

Off-Diagonal Long-Range Order in Solid ^4He

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Measurements of the moment of inertia by Kim and Chan have found that solid ^4He acts like a supersolid at low temperatures. To understand the order in solid ^4He , we have used path integral Monte Carlo simulations to calculate the off-diagonal long-range order (ODLRO) [equivalent to Bose-Einstein condensation (BEC)]. We do not find ODLRO in a defect-free hcp crystal of ^4He at the melting density. We discuss these results in relation to proposed quantum solid trial functions. We conclude that the solid ^4He wave function has correlations which suppress both vacancies and BEC.

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Whether bulk solid has a region of its equilibrium phase diagram with supersolid behavior has been of theoretical interest [1–3] for many years. Recently, Kim and Chan [4] have observed behavior similar to that of nonclassical rotational inertia (NCRI) at temperatures below 0.2 K. Analogous to behavior in a superfluid, NCRI would be expected in a supersolid, a state of matter in which crystallinity and superfluid behavior coexist. Two key theoretical quantities in establishing the order of a bosonic system are the superfluid fraction [estimated [5] to vanish] and off-diagonal long-range order (ODLRO) previously estimated only by variational methods.

Off-diagonal order tells us whether atoms at one end of the solid are in phase with atoms at the other end of the solid. It is formally equivalent (via a Fourier transform) to a nonzero condensate fraction or Bose-Einstein condensation (BEC). ODLRO would supply a mechanism for NCRI. The converse of this does not follow, a counterexample being 2D superfluidity, but all known superfluid systems in three dimensions manifest both NCRI and ODLRO. ODLRO [6] is a property of the single particle density matrix:

$$n(\mathbf{r}, \mathbf{r}'; \beta) = \frac{V}{Z} \sum_{\alpha} \int d\mathbf{r}_2 \dots d\mathbf{r}_n e^{-\beta E_{\alpha}} \Psi_{\alpha}(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_n) \times \Psi_{\alpha}^*(\mathbf{r}', \mathbf{r}_2, \dots, \mathbf{r}_n), \quad (1)$$

where Ψ_{α} and E_{α} are the α^{th} eigenfunction and value of the many body Hamiltonian, Z the partition function, V the volume, and $\beta = 1/k_B T$. A system is said to be Bose condensed if an eigenvalue of the matrix $n(\mathbf{r}, \mathbf{r}')$ is proportional to the number of atoms in the system in the thermodynamic limit. In this Letter, we consider a translationally invariant system in periodic boundary conditions. This implies that $n(\mathbf{r}, \mathbf{r}')$ only depends on $\Delta\mathbf{r} = \mathbf{r} - \mathbf{r}'$ and its eigenfunctions are momentum states. Considering the occupation of the $\mathbf{k} = 0$ momentum state, the condensate fraction is

$$n_0 = \frac{1}{V^2} \int d\mathbf{r} d\mathbf{r}' n(\mathbf{r}, \mathbf{r}'). \quad (2)$$

A system has ODLRO if, in the thermodynamic limit, the condensate fraction is greater than 0. This is equivalent to $n_0 = \lim_{|\Delta\mathbf{r}| \rightarrow \infty} n(\Delta\mathbf{r}) > 0$.

Reatto [7] showed that a pair-product (Jastrow) trial wave function (JWF), commonly used for liquid ^4He , has ODLRO. This trial function has the form $\Psi_J(R) = \exp[-\sum_{i<j} u(r_{ij})]$, where $u(r_{ij})$ is fixed by minimizing the variational estimate of the ground state energy. By interpreting the absolute square of the Jastrow wave function as a classical Boltzmann-Gibbs probability for a pair potential energy, it can be seen that the Jastrow trial function is equivalent to classical system interacting with a pair potential. The physical argument for BEC is then straightforward: to calculate $n(\Delta\mathbf{r})$ one displaces an arbitrary atom by $\Delta\mathbf{r}$; if the average amplitude for this is nonzero, the system has BEC. The condensate fraction will be nonzero as long as $u(r)$ is short ranged, except for special systems such as hard spheres at close packing density. It will also be true if the wave function has short-ranged three or higher body correlation factors. Chester [3] then pointed out that such a trial function can be a crystal, since it has the same spatial density as a classical solid interacting with a pair potential. This argument can be used to prove [8] that there exist quantum systems with both crystalline order and BEC. Chester further conjectures that under the same conditions, a crystal will have BEC only if there exist ground state vacancies (or interstitials). This argument has been recently elaborated [10]. The Jastrow form of trial function turns out to give a seriously incorrect density for freezing [11] and other properties. As is well known, melting of classical systems occurs when the rms vibration around a lattice site equals about 0.14 of the nearest neighbor distance: Lindemann's melting criterion. However, solid ^4He does not melt until much later [12], with a Lindemann's ratio of 0.30. Assuming Lindemann's criteria for the melting of a classical system, no Jastrow trial function can describe a solid ^4He near melting, nor can

it describe a quantum crystal without an intrinsic population of point defects.

A much better description of solid ^4He is obtained by multiplying the Jastrow function by a localization term; the Jastrow-Nosanow form [13] (JN) or “insulator” form:

$$\Psi_{\text{JN}}(R) = \frac{\Psi_J}{N!} \sum_P \prod_{i=1}^N \phi_{P_i}(\mathbf{r}_i). \quad (3)$$

Here $\phi_i(\mathbf{r})$ (a Wannier function) is localized about lattice site i , and P a permutation of atoms to lattice sites. The sum over P projects out the bosonic component of the wave function; the projected wave function is a “permanent.” In fact, the symmetrization lowers the variational energy by an amount proportional to the exchange energy, calculated in Ref. [14] to be about $3 \mu\text{K}/\text{atom}$, negligible for most properties but crucial for properties such as BEC or NCRI. The JN wave function is a very good description of the ground state judging by the computed energies, Debye-Waller factors, pair correlation function, and estimated melting density [11]. However, the solid order is put in “by hand” rather than coming about spontaneously. Broken translational symmetry is the hallmark of the crystal state [15,16]. Upon freezing a density wave arises which defines the lattice sites, a mean field potential and hence $\phi_i(\mathbf{r})$. It has been shown [17] that this type of trial function does not have BEC, assuming that the sum of the overlap of ϕ with those on other sites is less than unity as is expected to be the case. Because of the localized functions, the Reatto-Chester theorem on BEC does not apply.

An alternative trial function [18–20] (we will denote as a metal, Ψ_M) is obtained by making the single-body function $\phi(\mathbf{r})$ independent of the lattice site, but still having lattice symmetry. For electrons, $\phi(\mathbf{r})$ would be a Bloch function of band theory and would be obtained as a solution of a mean field with lattice symmetry. It is expected [1] that vacancy-interstitial (VI) fluctuations play an important role in supersolidity. In the JN function, VI pairs are bound, just as electron-hole pairs are in an electronic insulator. In the metallic function, vacancies will be locally attracted to interstitials but they are not bound as pairs; as a result the Ψ_M has both BEC and NCRI. Calculations on a similar quantum solid [19] have found that Ψ_M has a higher energy than Ψ_{JN} ; it costs energy to create unbound VI fluctuations. We note that calculations [21] and experiments [22] on solid ^4He suggest that there are no unbound vacancies or interstitials at low temperatures.

Another trial function, the “shadow” wave function [23] (SWF) has been introduced to allow a translationally invariant trial function to have the correct solid order. In this case, a single atom coordinate in the Jastrow trial function is replaced by a composite object, a linear polymer, with the inter- and intracorrelation factors being variationally determined. Typically the polymer is in fact a dimer, with the two ends separated by a distance on the order of the interatomic spacing. One of the ends (the shadow) is

integrated over to get the trial function. The great advantage of the SWF is that the crystal order is spontaneously generated, and one gets accurate properties after optimizing the wave function parameters. As more monomers are added to the trial function, the functional form is equivalent to the Feynman-Kacs path integral expression for the ground state wave function [24]. Though it has not been analytically shown, simple arguments involving displacing the polymer make it plausible that the shadow trial function will have always have BEC, as long as the interatomic correlation factors are short ranged. This has been verified in recent numerical calculations by Galli *et al.* [25].

Thus, we have a dilemma, not uncommon with arguments based on variational wave functions: one can have several satisfactory trial functions, all of them capable of good descriptions of solid helium, but some are BEC and some are not BEC. All of the usual properties one uses to test the quality of the trial function, e.g., the energy, the Debye-Waller factor, the pair correlation function, etc., are diagonal in coordinate space [expectations of $|\Psi(R)|^2$]; hence they are unreliable measures of how accurate the off-diagonal elements needed in Eq. (1) are. As we have mentioned above, it is not possible to state a general theorem covering whether all quantum crystals must or cannot have BEC, since the Jastrow trial functions can be used to define a Hamiltonian which is supersolid. We need a more direct, reliable method to decide whether the ground state of solid ^4He is BEC and, hence, which class of trial function, metal or insulator, is appropriate. Calculating $n(\Delta\mathbf{r})$ in solid bulk ^4He allows us to establish how good these trial functions are for computing BEC in quantum crystals.

To provide an unbiased answer, we use path integral Monte Carlo (PIMC) simulations [14], a numerical method that calculates integrals over the many body density matrix. It is ideally suited for this calculation since it can be done at finite temperature (under conditions where an experimental signature of NCRI has been seen), and is, in principle, exact, and has been validated on many properties [14] of liquid and solid ^4He . Most importantly, it is independent of a trial wave function bias or any assumption of lattice. Only the He-He potential enters: a semi-empirical form [26] is known to be accurate; in any case, experimental results suggest that supersolid behavior is a robust phenomenon insensitive to fine details of the interaction.

In PIMC, based on Feynman’s description of superfluid helium, one maps the quantum system onto a classical system of “polymers” which can permute onto one another. The value of $n(|\Delta\mathbf{r}|)$ is mapped to the end-to-end distribution of an open “polymer” in a sea of closed polymers representing the other helium atoms. While all particles are fully quantum mechanical, one polymer is open because we are computing the one particle momentum distribution. If the system has ODLRO, the two ends

will become separated from each other; the condensate fraction is the value of $n(\Delta\mathbf{r})$ at large r . On the other hand, if there is no ODLRO, the two ends will remain localized relative to each other and $n(\Delta\mathbf{r})$ will approach 0 at large $|\Delta\mathbf{r}|$. Superfluidity (i.e., NCRI), on the other hand, is represented in PIMC as a long cyclic permutation of paths, for example, as a complete row of atoms shifting down one element. One can immediately see the difference between ODLRO and NCRI in a PIMC solid calculation. Suppose we have N atoms and N lattice sites, so each site is, on the average, singly occupied. To perform the ODLRO calculation, one of the atom's paths is opened up, so now there will be $N - 1$ closed polymers and 2 open ends; clearly one of the N sites must be doubly occupied if we count the open ends as distinct atoms. For NCRI one can simultaneously shift all atoms to their new permuted sites; there need not be any double occupation, but such a simultaneous shift is unlikely for many atoms.

Techniques [14] developed and tested [27] on superfluid ^4He are used to calculate $n(\Delta\mathbf{r})$ efficiently, although new moves are used to ensure ergodicity in the solid. If one simply cuts open one polymer, one rarely finds large values of $\Delta\mathbf{r}$. To guarantee sufficient statistics on the end-end distance, we multiply the path integral density by a series of importance sampling functions having the effect of forcing apart the ends. A series of importance functions are used to get good statistics for a specific range of magnitudes of $|\Delta\mathbf{r}|$. The separate end-to-end distributions are then normalized with respect to each other by minimizing the χ^2 difference between them and using the definition $n(0) = 1$. We perform calculations of $n(\Delta\mathbf{r})$ both by performing an angular average over $\Delta\mathbf{r}$ as well as fixing $\Delta\mathbf{r}$ in the basal plane, specifically in the x direction. Calculations of $n(\Delta\mathbf{r})$ can much more easily access the full path space than calculations of the superfluid density because the ends of the open polymer can move more freely.

Calculations [28] have been performed in a nearly cubic box of 180 particles as well as a series of longer rectangular boxes extended in the basal plane ranging from 48 to 144 atoms. For the longer box, we altered our importance function to force the open ends apart only in the x direction (in the nearest neighbor direction of the basal plane). We examine values of $n(\Delta\mathbf{r})$ for a range of temperatures 0.1 to 2 K in a (periodic) rectangular box of size $\sim 18.5 \text{ \AA}$ corresponding to a density, 0.0286 \AA^{-3} near the experimental melting pressure of 25.3 bars. The random walk is started with the atoms in a perfect hcp crystalline lattice but no constraints are placed on how the atoms can arrange themselves. Since the box is chosen to be commensurate with a perfect hcp crystal, vacancies and interstitials are expected not to be common in the system, but they can form by a fluctuation. We note that throughout the PIMC simulation the system chooses to be consistently arranged in this hcp lattice. We have verified that the results presented here are independent of temperatures below 2.0 K.

The results of these calculations for $T = 0.5 \text{ K}$ are shown in Fig. 1. Note the curvature at small $\Delta\mathbf{r}$ is determined by the kinetic energy estimated at 24.0 K/atom. For both the spherical average value and the value in the basal plane $n(|\Delta\mathbf{r}|)$ decays exponentially for $|\Delta\mathbf{r}| > 3 \text{ \AA}$: we find no indication of ODLRO (BEC) in bulk solid ^4He . In fact the rate of decrease for $n(x)$, the SPDM in the x direction, is in agreement with the frequencies for straight line winding exchange [5], shown as the dashed line. We find oscillations in the computed $n(x)$ reflecting the underlying crystal lattice. The angular averaged $n(r)$ shows less structure than that in the x direction. Though it is possible that $n(x)$ will plateau for a longer distance scale, we see no indication of this in the results, nor can we think of a physical mechanism that would be responsible [29]. A system with ODLRO will be manifested when one end of the open polymer loses knowledge about the other end of the open polymer. But we find that pulling apart the two ends takes “work” per unit length, no matter how far apart the two ends are. This happens because additional atoms are displaced from their lattice sites.

The results of our PIMC calculations are in quantitative agreement with variational Monte Carlo calculations using a shadow wave function [25] (SWF) for distances less than 9 \AA ; they conclude that BEC does exist in the ground state of ^4He with a very small condensate fraction, $n_0 = 5 \times 10^{-6}$ at the melting density. However, with PIMC we find that $n(\Delta\mathbf{r})$ continues to decrease beyond 9 \AA . The SWF-computed $n(\Delta\mathbf{r})$ is remarkably accurate up to the second neighbor distance and systematically improves upon the Jastrow wave function. Nonetheless the SWF is still built from short range correlations, which leads inevitably to a

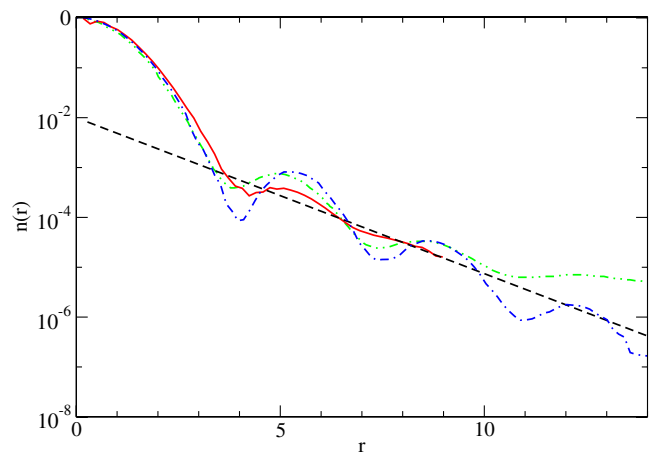


FIG. 1 (color online). The single particle density matrix as a function of distance (in \AA), estimated with PIMC, in hcp ^4He at a density 286 nm^{-3} and a temperature of 0.5 K. The solid (red) curve is the spherically averaged $n(r)$ while the dot-dashed (blue) curve is $n(x)$. The upper double-dot-dashed (green) curve is a variational MC calculation using the shadow wave function Ref. [25]. The dashed straight line (black) has a slope determined from the exchange calculations of Ref. [5].

nonzero superfluid fraction. We also expect the SWF will give a nonzero but very small vacancy concentration [30]. PIMC does not make a variational ansatz, and has the sole assumption that the results at low temperature smoothly approach the ground state values.

Among the proposed quantum solid wave functions, the symmetry-breaking Nosanow-Jastrow wave function gives results in agreement with PIMC, validating the insulator representation of solid helium. [Further details about this picture are in Ref. [15].] The implication of our calculation and the Reatto-Chester theorem is that a quantum solid trial function must include long-range correlations. This is most simply done by putting in localized functions about lattice sites, reflecting the broken symmetry. We have only done PIMC calculations at the melting density but we do not expect different behavior at higher density, since difficulty of exchange grows rapidly with density. The result reported here, together with the finding of zero superfluid density reported in Ref. [5], suggests that the mechanism for the measurements of Kim and Chan [4] involves more than equilibrium properties of a commensurate ^4He crystal.

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Note added.—After the calculation reported here was completed, we have learned of a similar PIMC calculation [32] done simultaneously. Although the numerical methods used in the Monte Carlo algorithm differ in a nontrivial way, the results are in substantial agreement.

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