Quasi-1D parahydrogen in nanopores

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The low temperature physics of parahydrogen ($p$-H$_2$) confined in cylindrical channels of diameter of the order of 1 nm is studied theoretically by Quantum Monte Carlo simulations. On varying the attractive strength of the wall of the cylindrical pore, as well as its diameter, the equilibrium phase evolves from a single quasi-1D channel along the axis, to a concentric cylindrical shell. It is found that the quasi-1D system retains a strong propensity to crystallization, even though on weakly attractive substrates quantum fluctuations reduce somewhat such a tendency compared to the purely 1D system. No evidence of a topologically protected superfluid phase (in the Luttinger sense) is observed. Implications on the possible existence of a bulk superfluid phase of parahydrogen are discussed.

I. INTRODUCTION

The speculative superfluid phase of condensed parahydrogen ($p$-H$_2$), predicted over forty years ago has so far eluded a direct, unambiguous experimental observation. The problem with the original prediction is that it assumes fluidlike behaviour of $p$-H$_2$ at low $T$, when in fact the system undergoes crystallization (at saturated vapor pressure) at $T = 13.8$ K, over a factor two higher than the temperature ($\sim 6$ K) at which Bose-Einstein Condensation and superfluidity ought to occur. Solidification takes place due to the depth of the attractive well of the intermolecular potential, roughly three times that between two helium atoms. The zero temperature equilibrium phase of $p$-H$_2$ is theoretically predicted to be a (non-superfluid) crystal in reduced dimensions as well.

First principle theoretical calculations based on realistic intermolecular potentials yield evidence that small $p$-H$_2$ clusters (thirty molecules or less) remain liquidlike down to temperatures of the order of 1 K, where they display superfluid behavior. This lends some credibility to the hypothesis that a bulk superfluid phase might be observable, if crystallization of the fluid could be suppressed. One way of lowering the freezing temperature of a fluid consists of confining it in a porous medium such as vycor glass. In the pores of vycor, whose characteristic size is $\sim$ 4 nm, $p$-H$_2$ freezes at a temperature $T \sim 8$ K, considerably lower than that of bulk $p$-H$_2$, but still significantly higher than the estimated superfluid transition temperature; indeed, the search for superfluid behaviour of $p$-H$_2$ in vycor has not met with success.

The solid phase, which has a different crystal structure than that of bulk $p$-H$_2$, nucleates at the pore walls, one may therefore wonder whether different physics (possibly including a superfluid phase) may be observed in a different confining environment, e.g., with pores of smaller size and/or less strongly adsorbing than silica.

It was recently shown that $p$-H$_2$ clusters of $\sim$ 30 molecules, confined in weakly adsorbing spherical cavities of size $\sim$ 2 nm, surprisingly feature an enhanced superfluid response, compared to that of free clusters. It is therefore conceivable that the same effect may take place in a different geometry, e.g., cylindrical channels, experimentally relevant to actual porous media. As the diameter of the channel is reduced to one nm or less, the physics of a fluid confined in it approaches the 1D limit, and becomes therefore amenable to interpretation within the framework of Luttinger liquid theory (LLT) as shown by computer simulation of $^3$He confined in nanopores of such a characteristic size.

No true long range order exists in 1D; rather, two-dimensional correlation functions display slow power-law decays at long distances. Of particular interest in this work is the pair correlation function $g(r)$, which at any finite temperature $T$ will take on the following behavior in the thermodynamic limit:

$$g(r) \sim 1 - \frac{1}{2\pi^2 K \rho^2 r^2} + A \cos(2\pi \rho r) \frac{1}{\rho^2 r^2 / K}$$

(1)

Here, $\rho$ is the linear density of particles and $A$ a non-universal, system-dependent constant. The Luttinger parameter $K$ describes how quickly the oscillations of $g(r)$ decay at long distance; based on its value one can meaningfully differentiate between phases that are “quasicrystalline” or “quasi-superfluid” in character. Specifically, if $K > 2$ the static structure factor will develop (Bragg) peaks at reciprocal lattice vectors, which is the experimental signature of a crystalline solid. On the other hand, if $K < 0.5$ the system features a robust propensity to superflow, and there exists a well-defined theoretical scenario in which a 3D bulk superfluid phase may arise in a network of interconnected, quasi-1D channels. For $0.5 \leq K \leq 1.5$, the system can be regarded as a “glassy” insulator (at the high end of the interval), or as a weak superfluid, subjected to pinning by either disorder or an external potential. Henceforth, whenever speaking of “crystal” versus “superfluid”, we shall refer to the above classification.

The ground state phase diagram of $p$-H$_2$ in one dimension only features a crystalline phase, with a value of $K \sim 3.5$ at the equilibrium density $\rho_0 = 0.218$ $\text{A}^{-1}$, monotonically increasing with density and remaining above $\geq 2$ all the way down to the spinodal density.

This low temperature phase diagram in 1D qualitatively mimics that of bulk $p$-H$_2$ in two and three dimensions, with no evidence of a superfluid phase.

In this work, we study theoretically the phase diagram of a quasi-1D fluid of $p$-H$_2$ in the narrow confines of a cylindrical channel of diameter of the order of 1 nm. The hypothesis being tested here is whether quantum excur-
sions of molecules in the direction perpendicular to the axis of the cylinder may act to screen the intermolecular potential, to the point of reducing the propensity of the system to form a crystal, possibly stabilizing a superfluid (in the Luttinger sense) phase.

We carried out first principle computer simulations at low $T$ of a reasonably realistic model of the system of interest, essentially the same model utilized in similar studies of $^4$He. We utilized different sets of potential parameters, in order to impart to the wall of the channel different adsorption properties, going from a substrate as strongly attractive as silica, to a much weaker one, such as Cs. Most of the results presented here are for channels of diameter $d=10$ Å, but we also performed simulations with $d=5$ and 20 Å.

Inside the narrower channel, an adsorbate is thermodynamically stable (i.e., there exists a bound state) only for the most strongly adsorbing substrate considered here; in such a tight confinement, molecules remain very close to the axis of the channel, and the system closely reproduces the physics of purely 1D $p$-$^2$H$_2$, with the same equilibrium (linear) density and the same value of the Luttinger parameter, within the uncertainty of our calculation. On the other hand, if the channel has a 2 nm diameter the equilibrium phase is consistently an insulating solidlike film adsorbed on the wall; growth takes place through successive solidlike layers, much like on a flat substrate.

Considerably more diversity of behavior is observed in channels of diameter 1 nm, once again pointing to the fact that this is the characteristic length scale within which $p$-$^2$H$_2$ displays the most interesting physics. For the weakest substrate considered in this work (Cs), $p$-$^4$H$_2$ forms inside the channel a quasi-1D adsorbate along the axis, always on the crystalline side of the LLT but with a reduced value of $K$ (2.7) with respect to the purely 1D case. As the strength of the substrate is gradually increased, molecules experience a greater pull toward the wall, their excursions away from the axis become increasingly significant, and the value of $K$ decreases, attaining a minimum (close to 2) on a Li substrate, for which the quasi-1D fluid takes on a helical structure. On stronger substrate, the system forms at equilibrium a shell coating the walls, the central region of the channel remaining empty. On increasing the density, a quasi-1D second layer eventually forms, again with physical properties that mimic those of the strictly 1D system.

The main physical conclusion of this investigation is that although nanoscale confinement in a cylindrical geometry can reduce its strong tendency to crystallization, nonetheless a regime of possible superfluidity of $p$-$^2$H$_2$ is never approached. This provides additional support to the notion that superfluidity in $p$-$^2$H$_2$ forms, again with physical properties that mimic those of the strictly 1D system.

The many-body Hamiltonian of the system is the following:

$$\hat{H} = -\lambda \sum_i \nabla_i^2 + \sum_{i<j} v(|\mathbf{r}_i - \mathbf{r}_j|) + \sum_i V(\mathbf{r}_i).$$

Here, $\lambda = 12.031$ KÅ$^{-2}$, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between any two $p$-$^2$H$_2$ molecules and $\mathbf{r}_i$ is the position of the $i$th molecule. The potential $v$ describes the pairwise interaction of $p$-$^2$H$_2$ molecules, whereas $V$ that of $p$-$^4$H$_2$ molecules with the wall of the channel. We used for $v$ a potential recently proposed by Moraldi modified at short distances as described in Ref. [24]. This potential has been shown to reproduce rather accurately the experimental equation of state of solid $p$-$^4$H$_2$, up to megabar pressure. Its use is motivated by the fact that the density of $p$-$^2$H$_2$ inside the channel is not uniform, and it could be quite high in the vicinity of the surface, in case of a strongly attractive substrate; it makes therefore sense to utilize a pair potential that is more accurate at high pressure than, for example, the standard Silvera-Goldman pair potential.

For the the interaction $V$ between a $p$-$^2$H$_2$ molecule and the wall, we use the expression arising from the integration of a Lennard-Jones potential over an infinite continuous medium surrounding the cylinder, regarded as infinitely long. The resulting expression only depends on the distance $\rho$ of the particle from the axis of the cylinder and contains two parameters, a characteristic length $a$ which is essentially the distance of closest approach to the wall of the channel, where the potential is strongly repulsive, and $D$, which has the dimensions of an energy and is basically the depth of the attractive well of the potential which particles experience from the wall.

### TABLE I: Potential parameters $D$ and $a$ utilized in this work.

| Substrate | $D$ (K) | $a$ (Å) |
|-----------|--------|--------|
| Cs        | 37.8   | 3.88   |
| Rb        | 39.7   | 3.87   |
| K         | 44.4   | 3.76   |
| Na        | 69.5   | 3.40   |
| Li        | 99.7   | 3.19   |
| Mg        | 191.8  | 2.76   |
| Glass     | 232    | 2.22   |

The values are taken from Ref. [27]. Substrates are listed in order of increasing strength, from top to bottom.
test cases was found to yield estimates indistinguishable from those extrapolated to the $\tau \rightarrow 0$ limit.

### III. RESULTS

![Graph](image)

**FIG. 2:** Energy per $p$-H$_2$ molecule $e$ (in K) versus linear density $\nu$ (in Å$^{-1}$), at $T=1$ K, inside a cylindrical channel of diameter $d=10$ Å. Results are shown for three different substrates, namely K (filled circles), Na (filled triangles) and Li (diamonds), listed in order of increasing strength (see Table I). Dashed lines are polynomial fits to the data. Statistical uncertainties are of the order of the symbol size.

Most of the results presented and discussed here pertain to adsorption of a $p$-H$_2$ fluid inside a cylindrical channel of diameter $d=10$ Å; the physical behaviour observed inside channels of greater or smaller diameter will be dealt with at the end. We begin by discussing the energetics. Fig. 2 shows computed values of the energy $e$ per $p$-H$_2$ molecule as a function of the linear particle density $\nu = N/L$, for three of the alkali substrates considered here. The results shown here are for a temperature $T=1$ K; energy estimates for this system have been consistently found not to change significantly below $T = 4$ K, at all physical conditions explored in this work.

The curves all display a minimum at the equilibrium density, corresponding to energy values all well below the bulk chemical potential of $p$-H$_2$, namely $-90$ K. It is noteworthy that a stable adsorbate also exists inside a Cs channel (the energy minimum in that case is $-95$ K), which is in contrast to the case of an infinite flat Cs substrate, which is actually not wetted by $p$-H$_2$ molecules. These are three substrates which are known to be weak adsorbers, for the purpose of identifying physical conditions in which the equilibrium phase of the system is quasi-1D, i.e., with $p$-H$_2$ molecules lined up along the axis of the channel.

We investigated the low temperature thermodynamic properties of our system of interest by means of first principle computer simulations based on the worm algorithm in the continuous-space path integral representation.

This methodology allows one to calculate finite temperature thermodynamic properties of Bose systems, with the Hamiltonian as the only required input and without any uncontrolled approximations. In particular, it grants one access to energetics as well as superfluid properties (both global and local) and relevant correlation functions, such as the reduced pair correlation function for the central quasi-1D channel along the axis of the cylindrical channel. As mentioned in the Introduction, we performed most of our simulations for a system with diameter $d=10$ Å, but we also carried out a few for a narrower channel, with diameter $d=5$ Å, as well as a wider one, with diameter $d=20$ Å.

The calculation performed here is standard, and we refer the readers interested in the methodology to the original references. We simply mention that all of the calculations were performed with the usual short-time propagator accurate to fourth order in the imaginary time step $\tau$, and with a value of $\tau = 1/640$ K$^{-1}$, which in a few cogent

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**FIG. 1:** Color online. Potentials describing the interaction between a $p$-H$_2$ molecule and the wall of the confining cylindrical channel, for some of the substrates considered here. Cs (cesium) is the weakest, Glass is the most strongly attractive, and Li (lithium) has intermediate strength. Here, $\rho$ is the distance of a particle from the axis of the channel.

These two parameters are adjusted to reproduce, as accurately as allowed by such a relatively simple model, the interaction of a particle with a substrate. The values of the parameters of the potential utilized in this work are reported in Table I. They were taken from Ref. 27 except those for Glass, which were obtained starting from those proposed in Ref. 28 for Helium atoms near a glass substrate, using Lorentz-Berthelot mixing rule to adjust them for $p$-H$_2$. Our focus here is mostly on metallic alkali substrates which are known to be weak adsorbers, for the purpose of identifying physical conditions in which the equilibrium phase of the system is quasi-1D, i.e., with $p$-H$_2$ molecules lined up along the axis of the channel.

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FIG. 3: Color online. Three-dimensional density of \( p-H_2 \) inside a cylindrical channel of diameter \( d=10 \, \text{Å} \), plotted as a function of the distance from the axis. Curves pertain to different substrates, at the corresponding equilibrium densities. Statistical errors are not visible on the scale of the figure.

the cylinder, the greater pull that they experience in the case of a Na substrate resulting in a greater spread of the molecular wave function in the transverse direction. At the opposite end, on the stronger substrates such as Mg and Glass, the density of \( p-H_2 \) is negligible on the axis, as the equilibrium phase consists of a single cylindrical shell coating the wall, with molecules sitting at a closer distance from it in the case of Glass.

The physics of the system on the substrate labeled as Li, on the other hand, in a way interpolates between strong and weak adsorption. The density profile displays a maximum off the axis, but the density on the axis itself remains finite. This suggests that molecules arrange on a helix, winding around the axis; this structure remains largely 1D in character.

An interesting question arises, namely, what is the physical effect of the significant molecular excursions away from the axis on the channel, on the physical character of a quasi-1D adsorbate. As mentioned in the Introduction, one may expect such excursions mainly to soften the intermolecular interaction, responsible for the strong propensity of the system to crystallize, possibly with the result of imparting to the system quasi-superfluid behaviour.

In order to address this issue, we study the reduced pair correlation function \( g(z) \), where \( z \) is the component of the distance between two particles along the axis of the channel. For systems that approach the 1D limit (and in our study that means equilibrium \( p-H_2 \) layers adsorbed inside channels whose walls have the adsorption properties of the alkali metals in Table I), the \( g(z) \) is expected to depend only on the product \( LT \) in the limit \( L \to \infty, T \to 0 \), and b) to conform to the behaviour predicted by Eq. 1 allowing one to infer the value of the Luttinger parameter \( K \) for the particular system of interest.

Fig. 4 shows pair correlation functions computed for \( p-H_2 \) inside a Cs (top) and a Na (bottom) channel, in both cases for two different temperatures, namely \( T = 0.5 \) and 1 K, and two different system sizes, comprising \( N = 40 \) and 80 molecules. In both cases, calculations are carried out at the equilibrium density, which, as mentioned above, is slightly above that in purely 1D. As one can see, collapse of the data is clearly observed. The value of the parameter \( K \) can be obtained by fitting the computed \( g(z) \) to the expression \( f(z) = 1 + A/z^2/K \).

For the weakest substrate, for which the adsorbate is closest to the 1D limit, i.e. for which molecular excursions in the transverse direction are most limited, the determined value of \( K \) is 2.70(5), appreciably lower than that for a purely 1D system (3.5). As the adsorption strength of the wall of the channel increases, our estimate of \( K \) gradually decreases, the lowest value (very close to 2) attained for a Li substrate. As shown above (fig. 3), if the wall of the channel is taken to be slightly more attractive than Li (i.e., Mg), then the equilibrium phase is a concentric cylindrical shell, with essentially no molecules in the central part of the channel. The effec-
tive 2D coverage of such a layer can be inferred from the data shown in Fig. 3 and is \( \sim 0.067 \, \text{Å}^{-2} \), i.e., the same with the equilibrium coverage of \( p\text{-H}_2 \) in 2D at \( T=0 \). Actually, the physics of such an adlayer is quite close to that of 2D \( p\text{-H}_2 \); that is, the system displays solidlike behaviour, with molecules localized in space, quantum-mechanical exchanges are virtually absent and, consequently, no trace of superfluidity can be observed. On increasing the density, a second, quasi-1D inner layer eventually forms; we studied this system for the case of a glass channel. For simplicity, we utilized in these calculations an effective harmonic potential, adjusted to reproduce, in the vicinity of the axis of the cylinder, the combined effect of the interaction of the molecules with the wall of the channel, as well as with the molecules in the shell coating it. The resulting, fairly tight confining effect for the molecules in the central region, combined with the relatively high linear density of thermodynamical effects for the molecules in the central region, combined with the relatively high linear density of thermodynamically stable inner layers, imparts to the system in the inner part a markedly solidlike behaviour. Indeed, characteristic values of the parameter \( K \) for quasi-1D inner \( p\text{-H}_2 \) layers surrounded by a \( p\text{-H}_2 \) cylindrical shell are generally \( \geq 3.5 \).

Summarizing, the largest reduction of the Luttinger parameter \( K \) that has been observed for \( p\text{-H}_2 \) in cylindrical confinement, with respect to its value in 1D, while substantial (from 3.5 to 2), still leaves the system in the “insulating” sector of the LLT.

We now comment on the results obtained in narrower and wider channels. Inside a channel of diameter \( d=5 \, \text{Å} \), no adsorption occurs except for the most attractive of the substrates considered here, namely glass. The quasi-1D inner layer closely approaches the physics of 1D \( p\text{-H}_2 \), with essentially the same value of the linear equilibrium density and Luttinger parameter \( K \). Inside a channel of wider diameter (\( d=20 \, \text{Å} \)), on the other hand, adsorption occurs for all substrates except Cs, and the equilibrium phase is again a single, solidlike cylindrical shell, concentric with the wall and with an equilibrium density close to that of 2D \( p\text{-H}_2 \).

IV. CONCLUSIONS

Extensive simulation studies have been performed for a realistic model of \( p\text{-H}_2 \) adsorbed in the interior of a cylindrical channel of diameter ranging from 5 to 20 Å. The results yield evidence that, although confinement can somewhat reduce the strong tendency of the system to crystallize, as observed in spherical cavities (Ref. 16), nevertheless the effect is quantitatively more limited in a cylindrical geometry.

Specifically, if the diameter of the channel is as large as merely 2 nm, then the physics observed is qualitatively very similar to that which takes place when \( p\text{-H}_2 \) is adsorbed on a flat substrate. On the other hand, inside narrow channels of diameter less than 1 nm, \( p\text{-H}_2 \) will form quasi-1D adsorbate (if the substrate is sufficiently strong) that closely reproduce the physics of the system in purely 1D, i.e., the phase is crystalline in nature (in the Luttinger sense).

A cylindrical channel of diameter close to one nm, with a substrate that is relatively weak (e.g., Li) provides a confining environment in which the interplay of reduced dimensionality and quantum excursions off the axis can lead to different physics, specifically to the stabilization of quasi-1D phases with a much reduced tendency to crystallize. This is qualitatively consistent with the recently reported enhancement of the superfluid response of \( p\text{-H}_2 \) clusters trapped inside a spherical cavity; however, the effect is quantitatively far less significant in the quasi-1D geometry considered in this work, as the predicted reduction of the Luttinger parameter \( K \) from its 1D value of 3.5 all the way to approximately 2 does not entail a fundamental change of the physical character of the system, which remains an insulator.

Consequently, any scheme aimed at stabilizing a bulk superfluid phase of \( p\text{-H}_2 \) in a network of interconnected cavities seems to face the hurdle that no superflow may be sustained inside narrow cylindrical channels connecting two adjacent cavities.

While this manuscript was undergoing review, we became aware of similar recent work claiming that the value of the Luttinger parameter \( K \) can be lowered considerably with respect to what found in this work, in fact to the point where \( p\text{-H}_2 \) could turn superfluid (in the Luttinger sense), inside Carbon nanotubes. The (cylindrical) geometry and diameters are similar to ours, but the model considered in Ref. 56 includes substrate corrugation. These predictions, seemingly at variance with the results presented here, were obtained with a different computational methodology with respect to that utilized here, specifically a ground state one. Clearly, further studies will be needed to resolve this discrepancy.

Acknowledgments

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The suggestion was made, almost two decades ago [M.-C. Gordillo and D. M. Ceperley, Phys. Rev. Lett. 79, 3010 (1997)] that SF might occur in a (quasi) two-dimensional (2D) \( p \)-H\(_2\) fluid embedded in a crystalline matrix of alkali atoms. Subsequent studies, however, showed that the equilibrium phase is a non-superfluid crystal, commensurate with the underlying impurity lattice. See, for instance, M. Boninsegni, New J. Phys. 7, 78 (2005).

It should also be mentioned that experimentally one observes the lowering of the superfluid transition temperature of liquid helium confined in vycor, i.e., confinement has also the effect of suppressing superfluidity. See, for instance, M. H. W. Chan, K. I. Blum, S. Q. Murphy, G. K. S. Wong and J. D. Reppy, Phys. Rev. Lett. 61, 1950 (1988).

The attractiveness of a wall potential depends both on the well depth \( D \) and on the distance of closest approach \( a \). In the following, when speaking in general terms of “attractive strength” of a substrate, or anything equivalent, we shall always refer to a particular combination of values of \( D \) and \( a \), not to the well depth \( D \) alone.

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A Li substrate is known to display unusual adsorption properties precisely due to the fact that it is neither too weak nor too strong. For example, it is the weakest substrate on which a superfluid \( ^4\)He mono-layer is predicted to exist. See M. Boninsegni, M. W. Cole and F. Toigo, Phys. Rev. Lett. 83, 2002 (1999).

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