Vacancy Excitation Spectrum in Solid ^{4}He and Longitudinal Phonons

D. E. Galli and L. Reatto

INFM and Dipartimento di Fisica, Universitá degli Studi di Milano, Via Celoria 16, 20133 Milano, Italy

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The first microscopic *ab initio* calculation of the excitation spectrum of a vacancy in solid ^{4}He is reported. The energy-wave vector dispersion relation has been obtained at melting density within a development of the shadow wave function variational technique. The calculation of the excitation spectrum of a vacancy gives a bandwidth which ranges from 6 to 10 K in the hcp solid ^{4}He, depending on the particular direction of the wave vector of the excitation. The effective mass of the vacancy turns out to be about 0.35 ^{4}He masses. We have also computed the spectrum of longitudinal phonons and we find rather good agreement with recent experimental results.

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The microscopic quantitative theory of a strongly interacting Bose fluid such as liquid ^{4}He has made enormous progress in the past couple of decades on one side on the basis of exact simulation of the system both for the ground state and at finite temperature and on the other side on the basis of variational theory for the ground state and for the elementary excitations. In comparison, less effort has been addressed to the solid phase. The equation of state has been studied in detail both with exact simulation and variationally with satisfactory results [1,2]. Scant results have been obtained for the excited states of the system on the basis of the modern theories. In the present Letter, we study two fundamental excitations, vacancy waves and phonons of longitudinal character on the basis of variational theory.

The general interest in solid ^{4}He lies in specific aspects of the system which displays phenomena related to the question of localization versus delocalization of atomic particles. In fact, solid ^{4}He is an example of what is customarily called a quantum solid, i.e., a solid for which the zero point motion of the atoms covers a significant fraction of the cell size. Exchange of atoms even at $T = 0$ K or delocalized defects such as a vacancy with a corresponding new branch of excitations are typical manifestations of a quantum solid due to the large freedom for the local motion of the atoms. This behavior changes over to the standard one of localized atoms when the density is well above the melting one. From an experimental point of view, the presence of delocalized vacancies in quantum solids such as ^{4}He or ^{3}He has been used in the interpretation of a number of experimental data, from NMR to specific heat, from x-ray diffraction to sound attenuation, but also ion or impurity mobility, pressure measurement, and plastic deformation (for a review, see [3]); furthermore, very recently experiments with acoustic waves in solid ^{4}He have provided evidence of nonphonon excitations at the lowest temperatures [4]. From a theoretical point of view, vacancy waves in quantum solids were first described by Hetherington [5], and later by Guyer [6]; a model for these excitations have been introduced in terms of a simple hopping Hamiltonian which gives the usual tight binding dispersion relation for the energy spectrum, but leaves the bandwidth and the effective mass of the vacancy as a parameter which has been found difficult to evaluate in a reliable way. Often, interpretation of the data coming from different experimental techniques has run into difficulty or has given conflicting results for the basic vacancy parameters and this might be due to the absence of a realistic model of a vacancy.

Intriguing as the notion of nonlocalized vacancies may be, a reliable experimental or an *ab initio* theoretical determination of the bandwidth of vacancies in a given solid helium phase is still not available. From the theoretical point of view, the difficulties arise from the fact that the large value of the zero point motion of the atoms in this system makes any theory which treats the vacancy as a small perturbation doubtful. On the other hand, it is essential to have a theory which embodies the basic Bose symmetry in any wave function (wf) of the system. These requirements made it very difficult to develop a realistic theory of a quantum solid with defects. The situation has changed in the past few years with the development of powerful simulation methods. Within the variational approach, the technique of shadow wave functions (SWF) [7] is able to treat disorder phenomena in a quantum solid, such as a vacancy [8] or even the interfacial region between a solid and a liquid at coexistence [9]. In a SWF, no *a priori* equilibrium positions are introduced and the crystalline order arises as an effect of broken symmetry induced by strong interparticle correlations. When the density ρ is above a value of the order of 0.029 Å^{-3}, the interparticle correlations are so strong that the solid phase becomes stable and its energy is below the one of the metastable liquid phase. The Bose symmetry is manifestly maintained by the SWF and defects can be delocalized and relaxation around them is allowed. With a SWF, the first quantitative treatment of the energy of formation of a vacancy in solid ^{4}He has been achieved [8]. Recently, we have also shown that in the presence of a finite concentration of vacancies in a low density solid

there is Bose-Einstein condensation of the ^{4}He atoms [10] at $T = 0$ K and at low temperatures; this is a result of increasing interest considering the recent experiment [4].

Here we present the first microscopic calculation of the excitation spectrum of a vacancy in solid ^{4}He based on a suitable extension of the SWF technique. With the SWF variational theory interparticle correlations are introduced also via subsidiary (shadow) variables $S = (\vec{s}_1, \ldots, \vec{s}_N)$, one for each of the atoms $R = (\vec{r}_1, ..\vec{r}_N)$. The wf can be written in the form

$$\Psi(R) = \int dS\, F(R, S), \tag{1}$$

where $F(R, S) = \phi_p(R)K(R, S)\phi_s(S)$. $\phi_p(R)$ contains the explicit part of the interparticle correlations, which are assumed of the Jastrow form, i.e., a pair product form, $K(R, S)$ is a Kernel which correlates each variable $\vec{r}_i$ to $\vec{s}_i$, and $\phi_s(S)$ is a Jastrow factor which correlates the $\vec{s}_i$. The variational principle for the energy allows the determination of the parameters contained in the various factors of the wf. In a previous work [8], the solid with one vacancy was obtained by reducing by one the number of particles as well as of the shadows and rescaling the volume V so that one compares the perfect crystal and the crystal with one vacancy at the same average density. As already mentioned, one observes a relaxation of the neighboring atoms toward the vacancy [8]. In addition, if the density is not too high, the vacancy is delocalized, i.e., it exchanges place with the ^{4}He atoms so that in a long MC run the vacancy can be found anywhere in the solid [8]. This means that a vacancy has a significant probability of tunneling to adjacent lattice sites. This phenomenon is expected to give rise to an allowed band of vacancy energies but the computation of this band requires the introduction of a wf suitable to describe also momentum carrying states. The form (1) for the SWF is not suitable to do this, but we have found a way to extend the SWF in such a way that it is able to describe also momentum carrying states, and in this way we are able to study the excitation spectrum of a vacancy. This has been obtained by associating one extra-shadow variable $\vec{s}_v$ with each vacancy. Because of the intershadow correlations, which are predominantly repulsive, this extra shadow localizes itself in the void left by the atoms, i.e., it localizes in the vacancy. By introducing a phase factor which depends on this extra-shadow variable, it is possible now to study the excitation at a finite $\vec{k}$. Our wf reads

$$\Psi^v_{\vec{k}}(R) = \int dS\, d\vec{s}_v\, F(R, S)L(\vec{s}_v, S)e^{i\vec{k}\cdot\vec{s}_v}. \tag{2}$$

The factor $L(\vec{s}_v, S) = \prod_i^N f_v(|\vec{s}_v - \vec{s}_i|)$ introduces the correlations between shadow variables and this extra shadow. As a functional form of the correlating factors, we have taken the ones used in Ref. [8]; the interatomic potential for ^{4}He has been represented by the Aziz potential [11]. For f_v, we have used the same functional form used for the correlations between the other shadow variables but with distinct coupling parameters. All expectation values have been computed with a Monte Carlo (MC) method. We want to stress that, by including the extra shadow and optimizing the factor $L(\vec{s}_v, S)$, the variational estimation of the vacancy formation energy is lowered by about 1 K at the melting density compared to the wf without the extra shadow, i.e., 15 K in place of 16 K. By studying the correlation function between the extra shadow and the real variables describing the position of the ^{4}He atoms, we have verified that indeed the extra shadow sets in the vacant site. One way to understand the role of this extra shadow is the following. It is known that the shadow variables are a way to represent the effects of the zero point motion of the atoms and to represent interparticle correlations beyond the pair level [2]. For an atom around the vacancy, this zero point motion is expected to differ from the one of the atoms far from the vacancy. As a consequence, also the interparticle correlations will be different for those atoms which are close to the vacancy. Integrations over the extra-shadow variable represent a way to change locally the effective two-, three-, and many-body correlations around the vacancy. One can show that the wf in Eq. (2) is an eigenstate of the total momentum operator with eigenvalue $\hbar k$. Because of the broken translational symmetry, this momentum is actually a quasimomentum. As usual, excitation energies $E(\hbar k)$ have been obtained as the difference between the total energy of the wf with quasimomentum $\hbar k$ and the total energy of the wf with zero momentum. The small size of the simulated system, a few hundred ^{4}He atoms, and the periodic boundary conditions stabilize the crystalline lattice which fits the simulation box and by suitably choosing its geometry and the number of particles in the box one can study both the fcc phase and the hcp one.

The energy spectrum $E(\hbar\vec{k})$ depends on the crystalline lattice and on the direction of $\vec{k}$, and the band is quite wide, of the order of 6–8 K, when the density is close to melting. As expected, $E(\hbar\vec{k})$ is equal within the statistical noise to the vacancy energy at $\vec{k} = 0$ when $\vec{k}$ is equal to one of the vectors of the reciprocal lattice. We might expect, however, that the vacancy has some coupling with phonon excitation. In order to explore if this effect has an influence on the bandwidth, we have also studied the longitudinal phonon within our approach. As a representation of a longitudinal phonon, we have used the same SWF that has been used for the phonon-roton excitation in the liquid phase [12] but without an explicit backflow contribution. Therefore the wf of the defected solid reads

$$\Psi^{ph}_{\vec{k}}(R) = \int dS\, d\vec{s}_v\, F(R, S)L(\vec{s}_v, S)\sum_j e^{i\vec{k}\cdot\vec{s}_j}. \tag{3}$$

In the perfect crystal, one simply drops the factor $L(\vec{s}_v, S)$.

This wf in a lattice with a basis similar to the hcp lattice represents longitudinal acoustic phonons. Solid ^{4}He, however, has an ideal hcp structure, so along the ΓA direction there is no gap between longitudinal acoustic and optical phonons and this wf represents also the optical branch for this special direction. The wf in Eqs. (2) and (3) are not mutually orthogonal; therefore the two wf do not give a proper treatment of the two branches of excitations. We have corrected this situation by building proper orthonormal excited states as linear combinations of $\Psi^{\rm v}_{\vec{k}}$ and $\Psi^{\rm ph}_{\vec{k}}$ and by performing the Hamiltonian diagonalization directly through the MC calculation of its matrix elements; this is the same technique we have introduced to study excitations in bulk liquid ^{4}He with one ^{3}He impurity [13].

It turns out that the coupling vacancy-longitudinal phonons have only a small effect on the excitation of the vacancy; for most k values it is well below 0.5 K. We show our results for the vacancy excitation in Fig. 1 for a density close to melting and along three directions in k space. We have computed the vacancy excitation spectrum for two different crystal structures: a fcc crystal (107 ^{4}He atoms in the simulation box) and a hcp crystal (179 ^{4}He atoms) with one vacancy. In Fig. 1, we show also the fits with the analytical dispersion relations obtained with a tight binding model for the fcc (Bravais) lattice:

$$E_{\rm v}(k_x, k_y, k_z) - E_{\rm v}(0) = \Delta_1(3 - \cos k_x a/2 \cos k_y a/2 - \cos k_z a/2 \cos k_y a/2 - \cos k_x a/2 \cos k_z a/2)/4, \quad (4)$$

where Δ_1 represents the bandwidth along the [100] direction and a is the side of the conventional unit cell, and for the hcp lattice:

$$\begin{aligned} E_{\rm v}(k_{\Gamma K}) - E_{\rm v}(0) &= -\Delta_{\Gamma A}(1 - \cos k_{\Gamma K} b)/6 + \Delta_{\Gamma K}(3 - \cos k_{\Gamma K} b - 2\cos k_{\Gamma K} b/2)/4, \\ E_{\rm v}(k_{\Gamma M}) - E_{\rm v}(0) &= \Delta_2(1 - \cos\sqrt{3}/2\, k_{\Gamma M} b)/2 + \Delta_{\Gamma A}(3 - \sqrt{5 + 4\cos\sqrt{3}/2\, k_{\Gamma M} b})/6, \\ E_{\rm v}(k_{\Gamma A}) - E_{\rm v}(0) &= \Delta_{\Gamma A}(1 - \cos\sqrt{2/3}\, k_{\Gamma A} b)/2, \end{aligned} \quad (5)$$

where $\Delta_{\Gamma A}$ and $\Delta_{\Gamma K}$ represent the bandwidth along the ΓA and ΓK directions, and where $\Delta_2 = \Delta_{\Gamma K} - 2/3\Delta_{\Gamma A}$ and b is the modulus of the basis vector of the hcp lattice along the ΓK direction. The agreement with the fits is rather good and this suggests that the hopping model for a vacancy introduced in the past is a reasonable approximation when the correct bandwidth is known. We want to stress that our calculation is truly *ab initio* and the only input is the interaction potential between helium atoms. From this calculation, it is possible to estimate the effective mass of a vacancy at small momenta.

The effective mass turns out to be about $0.39m_4$ in the fcc lattice, about $0.31m_4$ in the basal plane, and $0.38m_4$ along the ΓA direction in the hcp lattice. m_4 is the mass of one ^{4}He atom. The large value of the bandwidth implies that atoms jump very frequently in the vacant site and the residence time of a vacancy, of the order of $\tau = h/\Delta$, is 0.6×10^{-11} sec, and this is about 4 times larger than the period of the high frequency phonon of the crystal. Some recent experiments have suggested a large value of the vacancy bandwidth [14], of the order of what we find. At higher density, we find as expected that the bandwidth decreases, for instance, for the fcc Δ_1 decreases from 9.44 K at melting to 6 K at $\rho = 0.032\,94$ Å^{-3}. Unfortunately, the statistical noise on E_k of our present computational method increases very rapidly with the density, and we cannot follow in detail how the bandwidth decreases at density much above melting.

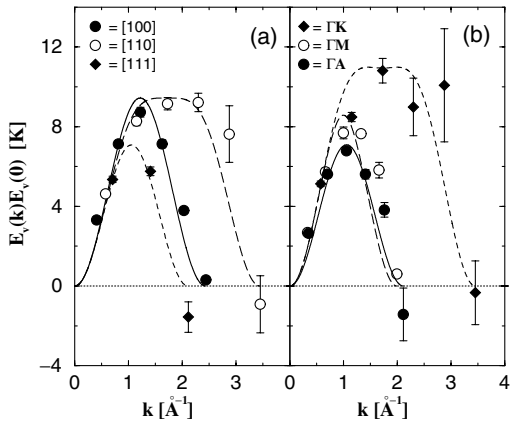

FIG. 1. Vacancy excitation spectrum in solid ^{4}He computed at $\rho = 0.028\,98$ Å^{-3} in a fcc (a) and in a hcp lattice (b). Lines in (a) and in (b) represent, respectively, a best fit with Eq. (4) ($\Delta_1 = 9.44$ K) and fit with Eq. (5) ($\Delta_{\Gamma K} = 10.94$ K, $\Delta_{\Gamma A} = 7.09$ K).

We discuss now the excitation spectrum of longitudinal phonons in the perfect crystal. In the crystal with one vacancy after diagonalization, the phonon spectrum agrees with that of the perfect crystal within the statistical errors in the computations. For this reason, we report here the excitation spectrum computed in the perfect solid only. In Fig. 2, we show the phonon frequencies computed with the wf (3) at $\rho = 0.028\,98$ Å^{-3} along three directions in the hcp lattice. We show also recent experimental data from inelastic neutron scattering [15] close to melting density and old theoretical prediction based on self-consistent phonon (SCP) theory at the same density [16]. Theoretical studies of the lattice dynamics in solid ^{4}He at low densities have been done in the past. Phonon frequencies and interesting multiphonon phenomena have been semiquantitatively interpreted using SCP theory [16] and recently also density functional

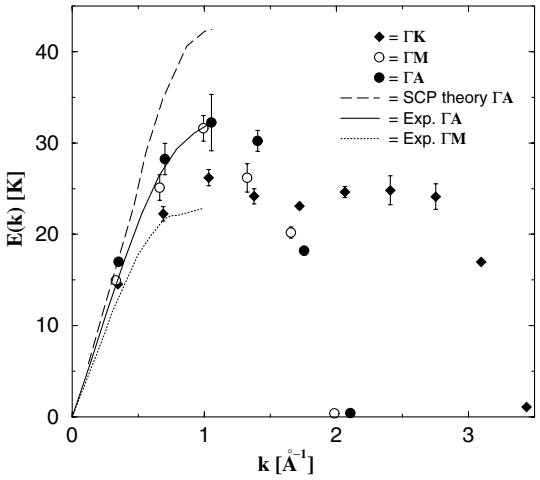

FIG. 2. Longitudinal phonons in an hcp solid ^{4}He computed at $\rho = 0.028\,98$ Å^{-3} close to the $T = 0$ K melting density along the ΓK, ΓA, and ΓM directions. The solid line and the dotted line represent recent experimental data from neutron scattering at melting density along the ΓA and ΓM directions [15], whereas the dashed line is the result of SCP [16] theory at melting density along the ΓA direction.

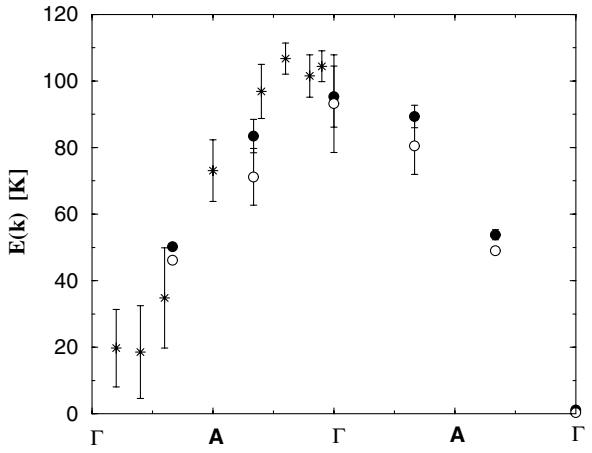

FIG. 3. Excitation energies for longitudinal phonons in an hcp solid ^{4}He computed along the ΓA direction at $\rho = 0.028\,98$ Å^{-3} (filled circles) and at $\rho = 0.0353$ Å^{-3} (open circles) and rescaled to a molar volume of 13.25 cm^3 together with inelastic x-ray scattering data [18] (stars).

theory [17]. The improvement of the present theory as compared to SCP is remarkable and there is a very good agreement with experiment in the ΓA direction. Along the ΓM direction, our theory overestimates the phonon frequency especially at the zone boundary. It should be noticed that in this region the one-phonon peak is a very weak feature over the multiphonon contribution so that the experimental values for $E(k)$ are rather uncertain. Our theory, as far as we know, is the most accurate and completely *ab initio* description of longitudinal acoustic phonons in solid ^{4}He near melting; this is remarkable because we have a wf which is able to reproduce quantitatively excited state properties in the solid and in the superfluid phase of ^{4}He starting from the same functional form. As suggested in [18], it is possible to scale the phonon frequencies in order to compare data measured at different densities; in Fig. 3, we show our phonon excitation energies along the ΓA direction computed at $\rho = 0.028\,98$ Å^{-3} and $\rho = 0.0353$ Å^{-3} and rescaled to a molar volume of 13.25 cm^3 using formula 3 in [18] (scaling factors: 2.96 and 1.78, respectively) together with inelastic x-ray scattering data [18]. We find a substantial agreement between the scaled phonon frequencies computed at different densities, so our theory seems to follow quantitatively the increasing of the phonon frequencies at higher densities.

We have investigated the excited state properties of solid ^{4}He on the basis of the shadow wave function variational technique. We have shown that this technique is a powerful method to study a quantum solid being able to treat in a natural way delocalized defects such as vacancies near the melting density. Longitudinal phonon excitations have been reproduced in good agreement with experimental data. We have been able also to compute for the first time in a fully microscopic and *ab initio* way the vacancy excitation spectrum in solid ^{4}He near the melting density where vacancies are highly mobile delocalized defects with a large bandwidth.

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