PHYSICAL REVIEW B **70**, 125405 (2004)

# Melting of a $p$-$H_2$ monolayer on a lithium substrate

Massimo Boninsegni
*Department of Physics, University of Alberta, Edmonton, Alberta, Canada T6G 2J1*

(Received 7 June 2004; published 8 September 2004)

Adsorption of $p$-$H_2$ films on alkali metals substrates at low temperature is studied theoretically by means of path integral Monte Carlo simulations. Realistic potentials are utilized to model the interaction between two $p$-$H_2$ molecules, as well as between a $p$-$H_2$ molecule and the substrate, assumed smooth. Results show that adsorption of $p$-$H_2$ on a lithium substrate, the most attractive among the alkali, occurs through completion of successive solid adlayers. Each layer has a two-dimensional density $\theta_e \approx 0.070$ Å$^{-2}$. A solid $p$-$H_2$ monolayer displays a higher degree of confinement, in the direction perpendicular to the substrate, than a monolayer helium film, and has a melting temperature of about 6.5 K. The other alkali substrates are not attractive enough to be wetted by $H_2$ at low temperature. No evidence of a possible superfluid phase of $p$-$H_2$ is seen in these systems.

DOI: 10.1103/PhysRevB.70.125405 PACS number(s): 67.70.+n, 61.30.Hn, 68.08.Bc

## I. INTRODUCTION

Much theoretical and experimental work has been devoted to the investigation of films of highly quantal fluids (e.g., condensed helium) adsorbed on a variety of substrates, from the most strongly attractive, such as graphite, to relatively weak ones, such as alkali metals.[1] The motivation underlying this effort is the understanding of the fascinating properties that quantum films display, often quite different than those of bulk materials.

Thin films of *para*-hydrogen ($p$-$H_2$) are of considerable interest. One of the reasons is that a fluid of $p$-$H_2$ molecules is regarded as a potential "second superfluid," due to the light mass and the bosonic character of its constituents.[2] In bulk $p$-$H_2$, superfluidity is not observed, because, unlike helium, $H_2$ solidifies at a temperature ($T \approx 13$ K) significantly higher than that ($\sim 4$ K) at which phenomena such as Bose condensation and, possibly, superfluidity (SF) might occur. This is due to the depth of the attractive well of the potential between two hydrogen molecules, significantly greater than that between two helium atoms. Several, attempts have been made[3–6] to supercool bulk liquid $p$-$H_2$, but the search for SF (in the bulk) has so far not met with success.

Confinement, and reduction of dimensionality, are widely regarded as plausible avenues to the stabilization of a liquid phase of $p$-$H_2$ at temperatures sufficiently low that a SF transition may be observed. Indeed, computer simulations yielded evidence of superfluid behavior in very small (less than 20 molecules) $p$-$H_2$ clusters,[7] and claims have been made of its actual experimental observation.[8] Theoretically, SF has also been predicted to occur in a strictly two-dimensional (2D) $p$-$H_2$ fluid embedded in a crystalline matrix of potassium atoms.[9]

Interesting as the above predictions undoubtedly are, they pertain to physical systems that are not easily realized in a laboratory, nor are controlled measurements of their properties always practical. On the other hand, adsorbed films of $p$-$H_2$ are readily accessible experimentally, and in fact have been extensively investigated, on different substrates. For example, the phase diagram and structure of monolayer $p$-$H_2$ films adsorbed on graphite have been studied by various techniques.[10–13] One of the most remarkable aspects[13] is that the melting temperature $T_m$ of a solid $p$-$H_2$ monolayer can be significantly less than bulk $p$-$H_2$. The question arises of whether a considerable reduction of $T_m$ could be achieved on a weak substrate, such as that of an alkali metal. It has been shown[14] that, for a $^4$He monolayer adsorbed on lithium, zero-point motion in the direction perpendicular to the substrate is quite significant, accounting for a doubling of the kinetic energy per atom, with respect to strictly 2D $^4$He. Such zero-point motion, conceivably important in a $p$-$H_2$ film as well, could result in an effective screening of the interaction of $p$-$H_2$ molecules, leading to a suppression of the melting temperature, perhaps to the point where quantum many-body phenomena may become observable in the liquid phase.

In this work, attention is directed to the physics of $p$-$H_2$ films adsorbed on alkali metals substrates. Besides the issue of SF, this system has elicited interest among condensed matter scientists for its intriguing wetting properties. It was suggested,[15] and experimentally verified,[15–17] that $H_2$, like $^4$He, should not wet cesium (Cs) or rubidium (Rb) substrates at low temperature, due to the relatively shallow depth of the substrate-adatom potential. It is not known whether a thermodynamically stable $p$-$H_2$ film should exist, at low $T$, on any of the other alkali substrates, namely potassium (K), sodium (Na) or lithium (Li). Particularly intriguing is the question of the existence of a $p$-$H_2$ monolayer on these substrates, and what its melting temperature $T_m$ should be.

Aside from the study of the phase diagram of 2D $p$-$H_2$ by Gordillo and Ceperley,[9] and of a $p$-$H_2$ surface by Wagner and Ceperley,[18,19] theoretical calculations for realistic models of adsorbed $p$-$H_2$ films have focused on graphite.[20] Only recently have the first theoretical studies of $p$-$H_2$ films on alkali substrates been carried out, based on path integral Monte Carlo (PIMC) simulations[21,22] as well as on semiempirical density functional (DF) methods.[22] PIMC studies have shown evidence of a wetting transition for liquid $p$-$H_2$ on Rb and Cs at temperatures well above 20 K.

Here, we present detailed PIMC results for a model of $p$-$H_2$ film adsorbed on Li and Na substrates, in the temperature range between 2 and 13 K, i.e., significantly lower than

1098-0121/2004/70(12)/125405(7)/$22.50

that studied in Ref. 21. The most accurate potentials currently available are utilized to describe the interactions among $p$-$H_2$ molecules, as well as between the molecules and the substrates, which are regarded as smooth (i.e., corrugation is neglected).

The main results of this study are the following:

(1) No stable $p$-$H_2$ film forms on a Na substrate, in the $T \rightarrow 0$ limit; the same is expected to hold true *a fortiori* on a K substrate, which is more weakly attractive than Na.

(2) Adsorption on a Li substrate occurs through completion of successive solid layers. A stable solid $p$-$H_2$ monolayer exists, whose equilibrium coverage (i.e., 2D density) is $\theta_e = 0.070 \pm 0.001$ Å$^{-2}$. This is the same value (within statistical uncertainty) found on a smooth graphite substrate,[20] only slightly greater than the theoretically computed equilibrium density of 2D $p$-$H_2$ (see Ref. 9).

(3) The spread of a $p$-$H_2$ monolayer in the direction perpendicular to the substrate is significantly less than for a $^4$He monolayer, and its melting temperature is $\sim$6.5 K, i.e., very close to what has been theoretically predicted[19] for 2D $p$-$H_2$.

The quantitative similarity of the results obtained in this work to those involving different substrates, of greatly varying strength, suggests that the basic physics of this system is driven by the interaction among hydrogen molecules, and that the role of the substrate (if it is assumed smooth) is rather marginal.

Although the PIMC method utilized in this work allows for the sampling of permutations of particles, which is essential in order to reproduce in the simulation any effect due to quantum statistics, permutations are not seen to occur, in the temperature range explored. This is consistent with the conclusion reached in previous work by others.[19] In the crystal phase, permutations are suppressed (as in most solids) by the localization of $p$-$H_2$ molecules; at higher temperature, on the other hand, though the crystal melts and molecules are less localized, they also behave more classically, as their thermal wavelength decreases. Consistently with permutations not being important, i.e., $p$-$H_2$ molecules obeying Boltzmann statistics in the temperature range explored here, no evidence of SF can be seen.[23]

The remainder of this paper is organized as follows: in the next sections, the model Hamiltonian is introduced, and a brief description is provided of the most important aspects of the computational method utilized (PIMC), of which comprehensive reviews exist in the literature; we then illustrate our results and outline our conclusions.

## II. MODEL

Consistently with other theoretical studies, our system of interest is modeled as an ensemble of $N$ $p$-$H_2$ molecules, regarded as point particles, moving in the presence of an infinite, smooth planar substrate (positioned at $z=0$). The quantum-mechanical many-body Hamiltonian is the following:

$$\hat{H} = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i<j} V(r_{ij}) + \sum_{i=1}^{N} U(z_i). \qquad (1)$$

The system is enclosed in a vessel shaped as a parallelepiped, with periodic boundary conditions in all directions. Here, $m$ is the $p$-$H_2$ molecular mass, $V$ is the potential describing the interaction between two $p$-$H_2$ molecules, only depending on their relative distance, whereas $U$ is the potential describing the interaction of a hydrogen molecule with the substrate, also depending only on the distance of the atom from the substrate. The Silvera-Goldman potential[24] was chosen to model the interaction between two $p$-$H_2$ molecules; this potential has been shown to provide an acceptable quantitative description of bulk $p$-$H_2$ in the condensed phase.[25]

The following potential, proposed by Chizmeshya, Cole, and Zaremba[26] was adopted to describe the interaction of a $p$-$H_2$ molecule with a smooth substrate [i.e., the $U$ term in (1)]

$$U(z) = U_0(1+\alpha z)e^{-\alpha z} - \frac{C_{\mathrm{vdw}} f_2[\beta(z)(z-z_{\mathrm{vdw}})]}{(z-z_{\mathrm{vdw}})^3} \qquad (2)$$

with $f_2(x) = 1 - e^{-x}(1+x+x^2/2)$ and $\beta(x) = \alpha^2 x/(1+\alpha x)$. The first term in (2) represents the Pauli repulsion between the electronic cloud of the molecules and the surface electrons, whereas the second term expresses the Van der Waals attraction. The values of the parameters $U_0$, $\alpha$, $C_{\mathrm{vdw}}$, and $z_{\mathrm{vdw}}$ used here are the ones supplied in Ref. 26.

The above model is, clearly, highly simplified. By far the most important simplification consists of the neglect of substrate corrugation, whose role is significant for attractive substrates such as graphite,[20] but can be expected to be less important on substrates such as those of alkali metals, which are relatively weak.

## III. METHODOLOGY

The path integral Monte Carlo method is a numerical (quantum Monte Carlo) technique that allows one to obtain accurate estimates of physical averages for quantum many-body systems at finite temperature. The only input of a PIMC calculation is the many-body Hamiltonian (1) (which includes the potential energy functions $U$ and $V$). PIMC yields results that are affected only by a (small) statistical uncertainty, as well as by an error due to the finite size of a many-particle system that can be practically simulated on a computer. Computing facilities commonly available nowadays comfortably afford PIMC computations for systems of several hundred particles; this size is normally sufficient to obtain fairly accurate estimates of energetics and most structural properties of interest. PIMC simulations have been extensively adopted to study physisorption of helium on a variety of substrates, including alkali metals.[14]

Because thorough descriptions of the PIMC method can be found in the literature,[27] it will not be reviewed here. We only provide some relevant details, namely, as follows.

(1) We have experimented in this work with a high-temperature approximation for the many-body density matrix $G(R,R',\tau)$ which is accurate up to order $\tau^4$ (see, for instance, Ref. 28). This form is not as effective as the pair-product approximation (PPA), more commonly used in PIMC simulations[27] of highly quantal fluids, such as helium. We have empirically observed convergence of the energy

estimates with a time step $\tau = (1/320)\ \mathrm{K}^{-1}$, almost three times shorter than in comparable PIMC studies based on the PPA.[18,20] The use of the high-temperature density matrix considered here simplifies (in our view) the calculation, without rendering it unacceptably inefficient computationally. Accurate estimates for quantities other than the energy, such as film density profiles, can be usually obtained with twice as large a time step.

(2) A multilevel metropolis scheme based on the staging algorithm[29] with free-particle sampling was used to sample many-particle paths through configuration space. This technique has been shown to be an effective remedy to the inefficiency of single-slice sampling, at low temperature. We adjusted the length $\overline{\tau}$ of the portion of individual single-particle paths that the algorithm attempts to update, so that the acceptance rate remains above 20%. Typically, $\overline{\tau} \approx 0.025\ \mathrm{K}^{-1}$. Rigid displacements of single particle paths were performed as well. The average displacement was chosen to ensure an acceptance rate of approximately 50%.

(3) We have included in our calculation the sampling of cyclic permutations of groups of $p$-$H_2$ molecules, based on an algorithm very similar to that illustrated in Ref. 27. This procedure is not restricted to sampling groups of two, three or four molecules, but allows in principle cycles of arbitrary lengths (up to $N$) to be constructed. As mentioned in the Introduction, however, we found that, at the physical conditions explored in this work permutations occur exceedingly rarely. This could be the result of using less than optimal a sampling algorithm, but we have verified that our procedure is capable of sampling permutations, with reasonable efficiency, for bulk $^4$He (a simulated system of 64 atoms) at $T = 2$ K and saturated vapor pressure. Thus, we believe the absence of permutations in our simulation reflects a physical effect, in agreement with other authors.[18,19]

Physical quantities of interest, besides the kinetic, potential, and total ($e$) energy per molecule, are the $p$-$H_2$ density profiles as a function of the distance $z$ from the substrate, i.e.,

$$n(z) \equiv \frac{1}{A} \int dx\, dy \rho(x,y,z), \tag{3}$$

where $A$ is the area of the substrate and $\rho(x,y,z)$ is the three-dimensional (3D) $p$-$H_2$ density, as well as the the angularly averaged, "reduced" pair correlation function $g(r)$, with $r = \sqrt{x^2+y^2}$ and

$$g(x,y) = \frac{1}{A\theta^2} \int dx'\ dy'\ n(x+x',y+y')n(x',y'), \tag{4}$$

where $\theta = N/A$ is the coverage and with $n(x,y) = \int dz\ \rho(x,y,z)$. The correlation function $g(r)$ provides a quantitative assessment of the two-dimensional character of an adsorbed film; the more two dimensional an adsorbed film, the more closely $g(r)$ mimics the pair correlation function of a strictly two-dimensional system of the same coverage.

As for the typical size of the physical systems simulated in this work, for $\theta \leqslant \theta_0 = 0.072\ \text{Å}^{-2}$, PIMC calculations were carried out on a system of 36 $p$-$H_2$ molecules, initially arranged on a triangular lattice at a distance of 3 Å from the substrate. At higher coverage, the initial arrangement was taken to be a series of successive solid (triangular) layers, arranged as in a hexagonal close-packed lattice, each layer of 2D density $\theta_0$ and with an incomplete top layer. Films of up to three layers are studied. At the monolayer equilibrium coverage $\theta_e = 0.070\ \text{Å}^{-2}$, we also obtained results for a system of 144 particles. No noticeable dependence of the estimates on the size of the system can be observed for the physical quantities discussed here, with the exception of the energy. In all calculations, the height of the simulation box (i.e., the distance between the periodically replicated images of the substrate) is 30 Å, i.e., much greater than the maximum film thickness observed, so as to make the use of periodic boundary conditions in the $z$ direction (perpendicular to the substrate) uninfluent.

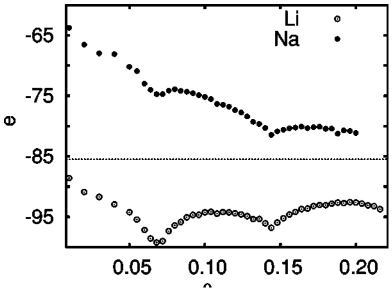

FIG. 1. Energy per molecule $e$ (in K) vs coverage $\theta(\text{Å}^{-2})$, for a $p$-$H_2$ film on Li (open symbols) and Na (filled symbols) substrates, computed by PIMC at a temperature $T = 2$ K. Dotted line represents the chemical potential of bulk $p$-$H_2$ at $T = 0$ (from Ref. 30). Statistical errors on the PIMC data are of the order of the symbol size.

## IV. RESULTS

PIMC result were obtained in this work for two substrates, namely Na and Li. Let us begin with an assessment of the energetics of the $p$-$H_2$ films on the two substrates.

Figure 1 shows computed values of the energy per $p$-$H_2$ molecule $e(\theta)$, as a function of coverage, on a Li and on a Na substrate, at a temperature $T = 2$ K. These numbers can be very reliably regarded as ground state estimates, as values of the energy computed below $T \approx 5$ K are found to be temperature independent, within the statistical uncertainties of the calculation. The dotted line in Fig. 1 represents the ground state energy per molecule ($e_b = -85.5$ K) of bulk $p$-$H_2$, in the fcc crystal structure, as computed by Silvera and Goldman[30] using self-consistent phonon theory.[31]

The two curves shown in Fig. 1 share some qualitative features, e.g., a succession of well-defined, equally spaced local minima, corresponding to adlayer completion. These minima occur at the same values of $\theta$ on both substrates, suggesting that the main player in the energy balance is the interaction potential among $p$-$H_2$ molecules.

Let us consider the case of Na first. Although it is (almost monotonically) decreasing, the $e(\theta)$ curve on Na appears to be flattening off, approaching the value $e_b$ from above, asymptotically. This indicates that no film of any thickness will form, i.e., that $p$-$H_2$ will not wet Na, at low $T$. Clearly, this conclusion can only be made tentatively, based on the results obtained up to a value of the coverage $\theta=0.2$ Å$^{-2}$. It is possible that a stable (thick) film may exist. On performing PIMC calculation on systems twice the size of that considered here, one could establish more robustly the trend observed here; however, even in that case one would need to supplement the information provided by PIMC with some other calculation (perhaps DF), capable (at least in principle) of making predictions in the $\theta\rightarrow\infty$ limit.

Assuming that on Na one indeed has a nonwetting situation, one question that arises is that of the temperature associated to the wetting transition; this issue was not addressed in this work.

On Li, on the other hand, the $e(\theta)$ curve is monotonically decreasing for $\theta\leqslant\theta_e$, with $\theta_e\approx0.070$ Å$^{-2}$; it attains a minimum at $\theta_e$, with $e(\theta_e)\approx-100$ K, i.e., below $e_b$, and displays a slowly increasing trend (while going through well-defined local minima, as mentioned above) for greater values of $\theta$. It seems physically reasonable to expect that $e(\theta)$ should also flatten off, and approach $e_b$ from below, in the $\theta\rightarrow\infty$ limit, though, again, the finite size limitation of this calculation does not allow us to make this conclusion firmly.

The local minima of $e(\theta)$ correspond to successive solid layers (more about this later in the paper); between these minima, films are thermodynamically unstable. This situation is physically quite different from the case of a $^4$He film on the same substrate, for which continuous growth of film thickness as a function of chemical potential is observed, with no layering.[33]

### A. $p$-H$_2$ monolayer on Li substrate

In the remainder of this paper, we shall concentrate on the substrate on which thermodynamically stable $p$-H$_2$ films are seen to form, i.e., Li. Completion of the first layer occurs at a coverage $\theta=0.070\pm0.001$. This value is consistent with that found on a smooth graphite substrate,[20] even though such a substrate is over four times more attractive (of course, corrugation plays a significant role on graphite). It is also only slightly above the equilibrium density[9] of pure 2D $p$-H$_2$.

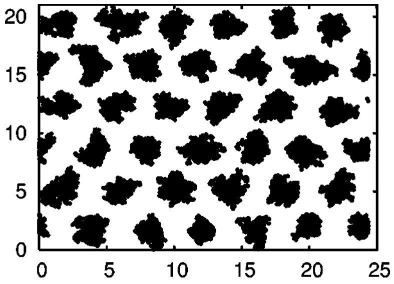

FIG. 2. Typical many-particle configuration for a $p$-H$_2$ monolayer film adsorbed on a Li substrate (top view) at a temperature $T=2$ K. Each black "cloud" represents one of 36 $p$-H$_2$ molecules. Periodic boundary conditions are used in both directions. The arrangement of the molecules on a triangular lattice is clearly seen, as well as the absence of overlap among different "clouds," to show that quantum exchanges are unimportant in this system, at this temperature.

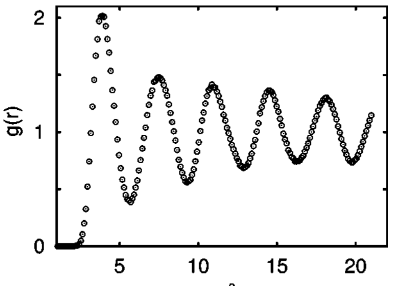

FIG. 3. Reduced pair correlation function $g(r)$, defined through Eq. (4), computed by PIMC for a $p$-H$_2$ monolayer film adsorbed on a Li substrate, at coverages $\theta=0.070$ Å$^{-2}$ and $T=2$ K. Statistical errors are smaller than symbol sizes. The curve is virtually indistinguishable from the pair correlation function for 2D $p$-H$_2$ at the same coverage, at $T=0$.

This suggests that, as long as the substrate is sufficiently strong to stabilize a film, the basic physics of an adsorbed $p$-H$_2$ monolayer film is largely substrate independent, driven primarily by the interaction potential between $p$-H$_2$ molecules. Figure 2 shows an instantaneous "snapshot" of a many-particle configuration for an adsorbed film at the equilibrium density (top view). Each fuzzy "cloud" represents a single molecule; the characteristic size of a cloud gives a quantitative measure of the effect of zero point motion. The arrangement of all molecules on a triangular lattice is fairly clear. Also apparent is the lack of any substantial overlap between different clouds, to indicate that permutations of particles are unimportant in this system.

More quantitative structural information is furnished by the density correlation function $g(r)$, defined in Eq. (4) and shown in Fig. 3. The computed $g(r)$ at $\theta=\theta_e$ is found to be virtually indistinguishable from the pair correlation function in strictly two-dimensional $p$-H$_2$, at the same coverage (and at $T=0$).[34]

Figure 4 shows the $p$-H$_2$ density profile in the direction ($z$) perpendicular to the substrate (solid line). Also shown, for comparison, is the corresponding density profile for a monolayer $^4$He film adsorbed on the same substrate, at $T=0$ (from Ref. 33). The $p$-H$_2$ film rests in closer proximity to

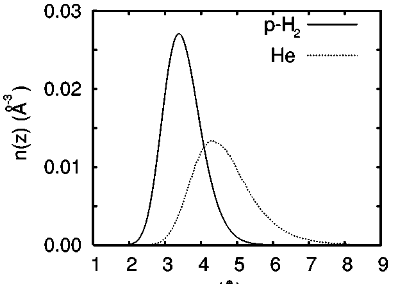

FIG. 4. Density profile $n(z)$ (Å$^{-3}$) in the direction $z$(Å) perpendicular to a Li substrate, for a $p$-H$_2$ monolayer film of coverage $\theta_e=0.070$ Å$^{-2}$ and at $T=2$ K (solid line). Statistical errors cannot be seen on the scale of the figure. Dotted line shows, for comparison, the corresponding density profile for a monolayer $^4$He film on the same substrate, at $T=0$ and at the equilibrium coverage $\theta_e=0.052$ Å$^{-2}$ (from Ref. 33).

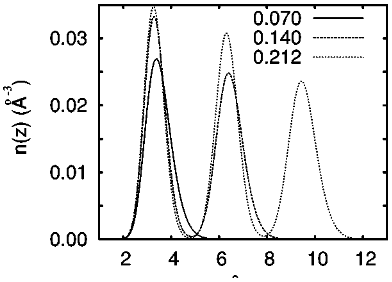

FIG. 5. Density profiles $n(z)$ (Å$^{-3}$) in the direction $z$(Å) perpendicular to a Li substrate, for $p$-$H_2$ films of varying coverage, corresponding to one, two, and three layers, at $T=2$ K. Statistical errors cannot be seen on the scale of the figure.

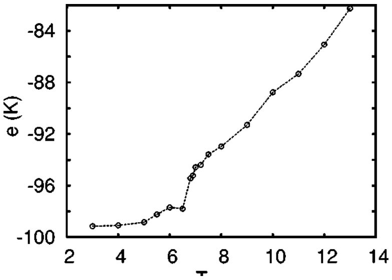

FIG. 6. Energy per molecule $e(T)$ for a $p$-$H_2$ monolayer adsorbed on a Li substrate. The coverage is 0.070 Å$^{-2}$. The change of slope of the curve at $T \approx 6.5$ K is evident. Results shown correspond to a system of 144 particles.

the substrate (by approximately 1.5 Å) with respect to the helium one, and has about half the width. Thus, the physics of a $p$-$H_2$ monolayer is even more 2D than that of one of He. Moreover, the kinetic energy per $p$-$H_2$ molecule at this coverage, in the $T \to 0$ limit is worth approximately 40 K, i.e., ~30% more than in a purely 2D $p$-$H_2$ system at the same coverage;[34] this should be compared to the factor of 2 difference in kinetic energy between 2D $^4$He and an adsorbed $^4$He film on Li (from Ref. 33).

In spite of their lighter mass, $p$-$H_2$ molecules experience a lesser degree of zero-point delocalization in the perpendicular direction, because of the much stronger attraction to the substrate,[26] as well as to the other molecules. As more layers are adsorbed on the substrate, zero-point molecular motion in the perpendicular direction is suppressed even further in the underlying layers, which become more compressed (see Fig. 5).

### B. Melting of a $p$-$H_2$ monolayer

In order to study the melting of a solid $p$-$H_2$ monolayer at the determined equilibrium coverage (namely $\theta = 0.070$ Å$^{-2}$), we computed the energy per molecule of the system as a function of temperature $[e(T)]$. Melting corresponds to a peak in the specific heat $c_V = (\partial e / \partial T)$. The specific heat can show several such "anomalies," corresponding to different transitions (e.g., solid to solid-vapor coexistence); several peaks are indeed observed in numerical simulations on graphite, for a commensurate solid layer with vacancies.[20] In order to reduce the smearing of the peaks, which inevitably occurs when one is performing a numerical study on a system of finite size, we increased the number of particles from 36 to 144 in this calculation, corresponding to a simulation cell in which the area of the substrate $A$ equals 48.74 Å × 42.21 Å. Results are shown in Fig. 6 and summarized in Table I. The energy estimates are not corrected for the long-range tail of the interaction potential between $p$-$H_2$ molecules, which is truncated at 21 Å in the simulation (potential truncation is routinely done when studying finite systems with periodic boundary conditions). We estimate the correction on the total energy to be worth no more than 0.03 K.

The results of Table I show that the dependence of the total energy per molecule on the temperature reflects essentially that of the potential energy alone, as the kinetic energy depends weakly on temperature, for this adsorbed monolayer film. The determination of values for the specific heat from the energy estimates can be made by numerical differentiation, but it is difficult to obtain accurate results in this way. Moreover, our primary objective was to locate the occurrence of the phase transition, and the figure clearly suggests a melting temperature $T_m \approx 6.5$ K, which is where the computed $e(T)$ curve displays a sudden, abrupt change of slope.

These results are similar to those obtained by Wagner and Ceperley, who studied the melting of a $p$-$H_2$ surface.[18,19] The computed melting temperature is also quite close to the theoretical 2D result.[19] This suggests that this system may pro-

TABLE I. Kinetic, potential, and total energy per $p$-$H_2$ molecule (in K) on a Li substrate, computed by PIMC at a coverage $\theta = 0.070$ Å$^{-2}$ at different temperatures. Results are for a 144-particle system. Statistical errors (in parentheses) are on the last digit(s). These estimates are not corrected for the long-range tail of the interaction potential between $p$-$H_2$ molecules, which is cut off at 21 Å. We estimate the correction on the total energy to be worth no more than 0.03 K.

| $T$ | Kinetic | Potential | Total |
|---|---|---|---|
| 3.0 | 39.86(5) | −139.007(13) | −99.15(5) |
| 4.0 | 39.87(4) | −138.949(14) | −99.08(4) |
| 5.0 | 39.99 (3) | −138.822(16) | −98.83(4) |
| 5.5 | 39.95(7) | −138.183(89) | −98.23(6) |
| 6.0 | 40.07(8) | −137.77(28) | −97.69(27) |
| 6.5 | 40.26(9) | −138.05(11) | −97.79(13) |
| 6.8 | 39.63(14) | −135.06(25) | −95.43(14) |
| 6.9 | 39.75(12) | −134.98(28) | −95.22(19) |
| 7.0 | 39.17(15) | −133.75(20) | −94.58(14) |
| 7.2 | 39.40(18) | −133.79(16) | −94.39(12) |
| 7.5 | 39.48(10) | −133.06(17) | −93.58(12) |
| 8.0 | 39.04(11) | −132.00(15) | −92.97(16) |
| 9.0 | 39.16(11) | −130.45(12) | −91.30(7) |
| 10.0 | 38.82(8) | −127.59(13) | −88.77(10) |
| 11.0 | 39.43(13) | −126.76(16) | −87.33(17) |
| 12.0 | 40.01(14) | −125.07(13) | −85.07(13) |
| 13.0 | 40.01(15) | −122.27(15) | −82.27(20) |

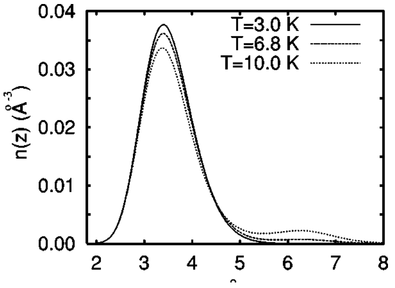

FIG. 7. Density profiles $n(z)$ (Å$^{-3}$) in the direction $z$(Å) perpendicular to a Li substrate, for $p$-$H_2$ films of coverage $\theta=0.070$ Å$^{-2}$, corresponding to one layer, at three different temperatures. The melting temperature is estimated at $T_m=6.5$ K. Statistical errors cannot be seen on the scale of the figure. As the temperature is raised, second layer promotion of molecules is observed.

vide a rather close experimental realization of a 2D system, in many respects even more so than an adsorbed helium film.

The problem of melting of a 2D solid is interesting and, to a considerable degree, still open. In particular, the transition from a solid to a liquid phase can be either discontinuous or continuous, the system going, in the latter case, through an intermediate, "hexatic" phase featuring local sixfold, bond-angle order.[35] Such a hexatic case can then melt into a disordered fluid as a result of unbinding of dislocations.[36] The results of this study point to a $p$-$H_2$ monolayer adsorbed on a Li substrate as a candidate to observe such a scenario experimentally.

In numerical simulations, on the other hand, unambiguous confirmation of dislocation-mediated melting is complicated by the finite size of the system that can be studied in practice.[37] Figure 7 shows density profiles computed at three different temperatures, below, above, and close to the melting temperature. They clearly suggest that melting occurs concurrently with second layer promotion; one can therefore opine that melting occurs microscopically with the formation of vacancies in the bottom layer. Visual inspection of instantaneous many-particle configurations (an example is shown in Fig. 8, for a temperature $T=8$ K) at temperatures just above $T_m$ indeed seems to indicate the presence of vacancies (and dislocations) in the bottom layer.

## V. CONCLUSIONS

Adsorption of $p$-$H_2$ on alkali metal substrates was studied theoretically by means of path integral Monte Carlo simulations. In order to assess the expected relevance of the results presented here to experiments, one clearly needs to assess quantitatively the limitations of the model utilized, as well as those of the calculation.

A major simplification of the model considered here is the neglect of substrate corrugation, i.e., the substrate is regarded as smooth; this is based on the relative weakness of these substrates, but clearly the validity of this assumption must be assessed with further study. Also absent in this work is any substrate-mediated interaction among $p$-$H_2$ molecules. In the system considered here, its neglect seems justified, again based on the weakness of the physisorption potential. In the case of more strongy attractive substrates, or of a nanostructure, a substantial renormalization of the effective interaction of $p$-$H_2$ molecules may ensue, possibly greatly enhancing quantum effects.

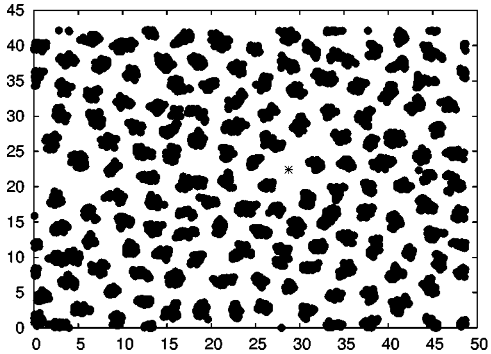

FIG. 8. Typical many-particle configuration for a $p$-$H_2$ film adsorbed on a Li substrate (top view) at a temperature $T=8$ K. Each fuzzy "cloud" represents one of 112 $p$-$H_2$ molecules in the bottom (first) adlayer, the remaining 32 molecules in the system having been promoted to the second layer. Periodic boundary conditions are used in both directions. The star at approximately (29,22) indicates the location of a vacancy.

The potential used here to describe the interaction between two $p$-$H_2$ molecules, namely the Silvera-Goldman potential, is the one for which most of the previous Monte Carlo simulations have been carried out. It is known to be reasonably accurate, even though a comprehensive, quantitative assessment is, to our knowledge, still lacking. Its main limitation is that of being merely a two-body potential. Although it is designed to incorporate, at least in part, effects of three-body interactions, this is done only in an effective way. Nonetheless, it seems unlikely (to us) that the use of a more refined version of the interaction would significantly, qualitatively change the results. More important seems the uncertainty of the substrate-adatom potential. The potentials used in this calculation are the most current, and are a significant improvement over the early "3-9" potential, both with respect to the functional form as well as the value of the most important parameters (e.g., the well depth). However, their absolute accuracy has not yet been quantitatively assessed; to that aim, additional experimental input may be needed.

We computed energetics for adsorbed films on both Li and Na substrates; results show that thermodynamically stable adsorbed $p$-$H_2$ films will form on Li, whereas a Na substrate (and therefore all other alkali metal substrates, which are even weaker than Na) is too weakly attractive for a stable film to form. This result is consistent with the experimental observation of a wetting transition on Cs and Rb.[15–17] Such a transition is predicted to occur on Na and K substrates as well, most likely at a temperature above the critical temperature, as observed on Rb. We also investigated thermodynamic properties of a $p$-$H_2$ monolayer on a Li substrate. This system has an equilibrium coverage at low temperature essentially identical to that on graphite, approximately 0.070 Å$^{-2}$, and is considerably more two-dimensional than a $^4$He monolayer adsorbed on the same (Li) substrate, owing to the much stronger attraction to the substrate experienced by a $p$-$H_2$ molecule with respect to a $^4$He atom. We determined the melting temperature of the monolayer to be approximately 6.5 K, which is very close to a theoretically computed 2D value. While this value is considerably lower than the 3D one ($\sim$13 K), it is still much higher than the temperature at which quantum exchanges are expected[9] to become significant ($\sim$1 K). As exchanges, and long cycles of particle permutations are known to be crucial to the onset of superfluidity,[27] this system does not appear to offer a promising avenue for the observation of a SF transition in $p$-$H_2$. Because a Li substrate is observed to be relatively strong, whereas a Na one is already too weak to allow adsorption, one might wonder whether a substrate made of an alloy of Li and Na (or, Li and another alkali metal) might have intermediate properties, possibly leading to enhanced zero point motion in the perpendicular direction and increased quantum character. Theoretical investigation of adsorption on such a "hybrid" substrate is under way.

## ACKNOWLEDGMENTS

This work was supported in part by the Petroleum Research Fund of the American Chemical Society under research Grant No. 36658-AC5, and by the Natural Science and Engineering Research Council of Canada under research Grant No. G121210893. The author wishes to acknowledge useful discussions with M. W. Cole.

---

[1] See, for instance, L. W. Bruch, M. W. Cole, and E. Zaremba, *Physical Adsorption: Forces and Phenomena* (Clarendon, Oxford, 1997).

[2] V. L. Ginzburg and A. A. Sobyanin, JETP Lett. **15**, 242 (1972).

[3] M. Bretz and A. L. Thomson, Phys. Rev. B **24**, 467 (1981).

[4] G. M. Seidel, H. J. Maris, F. I. B. Williams, and J. G. Cardon, Phys. Rev. Lett. **56**, 2380 (1986).

[5] H. J. Maris, G. M. Seidel, and F. I. B. Williams, Phys. Rev. B **36**, 6799 (1987).

[6] M. Schindler, A. Dertinger, Y. Kondo, and F. Pobell, Phys. Rev. B **53**, 11451 (1996).

[7] P. Sindzingre, D. M. Ceperley, and M. L. Klein, Phys. Rev. Lett. **67**, 1871 (1991).

[8] S. Grebenev, B. Sartakov, J. P. Toennies, and A. F. Vilesov, Science **289**, 1532 (2000).

[9] M. C. Gordillo and D. M. Ceperley, Phys. Rev. Lett. **79**, 3010 (1997).

[10] M. Nielsen, J. P. McTague, and L. Passell, in *Phase Transitions in Surface Films*, edited by J. Dash and J. Ruvalds (Plenum, New York, 1980).

[11] H. J. Lauter, H. Godfrin, V. L. P. Frank, and P. Leiderer, in *Phase Transitions in Surface Films 2*, edited by H. Taub, G. Torzo, H. J. Lauter, and S. C. Fain, Jr. (Plenum, New York, 1990).

[12] H. Wiechert, in *Excitations in Two-Dimensional and Three-Dimensional Quantum Fluids*, edited by A. F. G. Wyatt and H. J. Lauter (Plenum, New York, 1991).

[13] F. C. Liu, Y. M. Liu, and O. E. Vilches, J. Low Temp. Phys. **89**, 649 (1992).

[14] M. Boninsegni, M. W. Cole, and F. Toigo, Phys. Rev. Lett. **83**, 2002 (1999).

[15] E. Cheng, G. Mistura, H. C. Lee, M. H. W. Chan, M. W. Cole, C. Carraro, W. F. Saam, and F. Toigo, Phys. Rev. Lett. **70**, 1854 (1993).

[16] G. Mistura, H. C. Lee, and M. H. W. Chan, J. Low Temp. Phys. **96**, 221 (1994).

[17] D. Ross, P. Taborek, and J. E. Rutledge, Phys. Rev. B **58**, R4274 (1998).

[18] M. Wagner and D. M. Ceperley, J. Low Temp. Phys. **94**, 161 (1994).

[19] M. Wagner and D. M. Ceperley, J. Low Temp. Phys. **102**, 275 (1996).

[20] K. Nho and E. Manousakis, Phys. Rev. B **65**, 115409 (2002).

[21] W. Shi, J. K. Johnson, and M. W. Cole, Phys. Rev. B **68**, 125401 (2003).

[22] M. Boninsegni and L. Szybisz, J. Low Temp. Phys. **134**, 315 (2004).

[23] The possible occurrence of SF in a solid layer of $p$-$H_2$ was not explored in this work.

[24] I. F. Silvera and V. V. Goldman, J. Chem. Phys. **69**, 4209 (1978).

[25] Q. Wang, J. K. Johnson, and J. Q. Broughton, Mol. Phys. **89**, 1105 (1996).

[26] A. Chizmeshya, M. W. Cole, and E. Zaremba, J. Low Temp. Phys. **110**, 677 (1998).

[27] D. M. Ceperley, Rev. Mod. Phys. **67**, 279 (1995).

[28] S. Jang, S. Jang, and G. A. Voth, J. Chem. Phys. **115**, 7832 (2001).

[29] E. L. Pollock and D. M. Ceperley, Phys. Rev. B **30**, 2555 (1984).

[30] I. Silvera, Rev. Mod. Phys. **52**, 393 (1980).

[31] It is worth mentioning that an earlier analysis of experimental data by Schnepp (Ref. 32) yielded a lower value, namely −89.9 K.

[32] O. Schnepp, Phys. Rev. A **2**, 2574 (1970).

[33] M. Boninsegni and L. Szybisz, Phys. Rev. B **70**, 024512 (2004).

[34] The physical properties of a purely two-dimensional $p$-$H_2$ system at coverage 0.070 $\text{Å}^{-2}$ in the ground state have been studied separately by Quantum Monte Carlo simulations. Details of that calculation will be published elsewhere.

[35] See, for instance, P. M. Chaikin, and T. C. Lubenski, *Principles of Condensed Matter Physics* (Cambridge, University Press, Cambridge1995), p. 555.

[36] D. R. Nelson and B. I. Halperin, Phys. Rev. B **19**, 2457 (1979).

[37] See, for instance, K. J. Strandburg, Rev. Mod. Phys. **60**, 161 (1988).