

Ring Exchanges and the Supersolid Phase of ^4He

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Using path integral Monte Carlo simulations we calculate exchange frequencies in bulk hcp ^4He as atoms undergo ring exchange. We fit the frequencies to a lattice model and examine whether such atoms could become a supersolid, that is, have a nonclassical rotational inertia. We find that the scaling with respect to the number of exchanging atoms is such that superfluid behavior will not be observed in a perfect ^4He crystal.

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Recent torsional-oscillator observations by Kim and Chan on solid ^4He , both in the disordered absorbed vycor [1] and in bulk ^4He [2], have revived interest in the supersolid phase. In this phase, one has both long-range crystalline order and superfluidity. Experiments find a superfluid response to rotation at temperatures below 0.2 K. The low temperature superfluid density is about 1% of the solid density and is found to be independent of density within a pressure range of 25 to 60 bars. In the following, we assume the observed phenomena is described by equilibrium thermodynamics of pure bulk helium. In practice, whether this is the case is one of the most important issues. Assuming equilibrium [3], a supersolid is characterized by both long-range translational order and by a nonclassical response to rotation (NCRI).

In proposing such a state, Andreev and Lifshitz [4] postulated the existence of suitable defects (e.g., vacancies) and then estimated the properties of the dilute system of bosonic defects. The superfluid transition temperature of point bosons is $T_c = 3.31\rho^{2/3}\hbar^2/m$ where ρ is the density of the Bose condensing quasiparticles and m their effective mass. Taking the measured value for $T_c = 0.2$ K, writing the mass in terms of the bare helium atom mass $m = \mu m_4$ and their density as a fraction c of the bulk helium density at melting $\rho = 0.029 \text{ \AA}^{-3}$ we find that $c \approx 0.012\mu^{3/2}$: if the quasiparticle is heavier than a helium atom, at least one out of every 83 lattice sites must have a defect; if the mass is 1/10 the atom mass, the relative density of defects will need to be 4×10^{-4} . Such a dense collection of defects could not be associated with the much lower concentration of ^3He impurities.

Experiments, particularly the NMR experiments [5,6] on solid ^3He rule out zero point vacancy concentrations of more than one part in 10^{14} . Pederiva *et al.* [7] have done calculations of the energy of vacancies and find an energy of about 15 ± 4 K in the hcp phase of bulk ^4He at the

melting density, and 30 K at 50 bars, in agreement with various experiments, most notably x-ray scattering [8]. Using path integral calculations (described below) we estimate the energy to create an interstitial at the melting density is 48 ± 5 K; they are even more improbable than vacancies. Hence, the energies of point defects are substantially greater than zero; in equilibrium there should not be enough of them at 0.2 K to Bose condense; this precludes the Andreev mechanism for a supersolid.

In this Letter we examine the possibility that bulk solid hcp helium, assumed to be free of defects such as impurities and vacancies, could have a supersolid phase. One might think that there would always be ground state defects, arising from the large quantum zero point fluctuations. Near melting, the rms vibration about the lattice site is 30%, so that at any instant of time, a good fraction of atoms are closer to a neighboring site than to their home site. However, the absence of an atom from a lattice site is not sufficient for having a supersolid; if the empty site is always accompanied by a doubly occupied site, there can be no mass current. Chester [9] proved that any Jastrow (i.e., pair product) wave function of finite range has both Bose-Einstein condensation (BEC) and vacancies. However, Jastrow wave functions crystallize with much difficulty and with a transition density off by an order of magnitude [10] so that they are not reliable enough to be used to predict superfluidity. In general, variational wave function approaches are suspect, since the energy is not sensitive to the low probability regions of configuration space that are important for the superfluid density and Bose condensation.

Leggett [3] has written an upper bound to the superfluid density in terms of the zero temperature density of the solid. Using densities from path integral calculations, we find that the Leggett bound gives $\rho_s/\rho \leq 0.16$ at the melting density, a value consistent with experiment. In this Letter, we calculate values for ring exchange fre-

quencies and using them, find that the superfluid density should be zero in solid helium.

To determine whether bulk helium could be supersolid, path integrals give a much cleaner framework; they can be used to compute the superfluid density and the momentum distribution without the assumption of a trial wave function or any other uncontrolled approximation. The partition function of N bosons is

$$Z = \frac{1}{N!} \sum_P \int dR \langle R | e^{-\beta H} | PR \rangle, \quad (1)$$

where H is the Hamiltonian, β the inverse temperature, and $R = \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\}$. For numerical calculations, the density matrix operator is expanded into a path, beginning at the configuration R and ending at PR . In terms of these paths, the superfluid density (i.e., the number of atoms not moving with the walls of the torsional-oscillator) is given by

$$\frac{\rho_s}{\rho} = \frac{m \langle \vec{W} \vec{W} \rangle}{\hbar^2 \beta N}, \quad (2)$$

where $\vec{W} = \int_0^\beta dt \sum_{i=1}^N d\mathbf{r}_i(t)/dt$ is the winding number of the path around a torus. It is only exchanges on the order of the sample size that contribute to the superfluid density; local exchanges make no contribution. Using the path integral Monte Carlo (PIMC) method, superfluidity and freezing happen naturally at the right density and temperature, without imposing them in any way. The technical complications [11] concern ergodicity of the random walk, and finite size effects: one has to take the limit as $N \rightarrow \infty$.

PIMC calculations find a superfluid density on the order of 3% at melting density (molar volume 21.04 cm³) and about 1.2% at 55 bars (molar volume 19.01 cm³) in a 48 atom ($3 \times 4 \times 2$) hcp supercell. The superfluid density is larger than what is observed, and has a relatively weak pressure dependence. However, a cell with 180 atoms, has zero superfluid density. We cannot be sure that the lack of winding paths has a physical origin, or is due to a lack of ergodicity within the PIMC random walk. To change from one winding configuration to another involves a global move of the paths which becomes very unlikely as the box size gets large. To avoid this problem, we turn to a PIMC approach which directly estimates individual exchange probabilities.

The Thouless [12] theory of exchange in quantum crystals assumes that at low temperatures, the system will almost always be near one of the particular $N!$ arrangements of particles to lattice sites with rare, rapid, tunnelings from one arrangement to another. Hence, we label the particles with their initial lattice sites. Then the partition function is written as a sum over permutations of sites onto themselves. We break up the permutation into cyclic exchanges $\{p_1, p_2 \dots p_n\}$; each cycle is independent, so that

$$Z = Z_0 \sum_P \prod_{i=1}^{n_P} f_{p_i}(\beta), \quad (3)$$

where $Z_0 = \int dR \langle R | e^{-\beta H} | R \rangle$ is an uninteresting phonon partition function at low temperature. The contribution for a cycle

$$f_p(\beta) = \frac{1}{Z_0} \int dR \langle R | e^{-\beta H} | pR \rangle \equiv J_p \beta \quad (4)$$

is proportional to β because it is localized in time; the coefficient, J_p is the exchange frequency.

A special case of the above partition function is the Feynman-Kikuchi (FK) model [13] that assumes that $J_p = J_0 e^{-\alpha L_p}$ where L_p is the cycle length. The partition function is

$$Z = Z_0 \sum_P (\beta J_0)^{n_P} e^{-\alpha \sum_{i=1}^{n_P} L_{p_i}}. \quad (5)$$

We make contact with previous work by assuming $\beta J_0 = 1$. Calculations were done assuming a cubic 3D lattice, first by Feynman and Kikuchi analytically and then numerically by Elser [14]. It is found that the superfluid transition occurs as α becomes smaller from a localized state (small cycles) to large cycles for $\alpha_c \approx 1.44$. To understand this critical value, consider the free energy of adding a link to an existing loop. A cubic lattice has coordination number 6 but a return to the previously visited site is impossible since it is a cyclic permutation. Adding a link costs probability $e^{-\alpha}$ but the entropy of the new link is 5; hence $\alpha_c \sim \ln(5) = 1.6$. The critical value is smaller because of the ‘‘self-avoiding’’ restriction within a cycle and on overlapping cycles. Using the same argument for the hcp lattice gives a critical coupling of $\alpha_c \approx 2.3$.

Using methods [15,16] developed for solid ³He, we calculate the exchange frequencies and estimate how close they are to the critical value. We assume the helium interact with a semiempirical [17] pair potential. The frequencies for 2, 3, and 4 atom exchanges is very small [11], e.g., $J_2 \sim 3 \mu\text{K}$ at melting density. However, small cyclic exchanges are quite different from the long exchanges needed to get a supersolid. We have performed exchange calculations of 50 different exchanges involving from 5 to 10 atoms. All exchanges involve nearest neighbors, since calculations show that next-nearest exchanges are much less probable. We obtain accuracies on the order of 5% for the five-particle exchanges and 10% for the nine particle exchanges. More than half of the exchanges involve winding around the cell boundaries, important because they are representative of the type of exchanges in a supersolid.

Figure 1 shows the results of calculations of the frequency of the simplest winding exchanges: straight line exchanges in the basal plane. As assumed in the FK model, we find that the exchange frequencies decrease

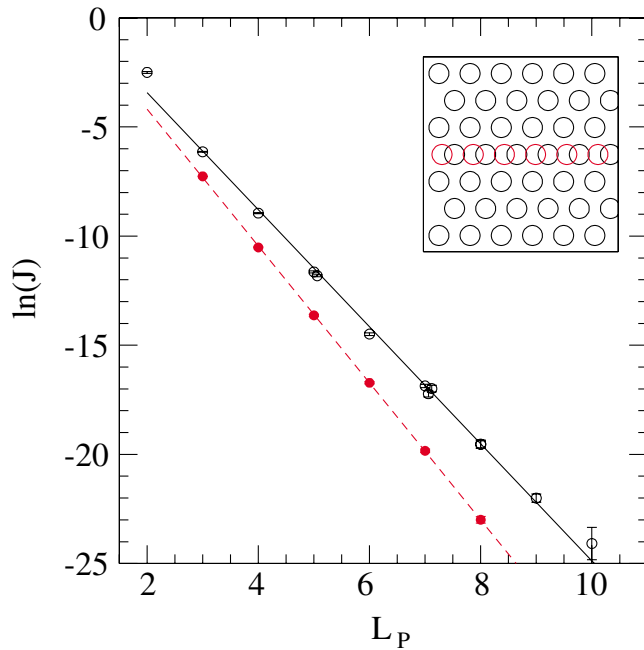


FIG. 1 (color online). The exchange frequencies (J in K) versus exchange length L_p for straight line exchanges in the basal plane that wind around the periodic cell. The inset shows the lattice sites in the basal plane for $L_p = 6$; the red (gray) atoms show the atoms midway through the exchange. The circles with error bars are the $\ln(J)$ at 2 M volumes; 21.04 cm³ (black, open circles, solid line) and 19.01 cm³ [red (black) solid circles, dashed line]. Multiple points at the same value of L_p are from cells with different number of atoms in the directions perpendicular to the exchange direction. The lines are least squares fits.

exponentially with the length of the exchange with an exponent of $\alpha = 2.64$ near the melting volume 21.04 cm³, and $\alpha = 3.14$ at the volume 19.01 cm³ corresponding to $P \sim 60$ bars.

To construct a more realistic model than the FK model, we need to take into account more details of the geometry of the exchange than just the number of exchanging atoms. We assume that it is the internal geometry of the exchange that matters [18]; the detailed arrangement of the neighboring spectator atoms is much less important. In particular, we assume the action of a given n cycle (the log of the exchange frequency) is the sum over the internal vertices of the exchange

$$J_p = J_0 \exp \left[- \sum_{k=1}^p \alpha(\theta_k) \right]. \quad (6)$$

Here θ_k are angles between successive displacements in the exchange cycle. In an hcp lattice there are seven possible angles between two nearest neighbor displacement vectors, but $\theta = 0$ occurs only in the pair exchange. We determine the parameters by fitting to the PIMC

exchange frequencies J_p . Good fits are obtained; the model predicts the exchanges frequencies with an accuracy of about 20%. The resulting coefficients are shown in Fig. 2. Typical errors on the coefficients are ± 0.03 . Note that there is a strong preference for exchanges that proceed in a straight line versus ones which have sharp angles; for them the incoming and outgoing particles are more likely to collide. The fitting coefficients are seen to depend linearly on $\cos^4(\theta/2)$. We find no preference for exchange in the basal plane beyond the effect induced by the selection of angles.

We also verified this model by comparing with results of the direct PIMC calculations (where permutations are generated dynamically) mentioned above and obtained rough agreement with the winding numbers and permutation cycle distributions. The two and three-particle exchanges are about twice the prediction of model. On the other hand, the exchanges in the 180 atom cell are somewhat smaller than Thouless theory. We expect such disagreements because Eq. (6) does not contain the effect of spectator atoms on the exchange process, and small exchanges have not been included in the fit.

The activation coefficient of the exchange is $J_0 = 7.2 \pm 0.5$ K. This is the order of magnitude but smaller than the vacancy energy. If it is related to vacancies, then J_0 should be of the same order of the vacancy energy at all

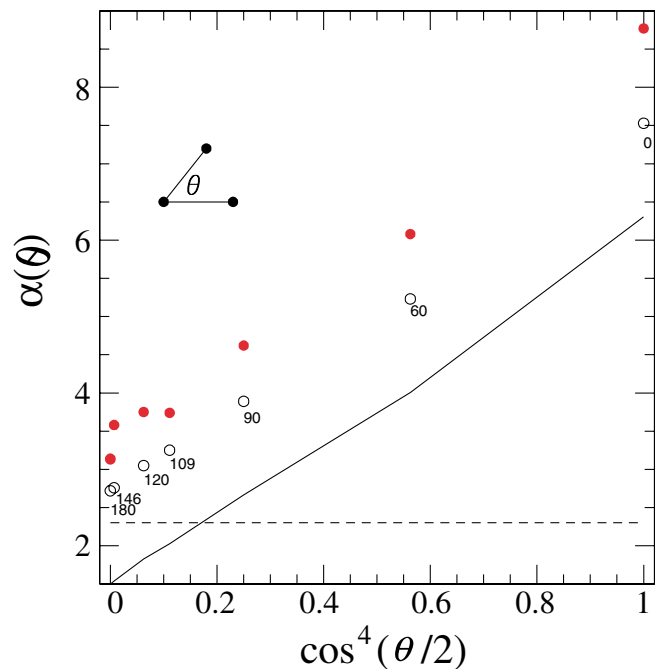


FIG. 2 (color online). The model parameters vs $\cos^4(\theta/2)$ at the melting density (open circles). The angle is the interior angle of the vertex as shown. The fits were done using 50 exchanges in a 180 atom cell. The solid red (black) circles correspond to a pressure 60 bars. The two lines show a critical supersolid Hamiltonian with (solid line) and without (dashed line) angular dependence.

densities, but on the contrary, we do not find a significant density dependence.

We now analyze the model. Because the probability of retracing is small, we initially neglect the self-intersections. This leads to a diffusion problem on a lattice, with a large probability of continuing in the same direction. Since a displacement only depends on the previous displacement, it is an un-normalized Markov process. (Because the hcp lattice has a basis, we have to label the displacements consistently on the A and B planes so that the transition probabilities are independent of the plane.) The probability of a given displacement vector Π_i will approach a steady state after many steps, (i refers to one of the lattice directions) and satisfy the eigenvalue equation

$$\sum_i \Pi_i e^{\alpha_{ij}} = \lambda \Pi_j. \quad (7)$$

By symmetry Π_i can only depend on whether the direction is in the basal plane Π_1 or out of the basal plane Π_2 . Define the partial sum $D_{i,j} = \sum_j e^{-\alpha_{ij}}$ where (i, j) are either in the basal plane (1) or out of it (2), e.g., D_{11} is the sum of the probability of both vectors being in the basal plane). The eigenvalue λ , is the solution to the secular equation

$$(D_{11} - \lambda)(D_{22} - \lambda) - D_{12}^2 = 0. \quad (8)$$

Putting in the model parameters, we find $\lambda = 0.303 \pm 0.005$. The probability of having an exchange of length p will equal a prefactor times λ^p , hence, since $\lambda < 1$, our PIMC results imply that solid ${}^4\text{He}$ will have only localized exchange and thus cannot be a supersolid.

Let us consider how the neglect of the self-intersections affects the critical value. Qualitatively, self-intersections must decrease the probability of long exchange cycles. To estimate the effect quantitatively, we perform random walks on the hcp lattice and count only nonintersecting walks. If we artificially change the model parameters α by subtracting 1.2, the model becomes critical when $\lambda \approx 1.03$ as opposed to $\lambda = 1$. This line is shown in Fig. 2. Our computed value of λ is much less than what is needed to allow for a supersolid. We expect that the presence of other exchange cycles will further increase the critical value of λ .

In summary, PIMC-computed exchange frequencies for hcp solid ${}^4\text{He}$ show that only localized exchanges will be present and thus should not exhibit the property of nonclassical rotational inertia. Based on other theoretical and experimental findings, we think it unlikely that the observed phenomena are due to vacancies, interstitials or ${}^3\text{He}$ impurities. Hence, one must look for an explanation of the experiments elsewhere, either to non-equilibrium effects or more complicated lattice defects.

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- [1] E. Kim and M.H.W. Chan, *Nature (London)* **427**, 225 (2004).
- [2] E. Kim and M.H.W. Chan, *Science* **305**, 1941 (2004).
- [3] A.J. Leggett, *Phys. Rev. Lett.* **25**, 1543 (1970).
- [4] A.F. Andreev and I.M. Lifshitz, *Sov. Phys. JETP* **29**, 1107 (1969).
- [5] R.A. Guyer, *Phys. Rev. Lett.* **26**, 174 (1971).
- [6] M.W. Meisel, *Physica (Amsterdam)* **178B**, 121 (1990).
- [7] B. Chaudhuri, F. Pederiva, and G.V. Chester, *Phys. Rev. B* **60**, 3271 (1999); F. Pederiva, G.V. Chester, S. Fantoni, and L. Reatto, *Phys. Rev. B* **56**, 5909 (1997).
- [8] B.A. Fraass, P.R. Granfors, and R.O. Simmons, *Phys. Rev. B* **39**, 124 (1989).
- [9] G.V. Chester, *Phys. Rev. A* **2**, 256 (1970).
- [10] J.P. Hansen and E.L. Pollock, *Phys. Rev. A* **5**, 2651 (1972).
- [11] D.M. Ceperley, *Rev. Mod. Phys.* **67**, 279 (1995).
- [12] D.J. Thouless, *Proc. Phys. Soc. London* **86**, 893 (1965); **55**, 1 (1983).
- [13] R.P. Feynman, *Phys. Rev.* **91**, 1291 (1953). See also R. Kikuchi, *Phys. Rev.* **96**, 563 (1954); R. Kikuchi, H.H. Denman, and C.L. Schreiber, *Phys. Rev.* **119**, 1823 (1960).
- [14] V. Elser, Ph.D. thesis, U.C. Berkeley, 1984.
- [15] D.M. Ceperley and G. Jacucci, *Phys. Rev. Lett.* **58**, 1648 (1987).
- [16] B. Bernu and D. Ceperley in *Quantum Monte Carlo Methods in Physics and Chemistry*, edited by M.P. Nightingale and C.J. Umrigar, NATO Advanced Study Institutes, Ser. C, Vol. 525 (Kluwer, Boston, 1999).
- [17] R.A. Aziz *et al.*, *Phys. Rev. Lett.* **74**, 1586 (1995).
- [18] B. Bernu and D.M. Ceperley, *J. Phys. Condens. Matter* **16**, 701 (2004).