Superfluidity of isotopically doped parahydrogen clusters

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It is shown by computer simulations that superfluid parahydrogen clusters of more than 22 molecules can be turned insulating and "solidlike" by the replacement of as few as one or two molecules, with ones of the heavier orthodeuterium isotope. A much smaller effect is observed with substitutional orthohydrogen. Substitutional orthodeuterium molecules prevalently sit in the inner part of the cluster, whereas orthohydrogen impurities reside primarily in the outer shell, near the surface. Implications on the superfluidity of pure parahydrogen clusters are discussed.

Clusters of molecular hydrogen are the subject of intense experimental investigation, especially after the claim of observation of superfluidity (SF) in clusters of $N=14-16$ para-H_2 molecules surrounding a linear carbonyl sulfide impurity [1]. Experimental data for pristine or isotopically mixed clusters are not yet available, but techniques based on Raman spectroscopy may soon be able to characterize their superfluid properties [2].

Quantitative information and physical insight in the properties of clusters of parahydrogen (para-H_2) molecules, both pristine [3–8] or doped [9–13], has been provided by microscopic calculations based on quantum Monte Carlo (QMC) simulations, making use of accurate intermolecular potentials [14–16]. In particular, a significant superfluid response has been predicted at $T \le 1$ K for pristine clusters comprising as many as 27 para-H_2 molecules [6,7].

To an excellent approximation, para-H_2 molecules, as well as those of the heavier orthodeuterium isotope (ortho-D_2) can be regarded as point particles of spin $S=0$, ortho-D_2 having 2 times the mass of para-H_2. A third isotope exists, namely orthohydrogen (ortho-H_2), which has the same mass of para-H_2, but different spin ($S=1$). Pairwise interactions between molecules of the different isotopes are very nearly the same [17]; thus, a mixed cluster of these components provides a simple experimental realization of a mixture of isotopic bosons. A number of fundamental questions can therefore be addressed by studying these systems, e.g., how does the presence of one component affect the superfluid properties of the other(s), or the structure of the cluster?

Classical binary Lennard-Jones (LJ) clusters have been extensively investigated; for example, it is known that, for equal concentrations of the two species, the one with the smaller depth of the pair potential well ϵ_{LJ} and/or with higher particle effective radius σ_{LJ} will sit prevalently at the cluster surface [18,19]. Because in a mixture of, e.g., para-H_2 and ortho-D_2, ϵ_{LJ} and σ_{LJ} are essentially the same for all pairwise interactions, the physics of the system is dominated by quantum effects, at low temperature.

Path integral Monte Carlo simulations of such mixed clusters have been carried out down to $T=2.5$ K, but without including quantum exchanges [20]. No theoretical predictions are presently available for the superfluid behavior of this system. Clearly, the sensitivity of the superfluid response of a finite cluster to its detailed isotopic composition, has a direct relevance to the design and interpretation of ongoing and future experiments.

In this paper, we present results of a microscopic study of para-H_2 clusters doped with isotopic impurities; specifically, we investigate the effect of the substitution of few ($N_D \le 4$) para-H_2 with ortho-D_2 (or ortho-H_2) molecules, in (para-H_2)$_N$ clusters that are entirely (or, almost entirely) superfluid. For definiteness, we focus on clusters with $N \ge 16$, at the two temperatures $T=0.5$ and 1 K.

The substitution of para-H_2 with ortho-D_2 molecules, generally causes pristine superfluid para-H_2 clusters to turn progressively solidlike, their structure increasingly mimicking that of pure ortho-D_2 clusters with the same numbers of molecules. For clusters comprising more than 20 molecules, however, the change from liquid to solidlike can occur abruptly. For instance, while the superfluid fraction of the pristine (para-H_2)$_{25}$ cluster at $T=1$ K is approximately 75%, substitution of a single para-H_2 molecule with an ortho-D_2 suppresses SF almost completely. Likewise, two such substitutional ortho-D_2 impurities suffice to suppress the superfluid response (close to 100%) of the same cluster at $T=0.5$ K.

A much smaller reduction of the superfluid response is observed if substitutional impurities are ortho-H_2 molecules. For example, (para-H_2)$_{24}$-(ortho-H_2)$_1$ is largely liquidlike at $T=1$ K. A crucial observation is that few substitutional ortho-D_2 molecules sit in the inner part of the cluster, whereas ortho-H_2 impurities are primarily located near its surface. These findings underscore the prominent role played by long exchanges, especially involving molecules in different shells of the cluster, in stabilizing a liquidlike structure of large clusters at low T, in turn allowing for SF to occur.

We model our system of interest as a collection of N_H para-H_2 and $N_D=N-N_H$ ortho-D_2 (ortho-H_2) molecules, regarded as Bose particles of spin $S=0$ ($S=1$), interacting via the Silvera-Goldman pair potential [14]. We study this system by QMC simulations, using the continuous-space worm algorithm [21,22]; technical details of our simulations are the same as in Ref. [7].

Figure 1 shows the superfluid fraction ρ_{S_H} of the para-H_2 component, as a function of the cluster size N at $T=1$ K (lower panel) and $T=0.5$ K (upper panel). Different symbols refer to a different number of substitutional ortho-D_2 or ortho-H_2 molecules (see figure caption). When a single para-H_2 molecule is replaced by an ortho-D_2 one, ρ_{S_H} is relatively
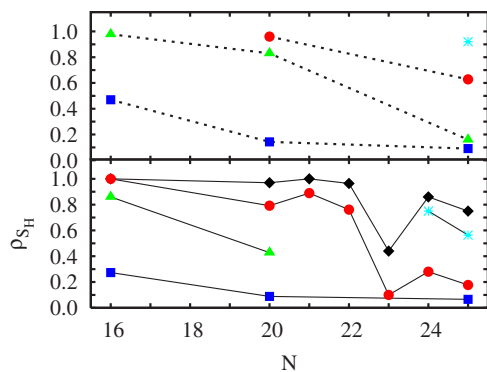
FIG. 1. (Color online) Superfluid fraction ρ_{S_H} of the parahydrogen component in clusters of N molecules with one (circles), two (triangles), and four (squares) substitutional orthodeuterium molecules, and with one (stars) orthohydrogen molecule. Upper panel shows data at $T=0.5$ K, lower panel shows data at $T=1$ K. Diamonds show results for the undoped clusters (entirely superfluid at $T=0.5$ K). Error bars are comparable to the size of the symbols.

little affected for $N<22$, with respect to a pristine para-H_2 cluster, but is depressed substantially in larger clusters, particularly at higher T. For example, the substitution of one ortho-D_2 in a (para-H_2)$_{25}$ cluster causes ρ_{S_H} to drop from 75% to less than 20% at $T=1$ K, while at $T=0.5$ K an almost complete suppression of the superfluid fraction is observed, in the same cluster, when two para-H_2 molecules are replaced by ortho-D_2. It should also be noted that pristine para-H_2 clusters with more than 22 molecules, generally display solidlike behavior even when undoped, albeit in different degrees [e.g., (para-H_2)$_{23}$ at $T=1$ K] [6,7].

Figure 2 compares the radial density profile (at $T=1$ K) of the (largely superfluid) pristine (para-H_2)$_{25}$ cluster, with that of the (essentially insulating) cluster with the same number of molecules, but with one para-H_2 replaced by an ortho-D_2. Profiles are computed with respect to the geometrical center of the cluster [23]. The main structural change arising from the substitution of a para-H_2 clearly occurs in the center of
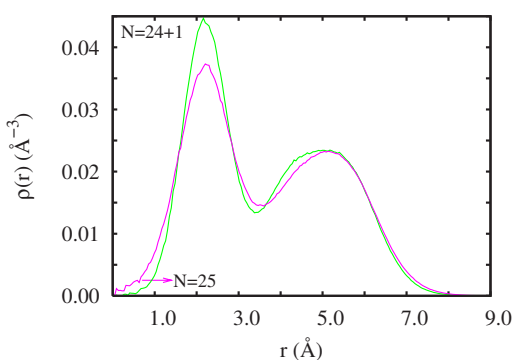

FIG. 2. (Color online) Radial density profiles for a pure (para-H_2)$_{25}$ (lower peak at short r) and a (para-H_2)$_{24}$-(ortho-D_2)$_1$ cluster, at $T=1$ K. Profiles are computed with respect to the geometrical center of the cluster. In the case of the doped cluster, no distinction is made between molecules of different types. Statistical errors are not shown for clarity; they are of the order of 5.0×10^{-4} Å^{-3}.
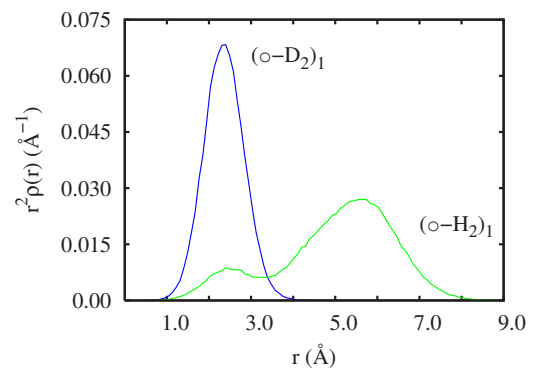

FIG. 3. (Color online) Radial density (multiplied by r^2) for the single ortho-D_2 and ortho-H_2 impurities in the doped (para-H_2)$_{24}$-(ortho-D_2)$_1$ and (para-H_2)$_{24}$-(ortho-H_2)$_1$ clusters, at a temperature of 1 K. Profiles are computed with respect to the geometrical center of the cluster.

the cluster, where molecules are considerably more localized (hence, the higher peak). In the vicinity of the surface of the system, density profiles are, in fact, almost identical.

If the dopant is ortho-H_2, on the other hand, then the structure of the cluster and its superfluid properties are much less sensitive to the substitution (see Fig. 1). For example, the corresponding profile for the cluster doped with one ortho-H_2 molecule is indistinguishable from that of the pristine cluster, on the scale of Fig. 2.

An important observation is that a lone ortho-D_2 molecule sits in the central part of the cluster; this is something that we observe for all clusters studied, with up to four ortho-D_2 substitutional impurities, in agreement with previous work [20]. The lighter ortho-H_2 dopant, conversely, is considerably more delocalized, and indeed is found prevalently in the external part of the cluster, as shown in Fig. 3.

The effect of cluster "crystallization," induced in relatively large clusters by one or two ortho-D_2 impurities (and the ensuing depression of para-H_2 SF) can also be observed in smaller systems, but a greater number of substitutions is needed. Figure 4 shows the structures of the two clusters (para-H_2)$_{16}$-(ortho-D_2)$_4$ [part (A) of the figure] and (para-H_2)$_{20}$ [part (B)]. These pictures were obtained using the procedure outlined in Ref. [10]. The pristine cluster has a featureless structure, and is entirely superfluid at $T\leq 1$ K. On the other hand, ρ_{S_H} is small in the doped cluster, whose solidlike structure is evident, with a central axis surrounded by rings of molecules. Two of the four ortho-D_2 molecules are
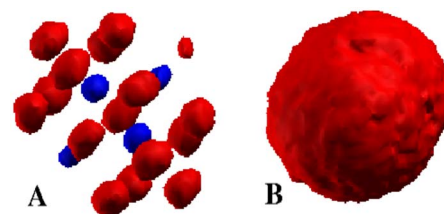

FIG. 4. (Color online) Three-dimensional representations of the clusters (para-H_2)$_{16}$-(ortho-D_2)$_4$ (A) and of (para-H_2)$_{20}$ (B). Darker color is used for impurity molecules.
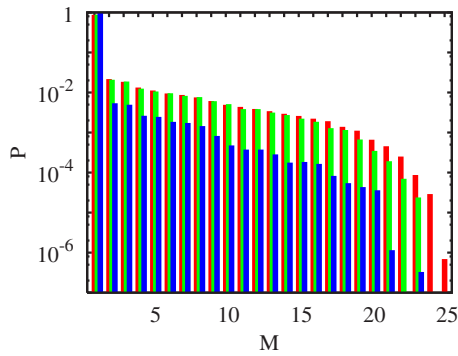
FIG. 5. (Color online) Frequency of occurrence of exchange cycles of length M (i.e., involving $1 \leq M \leq N_H$ para-H_2 molecules) at $T=1$ K. Spikes from left to right refer to a pristine (para-H_2)$_{25}$ cluster and to the mixtures (para-H_2)$_{24}$-(ortho-H_2)$_1$ and (para-H_2)$_{24}$-(ortho-D_2)$_1$.

placed on the axis, the other two on the central ring.

Numerical studies by other authors [10,13] had already yielded evidence of localization of para-H_2 molecules around a heavy impurity, rendering small, pristine clusters [e.g., (para-H_2)$_{13}$] significantly more rigid and solidlike. In all previous works, however, impurities were considered such as CO or HF, not only significantly heavier, but, more importantly, featuring a stronger (more attractive) interaction with the para-H_2 molecules, than that between the molecules themselves.

The results presented here, offer insight in the microscopic mechanism of SF in quantum clusters. In order for SF to occur, clusters (either doped or pristine) must be essentially liquidlike in character, i.e., molecules must enjoy a high degree of mobility and delocalization. The most important structural difference between clusters that are insulating or superfluid at $T \leq 1$ K, also based on the results for pristine clusters [6,7], is that the former feature a rigid, solidlike core, possibly with some loosely bound molecules on the surface; on the other hand, SF is enhanced in clusters whose inner region is floppy, with exchanges taking place between molecules in the inner and outer shells.

This is consistent with the notion of *quantum melting* of large clusters, at low T [6,7], originating from permutational exchanges involving *all* molecules, including those located in the inner part of the cluster. These exchanges become increasingly important at low temperature, where clusters become increasingly liquidlike, and consequently superfluid.

Figure 5 displays the frequency with which exchange cycles of varying length (i.e., involving a different number $1 \leq M \leq N_H$ of para-H_2) occur (spikes from left to right) in a pristine (para-H_2)$_{25}$ cluster as well as in the mixtures (para-H_2)$_{24}$-(ortho-H_2)$_1$ and (para-H_2)$_{24}$-(ortho-D_2)$_1$ at $T=1$ K. All exchange cycles are clearly suppressed in the cluster doped with a single ortho-D_2, but the reduction is most

dramatic for very long cycles. Conversely, when the cluster is doped with an ortho-H_2, exchanges (other than the very longest one) take place at almost the same frequency as in the pristine cluster.

Thus, a single substitutional ortho-D_2, which is located in the center of the cluster owing to its greater mass, has a strong inhibiting effect on long exchanges of para-H_2 molecules. As a result, the cluster turns solidlike, and SF is altogether depressed. Conversely, a single ortho-H_2 dopant molecule can effectively get out of the way, thereby allowing for a greater occurrence of long exchanges, including those involving para-H_2 molecules in the inner and the outer shell of the cluster. As a result, the doped (para-H_2)$_{24}$-(ortho-H_2)$_1$ cluster remains largely liquidlike, with a value of ρ_{S_H} close to 60%.

The suggestion that SF is underlain, or strongly enhanced by the occurrence of exchange cycles involving also molecules located in the central region of the cluster is not (as one may naively think) in contradiction with the observation that the superfluid density is largest at the surface [8]. For, as discussed above, the primary mechanism by which these exchanges promote SF is not by *locally* increasing the value of ρ_{S_H}, but by stabilizing an overall liquidlike phase of the whole cluster.

Summarizing, we have studied mixed hydrogen clusters of various sizes, down to $T=0.5$ K. To our knowledge, this is the first study of a mixed isotopic bosonic cluster including all quantum-mechanical effects, namely zero-point motion and permutations of identical particles. Gaining understanding of the effect of substitutional impurities, also affords insight into the microscopic origin of SF in pristine clusters of molecular hydrogen.

We find that the superfluid fraction ρ_{S_H} of pure para-H_2 clusters is depressed by replacement of a few para-H_2 by ortho-D_2 molecules. The depression is most dramatic for clusters with more than 22 molecules, which display incipient solidlike behavior even when pristine. The reduction of the superfluid fraction is considerably smaller in the presence of substitutional ortho-H_2 impurities. Lighter impurities, which are delocalized throughout the system, have less disruptive an effect on long exchanges than the heavier impurities, which sit in the inner part of the cluster. Our findings are consistent with the notion of melting of large clusters at low temperature as arising from purely quantum-mechanical effects, namely long exchanges of indistinguishable particles.

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