Superfluid Response of Parahydrogen Clusters in Superfluid $^4$He

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Abstract
First-principle computer simulations yield evidence of a finite superfluid response at low temperature of a parahydrogen cluster of 15 molecules in bulk superfluid $^4$He. The superfluid fraction is worth $\sim 44\%$ at $T = 0.25$ K, growing to about $\sim 66\%$ at $T = 0.15$ K, i.e., it is substantially reduced compared to that of the same cluster in vacuo, due to higher molecular localization. The implications of these findings on the interpretation of experiments with linear molecules embedded in parahydrogen clusters immersed in superfluid helium are discussed.

Keywords Superfluidity · Quantum clusters · Quantum Monte Carlo

1 Introduction

Almost half a century since the original prediction of Ginzburg and Sobyanin [1] of a possible superfluid transition at low temperature of a fluid of parahydrogen ($p$-$H_2$) molecules, its observation has eluded even the ablest experimenters and/or clever- est approaches. Meanwhile, there is now a wealth of robust theoretical predictions, based on the state-of-the-art many-body techniques and realistic intermolecular potentials, pointing to the following:

(a) Molecular hydrogen has a strong tendency to crystallize at temperatures well above those at which Bose condensation and superfluidity (SF) should occur, even in reduced dimensions [2, 3], disorder [4–6] and confinement [7, 8]

(b) Even if a metastable fluid phase of $p$-$H_2$ could be stabilized well below its 13.8 K freezing temperature, it may only turn superfluid at temperatures at least two

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1 There are neither theoretical predictions nor experimental evidence suggesting that a $p$-$H_2$ crystal might display superfluid behavior. See, for instance [9].
orders of magnitude lower than that (few K) predicted in the original 1973 work [10].

To date, the only quantitative prediction of superfluid behavior of \( p\text{-H}_2 \) has been made not for the bulk phase, but for small clusters (few tens of molecules), at temperatures of the order of 1 K [11–14]. Experimentally, the superfluid behavior of a quantum cluster can be inferred from the free rotation of a linear molecule embedded in it, as shown by high-resolution microwave or infrared spectroscopy [15]. This methodology has allowed for the remarkable observation of superfluidity in \( ^4\text{He} \) clusters of just a few atoms [16] and has also yielded some evidence of possible superfluid behavior of \( p\text{-H}_2 \) clusters comprising around fifteen molecules [17–19], in some cases backed by theoretical results [18, 20]. In some of these experiments [17, 21–24], the \( p\text{-H}_2 \) clusters are immersed in relatively large superfluid \( ^4\text{He} \) nanodroplets (comprising several hundreds to several thousands of atoms), rendering this a potentially unique example of a mixture of two superfluid Bose components.

The interpretation in terms of superfluidity of the \( p\text{-H}_2 \) clusters has been questioned, however, in the case of experiments in which the cluster is embedded in a \( ^4\text{He} \) matrix; in particular, recent simulation studies of small, mixed \( p\text{-H}_2/4\text{He} \) clusters with an embedded \( \text{CO}_2 \) dopant suggest that doped \( p\text{-H}_2 \) clusters may form a non-superfluid core in \( ^4\text{He} \) droplets [25] and that \( ^4\text{He} \) acts to suppress \( p\text{-H}_2 \) superfluidity in small, mixed clusters, a conclusion previously reached by others [26]. The question of the possible superfluidity of \( p\text{-H}_2 \) clusters in superfluid \( ^4\text{He} \) remains open, however, as there are at least two aspects that warrant further investigation. The first is that the simulations of Ref. [25] were carried out at temperature \( T = 0.5 \) K, considerably higher than that \( (T = 0.15 \) K) at which the onset of the superfluid response is reported in Ref. [17]. Second, the behavior of a small mixed cluster with a comparable number (of the order of ten) of \( ^4\text{He} \) atoms and \( p\text{-H}_2 \) molecules might be qualitatively different from that of the same number of \( p\text{-H}_2 \) molecules in a \( ^4\text{He} \) matrix of size such that its physical properties approach that of bulk \( ^4\text{He} \). Indeed, to our knowledge there are presently no theoretical predictions regarding structural and superfluid properties of \( p\text{-H}_2 \) clusters in superfluid \( ^4\text{He} \).

In this paper, we present results of first-principle computer simulations of a \((p\text{-H}_2)_{15}\) cluster in bulk superfluid \(^4\text{He}\), at temperature as low as \( T = 0.15 \) K. The purpose of this study is to gain further insight into this intriguing system and specifically on the effect of the \(^4\text{He}\) matrix on the superfluid properties of \((p\text{-H}_2)_{15}\), which in vacuo is predicted to be superfluid at relatively high temperature (close to 70% at \( T = 2 \) K and \( \sim 100\% \) at \( T = 1 \) K\(^2\)). Obviously, a second important goal is to weigh in on the existing controversy regarding the experiment of Ref. [17], by providing an upper bound on the superfluid response of a pristine \((p\text{-H}_2)_{15}\) cluster in \(^4\text{He}\).

We find here that the structure of the \((p\text{-H}_2)_{15}\) cluster in superfluid helium is fairly similar to that of a free \((p\text{-H}_2)_{15}\) cluster (i.e., in vacuo), the most significant difference being that \( p\text{-H}_2 \) molecules are more localized, especially in the inner shell, and

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\(^2\) The results for free clusters discussed here were obtained in Ref. [13].
as a result the superfluid response of the cluster is suppressed. It is not completely eliminated, though; for, at temperatures of the order of 0.3 K quantum-mechanical exchanges of \( p-H_2 \) molecules, virtually absent at \( T = 0.5 \) K, begin to occur, and the superfluid signal picks up, growing monotonically as \( T \to 0 \). At \( T = 0.15 \) K, the superfluid fraction of the cluster is close to 65%. This behavior is broadly consistent with the observations of Ref. [17].

It is important to note that the structure of the cluster remains essentially unchanged in the low temperature limit, even as exchanges become frequent and a finite superfluid response emerges. In other words, the system is not observed to undergo “quantum melting,” i.e., going from solid to liquidlike, as observed in simulations of some free clusters [12]. Rather, the physical behavior observed here in simulation, with simultaneous localization and superfluidity, is reminiscent of that of the free \((p-H_2)_{26} \) cluster, for which the denomination “supersolid” was proposed [27].

### 2 Model and Methodology

We considered an ensemble of \( \mathcal{N} = \sum_{a} N_{a} \) pointlike particles, \( \alpha = ^{4}\text{He}, \ p-H_2; \) all particles have spin zero, i.e., all components obey Bose statistics. The system is enclosed in a cubic cell, with periodic boundary conditions in the three directions (as we are simulating a \( p-H_2 \) cluster inside \( \text{bulk} \ ^{4}\text{He} \)). The volume of the cell \( \Omega \) is adjusted to make the total density \( \mathcal{N}/\Omega \) equal to the equilibrium density of \( ^{4}\text{He} \) at \( T = 0 \), i.e., \( 0.02183 \text{Å}^{-3} \). The quantum-mechanical many-body Hamiltonian reads as follows:

\[
\hat{H} = - \sum_{ia} \lambda_{a} \nabla_{ia}^{2} + \frac{1}{2} \sum_{a,\beta} \sum_{ij} v_{a\beta}(r_{ia}, r_{j\beta})
\]

where \( \lambda_{a} = 6.060(12.031) \text{KÅ}^{2} \) if \( \alpha = ^{4}\text{He} (p-H_2) \), \( r_{ia} \) is the position of the \( i \)th particle of component \( \alpha \), \( v_{a\beta} \) is the Aziz [28] (Silveira-Goldman [29]) pair potential to describe the interaction between two \( ^{4}\text{He} \) atoms (two \( p-H_2 \) molecules), and we make use of a potential proposed by Barnett and Whaley [30] to represent the interaction between a \( ^{4}\text{He} \) atom and a \( p-H_2 \) molecule. Although in principle different choices for \( all \) the pair potentials are possible, that made here is consistent with previous studies (see, for instance, Ref. [26]). Moreover, experience accumulated over decades of theoretical studies of both helium and parahydrogen suggests that the most important physical aspects are independent of the detailed form of the potentials utilized.

We performed first-principles QMC simulations of the system described by Eq. (1), based on the continuous-space worm algorithm (WA) [31, 32]. Since this technique is by now fairly well established and extensively described in the literature, we shall not review it here. A canonical variant of the algorithm was utilized, in which the numbers \( N_{a} \) of particles for each components are held fixed [12, 13]. Details of the simulation are standard; for instance, the short-time approximation to the imaginary-time propagator used here is accurate to the fourth order in the time step \( \tau \) (see, for instance, Ref. [33]). The results shown here are obtained with a value of
\[ \tau = (1/320) \, \text{K}^{-1}, \] which has been empirically found to yield results indistinguishable from those extrapolated to the \( \tau = 0 \) limit, within our statistical uncertainties.

The total number of particles in a typical simulation is \( N = 256 \), the number of \( p\text{-H}_2 \) molecules being, of course, equal to 15.

### 3 Results

Besides energetic and structural properties of the \( (p\text{-H}_2)_{15} \) cluster, of special interest here is the superfluid response of both the cluster and the \(^4\text{He}\) matrix. The superfluid fraction of bulk \(^4\text{He}\) is computed through the use of the standard “winding number” estimator \([34]\). On the other hand, superfluidity of a cluster (i.e., a finite system) is defined through its linear response to an externally imposed rotation around an axis going through the center of mass \([35]\). Specifically, the superfluid fraction of the cluster is defined as \( \rho_S = 1 - (I/I_{cl}) \), where \( I \) is the moment of inertia of the cluster with respect of the rotation axis and \( I_{cl} \) is its corresponding classical value. Within the path integral formulation of equilibrium statistical mechanics \([36]\), this definition leads to a relatively simple estimator of \( \rho_S \) (known as “area”), which is proportional to the square of the area swept by the many-particle paths in imaginary time \([37]\). Virtually, all quantitative calculations of superfluidity for quantum clusters (mostly helium and parahydrogen) reported in the literature have been carried out by utilizing the area estimator, in the context of numerical (Monte Carlo) evaluation of path integrals. We make use of the “area” estimator in this work as well.

We begin the illustration of our results with the observation that the \( (p\text{-H}_2)_{15} \) cluster does not break down but remains compact in superfluid \(^4\text{He}\), and its structure is essentially temperature-independent below \( T = 1 \) K. Figure 1 shows the radial density profile, computed with respect to the center of mass, at a temperature \( T = 0.25 \) K. Also shown for comparison is the corresponding profile in vacuo, at the same temperature. The structure is the same in both cases, with two well-defined shells. However, \( p\text{-H}_2 \) molecules in the cluster immersed in \(^4\text{He}\) feature a higher degree of localization, as shown by the greater height of the peaks, especially in the center of the cluster. The enhanced localization can be assessed quantitatively by looking at the kinetic energy per molecule, which is equal to \( \sim 41 \) K, some 60% higher than...
that in the free cluster, worth just \(~25\) K. Correspondingly, exchanges of \(p\)-H\(_2\) molecules, which are known to underlain superfluidity, are considerably less frequent than in the free cluster; for example, they are essentially nonexistent \(T = 1\) K, a temperature at which the free cluster is 100\% superfluid, and remain exceedingly rare even at \(T = 0.5\) K. (Consistently, there is no evidence of a superfluid response of the cluster at these temperatures.) Meanwhile, the surrounding \(^4\)He matrix is superfluid at \(T \leq 1\) K, the presence of the \(p\)-H\(_2\) cluster not affecting that to any significant degree.\(^3\)

The superfluid fraction of the \((p\)-H\(_2)\)\(_{15}\) cluster begins to be appreciably different from zero only at \(T \leq 0.3\) K. For example, at \(T = 0.25\) K it is equal to 0.44(4), while its value at \(T = 0.15\) K is 0.66(4). A quantitative assessment of the reduced propensity of a \((p\)-H\(_2)\)\(_{15}\) cluster in superfluid \(^4\)He to display quantum-mechanical exchanges, with respect to the same cluster in vacuo, can be obtained by comparing the computed frequency of occurrence \(P(n)\) of exchange cycles involving \(n\) \(p\)-H\(_2\) molecules for the two cases, as shown in Fig.

Although it does not directly correlate with the value of the superfluid response [38], \(P(n)\) provides a direct measure of the probability of occurrence of quantum mechanical exchanges in the cluster. In particular, exchanges involving (nearly) all of the molecules have been shown [38, 39] to be crucial to the onset of superfluidity of a \((p\)-H\(_2)\) cluster. Figure 2 shows that, for a cluster immersed in superfluid \(^4\)He, the reduction is especially significant precisely for cycles involving all of the molecules in the cluster. At the same time, long exchanges clearly do occur at this low temperature, even if the cluster immersed in superfluid \(^4\)He, consistently with the presence of a finite superfluid response.

\(^3\) In a system with \(N = 256\) particles, a small reduction (\(~10\%) of the superfluid fraction of \(^4\)He arises from the breaking of translational invariance caused by the presence of the \(p\)-H\(_2\) cluster. However, the cycle length distribution is very close to that of bulk superfluid \(^4\)He. On a system comprising \(N = 1024\) particles (i.e., 1009 \(^4\)He atoms), the superfluid fraction of \(^4\)He at \(T = 1\) K is essentially 100\%.
4 Conclusions

We now discuss the relevance of the results of this first-principle simulation of a \((p-H_2)_{15}\) cluster in superfluid \(^4\)He at low temperatures to experiments whose interpretation is still under debate. The results obtained in this work seem to lend support to the contention that the \((p-H_2)_{15}\) cluster immersed in superfluid \(^4\)He should turn superfluid at a temperature consistent with that of Ref. [17]. The question, of course, is the degree to which the experimental conditions of Ref. [17], chiefly the presence of a dopant molecule (CO\(_2\)), might quantitatively and qualitatively alter the physical behavior of the system, as predicted theoretically in this work. Theoretical calculations on free clusters [39] have shown that the mere replacement of one \(p-H_2\) molecule with a heavier \(o-D_2\), whose interaction with \(p-H_2\) molecules is very nearly the same, has a disruptive effect on the superfluid response of a cluster such as \((p-H_2)_{15}\). One could certainly expect a heavier and more complex object, such as a (CO\(_2\)), to have at least an equally significant effect; however, theoretical evidence has been reported of superfluidity at temperature as high as 0.5 K for a free \((p-H_2)_{15}\) cluster with an embedded CO\(_2\) [18]. Even making allowance for the difference between the embedded molecules, this suggests that the main physical agent causing the suppression of superfluidity in small clusters immersed in superfluid \(^4\)He nanodroplets and with embedded linear molecules is the surrounding \(^4\)He atoms and that the effect of the embedded linear molecule may be quantitatively less important. The results presented here indicate that superfluidity is recovered if the temperature is lowered to \(\sim 0.2\) K, and therefore the interpretation of the experimental results of Ref. [17] is plausible.

As a general remark, experiments with molecules embedded in a superfluid \(^4\)He matrix have long been predicated on the tenet that superfluid helium should act like “vacuum” [40]. Indeed, this calculation shows that \(^4\)He matrix leaves the cluster structure essentially unchanged, with respect to that of the free cluster; however, the interactions of the \(^4\)He atoms with the \(p-H_2\) molecules, albeit relatively weak, have the effect of rendering the \(p-H_2\) molecules less mobile and therefore suppressing quantum exchanges, consequently shifting the onset of superfluid behavior downward in temperature by an order of magnitude.

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Compliance with Ethical Standards

Conflict of interest The author declares that he has no conflict of interest.

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