Path-Integral Monte Carlo Study of Low-Temperature ^{4}He Clusters

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(Received 12 July 1989)

Path-integral Monte Carlo calculations have been used to study ^{4}He clusters at low temperatures. We develop a fluctuation formula for the superfluid fraction in terms of a projected area swept out by a path. Manifestations of superfluid behavior are shown to exist in a cluster of 64 atoms and a remnant of the λ transition persists in a cluster of 128 atoms. The temperature dependence of the superfluid fraction is similar to that observed in the liquid.

PACS numbers: 67.40.−w, 36.40.+d

The properties of ^{4}He clusters have attracted much experimental and theoretical interest.[1-6] Superfluidity has been reported in small (<110 Å) bubbles of ^{4}He confined in Cu foils.[7] One might therefore expect gas-phase ^{4}He clusters of analogous size to show superfluid behavior. However, attempts to provide experimental evidence of superfluid behavior in clusters has so far proved to be inconclusive.[1] By contrast, there has been considerable progress in theoretical work which has largely focused on the calculation of ground-state properties. Energy and density profiles have been computed using quantum Monte Carlo methods[2-5] and density-functional theory.[6] One remarkable result that emerged from these studies was the predicted smooth evolution of the ground-state energy as a function of the number of atoms in the cluster; i.e., there is an absence of magic numbers in *neutral* clusters. The ground-state condensate fraction has been investigated as a function of cluster size using variational calculations.[2-5] But, no finite-temperature investigations have yet been carried out.

Here, we report the results of a finite-temperature path-integral Monte Carlo study of ^{4}He clusters that includes the effect of Bose statistics. The method we employ, and the calculational procedures, have achieved notable success in probing the superfluid transition of the bulk liquid[8,9] and the two-dimensional counterpart.[10] Our main finding is that manifestations of superfluidity exist in a cluster of 64 atoms and that even in a cluster this small, at a given temperature the magnitude of the superfluid fraction is surprisingly similar to that in the bulk liquid.[11]

The statistical mechanical properties of an N-atom system are determined by the density matrix which, in the Feynman path-integral representation, is factored into M time slices

$$\rho(\mathbf{R},\mathbf{R}';\beta)=\int\cdots\int d\mathbf{R}_1\cdots d\mathbf{R}_{M-1}\rho(\mathbf{R},\mathbf{R}_1;\tau)\times\rho(\mathbf{R}_1,\mathbf{R}_2;\tau)\cdots\rho(\mathbf{R}_{M-1},\mathbf{R}';\tau)\,.$$

Here, $\tau=\beta/M$, the variables $\mathbf{R}$ are points in a $3N$-dimensional space, and $(\mathbf{R},\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}')$ denotes a discretized path. This device, along with an accurate approximation for the high-temperature (small-τ) density matrix, allows calculation of $\rho(\mathbf{R},\mathbf{R}';\beta)$ at a temperature a factor of $1/M$ lower than β. As in the studies of the bulk liquid, the small-τ approximation used here is of the pair product form

$$\rho(\mathbf{R},\mathbf{R}';\beta)=\prod_i\rho_1(\mathbf{r}_i,\mathbf{r}_i';\tau)\prod_{ij}\exp[-U(r_{ij},r_{ij}';\tau)]\,,$$

where, $i,j=1,N$; ρ_1 is the free-particle propagator and the nonideal part is contained in the second term.[9] For a Bose system, the density matrix is obtained by summing over all permutations P of particle labels

$$\rho(\mathbf{R},\mathbf{R}';\beta)=(1/N!)\sum_P\rho(\mathbf{R},P\mathbf{R}';\beta)\,.$$

Both the integration over paths and the summation over permutations are performed by a generalized Metropolis algorithm whose implementation is discussed in detail elsewhere.[9] The N atoms comprising the cluster interact via an accurate interatomic pair potential.[12]

In the two-fluid model description of liquid ^{4}He, the normal and superfluid parts can be defined (and experimentally measured) by their different responses to an external perturbation. Indeed, this fact allows the derivation of microscopic expressions for the superfluid or normal fractions. The superfluid fraction for a system with periodic boundary conditions (i.e., a homogeneous bulk liquid) can be computed either from the so-called *winding number* of the discretized paths or from the momentum density correlation function $\langle\mathbf{p}(r)\cdot\mathbf{p}(0)\rangle$.[9] Usually, one defines the normal fluid fraction from the response of a system to boundary motion or to an external field. In the present case, we imagine that the cluster has been placed in an external field, which is assumed to have cylindrical symmetry about an axis passing through the center of mass of the cluster. We then consider the

cluster's response to slow rotation of the field with an angular frequency, $\omega = \omega \mathbf{u}$. The setup closely resembles ^{4}He enclosed in a cylinder; a situation that has been extensively discussed in the literature.[13] As in that case, the superfluid fraction can be determined by the departure of the moment of inertia tensor $\mathbf{I}$ from its classical value $\mathbf{I}^*$ or from the angular momentum density correlation function $\langle \mathbf{L}(r) \cdot \mathbf{L}(0) \rangle$, where $\mathbf{L}$ denotes the total angular momentum.

The properties of the cluster are determined by ρ_ω, the density matrix of the system in the rotating field. The density-matrix operator in a frame at rest with respect to the field (primed frame) is determined by the Hamiltonian, $H' = H - \mathbf{L} \cdot \omega$. Since, the scalar operator $\mathbf{L} \cdot \omega$ is unchanged in going to the laboratory frame, $\rho_\omega = \rho' = \mathrm{Tr}\{\exp[-\beta H']\}$. The expectation value of $\mathbf{L} \cdot \mathbf{u}$ is $\langle L \rangle_\omega = \mathrm{Tr}\{L\rho_\omega\}/\mathrm{Tr}\{\rho_\omega\}$ and, by definition, the moment of inertia with respect to $\mathbf{u}$ is given by $I = (\partial \langle L \rangle_\omega / \partial \omega)_{\omega=0}$.

For a classical system with density distribution $\rho(r)$, the moment of inertia is given by $I^* = m \int d\mathbf{r} \rho(r) |\mathbf{u} \times \mathbf{r}|^2$. The normal fraction is the part of the cluster that responds as a classical system, namely,

$$I/I^* = \beta \{\langle \mathbf{L} \cdot \mathbf{L} \rangle - \langle \mathbf{L} \rangle \langle \mathbf{L} \rangle\}/I^* .$$

To proceed further, an appropriate estimator for the path-integral evaluation of I is required. This is obtained by twice differentiating $\mathrm{Tr}\{\rho_\omega\}$ with respect to ω. With the abbreviation $\lambda^2 = h^2\beta/m$ we find

$$I = \langle I^0 \rangle - 4\{\langle A^2 \rangle - \langle A \rangle \langle A \rangle\}\{m/\lambda^2\} ,$$

where

$$I^0 = m \sum_i \sum_\kappa (\mathbf{u} \times \mathbf{r}_{i,\kappa})(\mathbf{u} \times \mathbf{r}_{i,\kappa+1})/M$$

and

$$A = \sum_i \sum_\kappa (\mathbf{r}_{i,\kappa} \times \mathbf{r}_{i,\kappa+1})/2 .$$

The position of particle i at the time slice κ is $r_{i,\kappa}$ and $r_{i,M} = P r_{i,0}$. On the average, $\langle A \rangle = 0$ and $\langle I^0 \rangle = I^*$. For a given axis, the deviation of the moment of inertia from its classical value is related to the expectation value of the square of the surface area A enclosed by the Feynman paths projected onto a plane perpendicular to that axis.

The moment of inertia, and therefore the normal fraction, may also be computed from $P(n) = \langle \delta(L - n\hbar) \rangle$, the probability that the angular momentum has the value $n\hbar$. A path-integral estimator for $P(n)$ is

$$P(n) = (1/2\pi) \int d\theta g(\theta) \exp[-in\theta] ,$$

where the integration extends from $-\pi$ to π. For small τ (large M),

$$g(\theta) = \langle \exp[\{2A\theta - I^0\theta^2/2m\}\lambda^2] \rangle .$$

Since $g(\theta)$ is strongly peaked around $\theta = 0$, we can extend the integration limits to infinity and find

$$P(n) \approx \exp[-n^2(m\lambda^2/2I^*)/(1 - 4A^2 m/\lambda^2 I^*)] .$$

Thus, bosons will show fewer fluctuations in angular momentum than classical particles by an amount proportional to the superfluid fraction

$$(I^* - I)/I^* = 4m^2 \langle A^2 \rangle / \beta \hbar^2 I^* .$$

By direct computation, we find $\ln\{P(n)\}$ to be a linear function of n^2 for $n < 30$. Moreover, values for the normal fraction are essentially indentical using either approach.

We employed the full density matrix which allows for much larger values of τ than the primitive end-point approximation and choose a value of τ corresponding to a temperature of 40 K; a procedure which is known to yield satisfactory results for bulk.[9] The *lowest*-temperature simulations required more than 200 h of central-processing-unit time on an IBM 3090/200 E with

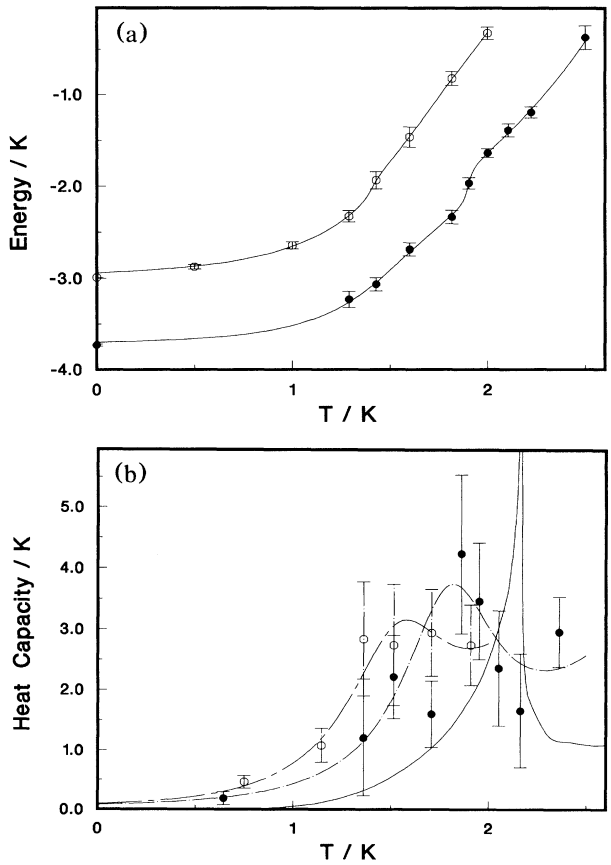

FIG. 1. Path-integral results for the (a) energy and (b) heat capacity of ^{4}He clusters with $N = 64$ (open circles) and 128 (solid circles). The $T = 0$ K energy values were taken from Green's-function Monte Carlo calculations (Ref. 2). The solid line refers to the bulk heat capacity (Ref. 11) and other lines are drawn as a guide to the eye.

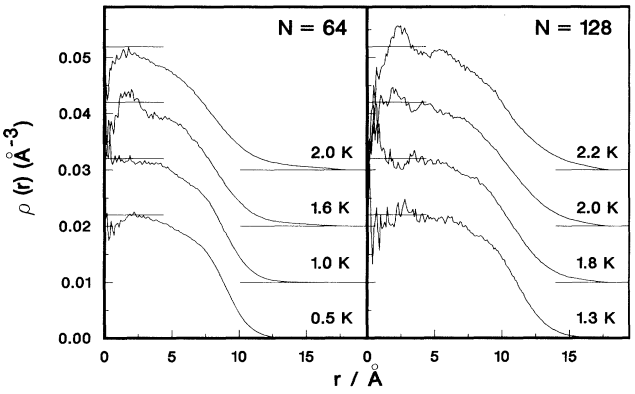

FIG. 2. Selected examples of radial density profiles for ^{4}He clusters. The bulk liquid density, $\rho = 0.022/\text{Å}^{-3}$, is indicated.

attached vector processors. The existence of correlated subaverages in analysis of the data points for the $N = 128$ cluster suggests that even longer runs may be necessary. Figure 1 shows results for the energy and the heat capacity as a function of temperature for $N = 64$ and 128. Around 1.9 K, a distinct bump can be discerned in the heat capacity of the larger cluster; a feature much less evident for the smaller one. This observation is consistent with the notion that the bulk λ transition becomes smeared out in a finite system. The present results extrapolate smoothly to ground-state energy values from previous calculations.[4,5]

There is always a chance that atoms will evaporate during the simulation at finite temperature; a problem that is particularly acute for helium. In order to circumvent this difficulty, we restricted the Feynman paths to lie within a radius R_c from the center of gravity of the paths. The choice of R_c is a somewhat delicate matter: It should be large enough to minimize the influence on the cluster, but it should also be sufficiently small to avoid having atoms in the vapor. The present choice ($R_c = 18$ Å) was guided by available zero-temperature density profiles[4,5] and is consistent with simple thermodynamic arguments. Figure 2 shows a selection of radial density profiles, at different temperatures, for both clusters. The density in the tail of the profiles increases slightly with temperature but overall the profiles are very similar to those reported previously for 0 K.[2-5] In all simulations, the density at R_c is very small.

The temperature dependence of the normal fraction is shown in Fig. 3. For both clusters, the normal fraction decreases strongly with temperature below 2 K; a behavior reminiscent of bulk ^{4}He. In the Feynman-path-integral representation, superfluidity is connected to the existence of very long paths involving several permuting atoms.[9] In bulk ^{4}He these paths result in the nonzero asymptotic value of the off-diagonal one-body density matrix (off-diagonal long-range order) and the presence of a Bose condensate. For an inhomogeneous fluid the probability that an atom is part of a permutation cycle involving p atoms provides a measure of the degree of superfluidity, provided that p is not too small.[9] Our cluster simulations reveal that the probability for large permutation cycles increases dramatically below the bulk λ-transition temperature. This effect is illustrated in Fig. 4. There we show the temperature dependence of $\Pi(r)$, the fraction of the radial density profile due to particles involved in permutation cycles of six or more atoms. This measure of the superfluid density is large in the surface region but, as expected, drops to zero at the cluster surface.

In summary, it is striking how little the presence of a surface has influenced the phenomenon of superfluidity. An investigation into the nature of dynamical excitations in these superfluid droplets would be most interesting.[14]

The research described herein was supported by the

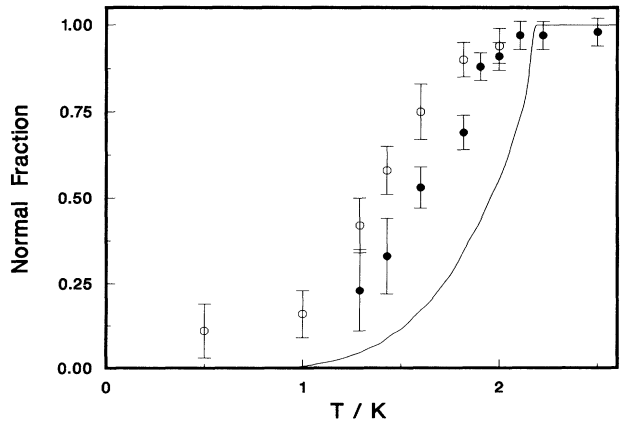

FIG. 3. Evolution of the normal fraction in ^{4}He clusters with $N = 64$ (open circles) and 128 (solid circles); the solid curve refers to the bulk (Ref. 11).

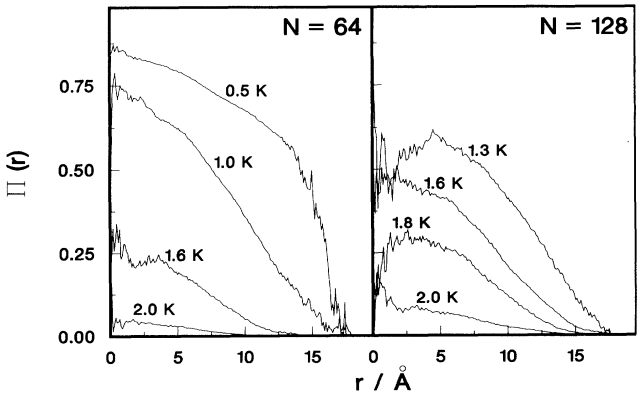

FIG. 4. Evolution of the fraction of the radial density profile due to permutation cycles involving six or more atoms in ^{4}He clusters with $N = 64$ and 128 atoms.

National Science Foundation under Grants No. CHE-8722481 and No. CHE-8815130.

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