Properties of the hcp phase of ^{4}He

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The Green's-function Monte Carlo method is used to investigate the ground-state properties of the hcp phase of ^{4}He with the Lennard-Jones potential. Within the errors of the calculation, about 0.05 K, the equation of state of the hcp phase cannot be distinguished from that of the fcc phase reported earlier. Other properties are essentially the same as well. The significant discrepancies between the experimental and computed equations of state must be due to the Lennard-Jones potential.

In a previous paper,[1] the equation of state and other properties of the fcc phase of crystalline ^{4}He were reported. The stable crystalline phase at zero temperature has been determined experimentally to be the hcp phase.[2] Earlier variational calculations by Hansen[3] had shown that the differences in energy between the fcc and the hcp phases were small and were within the statistical errors. Thus we chose to study the fcc phase since many previous theoretical calculations had also been done on this phase and because it was technically easier. However, properties such as the melting-freezing transition are rather sensitive to the equation of state. The discrepancies between our reported results and experiment may have been due to the use of an fcc crystal as well as to inadequacies in the Lennard-Jones two-body potential. In an attempt to address this question, accurate variational and Green's-function Monte Carlo computations were performed on the hcp phase of Lennard-Jones ^{4}He. The results of the calculations are presented below.

The computational methods used to investigate the hcp phase are similar to those used in our earlier paper. Variational calculations were done to provide populations of points $\{R\}$ suitable for starting Green's-function Monte Carlo (GFMC) iterations and to see whether the energies so obtained were in agreement for the two phases. The major part of the computations were done using the GFMC method to solve the Schrödinger equation. With this method, it is possible to compute exactly the energy and other properties of a Bose system, subject to statistical sampling errors. A detailed description of the GFMC method and the accompanying errors has been given elsewhere.[1,4]

The trail function used in the crystal variational calculations is

$$\psi_T(R) = \prod_{i<j} f(r_{ij}) \prod_m \phi(r_m - s_m) \quad ,$$

where the s_m are the lattice sites appropriate to the crystal order being studied. The trial function is also used as an importance function to accelerate the convergence of the GFMC method. In both the fcc and the hcp crystal calculations, $f(r_{ij})$ is a function of the type proposed by McMillan[5]

$$u(r) = -\ln f(r) = \tfrac{1}{2}(b/r)^5 \quad ,$$

and $\phi(r_m - s_m)$ is a Gaussian. The trial-function parameters used in the fcc computations were those published by Hansen and Levesque.[6] A series of variational calculations was done to find the optimal parameters for the hcp phase calculations. At each density, it was found that the same parameters could be used for both the fcc and the hcp phases with no loss in accuracy.

As is our standard practice, the dependence of the calculated energies on the size of the system was investigated. We observed a difference in behavior of the GFMC calculations for the fcc and hcp systems in this respect. A comparison of the 32-body with a 108-body system for the fcc phase yielded energy values which agreed well within the sampling errors. Such has not been the case for the hcp phase at all densities. Table I shows the size dependence of the energy at two densities. At the lower density, the difference between the 64-body and the 144-body energies is well outside the quoted sampling errors. The basis for such a difference may be understood by considering the pecularities of the hcp lattice. It is not cubic and therefore the periodic box used in our computations is also not cubic. That is, there are

TABLE I. Size dependence of the energy of the hcp phase. The first column gives the density in reduced units. The energy is in degrees K per particle and N is the number of particles in the system.

	E	
$\rho\sigma^3$	$N=64$	$N=144$
0.526	-4.832 ± 0.040	-4.671 ± 0.044
0.589	-2.991 ± 0.029	-2.966 ± 0.011

TABLE II. Variational energies for the fcc and hcp phases. The first column gives the density in reduced units. The energies are all in degrees K per particle.

$\rho\sigma^3$	fcc	hcp
0.468	-4.315 ± 0.032	-4.337 ± 0.044
0.496	-4.035 ± 0.029	-4.100 ± 0.032
0.526	-3.502 ± 0.072	-3.382 ± 0.086
0.557	-2.463 ± 0.062	-2.513 ± 0.043
0.589	-0.965 ± 0.075	-0.892 ± 0.049

differing numbers of unit cells in each direction. For a system with a large number of particles, the departure from a cubic structure can be slight, but in the small systems which we have studied the box is far from cubic. The largest phonon wavelength which is treated is determined by the shortest box side. Thus a 64-particle system with hcp order is effectively smaller than a 32-body system in an fcc simulation. Also, the tail correction to the energies obtained by extrapolating $g(r)$ is much larger in the smaller system. For a 64-body hcp system, the tail correction can be at least 15% of the potential energy and is somewhat uncertain. As we go to the larger systems, the corrections become minor and we have more confidence in the calculated energies.

Finally, we would like to comment on the optimistic statistical errors quoted in Table I. These errors reflect the range of energy values encountered in the course of the GFMC iterations. Once equilibrium is attained, the energy of the hcp crystal is stable and leads to a small statistical error. In our fcc crystal study, we concluded that the error in using the 108-body results was less than 0.05 K. A similar analysis in this case would suggest that the error in using the 144-body results is about 0.11 K, which greatly overshadows the statistical errors. However, we have much more confidence in the energy values calculated with 144 particles than with 64 particles, and we conclude that the error in using the 144-body values is no more than 0.05 K.

One primary reason for studying the hcp phase of ^{4}He was to ascertain how the equation of state of the solid and the parameters of the melting-freezing transition change when hcp order rather than fcc order is used in the GFMC calculation. Our first computation was to check how closely the energy values of the two crystals agreed in variational calculations. This is essentially a repetition of the work of Hansen and Levesque and of Hansen, except that we used much smaller systems. The comparison of the energies of the two crystals was simplified by cutting off the potential energy at the same value of r in both systems. Table II lists the energies of the two phases as a function of density. Within the statistical errors of 0.05 to 0.08 K, the variational energies are the same.

In Table III the crystal energies from GFMC calculations are given as a function of density. At most densities, a perturbative estimate of the contribution of the Axilrod-Teller three-body potential is added to the energies. The estimated value of the correction is the same for both crystals. No systematic difference between the fcc and hcp crystal energies is observed. Use of the hcp energies to derive an equation of state for the crystal yields numerically equivalent results to

TABLE III. Comparison of the energies of the fcc and hcp phases in a GFMC calculation. The first column gives the density in reduced units. E_2 is the GFMC energy without the three-body energy correction and E is the energy with the correction. All energies are in degrees K per particle.

	fcc		hcp	
$\rho\sigma^3$	E_2	E	E_2	E
0.468	-5.50 ± 0.05	-5.20 ± 0.05	-5.64 ± 0.03[a]	...
0.526	-4.72 ± 0.03	-4.30 ± 0.03	-4.67 ± 0.04	-4.26 ± 0.04
0.589	-2.93 ± 0.09	-2.37 ± 0.09	-2.97 ± 0.01	-2.40 ± 0.01

[a]This value of the hcp crystal energy was calculated in a 64-body system. All other hcp energies are from 144-body systems.

TABLE IV. Moments of the single-particle distribution function. The first column gives the density in reduced units. The succeeding columns give the second, fourth, and sixth moments of the single-particle distribution. $\bar{\beta} = \langle r^4 \rangle - \frac{5}{3}\langle r^2 \rangle^2$. All lengths are in units of σ. A measure of the departure of the single-particle distribution from Gaussian form is $\bar{\beta}/\langle r^2 \rangle^2$.

$\rho\sigma^3$	Phase	$\langle r^2 \rangle$	$\langle r^4 \rangle$	$10\langle r^6 \rangle$	$\frac{1}{25}\bar{\beta}$
0.526	fcc	0.127 ± 0.002	0.029 ± 0.001	0.096 ± 0.006	$(0.68 \pm 0.18) \times 10^{-4}$
0.526	hcp	0.120 ± 0.004	0.023 ± 0.001	0.063 ± 0.005	$\simeq 10^{-5}$
0.589	fcc	0.099 ± 0.003	0.016 ± 0.001	0.037 ± 0.003	$\simeq 10^{-6}$
0.589	hcp	0.102 ± 0.002	0.017 ± 0.001	0.042 ± 0.003	$\simeq 10^{-6}$

that of the fcc equation of state. Thus the melting-freezing transition remains that reported in the earlier paper.

To clarify the behavior of the fcc crystal at higher densities, an additional simulation at $\rho\sigma^3 = 0.622$ was carried out. The energy at this density, including three body corrections is -1.081 ± 0.088 K and was used in redetermining the equation of state for the fcc crystal. The revised equation of state is fitted by the polynomial

$$\frac{E}{N} = A' + B'\left(\frac{\rho - \rho_1}{\rho_1}\right)^2 + C'\left(\frac{\rho - \rho_1}{\rho_1}\right)^3 ,$$

and the new values for the parameters are

$$A' = -5.680 \pm 0.039, \quad B' = 18.56 \pm 6.5 ,$$

$$C' = 2.39 \pm 10$$

and

$$\rho_1 = (0.429 \pm 0.012)\sigma^{-3} .$$

The addition of the higher-density datum has not changed the equation of state since the new parameters are within the errors of the original parameters. Use of the new equation of state for the crystal in a Maxwell construction yields the same melting and freezing densities as published earlier. That is, the melting density is $(0.515 \pm 0.009)\sigma^3$, the freezing density is $(0.475 \pm 0.011)\sigma^3$, and the volume difference between the solid and the liquid is 1.63 ± 0.60 cm^3/mole.

Other crystal characteristics were also determined for the two phases. Our investigations of the fcc crystal had shown that the single-particle density $\rho(r)$ is essentially Gaussian with only small deviations from Gaussian behavior in the tail of the distribution. A similar behavior is also observed for the single-particle density in the hcp crystal. In Table IV we enumerate the values of $\langle r^2 \rangle$, $\langle r^4 \rangle$, $\langle r^6 \rangle$, and $\bar{\beta}$ for the two phases. The quantity $\bar{\beta}$ is a linear combination of the fourth moment and the square of the second moment of $\rho(r)$ which should be zero for a Gaussian distribution.

A perusal of the table shows little difference between the fcc and hcp crystals, although higher moments suggest that the latter may be slightly more localized at the lower density. From the evidence obtained, we conclude that $\sigma(r)$ is very nearly Gaussian for the hcp crystal as well as for the fcc crystal in the density range studied.

Our final comparison between the two phases is to compare the pair-correlation function and the structure function. The outcome is that the values of these two functions for the two phases are the same within their errors at each density.

The study of the hcp phase of Lennard-Jones ^{4}He was initiated to answer questions raised by the GFMC simulation of the fcc phase. We were uncertain whether the discrepancies observed between the experimental values and GFMC values were the result of using the "wrong" crystal phase; i.e., fcc, in the calculations or a result of using the Lennard-Jones potential. Earlier Monte Carlo variational calculations seemed to suggest that the hcp phase and the fcc phase could not be distinguished when the Lennard-Jones two-body potential was used. This conclusion has been borne out by our more accurate GFMC calculations. The small differences between the hcp and fcc phases are not discernible through a GFMC computation, and thus the ground state of Lennard-Jones ^{4}He is accurately described by an fcc crystal. We conclude that the shortcomings in the calculated equation of state for solid ^{4}He are a result of the Lennard-Jones potential.

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