Variational Monte Carlo Calculations of Liquid ^{4}He with Three-Body Correlations

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The first Monte Carlo calculations explicitly employing triplet correlations in the variational wave function for the ground state of ^{4}He are presented. A significant lowering of energy is obtained, accounting for 75% of the discrepancy between previous Jastrow variational calculations and the known exact numerical results. An improved density dependence of the energy is obtained and the pair correlation function is sharpened leading to much better agreement with the exact ground state.

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Many variational calculations of the ground-state energy of liquid ^{4}He with use of the Metropolis Monte Carlo method[1] to calculate the energy expectation value have been done with trial wave functions of the Jastrow form,[2]

$$\Psi_J = \prod_{i<j} f_{ij} = \exp\Big(-\tfrac{1}{2}\sum_{i<j} u_{ij}\Big). \tag{1}$$

The correlation function f_{ij} and the pseudopotential u_{ij} are functions only of the distance $|\vec{r}_{ij}|$ between particles i and j.

Recent Green's-function Monte Carlo (GFMC) calculations,[3] which can integrate *exactly* the N-body Schrödinger equation for a given potential, have given energies significantly lower (1.2 °K) than those obtained by the Jastrow variational method (see Fig. 1). Several authors[4,5] have investigated the effects of including limited triplet correlation in the trial wave function,

$$\Psi_3^{\,2} = \exp\Big(-\sum_{i<j} u_{ij} - \sum_{i<j<k} w_{ijk}\Big). \tag{2}$$

These calculations suggest that three-body correlations account for much of the energy difference.

The errors in the approximate integral equations employed in these calculations are difficult to assess. By contrast, the treatment by Monte Carlo integration yields a strict variational upper bound for the energy within a small statistical uncertainty. The major drawback of using Eq. (2) with the Monte Carlo method is that, for a general function w_{ijk}, explicit three-body sums are required to calculate the energy expectation. For a simulation of N particles the inclusion of these three-body sums would in general increase the computation time by a factor of order N over that required in a Jastrow calculation. In this paper we will show that for a class of physically reasonable triplet correlations no explicit three-body sums are required and thus the computation time is of the same order as in a Jastrow calculation. We also show that the inclusion of these triplet correlations brings the variational and GFMC results into much better agreement.

The trial wave function we have used is

$$\psi_3^{\,2} = \exp\Big[-\sum_{i<j}\tilde{u}_{ij} - \tfrac{1}{2}\lambda\sum_{l}\vec{G}(l)\cdot\vec{G}(l)\Big], \tag{3}$$

where

$$\vec{G}(l) = \sum_{i\neq l}\xi_{li}\vec{r}_{li}, \quad \tilde{u}_{ij} = u_{ij} - \lambda\xi_{ij}^{\,2} r_{ij}^{\,2},$$

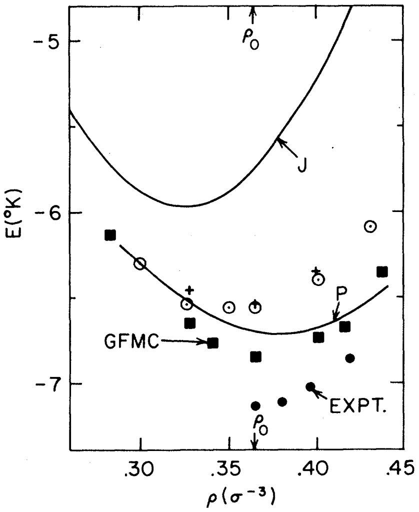

FIG. 1. Comparison of energy vs density. J indicates pure Jastrow results of Ref. 10; P indicates triplet calculations of Ref. 5; experimental results from Ref. 11; exact Lennard-Jones from Ref. 3; cross indicates present calculation; dot in circle indicates results from Ref. 4.

with λ and ξ to be obtained variationally. The principal motivation for this choice is as follows. For an exact solution $(H\psi_0)/\psi_0$ is a constant, but when one uses a pure Jastrow trial function $(H\psi_J)/\psi_J$ contains terms like $u_{ij}'u_{ik}'\vec{r}_{ij}\cdot\vec{r}_{ik}$. The form of Eq. (3) permits the partial cancellation of such terms by terms arising from w_{ijk}. Furthermore, Pandharipande has shown[5] that a three-body form similar to ours includes effects of Feynman-Cohen[6] backflow. Since the calculation of $\sum_i \vec{G}(i)\cdot\vec{G}(i)$ requires only two-body sums, this wave function is well suited for Monte Carlo calculation.[7]

We employ the standard Metropolis Monte Carlo procedure. The energy is computed from the identity

$$E = N^{-1}\langle (H\Psi)/\Psi\rangle = \langle 2T_i + V_i - \vec{F}_i^{\,2}\rangle,$$

where i refers to the coordinates of one particle, and

$$T_i = -(\hbar^2/4m)\nabla_i^{\,2}\ln\Psi,$$

$$\vec{F}_i^{\,2} = (\hbar^2/2m)(\nabla_i \ln\Psi)^2,$$

$$V_i = \tfrac{1}{2}\sum_{j\neq i} v_{ij}.$$

The angular brackets indicate an average over configurations. Here v_{ij} is the interparticle potential which is taken to be the Lennard-Jones potential with the DeBoer-Michels parameters,

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

$$\sigma = 2.556\ \text{Å},\quad \epsilon = 10.22\ ^\circ\text{K}.$$

The T_i and the $\vec{F}_i$ are most easily calculated by defining the symmetric tensors

$$\overleftrightarrow{T}(j) = \nabla_i \vec{G}(j) = \begin{cases} \sum_{k\neq i}\left(\dfrac{\xi_{ik}'}{r_{ik}}\right)\vec{r}_{ik}\vec{r}_{ik}, & i = j \\ \left(\dfrac{\xi_{ji}'}{r_{ik}}\right)\vec{r}_{ji}\vec{r}_{ji}, & i \neq j, \end{cases}$$

and the vectors

$$\vec{L}(j) = \nabla_i^{\,2}\vec{G}(j).$$

The primes indicate a derivative. T_i and $\vec{F}_i$ become

$$T_i = (\hbar^2/8m)\{\nabla_i^{\,2}\tilde{u}_{ij} + \lambda\textstyle\sum_j[\overleftrightarrow{T}(j)\cdots\overleftrightarrow{T}(j) + \vec{L}(j)\cdot\vec{G}(j)]\},$$

$$\vec{F}_i^{\,2} = (\hbar^2/8m)[\nabla_i\tilde{u}_{ij} + \lambda\textstyle\sum_j\overleftrightarrow{T}(j)\cdot\vec{G}(j)]^2$$

which include only simple inner products.

We have chosen for purposes of comparison two different forms for $u(r)$: the McMillan form,[2]

$$u(r) = (b/r)^5, \tag{4}$$

where b is a variational parameter, and a form suggested by Reatto,[8]

$$u(r) = \begin{cases} u_{\text{KLV}}(r) + C\exp-(r-d)^2/D^2 - A\exp-(r-s)^2/\sigma^2 - F, & r < s, \\ u_{\text{KLV}}(r) + C\exp-(r-d)^2/D^2 - A - F, & r_{\min} > r > s, \\ 0, & r > r_{\min}; \end{cases} \tag{5}$$

TABLE I. Comparison of variational energies with (E) and without (E_J) triplet correlation. Parameters are as defined in the text. "M" implies a two-body pseudopotential as in Eq. (4) with $b = 1.17\sigma$. "R" implies use of Eq. (5).

u	E_J	$\rho(\sigma^{-3})$	E (°K)	λ	r_t	ω
M[a]	−5.96	0.333	−6.46 ± 0.02	−6.5	0.85	0.52
M[a]	−5.73	0.365	−6.53 ± 0.02	−8.0	0.82	0.50
M[a]	−5.25	0.400	−6.37 ± 0.02	−9.0	0.85	0.45
R[b]	−5.94 ± 0.03	0.365	−6.55 ± 0.03	−9.0	0.80	0.50

[a] Jastrow results from Ref. 10.

[b] Jastrow results with use of Eq. (5).

TABLE II. The values and positions of the first few maxima and minima of $g(r)$ at experimental equilibrium density ($\rho = 0.365$). Variational parameters are the same as in Table I. Results including triplet correlations are indicated by "T".

Trial function	$r_{\max 1}$	$g_{\max 1}$	$r_{\min 1}$	$g_{\min 1}$	$r_{\max 2}$	$g_{\max 2}$
M	1.32 ± 0.02	1.265 ± 0.003	2.03 ± 0.02	0.947 ± 0.001	2.68 ± 0.02	1.014 ± 0.002
$M+T$	1.35 ± 0.02	1.30 ± 0.005	2.03 ± 0.02	0.918 ± 0.003	2.68 ± 0.02	1.030 ± 0.005
R	1.34 ± 0.01	1.33 ± 0.005	1.97 ± 0.02	0.912 ± 0.006	2.62 ± 0.04	1.028 ± 0.005
$R+T$	1.36 ± 0.01	1.365 ± 0.005	1.99 ± 0.01	0.883 ± 0.003	2.58 ± 0.04	1.043 ± 0.004
GFMC	1.36 ± 0.02	1.35 ± 0.01	2.04 ± 0.04	0.90 ± 0.02	2.68 ± 0.02	1.040 ± 0.01

$C = 0.3$, $d = 1.8\sigma$, $D = 0.6\sigma$, $A = 0.3$, $s = 1.5\sigma$; $u_{\mathrm{KLV}}(r)$ is given in Ref. 9; F and $r_{\min}$ were chosen so that the $u(r)$ goes smoothly to zero at $r_{\min} = 2.667\sigma$ and $F = 0.0397$.

The $u(r)$ of Eq. (5) gives a lower energy (-5.9 °K) at the experimental equilibrium density, $\rho_0 = 0.3648\sigma^{-3}$, than that of Eq. (4) ($-5.7$ °K), but its optimal parameters have not been determined at other densities. The pseudopotentials are modified to go smoothly to zero at $r = r_B$, half the side of the simulation cube.

We introduced a form for the triplet correlation function which is effective at intermediate ranges:

$$\xi(r) = \left[\exp\left(\frac{r - r_t}{\omega}\right)^2\right]\left(\frac{r - r_B}{r_B}\right)^3,$$

where r_t and ω are new variational parameters.

Table I gives the energies calculated for 108 particles at various densities. The optimum values of the variational parameters are also given. These energies are shown in Fig. 1 along with results for the Jastrow wave function and GFMC. It can be seen that the inclusion of the triplet correlation greatly improves the agreement between the variational and the exact results. The energy is lowered to within 0.5 °K of the equilibrium Lennard-Jones ground state and the equilibrium density is shifted from $0.9\rho_0$ to about $0.96\rho_0$.

The two-body distribution function $g(r)$ calculated with the pure Jastrow wave function with the McMillan pseudopotential is known[3] to have too little structure. The Reatto form for the pseudopotential gives an improved $g(r)$. We find that the inclusion of the triplet correlation improves both estimates of $g(r)$ by about the same amount. This may be seen in Table II where the positions and magnitudes of the first few maxima and minima of $g(r)$ are given for the various computations at $\rho = 0.365\sigma^{-3}$.

Our results constitute strong confirmation that the inclusion of three-body correlations in a variational trial function significantly improves the energy and structure as compared with a pure Jastrow *Ansatz*. Whether the remaining disagreement with exact results may be resolved by considering a broader class of three-body functions or whether four body and higher correlations will be required remains an open question. It is interesting to note that our results agree well with those of Campbell in spite of the different motivation and formally rather different wave function used. The discrepancy between experiment and exact Lennard-Jones calculations is almost entirely removed if one uses the HFDHE2 potential for helium suggested by Aziz *et al.*[12] We plan calculations of the equation of state of helium using this improved potential.

We conjecture that the effects explored here are important corrections in the structure of ^{3}He; but the effect of backflow on the orbitals of the Slater determinant is likely also to be significant. Calculations are underway to test this hypothesis.

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Broken Hexagonal Symmetry in the Incommensurate Charge-Density Wave Structure of $2H$-TaSe$_2$

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High-resolution x-ray scattering studies show a new charge-density wave (CDW) structure on warming through the commensurate-incommensurate transition in $2H$-TaSe$_2$ at 93 K. In contrast to the fully incommensurate CDW structure seen on cooling, hexagonal symmetry is broken in the new phase and the triple-$\vec{q}$ CDW has one commensurate and two incommensurate wave vectors. At 112 K (warming) the CDW transforms to the fully incommensurate structure.

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Systems with incommensurate periodicities have been the focus of many experimental[1-4] and theoretical studies.[5-9] These systems include charge-density waves[1,2] (CDW's) and rare gases physisorbed onto surfaces.[3,4] If the incommensurate periodicity is close to registry with the host lattice, one expects the interaction between the two subsystems to favor the formation of large commensurate regions separated by narrow domain walls with rapidly varying superlattice phase.[5,6] Domain walls may be either ordered in a regular hexagonal honeycomb array or linear striped pattern, for example, as suggested by Bak and Mukamel,[7] or disordered as described by Villain.[8] These arrangements are determined by the competition between wall-wall interactions, wall-crossing energies, and entropy. There may be phase transitions from the disordered to ordered states and between the different ordered states. Thus far the evidence in support of domain walls has come from the observation of higher-order diffraction satellites of the CDW superlattice in $2H$-TaSe$_2$ (Ref. 2) and satellite intensity variations attributed to coherent interference from ordered domains in the krypton/pyrolytic-graphite systems.[3]

In this Letter we present observations of a previously undetected CDW phase in $2H$-TaSe$_2$ with broken hexagonal symmetry. In the new phase the triple-$\vec{q}$ CDW contains one commensurate and two incommensurate wave vectors. We will show that diffraction satellites identify the new phase as having the striped geometry. Further we report a first-order transition from this state to a fully incommensurate state which has the hexagonal geometry. This transition was initially seen in dilatometry studies by Steinitz and Grunzweig-Genossar.[10]

High-resolution x-ray scattering was performed on a triple-axis spectrometer with a cleaved TaSe$_2$ platelet mounted in $(h0l)$ or (hhl) scattering planes. Copper $K\alpha_1$ x rays from a 50-kW rotating anode were focused with a vertically bent LiF monochromator. A flat Ge analyzer was used on the diffracted beam. This arrangement resulted in a resolution function with a full width at half maximum of 0.003 Å^{-1} in the diffraction plane and about 0.1 Å^{-1} normal to the plane.

Neutron scattering experiments[2] have shown that on cooling[11] an incommensurate CDW forms at a normal-incommensurate (NI) transition at $T_{\rm NI} = 123$ K and becomes commensurate at a commensurate-incommensurate (CI) transition at $T_{\rm CI} \sim 90$ K. The CDW has a triple-$\vec{q}$ structure with