Two-dimensional H$_2$ clusters: A path-integral Monte Carlo study

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We performed path-integral Monte Carlo simulations of two-dimensional H$_2$ clusters of different sizes. The smaller of these clusters are superfluid at low temperatures. On increasing the size we observe the formation of a solidlike inner core and a liquidlike outer shell.

I. INTRODUCTION

The possibility of maintaining H$_2$ in a fluid state at temperatures low enough to produce a superfluid has recently attracted considerable attention.[1–7] Unfortunately, the H$_2$-H$_2$ interaction is too strong to allow molecular hydrogen to be a liquid below its bulk triple point of 14 K.

One way to attain a liquid ground state is to reduce the effective attraction between the H$_2$ molecule or alternatively, to reduce the number of H$_2$ neighboring molecules by, for example, using a two-dimensional(2D) geometry.[2] In 2D, there are six particles around any given H$_2$, instead of the ~ 12 in a three-dimensional structure. This is not enough, however. It is experimentally known[5] that the surface melting temperature of solid H$_2$ (the melting of the monolayer next to the gas phase) is ~ 6 K, still above the 2D superfluid transition temperature. A second way to reduce the number of neighbors is to consider 3D clusters. Simulation results and experimental data suggest[1,7] that this approach is good if the number of hydrogen molecules in the cluster is <20. A third possibility is to introduce repulsive fixed impurities to frustrate the solid. This has been shown to produce a 2D superfluid[2] in simulations, but such tailored substrates have yet to be constructed in the laboratory. The other possibility is to create a quasi-one-dimensional environment in which the number of neighbors would be reduced further more. That produces a liquid even at 0 K (Ref. 4) but superfluidity will be suppressed in a truly 1D system at finite temperature.

In this paper, we study what happens with 2D clusters of H$_2$. As mentioned above, a 2D bulk liquid phase does not exist below 6 K. However, in finite clusters, the temperature of the freezing transition will be reduced. One can ask how big a cluster is needed to have a localized core at very low temperatures. For those clusters, it is possible to have a surface that remains liquid at very low or zero temperature.

We study here strictly 2D H$_2$ clusters with sizes ranging from $N=6$ to $N=61$ molecules to determine the fraction of molecules considered to be superfluid (i.e., decoupled from motions of the substrate) as a function of temperature. We checked also the relation between superfluidity and cluster structure and between the number of particles and the formation of a solidlike inner shell.

II. METHOD

The path integral Monte Carlo (PIMC) method allows us to calculate the thermodynamic and structural properties of a quantum system by mapping it into an equivalent classical model.[8] The only necessary input is the intermolecular potential. The H$_2$ molecules are modeled as spherical particles interacting with an empirical potential,[10] which reproduces reasonably well the available experimental data.[5] We found that the intermolecular interaction was strong enough to prevent the evaporation of the cluster at low temperatures even when surrounded by a perfect vacuum. We changed the position of the cluster after each Monte Carlo step to always have the center of mass at the center of the simulation cell. The imaginary time step τ was taken to be 1/80 K, a value that was found to be small enough to give good accuracy in 3D hydrogen clusters.[11] That means that, for instance, for $T = 1$ K, we need to have 80 *beads* (time slices) to describe each hydrogen molecule. Additional details about the method are given elsewhere.[8]

III. RESULTS

We performed PIMC simulations in clusters with different number of particles ($6 < N < 60$) in a temperature range $0.33 < T < 3$ K and calculated the superfluid response as well as other static properties. The superfluid fraction is shown in Figs. 1 and 2. We observe that for $N \leq 10$ the superfluid fraction vs T has a similar form: $\rho_s/\rho \sim 1$ for $T < 1$ K and decreases slowly until it reaches the value zero at $T \sim 3$ K. For temperatures for which $\rho_s/\rho < 1$ the larger the cluster, the smaller the superfluid fraction. These small clusters have a simple structure, basically one central molecule surrounded by one more or less complete shell (see below and Fig. 3). One might think that the structure for $N=7$ would be special since it could correspond to a central particle with complete layer as in classical clusters with complete shells. However, such shell effects are not observed here. Because of the strong quantum fluctuations, the superfluid fraction depends smoothly on N. We also observe that due to the small size of the clusters, the transition from superfluid to normal fluid is smeared out over a wide temperature range ($1 < T < 3$).
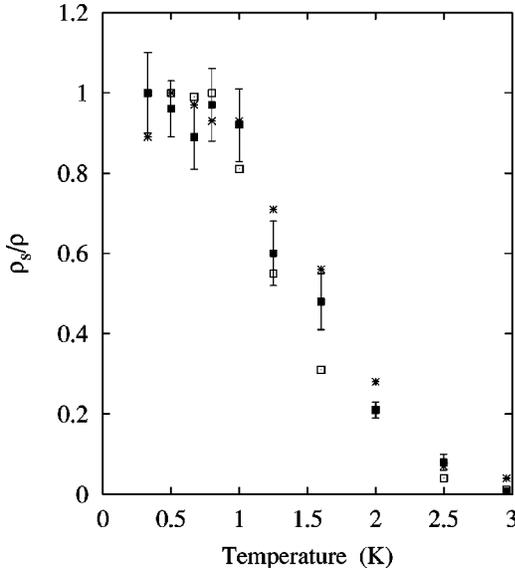
FIG. 1. Superfluid fraction for clusters with $N=7$ (full squares); $N=6$, (stars), and $N=8$ (squares). The error bars displayed are typical of each temperature.

Figure 2 gives the same magnitude as Fig. 1 but for $N=10$, 13, 16 and 20 molecules. We observe a further decrease in the superfluidity with increased cluster size. A big difference with the previous figure is that we do not have plateaus for $\rho_s/\rho \sim 1$, and for $N>10$ the superfluid fraction does not approach unity at low temperatures. Furthermore, the temperature at which $\rho_s/\rho \sim 0$ also decreases in going from $N=10$ ($T \sim 3$ K), to $N=13$ (diamonds; $T \sim 2$ K) and $N=16$ (full squares; $T<1$ K) until $N=20$ (squares; $T<0.5$ K). For $N>20$, ρ_s is very small in the temperature range $T>0.33$ K indicating that at most few atoms in the cluster remain delocalized. (At $T=0.33$ K, $\rho_s/\rho=0.029$
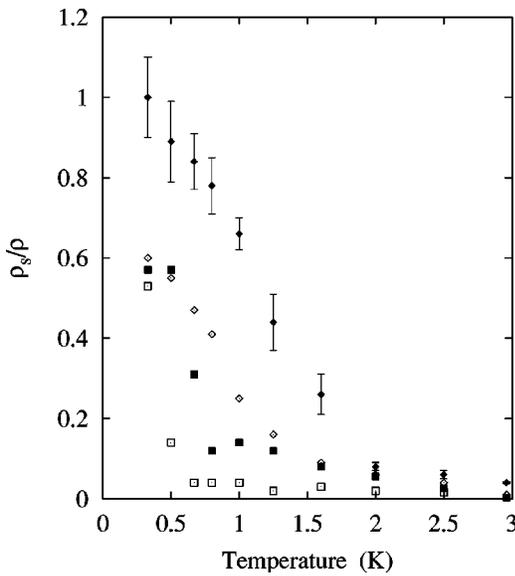
FIG. 2. Same as in Fig. 1 but for larger values of N. From top to bottom: $N=10$, 13, 16, 20. As before, the error bars represent their common values.
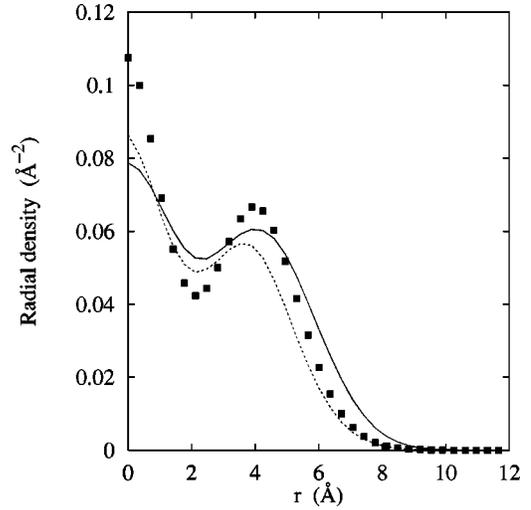
FIG. 3. Radial density for the clusters shown in Fig. 1 ($N=7$, full squares; $N=6$, dotted line; $N=8$, solid line).

± 0.004 for a cluster of 30 molecules, and 0.017 ± 0.001 when $N=37$.)

The average radial density (with respect to the cluster center of mass) gives some insight into the physical state of the clusters. In Fig. 3 we display the density for $N=6$, 7, 8 and in Fig. 4 for $N=10$, 13, 16, and 20 molecules at $T=0.33$ K. The general features are common to all temperatures. In Fig. 3 we observe that the three clusters share basically the same structure: one molecule in the center and an outer shell. However, we can see that when $N=7$ (full squares), the molecule in the center is more localized (with a higher central density and a lower density minimum surrounding) than for $N=6$ and $N=8$. In the region $r>6$ Å, the density increases with the number of particles, as one would expect.

Figure 4 gives the same information as Fig. 3, but for clusters with $10 \leq N \leq 20$ H_2 molecules. The last two systems, follow the same structure model described in Fig. 3:
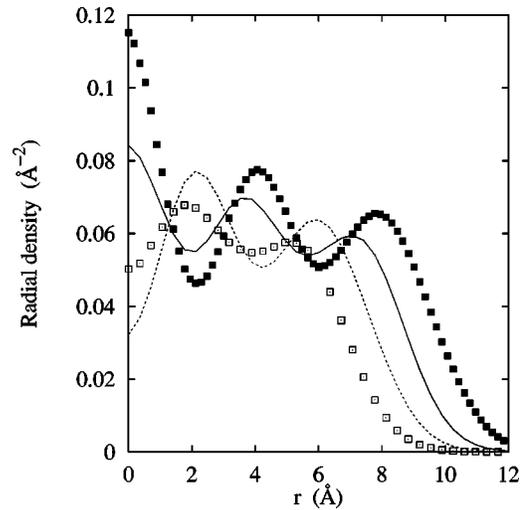
FIG. 4. Same as in Fig. 3 but for $N=10$ (squares); $N=13$ (dotted line); $N=16$ (solid line), and $N=20$ (full squares).

one particle at the center of mass of the cluster and two surrounding layers necessary to accommodate all the H$_2$ molecules. For smaller clusters $N=13$ (dotted lines) and $N=10$ (squares), the center of mass is not always occupied by a hydrogen molecule, a conclusion suggested by the minimum at $r=0$. Surrounding that empty core, we have two shells. As before, in the regions further from the origin, the density depends basically on the number of molecules present.

The structures of these 2D H$_2$ clusters are similar to those calculated in 3D, the H$_2$-H$_2$ interaction is strong enough to create that pattern. This is not what happens in ^{4}He clusters. A recent paper[9] suggest that the helium density is homogeneous and constant in the inner parts, and decreases slowly in the border limit of the cluster, just the same as in the 3D counterparts.

If we compare now the cluster structures with the superfluid density, one can see that the maximum values of ρ_s/ρ correspond to clusters with only two layers (if a central molecule can be considered as such), or in the limit case of $N=16$, with a shell structure not completely developed. When we have a large superfluid density, then the molecules will be delocalized and not in a fixed crystal structure. The next step would be to characterize the number of delocalized molecules.

To estimate directly the localization of the molecules, we calculated the rms deviation of the molecular diffusion with respect to its average position [Lindemann's ratio (LR)]. This parameter changes at a liquid-solid transition. To do that, we compute the average of the squared distance of each molecule to a its initial position. The reference positions consist of all the sites in a triangular lattice with lattice spacing 3.8 Å within a fixed distance of the origin. The LR is then $\gamma=[\langle(r_i-Z_i)^2\rangle]^{1/2}/3.8$ Å. However, there is a problem in calculating the LR in this way: the cluster can rotate about its center of mass since the system has circular symmetry. In addition, neighboring molecules can interchange positions. Both processes will lead to a gradual increase of the apparent rms deviation. That means that the LR's ratios we obtained are in fact upper bounds to the real ones. That accounts for the large numbers obtained.

We obtained the LR at 1 K for different clusters ranging in size from $N=16$ to $N=61$ molecules and the results are given in Fig. 5. Between $N\sim19$ (two complete shells plus the central particle) and $N\sim37$ molecules (three completed shells), there is an appreciable decrease in the LR. From there on, the reduction continues, but more slowly, to get the value for a 2D solid (dashed line, 0.176) in large enough clusters. The difference in the LR for $N=61$ and the limit $N\rightarrow\infty$ is due in part to the rotation of the cluster, and partially to the liquidlike outer shell. To check that, we calculated the LR for the 37 innermost molecules in the $N=61$ cluster and compared it with the result for a bare $N=37$ arrangement. In the first case, the LR is 0.39 ± 0.12 instead of the 0.88 ± 0.17 in the second, a factor of 2 greater. 0.39 is also smaller than the average value for the entire $N=62$ cluster (0.48 ± 0.10), indicating that the molecules move around more in the outer shell. The same could be said of a cluster of 19 molecules inside a bigger cluster of 37. Its LR is
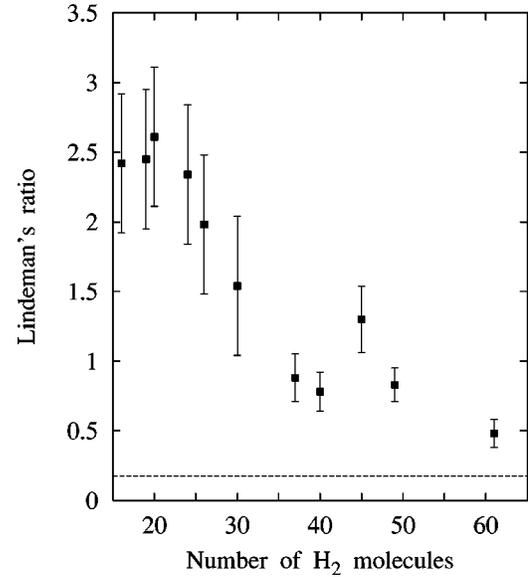
FIG. 5. Lindemann's ratio at $T=1$ K for clusters ranging form $N=16$ to $N=61$ molecules. The dotted line represents the same magnitude for a 2D bulk solid at the same temperature. See text for details.

0.49 ± 0.17 compared with 2.45 for the smaller cluster alone.

The thermodynamic stability of the clusters was also checked. Figures 6 and 7 show the energy per hydrogen molecule as a function of temperature for six of the 2D clusters studied. In both figures the dotted lines represent least-squares fits of the internal energies to cubic polynomials. Using them, we can obtain by extrapolation the ground-state energies per particle, that we displayed in Fig. 8. According to Ref. 9, the dependence of the energy on the size of the cluster is accurately described by an expression of the form

$$e=e_0+e_1/N^{1/2}+e_2/N. \quad (1)$$
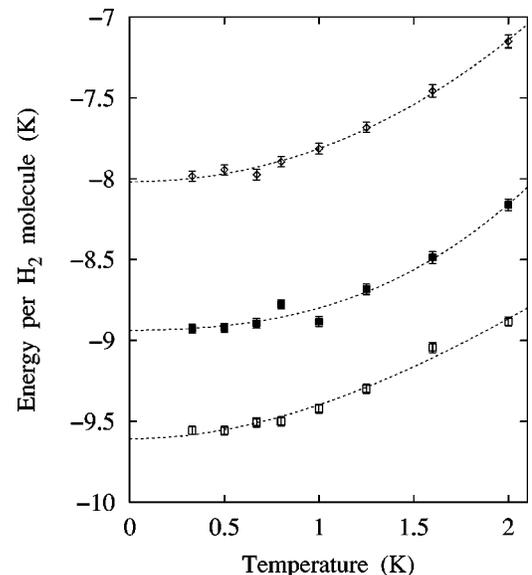
FIG. 6. Energy per H$_2$ molecule as a function of temperature. From top to bottom $N=6$, $N=7$, and $N=8$. The dotted lines are fits to a cubic polynomial in temperature.
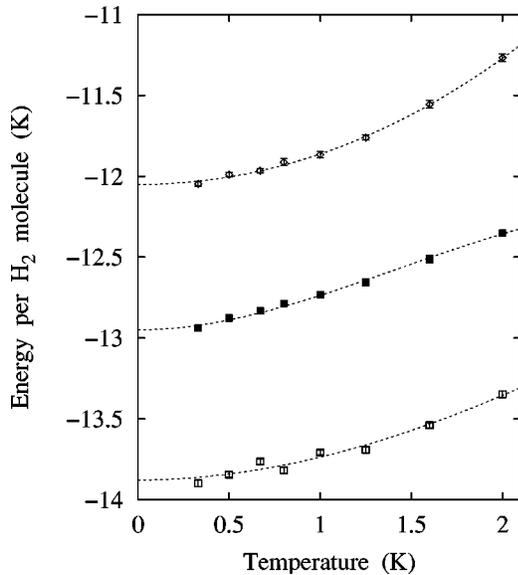
FIG. 7. Same as in Fig. 6, but for $N=13$ (squares), $N=16$, (full squares) and $N=20$ (diamonds).

FIG. 8. Zero-temperature energies per hydrogen molecule as a function of cluster size N. The error bars are of the same size as the symbols. See text for details.

The parameters we obtained are $e_0 = -22.61 \pm 0.24$ K, $e_1 = 43.2 \pm 1.5$ K/molecule, and $e_2 = -18.1 \pm 2.4$ K/molecule, with a χ^2 per degree of freedom lower than one. We found that e_0 is comparable with the energy per particle in the 2D bulk.[2] All the clusters considered are self bound since their ground-state energy is negative.

We obtain an estimate of the surface energy[9] from $\gamma = (\sigma/4\pi)^{1/2} e_1 = 3.45 \pm 0.12$ K/Å, where we have estimated the 2D density as the equilibrium value in bulk ($\sigma = 0.08$ Å^2). This is much greater than for 2D ^{4}He clusters.

One can imagine making such 2D clusters by dropping 3D droplets (say formed by expanding supercritical hydrogen through a nozzle) on a flat surface, such as graphite, though the effect of the corrugation could modify the cluster properties. Helium clusters with a hydrogen core can be formed in such nozzles.[7] If those are allowed to condense on a surface, the helium could then be boiled off to leave the smaller hydrogen clusters. To experimentally detect the superfluid properties at least two possibilities suggest themselves. The hydrogen droplets could trap an adequate impurity. If the hydrogen interaction with the impurity is as weaker or weaker than the substrate hydrogen impurity the cluster will remain as a monolayer. The motion of the hydrogen around the impurity might be related to properties of the rotovibrational state of the impurity and observable in its spectrum. Such analysis has been perfected for 3D clusters of hydrogen and helium. In addition, one might observe changes in the diffusional motion of the clean clusters on a very flat substrate. Clusters that are primarily superfluid should have an enhanced diffusion constant.

IV. CONCLUSIONS

We reported PIMC simulations on strictly 2D H_2 clusters. We found that for clusters with only two complete shells around the center of mass are delocalized and fully superfluid at $T \lesssim 1$ K. For larger clusters with between two and three complete layers of atoms, a transition between liquidlike and solidlike puddles is observed. However, even at $N = 61$, we have at least part of the outer structure not completely solid.

ACKNOWLEDGMENTS

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