressibility in the ground state is derived in that section but it turns out to be difficult to handle in a variational calculation. In Sec. IV we extend our variational calculations to higher densities covering the molar volume down to $9 \text{ cm}^3/\text{mole}$. The importance of this work is enhanced by the fact that the cluster expansion breaks down already for considerably larger molar volumes.

The influence of the interatomic two-body potential is systematically investigated in Sec. V, over the whole density range covered in Sec. IV. A few remarks on the melting transition of He³ and He⁴ and on the possibility of Bose-Einstein condensation in solid He⁴ are presented in Sec. VI.

II. GENERALIZED TRIAL WAVE FUNCTION

In previous Monte Carlo studies of solid helium-4 and -3 (see I and II) a variational ground-state wave function of the following type has been used:

$$\psi = \prod_{i < j} f(r_{ij}) \prod_i \varphi(r_i), \quad r_{ij} = |\vec{r}_i - \vec{r}_j|, \quad (2)$$

where the indices i and j run from 1 to N (total number of atoms), $f(r_{ij})$ is a spherically symmetric two-body correlation function, and φ_i is a one-particle wave function centered at lattice site \vec{R}_i . In I and II, the function $f(r)$ was taken to have the analytic form of the WKB solution for tunneling into an r^{-12} core,

$$f(r) = \exp[-\frac{1}{2}(B/r^5)], \quad (3)$$

where B is a variational parameter. The φ_i are Gaussians used to localize the particles at the lattice sites,

$$\varphi_i = \exp[-\frac{1}{2}A(\vec{r}_i - \vec{R}_i)^2], \quad (4)$$

where A is another variational parameter.

In the trial ground-state wave function assumed

in the SCP theory,⁵ the single-particle Gaussian used above, corresponding crudely speaking to an Einstein model of the crystal, is replaced by a correlated Gaussian corresponding to some harmonic model of the crystal. Specifically,

$$\psi = \prod_{i < j} f(r_{ij}) \psi_{\text{harm}}, \quad (5)$$

$$\psi_{\text{harm}} = \exp\left[-\frac{1}{2} \sum_{i,j} (\vec{r}_i - \vec{R}_i) \cdot \vec{G}_{ij} \cdot (\vec{r}_j - \vec{R}_j)\right], \quad (6)$$

where \vec{R}_i is the equilibrium (lattice) position of the i th atom. The matrix \vec{G}_{ij} is determined variationally and in all SCP calculations a restricted class of $f(r)$ introduced by Nosanow has been used to ensure the fast convergence of the cluster expansion which is almost always truncated after the two-body term. In a purely harmonic crystal the $f(r)$ is just a constant, and the force-constant matrix Φ is related to the G matrix appearing in the correlated Gaussian by $\Phi = (\hbar^2/m) G^2$.

To determine the effect on the ground-state energy of replacing the single-particle Gaussian used in I and II by a correlated Gaussian we have recalculated some of the ground-state properties of the bcc lattice using a simple correlated Gaussian model together with the Jastrow factors (3).

The G_{ij} chosen has the form

$$G_{ij}^{\alpha\beta} = \begin{cases} e_{ij}^{\alpha} e_{ij}^{\beta} A'' + (\delta_{\alpha\beta} - e_{ij}^{\alpha} e_{ij}^{\beta}) A^{\perp}, & i \neq j \\ A \delta_{\alpha\beta}, & i = j \end{cases} \quad (7)$$

where

$$e_{ij}^{\alpha} = (R_j^{\alpha} - R_i^{\alpha}) / |R_{ij}|, \quad \alpha = x, y, z,$$

with the additional restriction that for the bcc crystal considered here, G_{ij} is nonzero only for the pair ij nearest or next-nearest neighbors. A , A'' , and A^{\perp} are determined variationally. This form allows the transverse and longitudinal correlations to be treated independently and has the single-particle Gaussian as a limiting case. With this G and $f(r)$ from Eq. (3), Eq. (5) gives the explicit form of our trial wave function.

In a harmonic crystal the force-constant matrix Φ must satisfy certain requirements owing to the symmetry of the crystal. In particular, translational invariance requires that

$$\sum_i \Phi_{is} = 0 \quad \text{for all } s. \quad (8)$$

Our trial wave function is an eigenstate of some "fictitious" Hamiltonian which can be obtained by applying the kinetic energy operator to Eq. (5). The potential of this fictitious Hamiltonian contains the harmonic potential appropriate to ψ_{harm} plus various terms arising from the Jastrow factors. By demanding that this fictitious Hamiltonian be translationally invariant we are able to derive the following restriction on A , A'' , and A^{\perp} :

$$A + \frac{1}{3} \times 14(A'' + 2A^{\perp}) = 0. \quad (9)$$

The number 14 which appears in (9) is just the number of particles in the first two shells for a bcc lattice. This relation is similar to that obtained by imposing Eq. (8) on the force constants for a purely harmonic crystal. With the sum rule (9) the number of independent variational parameters in the trial wave function is reduced to three (e.g., A'' , A , and B).

We may remark that a calculation of the dispersion curves for a harmonic crystal with force-constant matrix corresponding to the G of Eq. (7) gives results typical of most Bravais lattices except for very small k , where owing to the finite-range property of G in Eq. (7), an ω linear in k is not obtained. This suggests that this limited form for G is sufficient to introduce some phonon correlations.

With this wave function the energy expectation value is

$$\langle H \rangle = \langle T \rangle + \langle V \rangle,$$

with

$$\langle T \rangle = N \frac{3\hbar^2}{4m} A + \frac{5\hbar^2}{m} \sum_{i < j} \left\langle \frac{B^5}{r_{ij}^7} \right\rangle, \quad (10)$$

and for the Lennard-Jones potential (1),

$$\langle V \rangle = \left\langle \sum_{i < j} v(r_{ij}) \right\rangle = 4\epsilon \sum_{i < j} \left[\left\langle \left(\frac{\sigma}{r_{ij}} \right)^{12} \right\rangle - \left\langle \left(\frac{\sigma}{r_{ij}} \right)^6 \right\rangle \right].$$

Here the brackets denote normalized averages weighted by the square of the trial wave function [see Eqs. (9) and (10) in I].

As pointed out in I, the simple trial function (5) allows a straightforward scaling procedure [Eq. (16) of I] which makes it possible to perform a complete variational calculation at a fixed density, the expectation values for different densities being simply related to those computed at the fixed density. This results of course in a considerable saving of computer time. We carried through a complete variational calculation for bcc He³ for a 250-particle system enclosed in a cubic box with periodic boundary conditions. Around 150 000 configurations were generated on each run, requiring about 5 min of computer time on the CDC 6600 of the Courant Institute for Mathematical Sciences (New York). Our results for a number of densities close to melting are summarized in Table I. They are compared to the previous bcc results using an "Einstein"-type wave function (2) which were briefly reported earlier in II. These previous results had been obtained for a larger system (686 atoms) and a larger number of configurations had been generated (around 400 000). Accordingly the statistical error on the expectation values, which was roughly 0.2 °K on the total energy, is larger on the new results, but does not exceed 0.5 °K. It

TABLE I. bcc He³ results with LJ1 potential. For each density the results on the upper line are computed with the wave function defined by Eq. (5); the lower line corresponds to Eq. (2). $\langle V \rangle$, $\langle T \rangle$, E , and E^{expt} are the calculated potential, kinetic, and total energy per atom and the experimental energy, respectively (in °K). p^{virial} , p^{thermo} , and p^{expt} are the pressures calculated from Eq. (11), Eq. (12), and experiment (in atm.). S is the rms displacement and $S(\Theta_D)$ is an "experimental" estimate of this quantity using Eq. (13) and the measured Debye temperature. K and K^{expt} are the calculated and experimental compressibilities (in atm⁻¹). This notation is maintained in all other tables.

ρ (atom/ σ^3)	v (cm ³ /mole)	$\langle V \rangle$ (°K)	$\langle T \rangle$ (°K)	E (°K)	E^{expt} (°K) ^a	p^{vir} (atm)	p^{thermo} (atm)	p^{expt} (atm) ^a	S (Å)	$S(\Theta_D)$ (Å) ^b	$10^2 K$ (atm ⁻¹)	$10^2 K^{\text{expt}}$ (atm ⁻¹) ^c
0.4	25.14	-21.2	21.55	0.35		28	31		1.17		0.81	
		-22.0	22.4	0.4		•••	36		1.14		•••	
0.42	23.94	-22.7	23.55	0.85	-1.03	32	37	35	1.11	1.35	0.65	
		-22.7	23.6	0.9		34	39		1.11		•••	0.46
0.44	22.85	-24.3	25.75	1.45	-0.50	36	46	47	1.08	1.28	0.46	0.37
		-23.5	25.0	1.5		47	45		1.05		0.55	
0.46	21.86	-25.3	27.35	2.05		52	58	62	1.05	1.22	0.31	0.29
		-24.5	26.6	2.1	0.15	64	55		0.99		0.33	
0.48	20.95	-26.3	29	2.7		72	75	78	1.02	1.16	0.21	0.23
		-25.7	28.4	2.7	0.90	82	71		0.95		0.22	
0.5	20.11	-26.25	29.85	2.6		115	98	97	0.99	1.11	0.15	0.18
		-26.95	30.75	2.8	1.82	96	94		0.92		0.15	

^aReference 18.^bReference 19.^cReference 20.

should however be stressed that this fairly small statistical error on the ground-state energy, combined with the slow variation of this extremum quantity as a function of the variational parameters, at least in the vicinity of the minima, causes a considerably larger uncertainty (not a statistical error) on the potential and kinetic energies separately, because these are not extremum functions of the variational parameters. The same remark holds for the pressure calculated by the virial theorem:

$$P = \rho \left[\frac{2}{3} \langle T \rangle - (1/3N) \sum_i \langle \vec{r}_i \cdot \vec{\nabla}_i V \rangle \right]. \quad (11)$$

The "variational uncertainty" is estimated to be less than 10% of the quoted potential and kinetic energy values and roughly 15% on the virial pressure values. These uncertainties turn out to be largest at low densities and tend to become less important when the solid is compressed (see the results quoted in Sec. IV).

Another way of computing the pressure P and the compressibility K at $T=0$ °K consists in differentiating numerically the energies as a function of molar volume:

$$P = - \frac{dE}{dv}, \quad K = - \frac{1}{V dP/dv}. \quad (12)$$

In practice a simple polynomial is fitted to the energy-vs-volume curve and differentiation then yields the pressures with an estimated error of 5% and the compressibilities with an error of about 10%. It is a remarkable feature of all our results presented in this and the following sections that the difference between the pressures computed through formulas (11) and (12) is always within the quoted uncertainties and, moreover, this differ-

ence appears to be nonsystematic and tends to be zero on the average.

Returning to Table I we clearly see that the ground-state energies per atom, computed with wave functions (2) and (5), respectively, are very close, the differences being well within the statistical errors. The theoretical values lie less than 2 °K above the experimental data of Pandorf and Edwards.¹⁸ As to the kinetic and potential energies, their differences are also within the above-mentioned uncertainties. The pressures also agree very closely, especially the more accurate estimates from formula (12) ("thermodynamic" pressures), and they lie very close to the experimental values of Ref. 18. The compressibilities also agree within the quoted uncertainties, but appear to be generally higher than the experimental values. Another interesting quantity is the rms displacement of the atoms from their equilibrium positions; again the values computed with both wave functions agree within statistical errors (of the order of 5%) although as expected the values obtained from the "correlated Gaussian" wave function appear to be systematically slightly larger than those from the Einstein-type wave function. An "experimental" estimate of the rms displacement can be obtained from the measurements of the Debye temperature Θ_D at very low temperatures through the Debye formula⁹

$$S^2 = \frac{9}{4} \frac{\hbar^2}{mk\Theta_D}, \quad (13)$$

where S^2 denotes the square of the rms displacement. Precise measurements of Θ_D are available both for He³¹⁹ and He⁴.²¹ The rms estimates from (13) are also given in Table I; they turn out to be

in reasonable agreement with the theoretical values.

Our conclusion from the comparison made in Table I between correlated and uncorrelated Gaussian results is that no significant change of ground-state properties follows from the use of a more general phonon wave function and, in particular, the ground-state energy is not lowered significantly despite the presence of an additional variational parameter, at least in the relatively restricted density range considered here. This lends strong support to our feeling that short-range correlations are dominant in solid helium for these densities and that a correct treatment of these correlations is crucial if quantitatively reasonable data are to be computed. In the remainder of the present work we restrict ourselves to the simpler form of the wave function, formula (2).

As regards the special choice of the short-range correlation function we feel that there is no basic physical reason why it should be very different from the liquid-helium case. For liquid helium the choice of Eq. (3) appears to be close to optimal.¹³ In the case of the solid two other choices (including the Nosanow form) have been considered in Ref. 14, where it was shown that those Jastrow factors gave significantly higher energies when used in conjunction with Monte Carlo computations. However a more complicated form than (3) might very well allow a further slight lowering of energy expectation values; the price to be paid would then be the loss of the simple scaling relations which greatly reduce the amount of computations.

III. HELIUM-4 RESULTS

We present here in some detail the earlier results obtained by one of us for hcp He⁴, which had been briefly quoted in II. These results were obtained with the two-parameter trial wave function defined by formulas (2)–(4) for an 800-atom system in a nearly cubical box with periodic boundary conditions; 400 000 configurations were generated on the average for each run; the statistical error (standard deviation) on the ground-state energy is estimated to be 0.2 °K and the other error esti-

mates have been mentioned earlier (Sec. II). The variational results in the molar volume range between 17 cm³/mole and melting are shown in Table II together with available experimental data. We are able to draw conclusions quite similar to those of Sec. II: The ground-state energy is everywhere within 1.5 °K of experimental values, the difference between theory and experiment decreasing with increasing density; the “thermodynamic” and virial pressures are very close, well within the above-mentioned uncertainties and are systematically lower than experimental values. The calculated compressibilities on the other hand are reasonably close to experimental values but systematically larger. The calculated rms displacement values are again fairly close to their experimental “estimate” from formula (13). As expected the variational parameter *A* of the Gaussian single-particle wave function (4) increases with increasing density, resulting in an increasing localization of the atoms around their equilibrium positions as illustrated by the rapidly decreasing rms displacement values. However, the parameter *B* in the Jastrow factors (3) varies very little with density and remains everywhere very close and slightly below the WKB value *B* = 1.135σ.

Among the other published theoretical results for hcp He⁴ Horner’s¹⁰ come closest to ours; his energies lie roughly 2 °K above our energy values. Horner attributes the discrepancy between his results and experiment to the absence of phonon correlations in his mean-field treatment. In the light of our results of the Sec. II the discrepancy might also be due to the neglect of higher-order terms in Horner’s treatment of short-range correlations. In Sec. IV, we extend our variational results to smaller molar volumes, essentially the region between 9 and 18 cm³/mole, which has been much less explored both by theoretists and experimentalists. But before that we discuss briefly the problem of the computation of the compressibility in the ground state of a quantum system. The compressibility is usually computed by numerically differentiating twice the energy-vs-molar-volume

TABLE II. hcp He⁴ results with LJ1 potential. All experimental data are taken from Ref. 20.

<i>v</i> (cm ³ /mole)	$\langle V \rangle$ (°K)	$\langle T \rangle$ (°K)	<i>E</i> (°K)	<i>E</i> ^{exp} (°K)	<i>p</i> ^{vir} (atm)	<i>p</i> ^{themo} (atm)	<i>p</i> ^{expt} (atm)	10 ⁴ <i>K</i> (atm ⁻¹)	10 ⁴ <i>K</i> ^{exp} (atm ⁻¹)	<i>S</i> (Å)	<i>S</i> (θ _{<i>p</i>}) (Å)
21.5	-26.35	21.68	-4.67	-6.08	20	19		41.9		0.963	
20.87	-27.72	23.22	-4.5	-5.9	26	26	28	38.9		0.935	1.02
20.28	-28.3	24.0	-4.3	-5.7	33	34	36	37.2	31.4	0.91	0.98
19.69	-29.61	25.61	-4.	-5.39	40	42	47	34.7	26.1	0.877	0.94
19.12	-31.23	27.55	-3.68	-5.	49	51	60	30.7	21.8	0.843	0.91
18.59	-31.97	28.64	-3.33	-4.6	59	61	74	26.0	18.2	0.815	0.88
18.06	-32.69	29.77	-2.92	-3.97	71	73	92	21.1	15.1	0.787	0.85
17.56	-33.95	31.55	-2.39	-3.35	84	88	111	17.0	13.0	0.76	0.815

function. This always results in some loss of accuracy; especially if the ground-state energies are computed for relatively few molar volumes. For this reason we have tried to derive a formula for the compressibility in the ground state in a way similar to the derivation of the virial formula for the pressure. Incidentally the same virial formula holds both for classical and quantum systems²² but the classical relation giving the compressibility as the $k \rightarrow 0$ limit of the structure factor does not hold for a quantum system. By differentiating both sides of the Schrödinger equation twice with respect to volume, we are able to derive the following simple relation for the inverse compressibility:

$$K^{-1} = \frac{5}{3} P + \frac{4}{3} (\langle W\Phi \rangle - \langle W \rangle \langle \Phi \rangle), \quad (14)$$

where P is the pressure (from the virial formula), $W = V + \frac{1}{2} \sum_i \vec{r}_i \cdot \nabla_i V$, with V the potential part of the Hamiltonian, and Φ is defined by

$$\frac{\partial' |\psi\rangle}{\partial v} = \Phi |\psi\rangle, \quad (15)$$

with $|\psi\rangle$ the ground-state wave function and the prime meaning that differentiation with respect to volume does *not* include the contribution coming from the scaling of the particle coordinates with volume. To the best of the authors's knowledge the formula had not been previously derived. Some details of the derivation of formula (14) are given in Appendix A. The first term on the right-hand side of (14) is the ideal-gas contribution (which is the same for fermions, bosons, or particles that obey Boltzmann statistics) and the second term is a fluctuation term arising only for systems of interacting particles. Unfortunately relation (14) is difficult to use in our variational calculations because the differentiation (15) introduces the derivatives of the optimum variational parameters with respect to volume, which are not known very accurately because of statistical uncertainties. Moreover the fluctuation term in formula (14) cannot be calculated with sufficient accuracy for our choice of the wave function by the Monte Carlo method; consequently formula (14) is of little use in the present context, but might prove more useful to test the consistency of other approximate ground-state calculations.

IV. EXTENSION TO HIGHER DENSITIES

As pointed out earlier, theoretical results for the ground-state properties of solid helium are scarce at molar volumes less than about 18 cm³/mole. This is due partly to the breakdown of the truncated cluster expansions at smaller molar volumes. Horner's perturbation results extend to about 12 cm³/mole. Morely and Kliewer²³ have computed self-consistent phonon spectra without including short-range correlations at 10 and 12

cm³/mole. The results presented in this section seem to indicate on the contrary that short-range correlations are still crucial at such high densities. On the other hand the increasing discrepancies between variational results and experiment at high density must almost certainly be traced back to an inadequate interatomic pair potential.

Our high-density variational calculations were based on the trial wave function described by Eqs. (2)–(4) for a system of 256 atoms on an fcc lattice; this close-packed crystal structure is sufficiently close to the physical hcp structure that Monte Carlo computations with their inherent statistical uncertainties cannot distinguish between them; the fcc structure was chosen for convenience. The computations were done at the single reduced density $\rho = 0.65$ atom/ σ^3 (15.47 cm³/mole) and the results scaled to higher and lower densities as outlined earlier. A few technical details describing our numerical procedure are given in Appendix B. The parameters A and B [Eq. (3) and (4)] were varied over sufficiently large intervals to cover, after scaling, the molar-volume range between 9.5 and 18 cm³/mole. In the low-density region the new results overlap within statistical uncertainties the previous hcp data obtained with the 800-atom system. This confirms the generally accepted independence of computer-“experiment” results on the size of the system, as already observed for various classical systems, at least for reasonably short-range interactions (in our case essentially an inverse fifth-power law). The results for fcc He³ and He⁴ are summarized in Tables III and IV, respectively. Experimental data are indicated whenever available. Horner's energy results, as read off from his figure,¹⁰ are added for comparison. From our rms displacement values we have computed estimates of the Debye temperatures through formula (13); they agree reasonably well with existing experimental data. For this reason we have also indicated the corresponding estimates for the average sound velocity of solid He³ and He⁴ as a function of molar volume.

Inspection of Tables III and IV calls for the following remarks: As the molar volume decreases, the ground-state energies drop below their experimental values; for He⁴ the calculated energy is roughly 15 °K lower than experiment around 9 cm³/mole. This situation will be discussed in more detail in Sec. V. As a consequence of this behavior it is not surprising that the computed pressures lie considerably below experimental values over the whole volume range considered here. The estimated relative error of the virial pressure decreases with increasing density and it is the more remarkable that the virial predictions agree so well with the “thermodynamic” pressures. On the other hand, the statistical uncertainties of the en-

TABLE III. fcc He³ results with LJI potential.

ν (cm ³ /mole)	$\langle V \rangle$ (°K)	$\langle T \rangle$ (°K)	E (°K)	$E^{\text{ext a}}$	$E^{\text{HORNER b}}$	ρ^{vital} (atm)	ρ^{thermo}	$\rho^{\text{ext c}}$	$10^4 K$ (atm ⁻¹)	$10^4 K^{\text{ext c}}$ (atm ⁻¹)	S (Å)	Θ_D (°K)	Θ_D^{ext} (°K)	\bar{C} (m/sec)
20.11	-28.75	32.45	3.7			61			14.0	10.75	0.846	50.5	43.5	530
18.28	-30.9	36.7	5.8	4.47	7.7	125	140	156	8.8	7.68	0.80	56.4	54.5	574
16.76	-31.9	40.7	8.8	8.16	11.2	235	225	247	6.6	5.23	0.76	63.2	66.5	626
15.47	-32.8	46.1	13.3	12.83	15.2	360	328	372	4.6	3.6	0.67	81.5	79	788
14.36	-35.95	54.55	18.6	18.85	20.1	490	461	551	3.2	2.6	0.63	91.4	91	864
13.41	-38.3	62.7	24.4	26.53		615	639	770	3.2	1.95	0.59	104.2	104.5	964
12.57	-37.3	69.75	32.45	35.97		890	879	1057	1.69		0.546	121.3	118	1100
11.83	-38.	80.1	42.1			1170	1189		1.29		0.52	132		1174
11.17	-37.25	89.75	52.5			1490	1577		1.03		0.503	143		1249
10.58	-29.5	94.55	65.05			2095	2042		0.85		0.47	164.1		1410
10.05	-26.	106.7	80.7			2640	2581		0.72		0.43	193.4		1634
9.57	-23.9	121.2	97.3			3180	3189							

^aExperimental energies are based on the value 2.53 °K at 19.5 cm³/mole (Ref. 18) and then computed for higher densities by integrating the equation of state given in the table.

^bReference 10.

^cReference 33.

\bar{C} is a measure of the average sound velocity obtained here essentially from the calculated Debye temperature divided by the Debye wave vector.

TABLE IV. fcc He⁴ results with LJI potential.

ν (cm ³ /mole)	$\langle V \rangle$ (°K)	$\langle T \rangle$ (°K)	E (°K)	E^{ext} (°K) ^a	E^{HORNER} (°K)	ρ^{vital} (atm)	ρ^{thermo} (atm)	$\rho^{\text{ext b}}$ (atm)	$10^4 K$ (atm ⁻¹)	$10^4 K^{\text{ext}}$ (atm) ^b	S (Å)	Θ_D (°K)	Θ_D^{ext} (°K) ^c	\bar{C} (m/sec)
18.28	-32.3	29.25	-3.05	-4.1	-1.8	70	75	84	23	16.5	0.84	38.5	37	403
16.76	-34.2	32.8	-1.4	-2.5	-0.4	150	119	155	12.5	11.0	0.78	45.1	47	459
15.47	-37.8	39	1.2	-1.0	2.4	215	188	249	7.8	6.15	0.71	54.1		536
14.36	-40.75	44.85	4.1	3.0	6.3	296	309	411	4.9	4.25	0.647	65.1		630
13.41	-41.6	50.3	8.7	9.0	10.2	475	469	590	3.6	3.0	0.602	75.1		710
12.57	-43.4	58.35	14.95	15.7		650	672	846	2.7	2.15	0.569	84.2		779
11.83	-43.95	65.45	21.5	24.0		886	925	1170	2.07	1.65	0.527	94.9		887
11.17	-38.90	69.05	30.15	35.5		1332	1244	1630	1.55	1.27	0.512	103.9		925
10.58	-37.4	78.5	41.1	48.5		1720	1647	2110	1.19	0.98	0.473	121.9		1065
10.05	-36.15	88.8	52.65	60.7		2140	2146	2700	0.93	0.78	0.437	142.3		1222
9.57	-26.	93.1	67.1	81.6		2900	2755	3480	0.76	0.64	0.427	149.4		1262

^aEnergies for molar volumes larger than 11 cm³/mole from Ref. 33; the values for smaller molar volumes were obtained by integrating the experimental equation of state.

^bReferences 20 and 37.

^cReference 20.

ergy values are inflated by the scaling procedure and the estimated error on the ground-state energy is about 1 °K at the highest densities considered here. The calculated compressibility is everywhere higher than experiment. Another remarkable feature of our results is that the optimum value of the B parameter [Eq. (3)] stays practically constant over the whole density range, both for He³ ($B \approx 1.07 \sigma$) and He⁴ ($B \approx 1.09 \sigma$). Thus there is no indication of any decrease in importance of the short-range correlations. As $B=0$ corresponds to a noncorrelated trial wave function, we would expect at least a decrease in the optimum value of B if short-range correlations became less and less important. Moreover the Jastrow factors contribute roughly half of the kinetic energy up to the highest densities considered here.

Another important remark to be made is that by the time the potential energy goes through its lowest value, i. e., around 12 cm³/mole, which corresponds roughly to nearest neighbors sitting at the position of the potential minimum, the kinetic energy is about twice as large in absolute value, contrary to the situation near melting where both energies are of the same order. Thus in a certain sense solid helium is even more extremely "anharmonic" at roughly half the melting volume than it is near melting. This explains why, even at the lowest molar volume studied here, the predictions of harmonic theory²⁴ are so strikingly different, from the present variational results. The result also sheds some doubt on the validity of SCP results without short-range correlations in this volume range.²³

V. INFLUENCE OF TWO-BODY POTENTIALS ON GROUND-STATE PROPERTIES

As emphasized by Tables I–IV, the assumed two-body potential, i. e., the Lennard-Jones potential with de Boer parameters, defined by Eq. (1) and labeled by LJ1, seems inadequate for the description of solid helium. The fact that the variational ground-state energies, which constitute an upper bound for a given two-body potential, drop below experimental values at small molar volumes can only be due to the inadequacy of that pair potential. It might be argued that many-body forces are responsible for the discrepancy, but it seems quite unlikely that they could make up the total difference in the case of helium which has a very weak electronic polarizability. The best known triplet interaction is the triple-dipole or Axilrod-Teller interaction²⁵ resulting from the three-body potential:

$$\rho_3(\vec{r}_{12}, \vec{r}_{13}, \vec{r}_{23}) = \frac{\nu}{r_{12}^3 r_{13}^3 r_{23}^3} (1 + 3 \cos \theta_1 \cos \theta_2 \cos \theta_3), \quad (16)$$

where the θ_i are the interior angles of the triangle formed by the three vectors \vec{r}_{12} , \vec{r}_{13} , \vec{r}_{23} , and $\nu = 0.324$ °K for helium if the distances are expressed in units of σ . The contribution of these forces to the ground-state energy of liquid and solid helium has been estimated in II and also by Murphy and Barker.²⁶ These estimates yield a contribution of roughly 1% of the total potential energy near the melting density. A simple lattice-sum gives the following estimate for the triple-dipole contribution to the ground-state energy²⁶:

$$\epsilon_3 \approx 0.1 (\rho/\rho_0)^3 \text{ °K}, \quad (17)$$

where ρ is the reduced density and ρ_0 is the reduced equilibrium density of liquid He⁴, $\rho_0 = 0.364$ atom/ σ^3 . The resulting contributions are consequently quite small at low density. At the highest density considered here, i. e., $\rho = 1.05$ atom/ σ^3 ($V = 9.57$ cm³/mole), formula (17) predicts a contribution of 2.4 °K per atom, which is considerably less than the difference between experiment and our theoretical ground-state energy using the LJ1 potential. It is generally believed that the triple-dipole forces are the dominant three-body interactions, and we conclude that triplet forces cannot account completely for the low theoretical values of the energy. Moreover an estimate of the contribution of triplet forces to the pressure is obtained by differentiating (17) with respect to volume:

$$p_3 \approx 2.4 \rho (\rho/\rho_0)^3 \text{ atm.} \quad (18)$$

This results in a correction of only 2% of the total pressure around 10 cm³/mole, again much less than the difference between experimental and theoretical pressures. A similar remark holds for the compressibility results.

For these reasons we have investigated the influence of two-body potentials on the ground-state properties of solid helium. The low-density results for He⁴ have been reported earlier¹⁶ and we concentrate here on the density range studied in Sec. IV. As pointed out in Ref. 16, the spherical radial functions, defined by Eq. (11) of I and computed with wave function (2) for various values of the parameters A and B , can readily be reused to calculate potential energy expectation values for various interatomic potentials without any new lengthy computations, according to formula (13) of I. Adding to the potential energy the unchanged kinetic energy, one can then minimize anew the total energy with respect to the variational parameters on which $g(r)$ depends. We investigated in this way the two-body potentials already used in Ref. 16 plus another potential recently proposed by Beck.²⁷ This potential has the correct theoretical long-range dependence on the separation (van der Waals dispersion forces) as well as a short-range repulsive part fitted to theoretical potential

values. The region in the vicinity of the potential minimum is chosen so as to fit experimental second virial coefficient data. The resulting potential is in reasonable agreement with recent first principles calculations of the He-He potential.²⁸ Its rather simple analytic expression is

$$v(r) = A e^{-\alpha r - \beta r^6} - \frac{B}{(r^2 + a^2)^3} \left(1 + \frac{2.709 + 3a^2}{r^2 + a^2} \right), \quad (19)$$

where

$$\begin{aligned} A &= 4.638 \times 10^6 \text{ }^\circ\text{K}, & B &= 1.00685 \times 10^4 \text{ }^\circ\text{K } \text{\AA}^6, \\ \alpha &= 0.675 \text{ } \text{\AA}^{-1}, & \beta &= 4.390 \text{ } \text{\AA}^{-6}, \\ \beta &= 3.746 \times 10^{-4} \text{ } \text{\AA}^{-6}. \end{aligned}$$

Significant differences between the Beck and LJ1 potentials are the relative "softness" of Beck's potential in the repulsive region and a slight shifting of the minimum to a larger radius.

Bruch and McGee²⁹ have derived a semiempirical pair potential in a spirit very similar to Beck's. These authors have also included the exact theoretical long-range behavior in their potential and have added to this part a Morse potential with parameters adjusted to give best agreement with various dilute-gas properties over a wide range of temperatures. Again the resulting potential has a softer and slightly wider repulsive core than the LJ1 potential. Analytically the Bruch-McGee potential (which we shall refer to as Morse potential for brevity) splits into two pieces ("hybrid" potential):

$$\begin{aligned} v(r) &= \epsilon (e^{2c(1-x)} - 2e^{c(1-x)}), \\ x &= r/r_m, & r < r_2 \\ &= -\alpha/r^6 - \beta/r^8, & r > r_2 \end{aligned}$$

where

$$\begin{aligned} \epsilon &= 10.75 \text{ }^\circ\text{K}, & c &= 6.12777, \\ r_m &= 3.0238 \text{ } \text{\AA}, & r_2 &= 3.6828 \text{ } \text{\AA}, \\ \alpha &= 10214 \text{ }^\circ\text{K } \text{\AA}^6, & \beta &= 27670 \text{ }^\circ\text{K } \text{\AA}^8. \end{aligned}$$

Finally we have used a Lennard-Jones 12-6 potential with a slightly larger value of the repulsive core parameter $\sigma = 2.62 \text{ } \text{\AA}$. This value gives a significantly improved fit to recent precise scattering measurements³⁰ over the older de Boer value¹⁷; unfortunately these experiments do not allow a precise determination of the parameter ϵ , and we have kept the old value $\epsilon = 10.22 \text{ }^\circ\text{K}$. This may seem somewhat artificial, but the procedure gives results in excellent agreement with experiment when the high-temperature equation of state is calculated "exactly" for gaseous helium (with proper inclusion of quantum corrections).³¹ This second Lennard-Jones potential will be labeled LJ2. The common

feature of the LJ2, Morse and Beck potentials, pictured in Fig. 1, is a wider repulsive core compared to the LJ1 potential.

Results obtained with these various potentials are compared with existing experimental data in Tables V-VII. Table V lists the ground-state energies of both He³ and He⁴. In the range where experimental data are available, the energies computed from the Morse potential are everywhere too high, the discrepancy rising up to almost 20 °K below 10 cm³/mole for He⁴. The LJ2 energies are very close to experiment at the lower densities, but become somewhat higher for He⁴ when the density is increased. The energies obtained from the Beck potential are systematically a few °K above experiment. Turning to the pressures, listed in Table VI, it appears that the Morse results are consistently too high; the LJ2 results are in fair agreement with experiment except at the very highest densities. The Beck pressures agree best with experiment, the relative difference exceeding 5% only at the very lowest and highest densities. The low-density discrepancy may be spurious and due to our numerical differentiation procedure (no energy values were

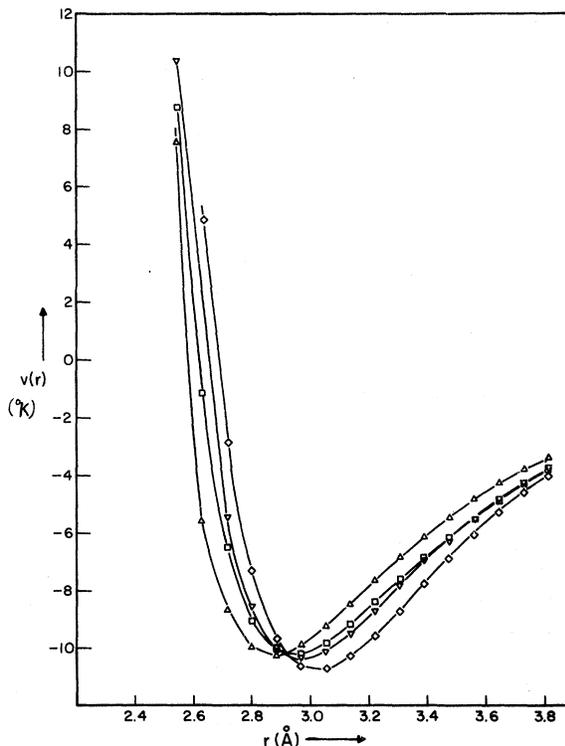


FIG. 1. He-He potentials (in °K) as a function of inter-atomic spacing (in Å). The potentials used in the calculation are represented by: triangles, LJ1 potential; squares, LJ2 potential; diamonds, Morse potential; upside-down triangles, Beck potential.

TABLE V. Ground-state energies per atom ($^{\circ}\text{K}$) as computed with various potentials for solid He^3 and He^4 . The experimental data for Table V–VII are taken from the same sources as the data in Table III.

v (cm^3/mole)	He^3						He^4					
	LJ1	LJ2	Morse	Beck	Expt.	Horner	LJ1	LJ2	Morse	Beck	Expt.	Horner
18.38	5.8	4.4	7.25	6.65	4.47	7.7	-3.05	-4.8	-3	-2.7	-4.1	-1.8
17.49	7.4	6.3	9.35	8.35	6.17	9.3	-2.3	-3.95	-1.7	-1.6	-3.4	-1.2
16.76	8.8	8.5	12	10.45	8.16	11.2	-1.4	-2.85	-0.1	-1.15	-2.5	-0.4
16.09	10.9	10.8	14.8	13.1	10.38	12.9	-0.16	-1.65	1.8	1.2	-2.0	0.8
15.47	13.3	13.1	17.4	16.15	12.83	15.2	1.2	-0.1	3.95	2.75	-1.0	2.4
14.9	16	15.8	20.5	18.6	15.60	17.2	2.55	1.95	6.55	4.75	1.0	4.2
14.36	18.6	18.9	24.3	21.6	18.85	20.1	4.1	4.5	9.35	7.4	3.0	6.3
13.87	21.25	22.6	28.7	25.15	22.46		6.17	7.3	12.55	10.15	6.0	8.2
13.41	24.4	27.25	33.55	29.35	26.53		8.7	10.15	16.40	13.15	9.0	10.2
12.97	27.9	31.85	38.55	34.15	31.13		11.65	13.25	20.10	16.7	12.2	13.1
12.57	32.45	36.6	44.25	38.8	35.97		14.95	17.05	24.45	20.35	15.7	
12.19	36.85	41.6	50.4	44.1			18.03	21.5	29.55	24.4	19.5	
11.83	42.1	47.56	56.75	50.1			21.5	26.7	34.95	29.1	24.0	
11.49	49.25	54.1	63.8	56.05			25.52	31.65	41.65	34.4	30.	
11.17	52.5	61.65	71.65	62.55			30.15	37.1	48.2	40.2	35.5	
10.87	58.4	69.45	80.2	69.75			35.5	43.3	55.1	46.45	41.4	
10.58	65.05	77.2	89.4	77.7			41.1	50.35	62.55	52.8	48.5	
10.31	72.5	85.85	99.4	86.25			46.55	58.3	70.85	59.6	55.7	
10.05	80.7	95.45	109.5	95.5			52.65	67.2	80.05	67.1	60.7	
9.81	88.95	106.	119.95	105.35			59.5	77	90.05	75.4	72.1	
9.57	97.3	117.6	131.3	114.9			67.1	88	100.9	84.4	81.6	

computed beyond 18.28 cm^3/mole for the various "new" potentials); on the other hand the high-density experimental data of Stewart³² may not be very accurate. The various pressure data are pictured in Figs. 2 and 3.

A similar situation holds for the compressibilities (Table VII): The agreement with experimental val-

ues is best for the Beck potential. The LJ2 values are too high at low density and too low at higher densities. The Morse compressibilities are systematically too low, with the exception of the lowest He^3 densities, which might again be due to our numerical differentiation procedure in that region. The conclusion drawn from the detailed comparisons

TABLE VI. Ground-state pressures as computed with various potentials for solid He^3 and He^4 (in atm).

v (cm^3/mole)	He^3					He^4				
	LJ1	LJ2	Morse	Beck	Expt.	LJ1	LJ2	Morse	Beck	Expt.
18.28	140	180	208	168	156	75	89	118	105	84
17.49	180	218	250	210	204	94	111	152	130	117
16.76	225	260	295	260	247	115	141	196	161	155
16.09	274	307	353	318	305	145	181	253	202	205
15.47	328	370	429	386	372	189	240	322	257	249
14.9		452	521	464	455	240	316	400	324	329
14.36	461	555	632	555	551	309	406	491	405	411
13.87	543	672	755	655	657	384	501	591	496	494
13.41	639	803	894	770	770	469	604	706	599	590
12.97	757	951	1053	902	910	566	716	841	717	715
12.57	879	1108	1225	1049	1057	672	837	989	845	846
12.19	1024	1283	1418	1217		791	977	1158	990	986
11.83	1190	1478	1634	1407		925	1143	1351	1152	1170
11.49	1374	1697	1872	1619		1075	1342	1568	1334	1380
11.17	1577	1944	2133	1855		1245	1581	1812	1535	1630
10.87		2222	2417	2111		1435	1862	2081	1756	1860
10.58	2047	2545	2732	2397		1647	2201	2386	2004	2110
10.31	2310	2906	3070	2702		1880	2589	2722	2272	2400
10.05	2595	3320	3432	3034		2146	3030	3082	2569	2700
9.81	2895	3770	3780	3379		2420	3500	3469	2881	3050
9.57	3220	4305	4236	3764		2756	4020	3905	3226	3480

TABLE VII. Ground-state compressibilities as computed with various potentials for solid He³ and He⁴: 10⁵K in atm⁻¹.

v (cm ³ /mole)	He ³					He ⁴				
	LJ1	LJ2	Morse	Beck	Expt.	LJ1	LJ2	Morse	Beck	Expt.
18.28	140	145	135	118	107.5	230	240	160	190	165
17.49	105	115	105	94		160	165	110	150	129
16.76	88	99	81	76	68	125	120	82	115	110
16.09	77	75	60	63	64	105	85	64	82	75
15.47	66	54	46	52	52.3	78	60	53	63	61.5
14.9		41	37	44	43.1	61	48	43	50	49.6
14.36	46	32	30	37	36	49	38	36	41	42.5
13.87	39	27	26	32	30.6	42	34	31	35	35.5
13.41	32	24	22	27	26	36	31	26	30	30
12.97	27	21	19.4	23	22.4	31	28	23	26	25.3
12.57	22	19.1	17	19.7	19.5	27	24	19.6	22.7	21.5
12.19	19.6	16.8	14.9	17	17	24	20	16.8	19.8	17.5
11.83	16.9	14.5	13	14.7		20.7	16.3	14.4	17.2	16.5
11.49	14.7	12.4	11.5	12.8		17.9	13.2	12.4	15	14.6
11.17	12.9	10.6	10.1	11.2		15.5	11	10.8	13.1	12.7
10.87		9.1	9.1	10		13.5	9.6	9.6	11.6	11.1
10.58	10.3	7.8	8.0	8.9		11.9	8.3	8.4	10.2	9.8
10.31	9.3	6.7		8.1		10.5	7.2		9.1	8.7
10.05	8.5	5.9	6.5	7.3		9.3	6.3	6.7	8.1	7.8
9.81	7.8	5.1		6.7		8.4	5.5		7.3	7
9.57	7.2	4.3	5.5	6.2		7.6	4.7	5.6	6.6	6.4

made in Tables V–VII is that the Beck and LJ2 potentials give considerably better agreement with

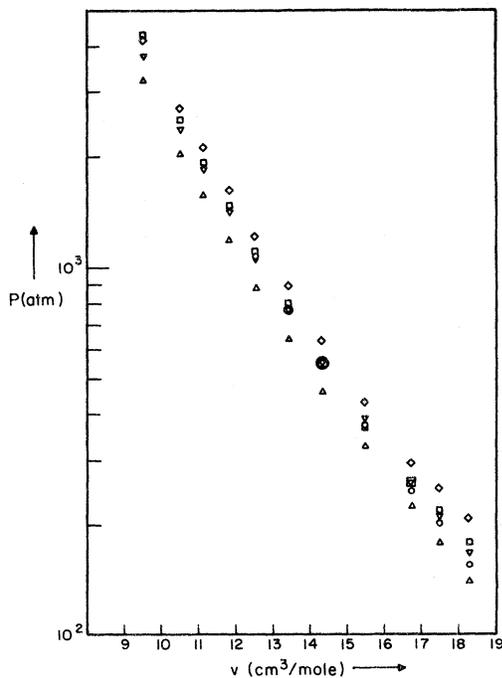


FIG. 2. Solid He³ equation of state. The pressures are in atm (logarithmic scale) and the molar volumes in cm³. The experimental points, Ref. 33, are represented by circles, LJ1 potential by triangles, LJ2 potential by squares, Morse potential by diamonds, and Beck potential by upside-down triangles.

experimental values than the commonly used LJ1 potential. The Morse potential on the other hand is not very satisfactory, except perhaps at low densities.¹⁶ The best over-all agreement with ex-

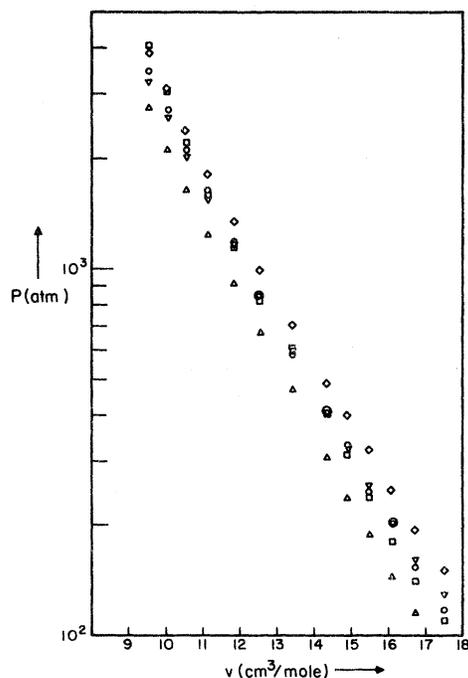


FIG. 3. Solid He⁴ equation of state. The various points correspond to the same potentials as in Fig. 2. Experimental data from Refs. 20 and 32.

perimental data is obtained with the Beck potential which we recommend to be used in any further theoretical calculations of low-temperature condensed-helium properties.

VI. REMARKS ON PHASE TRANSITIONS AND BOSE-EINSTEIN CONDENSATION

We would like to make here two brief remarks on the melting properties and on the possibility of Bose-Einstein (BE) condensation in solid helium. The melting and crystallization volumes and pressures for He³ and He⁴ obtained from our variational results combined with Schiff and Verlet's¹³ liquid-helium results, and the pressure and volume at which the bcc-hcp transition occurs in solid He³, have been quoted in II. They are summarized for convenience in Table VIII together with experimental values.

The melting mechanism of solid helium is probably a very complex one, but two somewhat academic "experiments" strongly indicate that attractive forces between helium atoms are not essential in that mechanism. The first experiment consisted in estimating the volumes of the coexisting phases for model systems of particles having the same mass as He³ or He⁴, but interacting only through the repulsive part of the Lennard-Jones potential, i. e., through the truncated potential:

$$v(r) = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6], \quad r < \sigma$$

$$= 0, \quad r > \sigma.$$

Again the sphericalized radial distribution functions obtained from our trial wave function (2), or from Schiff and Verlet's liquid wave function, can readily be reused to compute the ground-state energy of a system of atoms interacting through this truncated pair potential. The important result is that the liquid-solid transition volumes for this artificial system turn out to be identical, within statistical errors, with the corresponding values for the more realistic system, interacting via the full potential (1).

The second experiment compares the helium melting properties with those of a rather crude model which has frequently been used to discuss qualitative features of condensed helium: the quantum hard-sphere model. Obviously because the

true He-He potential is soft, the "effective hard-sphere diameter" should be smaller than the repulsive core diameter of the more realistic potentials, resulting in a smaller value of the reduced density. This explains why the volumes of the coexisting liquid and solid for the quantum hard-sphere model, as estimated by Hansen, Levesque, and Schiff,³⁴ are larger, but still of the same order, as those of helium. Both these experiments seem to suggest that the crystallization of helium is due essentially to geometrical (or packing) effects, a situation quite similar to that encountered in classical systems.

A certain amount of speculation has recently been going on about the possibility of superfluidity or of Bose-Einstein condensation in solid He⁴.³⁵ We shall only briefly consider the possibility of BE condensation in conjunction with a theorem due to Reatto.³⁶ Clearly the general structure of the wave function (2) is quite unsatisfactory for two reasons: First it is not symmetric as requested by Bose statistics; this defect probably does not have an important effect on the computed ground-state properties because of the localization of the helium atoms around their lattice sites, but it is crucial if the possibility of BE condensation is examined.³⁷ Secondly the trial wave function is unsatisfactory because it contains information *not* present in the Schrödinger equation it is supposed to solve, i. e., the equilibrium positions of the atoms. A more satisfactory trial wave function would be a pure Jastrow wave function (completely symmetric) as used by McMillan¹² and Schiff and Verlet¹³ for liquid helium. Reatto's theorem³⁶ states that a Jastrow wave function always implies the presence of a finite BE condensate. Hence if it were possible to construct a Jastrow wave function which would yield reasonable ground-state properties *and* long-range (crystalline) order, we would have a strong argument in favor of BE condensation in solid He⁴. The possibility of long-range order resulting from a Jastrow-type wave function is a direct consequence of the analogy with classical systems of particles interacting through a pair potential; the Boltzmann factor for these systems is formally analogous to a Jastrow wave function and, depending on density and temperature, the systems described by this Boltzmann factor will be fluid or crystalline. Consequently it is reasonable to look for a Jastrow function yielding long-range order in a certain density range. In fact Levesque and Schiff³⁸ have looked for "localized states" (i. e., states with crystalline order) using the Jastrow factors (3). They found that at densities close to the helium melting density a localized state could only be obtained with such a large value of the parameter *B* that the corresponding total energy was unreasonably high, which means that

TABLE VIII. Phase transitions of He³ and He⁴ at 0°K. The molar volumes are in cm³, the pressures in atm.

	Theory	Expt.	Theory	Expt.
V_{liq}	38.2	25.8	26.5	23.4
V_{sol}	24.9	24.5	22	21.5
P_{melt}	24	35	15	25
$V_{\text{bcc-hcp}}$	22	19.8		
$P_{\text{bcc-hcp}}$	58	105		

the Jastrow wave function gives a very poor description of the solid. A recent study by Hoover, Gray, and Johnson,³⁹ who systematically investigated, by Monte Carlo methods, classical systems of particles interacting through various inverse power laws, gives us a hint for the failure of pure Jastrow functions to yield a good description of solid helium. The clue lies in the rms displacement of the atoms, computed by these authors at the melting density for the various inverse power potentials. The Lindemann ratio, i. e., the ratio of the rms displacement to the nearest-neighbor distance, turns out to be practically constant for all power laws investigated, from the hard-sphere limit (infinite power) to the Coulomb limit. Their findings agree with Hansen's computer results for the inverse-12 power law and the Lennard-Jones interaction.⁴⁰ The Lindemann ratio found for these various classical systems is always close to the "magical ratio" $f = \frac{1}{7} = 0.143$. It is immediately seen from Tables I and II that this ratio is considerably larger for solid He³ and He⁴ at melting; the values are $f_3 = 0.29$ and $f_4 = 0.26$, roughly twice the practically constant value for classical systems. In other words, near melting, the helium atoms have considerably larger vibration amplitudes than any of the investigated classical systems. It seems quite doubtful that there exists a pair interaction which, in conjunction with classical statistical mechanics, would yield a melting Lindemann ratio as large as that calculated for solid helium. Hence it appears impossible to construct a purely Jastrow wave function allowing a large zero-point motion of the atoms while conserving long-range crystalline order. Consequently Reatto's theorem cannot be invoked to prove the existence of BE condensation in solid He⁴.

However our argument does not rule out completely the possibility of BE condensation, because it may be possible to construct a generalized Jastrow function including multiple correlations, formally equivalent to a classical Boltzmann factor for a system with many-body interactions. Such a classical system might yield a Lindemann ratio comparable to that calculated for solid helium and Reatto's theorem can be extended to include such wave functions. However a multiple correlation wave function would be too complicated to handle in a variational scheme, and as yet no computer experiments have been made on classical systems including many-body forces explicitly.

VII. CONCLUSION

We have presented a rather detailed calculation of various ground-state properties of solid He³ and He⁴ in the volume range between 9 cm³/mole and melting, using a simple two-parameter trial wave function in conjunction with the Metropolis-

Monte Carlo method to compute normalized expectation values. The addition of a supplementary variational parameter to include "phonon correlations" in the wave function does not change the results significantly in the volume range close to melting. Our extension of previous variational results to higher densities clearly demonstrates the inadequacy of the usual Lennard-Jones potential with de Boer parameters. Significant improvement in the agreement with available experimental data is obtained if the recently proposed Beck potential is used instead of the Lennard-Jones potential. The strongly anharmonic nature of solid helium at less than half its melting volume is stressed by the large kinetic- to potential-energy ratio in that region. There is no indication that short-range correlations become less important as the molar volume decreases.

We have pointed out the predominance of repulsive forces in the melting process of solid helium, but were unable to reach any definite conclusion concerning the possibility of BE condensation.

Finally we remark that low-lying excited states may be formulated by a variational approach patterned after Feynman's theory of liquid helium. Results of a Monte Carlo calculation of low-lying energy levels using these states will be presented in a subsequent publication.

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APPENDIX A

We give here a few details for the derivation of formula (14). Following Cottrell and Paterson's proof of the virial theorem in the quantum case,²² we define new, reduced, coordinates $\tilde{\xi}_i$ by

$$\tilde{\mathbf{r}}_i = a \tilde{\xi}_i \quad (i = 1, \dots, N),$$

where the scaling factor $a = V^{1/3}$ (V = total volume of the system); in the reduced coordinates we define the wave function corresponding to the system in a unit box by

$$\Phi(\xi_1, \dots, \xi_N; a) = \psi(\tilde{\mathbf{r}}_1, \dots, \tilde{\mathbf{r}}_N; a).$$

Differentiation with respect to a yields the basic relation

$$\left(\frac{\partial}{\partial a}\Phi\right)_{\vec{r}_i} = \frac{1}{a} \sum_i \vec{r}_i \cdot \vec{\nabla}_i \psi + \left(\frac{\partial \psi}{\partial a}\right)_{\vec{r}_i}.$$

In reduced coordinates, the Hamiltonian becomes

$$H(\vec{\xi}_1, \dots, \vec{\xi}_N; a) = -\frac{\hbar^2}{2ma^2} \sum_i \nabla_{\vec{r}_i}^2 + v(\vec{\xi}_1 a_1, \dots, \vec{\xi}_N a).$$

We differentiate twice the Schrödinger equation with respect to a :

$$\begin{aligned} \frac{\partial^2 H(\vec{\xi}_1, \dots, \vec{\xi}_N; a)}{\partial a^2} \Phi(\vec{\xi}_1, \dots, \vec{\xi}_N) \\ + 2 \frac{\partial H}{\partial a} \frac{\partial \Phi}{\partial a} + M \frac{\partial^2 \Phi}{\partial a^2} \\ = \frac{\partial^2 E}{\partial a^2} \Phi + 2 \frac{\partial E}{\partial a} \frac{\partial \Phi}{\partial a} + E \frac{\partial^2 \Phi}{\partial a^2}. \end{aligned}$$

We multiply this equation on the left by Φ^* and integrate over the volume of the unit box. Next we integrate certain terms by parts, keeping in mind that Φ is a solution of the Schrödinger equation. Surface terms vanish for rigid boundary conditions, as shown by Cottrell and Paterson. But it is easily seen that the proof also holds for periodic boundary conditions. After a certain amount of rather tedious algebra we obtain, after returning to the old coordinates

$$\begin{aligned} \frac{\partial^2 E}{\partial a^2} = -\frac{3}{a} \frac{\partial E}{\partial a} + \frac{4}{a} \frac{\langle \psi | w \partial / \partial a | \psi \rangle}{\langle \psi | \psi \rangle} \\ - 2 \frac{\langle \psi | \partial / \partial a | \psi \rangle}{\langle \psi | \psi \rangle} \left(\frac{\partial E}{\partial a} + \frac{2E}{a} \right), \end{aligned}$$

where w is defined by (15).

From this formula, (14) is immediately recovered by switching to derivatives with respect to V and using the virial theorem.

APPENDIX B

The standard Metropolis-Monte Carlo method is described in detail by Wood in his excellent review paper.⁴¹ The long-range order of the solid and the rapid decrease with distance of the Jastrow correlations allows one major simplification in our solid-helium computations: We replace the "nearest-image" convention by letting each particle "interact" with a fixed number of nearest-neighbor shells. Generally five shells (i. e., 58 atoms) were included in the bcc computations and four shells (i. e., 54 atoms) in fcc runs. No significant changes in the computed averages occurred when more shells were included, as expected, because the Jastrow

factors are practically equal to 1 beyond the third shell, at least for the physically important values of the parameter B . This procedure cuts down considerably on the number of pairs to be considered at each step of the random walk. A "step" of the random walk consists in moving one atom; we chose to move atoms in a definite order.

To illustrate our numerical results, we give here the detailed data from one particular run on the CDC 6600. All quantities are given in reduced units (i. e., $\sigma = \epsilon/k = 1$) for the density $\rho = 0.65$ atom/ σ^3 and the following values of the variational parameters $B = 1.12$ and $A = 15$.

The RANFNYU random-number generator of the Courant Institute for Mathematical Sciences was used with the initial argument set equal to 1. The maximum displacement of each atom along the three Cartesian coordinates was chosen equal to 0.175. Starting from a perfect-lattice initial configuration, 25 600 configurations were generated before "equilibrium"; then all averages were again initialized, and a total of 128 256 more configurations generated from that point. The final averages per atom were

$$\frac{1}{N} \sum_{i < j} \langle 1/r_{ij} \rangle = \langle 1/r^6 \rangle = 1.8516,$$

$$\langle 1/r^7 \rangle = 1.5141, \quad \text{and} \quad \langle 1/r^6 \rangle = 0.8700;$$

the rms displacement had a final value of 0.241. Of the 128 256 configurations, 65 493 had been "accepted" in the course of the random walk.

A small correction term has to be added to the $\langle 1/r^6 \rangle$ and $\langle 1/r^7 \rangle$ results, owing to neighbors beyond the fourth shell. For small rms displacements a static lattice correction is accurate enough, but for the larger rms displacements we calculated slightly more accurate corrections by factorizing the two-particle distribution function into a product of two Gaussian one-particle distribution functions of width determined by the rms displacement value. For an inverse- n power law, the correction then reduces to

$$\begin{aligned} \frac{1}{N} \sum_{i < j} \left\langle \frac{1}{r_{ij}^n} \right\rangle_{\text{corr}} = \frac{1}{2} \left(\frac{3}{4\pi S^2} \right)^{1/2} \\ \times \sum_{\nu} \frac{n_{\nu}}{R_{\nu}} \int_0^{\infty} \frac{e - (3/4S^2)(r - R_{\nu})^2}{r^{n-1}} dr, \end{aligned}$$

where S^2 is the square of the rms displacement, R_{ν} is the distance to the ν th shell of neighbors, n_{ν} is the number of atoms in that shell, and the sum runs over all shells not included in the Monte Carlo computation.

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