

Zero-Temperature Equation of State of Quasi-One-Dimensional H₂

M. C. Gordillo, J. Boronat, and J. Casulleras

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

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We have studied molecular hydrogen in a pure 1D geometry and inside a narrow carbon nanotube by means of the diffusion Monte Carlo method. The one dimensionality of H₂ in the nanotube is well maintained in a large density range, this system being closer to an ideal 1D fluid than liquid ⁴He in the same setup. H₂ shares with ⁴He the existence of a stable liquid phase and a quasicontinuous liquid-solid transition at very high linear densities.

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The experimental finding in 1991 [1] of carbon nanotubes opened brand-new possibilities both in technology and in fundamental physics. The nanoscale provided by these new materials led to the discovery of novel mechanical, chemical, and electrical properties [2] which suggest exciting new technological applications. One of the more relevant features that these new materials have shown is their large adsorption energy compared with a graphite planar substrate. Special interest exists in the physisorption of hydrogen [3–7] in the quest for a fuel cell efficient enough to be used as a pollution-free energy carrier. In fact, single wall carbon nanotubes (SWCN) with diameters of the order of a nanometer have been proposed as one of the possible candidates to approach the pursued level of packing [3].

From a more fundamental point of view, the strong confinement of particles adsorbed in the carbon channels of a SWCN bundle, with diameters ranging from 7 to 40 Å and an aspect ratio of ~1000, offers the possibility of an experimental realization of a quasi-one-dimensional system. Moreover, if the temperature is low enough, one is dealing with a unique opportunity of studying a nearly one-dimensional (1D) quantum fluid. In a recent experiment, Teizer *et al.* [8] have unambiguously observed the quasi-one-dimensional behavior of ⁴He adsorbed in a SWCN bundle by measuring its desorption rate. On the other hand, theoretical studies in the limit of zero temperature and strictly one dimension have proved the existence of a liquid state with a binding energy in the millidegrees Kelvin scale [9–11]. The aim of this paper is to extend the theoretical study to the appealing case of H₂ that, besides its technological relevance, might offer the existence of a homogeneous liquid phase at zero temperature. It is worth noticing that both, bulk and two-dimensional (2D) H₂ are solid in this temperature limit. Liquid phases have been observed only in theoretical calculations of small clusters [12] and in 2D geometries with localized alkaline impurities [13].

We have studied molecular hydrogen at zero temperature in a one-dimensional array and inside a single walled carbon nanotube (T) of radius $R = 3.42$ Å [a (5,5) arm-chair tube [14]] that is one of the narrowest experimen-

tally obtained [15]. The technique used is the diffusion Monte Carlo (DMC) method, which has become, in the past decades, one of the most efficient theoretical tools, from the microscopic point of view, to deal with quantum fluids [16,17].

A relevant issue in a microscopic study is the nature of the interspecies interaction. We have considered the H₂ molecules interacting via the isotropic semiempirical potential from Silvera and Goldman (SG) [18] that has been extensively used in path integral Monte Carlo (PIMC) and DMC calculations of bulk [19], clusters [12], and H₂ films [20]. In the simulations of H₂ inside a nanotube, we consider a cylindrically symmetric potential as suggested by Stan and Cole [21]. In that simplified model, the interactions between C atoms and H₂ molecules are axially averaged out, resulting in a potential which depends only on the distance to the center of the tube. It has been proved [5] that the differences between that smoothed potential and a potential which is built up as an explicit sum of individual C-H₂ interactions are not significant and surely smaller than the relative uncertainty in the (σ, ϵ) Lennard-Jones parameters. Considering $\sigma = 2.97$ Å and $\epsilon = 42.8$ K, the symmetric potential felt by a H₂ molecule in a (5,5) tube has a depth of 42ϵ , 3 times larger than the attraction of the same molecule in a flat graphitic surface.

The use of importance sampling in DMC requires the introduction of a trial wave function that guides the diffusion process to relevant regions of the walkers phase space. In the 1D system, we consider

$$\Psi^{1D}(\mathbf{R}) = \Psi_J(\mathbf{R}), \quad (1)$$

with $\Psi_J(\mathbf{R}) = \prod_{i<j} \exp[-\frac{1}{2}(\frac{b}{r_{ij}})^5]$ being a Jastrow wave function with a McMillan two-body correlation factor. Inside the nanotube, H₂ molecules interact with the walls of the cylinder and therefore we have added an additional one-body term,

$$\Psi^T(\mathbf{R}) = \Psi_J(\mathbf{R})\Psi_c(\mathbf{R}), \quad (2)$$

with $\Psi_c(\mathbf{R}) = \prod_i^N \exp(-c r_i^2)$ and r_i being the radial

distance of the particle to the center, to avoid the hard core of the H₂-nanotube interaction.

Theoretical calculations of 1D ⁴He agree in predicting a liquid-solid phase transition at high linear densities [9–11]. This transition, which is only possible at absolute zero temperature, looks like a nearly continuous one without a measurable difference between the melting and freezing densities. Following the same procedure as in our previous work in helium [10], we have explored the existence of such a transition in H₂. In this ordered phase, we modify the trial wave function in both the 1D system and inside the nanotube by multiplying them by a z -localized factor $\Psi_s(\mathbf{R}) = \prod_i^N \exp[-a(z_i - z_{is})^2]$. The sites z_{is} are equally spaced points in both the 1D line and the axial direction of the nanotube.

The variational parameters a , b , and c have been optimized by means of variational Monte Carlo calculations. In the liquid phase and near the equilibrium density $b = 3.759 \text{ \AA}$, with a slight increase with density (at $\lambda = 0.277 \text{ \AA}^{-1}$, $b = 3.789 \text{ \AA}$), whereas $c = 4.908 \text{ \AA}^{-2}$ is kept fixed for all λ values. In the solid phase, $b = 3.404 \text{ \AA}$, $a = 0.799 \text{ \AA}^{-2}$, and $c = 5.136 \text{ \AA}^{-2}$, with a negligible λ dependence in the region analyzed.

The possible existence of a liquid-solid phase transition at high linear density has been studied in both 1D and inside a narrow nanotube. In Table I, results for the energy per particle of both systems are reported for the liquid ($a = 0$) and solid ($a \neq 0$) phases. The comparison between the energies of both phases at the same density shows that their difference changes sign when going from $\lambda = 0.312 \text{ \AA}^{-1}$ to $\lambda = 0.304 \text{ \AA}^{-1}$ in 1D and from $\lambda = 0.320 \text{ \AA}^{-1}$ to $\lambda = 0.312 \text{ \AA}^{-1}$ in the tube. Above these densities, the system prefers to be localized in a solidlike structure with a difference $|E(s) - E(l)|$ that increases with λ . When the density decreases, the liquid phase is energetically preferred and again the size of the difference $|E(s) - E(l)|$ increases when λ diminishes. The density value at which this difference becomes zero is estimated to be $\lambda = 0.309 \text{ \AA}^{-1}$ in 1D and $\lambda = 0.315 \text{ \AA}^{-1}$ in the tube, being impossible to distinguish between freezing and melting densities. As previously studied in ⁴He [10] it appears to be a nearly continuous phase transition located at a density close to the inverse of the location of the minimum of the respective pair potential ($r_m^{-1} = 0.337 \text{ \AA}^{-1}$ vs $\lambda_s = 0.358 \text{ \AA}^{-1}$ for helium, and $r_m^{-1} = 0.291 \text{ \AA}^{-1}$ vs $\lambda_s = 0.309 \text{ \AA}^{-1}$ for molecular hydrogen).

Inside the nanotube, the energies are much more negative than in 1D due to the strong attraction of the carbon substrate: the binding energy of a single H₂ molecule in the tube is $E_b = -1539.87 \pm 0.11 \text{ K}$. Looking at the T-energy results contained in Table I, one realizes that, also in this case, a transition occurs at a density very close to the 1D one. It is remarkable that, both in 1D and T, H₂ remains liquid below the liquid-solid transition density, and thus a homogeneous liquid phase at zero pressure is predicted. That result contrasts with the theoretically and experimentally well-established solid phase in 3D [22] and the 2D solid phase predicted by a PIMC calculation [20].

The equations of state of liquid H₂ near the equilibrium density for both the 1D and T systems are shown in Fig. 1. In order to make the energy scales compatible we have subtracted the single binding energy E_b to the T results. The lines in the figure correspond to the third-degree polynomial fits in the form

$$\frac{E}{N} = e_0 + A \left(\frac{\lambda - \lambda_0}{\lambda_0} \right)^2 + B \left(\frac{\lambda - \lambda_0}{\lambda_0} \right)^3. \quad (3)$$

The best set of parameters e_0 , λ_0 , A , and B are reported in Table II. The equilibrium densities in both systems are the same considering their respective uncertainties but the binding energy $e_0 = e(\lambda_0)$ is larger when H₂ is inside the nanotube. The difference between the 3D geometry (T) and the idealized one (1D) can be quantified by means of the adimensional parameter

$$\Delta^T = \frac{(E^T - E_b^T) - E_{1D}}{(E^T - E_b^T)}. \quad (4)$$

In the present system, around λ_0 , $\Delta^T = 3.5\%$ which emphasizes the proximity between the real system and the idealized one. It is worth noting that in ⁴He inside the same nanotube we obtained $\Delta^T = 90\%$ [10], and therefore H₂ seems a better candidate to experimentally achieve a 1D condensed phase. That significant difference between helium and hydrogen may be understood by taking into account the fact that the difference between the hard-core size of the C-He interaction ($\sigma_{C-He} = 2.74 \text{ \AA}$) and the C-H₂ interaction ($\sigma_{C-H_2} = 2.97 \text{ \AA}$) is magnified in a (5, 5) tube because of its small radius ($R = 3.42 \text{ \AA}$).

In Fig. 2, the density dependence of the pressure for both the 1D and T systems is reported from equilibrium up to the liquid-solid transition density. As a matter of comparison, the same results for ⁴He are also plotted.

TABLE I. Energies per particle in K at high linear densities λ for 1D and T H₂ systems. $a = 0$ and $a \neq 0$ correspond to the liquid and solid phases, respectively.

λ (\AA^{-1})	E/N (1D, $a = 0$)	E/N (1D, $a \neq 0$)	E/N (T, $a = 0$)	E/N (T, $a \neq 0$)
0.329	98.083 ± 0.034	97.963 ± 0.016	-1453.99 ± 0.06	-1454.69 ± 0.04
0.320	72.567 ± 0.013	72.523 ± 0.007	-1476.74 ± 0.05	-1476.88 ± 0.01
0.312	53.264 ± 0.010	53.227 ± 0.010	-1493.790 ± 0.019	-1493.720 ± 0.002
0.304	38.581 ± 0.018	38.636 ± 0.014	-1506.570 ± 0.03	-1506.540 ± 0.011
0.290	19.203 ± 0.010	19.260 ± 0.003	-1523.730 ± 0.017	-1523.600 ± 0.02

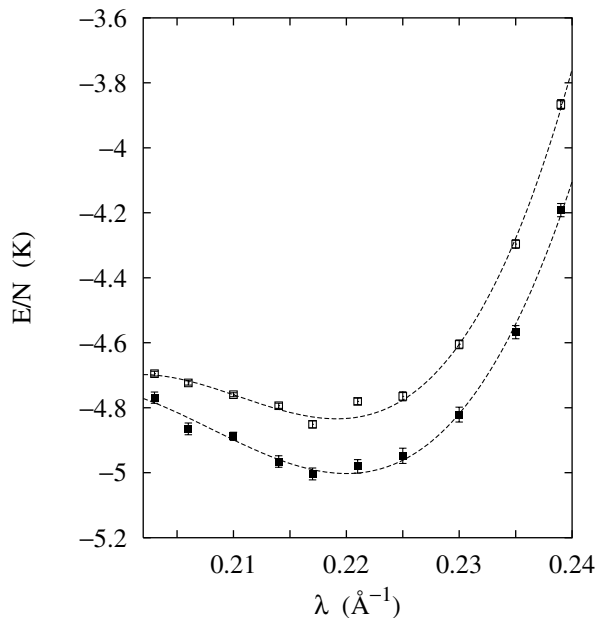


FIG. 1. Energy per particle of H_2 as a function of the linear density. Open squares are the 1D results, and filled squares are the T energies having subtracted the binding energy of a single molecule E_b . The lines are the result of the polynomial fit [Eq. (3)] with the optimal parameters reported in Table II.

Both in H_2 and 4He the pressure increases faster in the 1D geometry (P_λ) than in the tube (P) due the transverse degree of freedom that particles have in the latter case (notice the proportionality between the scales of P and P_λ in Fig. 2, $P_\lambda/P = \pi R^2$). At a given density λ , the difference between the T and 1D pressures is smaller in H_2 than in 4He . For example, at the respective transition densities that difference is more than one and one-half times larger in helium than in hydrogen. Therefore, the one dimensionality of H_2 inside the nanotube is well maintained in all of the liquid regime, in contrast with 4He in which the departure from such an idealized model already appears around the equilibrium density and increases significantly with λ . Also apparent from Fig. 2 is a much smaller compressibility in H_2 than in 4He . In the 1D geometry at $\lambda = \lambda_0$ the velocity of sound in H_2 is $c = 736.1 \pm 0.2$ m/sec to be compared with $c = 7.98 \pm 0.07$ m/sec in 4He at $\lambda = \lambda_0(^4He) = 0.062 \text{ \AA}^{-1}$. The velocity of sound drops to zero at the spinodal point that, according to the equation of state (Table II), is located at densities $0.210 \pm 0.001 \text{ \AA}^{-1}$ and $0.209 \pm 0.001 \text{ \AA}^{-1}$ for the 1D and T systems, respectively.

TABLE II. Parameters of the equation of state [Eq. (3)] for the two systems studied.

Parameter	1D H_2	H_2 in a tube
λ_0 (\AA^{-1})	0.2191 ± 0.0004	0.2200 ± 0.0006
e_0 (K)	-4.834 ± 0.007	-1544.880 ± 0.016
A (K)	65.7 ± 3.6	69.7 ± 4.9
B (K)	556.0 ± 46.6	429.7 ± 73.9
χ^2/ν	1.98	1.5

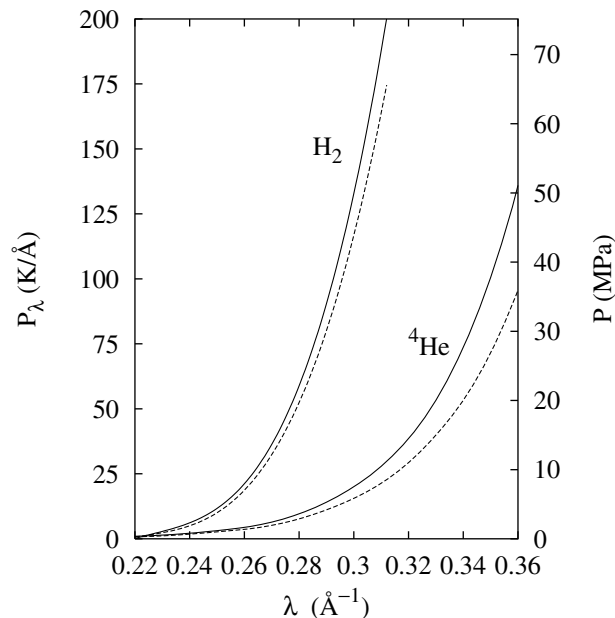


FIG. 2. 1D (P_λ , solid line) and T (P , dashed line) pressures for H_2 and 4He as a function of the linear density.

The spatial structure of molecular hydrogen in the 1D array and inside the nanotube has also been analyzed by means of the two-body radial distribution function $g(z)$ and its Fourier transform, the static structure factor $S(k)$. In Fig. 3, the 1D results for $g(z)$ are reported at both the equilibrium density for the liquid phase and in the solid-liquid transition region ($\lambda = 0.312 \text{ \AA}^{-1}$). The corresponding results for H_2 inside the nanotube are indistinguishable from

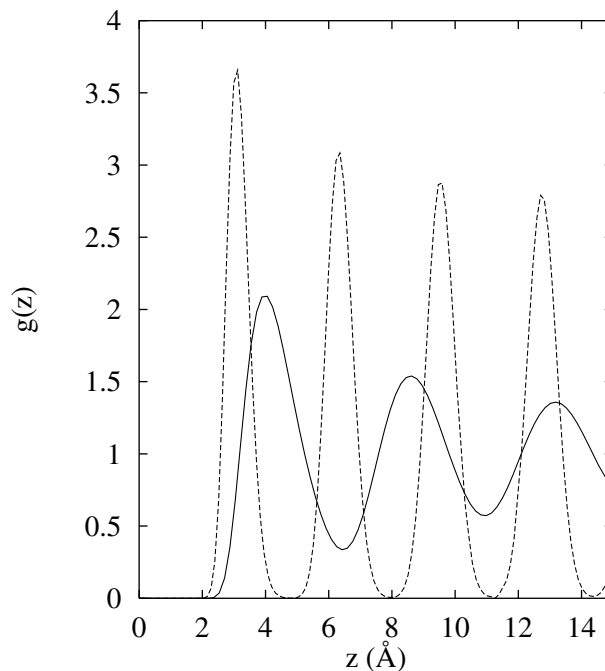


FIG. 3. Two-body radial distribution function for 1D H_2 at equilibrium (solid line) and at the liquid-solid transition density (dashed line).

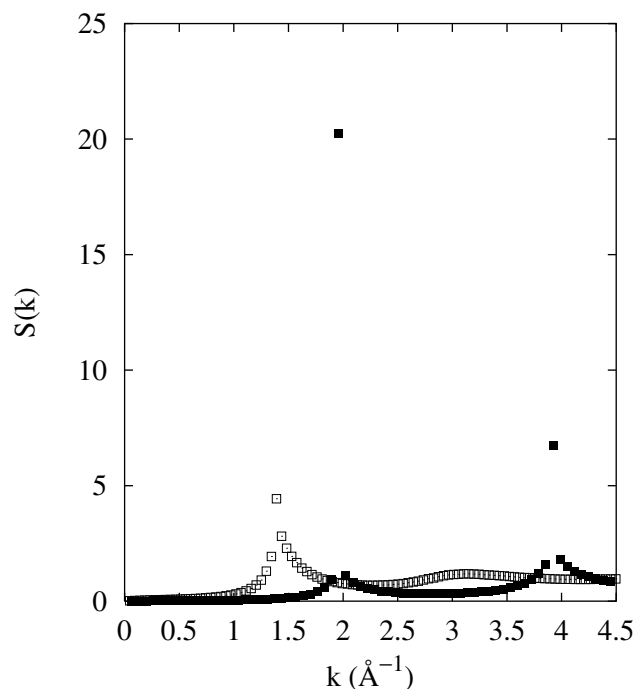


FIG. 4. Static structure function for 1D H_2 near equilibrium (open symbols) and at the liquid-solid transition density (solid symbols).

the 1D results in the scale shown in Fig. 3. The solid $g(z)$ shows a strongly localized order around the equally spaced z sites that decreases very slowly when z increases. The result for $g(z)$ at $\lambda = \lambda_0$ manifests the nature of a dense fluid with an appreciable structure that decreases faster than in the solid but shows residual ordering up to large z distances.

The significant differences in structure between the low and high density regimes are reflected even more clearly in the static structure factors. In Fig. 4, the results for $S(k)$ corresponding to the same densities reported in Fig. 3 are shown. At high density, a characteristic result for a solid phase is obtained with regular k spacing according to the only periodicity allowed by the 1D geometry. At $\lambda = \lambda_0$, $S(k)$ shows a first peak, reflecting the localization observed in $g(z)$ (Fig. 3), and a subsequent very smoothed maximum, as expected in a homogeneous liquid phase.

In conclusion, we have studied the zero-temperature equation of state of molecular hydrogen in a 1D geometry and inside a narrow nanotube by means of the diffusion Monte Carlo method. The 1D calculation predicts the existence of a self-bound system with a binding energy of -4.8 K and a quasicontinuous liquid-solid transition at high density. The comparison with a real system, hydrogen in a nanotube, points to a close proximity between its properties and the ones of the 1D limit. The prediction of a liquid H_2 phase inside a (5, 5) carbon nanotube is one of the main conclusions of this paper. The high one dimen-

sionality of this system would preclude a superfluid behavior but the use of wider nanotubes can provide a proper setup to observe the long-desired superfluidity in molecular hydrogen. We expect that this work could encourage experimentalists to explore such a intriguing possibility.

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