Bose-Einstein Condensation of Incommensurate Solid ^{4}He

D. E. Galli and L. Reatto
Dipartimento di Fisica, Università degli Studi di Milano, Via Celoria 16, 20133 Milano, Italy
(Received 2 February 2006; published 26 April 2006)

It is pointed out that the simulation computation of energy performed so far cannot be used to decide if the ground state of solid ^{4}He has the number of lattice sites equal to the number of atoms (commensurate state) or if it is different (incommensurate state). The best variational wave function, a shadow wave function, gives an incommensurate state, but the equilibrium concentration of vacancies remains to be determined. We have computed the one-body density matrix in solid ^{4}He for the incommensurate state by means of an exact ground state projector method in which incommensurability occurs spontaneously. We find a vacancy induced Bose-Einstein condensation of about 0.23 atoms per vacancy at a pressure of 54 bar. This means that bulk solid ^{4}He is supersolid at low enough temperature if the exact ground state is incommensurate.

DOI: 10.1103/PhysRevLett.96.165301 PACS numbers: 67.80.−s

Introduction.—Experiments by Kim and Chan [1,2] give evidence for nonclassical rotational inertia of solid ^{4}He, one hallmark of the supersolid state of matter [3]. These results have generated large interest because this would be a novel state characterized, in a bulk sample, by spontaneous broken translational symmetry and by a suitable rigidity of the phase of the wave function (WF) giving rise to superfluid properties. The standard mechanism for this rigidity is the presence of Bose-Einstein condensation (BEC). Such as state with BEC was suggested long ago [4,5] as a possibility for a quantum solid of boson particles. Early theoretical works [3–6] were based on simplified models so that it was not possible to draw specific predictions for solid ^{4}He. Powerful simulation methods have been applied to study a realistic model of solid ^{4}He in the last two years. A path integral Monte Carlo (PIMC) simulation has been applied to study crystalline ^{4}He at a finite temperature, and the authors conclude that the superfluid fraction ρ_s at $T = 0.2$ K is zero [7] and that [8] there is no off-diagonal long range order (ODLRO); i.e., there is no BEC at $T = 0.2$ and 0.5 K. On the other hand, the *ground state* of crystalline ^{4}He has been studied by variational methods based on the shadow wave function (SWF), and this study shows that ODLRO is present [9] for a range of densities above melting with a rather small value of BEC fraction. One important point to mention is that in these PIMC and SWF computations the crystal is commensurate in the sense that the number M of lattice sites is equal to the number N of particles, i.e., $M = N$. One finds in the literature [7,8,10] statements that it is certain that the ground state of solid ^{4}He is commensurate because microscopic computations [11,12] have shown that a vacancy increases the energy of the system by at least 15 K and by an even higher value in the case of an interstitial. The first purpose of this Letter is to present a critical discussion of such statements and to examine if the ground state of crystalline ^{4}He is commensurate (i.e., $N = M$) or if it is incommensurate ($N \neq M$) in the sense that the lattice parameter inferred from bulk density measurement differs from the one deduced from Bragg scattering. Present experiments [13] do not give evidence for vacancies at low T, but new measurements seem needed to put a stringent bound on ground state vacancies. The nature of the ground state, commensurate (C) or incommensurate (I), is a very important point, and a phenomenological theory [14] has shown that the low T properties of crystalline ^{4}He would be strongly modified should the ground state be incommensurate. Our conclusion will be that the microscopic computations of solid ^{4}He present in the literature do not allow one to infer if the ground state is C or I. Since the presence of vacancies in the ground state cannot be excluded, it is important to study their properties; in particular, we study if there is BEC induced by vacancies. This has been studied variationally [15], and here we present an exact computation by a shadow path integral ground state (SPIGS) method [12] that confirms a vacancy induced BEC.

Commensurate or incommensurate?—First, we notice that the computations [11,12] at the basis of the estimate of the formation energy of a vacancy are actually based on the computation of the ground state energy of two different systems. To be specific let us consider the SPIGS computation. The method is based on the application of the imaginary time evolution operator $\exp\{-\tau\hat{H}\}$ to an assumed trial function, on a SWF in the case of SPIGS and on a splitting of this operator $\exp\{-\tau\hat{H}\} = [\exp(-\frac{\tau}{P}\hat{H})]^P$ which gives rise to a path integral of *linear* polymers. When τ is large enough, a sampling of the exact ground state of the system is obtained. Notice that in both the SWF and the projection procedure equilibrium sites of the solid are not introduced at any stage of the computation, but the crystalline order, if stable, arises as spontaneous broken symmetry. With this method two computations are performed, one in which the number N of particles is equal to the number M of lattice sites, which fits in the simulation box and satisfies the periodic boundary conditions (PBC), and one in which $N = M - 1$. In the second case the simulation shows that the local density continues to have M maxima with essentially the same degree of crystalline order, as measured by the height of the Bragg peaks, as in the case $N = M$. This means that in the second case the crystalline order is stable with one mobile vacancy and such a state is I. The SPIGS computation in the two cases gives a converging energy, and one example of the evolution of E as a function of τ is shown in Fig. 1 for the fcc lattice. State C is for $N = M = 108$ at $\rho = 0.031$ Å^{-3}, and state I is for $N = M - 1 = 107$ at the same *site* density. Starting from a fully optimized SWF [16] just a few projections are enough to get convergence in both cases. As an interatomic potential we have used a standard Aziz potential [17], the time step $\delta = \tau/P$ is $(80\ \mathrm{K})^{-1}$, and the pair-product approximation [18] has been used for the imaginary time propagator. Both WFs are non-negative so both computations produce ground state energies, but the value E_I is slightly larger than E_C. Since we are comparing the energy for two different choices of N, it makes no sense to minimize the energy; both values represent a ground state energy of two periodically repeated small systems. We conclude that this kind of computation cannot be used to determine if the ground state of bulk solid ^{4}He is C or I unless one is able to extrapolate these finite size results to the bulk limit also taking into account the effects of the PBC. The difference $E_I - E_C$ has been used [12] to estimate the formation energy of an extra vacancy in bulk under the hypothesis of noninteracting vacancies, but this is only a derived quantity [19]. Also in the classical case it is well recognized [20] that no direct computation of the equilibrium concentration $\bar{X}_v$ of vacancies of a solid at finite temperature is available yet exactly for the same reasons as in the quantum case: due to the finite size of any system that can be simulated and to the commensurability effect between the crystal lattice and the simulation box, the crystal cannot achieve its true equilibrium concentration of vacancies [20]. $\bar{X}_v$ in the classical case has been obtained only indirectly by a statistical thermodynamics analysis of an extended system. In a similar way we can expect to get information on the nature C or I of the ground state of bulk crystalline ^{4}He only by considering the WF of an extended system, not of the one which is simulated.

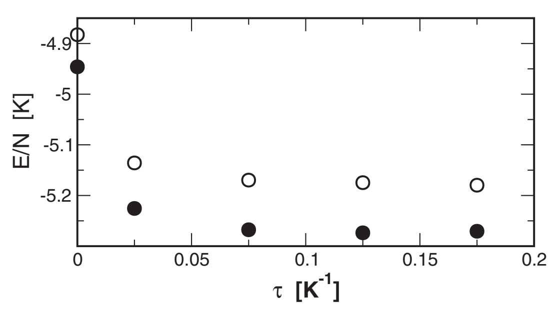

FIG. 1. Energy per particle as a function of the evolution in imaginary time τ of a SPIGS simulation of fcc solid ^{4}He in a box with $M = 108$. Solid circles, state C ($N = M$) at $\rho = 0.031$ Å^{-3}; open circles, state I ($N = M - 1$). The largest value of τ corresponds to 14 projections. Statistical errors are below symbol size.

In the framework of variational theory the WFs fall in two categories. One category is a WF which contains as a factor one-body terms which explicitly break the translational symmetry. Such a WF has great difficulty in describing a vacancy, and in fact, we are not aware of any such computation. In addition, the nature C or I is built into the WF by construction. Finally, such WFs with explicitly broken translational symmetry give a worse energy [16] than the one given by WFs of the next category. This second category represents translationally invariant WFs for which the crystalline state arises as spontaneously broken symmetry. One such WF is the time honoured Jastrow WF. The other one is the SWF which presently gives the best representation [16] of the ground state of solid ^{4}He in the sense that it gives the lowest energy.

An important point is that both these translationally invariant WFs give a ground state with a finite concentration of vacancies and with BEC. In the case of a Jastrow WF, this was shown by Chester [5] and we briefly repeat here the argument. Consider a Jastrow WF of a very large system of $\mathcal{N}$ particles in volume $\mathcal{V}$:

$$\Psi_J(R) = \prod_{i<j}^{\mathcal{N}} e^{-1/2u(r_{ij})}/Q_{\mathcal{N}}^{1/2}, \tag{1}$$

where $r_{ij} = |\vec{r}_i - \vec{r}_j|$, $R = \{\vec{r}_1, \ldots, \vec{r}_{\mathcal{N}}\}$, and $Q_{\mathcal{N}}$ is the normalization constant of Ψ_J^2, i.e.,

$$Q_{\mathcal{N}} = \int_{\mathcal{V}} dR \prod_{i<j}^{\mathcal{N}} e^{-u(r_{ij})}. \tag{2}$$

As noticed long ago [21] computation of averages with Ψ_J^2 and the normalization $Q_{\mathcal{N}}$ have a straightforward interpretation in classical statistical mechanics: Ψ_J^2 coincides with the normalized probability distribution in configurational space of $\mathcal{N}$ classical particles at inverse temperature $\beta^* = 1/k_B T^*$ and interacting with a pair potential $v^*(r)$ such that $\beta^* v^*(r) = u(r)$. $Q_{\mathcal{N}}$ is the canonical configurational partition function of this classical system and its logarithm is proportional to the excess Helmohltz free energy. It has been proved [22] that Ψ_J has a finite BEC fraction, but it is also known that the equivalent classical system corresponding to Ψ_J^2 is a crystalline solid, when the density is large enough, and this solid has a finite concentration of vacancies. For a classical system the fact that a solid in equilibrium at a finite temperature has a finite concentration $\bar{X}_v = (\mathcal{M} - \mathcal{N})/\mathcal{N}$ of vacancies, where $\mathcal{M}$ is the number of lattice sites, even if a single vacancy has a finite cost of local free energy, derives from the gain in configurational entropy when the number $\mathcal{M} - \mathcal{N}$ of vacancies is proportional to $\mathcal{N}$ [23]. Another way of expressing this is that the configurational partition function $Q_{\mathcal{N}}$ of this equivalent classical system has contributions from different pockets in configurational space, from a pocket Ω_0 in which the positions $\{\vec{r}_i\}$ of the particles correspond to vibrations around the equilibrium positions of the commensurate $\mathcal{N} = \mathcal{M}$ lattice but also from pockets $\Omega_1, \Omega_2, \ldots,$ corresponding, respectively, to $\mathcal{M} = \mathcal{N} + 1$, i.e., a state with one vacancy, to $\mathcal{M} = \mathcal{N} + 2$, and so on. It turns out [20,23] that the overwhelming contribution to $Q_{\mathcal{N}}$ is associated with pockets $\Omega_{\mathcal{M}-\mathcal{N}}$ with a macroscopic number $\mathcal{M} - \mathcal{N}$ of vacancies. These observations have an immediate interpretation in the quantum case: the WF (1) of a bulk system is describing at the same time states with no vacancies but also with vacancies and the overwhelming contribution to the normalization constant $Q_{\mathcal{N}}$ derives from the pockets corresponding to a finite concentration of vacancies. The simulation of a small system of N particles with PBC is mimicking the expectation values of the quantum Hamiltonian of the extended system in a restricted pocket in configurational space, for instance, the pocket Ω_0 of the commensurate state or the pocket Ω_1 of the state with one vacancy depending on if $N = M$ or $N = M - 1$. Notice that in a Monte Carlo (MC) computation the normalization constant (2) is never computed explicitly but averages are implicitly normalized to the set of configurations that are explored in the MC simulation, i.e., to the pocket Ω_0 or Ω_1 that one has implicitly chosen at the start of the computation by choosing $N = M$ or $N = M - 1$. If we try to estimate the ground state energy per particle $e_G = E_G/\mathcal{N}$ of a truly macroscopic system, the answer is clear as long as the concentration of vacancies is small so that they can be considered as independent: If $e_0 = E_{M=N}/N$ is the energy per particle from simulation of the C state and $E_1 = Ne_0 + \Delta e_v$ the total energy from simulation of the I state with one vacancy, the inferred ground state energy of the extended system is

$$e_G = e_0 + \bar{X}_v \Delta e_v, \tag{3}$$

where $\bar{X}_v$ is the average concentration of vacancies that should be obtained from an analysis of $Q_{\mathcal{N}}$ of the extended system. This is the true variational energy of Ψ_J and not e_0. Notice that e_G will differ from e_0 only by a very small amount if $\bar{X}_v$ is well below 1%.

At present the best variational representation of solid ^{4}He is given by a SWF [16], Ψ_{SWF}. Also Ψ^2_{SWF} has a classical interpretation; in fact, the normalization of Ψ^2_{SWF} coincides with the configurational partition function of a classical system of suitable flexible triatomic molecules [24] because every particle has two subsidiary variables in Ψ^2_{SWF}. For this equivalent classical system the concentration $\bar{X}_v$ of vacancies is finite since in the previous argument it makes no difference that the "particles" are monoatomic or molecular species. We also conclude that Ψ_{SWF} describes a quantum solid with vacancies in it and the ground state energy of an extended system is given by Eq. (3) [25].

We now consider the size of $\bar{X}_v$. An estimate of $\bar{X}_v$ for a Jastrow function has been performed some years ago [26], but unfortunately Ψ_J gives an unrealistic representation of solid ^{4}He because Ψ_J gives a much too large localization of atoms. For Ψ_{SWF}, $\bar{X}_v$ is not known and this is a priority computation for the future.

We consider now the exact ground state as given by SPIGS [12]. The projection maps the quantum problem into an equivalent classical problem of flexible linear polymers with the number D of monomers equal to $D = 2P + 1$, where P is the number of projections. Such a classical system has vacancies for any finite P, but the concentration $\bar{X}_v$ of vacancies might vanish in the limit $P \rightarrow \infty$. Only a study of $\bar{X}_v$ as a function of P will be able to say whether ground state vacancies are present in the exact ground state of solid ^{4}He.

Vacancy induced BEC.—Given that vacancies might well be part of the ground state of solid ^{4}He, we present a microscopic calculation of the one-body density matrix ρ_1 in the presence of vacancies with the exact SPIGS method. Computation of $\rho_1(\vec{r}, \vec{r}')$ is performed by cutting one of the linear polymers at the central monomer and sampling the distance $|\vec{r} - \vec{r}'|$ of the two cut ends. Notice that in SPIGS computations, contrary to the case of PIMC calculations, no exchange moves between polymers have to be performed; this is a great advantage due to ergodicity problems arising from exchange moves. In any case, the calculation of ρ_1 by means of SPIGS in the solid is computationally very intensive due to the low relaxation (to get converged results one needs more than 10^7 MC steps) and to the large number of degrees of freedom (i.e., coordinates of monomers) as the imaginary time evolution τ becomes greater. There is also the necessity to compute ρ_1 as a function of τ in order to control the convergence. We have worked with a box which fits $M = 108$ fcc lattice sites and with $N = 107$ and $N = 106$ so that we have one or two vacancies which corresponds, respectively, to $X_v = 0.93\%$ and $X_v = 1.89\%$. In Fig. 2 we show the results for three values of τ [27] as well as the variational SWF results at density 0.031 Å^{-3}, which corresponds to a pressure of about 54 bar. ρ_1 has been computed with $\vec{r} - \vec{r}'$ along the nearest neighbor direction ([110] in fcc). One can see that ρ_1 develops a plateau for distances greater than about 5 Å, and this is a signature of BEC. We have estimated the condensate fraction by averaging the plateau for distances greater than 5.5 Å, and the values with their statistical uncertainty are shown in Fig. 2. The value of n_0 is only weakly dependent on τ and similar to the SWF results. With SWF it is known that n_0 for the hcp lattice is very similar to the fcc one [15]. ρ_1 in the plateau region has oscillations and the maxima correspond to multiples of the nearest neighbor distance; this can be interpreted in terms of a sequence of jumps of atoms which make use of the vacancy. This process is distinct from the vacancy-interstitial pairs that were found to be important for the commensurate state in a SWF computation [9]. In order to explore larger distances, we have computed ρ_1 with SWF also for a system with $N = M - 1 = 191$, which corresponds to $X_v = 0.52\%$. One sees from Fig. 2 the persis-

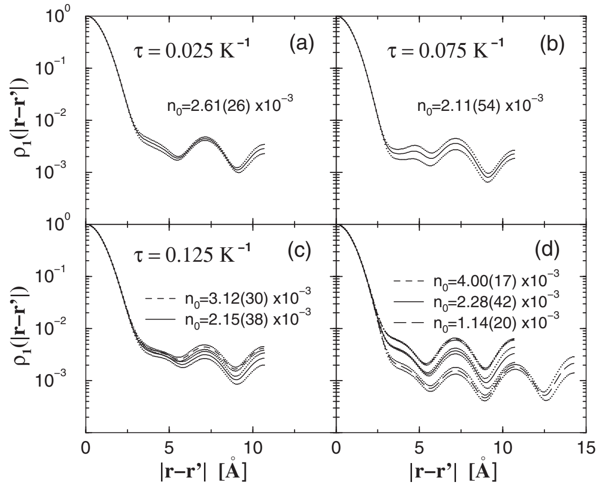

FIG. 2. One-body density matrix ρ_1 computed in fcc solid ^{4}He at $\rho = 0.031$ Å^{-3} with SPIGS (a)–(c) for different imaginary time evolutions τ and with SWF (d). $N = M - 2 = 106$ (dashed lines); $N = M - 1 = 107$ (continuous lines); $N = M - 1 = 191$ (long dashed lines). The dotted lines represent statistical uncertainty.

tence of the oscillations around a finite plateau. The three SWF computations give n_0, which scales with X_v within the statistical uncertainty. In the case of SPIGS, n_0 does not scale so well with X_v, and this might arise from the presence of some correlation between the two vacancies. We consider more reliable the SPIGS result with one vacancy so that we estimate a condensate fraction of about 0.23 ^{4}He atoms per vacancy at the pressure of about 54 bar. Therefore vacancies are very efficient in inducing BEC. Using, as an order of magnitude, $T_{\rm BEC}$ of an ideal gas with the effective mass [28] $m^* = 0.35 m_{\rm He}$, we get $T_{\rm BEC} \simeq 11.3 \times (\bar{X}_v)^{2/3}$; for example, $T_{\rm BEC} \simeq 0.2$ K for $X_v = 2.3 \times 10^{-3}$ and $T_{\rm BEC} \simeq 10^{-3}$ K for $X_v = 10^{-6}$. Therefore we expect supersolidity at low T in bulk solid ^{4}He if vacancies are present either as part of the ground state or as the nonequilibrium effect.

Conclusion.—On the basis of an exact microscopic theory of solid ^{4}He, the SPIGS projector method, we have shown the presence at the same time of spatial order and of BEC when a finite concentration of vacancies is present at $T = 0$ K, i.e., if the ground state is incommensurate. Based on the argument by Leggett [3] this system would show nonclassical rotational inertia effects. In addition, we have shown that the question of whether the ground state of bulk solid ^{4}He is C or I is still undecided but we noticed that the ground state is I for the best variational WF. The quantitative evaluation of the concentration of vacancies X_v for the SWF and the study of what happens to X_v under projection with the SPIGS method remain an open problem.

We thank D. M. Ceperley for useful discussions. This work was supported by the Mathematics Department "F. Enriques" of the Università degli Studi di Milano and by the INFM Parallel Computing Initiative.

[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] G. V. Chester, Phys. Rev. A **2**, 256 (1970).
[6] W. M. Saslow, Phys. Rev. Lett. **36**, 1151 (1976).
[7] D. M. Ceperley and B. Bernu, Phys. Rev. Lett. **93**, 155303 (2004).
[8] B. K. Clark and D. M. Ceperley, Phys. Rev. Lett. **96**, 105302 (2006); M. Boninsegni, N. Prokof'ev, and B. Svistunov, Phys. Rev. Lett. **96**, 105301 (2006).
[9] D. E. Galli, M. Rossi, and L. Reatto, Phys. Rev. B **71**, 140506(R) (2005).
[10] J. Day and J. Beamish, Phys. Rev. Lett. **96**, 105304 (2006).
[11] F. Pederiva *et al.*, Phys. Rev. B **56**, 5909 (1997).
[12] D. E. Galli and L. Reatto, Mol. Phys. **101**, 1697 (2003); J. Low Temp. Phys. **134**, 121 (2004).
[13] R. O. Simmons, J. Phys. Chem. Solids **55**, 895 (1994).
[14] P. W. Anderson, W. F. Brinkman, and D. A. Huse, Science **310**, 1164 (2005).
[15] D. E. Galli and L. Reatto, J. Low Temp. Phys. **124**, 197 (2001); D. E. Galli and L. Reatto, in *Recent Progress in Many-Body Theories*, edited by R. F. Bishop *et al.* (World Scientific, Singapore, 2002), Vol. 6.
[16] S. Moroni *et al.*, Phys. Rev. B **58**, 909 (1998).
[17] R. A. Aziz *et al.*, J. Chem. Phys. **70**, 4330 (1979).
[18] D. M. Ceperley, Rev. Mod. Phys. **67**, 279 (1995).
[19] Using the method of Ref. [12] from E_I and E_C we estimate a vacancy formation energy at fixed lattice parameter of 8 ± 1 K, which corresponds to 25 ± 2 K at fixed density.
[20] W. C. Swope and H. C. Andersen, Phys. Rev. A **46**, 4539 (1992).
[21] W. L. McMillan, Phys. Rev. **138**, A442 (1965).
[22] L. Reatto, Phys. Rev. **183**, 334 (1969).
[23] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1976).
[24] S. Vitiello, K. Runge, and M. H. Kalos, Phys. Rev. Lett. **60**, 1970 (1988); L. Reatto and G. L. Masserini, Phys. Rev. B **38**, 4516 (1988).
[25] At melting density the best energy [16] obtained with a WF with localizing factors is 0.056 K per atom above the SWF result. This means that even by allowing for the extra term $\bar{X}_v \Delta e_v$ the SWF energy is below the one of the WF with localizing factors for any $\bar{X}_v < 0.8\%$ (we have estimated $\Delta e_v = 6.8 \pm 0.9$ K at fixed lattice parameter).
[26] J. A. Hodgdon and F. H. Stillinger, J. Stat. Phys. **78**, 117 (1995).
[27] In the computation of ρ_1 we have used $\delta = (40\ {\rm K})^{-1}$. The pair-product approximation for this δ is slightly inaccurate but the effect on the energy is only 0.4%.
[28] D. E. Galli and L. Reatto, Phys. Rev. Lett. **90**, 175301 (2003).