

Quantum crystals: from quantum plasticity to supersolidity

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ABSTRACT

We have discovered that helium-4 crystals are anomalously soft around one tenth of a Kelvin (100 mK) if totally free of impurities. Their plasticity is large, due to quantum effects. This is because their dislocations can move macroscopic distances (typically 0.1 mm) at high speed (meters per second) under the effect of stresses as small as 1 microbar.

In classical crystals all atoms are completely frozen at low temperature. But in quantum crystals such as helium-4, quantum fluctuations are large and atoms can jump by quantum tunneling from site to site, especially at the core of dislocation lines where the packing is not as compact as elsewhere. We have shown that highly mobile dislocations reduce the stiffness of helium-4 crystals by one order of magnitude.

However, very tiny traces of helium-3 impurities are sufficient to stop the motion of dislocations when they attach to them below temperatures of order 100 mK. Apparently, this is what drives these crystals to a “supersolid state”, an astonishing new state of matter where superfluidity coexists with crystalline order. We think that the core of dislocations becomes superfluid only when the dislocation lines themselves stop moving.

Keywords: Quantum crystals, supersolidity, plasticity, dislocations

1. INTRODUCTION

A crystal is quantum if the quantum fluctuations of its atoms are large. Let us first explain what “large” means and why quantum fluctuations are larger in helium 4 crystals than in any other crystal.

In a classical crystal at low enough temperature, all the atoms are frozen on one site of the lattice. But if an atom is localized in a box of size a , the Heisenberg uncertainly relations imply that this atom has a momentum $p = \hbar/a$. If the hard core diameter of the atom is d , this momentum should actually be of order $\hbar/(a-d)$. To this momentum is associated a quantum kinetic energy $E_c = \hbar^2/2m(a-d)^2$ known as its “zero point energy” because it exists at the absolute zero (m is the atomic mass). In the case of helium 4, the mass $m = 4/N$ is small, the typical interatomic distance is $a = 0.37$ nm and the hard core diameter is $d = 0.26$ nm, so that the kinetic energy E_c is about 15K.

In order to see if E_c is large, one needs to compare it to the interatomic potential energy between atoms. Helium atoms are the smallest rare gas atoms with two electrons on a complete 1s shell. As a consequence, not only helium atoms do not have any chemical properties but their attractive interactions are the weakest possible ones because their polarizability is the smallest. When adding a hard core repulsion, one obtains a full interaction energy with a minimum around 0.3 nm, whose amplitude has the same order of magnitude as E_c . Quantum fluctuations are large in both liquid and solid helium. In molecular hydrogen, the mass of the molecule is smaller but the polarizability is much larger so that the quantum fluctuations are not as important as in helium crystals. For heavier atoms E_c is smaller and the interatomic potential is also larger. Helium is the best candidate to study the properties of quantum crystals.

There are two isotopes, helium 4 and helium 3. Natural helium is extracted from gas wells where it accumulates. Most of this natural helium is helium 4 because it comes from the α -decay of Uranium. It usually contains 0.3 ppm ($3 \cdot 10^{-7}$) only

of the light isotope helium 3. In helium 3 the zero point energy is even larger than in helium 4. Furthermore, helium 3 is a Fermi particle while helium 4 is a Bose particle, so that liquid helium 3-4 mixtures spontaneously phase separate below 0.8K. Natural helium 4 can be purified by distillation down to the ppb level. It is also possible to buy pure helium 3 which is produced by the β -decay of Tritium in the military nuclear industry. Since the 1970's, helium 3-4 mixtures are used in so-called "dilution refrigerators" to cool matter down to 2 mK.

As early as in the 1930's, F. Simon[1] and F. London[2] understood that the magnitude of quantum effects is the reason for the particular phase diagram of helium at low temperature. Fig.1 shows that the liquid phase of helium 4 is stable down to $T=0$ at low pressure. Liquid helium 4 crystallizes only at pressures higher than 25 bar (29 bar in helium 3). The melting line is roughly independent of T showing that the transition from liquid to solid helium is mostly a question of quantum fluctuations.

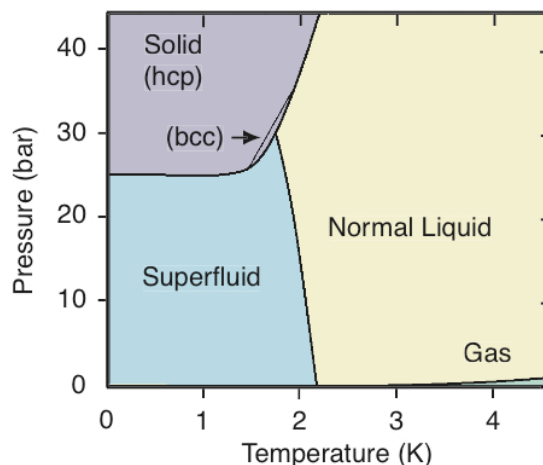


Figure 1. The phase diagram of helium 4 at low temperature. Due to the large magnitude of E_0 , the quantum kinetic energy of atoms, the liquid phase is stable down to $T=0$ and the solid phase only exists above 25 bar. There is no triple point where the gas, the liquid and the solid phase would coexist. Moreover, the liquid becomes superfluid below a "lambda" transition line around 2K. It has now been discovered that there is a similar transition to a "supersolid" state in the solid around 0.1K.

These quantum fluctuations have other consequences on macroscopic quantities. For example, the molar volume of liquid helium 3 is much larger than that of liquid helium 4 (36.8 cm^3 compared to 27.6 for helium 4 at zero bar). For the purpose of this article, it is important to notice that helium crystals do not obey the "Lindemann" criterion for melting. This criterion says that a crystal melts when the amplitude of the fluctuations reach 10% of the nearest neighbor distance. It is basically obeyed in all classical crystals. But in the case of helium 4 crystals, the fluctuations are much larger, 27% on the melting line (even more for helium 3). It means that atoms are not as well localized on their lattice sites as in classical crystals. In the case of helium 3, atoms can exchange their positions by quantum tunneling through energy barriers, which are low. A well-known consequence of this exchange is magnetic "exchange interactions" which lead to nuclear magnetic ordering below 1 mK (helium 3 has a non-zero nuclear spin).

At the end of the 1970's, it had been predicted by A.F. Andreev that the surface of helium crystals should be rough down to $T=0$ due to these quantum fluctuations. However this prediction was shown incorrect. It has been proven by several research groups that both helium 4 and helium 3 crystals show roughening transitions to faceted shapes (see Fig.2) below a series of roughening temperatures corresponding to facets of higher and higher Miller indices appearing at lower and lower temperature as for classical crystals (for a review, see Ref. [3]).

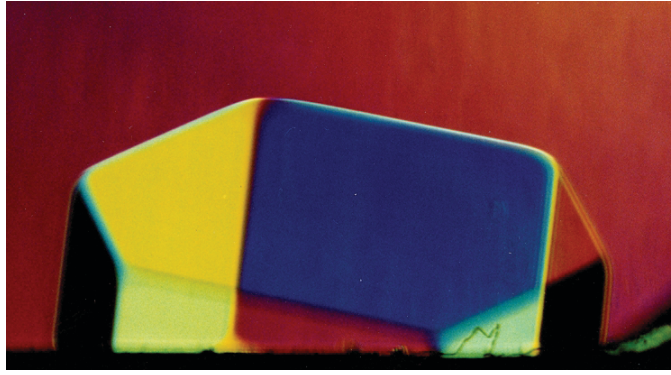


Figure 2. A helium 4 crystal growing at 100 mK in the optical cryostat of the ENS (Paris). The colors are obtained by illuminating it through a glass prism. The growth shape reveals the presence of facets in high symmetry directions and allow the determination of the crystal orientation.

In 2004, another astonishing property was proposed, namely that helium 4 crystals could be “supersolid” which means superfluid and solid at the same time. Supersolidity is the subject of this article. It is highly paradoxical and its understanding is still controversial but, in my opinion, its existence is now well established by robust experimental evidence. As already mentioned above, liquid helium 4 has a phase transition from a normal liquid above 2K to a superfluid phase below this temperature. At the time of its discovery, the origin of superfluidity was also controversial [4], but it is now well established that it is a consequence of Bose Einstein condensation in a sense generalized to systems of interacting identical bosons after the famous work by Penrose and Onsager[5]. Superfluid helium 4 is described by a macroscopic wave function that implies phase coherence at a macroscopic scale. Superfluid helium is an ensemble of undistinguishable particles forming a macroscopic wave of matter. As we shall see below, it is also possible that a crystal is partially superfluid, that is “supersolid”. However, in the case of helium 4 supersolidity has been shown to be associated with disorder, probably dislocations, and we shall see that it is surprisingly related to a kind of quantum plasticity of the crystals.

2. THE ROTATION ANOMALY OF HELIUM 4 CRYSTALS

2.1 The 2004 experiment by Kim and Chan

In 2004, E. Kim and M. Chan published two articles suggesting the supersolidity of solid helium 4. They used a so-called “torsional oscillator” (TO) which is a little box typically 1 cm in size, suspended to a torsion rod usually made of BeCu bronze (Fig.3). The box oscillates around the torsion rod with a resonance around 1kHz. The resonance period τ is about 1 ms, given by $\tau = 2\pi\sqrt{I/K}$, where I is the rotational inertia and K an elastic constant which mainly depends on the stiffness of the torsion rod. Torsional oscillators had already been used to study the superfluid transition. Indeed, when the box is filled with liquid helium, one observes a decrease of the inertia I as the box is cooled down through the superfluid transition. This is because the ground state of a superfluid is irrotational so that it does not rotate with the box walls; it stays at rest (except if the rotation velocity exceeds a critical value). In 2004, Kim and Chan have discovered that a torsional oscillator filled with *solid* helium shows a decrease of its resonance period when cooled below about 100 mK, as if 1% of the helium mass stopped rotating with the box walls. This observation was so surprising that many possible artifacts were considered: the solid could slip against the walls, the change in period could be a consequence of a change in the stiffness K more than a change in the inertia I etc. In my opinion, all possible artifacts have been successively ruled out [7]. Apparently, a fraction of solid helium 4 flows through the rest without friction. This fraction varies from sample to sample in the range from 10^{-4} in bulk single crystals to a few percent in quenched frozen thin polycrystals. The temperature of the transition to the supersolid state increases with helium 3 impurity concentration which could be varied from 1 ppb to a few ppm. The change in period depends on the oscillating velocity as in superfluid *liquid* helium due to the existence of a critical velocity for the appearance of dissipation in the flow. Eventually, in pure helium 3, a Fermi system, there is no inertia change.

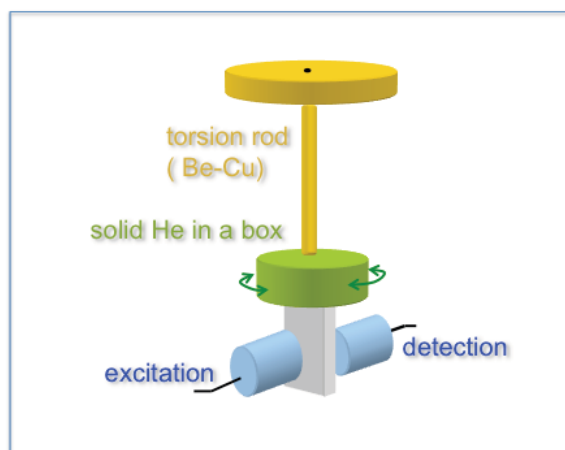


Figure 3. The torsional oscillator used in 2004 by E. Kim and M.H.W. Chan [6] to measure the rotational inertia of solid helium 4.

2.2 Two possible interpretations

The possibility that solid properties could coexist with superfluidity had been considered in 1969 D.J. Thouless and by A.F. Andreev and I.M. Lifshitz [7,8]. At that time, one imagined that a quantum crystal could be invaded by superfluid vacancies. In a classical crystal, a vacancy has a positive energy because removing one atom on a lattice site implies cutting bonds, which costs a large potential energy. But in a quantum solid, this vacancy can exchange its position with neighboring atoms by quantum tunneling and become delocalized. It becomes a wave with a bandwidth proportional to the tunneling frequency. Supposing that this frequency is very large, the bottom of the band could be negative and the crystal invaded by delocalized vacancies. If vacancies repel each other, the crystal should contain a finite density of vacancies even in its ground state at $T=0$ (the crystal would be “incommensurate” because it would have less atoms than lattice sites). Since helium 4 atoms are bosons, vacancies in helium 4 crystals should also be bosons and a gas of zero point vacancies should Bose-condense below a certain temperature depending on the mass and the density of these vacancies. A superflow of vacancies would be an inverse flow of mass and this hypothetical crystal would stay elastic (the lattice would not disappear) while part of the mass would flow without dissipation through the rest. Unfortunately this exciting model was proven wrong: numerical simulations and experiments have shown that the bandwidth is small so that the bottom of the vacancy band is positive, about $+10\text{K}$, so that the probability of having vacancies at 0.1K is negligible (The atom-atom exchange frequency is about 2MHz in solid helium [9], which corresponds to an energy $h\nu/k_B = 1.3 \cdot 10^{-27}/1.4 \cdot 10^{-23} \sim 10^{-4}\text{K}$ or 0.1mK . As for the vacancy-atom exchange energy, which gives an order of magnitude for the vacancy bandwidth, it has been numerical found to be about 1.6K [10]).

Since various experiments had shown that supersolidity increased with disorder, it was proposed more recently that the inside of crystalline defects could be supersolid. At this stage of this presentation, it must be useful to remind that “supersolid” means that the system is solid with a non zero shear modulus and that a fraction of its mass is superfluid. Grain boundaries are interesting [11] but, for simplicity, let us consider dislocations only. A dislocation line is a one dimensional defect inside which atoms are not as compactly packed as in the bulk crystal so that atom exchange must be easier. Numerical simulations have shown that it is sufficient to drive them to a superfluid state. Strictly speaking, a 1D-system is not superfluid but the dislocations form a 3D-network and if the temperature is low enough, the coherence length is larger than the distance between nodes in the network, and the phase coherence percolates through the whole network which becomes a 3D-superfluid. This is the model which looks most plausible to me but there is no real consensus about it, in particular because it is difficult to build a supersolid fraction of 1% with the core of dislocation lines with an atomic width, also because one may need very low temperatures for the coherence length to be large enough.

2.3 Supersolid helium 4 is stiffer than normal solid helium

If some of the mass starts flowing through the rest, one could naively imagine that the crystal becomes softer, more precisely that its elastic shear modulus is reduced. In 2007, Day and Beamish discovered that the opposite happens [12]. They measured the shear modulus μ of polycrystals in the thin space between two piezoelectric transducers and they found that μ increases when supersolidity appears. The temperature variation of μ is exactly the same as that of the supersolid fraction, showing that the newly discovered elastic anomaly and the previously found rotation anomaly are the two consequences of a unique phenomenon. For the elastic anomaly they proposed the following explanation.

A solid with mobile dislocations is softer than if its dislocations are pinned by some mechanism. Since any helium 4 sample contains some helium 3 impurities, and since the latter have a binding energy to dislocations of about 0.7K, they should bind to the dislocations and pin them below a temperature of order 100 to 200 mK depending on their concentration. This simple interpretation was supported by varying the helium 3 concentration from 0.3 ppm down to 1 ppb. The elastic anomaly and the rotation anomaly are shifted to low temperature in the same manner. A latter study as a function of frequency has shown that there is actually a distribution of binding energies around 0.73K with a width of 0.45K, so that the transition to the stiff supersolid state is broad [13].

The model by Beamish's group appears well supported by their observations but the relevance to supersolidity of changes in elastic properties remains to be found.

3. THE QUANTUM PLASTICITY OF ULTRAPURE HELIUM CRYSTALS

Since Beamish et al. had studied helium 4 samples with a large amount of disorder (polycrystals grown at constant volume), it appeared important to compare the elastic properties of polycrystals to high quality single crystals in order to investigate the role of disorder. This is what was recently achieved in our group [14].

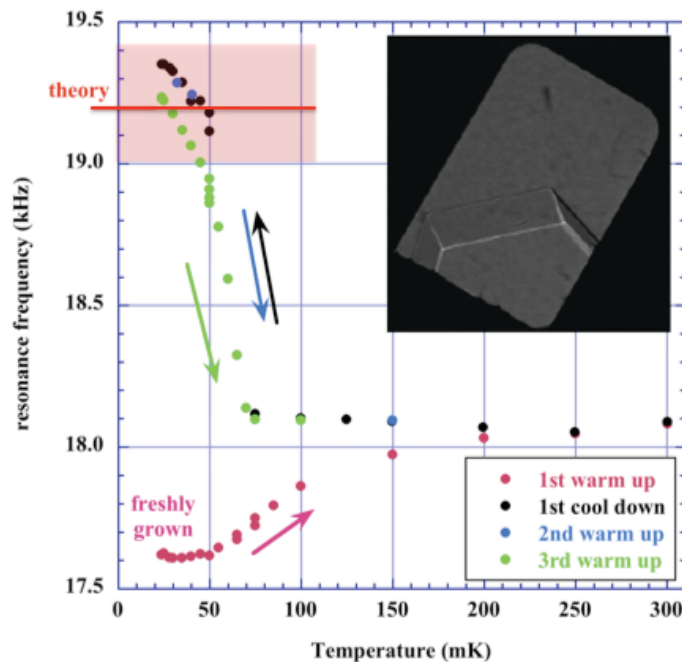


Figure 4. The measurements by Rojas et al.[14] of the elasticity of helium 4 crystals.

Rojas et al. [14] built a rectangular cell about 2 cm³ in volume (see inset in Fig.4) where the growth of solid helium could be monitored since it is transparent in an optical cryostat. Two piezo-electric transducers allowed measurements of the resonance frequency of the first acoustic mode in the cell. This frequency depends on all elastic coefficients since the

resonant wave is nowhere purely longitudinal nor transverse in such a cell, but it can be calculated numerically. Measurements were made either on polycrystals grown at constant volume from normal liquid helium, or on low quality single crystals grown from the superfluid at constant temperature $T \sim 1.4\text{K}$ and pressure $P_m(T)$ but damaged during cool down after growth (this is because the liquid-solid equilibrium pressure $P_{eq}(T)$ has a substantial temperature variation above 1K so that cooling from 1.4K to 1K produces large stresses of order 1 bar), eventually on very high quality single crystals grown slowly at constant T and P from the superfluid at 25 mK. Any crystal could be melted down to a small seed and regrown with the same orientation but different growth conditions so that the crystal quality could be changed at fixed orientation in order to study the effect of disorder.

Low quality single crystals and polycrystals showed similar elastic anomalies, confirming Beamish's assumption that the relevant defects are dislocations not grain boundaries. In fact, grain boundaries had already been shown to be solid not liquid, even at liquid-solid equilibrium where they are not wet by the liquid phase[11]. The grains do not slip against each other, it is really their own rigidity which changes at the transition.

Fig. 4 shows some results obtained with very high quality single crystals. The inset in this figure shows the orientation of one particular crystal. Knowing this orientation, H.J. Maris was able to calculate what should be the resonance frequency given the values of the elastic coefficients previously measured by Greywall[15] at 1.2K. At this temperature, the motion of dislocations is damped by thermal fluctuations so that the elastic coefficients should be the intrinsic ones that are related to the elasticity of the lattice only. The numerical calculation predicts a resonance frequency at $19.2 \pm 0.2\text{ kHz}$. In contrast, this crystal resonated at 17.6 kHz if fresh from growth. During warm up to 300 mK, the resonance frequency increased to 18 kHz. Cooling down drove the resonance frequency up to 19.4 kHz, close to the predicted value. This surprising behavior was interpreted as follows.

Fresh from growth at 25 mK, helium 4 crystals should be absolutely free of any impurity. This is because impurities are more soluble in the liquid phase than in the solid phase, as usual. In the particular case of helium, whose thermodynamic properties are very well established, helium 3 impurities have a potential energy 1.359K lower in liquid helium 4 than in solid helium 4. As a consequence, at 25 mK, the concentration of helium 3 atoms in the helium 4 crystal is 10^{21} times less than in liquid helium 4 where it is only 0.4×10^{-9} . It means that growing a crystal at 25 mK rejects all helium 3 impurities in the liquid, in front of the moving crystal surface[14]. Obviously, this ultrapure crystal is anomalously soft. This observation confirms that dislocations are highly mobile in helium 4 crystals if they are not pinned by helium 3 impurities.

The increase of the crystal stiffness during the first warming is a consequence of helium 3 impurities escaping from the nearby liquid and invading the crystal as T increases, binding to deep sites, perhaps to the nodes of the dislocation network. Afterwards, when the crystal is cooled down, it contains some free moving helium 3 impurities, which progressively bind to all dislocations and anchor them. As a result the dislocations no longer move and one recovers the normal elasticity of the crystal. A first conclusion of these results is that helium 4 crystals are not anomalously stiff at low T , they are anomalously soft in an intermediate temperature range between very low T where dislocations are pinned by impurities (if present, of course) and high temperature (1K in our case) where their motion is damped by thermal fluctuations. Rojas et al.[14] repeated these observations with other crystals. They also annealed them up to 0.95 K. Probably because this annealing rearranged the dislocation network, an even larger softening was observed (the resonance frequency was as low as 15.9 kHz between 60 and 300 mK). One usually assumes that, in hcp crystals, edge dislocations glide easily along the basal plane only. As a consequence, only one elastic coefficient is expected to change when dislocations move, namely the shear modulus c_{44} which governs the velocity of transverse sound $c_t = (c_{44}/\rho)^{1/2}$ along the 6-fold symmetry axis. If thus attributed to a change of c_{44} only, our observation means that the reduction of c_{44} is very large (86%) when dislocations are free to move. For such a very large variation of c_{44} , dislocations must cooperate by grouping together in the low angle grain boundaries of a mosaic structure [16].

The observations by Rojas et al. [14] deserve some more comments. The sound amplitude in our cell is very small, typically 1 microbar corresponding to a maximum strain of 10^{-8} at resonance. Such a small amplitude was used to avoid unpinning of dislocations from helium 3 impurities. The response to this 1 mbar stress oscillating at 15 – 20 kHz must be a displacement of at least 80 micrometers at the same frequency if one assumes that the dislocation density is less than 100 cm^{-2} as seems reasonable from previous studies[3]. This means that dislocations move macroscopic distances at very large velocities (several m/s) under minute stresses. Such a motion cannot be classical. It must be the consequence of the quantum tunneling of kinks on these dislocations, which appears possible at low temperature. We have thus discovered a spectacular softening of helium 4 crystals when their dislocations are free to move. We call it “quantum plasticity”.

Now an important question remains: what is the relation of quantum plasticity with supersolidity? As explained in Ref. [7], we believe that the transverse fluctuations of mobile dislocations are able to destroy the phase coherence along the dislocations themselves. This is perhaps because fluctuating mass current are associated to transverse fluctuations of the dislocation lines and it is well known that mass currents in a superfluid are proportional to phase gradients. We thus propose that quantum plasticity has to disappear (the crystal gets stiffer) for supersolidity to appear. Inversely, if the dislocation core is supersolid, its phase coherence implies that the dislocation lines do not fluctuate. Superflow of mass would be possible along the dislocation cores only if the dislocations lines themselves do not move.

In order to check that this rough model has some truth in it, we prepare experiments in which both the rotational inertia and the shear modulus could be measured at the same time and in samples with variable disorder. When the dislocation density decreases, the amount of superfluid mass should decrease and become negligible for low densities. The rotation anomaly should vanish. At the same time, the dislocation network being more loose, the pinning length of dislocations should be larger as well as their possible displacement, so that the elastic anomaly should increase in magnitude. On the contrary, with an increasing density of dislocation density, the magnitude of the rotational anomaly should increase while the elastic anomaly should decrease because the dislocation network would become very tight. To do this, we have constructed a transparent torsional oscillator where we can monitor the crystal growth and measure the crystal orientation. In this transparent TO, we will install piezoelectric transducers to measure the shear modulus and the dislocation density. These experiments are obviously not easy to do, but we hope that they clarify our understanding of two astonishing properties of quantum crystals, namely their supersolidity and their quantum plasticity.

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