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# Classical and quantum physics of hydrogen clusters

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## Abstract

We present results of a comprehensive theoretical investigation of the low temperature ( $T$ ) properties of clusters of *para*-hydrogen ( $p$ -H<sub>2</sub>), both pristine as well as doped with isotopic impurities (i.e., *ortho*-deuterium,  $o$ -D<sub>2</sub>). We study clusters comprising up to  $N = 40$  molecules, by means of quantum simulations based on the continuous-space Worm algorithm. Pristine  $p$ -H<sub>2</sub> clusters are *liquid-like* and superfluid in the  $T \rightarrow 0$  limit. The superfluid signal is uniform throughout these clusters; it is underlain by long cycles of permutation of molecules. Clusters with more than 22 molecules display solid-like, essentially classical behavior at temperatures down to  $T \sim 1$  K; some of them are seen to turn liquid-like at sufficiently low  $T$  (*quantum melting*).

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Clusters of molecular hydrogen are of interest for a number of fundamental reasons. Firstly, their investigation fits in the general theme of quantum few-body systems and the study of the evolution of the physical properties of a finite system as its size (number of particles) grows.

Secondly, molecular  $p$ -H<sub>2</sub> has long been speculated to be a potential superfluid, owing to the low mass of its constituents (about one half of that of a helium atom) [1].

In the bulk, superfluidity (SF) is not observed because, unlike helium, H<sub>2</sub> solidifies at a temperature ( $T \approx 13$  K) significantly higher than that ( $\sim 4$  K) at which phenomena such as Bose condensation and possibly SF might occur. This is due to the depth of the attractive well of the potential between two hydrogen molecules; significantly greater than that between two helium atoms. Although several avenues have been explored, both theoretically as well as experimentally, aimed at stabilizing a fluid phase of *para*-hydrogen at low  $T$ , thus far the search for bulk SF has not met with success (and there are reasons to be skeptical about its future prospects [2, 3]).

On the other hand, sufficiently small clusters of  $p$ -H<sub>2</sub> ought to remain liquid-like<sup>2</sup>, owing to the competition between

bulk and surface energy contributions, the latter promoting a ‘disordered’, liquid-like, arrangement of molecules. Theoretical calculations carried out some seventeen years ago, indeed, predicted that clusters of  $p$ -H<sub>2</sub> with fewer than 20 molecules should be liquid-like, turning superfluid at temperatures of the order of 2 K [4].

It should be noted that molecular hydrogen provides, in many respects, a richer playground than helium. Firstly, isotopes of different masses but with the same quantum statistics are easily accessible, and because intermolecular interactions among isotopes are reasonably similar (at least in pure clusters), it is feasible to isolate the effects of mass. Secondly, because the physics of bulk H<sub>2</sub> is expected to be noticeably different than that of small clusters thereof (unlike the case of helium), the investigation of clusters of varying size allows one to study systematically the emergence of bulk physics.

The experimental investigation of SF in clusters received renewed impetus following the introduction of helium nanodroplet isolation spectroscopy (HENDI), allowing one to investigate a single molecular impurity embedded in clusters comprising from a few, to several thousand helium atoms [5]. In these experiments, SF of the medium surrounding the molecule (i.e., the cluster) can be inferred by studying the rotational spectrum of the dopant. Specifically, the observed decoupling of the rotation of the molecule from that of the cluster is interpreted as a sign of the onset of SF in the cluster. Evidence of SF has been reported in clusters of

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<sup>2</sup> It must be stressed that for a finite size system no *rigorous* distinction can be made between ‘solid’ and ‘liquid’ phases. Therefore, this terminology is used somewhat loosely, for illustrative purposes, in the remainder of this paper. In general, when speaking of a ‘solid’ cluster one refers to the presence of order on a length scale comparable to that of the cluster itself.

$N \sim 15$   $p$ -H<sub>2</sub> molecules surrounding a linear carbonyl sulfide (OCS) impurity; these clusters are enclosed in a larger helium droplet [6]. Moreover, novel techniques based on Raman spectroscopy might even hold promise for the investigation of SF in pristine (i.e., undoped) clusters [7].

Motivated by the above developments, we have undertaken a systematic theoretical study of the physical properties of clusters of hydrogen molecules at low temperature (i.e., below 4 K). We have considered both pristine clusters of  $p$ -H<sub>2</sub> and  $o$ -D<sub>2</sub>, as well as clusters of  $p$ -H<sub>2</sub> doped with few substitutional  $o$ -D<sub>2</sub>.

Our results show that clusters with a number of molecules less than  $\sim 22$  are essentially liquid-like at temperatures lower than  $\sim 4$  K, and turn superfluid in the low  $T$  limit, much like clusters of helium atoms were predicted to do a long time ago [8]. More interesting physics is seen for clusters comprising between 22 and 30 molecules. At temperatures of the order of 2 K, these clusters display a rather classical behavior, with molecules arranged in an orderly, ‘crystalline’ fashion. On the other hand, as  $T \rightarrow 0$  clusters turn superfluid; in some of them, pronounced liquid-like behavior sets in, as clusters appear to undergo ‘melting’, driven purely by quantum effects, a mechanism reminiscent of that which stabilizes a liquid phase of condensed helium at low temperature.

In the remainder of this paper, we discuss the most significant signatures of the above physical behavior, inferred from our computer simulations.

## 2. Theoretical model

Our microscopic model of a droplet of hydrogen molecules is the one adopted in all other studies of clusters of molecular hydrogen since the pioneering work of [4]. In the most general case, we assume a collection of point-like particles obeying Bose statistics; each particle is either a  $p$ -H<sub>2</sub> or  $o$ -D<sub>2</sub> molecule. Particles interact via a spherically symmetric pair potential. Here, we make the simplifying assumption that the interaction for all species is the same; this approximation is actually quantitatively acceptable for many purposes [9]. Several choices are possible for the model interaction; in most previous calculations, the Silvera–Goldman pair potential [10] has been used, and the results presented here are obtained with this potential. It should be noted, however, that results of calculations making use of other pairwise interactions display the same qualitative physics (albeit quantitative differences exist) [11].

## 3. Methodology

Quantum-mechanical calculations at finite temperature for energetics, structural and superfluid properties of the clusters were carried out using the continuous-space Worm algorithm (WA) [12]. This quantum Monte Carlo (QMC) method, introduced in 2006, allows for numerically *exact* calculations of physical properties of Bose systems at finite temperature, especially those properties that hinge on a reliable simulation of quantum exchanges (chiefly SF). While the full power

of this methodology is harnessed when performing large-scale calculations of bulk properties of matter (for which a number of particles of the order of  $10^4$  is well within reach [13]), calculations for finite clusters are also carried out quite efficiently.

A general description of this method is provided in [12], whereas details related to this specific calculation are given in [14, 15].

## 4. Results

### 4.1. Magic numbers

The chemical potential  $\mu(N)$  associated to a cluster of  $N$  molecules is defined as

$$\mu(N) = E(N - 1) - E(N) \quad (1)$$

where  $E(N)$  is the total energy of the cluster in the  $T \rightarrow 0$  limit. A peak in the chemical potential for a particular value of  $N$  is a sign of enhanced stability of the cluster, typically in correspondence to a particular geometrical arrangement of the molecules (i.e., a local minimum of the potential energy).

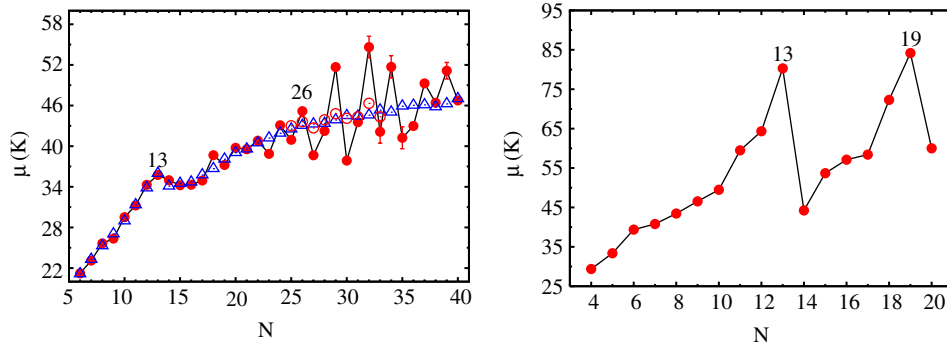
Figure 1 shows computed values of  $\mu(N)$  for clusters of  $p$ -H<sub>2</sub> and  $o$ -D<sub>2</sub>, based on energy estimates obtained at finite  $T$ . In both cases well-defined peaks can be seen at  $N = 13$ , and for  $o$ -D<sub>2</sub> clusters at  $N = 19$  as well, using energy values computed at  $T = 1$  K for  $p$ -H<sub>2</sub>, 0.5 K for  $o$ -D<sub>2</sub> (filled circles in figure 1). For  $o$ -D<sub>2</sub> clusters, energy estimates do not appreciably change on lowering the temperature (at least down to 0.25 K). For  $p$ -H<sub>2</sub> clusters, on the other hand, the additional structure seen for  $N > 25$  at  $T = 1$  K is ‘washed out’ at lower  $T$ . Indeed, our extrapolated ground state results are consistent with those of other authors, whose calculations only show the  $N = 13$  peak in the 1–30  $N$  range, at  $T = 0$  [16, 17]. The picture becomes more complex for larger clusters, as calculations at lower and lower temperatures are needed in order to ascertain whether some peaks that are present at finite  $T$  persist in the  $T \rightarrow 0$  limit.

In any case, this behavior suggests that, at temperatures of the order of 1 K, clusters of  $p$ -H<sub>2</sub> in the size range between  $\sim 23$  and 30 behave as more classical objects than in the  $T \rightarrow 0$  limit, wherein, as we shall see, in some cases distinct liquid-like behavior can be observed.

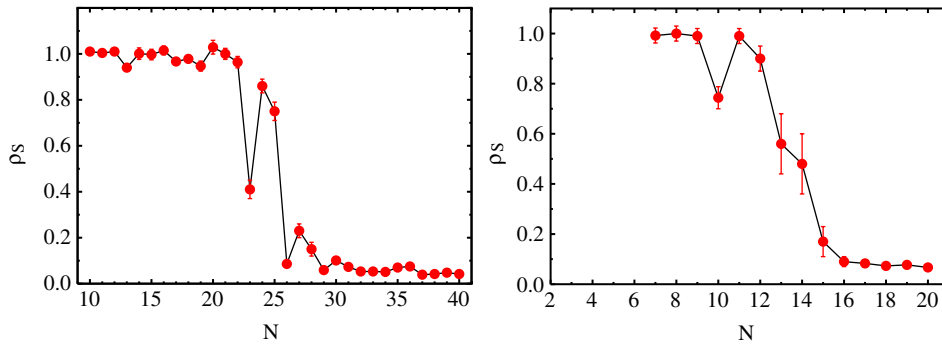
### 4.2. Superfluidity

The global superfluid response of a cluster can be computed by QMC simulations using the well-known ‘area’ estimator, originally introduced in [8]. Results for the superfluid fraction  $\rho_S$  are shown in figure 2 (from [15]).

Clusters of  $p$ -H<sub>2</sub> ( $o$ -D<sub>2</sub>) below a given size (approximately 23 for  $p$ -H<sub>2</sub> and 8 for  $o$ -D<sub>2</sub>) are entirely superfluid at 1 K (0.5 K); the superfluid fraction then decreases with  $N$ , but in a non-monotonic fashion, markedly so for  $p$ -H<sub>2</sub>. In particular, in a size range between 23 and 30, the superfluid fraction oscillates sharply, even on adding a single  $p$ -H<sub>2</sub> molecule. It is



**Figure 1.** Chemical potential as a function of the number  $N$  of molecules in clusters of  $p$ -H<sub>2</sub> (left) and  $o$ -D<sub>2</sub> (right). Filled circles are estimates obtained at  $T = 1$  K for  $p$ -H<sub>2</sub>, 0.5 K for  $o$ -D<sub>2</sub>. The latter remain unchanged at lower  $T$ . Open circles show estimates at  $T = 0.25$  K, triangles refer to results of [16].



**Figure 2.** Superfluid fraction of  $p$ -H<sub>2</sub> (left) and  $o$ -D<sub>2</sub> (right) clusters with varying numbers of molecules, at  $T = 1$  K ( $T = 0.5$  K for  $o$ -D<sub>2</sub>). When not shown explicitly statistical error bars are of the order of the symbol size.

plausible that such large oscillations reflect structural changes that take place as the number of molecules is changed<sup>3</sup>.

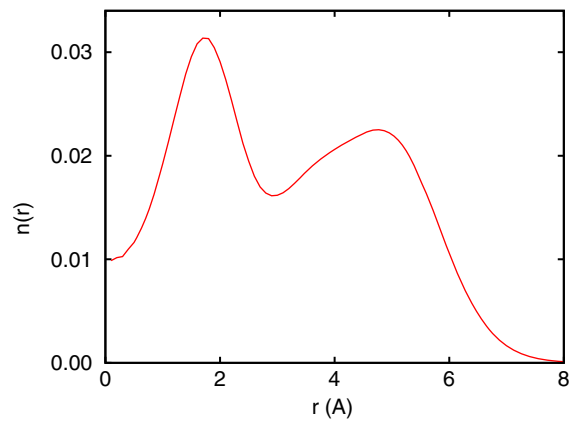
The superfluid response of  $o$ -D<sub>2</sub> clusters is considerably suppressed with respect to the corresponding clusters of  $p$ -H<sub>2</sub>, due to the larger molecular mass. There are reasons to expect, however, that the fundamental physical picture may be very similar, only ‘shifted’ to lower temperature.

In the remainder of this paper, we shall concentrate on clusters of  $p$ -H<sub>2</sub>;  $o$ -D<sub>2</sub> will only be discussed again as an isotopic dopant for these clusters.

#### 4.3. Clusters with $N < 23$

Clusters with fewer than 23  $p$ -H<sub>2</sub> molecules show a behavior quite similar to that of helium clusters. The radial density profile of the  $(p$ -H<sub>2</sub>)<sub>20</sub> cluster at  $T = 1$  K is shown in figure 3. A floppy structure is observed, featuring an inner and an outer shell with no sharp separation between them. An examination of many-particle configurations generated by the simulation reveals no preferred molecular arrangement, consistent with liquid-like character.

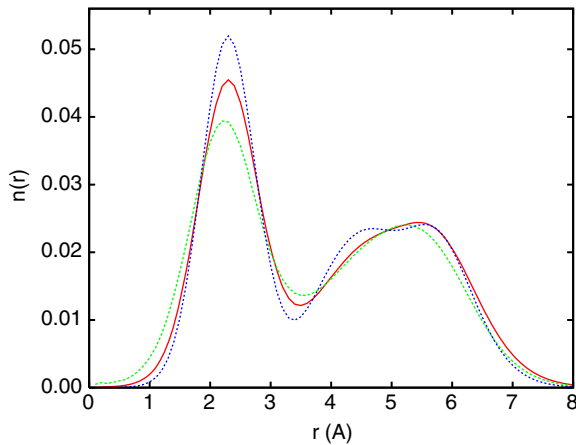
<sup>3</sup> The distinction between clusters of size less than 23 molecules and those of size between 23 and 40 pertains to results obtained with the Silvera–Goldman interaction potential. On using a weaker potential, such as the Lennard-Jones, clusters of size greater than 23 are liquid-like at  $T = 1$  K. Conversely, if a stronger binding model interaction is adopted (e.g., the Buck potential), superfluidity is depressed. Qualitatively, however, the overall physical picture is unaltered; see [11].



**Figure 3.** Radial density profile for a  $(p$ -H<sub>2</sub>)<sub>20</sub> droplet, computed with respect to the center of mass of the system, at  $T = 1$  K. Density is expressed in  $\text{Å}^{-3}$ .

Indeed, the peak in the chemical potential for  $N = 13$ , initially thought of as possibly representative of a solid-like cluster, at least for  $p$ -H<sub>2</sub> corresponds instead to the completion of the first molecular shell, and there now seems to be theoretical agreement that such a cluster is liquid [16–18].

At  $T = 1$  K these clusters are essentially entirely superfluid, within the statistical errors of our calculation [14, 15]. The superfluid response of the system can be spatially resolved, using an estimator recently proposed by Kwon *et al* [19]. It



**Figure 4.** Radial density profile for a  $(p\text{-H}_2)_{25}$  (lowest main peak),  $(p\text{-H}_2)_{26}$  (highest) and  $(p\text{-H}_2)_{27}$  (intermediate) droplets, computed with respect to the center of mass of the system, at  $T = 0.5$  K. Density is expressed in  $\text{\AA}^{-3}$ .

is observed [20] that these clusters are uniformly superfluid, i.e., with no concentration of the response in particular regions (e.g., the surface).

#### 4.4. Clusters with $N > 23$

Figure 4 shows radial density profiles for clusters with  $N = 25$ , 26 and 27 molecules at  $T = 0.5$  K. They are generally sharper than that of  $(p\text{-H}_2)_{20}$ , pointing to increased molecular localization and greater rigidity of the cluster inner shell, as evidenced by the absence of particles in the middle of the cluster.

However, some relative differences are clear, even within these three systems. For instance, the radial density profile of  $(p\text{-H}_2)_{26}$  displays a noticeably sharper peak than that of both other clusters, as well as a lower inter-shell minimum (albeit in no case are the two shells sharply separated), and additional structure further away from the center. In particular, while the addition of a single molecule to the  $(p\text{-H}_2)_{25}$  has the effect of enhancing localization and the rigidity of the inner shell, the addition of a second molecule (yielding the  $(p\text{-H}_2)_{27}$  cluster) has the opposite effect, namely that of ‘softening’ the

inner shell. This fact by itself points to the importance of quantum exchanges involving particles in different shells. The superfluid fraction of the  $(p\text{-H}_2)_{25}$  cluster at this temperature is close to 85%, that of  $(p\text{-H}_2)_{27}$  is around 25%, whereas that of the  $(p\text{-H}_2)_{26}$  is less than 10%.

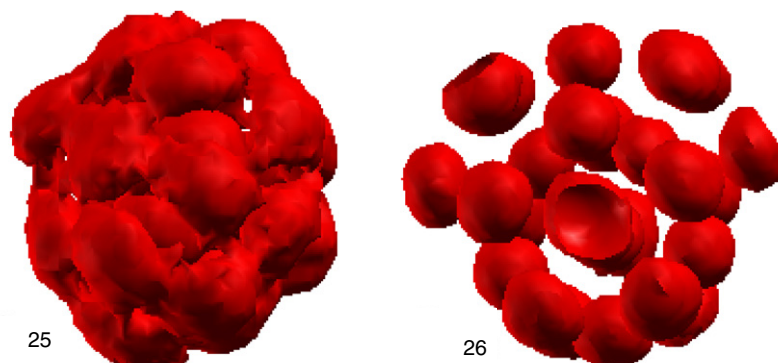
In order to gain more visual understanding of the structure of the different clusters, we use a graphical representation of their density, obtained as proposed in [18]. Figure 5 shows  $p\text{-H}_2$  clusters consisting of 25 and 26 molecules at  $T = 1$  K. The cluster  $(p\text{-H}_2)_{26}$  displays remarkably solid-like properties. Its structure consists of three rings of five molecules, with four other molecules linearly arranged along the axes of the rings, while the remaining seven molecules form an outer shell. Although their position is smeared by zero-point fluctuations the various molecules in the cluster can be clearly identified, indicating that they enjoy a fairly high degree of spatial localization; consequently, exchanges among different molecules are highly suppressed (though not completely absent), and the superfluid response is weak. Conversely, the molecules in the cluster  $(p\text{-H}_2)_{25}$  cannot be clearly identified, and the entire system appears amorphous. Because of their pronounced delocalization, molecules have a strong propensity to be involved in quantum exchanges, hence the larger superfluid response observed.

On the other hand, in the  $T \rightarrow 0$  limit *all* of these clusters, including  $(p\text{-H}_2)_{26}$ , turn superfluid. Indeed, the superfluid fraction of the  $(p\text{-H}_2)_{26}$  cluster reaches essentially 100% below  $\sim 0.1$  K.

Ground state calculations of the Lindemann ratio [17] suggest that even  $(p\text{-H}_2)_{26}$ , the most clearly solid-like at higher temperature, is essentially liquid at  $T = 0$ . Numerical evidence points to a structural transformation (see footnote 2) taking place at low  $T$  from a classical, solid-like to a liquid ‘phase’ of some of these clusters. Indeed, computer simulation gives evidence of such a transformation, as we next show.

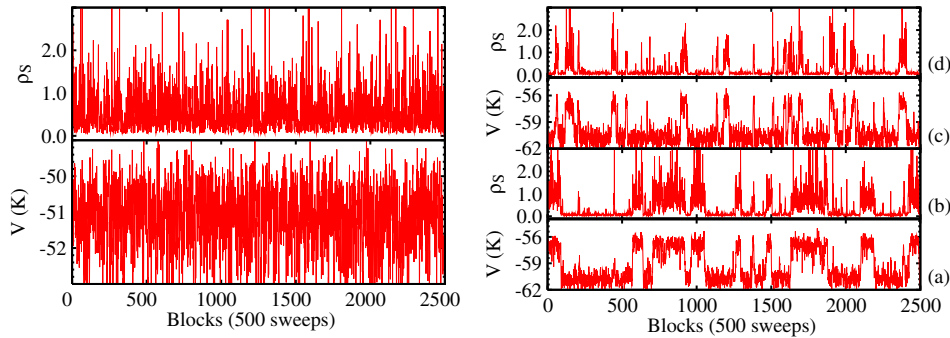
#### 4.5. Quantum melting

Figure 6 shows the values of the superfluid fraction and of the potential energy per molecule, recorded during a typical Monte Carlo run for clusters of 18 and 23  $p\text{-H}_2$  molecules, the former at  $T = 2$  K, the latter at both  $T = 1.0$  and 1.4 K. In particular,



**Figure 5.** Three-dimensional representation of the molecular density of the two clusters  $(p\text{-H}_2)_{25}$  and  $(p\text{-H}_2)_{26}$ .





**Figure 6.** Potential energy per molecule and superfluid fraction observed during a typical Monte Carlo run (see text) for a cluster of  $N = 18$   $p$ -H<sub>2</sub> molecules at  $T = 2$  K (left) and for one of 23  $p$ -H<sub>2</sub> molecules (right) at  $T = 1$  K (panels a and b) and  $T = 1.4$  K (panels (c) and (d)).

we show consecutive block averages of  $\rho_S$  and  $V$ , each block consisting of 500 QMC sweeps (see [15] for details).

For a  $(p\text{-H}_2)_{18}$  cluster, both quantities simply fluctuate about their average values. On the other hand, for  $(p\text{-H}_2)_{23}$ , despite the large fluctuations, two different regimes can be easily identified, namely one in which the superfluid fraction is high (with an average value close to 1) and the other characterized by low values of  $\rho_S$  (average value close to zero). The potential energy, correspondingly, takes on high (low) values when  $\rho_S$  is large (small). The switching of the values of the potential energy between the two different regimes, separated by some  $\sim 6$  K, can be interpreted as due to the system visiting relatively ordered, solid-like, insulating configurations (characterized by low potential energy), and disordered, liquid-like, superfluid ones.

The remarkable observation is that ‘melting’ of this cluster takes place as the temperature is *lowered*, due to quantum effects. On comparing the results for the cluster  $(p\text{-H}_2)_{23}$  at the two different temperatures, we can see that the liquid-like superfluid phase becomes dominant at lower  $T$ . Correspondingly, there is a sharp increase in the frequency of occurrence of permutation cycles involving *all* of the particles in the cluster.

One might speculate that the same physical behavior may be present in most (all ?) of the clusters in the range explored here, possibly even above  $N = 30$ . In principle, such *quantum melting* (QM) ought to take place at increasingly lower temperature, as the size of the cluster is increased. As shown by the results in figure 2, however, the trend is non-monotonic. In our simulations, we have observed clear evidence of QM for at least two clusters (namely  $N = 23$  and 27) in the temperature range between 0.25 and 1.25 K. Using a different interaction potential does not eliminate the effect, it simply shifts it to a higher (lower) temperature, depending on which potential is utilized [11].

It should be noted that the melting at low  $T$  of a cluster (specifically,  $(p\text{-H}_2)_{26}$ ) that displays solid-like, insulating properties at high  $T$  ( $\sim 1$  K), has also been reported by other authors, who performed similar numerical simulations, based on the Path Integral Monte Carlo method [21]<sup>4</sup>. Although

<sup>4</sup> It should be noted that large numerical discrepancies exist between their results and ours, whose explanation might have to do with different intermolecular potentials utilized. See also [11].

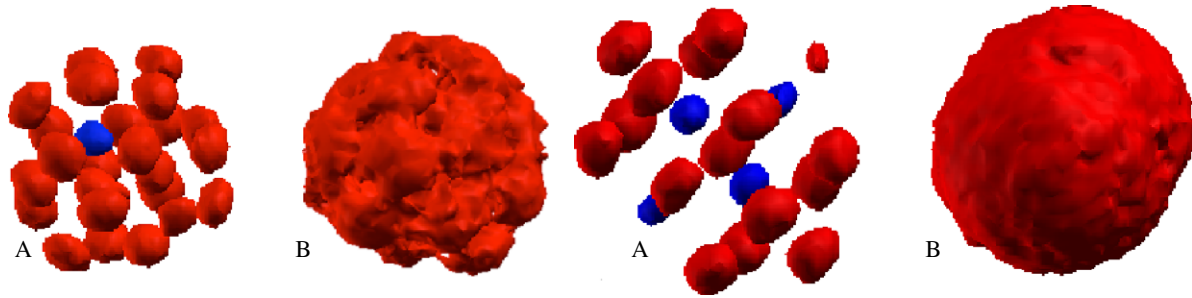
there are substantial quantitative discrepancies between their estimates and ours (e.g., we find  $(p\text{-H}_2)_{26}$  to be insulating at  $T = 0.5$  K), their physical interpretation is equivalent to the one that we are providing here.

It has been suggested that the emergence of SF in the low  $T$  limit in these clusters may be related to exchanges involving primarily ‘loosely bound surface molecules’, surrounding an otherwise essentially rigid core [21] (see footnote 4). Such a picture is at variance with the observation that the superfluid response remains homogeneous throughout the system, in the middle as on the surface, much like in clusters with fewer than 23 molecules, and that it approaches unity in the low  $T$  limit. An examination of the frequency of occurrence of permutation cycles of a given length shows that the superfluid response of clusters with  $N > 22$  crucially hinges on the onset of permutations involving all of the molecules in the clusters, *not* just those on the surface [20]. Finally, results obtained in the presence of an isotopic impurity (see below), showing that a single substitutional  $o\text{-D}_2$  molecule can turn a  $p\text{-H}_2$  cluster (that is otherwise entirely superfluid when undoped) insulating and solid-like rules out altogether the picture of loosely bound surface molecules, as the impurity sits in the center of the cluster, and therefore its effect on exchanges involving only surface molecules is negligible.

A possible alternate scenario consists of regarding the system as a rigid rotator; as soon as the temperature is lowered below the characteristic separation between the first two energy levels of a spherical rotator with the same classical moment of inertia of the cluster, the system may rotate freely, and therefore be a ‘superfluid’ according to the definition. However, the computation of the moment of inertia  $I$  carried out in this work, yields a ‘transition temperature’  $\hbar^2/I \sim 0.06$  K for clusters with  $N > 22$ , rapidly decreasing for greater size clusters. On the other hand, our results show the onset of superfluid behavior at temperatures an order of magnitude higher than that for  $(p\text{-H}_2)_{23}$ , and for other clusters (e.g.,  $(p\text{-H}_2)_{27}$ ) which display QM.

#### 4.6. Doped clusters and exchange cycles

In order to gain additional insight into the mechanism underlying SF in these clusters, and the importance of quantum



**Figure 7.** Three-dimensional representations of  $p$ -H<sub>2</sub> clusters doped with one (left) and four (right)  $o$ -D<sub>2</sub> molecules. Left:  $(p\text{-H}_2)_{24}-(o\text{-D}_2)_1$  (A) and  $(p\text{-H}_2)_{25}$  (B). Right:  $(p\text{-H}_2)_{16}-(o\text{-D}_2)_4$  (A) and  $(p\text{-H}_2)_{20}$  (B). A darker color is used for impurity molecules.

exchanges, we have performed additional simulations of  $p$ -H<sub>2</sub> clusters, in which one or more  $p$ -H<sub>2</sub> molecules were replaced by molecules of  $o$ -D<sub>2</sub>. As stated above, the only difference between  $o$ -D<sub>2</sub> and  $p$ -H<sub>2</sub> in our microscopic model is the mass of the substitutional particles.

In figure 7 we make use of the same schematic three-dimensional representations used above to illustrate the structural changes that occur upon doping, with substitutional  $o$ -D<sub>2</sub> impurities, two different  $p$ -H<sub>2</sub> clusters, namely  $(p\text{-H}_2)_{25}$  and  $(p\text{-H}_2)_{20}$ . The main effect in both cases is the same, i.e., the introduction of heavier impurities, whose energetically favored position is at (or, near) the geometrical center of the cluster, has the effect of rendering a liquid-like, superfluid pristine cluster *insulating and solid-like*.

Firstly consider the case of a single  $o$ -D<sub>2</sub> impurity substituted into a  $(p\text{-H}_2)_{25}$  cluster (left part of figure 7). The lone  $o$ -D<sub>2</sub> molecule sits in the central part of the cluster. The cluster turns from liquid (A) to solid-like (B); correspondingly, SF is altogether depressed [22]. By contrast, if the dopant molecule is taken to have *the same mass* as all other molecules but *distinguishable* from them, and thus it is not allowed to take part in exchanges of  $p$ -H<sub>2</sub> molecules (this is actually a reasonable model for an  $o$ -H<sub>2</sub> dopant molecule), then the structure of the cluster and its superfluid properties are much less affected by the substitution. Indeed, a doped cluster of 25 molecules retains most of its SF in this case. The physical difference arises from the fact that a lone  $o$ -D<sub>2</sub> molecule will sit in the central part of the cluster, where it has a strong inhibiting effect on long exchanges of  $p$ -H<sub>2</sub> molecules; the lighter  $o$ -H<sub>2</sub> dopant, conversely, is considerably more delocalized, and indeed is found prevalently near the surface [22]. As a result, long exchanges of  $p$ -H<sub>2</sub> molecules, also involving those in the inner shell of the cluster, remain possible.

The effect of cluster ‘crystallization’, induced in the  $(p\text{-H}_2)_{25}$  clusters by the substitution of one or two  $o$ -D<sub>2</sub> impurities (and the ensuing suppression of SF), can also be observed in smaller systems, but a greater number of substitutions is needed in order to produce the same dramatic change. Figure 7 (right part) shows the structures of the two clusters  $(p\text{-H}_2)_{16}-(o\text{-D}_2)_4$  (part A of the figure), and  $(p\text{-H}_2)_{20}$  (part B)); the pristine cluster is featureless and liquid-like, entirely superfluid at  $T \leq 1$  K. On the other hand, the superfluid component is small in the doped cluster, whose solid-like structure is evident, with a central axis surrounded

by rings of molecules. Two of the four  $o$ -D<sub>2</sub> molecules are placed on the axis, the other two on the central ring.

All of this shows that it is not only zero-point motion that underlies a liquid-like behavior of these systems; quantum exchanges play actually a crucial role.

## 5. Conclusions

A systematic theoretical study of the physical properties of clusters of hydrogen molecules at low temperature has been carried out, with the aim of understanding the interplay between superfluid and structural properties. We have considered both pristine clusters of  $p$ -H<sub>2</sub> and  $o$ -D<sub>2</sub>, as well as clusters of  $p$ -H<sub>2</sub> doped with few substitutional  $o$ -D<sub>2</sub>.

While the more quantitative details depend on the specific choice of interaction potential, there are some interesting general aspects that emerge in numerical simulations based on any reasonable pairwise, spherically symmetric interaction. We do not expect that the inclusion of non-spherical corrections would significantly alter the picture.

Our results show that clusters with a number of molecules less than  $\sim 22$  are essentially liquid-like at temperatures lower than  $\sim 4$  K, and turn superfluid in the low  $T$  limit, much like clusters of helium atoms. To the extent that such a terminology can be accepted, there appears to be a conventional ‘normal-to-superfluid’ transition. On the other hand, clusters of size between 22 and  $\sim 30$  molecules display a richer behavior in many respects. Firstly, they behave classically in a range of low temperatures, at which they display a relatively ordered structure, with molecules arranged in some preferred geometrical fashion. This is more pronounced for some clusters (e.g.,  $N = 26$ ) than others. At sufficiently low temperature, however, most of these clusters display superfluid properties. Although we cannot rule out a possible ‘supersolid’ phase (i.e., one characterized by SF as well as an orderly arrangement of molecules), we have seen so far little evidence of that in *any* of the clusters studied. On the contrary, numerical evidence accumulated by others suggests that the ground state of all these clusters is liquid-like. However, further study is under way to clarify this intriguing issue.

We have observed at least two cases in which a distinct change of physical character occurs as the temperature is lowered, going through a stage in which a solid-like non-superfluid ‘phase’ of these droplets co-exists with a liquid-like superfluid one, the latter becoming predominant at lower

$T$ . This conclusion is mostly based on the observation of large, concomitant oscillations, recorded during the computer simulation, of the superfluid density and the potential energy per particle. This intriguing phenomenon, to which we have come to refer as *quantum melting*, might conceivably be experimentally observable in  $p$ -H<sub>2</sub> droplets, as well as in other physical systems, e.g., dipolar cold molecules confined in external harmonic potentials.

Examination of the statistics of permutation cycles, as well as the observation that the replacement of a single  $p$ -H<sub>2</sub> molecule with an  $o$ -D<sub>2</sub> can turn a cluster (that is superfluid and liquid-like when undoped) solid-like and insulating, directly points to the importance of long exchanges, especially involving particles in the inner and outer shells of the cluster, in stabilizing a liquid-like, superfluid phase of these objects. Information coming from structural quantities is also consistent with the melting of the clusters at low temperature, but the signal is smaller and sometimes ambiguous (especially at the lowest temperatures).

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