Supersolid State of Matter

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We prove that the necessary condition for a solid to be also a superfluid is to have zero-point vacancies, or interstitial atoms, or both, as an integral part of the ground state. As a consequence, in the absence of symmetry between vacancies and interstitials, superfluidity has a zero probability to occur in commensurate solids which break continuous translation symmetry. We discuss recent ^{4}He experiments by Kim and Chan in the context of this theorem, question its bulk supersolid interpretation, and offer an alternative explanation in terms of superfluid interfaces.

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A recent discovery by Kim and Chan [1,2] that solid ^{4}He samples have a nonclassical moment of inertia (NCMI) is a breakthrough result which has prompted renewed interest in the supersolid (SFS) state of matter. Early theoretical work by Andreev and Lifshitz [3] and by Chester [4] showed that solids may feature a Bose-Einstein condensate of vacancies. One may consider this work as establishing *sufficient* conditions for SFS. It was natural then to interpret mass decoupling in the torsion oscillator experiments as originating from a small ($\sim$1%) concentration of zero-point vacancies present in the crystal ground state with more unit cells than atoms [1].

However, the overwhelming bulk of experimental work (for a review, see, e.g., [5]) indicates that vacancies and interstitials in ^{4}He are *activated* and their concentration is negligible below 0.2 K. The most recent study [6] looked at the density variations of solid ^{4}He between two capacitor plates and did not reveal any presence of vacancies. To deal with these facts, an idea was put forward that exchange processes in quantum crystals may lead to superfluidity (SF) even in the absence of vacancies [7,8]. Mistakenly, this idea is attributed to Leggett's work [9], which established a link between the SF response and the *connectivity* of the ground state wave function (see below) and derived a rigorous upper bound on the superfluid density, ρ_s. Crystal defects and their relation to the connectivity was *not* discussed in Refs. [9,10].

The central point of the discussion to follow is to understand whether SF is possible in commensurate solids (crystal structures with the number of atoms being an integer multiple of the number of lattice points as in ^{4}He) and what the necessary conditions are for this to happen.

Below we reexamine Leggett's work and show that it implies vacancies and/or interstitial atoms as a *necessary* condition for SFS in bosonic systems similar to ^{4}He. Chester's "final speculation" that without them the solid state of matter is insulating [4] proves to be a theorem. We present an alternative proof using path-integral language in which the presence of vacancies in the SF state is seen explicitly. It also provides a picture showing why exchange processes on their own do not lead to SF. Finally, we consider a general argument based on the phase–particle-number uncertainty relation [11] which connects SF, compressibility of solids pinned by external fields and vacancies (pinning is crucial to separate and suppress the acoustic phonon contribution to the compressibility from that due to adding/removing particles to/from the bulk [12]). We find that SFS ground states in commensurate solids have a zero probability to be found in nature, because they require an accidental symmetry between the vacancies and interstitials which is immediately broken by changing system parameters [13]. This result does not apply to systems with explicitly broken translation symmetry, e.g., by external periodic potential, where commensurability may be enforced by hand and the lattice constant may not be changed continuously. By excluding the bulk SFS interpretation of the Kim-Chan results, we are forced to look for an alternative explanation of their data based on the physics of disordered and frustrated ^{4}He interfaces.

As shown by Feynman [14], the ground state of a bosonic system has no zeros, $\Psi_G(x_1, x_2, \ldots, x_N) \neq 0$. Moreover, in superfluid Ψ_G does not decay exponentially when one or several coordinates, say, $x_1, x_2, \ldots, x_m$, are taken around the system while other coordinates are kept fixed. This property (called connectivity by Leggett [9]) is key for SF, and is just another way of saying that topological off-diagonal long-range order is required for SF [15–17]. The requirement that connected Ψ_G be single-valued leads to the quantization of velocity circulation and thus stability of persistent currents in samples with the cylindrical annulus geometry [9].

To illustrate the point, consider a one-dimensional system of two identical bosons forming a bound (molecular) ground state, $\varphi_0(|r_1 - r_2|)$, with localization length l. Naively, the first rotating state of the molecule on a ring of large circumference, $L \gg l$, is written as a product of the plane wave for the center of mass coordinate, $R = (r_1 + r_2)/2$, times the bound state: $\varphi_1 = e^{i2\pi R/L}\varphi_0(|r_1 - r_2|)$. This expression, however, is not single valued, because if r_1 or r_2 is taken around the ring we get $\varphi_1 \to -\varphi_1$.

The correct solution is to replace φ_0 with $\tilde{\varphi}_0$, which has a zero at $|r_1 - r_2| \approx L/2$, i.e., in the region where φ_0 is exponentially small; at distances $|r_1 - r_2| \ll L$, the two functions are almost identical, $|\tilde{\varphi}_0| \approx \varphi_0$. An energetic cost of creating a zero in the above example is exponentially small and vanishes in the limit of infinite system size.

The same considerations apply to the disconnected crystal state consisting of N bosons when Ψ_G decays exponentially when any finite number of coordinates are moved around while other coordinates are kept fixed. The first rotating state in the system of linear size L with periodic boundary conditions can be written as $\phi_1 = e^{i2\pi R/L}\tilde{\Psi}_G$, with $R = \sum_{i=1}^{N} r_i/N$ and $\tilde{\Psi}_G$ having hyperplanes of zeros in regions where the modulus of Ψ_G is exponentially suppressed and thus extra zeros do not cost finite (system-size independent) energy. The phase gradient circulation of ϕ_1 is $\sim 1/N$, and such a system will not show the NCMI which is based on the impossibility of setting system in rotation with arbitrary small (in thermodynamic limit) velocity circulation. For comparison, the first rotating state of the single-atom superfluid system, $\phi_1^{(\mathrm{SF})} = e^{i2\pi \sum_{i=1}^{N} r_i/L}\Psi_G$, has the phase gradient circulation 2π and no zeros because creating them in the connected Ψ_G is so energetically costly that the lowest energy state corresponds to the relatively high kinetic energy of rotation [9]. For definiteness, we consider below only single-atomic superfluids, but all considerations are readily generalized to the m-atomic case.

By definition, $|\Psi_G(x_1, x_2, \ldots, x_N)|^2$ is the probability density to find particles at the specified positions. We fix all coordinates except one, x_1, and observe that connected $|\Psi_G(x_1)|^2$ remains finite when x_1 is taken arbitrary far from the initial position. Formally, this property is identical to statistical properties of atomic configurations in classical crystals at finite temperature and was used by Chester to introduce vacancies in the ground state. This correspondence was not elaborated in Ref. [9].

How do we ''visualize'' vacancies or interstitials in the state of identical particles with large zero-point vibrations of atoms, *especially when the solid is commensurate*? The common perception is that commensurate solids do not have vacancies and interstitials by definition, or else there is no way to separate them from the picture of standard zero-point motion. Imagine a solid sample pinned by an (arbitrarily weak) external potential preventing it from moving as a whole. There is no problem identifying lattice points using the average (periodic in space) particle density profile, $\rho(r)$. Now consider a typical spatial configuration of particle positions and lattice points and start the coarse-graining procedure of ''erasing'' the closest particle—lattice point pairs in the spirit of the spatial renormalization group treatment. As we progress towards mesoscopic length scales, all short-range zero-point fluctuations of atoms away from lattice points will be erased from the picture. The procedure continues until we have erased all pairs with sizes much smaller than L but much larger than all microscopic scales. We say that the state has no vacancies and interstitials if the final coarse-grained configuration is empty. If the configuration still contains lattice points, or particles, or both, at arbitrary large distances, we say that it has zero-point vacancies or interstitials. In what follows, we always refer to vacancies and interstitials only in the above mentioned sense, which excludes *bound exciton-type vacancy-interstitial pairs*. The decimation procedure explains how vacancies and interstitials are possible in commensurate solids, and works equally well for classical crystals at finite temperature. For the commensurate solid with connected Ψ_G, we may start with the perfect-lattice configuration of particle coordinates and its empty coarse-grained picture, and then move x_1 an arbitrary distance away to produce an image of the vacancy and interstitial. This will *not* result in the exponential suppression of the configuration probability (in fact, such configurations will dominate in the normalization integral); i.e., vacancies and/or interstitials are necessarily present in the SFS ground state.

Since in the SFS state vacancies and interstitials do not form bound pairs and can be found arbitrarily far from each other, there is no *microscopic* mechanism to fix their number densities at the same value, and one may consider creating them in the equilibrium thermodynamic state independently [13]. Formally, it means that the particle-number density n and the unit-cell number density n_u should be treated as independent thermodynamic parameters to be determined from the minimization of free energy. In the absence of exact interstitial-vacancy symmetry, $n = n_u$ may occur only accidentally. The most likely outcome is that $n < n_u$, since energy cost to produce vacancies is typically smaller than that for interstitials.

Our second consideration is based on the path-integral formulation of quantum statistics [14] in terms of many-body trajectories, $\{x_i(\tau)\}$, in imaginary time $\tau \in [0, \beta]$ with periodic boundary conditions $\{x_i(\beta)\} = \{x_i(0)\}$. The most important superfluid characteristic of particle trajectories, or world lines, is their winding numbers, M^α, $\alpha = 1, 2, \ldots, d$, where d is the space dimension. To determine M^α, imagine a cross section going through point $\mathbf{R}$ perpendicular to the direction α and count how many times particles cross it from left to right, k_-^α, and from right to left, k_+^α. By definition, winding numbers are $M^\alpha = k_+^\alpha - k_-^\alpha$. They are independent of the cross-section location $\mathbf{R}$ because trajectories are continuous and periodic in imaginary time. The superfluid density is then given by [18]

$$\rho_s^{\alpha\gamma} = 2mTL^{2-d}\langle M^\alpha M^\gamma \rangle, \tag{1}$$

where m is the particle mass. In $d = 3$, the superfluid density is finite in the thermodynamic limit, $L \to \infty$, $T \to 0$, and $T/L \to 0$, only if the probability of having world lines with nonzero winding numbers in the ground state is close to unity. We now demonstrate that crystal states without vacancies are described by world-line configurations with $\mathbf{M} = 0$; i.e., they are not superfluid. We start

with the picture of a perfect crystal with particles tightly localized around equilibrium lattice points. This state with $\mathbf{M} = 0$ is shown in Fig. 1(a). When exchange processes are added into the picture, the world lines are no longer in one-to-one correspondence with the lattice points. The nature of the exchange process, however, is such that when one particle leaves its equilibrium crystal point R_1 and goes to point R_2, the other particle goes from R_2 to R_1 (for pairwise exchange). Thus, the net current of world lines through any cross section remains zero. The same conclusion follows by considering multiparticle exchange events [19]; see Fig. 1(b).

Now consider a world-line configuration with $\mathbf{M} \neq 0$ [Fig. 1(c)]. At any moment of imaginary time, we consider the spatial configuration of particle positions and lattice points and apply the coarse-graining procedure discussed above. All short-range exchange process and zero-point fluctuations will be erased once we pass several atomic distances. In the insulating state, the "movie" of the coarse-grained configuration evolution in time will show an empty "screen" for Figs. 1(a) and 1(b). If $\mathbf{M} \neq 0$, as in Fig. 1(c), it is impossible to erase all particles and lattice points at all moments in time, since topologically winding numbers correspond to particle trajectories moving continuously in the same spatial direction and thus create an imbalance between particles and lattice points at arbitrary large distances. A coarse-grained trajectory with $M = 1$ will then feature an interstitial and a vacancy which separate over distances of order L and eventually make a closed loop around the system; see Fig. 2. For the statistics of such loops to give finite ρ_s in the thermodynamic limit, they have to be typical and numerous; i.e., vacancies and/or interstitials must be an integral part of the ground state.

Our last consideration is based on the relation between the compressibility of *pinned* solids, κ, and vacancies. Compressibility can be calculated through the energies of states with one interstitial, E_{N+1}, and one vacancy, E_{N-1}, as $\kappa = 1/V\Delta E$, where V is the system volume, and $\Delta E = E_{N+1} - E_{N-1} \equiv (E_{N+1} - E_N) + (E_N - E_{N-1})$. Incompressible states have finite, system-size independent ΔE, which is the sum of activation energies for vacancies and interstitials. Correspondingly, crystals without interstitials and vacancies have finite $\Delta E > 0$ (otherwise, these defects would be an essential part of the ground state) and thus are incompressible (if pinned) and vice versa. Going one step further, this implies that SF and pinned compressibility come together, and either one (including long-wave acoustic properties with additional sound mode) can be used for the detection of the SFS state experimentally. This conclusion is in line with the famous uncertainty relation

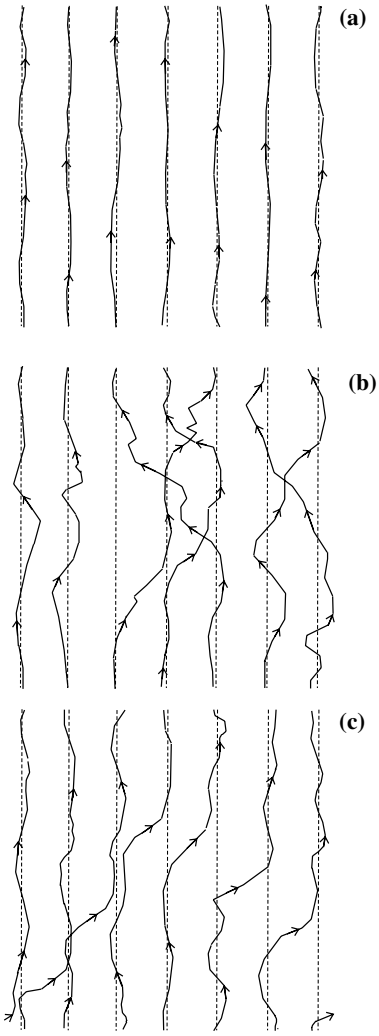

FIG. 1. Particle world lines in different crystals at low temperature. The time axis is vertical. The dashed lines show the equilibrium lattice points. (a) Nearly classical crystal at low temperature; $\mathbf{M} = 0$. (b) Insulating quantum crystal with large zero-point fluctuations and frequent particle exchange processes; $\mathbf{M} = 0$. (c) Particle world lines with a nonzero winding number.

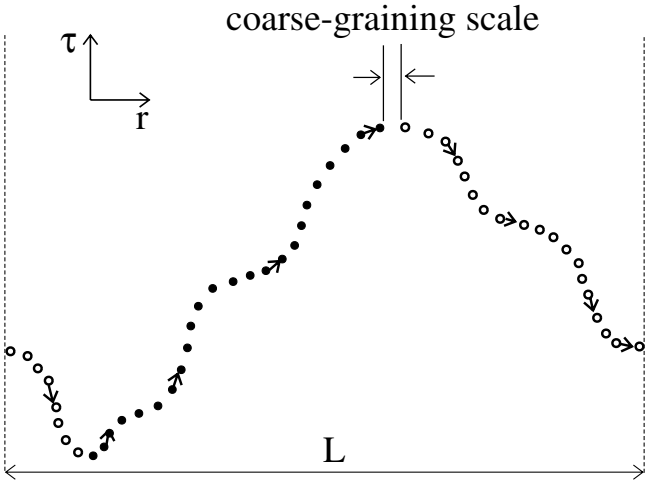

FIG. 2. Evolution of the coarse-grained picture (see text) for a trajectory with a nonzero winding number similar to Fig. 1(c). Solid and open circles show particle and lattice site positions correspondingly. Arrows indicate the direction of the particle-number current.

[11] between the phase of the superfluid order parameter, ϕ, and particle number, $\Delta\phi\Delta N \geq 1/2$. Because of this relation, one may not introduce a well-defined phase field for the incompressible state of matter which tends to *completely* suppress particle-number fluctuations.

We have little doubt that large activation energies for vacancies and interstitials in ^{4}He measured down to $\sim$1 K temperatures [5] will not radically change to near zero values at lower temperatures, and that ^{4}He is a commensurate solid at $T = 0$ (it has no symmetry between vacancies and interstitials either). We thus conclude that bulk solid ^{4}He cannot be in the SFS state. By excluding superflow through the crystal bulk, we are forced to look more closely at the superfluid properties of disordered helium-substrate layers in the helium-Vycor system [1] and frustrated interfaces between microcrystallites in the helium-only system [2].

There are indications of strong disorder in the experimental systems of Refs. [1,2]. For the bulk normal-SF transition one expects the dependence of ρ_s on reduced temperature parameter $t = (T_c - T)/T_c$ (in the limit of $t \to 0$) to be the same as in liquid ^{4}He, namely, $t^{0.671}$. Instead, ρ_s appears to vanish at T_c with zero derivative. Such a behavior can be modeled by a broad distribution of transition temperatures in the heterogeneous sample. This observation correlates with the gradual decrease of the decoupled mass with the increase of the torsion oscillator amplitude by orders of magnitude. We suggest that helium samples consist of microcrystallites of linear size D with SF interfaces of typical thickness d between them. The SF fraction coming from the foamlike system of interfaces is estimated from the surface-to-volume ratio as $\rho_s/\rho \sim 2d/D$. To get $\rho_s/\rho \sim 1\%$ from interfaces with $d \sim 10$ Å, one will need crystallite sizes about a fraction of a micron. The variety of interfaces with different crystallographic indexes provides a distribution of transition temperatures. For the Vycor system, one may imagine that SF persists at the disordered helium-Vycor interface.

One of the experimental mysteries is extreme sensitivity to ^{3}He impurities at the level of $n_3 \sim 100$ ppm. To minimize kinetic energy, light ^{3}He atoms are likely to end up at frustrated interfaces, and then at the edges where different interfaces meet. This may increase ^{3}He edge versus bulk concentration by a large factor of $\sim(D/d)^2$ and produce $n_3^{(\mathrm{edge})} \sim 1$ with a profound effect on the edge-connected interface SF (^{3}He-rich edges act as a disordered two-dimensional network of Josephson junctions). In Vycor, ^{3}He atoms may go to places where disorder is the largest and block channels between the pores.

We are not aware of studies looking at superfluidity of interfaces between ^{4}He crystals and ^{4}He crystals on disordered substrates at elevated pressures. Model simulations of domain wall boundaries in the checkerboard solid (obtained for interacting lattice bosons at half-integer filling factor) show that they remain superfluid deep into the bulk solid phase [20]. In the outlined picture, three predictions are certain: (i) the superfluid fraction must strongly depend on the crystal growth process; (ii) the amount of ^{3}He sufficient to suppress superfluidity scales as $n_3 \propto \rho_s^2$; (iii) transition temperatures on interfaces do not depend on D or on $\rho_s(T = 0)$.

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