Parahydrogen Clusters: Numerical Estimates and Physical Effects

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Abstract. We study by means of Quantum Monte Carlo simulations based on the Worm Algorithm the low temperature (down to \(T = 0.05\) K) properties of parahydrogen clusters comprising up to 40 molecules. Three different intermolecular interactions are employed: the Silvera-Goldman, the Buck and the Lennard-Jones potential. Despite important discrepancies observed in the numerical estimates of energy and superfluid fraction, the mechanism by which clusters melt at low \(T\) is independent of the particular choice of the potential, whose only effect is to alter the temperature scale.

1. Introduction

After the observation of some superfluid response in clusters of parahydrogen (\(p\)-H\(_2\)) comprising \(N \approx 15\) molecules [1], an intense theoretical effort, spanning now almost a decade, has been devoted to the characterization of structural and superfluid properties of doped or pristine molecular hydrogen clusters. Quantum Monte Carlo (QMC) computer simulations both at zero and finite temperature have quickly emerged as the most powerful theoretical method for this kind of investigation [2, 3, 4, 5, 6, 7, 8, 9, 10, 11]. In particular \(p\)-H\(_2\) clusters of size up to \(N=21\) are predicted, by means of QMC simulations by us based on the Worm Algorithm (WA) [12, 13], to be liquid-like and superfluid (the value of the superfluid fraction \(\rho_S\) is approximately 1) at \(T \leq 1\) K; for \(N \geq 22\), \(\rho_S\) displays important variations with \(N\) reflecting structural changes that occur by adding even a single molecule. Some cluster undergoes quantum melting going from solid-like to liquid-like (superfluid) as \(T \to 0\) K.

It has to be mentioned that the methodology (i.e., the WA) employed to obtain these predictions is formally exact [14], the only source of uncertainty for the calculation being the model potential adopted to describe the interaction between two \(p\)-H\(_2\) molecules. Obviously the choice of the potential could affect the reliability of the numerical estimates as well as, in the worst-case scenario, the whole physical picture.

In this paper we show estimates, obtained with the WA, for the energy per molecule and the superfluid fraction, of \(p\)-H\(_2\) clusters of size up to \(N=40\) molecules at low temperature (down to \(T =0.5\) K). Three different model interactions are employed: the Silvera-Goldman [15], commonly used for this kind of calculations, and two other popular choices, namely the Buck [16], and the Lennard-Jones [17] potentials.

We find that the values of the energies computed with the Buck potential are sensibly lower than those obtained with the Silvera-Goldman (SG) or the Lennard-Jones (LJ ) one; on the other
hand, the values of $\rho_s$ are nearly independent of the potential utilized for $N < 20$ displaying conversely important discrepancies for larger clusters. However the phenomenon of quantum melting by which some cluster of size $N \geq 22$ turns liquid-like at sufficiently low $T$ is independent of the choice of the model interaction which is only responsible for a shift in the temperature scale.

The reminder of this paper is organized as follows: in the next section we briefly introduce the physical model adopted in our calculation referring the reader to Refs. [5, 12, 13] for an exhaustive description. Then we present and discuss our results. Finally we outline the conclusions of our work.

2. Physical model

We model a $p$-H$_2$ cluster, as a collection of $N$ $p$-H$_2$ molecules, regarded as spin-0 Bose particles. The quantum mechanical hamiltonian is the following:

$$H = -\lambda \sum_i^{N} \nabla^2_i + V(R)$$

where $\lambda=12.031$ KÅ$^2$; $R \equiv r_1, r_2 \cdots r_N$ is a collective coordinate referring to all $N$ particles in the system, and $V(R)$ the total potential energy of the configuration $R$.

In most of the published numerical works on clusters of molecular hydrogen, the potential energy $V$ is expressed as a sum of pair-wise contributions, each represented by a spherically symmetric potential; the SG, Buck and LJ potentials used here are no exception, in this regard. We study the system of our interest (i.e., a $p$-H$_2$ cluster) by QMC computer simulations, using the continuous-space Worm Algorithm [12, 13]; technical details of our calculation are the same as in Ref. [5].

3. Results

The left part of Fig. 1 shows the energy per $p$-H$_2$ molecule as a function of the cluster size $N$ at a temperature of 1 K, computed with the LJ (triangles), Buck (diamonds) and SG (circles) potentials. The right part of Fig. 1 shows the superfluid fraction $\rho_s$ of $p$-H$_2$ clusters as a function of the cluster size $N$. Estimates are obtained using the Buck (diamonds), SG (circles) and LJ (triangles) potentials at $T=1$ K (full symbols) and $T=0.5$ K (open symbols).

Figure 1. (color online). Energy per molecule (left) and superfluid fraction (right) of $p$-H$_2$ clusters as a function of the cluster size $N$. Estimates are obtained using the Buck (diamonds), SG (circles) and LJ (triangles) potentials at $T=1$ K (full symbols) and $T=0.5$ K (open symbols).
Figure 2. (color online). Potential energy per molecule and superfluid fraction observed during a typical Monte Carlo run for a cluster of $N=26$ $p$-$H_2$ molecules at $T=1$ K (panels a and b) and $T=1.5$ K (panels c and d). The coexistence of two phases can be easily recognized since the averages of $\rho_S$ and $V$ simultaneously switch between high (liquid-like superfluid phase) and low (solid-like insulating phase) values. The liquid-like superfluid phase becomes dominant as $T$ is lowered. Results are obtained with the LJ potential.

Estimates of the superfluid fraction at $T=0.5$ K and $T=1$ K, as a function of the number of molecules in a $p$-$H_2$ cluster, are shown in the right part of the same figure. Clusters of size up to $\sim 20$ molecules are largely superfluid at $T \leq 1$ K, and the computed values of $\rho_S$ are essentially independent of the potential. When the cluster size increases, although a similar non monotonic trend of the superfluid fraction is observed regardless of the choice of the potential, important numerical discrepancies between results obtained with different model interactions are evident. For example, a cluster comprising $N=26$ molecules at $T=0.5$ K is found to be insulating with the Buck or SG potential (open circles or diamonds), but 100% superfluid with the LJ one (open triangles). Moreover we notice that, irrespectively of the chosen interaction, the values of the superfluid fraction, in this case, differs substantially from that ($\rho_S \approx 0.5$) reported in Ref. [6] obtained by conventional Path Integral Monte Carlo simulations [19]. The reason for this discrepancy is unclear at this time. In general, the LJ potential yields a large superfluid response at a temperature considerably higher than that needed to detect the same superfluid response with the SG (or Buck) potential. Therefore it is crucial to understand, also in view of future experiments that will probably provide a characterization of the superfluid properties of pure $p$-$H_2$ cluster [20], whether the main physical effects (i.e., the quantum melting) predicted for $p$-$H_2$ clusters [2, 5, 9] are potential dependent or represent genuine physics.

Figure 2 illustrates the quantum melting phenomenon (extensively discussed in the case of the SG potential in Refs. [2, 5, 9]) when the LJ potential is used. Estimates, computed in a typical Monte Carlo run, of the potential energy per particle ($V$) and the superfluid fraction...
(\(\rho_S\)) of the cluster \((p-H_2)_{26}\) are shown at \(T=1\) K (panels a and b) and at \(T=1.5\) K (panels c and d). The behavior of \(\rho_S\) and \(V\) indicates the coexistence of a liquid-like (superfluid) and a solid-like (insulating) “phase” associated respectively to portions of the simulation in which the averages of \(\rho_S\) and \(V\) take simultaneously high and low values. The liquid-like (superfluid) regime becomes dominant at low \(T\); it is in fact at low \(T\), that the cluster quantum melts. Quantum melting occurs (at much lower \(T\)) even when the Buck potential is used. In fact we find that the superfluid fraction of the cluster \((p-H_2)_{26}\) computed with the Buck potential approaches 1 at a temperature as low as \(T \approx 0.05\) K. This is consistent with the observation that \((p-H_2)_{26}\), a particularly stable (i.e., “magic”) cluster at \(T = 1\) K (temperature at which it is solid-like and its nearest neighbors \((p-H_2)_{25}\) and \((p-H_2)_{27}\) are more liquid-like [5]) is not a magic cluster at \(T = 0\) K [8] (when it is liquid-like as well, due to quantum melting).

4. Conclusions

Low temperature QMC computer simulations have been carried out to investigate the dependence of superfluid and structural properties of \(p-H_2\) clusters comprising up to 40 molecules on the model interaction. Strong dependence on the potential is found for the numerical estimates of the energy per molecule and (especially in clusters of \(N \geq 20\) \(p-H_2\) molecules) the superfluid fraction.

The phenomenon of quantum melting, as well as all the relevant physical effects described in Refs. [2, 5, 9], is predicted (at different temperatures) independently of the interaction potential employed.

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