Superfluid behavior of quasi-1D \( \text{p-H}_2 \) inside carbon nanotube

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(Dated: August 26, 2016)

We perform ab-initio Quantum Monte Carlo simulations of para-hydrogen (pH\(_2\)) at \( T = 0 \) K confined in carbon nanotubes (CNT) of different radii. The radial density profiles show a strong layering of the pH\(_2\) molecules which grow, with increasing number of molecules, in solid concentric cylindrical shells and eventually a central column. The central column can be considered an effective one-dimensional (1D) fluid whose properties are well captured by the Tomonaga-Luttinger liquid theory. The Luttinger parameter is explicitly computed and interestingly it shows a non-monotonic behavior with the linear density similar to what found for pure 1D \(^3\)He. Remarkably, for the central column in a (10,10) CNT, we found an ample linear density range in which the Luttinger liquid is (i) superfluid and (ii) stable against a weak disordered external potential, as the one expected inside realistic pores. This superfluid behavior could be experimentally revealed in bundles of carbon nanotubes, where deviations from classical inertial values associated with superfluid density could be measured by using quartz crystal microbalance techniques. In summary, our results suggest that pH\(_2\) within carbon nanopores could be a practical and stable realization of the long sought-after, elusive superfluid phase of parahydrogen.

PACS numbers: 67.25.D-, 67.25.dr
calculations seem to contradict this claim, by showing that the 1D pH$_2$ equilibrium phase is a crystal [17], as it also is in 2D pH$_2$ [18].

So far the only reported enhancement of superfluid response was obtained within PIMC simulations for pH$_2$ confined inside nano-cavities [19]. The confining medium discussed in this paper is however not realistic, being composed of spherical nano-sized cavities coated with alkali metal thick films in order to reduce the adsorption properties of the cavity walls, which seems hardly feasible at the present time.

We follow here a different approach by addressing a more realistic system made of pH$_2$ molecules in a confining system that is routinely provided by existing nanotechnologies, i.e. armchair carbon nanotubes (CNT) of different radii. Although strictly 1D geometry precludes superfluid behavior, wider tubes where pH$_2$ forms a quasi-1D system coexisting with solid-like concentric cylindrical shells could provide the ideal environment where strong evidence of the elusive superfluidity of para-hydrogen could be collected, as shown in the present work.

Our calculations are based on exact zero temperature Path Integral Ground State (PIGS) Monte Carlo method [20, 21]. Because PIGS is a well-established computational methodology we shall not review it here. We recall only that the most relevant feature is that it provides unbiased estimates of the $T = 0$ K ground state properties directly by the microscopic Hamiltonian, by projecting in imaginary time a trial wave function. The quality of the trial wave function has the sole role to fix the length of the total imaginary time projection. Here we have considered a shadow wave function (SWF) [22], which has provided an optimal trial wave function for bulk [23], confined [24], overpressurized [25] and dimensionally reduced [26] He systems, whose parameters have been optimized to describe pH$_2$ [27]. All the approximations involved in the PIGS method, i.e. the choice of the total imaginary time $\tau$, of the imaginary time step $\delta \tau$ and the approximation for the short imaginary time propagator, are so well controlled that the resulting systematic errors can be reduced within the unavoidable Monte Carlo statistical error making of PIGS an exact zero-temperature method [20, 21].

In our calculations we consider $N$ pH$_2$ molecules, described as point-like particle with zero spin adsorbed within CNT of different radii, described by the following Hamiltonian

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

where $\vec{r}_i$ are the positions of the pH$_2$ molecules, $\lambda = \hbar^2/2m = 12.031$ KÅ$^2$, $v$ describes the interaction between a pair of molecules and $V$ describes the interaction of a molecule with the CNT. We assume periodic boundary conditions along the tube axis. As for $v$, which is considered spherically symmetric, we use the well-known Silvera-Goldman potential (SG) [28]. We specifically consider three different armchair CNTs: the (10,10) CNT with radius $R = 6.80$ Å, the (12,12) CNT with radius $R = 8.19$ Å and the (15,15) CNT with radius $R = 10.17$ Å. To model the H$_2$-carbon interaction we used a pair potential fitted to high level ab initio results on the interaction between H$_2$ and graphite [1]. This procedure provides a corrugated potential $V$, but implicitly neglects the effects of curvature, which however are found to have very little consequences for the considered CNTs [30]. By using the fourth order pair-Suzuki approximation [21] for the short imaginary time propagator we observe convergence of ground state estimates with a projection time $\tau = 0.250$ K$^{-1}$ using a time step $\delta \tau = 1/640$ K$^{-1}$.

We made a number of simulations with varying number $N$ of pH$_2$ molecules from 38 up to a maximum of 432, adsorbed within the three different CNTs of increasing length $14.77 < L < 59.00$ Å. Similarly to the case of $^4$He adsorbed in nanotubes [31, 32], the pH$_2$ radial density profiles $\rho_R(r)$, reported in Fig. 1 show a marked layered structure: the pH$_2$ molecules form a cylindrical shell adsorbed on the inner tube wall plus a central column in the (10,10) CNT, two concentric cylindrical shells in the (12,12) CNT, and two concentric cylindrical shells plus a central column in the (15,15) CNT. The promotion to the second (lower density) layer (or to the central column for the (10,10) CNT) occurs at an areal density value $\theta_P = 0.108$ Å$^{-2}$, which is about 15% higher than the promotion coverage to the second layer found for pH$_2$ adsorbed on graphite [37]. For all the three CNT, the adsorbed layer adjacent to the tube inner surface turns out to be a crystalline two dimensional triangular solid wrapped to form a cylinder, whose structure is incommensurate with the underlying carbon lattice. The intermediate shells (in the (12,12) and (15,15) tubes) are

![FIG. 1: (Color online) Typical radial density profiles $\rho_R(r)$ for pH$_2$ inside the considered CNTs. Statistical errors are smaller than the used symbols.](image-url)
also two dimensional solid wrapped on a cylindrical surface for all the considered values of $N$, with no evidence whatsoever of a liquid-like behavior.

Within the PIGS method it is possible to obtain a direct estimate of the superfluid fraction $\rho_s$ from the imaginary time diffusion of the center of mass of the system \cite{38, 39}. For the (10,10) and (12,12) CNTs, we found a sizable superfluid response, comparable with the (debated \cite{40}) one calculated for $\text{pH}_2$ embedded in a 2D Na crystal \cite{41}. However, this large $\rho_s$ has to be ascribed to the presence of defects in the crystalline structure of the adsorbed layer due to the mismatch between the $\text{pH}_2$ lattice and the underlying carbon structure, i.e. to the actual length $L$ of the simulated CNT. The effective ability of such defects to sustain a detectable superfluid flow \cite{42}, or rather their pinning at the structural defects in real CNTs is beyond the scope of this paper.

Our systems provide however a better candidate for superfluidity: the central column in (10,10) and (15,15) CNTs, that behaves as a quasi-1D superfluid whose properties are well captured by the Tomonaga-Luttinger liquid theory (TLL) \cite{43, 45}. The description of a confined liquid by means of the TLL has been successfully applied to $^4\text{He}$ in nanopores \cite{33, 34}. TLL is a phenomenological theory than captures the low-energy properties of a wide class quantum 1D systems with short range interaction \cite{43, 46} in terms of two bosonic fields, $\phi(x)$ and $\theta(x)$ representing respectively the density and the phase fluctuations of the particle field operator $\psi(x) = \sqrt{\rho + \partial_x \phi(x)} e^{i\theta(x)}$ ($\rho$ being the average density) via the low-energy effective Hamiltonian

$$H_{LL} = \frac{\hbar}{2\pi} \int dx \left( cK_L \partial_x \theta(x)^2 + \frac{c}{K_L} \partial_x \phi(x)^2 \right). \quad (2)$$

The parameter $K_L$ (known as Luttinger parameter \cite{47}) and the velocity $c$ are generally independent quantities fixed by the microscopic details of the system. Such Hamiltonian is exactly solvable, thus the knowledge of $c$ and $K_L$ is enough to characterize the correlation functions and the thermodynamic properties of the system. For Galilean-invariant systems, as the ones we are going to consider here, $c = \hbar \rho / m K_L$ \cite{47}, thus the only parameter to be determined is $K_L$. Here we determine the Luttinger parameter via QMC simulations, that have largely been proven to be efficient in estimating $K_L$ \cite{17, 48, 50}.

$K_L$ governs the decay of correlations function and can be used to draw a well defined definition of (quasi) crystal and (quasi) superfluid. For $K_L < 1/2$ the static structure factor develops Bragg peaks at reciprocal lattice vectors, which is the signature of a (quasi) crystalline solid. For $K_L > 1/2$ no (quasi) diagonal-long range order is present, but the system displays a (quasi) off-diagonal long-range order. Thus, even if no true long-range order can exist in 1D for a system of particles with short range interaction \cite{51}, there can be a phase, known as Luttinger liquid (LL), featuring power-law decaying correlations \cite{45}, that is superfluid in the sense that it displays a quasi-off diagonal long range order \cite{52, 53}. Such a superfluidity manifests different degree of robustness against disorder or external potentials. Specifically, if $K_L > 3/2$ the superfluid is insensitive to a weak external disordered potential \cite{54}, while for a periodic external potential commensurate with the density with filling fraction $1/\rho$, the transition is located at $K_L = 2/\rho^2$ \cite{53}.

It was found that for narrow pores $^4\text{He}$ obeys the TLL theory with a small Luttinger parameter corresponding to solid-like character of the adsorbed phase \cite{33, 34}. On the other hand, for wider pores, the central region appears to behave like a LL but with a larger $K_L$ indicating that the system is dominated by superfluid fluctuations, as indeed expected for superfluid $^4\text{He}$. We will show here that a similar behavior occurs for $\text{pH}_2$ in CNTs. Since the exchanges of molecules with the surrounding shells are null, the central column of $\text{pH}_2$ in (10,10) and (15,15) CNT can be considered an effective one-dimensional system that can be well described via the TLL \cite{34}. The surrounding shells have the crucial role to screen (reduce) the bare $\text{pH}_2-\text{pH}_2$ interaction, and the molecules inside the central column can be depicted as pure 1D particles (with the same mass of the initial ones) interacting via the effective potential \cite{34}

$$v_{1D}(z) = \frac{1}{\rho_L} \int d^2 r \int d^2 r' v(\vec{r} - \vec{r}') \rho_R(r) \rho_R(r') \quad (3)$$

where $\vec{r} = (r, \varphi, z)$ is a vector in cylindrical coordinates and

$$\rho_L = \frac{N}{L} = 2\pi \int dr \; r \rho_R(r) \quad (4)$$

is the linear density. The resulting effective potential is almost insensitive to the actual pore length and to the density of the central column itself. The obtained $v_1$ for the (10,10) and (15,15) CNT are shown in Fig. 2 where they are also compared to the SG $\text{pH}_2-\text{pH}_2$ bare interaction potential. Notably, they can be fairly fitted by using a Lennard-Jones like formula \cite{55}. As already observed for $^4\text{He}$ \cite{34}, the effect of the surrounding shells is that of reducing the potential well depth and of shifting the minimum to smaller separations. This can change dramatically the low-density behavior of the effective 1D system when compared to the strictly 1D $\text{pH}_2$. In fact, for example, pure 1D $\text{pH}_2$ is expected to display a spinodal decomposition at densities below 0.209 Å$^{-1}$ \cite{17}, while we have been able to simulate such effective pure 1D system down to $\rho = 0.02$ Å$^{-1}$ without any signature of spinodal decomposition. For this pure 1D system, we have simulated $N = 50$ particles in order to minimize the finite size effects \cite{17, 56}, taking $\tau = 2.50$ K$^{-1}$ and $\delta \tau = 1/320$ K$^{-1}$ to guarantee convergence to the ground state.
fluid) and (which discerns from a (quasi) crystal and a (quasi) superfluid response should be expected could be easily extracted by the quartz microbalance techniques [30], by measuring the frequency shifts in the shear modes of the microbalance parallel to the bundle axis. The density range where a superfluid response should be expected could be easily reached by changing the pressure (chemical potential) of the pH2 vapor surrounding the nanotube bundles, which determines the actual amount of fluid adsorbed inside the central columns.

While preparing this manuscript, we were made aware of a recent paper where quasi-1D pH2 in model nanopores with smooth walls was studied by using PIMC [57] with no sign of any LL-superfluid phase. When their radius is such that the pore houses a single pH2 column, $K_L$ is found to grows from the value 0.28 of the pure 1D pH2 [17] to values close to 1/2 but still in the (quasi) crystalline state. Even the combination of cylindrical shell plus central column has been explored in Ref. [57] for a glass pore of radius $R = 5$ Å, but with opposite results than ours. We argue that the less attractive substrate and the small radius with respect to the (10,10) CNT considered here, provide a tighter confinement for pH2 that strongly localizes the molecules, resulting in a Luttinger parameter even lower than the one of the pure pH2.

In conclusion we have studied, by using PIGS exact simulations and the TLL theory, pH2 within geometric confinement provided by realistic CNT of different radii. The results show the appearance, for the (10,10)
and (15,15) CNTs, of a central column along the NT axis, that can be described within the TLL theory. The molecules belonging to the inner column are screened by the solid pH$_2$ layers adsorbed on the surrounding CNT inner wall, resulting in pronounced quantum exchanges between molecules within the column, leading to a clear superfluid behavior in the (10,10) CNT. Our QMC simulations do indeed confirm this scenario, suggesting that pH$_2$ within bundles of carbon nanotubes could be a practical realization of the elusive superfluid phase of parahydrogen.

We thank M. Boninsegni, G. Bertaina, D.E. Galli, G. Mistura and P.L. Silvestrelli for stimulating discussions.

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[55] We have fit our $v_{LD}$ with the formula $v_{LD}(z) = 4\epsilon \left( \frac{z}{\sigma} \right)^m - \left( \frac{z}{\sigma} \right)^m/2$ obtaining $\epsilon = 8.845$ K, $\sigma = 2.726$ Å and $m = 9.230$ for the (10,10) CNT and $\epsilon = 3.683$ K, $\sigma = 2.658$ Å and $m = 8.957$ for the (15,15) one.
The external potential experienced by the pH\textsubscript{2} molecules in the central column is the sum of the potential due to the CNT itself and the one due to the adsorbed layer. The CNT produces a periodic potential whose maximum excursion in energy (i.e., the energy difference between top and hollow site adsorption energies) are of the order of 0.03 K, i.e., $10^{-3}$ times the SG well and $4 \times 10^{-3}$ times the $v_{1D}$ well. The adsorbed layer produces a potential which is disordered due to the presence of defects induced by incommensurability, whose maximum excursion in energy is $0.3$ K, i.e., $10^{-2}$ times the SG well and $4 \times 10^{-2}$ times the $v_{1D}$ well.

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**SUPPLEMENTAL MATERIAL: SUPERFLUID BEHAVIOR OF QUASI-1D P-H\textsubscript{2} INSIDE CARBON NANOTUBE**

**PH\textsubscript{2}-CNT INTERACTION POTENTIAL**

The effective pH\textsubscript{2}-CNT interaction potential $V$ is constructed by summing all the pairwise pH\textsubscript{2}-C contributions among the pH\textsubscript{2} molecule and the Carbon atoms of an armchair CNT tube of indices $(n,n)$ and stored on a grid for computational efficiency. To prevent spurious boundary effects due to the truncation of the tube (and on the imposed periodic boundary conditions along the axis) we construct tubes longer than 100 Å to perform the summation but retain only the central portion of length $L_0 = 14.77$ Å (corresponding to 5 elemental cells of the Carbon hexagonal lattice). Thus the simulated CNTs described in the paper will have lengths that are integer multiples of $L_0$.

**Curvature effects.**

In order to describe the pH\textsubscript{2}-C interaction we have considered an exp-6-8-10 potential obtained by fitting high-quality \textit{ab initio} results for the H\textsubscript{2}-graphite interaction \cite{1}. Although our potential construction accounts for the cylindrical geometry of the C atoms, it misses the curvature related $sp^2 \rightarrow sp^3$ hybridization of the Carbon bonds that may modify the pH\textsubscript{2}-C interaction. Curvature-dependent corrections to the coefficients of a Lenard-Jones potential describing the C-H\textsubscript{2} pairwise interaction have been proposed in the past to include effects due to the increasing $sp^2 \rightarrow sp^3$ hybridization in Carbon nanotubes as the CNT radius decreases\cite{2}. Such corrections are based on interpolation formulas between the two extreme limits of pH\textsubscript{2} interacting with a C atom in a graphite plane (pure $sp^2$ character) and in an ideal $sp^3$ environment. However, this model potential was later found inadequate to quantitatively describe the H\textsubscript{2}-graphite interaction and thus a better, albeit curvature independent, C-H\textsubscript{2} pair potential has been proposed \cite{3}, which we are using here. Corrections due to mixed hybridization effects mentioned above (which are important for CNTs with very small radii) are expected however to have small impact for the CNT investigated in our work. In fact, for the radii of interest here, the $sp^2$ component in the interaction parameter predicted by the interpolation formulas of Ref. \cite{2} would be dominant (being 86% for the (10,10) tube and 91% for the (15,15) one). We should also add that among physisorbed system, Carbon materials represent rather attractive substrates for pH\textsubscript{2}.
adsorption, and thus relatively small changes in the adsorption well depth/position of the \(\text{PH}_2\)-C potential are expected to affect only slightly the structure of the solid-like \(\text{PH}_2\) layer adsorbed on the CNT inner wall, and have even smaller effects on the central column structure.

In order to check that curvature effects are indeed negligible in the present study, we proceeded as in Ref. [2] to compute the interaction between \(\text{H}_2\) and an \(sp^3\)-coordinated Carbon atom with a dangling bond, and then use their interpolation formulas to find the correction to the pair potential well-depth used in our calculation (appropriate for a flat, \(sp^2\) coordinated substrate). We performed state-of-the-art \textit{ab initio} calculations (using the QUANTUM-ESPRESSO package[3]) to compute the interaction between a \(\text{H}_2\) molecule and a t-butyl radical (used in Ref. [2] to model the environment of an unsaturated \(sp^2\) carbon). The exchange-correlation functional used in our calculations explicitly includes the contributions of dispersion (Van der Waals) forces [4] (which were neglected in the calculations of Ref. [2]), which are known to provide important corrections to the energetics of physisorbed systems like the one considered here. We find that in order to reproduce the \textit{ab-initio} results described above for the \(\text{H}_2\)-C\((sp^3)\) interaction, the well depth of the \(exp\)-6-8-10 pair potential should be \(\epsilon = 6.2\,meV\), to be compared to the value \(\epsilon = 5.3\,meV\) describing the \(\text{PH}_2\)-C\((sp^2)\) two-body interaction. By using the above values in the interpolation formula that gives the curvature-corrected well depth parameter of the two-body interaction appropriate for a CNT with a given radius [2], we find that in the case of the (10,10) tube, the pair-potential well depth should be decreased by 23% with respect to the value (appropriate for the \(\text{H}_2\)-C\((sp^2)\) interaction) used in our calculations. An even smaller change is found for the (15,15) tube. In order to estimated the consequences of such a reduction, we compare the results of the QMC calculations for the radial density profile in the (10,10) CNT by summing (i) the pair potential without curvature corrections \(V\) (i.e. the one used for the computation in the main paper) and (ii) a rescaled one \(\eta V\) with \(\eta = 0.9, 0.8\) and 0.7. We find, as it appears in Fig. 4 where our results are reported, that the differences in the two cases (i.e. with and without curvature corrections) are indeed very small. The maximum of the density peak is reduced by a factor about 9% for the largest considered \(\eta\), but even in this case the number of \(\text{PH}_2\) molecules housed by the adsorbed layer is the same as for \(\eta = 1.0\). Since the curvature effects on the density profiles are small, the obtained effective one-dimensional interaction potential \(v_{1D}\) (Eq. (3) in the main paper) is practically insensitive to such corrections, as can be inferred from the right panel of Fig. 4. This confirms that curvature effects are completely negligible for the present study.

![Graph](image)

**FIG. 4**: (Color online) Left panel: radial density profiles \(\rho_R(r)\) for \(\text{PH}_2\) inside a \((10,10)\) CNTs with the potential \(V\) rescaled by a factor \(\eta\) as described in the text. Statistical errors are smaller than the used symbols. Right panel: corresponding effective one-dimensional interaction potential \(v_{1D}\).

**POSSIBLE EXPERIMENTAL SETUP TO OBSERVE \text{PH}_2\) SUPERFLUID BEHAVIOR IN CNTS.**

Aligned structures of CNTs (of lengths up to hundreds microns) with controllable radii can be routinely grown on different substrates (see for instances Ref. [5], and references therein). Micrometer-sized bundles of aligned parallel carbon nanotubes have been grown, in particular, on silicon or quartz surfaces [6], which can be up to 300 micron tall, with a bundle aspect ratio (height-to-width) of 5:1. This is a particularly favorable method in the present context, which allow in principle to grow the CNTs bundle directly over a quartz crystal microbalance (QCM) surface. Once filled with hydrogen (whose amount can be controlled through the environmental pressure), frequency shifts in the shear modes of the microbalance parallel to the bundle axis should allow detection of mass decoupling due to the appearance (e.g. by lowering the temperature) of a superfluid fraction within the central column of \(\text{PH}_2\) in each CNT. The latter corresponds to about 3% of the total amount of \(\text{PH}_2\) adsorbed in a \((10,10)\) CNT. For a QCM driven at a fundamental frequency of 5 MHz, adsorption of \(\text{PH}_2\) in the nanotubes will determine a frequency shift of 30 Hz if the total open volume of the nanotubes amounts to, say, \(10^{-7}\,cc\) (which is well below the theoretical values accessible in the microscopic bundles described above). If about 3% of the total \(\text{PH}_2\) mass decouples from the QCM oscillations in the superfluid phase, this will determine an increase in the resonance frequency of about 1 Hz, which is well above the standard resolution of 0.1 Hz (or less) typical of a QCM setup (see, for instance, Ref. [7]), thus allowing, in principle, to detect the normal-to-superfluid transition.
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