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# Crystallization of *para*-Hydrogen: a quantum phase transition at finite temperature?

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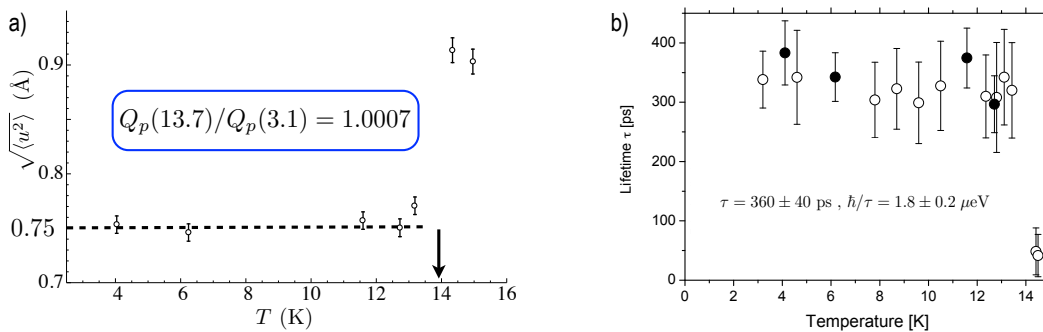
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**Abstract.** Recent neutron scattering measurements have revealed that *para*-Hydrogen prepared in its fundamental state solidifies in a crystal that do not show temperature response (temperature independent molecular displacement and first rotational level linewidth as well as negligible thermal expansion). Here, it is argued that such unique behaviour in the crystal phase can be understood if the crystallization is driven by pure quantum fluctuations.

## 1. Introduction

Local density fluctuations triggers crystal growing within a liquid at the freezing temperature. Conversely, as Lindemann observed long time ago [1], the crystal melts when the root mean square (rms) displacement is a sizeable portion of the first neighbour distance. At that point, some particle displacements explore too much the core part of the interaction potential acquiring enough kinematic energy to scape the crystal ordering. That is, phase transitions are driven by fluctuations. Once the crystal emerges, fluctuations decrease as temperature decreases. Eventually, the rms displacement is small enough for the harmonic approximation to be valid. Unless that quantum delocalization imposes a minimum size of the fluctuations too large. That being so, even at the lowest achievable temperature the harmonic approximation breakdowns and the solid is considered a quantum solid. Such is the case of the hydrogen family of molecular solids [2]. As the temperature decreases eventually quantum fluctuations overcome the diminishing thermal contribution so that both the rms displacement and the thermal expansion eventually stop diminishing to accommodate to the finite value of quantum fluctuations. Recently we have discovered that this athermal behaviour is stretched to its maximum in the case of *para*-Hydrogen in its fundamental state ( $J = 0$ ). Remarkably, the *para*- $H_2^{J=0}$  molecular crystal shows no discernible thermal expansion nor increasing rms displacement from  $\sim 3$  K to melting ( $\sim 13.8$  K) as attested by neutron scattering measurements of the  $J = 0 \rightarrow 1$  transition linewidth, rms molecular displacement and Bragg scattering [3]. As we all know, in Helium the effect is even stronger. Quantum fluctuations are so large that at its saturated vapour pressure Lindemann melting criterion is fulfilled even at zero temperature: at the lowest temperatures the condensate phase remains liquid (a quantum liquid). The survival of fluctuations, albeit quantum, immediately opens the possibility of phase transitions even at  $T = 0$  K. Necessarily driven by quantum fluctuations they are known as Quantum Phase





**Figure 1.** a) White circles are the rms of molecular displacements of the *para*-H<sub>2</sub><sup>J=0</sup> crystal at various temperatures. The arrow marks the triple point temperature (13.8 K). The blue box display the ratio of  $Q$  corresponding to the ( $\bar{1}02$ ) reflection of the *hcp* crystal structure (denoted by  $Q_p$ ), at 13.7 K and 3.1 K. b) The temperature dependence of the lifetime of the  $J = 0 \rightarrow 1$  transition. The average value and its corresponding value in  $\mu\text{eV}$  are also given.

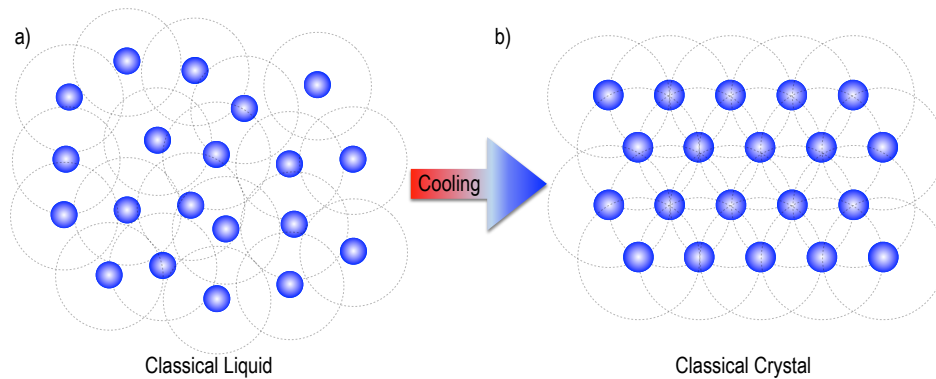
Transitions (QPTs), a field of considerable interest in the last two decades [4]. Indeed, <sup>4</sup>He below 1 K undergoes a first order transition towards a hcp crystal at around a pressure of 25 bar. Second order QPTs are also observed and, as in the classical case, are far more fashionable. Here, we will argue that the very peculiar athermal behaviour of the *para*-H<sub>2</sub><sup>J=0</sup> crystal can be understood if the corresponding crystallization is driven by fluctuations which are quantum in nature in spite of being at a finite temperature. As such, it can be considered a QPT between a so called quantum Boltzmann liquid and a “high temperature” quantum crystal.

## 2. Experimental results

The main goal of the experiment above mentioned was to measure the spectral broadening of the first  $J = 0 \rightarrow 1$  rotational transition in solid *para*-H<sub>2</sub>. Previous to the neutron scattering measurements a  $J = 0$  sample was prepared carefully by passing the liquid H<sub>2</sub> through chromium oxide within a gel during five days. All measurements were performed on the IN20 thermal neutron spectrometer at the Institut Laue Langevin, France. The instrument was used either in polarised triple-axis (TAS) mode or in TAS-spin-echo (TASSE) mode, in both cases with fixed final wave vector ( $2.66 \text{ \AA}^{-1}$ ). In TASSE mode, the accessible Fourier time spanned 3.2 ns at  $\sim 2.7 \text{ \AA}^{-1}$  with a time constant of 440 ps yielding an energy resolution of  $1.15 \text{ } \mu\text{eV}$  half width at half maximum at  $\sim 15 \text{ meV}$ . We not only measured the sought for linewidth but Bragg diffraction and the rms displacement in a temperature range between  $\sim 3 \text{ K}$  and the triple point at 13.8 K. The results are summarized on Fig. 1. For the details see [3]. Here, our interest is in the fact that the crystal show an essentially athermal behaviour, as it is illustrated in the Figure.

## 3. Discussion

Probably the only indisputable fact coming out from the result referred to above is that the *para*-H<sub>2</sub> cryocrystal cannot be described classically. A full quantum calculation of the system is unaffordable. We can, however, eliminate the rotational degrees of freedom since we are dealing with a  $J = 0$  population of diatomic molecules with a first rotational level at  $\sim 171 \text{ K}$  while the system temperature is below 20 K. Silvera and Goldman [5] developed an accurate effective pair potential for the H<sub>2</sub><sup>J=0</sup> molecule some time ago. Using this potential (isotropic as it corresponds to a  $J = 0$  wavefunction) we have performed a classical Molecular Dynamics study

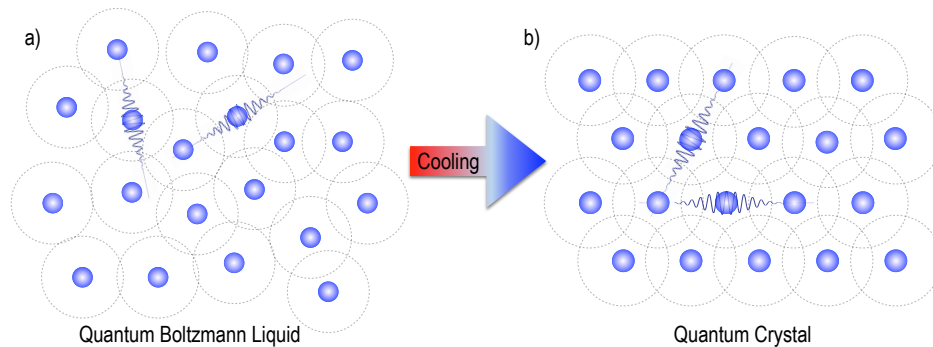


**Figure 2.** Crystallization of a classical 2D crystal. In a) temperature is near but above  $T_{tp}$ . In b) the crystal is shown at  $T = 0$ .

of the condensate phases. This classical analog melts at  $T_{tpcl} \sim 25$  K, around 1.8 times higher than the experimental value (at any rate, consistent with classical law-of-corresponding-states arguments). Scaling to the respective triple point temperature the corresponding calculated  $S(Q)$ 's yield a ratio  $Q_p(0.95 T_{tpcl})/Q_p(0.22 T_{tpcl})$  that amounts to 1.04 to be compared with the measured value of 1.0007. Finally, the classical crystal show a temperature dependent rms displacement. However, Lindemann's argument is vindicated (and subsidiarily Silvera-Goldman potential) since it melts at a  $\sqrt{\langle u^2 \rangle} \sim 0.75$  Å in agreement with the measurements.

As expected, the classical analog cannot reproduces the observed behaviour but, since it melts at the correct  $\sqrt{\langle u^2 \rangle}$ , we gain a strong confidence in the adequacy of the Silvera-Goldman potential. Under such an assumption, the classical analog tell us that quantum delocalization starts to be relevant somewhere above 25 K, i.e., very well above the triple point. This is consistent with a good deal of previous observations regarding liquid *para*-H<sub>2</sub>. The excess of kinetic energy arising from the Heisenberg uncertainty Principle has been observed [6, 7] and it results in a remarkable isothermal dependence of the kinetic energy on density [8]. As in the case of  $\sqrt{\langle u^2 \rangle}$  in excess in a quantum crystal, this phenomenology can be understood in terms of single-molecule wavefunction exploring the repulsive core of the intermolecular potential. Such a wave mechanics behaviour explain also why the liquid avoid crystallization at 25 K. Similarly, owing to the effects of particle delocalization on the overall magnitude of attractive intermolecular interactions, liquid *para*-H<sub>2</sub> near its triple point can sustain collective excitations which are otherwise absent in the classical computational (supercooled) counterpart [9]. All things considered, liquid *para*-H<sub>2</sub> qualifies as a quantum liquid. Since it crystallizes before Bose-Einstein condensation takes place, the term Boltzmann quantum liquid has been coined.

Being the quantum effects so manifest from so high temperatures, we are induced to consider what are the consequences of a fully developed wavelike behaviour already in the liquid, i.e., the consequences of classical thermal fluctuations playing no role. At a first glance, crystallization would be avoided altogether as in the case of He. However, excluded volume arguments make clear that it is not necessarily the case. To illustrate the point we will recourse to a 2D pictorial representation. Fig. 2 represents a classical picture of a 2D simple liquid crystallization. There, the blue spheres represents the core of the potential while the dotted line circle corresponds to the minimum of the pair potential. In the liquid side, the kinetic energy is too high for the crystal to form. Below  $T_{tp}$ , it is more energetically favorable for the particles to remain around the attractive well of the pair potential. At the transition, the excess of kinetic energy is released as heat more than compensating the diminution of configurational entropy. At sufficiently low temperature, the particles moves around the minima in the potential energy and the harmonic



**Figure 3.** Crystallization of a quantum Boltzmann 2D liquid. In a) temperature is near but above  $T_{tp}$ . In b) the representation is valid for any temperature below  $T_{tp}$ .

approximation works. At  $T = 0$  the particles sit at the minima as shown in Fig. 2 b).

Figure 3 represents the case of a quantum Boltzmann liquid fully dominated by quantum fluctuations (blue wavelets represent wavepackets). The scale of the quantum delocalization is commensurable with the interparticle distance. In fact, the wavepacket width determines the equilibrium density in order to avoid a substantial penetration of the wavefunctions within the repulsive core of the neighbour particles. Excluded volume around each particle is then maximized at the scale of the wavepacket width, not to the size of the repulsive core. If the well of the pair potential is shallow enough, decreasing the temperature would never drives the system to a crystalline phase. The balance between kinetic and potential energy will remain always in the kinetic side. But the configurations maximizing the available volume per particle are ordered close-packed structures (the triangular lattice in the 2D case). Furthermore, there is a gap in the available volume per particle between a close-packed arrangement and any other disordered configuration. Therefore, for a given density, by adopting a close-packed configuration, the system minimizes the wavepacket exploration of the neighbor particles core optimally: maximum first-neighbour distance for each and every particle in the system. If it happens that for a given density the potential well is able to move the energy balance to the potential side for the close-packed configuration, the liquid will crystallize. But, under the assumption referred to above of no role of classical thermal fluctuations at the transition, decreasing the temperature does not change the picture and the crystal will remain fully expanded whatever the temperature. We conclude then, that the unique athermal behaviour observed in the *para*- $\text{H}_2^{J=0}$  crystal is a strong evidence in favour of a quantum nature of its crystallization transition.

### Acknowledgments

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