

Quantum Monte Carlo Study of Two-Dimensional H_2 on a Rb Substrate

C. Cazorla and J. Boronat

*Departament de Física i Enginyeria Nuclear, Campus Nord B4-B5,
Universitat Politècnica de Catalunya, E-08034 Barcelona, Spain*

A quantum Monte Carlo study at zero temperature of two-dimensional H_2 on top of a solid Rb surface is presented. The lattice constituted by the alkali atoms frustrates the formation of solid H_2 , which is the natural phase of pure two-dimensional H_2 . Therefore, H_2 with the Rb atoms acting like fixed impurities remains in a liquid phase even at zero temperature. We present results for the H_2 equation of state, structural properties, superfluid density and condensate fraction for a fixed Rb lattice.

PACS numbers: 67.70.+n, 67.90.+z.

1. INTRODUCTION

The search for a superfluid phase of molecular hydrogen has deserved the attention of theorists and experimentalists for a long time. H_2 is an *a priori* optimal candidate due to its light mass, one half of the ^4He mass. However, the H_2 - H_2 interaction is stronger than the He-He one (more than a factor three in the well depth), and contrary to ^4He , bulk molecular hydrogen freezes at 13.8 K. Therefore, a possible H_2 superfluid phase is very hard to achieve and, in fact, it has never been observed. In the last years, the effort has been addressed mainly to molecular hydrogen in inhomogeneous systems due to the decrease of its freezing density. This feature is known from experiments: a H_2 film adsorbed on several substrates freezes at temperatures around 5 K.¹

At present, there are several theoretical works which prove the existence of a superfluid phase of molecular hydrogen in restricted geometries. In a purely one-dimensional array H_2 may remain in the liquid state; this limiting situation can be nowadays carried out by adsorption inside a carbon nanotube or into the interstitial channels of a carbon nanotube bundle.

Actually, zero-temperature calculations of H_2 adsorbed in nanotubes have proved its superfluid state.² On the other hand, path integral Monte Carlo simulations of H_2 droplets have also detected superfluidity but it disappears when the number of molecules is larger than twenty.³ Finally, a third alternative was suggested by Gordillo and Ceperley⁴ who observed superfluidity in a purely two-dimensional H_2 system with alkali impurities arranged in a triangular lattice. In the latter case, the alkali impurities which interact weakly with H_2 frustrate the formation of the H_2 solid phase, the ground state of pure two-dimensional H_2 .

Following the Gordillo and Ceperley's proposal,⁴ we have carried out a similar study at zero temperature by using the diffusion Monte Carlo (DMC) method. In Ref. 4, the substrates were K and Cs disposed in different lattices and with alkali- H_2 interactions modeled by Lennard-Jones potentials with parameters estimated by Gordillo and Ceperley. However, the lattices used in those calculations do not exist in nature making their predictions difficult to validate experimentally. In the present work, we explore a similar system but using Rb instead of K since there are experimental measures⁵ which confirm the existence of a solid Rb film with the right lattice constant to block the H_2 crystallization. Our results show that in this more realistic substrate the superfluidity is strongly suppressed with respect to estimations of Ref. 4, mainly due to the more attractive Rb- H_2 interaction compared with the K- H_2 one.

2. THEORETICAL MODEL

The influence of alkali impurities in the properties of two-dimensional H_2 is studied at zero temperature by means of the diffusion Monte Carlo (DMC) method. This fully microscopic approach solves stochastically the imaginary-time Schrödinger equation,

$$-\hbar \frac{\partial \Phi(\mathbf{R}, t)}{\partial t} = (H - E)\Phi(\mathbf{R}, t), \quad (1)$$

with hamiltonian $H = -D \sum_{i=1}^N \nabla_i^2 + \sum_{i<j}^N V(r_{ij})$, $D = \hbar^2/(2m)$, and E being a constant acting as a reference energy. When $t \rightarrow \infty$ only the ground state survives, and in the case of bosons like para- H_2 the results are exact apart from statistical errors. Instead of solving Eq. (1), DMC introduces a trial wave function $\psi(\mathbf{R})$ for importance sampling, and thus the Schrödinger equation is solved for the wave function $f(\mathbf{R}, t) = \Phi(\mathbf{R}, t) \psi(\mathbf{R})$.

The trial wave function for the present problem contains correlations between N H_2 molecules ($f(r_{ij})$) and between H_2 and the n Rb atoms

Table 1. Total and partial energies per particle of liquid H₂ immersed in the Rb lattice.

$\sigma(\text{\AA}^{-2})$	$E/N(\text{K})$	$V/N(\text{K})$	$T/N(\text{K})$
0.011	-43.40 ± 0.06	-58.14 ± 0.08	14.74 ± 0.03
0.015	-43.28 ± 0.03	-57.78 ± 0.03	14.50 ± 0.03
0.018	-44.06 ± 0.01	-59.83 ± 0.01	15.78 ± 0.01
0.023	-44.68 ± 0.03	-61.46 ± 0.10	16.77 ± 0.08
0.026	-44.48 ± 0.02	-64.26 ± 0.02	19.78 ± 0.01

$(F(R_{ij}))$,

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \prod_{i < j}^N f(r_{ij}) \prod_{i,k}^{N,n} F(R_{ik}) . \quad (2)$$

Both two-body correlation factors have been chosen of McMillan type $\exp(-0.5(b/r)^5)$, the parameters being selected through a previous variational Monte Carlo (VMC) calculation. The optimal values are $b = 3.7$ and 6.4 \AA for the pairs H₂-H₂ and H₂-Rb, respectively.

The internal structure of the para-H₂ molecules is neglected and their interactions are modeled by the standard Silvera-Goldman potential.⁶ The interaction between H₂ and alkali atoms is much less well known. We have taken for it a Lennard-Jones potential with the parameters reported in Ref. 7. In particular, for Rb-H₂ these are $\sigma = 4.54 \text{ \AA}$ and $\epsilon = 27.0 \text{ K}$, values appreciably much larger than the ones used in Ref. 4 for the interaction K-H₂.

Both the Rb atoms and the H₂ molecules are arranged in a strictly two-dimensional geometry. The Rb atoms are considered as fixed impurities distributed according to a triangular solid phase with lattice parameter 10 \AA . As commented previously, this solid Rb film is realistic since it has been observed experimentally.⁵ The number of alkali impurities in the simulation box is kept fixed to 30 and the number of H₂ molecules is progressively increased to obtain the equation of state. It is worth noticing that a solid H₂ film commensurate with this substrate is not possible if the size of the core of the alkali-hydrogen interaction is taken into account.

3. RESULTS

The energy of 2D H₂ with the fixed array of alkali impurities is calculated using the DMC method for different numbers of H₂ molecules and a fixed

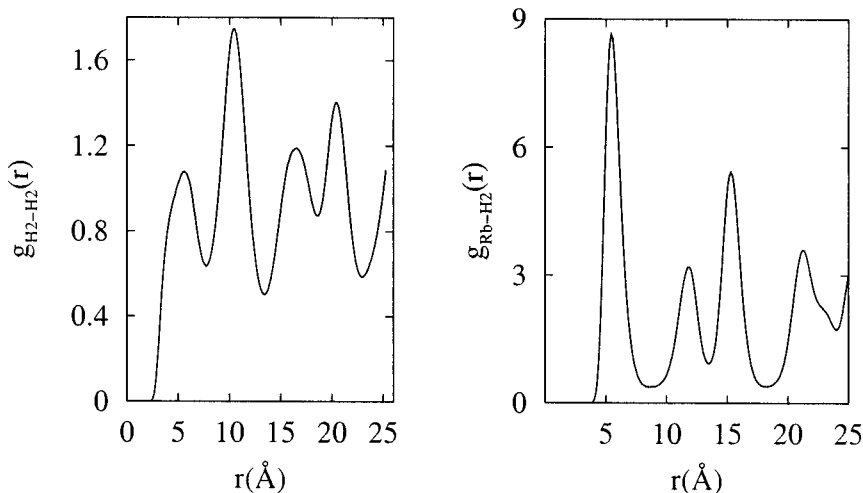


Fig. 1. Left: $\text{H}_2\text{-H}_2$ radial distribution function. Right: Rb-H_2 radial distribution function. Both calculated at a density $\sigma = 0.023 \text{ \AA}^{-2}$.

simulation box to cover a wide range of densities. The results obtained for the total and partial energies when the substrate is Rb are reported in Table 1. The equilibrium point is obtained through a polynomial fit to the data; it is located at a density 0.023 \AA^{-2} with a ground state energy -44.68 K . This point is rather far from that corresponding to a pure solid H_2 film: the density is much larger, 0.067 \AA^{-2} , and the energy is smaller, -23.41 K . The sizeable increase in the total energy is due to the potential energy between the substrate and H_2 . If the Rb substrate is replaced by a K one, with the same lattice constant, the equilibrium point is nearly unchanged since the Lennard-Jones parameters (σ, ϵ) for the pair K- H_2 do not differ significantly of the ones for Rb- H_2 .⁷ The results change dramatically if one considers the K- H_2 parameters estimated in Ref. 4 ($\sigma = 3.75 \text{ \AA}, \epsilon = 9.54 \text{ K}$). Our calculation for this latter case gives an energy -20.17 K corresponding to an equilibrium density of 0.038 \AA^{-2} . This result for the equilibrium density is in agreement with the one reported in Ref. 4 but our energy is larger due to the fact that we have reduced the size effects in the simulation.

The relatively large core of the Rb- H_2 interaction does not leave much space for the diffusion of the H_2 molecules. This feature is reflected in the $\text{H}_2\text{-H}_2$ and Rb-H_2 two-body radial distribution functions shown in Fig. 1. The $g_{\text{H}_2\text{-H}_2}(r)$ shows a periodic-like structure which slowly vanishes at long distances; the position of the peaks correspond to an hexagonal pattern corresponding to the *holes* in the middle of the triangles of the Rb lattice. This most probable position for the H_2 molecules appears also clearly as the

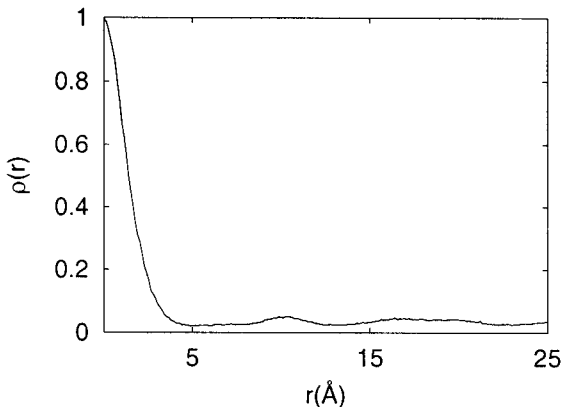


Fig. 2. One body density matrix of 2D H₂ in the Rb substrate.

main peak of the mixed distribution $g_{Rb-H_2}(r)$.

A fundamental magnitude which characterizes the expected superfluid character of liquid H₂ is the non-zero condensate fraction n_0 . The value of n_0 is obtained as $n_0 = \lim_{r \rightarrow \infty} \rho(r)$, with $\rho(r)$ the one-body density matrix. The result for $\rho(r)$ at the equilibrium density is shown in Fig. 2. As one can see, $\rho(r)$ becomes constant at large distances in spite of some oscillations induced by the substrate. The condensate fraction extracted from $\rho(r)$ is very small, about 0.03; this value is approximately seven times smaller than n_0 in 2D ⁴He at zero temperature.

In order to complete the description of the system, we have calculated its superfluid fraction ρ_s/ρ . This quantity is accessible in a DMC calculation by extending to zero temperature the winding-number technique employed in PIMC calculations, as discussed for bosons in a lattice in Ref. 8. The superfluid fraction is obtained as the ratio of two diffusion constants $\rho_s/\rho = D_s/D_0$ when $t \rightarrow \infty$, with $D_0 = \hbar^2/(2m)$ and

$$D_s = \lim_{t \rightarrow \infty} \frac{N}{4t} \frac{\int d\mathbf{R} f(\mathbf{R}, t) [\mathbf{R}_{CM}(t) - \mathbf{R}_{CM}(0)]^2}{\int d\mathbf{R} f(\mathbf{R}, t)} \quad (3)$$

is the diffusion constant of the *center of mass* of the system, i.e., $\mathbf{R}_{CM} = (1/N) \sum_{i=1}^N \mathbf{r}_i$. In Fig. 3, we show the result for D_s/D_0 at the equilibrium density. From the asymptote one extracts the superfluid fraction; the result for the present system is 0.08, again a very small figure. In Ref. 4, with K instead of Rb and different Lennard-Jones parameters a value much larger (0.25) was reported. This sizeable decrease is mainly due to the more attractive potential used in this work that we consider as more realistic.

Summarizing, we have carried out a DMC calculation of 2D H₂ with fixed alkali impurities distributed according to a realistic solid lattice. The

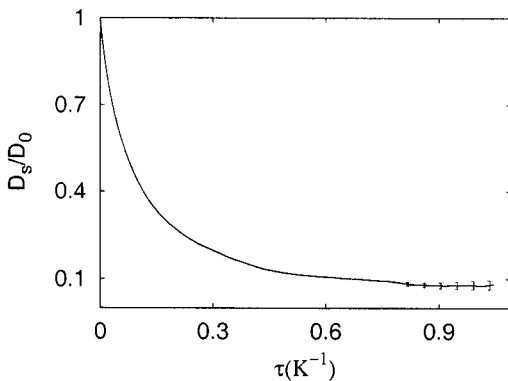


Fig. 3. Diffusion coefficient of the center of mass in imaginary time. The asymptotic value is the DMC estimation of the H_2 superfluid density.

simulation concerns mainly to Rb since it presents in nature the proper lattice to frustrate the H_2 crystallization. The results obtained show a highly structured liquid phase with a superfluid fraction practically suppressed. Therefore, this not very optimistic result does not confirm previous results obtained with a K lattice and appreciably different potentials. A final and more conclusive answer would require more accurate alkali- H_2 interatomic potentials.

ACKNOWLEDGMENTS

This work was supported in part by DGES (Spain) Grant No. BFM2002-00466 and Generalitat de Catalunya Grant No. 2001SGR-00222.

REFERENCES

1. F. C. Liu, Y. M. Liu, and O. E. Vilches, *Phys. Rev. B*, **51**, 2848 (1995).
2. M. C. Gordillo, J. Boronat, and J. Casulleras, *Phys. Rev. Lett.* **85**, 2348 (2000).
3. P. Sindzingre, D. M. Ceperley, and M. L. Klein, *Phys. Rev. Lett.* **67**, 1871 (1991).
4. M. C. Gordillo and D. M. Ceperley, *Phys. Rev. Lett.* **79**, 3010 (1997).
5. Gerald S. Leatherman and Renee D. Diehl, *Phys. Rev. B*, **53**, 4939 (1996).
6. I. F. Silvera and V. V. Goldman, *J. Chem. Phys.* **69**, 4209 (1978).
7. F. Ancilotto, E. Cheng, M. W. Cole, and F. Toigo, *Z. Phys. B* **98**, 323 (1995).
8. S. Zhang, N. Kawashima, J. Carlson, and J. E. Gubernatis, *Phys. Rev. Lett.* **74**, 1500 (1995).