PATH INTEGRAL MONTE CARLO SIMULATIONS OF
H₂ SURFACES

Marcus Wagner and David M. Ceperley

Beckman Institute,
National Center for Supercomputing Applications,
and Department of Physics
University of Illinois at Urbana-Champaign
1110 W. Green St., Urbana, IL 61801

Abstract

The (1,1,1)-surfaces of bulk solid molecular hydrogen have been studied at temperatures between 0.5K and 1.3K, using path integral Monte Carlo. A general method is introduced for constructing an external potential to represent the tail correction for an arbitrary heterogeneous layered bulk substrate-adsorbate system. We compute density profiles parallel and perpendicular to the free H₂ surface, total energies, and the surface tension. The structure of partial (not completely filled) surface layers is investigated and found liquid for some filling fractions. Quantum exchange of H₂ molecules at the free surface is observed and the possibility of superfluidity in a surface layer of H₂ is discussed.
I. INTRODUCTION

Little is known about the surface of solid H\textsubscript{2}. Silvera\textsuperscript{1} gives a comprehensive review of its molecular bulk solid. Due the small mass, the zero point energy of H\textsubscript{2} molecules in bulk is on the same order of magnitude as the potential energy, leading to a rather weak binding energy. The thermal wavelength of H\textsubscript{2} (\(\approx 12.3 \text{\AA} \, K/T^{1/2}\)) is several times the nearest neighbor distance for \(T \lesssim 9\text{K}\). Therefore delocalization effects are essential and quantum exchange needs to be considered at the surface.

Experimental observations\textsuperscript{2} show the solid hydrogen surface to be very dynamic, and it may have a terrace structure\textsuperscript{3,4,2}. Since H\textsubscript{2} molecules are bosons, Ginzburg and Sobbyanin\textsuperscript{5} argued that in analogy to \(^4\text{He}\), liquid hydrogen will be superfluid, if it could be supercooled from its melting temperature (\(T=13.8\text{K}\) at low pressure) down to about 6K. They further suggested that superfluidity of H\textsubscript{2} films might be possible, because the lower density might allow hydrogen to stay liquid at low enough temperatures. Their work sparked a continuing search for thin liquid H\textsubscript{2} films at low temperatures\textsuperscript{6-8}. However, the goal of finding a new superfluid has so far proved elusive. The lowest freezing temperature of para-hydrogen Torii \textit{et al.}\textsuperscript{6} have observed in Vycor glass is 8.5K. Vilches\textsuperscript{7} and Liu \textit{et al.}\textsuperscript{8} succeeded in keeping H\textsubscript{2} monolayers on preplated graphite liquid down to \(T=5.74\text{K}\), which is, however, still too high for superfluidity in two dimensions.

Clearly, these fascinating aspects of the hydrogen surface require further investigation. In the present work, we will focus on the free surface of bulk H\textsubscript{2} in the temperature range between 0.5K and 1.3K. The next section is a brief review of some aspects of the Path Integral Monte Carlo (PIMC) method underlying our computations. The third section introduces a procedure to incorporate the long range contributions to the system with an external
potential, and our choice of the pair potential between H\textsubscript{2} molecules will be motivated in section IV. Section V discusses energies and profiles, beginning with bulk H\textsubscript{2} at T=0.5K. This is followed by the results for the free H\textsubscript{2} surface, i.e. the bulk H\textsubscript{2}-vacuum interface, which is taken in (1,1,1) direction, where it is close packed. Then, we elaborate on the case of a free H\textsubscript{2} surface with a “partially filled” top layer. This is a particularly interesting topic, because it not only allows the simulation of surface imperfections, such as steps and islands, but also enables us to investigate the possibility of the existence of a thin liquid surface layer of H\textsubscript{2} on the H\textsubscript{2} substrate, which would at these temperatures be a candidate for a superfluid transition\textsuperscript{9}. Section VI concludes this paper with a discussion of quantum exchange effects in the partial adlayer and the prospect of superfluidity.

**II. COMPUTATIONAL METHOD**

Path Integral Monte Carlo (PIMC) is a computational method for quantum many-body properties at finite temperatures, based on Feynman’s\textsuperscript{10,11} path integral formalism which is an exact mapping of a quantum system on a classical particle system. It has proven\textsuperscript{12,13} an accurate tool for computing the static properties of quantum systems, such as bulk \textsuperscript{4}He. A detailed description of the method has been given elsewhere\textsuperscript{14}.

All equilibrium properties of the N-particle system at the inverse temperature $\beta = 1/k_B T$ can be obtained from the many-body density matrix

$$\rho(R, R'; \beta) = \langle R | e^{-\beta H} | R' \rangle$$

which is expanded into a path of $M$ steps in imaginary time, each step or “time slice” of duration $\tau = \beta / M$
\[ \rho(R, R'; \beta) = \int dR_1 \cdots dR_{M-1} \rho(R, R_1; \tau) \rho(R_1, R_2; \tau) \cdots \rho(R_{M-1}, R'; \tau) \]  

(2)

where \( R \) stands for the \( 3N \) coordinates in continuous real \( 3D \) space. One can think of a particle’s path as a polymer with \( M \) beads. The beads of a polymer interact only with beads of other polymers on the same time slice. One splits the many-body density matrix at \( \beta \) into \( M \) density matrices at \( \tau = \beta/M \) since one can accurately approximate the many body density matrix at high temperature. If only the diagonal of the many-body density matrix is needed, i.e. \( R = R' \) in Eq.(2), then each particle’s path corresponds to a ring polymer.

Figs. (1.a) and (1.b) show a crystalline layer of 56 \( \text{H}_2 \) molecules in the \( x-y \) plane with periodic boundary conditions, and a liquid layer of 28 \( \text{H}_2 \) molecules. The first of 80 time slices of each molecule is marked by a circle. These figures will be discussed below in the context of partially filled hydrogen layers.

Define the action in time slice \( k \) as

\[ S_k = -\ln \rho(R_k, R_{k+1}; \tau) . \]  

(3)

We used the following approximation for the action:

\[ S_k = \frac{3N M}{2} \ln(4\pi \lambda \tau) + \sum_i \frac{(\Delta \vec{r}_i)^2}{4 \lambda \tau} + \sum_{i<j} U(\vec{r}_{ij}, \vec{r}_{ij}'; \tau) + \sum_i U_{\text{ext}}(r_i; \tau) , \]

(4)

where \( U(\vec{r}_{ij}, \vec{r}_{ij}'; \tau) \) is the exact two-body density matrix, for the interaction between particles \( i \) and \( j \), and \( \vec{r}_{ij} \) the distance vector between \( i \) and \( j \) at time slice \( k \); \( \vec{r}_{ij}' \) at time slice \( k + 1 \), \( \lambda \equiv \hbar^2/2m \), and \( \Delta \vec{r}_i \) is the displacement of particle \( i \) from one time slice to the next. \( U_{\text{ext}} \) is the action due to an arbitrary external potential. Because the external potentials used here are weak and slowly varying, we use the primitive approximation:

\[ U_{\text{ext}}(r; \tau) \simeq \tau V_{\text{ext}}(r) . \]  

(5)
The external potential $V_{ext}$ will play an important role in characterizing layered systems and surface adsorption, and will be the central issue of the next section. To minimize computer time a large time step is desirable. Conversely, the smaller the time step the more precise $\rho(R_k, R_{k+1}; \tau)$ can be expressed. For simulations of $^4$He below the superfluid transition, a "time step" of $\tau = 1/40K$ has been found sufficient\textsuperscript{14} implying that we use 80 time steps for a simulation at $T=0.5K$.

The many-body density matrix from Eq. (1) must be symmetrized to account for the particle exchanges in a Bose system:

$$\rho_{\text{Bose}}(R, R'; \beta) = \frac{1}{N!} \sum_P \rho(R, P R'; \beta),$$

where $P$ is a permutation. The total configuration space is thus given by the permutation, $P$, i.e. the labelling of the particles, and the spatial coordinates $R_k$ at all $M$ time slices. For further details on the construction of the many body density matrix, the sampling algorithm, and the implementation, see Ref. [14].

### III. THE EXTERNAL POTENTIAL

To extend the range of applications of PIMC to layered quantum systems and surface adsorption we introduce an external potential, so that our small finite system will be closer to the thermodynamic limit. In particular, there are two effects we wish to approximate: the interaction of the surface particles with the substrate not explicitly represented, and the effect of interaction of two particles on the surface with a separation greater than half the size of the simulation box.

Let us introduce a terminology which we will use throughout the remainder of the paper. By an **explicit** layer, we mean one where the particles’ coordinates are explicitly represented.
An explicit layer can either be dynamic, in which case the particles’ paths are dynamically sampled or frozen, in which case the coordinates of the path are unchanged from the beginning of the calculation to the end. In contrast to explicit, in a model layer, only the mean density of its atoms interacts with the explicit particles. We use the model layers to represent all of the particles deep inside the bulk that we do not wish to explicitly carry along in the simulation. They simply contribute to an external potential which the explicit layers see. By $\rho^i(\vec{r})$ is meant the number density of the $i$-th layer, either explicit or model.

We apply periodic boundary conditions in two directions parallel to the surface, and use the minimum image convention, and cut-off all pair interactions beyond a distance $r_c \leq \min(L_x, L_y)/2$. To avoid a discontinuity at $r_c$ which could cause unphysical correlations, we shift the potential so that it is continuous at $r_c$. Thus the short-ranged potential used is:

$$\tilde{\phi}(r) = \begin{cases} 
\phi(r) - \phi(r_c) & , r < r_c \\
0 & , r \geq r_c .
\end{cases} \quad (7)$$

To correct for this shift we add a contribution to the external potential. The potential energy due to the cutoff potential on explicit layer $E$ seen by a particle $i$ at position $\vec{r}$ is:

$$w^E_i(\vec{r}) = \int d^3r' \delta \phi^E_i(|\vec{r} - \vec{r}'|) \rho^E(\vec{r}') , \quad (8)$$

where $\delta \phi = \phi - \tilde{\phi}$. We have assumed that we can take the mean density $\rho^E$ of the explicit layer instead of the actual two particle density i.e., the deviation of the actual density from the mean density at a distance larger than $r_c$ is neglected.

The second effect we included in the external potential is the interaction of an explicit atom with a model layer. The effect on the potential energy of particle $i$ at position $\vec{r}$ is:

$$w^M_i(\vec{r}) = \int d^3r' \phi^M_i(|\vec{r} - \vec{r}'|) \rho^M(\vec{r}') . \quad (9)$$
Assuming the density is uniform in the $x$-$y$ plane one can write the above two integrals in cylindrical coordinates as:

$$w(z) = 2\pi \int_{-\infty}^{\infty} dz' \rho(z') \int_{0}^{\infty} x dx \phi(\sqrt{x^2 + (z-z')^2})$$

$$= 2\pi \int_{-\infty}^{\infty} dz' \rho(z') t(|z-z'|) ,$$

where $t(s) = \int_{s}^{\infty} s' ds' \phi(s')$.

Then the total action seen by particle $i$ at position $\vec{r}$ is:

$$U_i(\vec{r}) = \sum_{j \neq i} u_{ij}(\vec{r}_{ij}; \tau) + \tau \sum_{k} w_{ij}^k(\vec{r}) ,$$

where the sum $k$ is over explicit and model layers, including the one particle $i$ belongs to. This external action is used in the PIMC simulation.

There is an important distinction between explicit and model layers in the way in which the external potential contributes to the total energy. We define the total energy of the explicit layers as:

$$E_t = \left\langle \sum_{i<j} \phi_{ij}(\vec{r}_{ij}) + \sum_{i,M} w_{i}^{M}(\vec{r}_{i}) + \frac{1}{2} \sum_{i,E} w_{i}^{E}(\vec{r}_{i}) \right\rangle ,$$

where the brackets $<>$ indicate averaging over the paths. The factor of $\frac{1}{2}$ for explicit layer interaction needs to be there to avoid double counting. Thus our zero of energy is when the explicit layers are absent.

Now, to represent the density of either an explicit or model layer, we assume it is Gaussian, and homogeneous in the $x$ and $y$ direction:

$$\rho_k(\vec{r}) = \frac{\sigma_k}{(2 \pi w_k^2)^{1/2}} e^{-\frac{(x-z_k)^2}{2w_k^2}} .$$

The parameters here are the coverage $\sigma_k$ (number of particles per area), the center, $z_k$, and the width, $w_k$. Deep inside the surface, solid hydrogen is a typical quantum crystal and its
density distribution around the lattice sites is known to be Gaussian. In this case, we use experimental data\(^1\) to determine our layer parameters. The layer separation in the \((1,1,1)\) direction of the fcc crystal \(z_k - z_{k-1} = 3.09\text{Å}\), the coverage \(\sigma_k = 0.0804\text{Å}^{-2}\) comes from the density, and the layer width, \(w_k = 0.40\text{Å}\) is the experimental rms value of the zero point motion in the \(z\)-direction. For the explicit layers we also use Gaussians. Fig. (2) shows \(\text{H}_2\) density profiles perpendicular to the surface obtained from the PIMC simulation overlayed with the “explicit” Gaussian layers to represent them in the external potential. We determine \(z_k\) and \(w_k\) by calculating the first and second moments of the density profile. Iterating an input set of layers once with PIMC is usually sufficient to obtain self consistency in potential energy per particle to the order of 0.1K. In the case when the layer profile is not well described by a Gaussian it is straightforward to use a computed density in Eqs. (8) and (9).

IV. \(\text{H}_2\)-\(\text{H}_2\) PAIR POTENTIAL

The simulations described in this paper always represent the \(\text{H}_2\) molecules as spherical particles interacting via a semi-empirical pair potential. The spherical approximation is good because in thermal equilibrium at \(T=0.5\text{K}\), almost all \(\text{H}_2\) is of the para-hydrogen species, i.e. in the rotational ground state (\(J=0\)). The ratio of the minor to the major axis of the ellipsoidal electronic charge distribution of the \(\text{H}_2\) molecule is 0.94\(^1\). At low temperature one can average over the angular dependence of the \(\text{H}_2\)-\(\text{H}_2\) pair potential\(^{15}\), due to the large inter-molecular separation. Consider the averaging due to zero point rotation. The first excited state of a free para-hydrogen molecule (\(J=2\)) has an energy 509.9K higher than the ground state, and is not thermally occupied. The characteristic time for rotational excitations is
short compared to the time step $\tau = 1/40K$ in our PIMC simulations, introduced in Eq. (2). Therefore, the molecule will have rotated many times between two steps in the simulation and will have done the rotational averaging. To be more specific, consider the expansion of the density matrix of a single $\text{H}_2$ molecule:

$$\langle \Omega | e^{-H\tau} | \Omega' \rangle = \sum_{l=0}^{\infty} \frac{(2l+1)}{4\pi} P_l(\cos \Theta) e^{-E_l \tau},$$

where $\Omega$ is the unit bond vector, $\Theta$ is the angle between $\Omega$ and $\Omega'$, and $P_l$ is a Legendre polynomial. Thus, the first allowed excited state is weighted by $exp\{-509.9K/40K\} \approx 3 \times 10^{-6}$ less than the ground state, rendering it insignificant for our purposes.

We choose the semiempirical potential from Silvera and Goldmann\textsuperscript{15} as shown in Fig. (3) to represent the interaction between two $\text{H}_2$ molecules because it seems to be the most reliable pair potential in the regime of low pressure and temperature, and has already been used successfully in PIMC simulations of $\text{H}_2$ clusters by Sindzingre et al.\textsuperscript{16} and, more recently, by Scharf et al.\textsuperscript{17}.

V. ENERGIES AND PROFILES

A. Bulk Hydrogen

At zero temperature, bulk $\text{H}_2$ is experimentally known to be an $f\text{cc}$ crystal with density $\rho = 0.026\text{Å}^{-3}$, and energy per molecule $e_o = -85.5K\text{1}$. From a simulation of the bulk at that density at $T=0.5K$ with 96 molecules, we obtain a kinetic energy of $69.3 \pm 0.1K$ and a potential energy of $-156.3 \pm 0.1K$ giving an energy $-87.0 \pm 0.2K$. Thus, our value is $1.5 \pm 0.2K$ lower than the experimental one. We obtain a pressure of $0.04 \pm 0.07$ atm. We believe that our intermolecular potential is sufficiently accurate to study surface effects, and it further
justifies the use of the spherically averaged pair potential for the pair potential between H$_2$ molecules. Using the Debye temperature $\Theta_D \simeq 108$K$^{18}$, the change in internal energy of H$_2$ between zero temperature and $T = 0.5$K, according to $U(T) \simeq 3\pi^4 T^4 / 5 \Theta_D^2$, is only $3 \times 10^{-6}$K. Having established that the PIMC simulation of bulk H$_2$ gives reliable energies, we can proceed with the H$_2$ surface.

**B. Hydrogen Surface: Complete Top Layer**

The surface tension $\gamma$ of a bare surface is the energy necessary to create a surface, calculated by comparing the energy per particle of a bulk simulation to that of a slab. From a calculation with 64 H$_2$ molecules and four layers at T=0.5K making up a system with two free surfaces of 199Å area each, we obtain $\gamma = 3.41 \pm 0.05$KÅ. The experimental value for the surface tension given by Souers$^{18}$ is $\gamma_{expt} = 3.83$KÅ$^2$ which, however, pertains to liquid H$_2$ and the extrapolation is meant only for the range from 14.7K to 25K. A more current experimental reference for the surface tension of hydrogen, Pashkov et al.$^{19}$, provides values between the critical point and the triple point (32.98K), all in the liquid phase. At 15K, they quote $\gamma = 2.02$KÅ, but extrapolating their empirical formula $\gamma = \gamma_o (1 - T/T_c) \mu$ down to 0.5K gives $\gamma = 5.27$KÅ. Obviously, extrapolating the surface tension that far outside the intended temperature interval is unreliable.

In a crystal the Lindemann’s ratio, $\Gamma$, is the rms displacement of a particle from its lattice site $\vec{z}$ divided by the nearest neighbor distance, 3.79Å. At $T = 0.5$K, we obtain for bulk H$_2$, $\Gamma = 0.21 \pm 0.03$, which is within the experimental value of the Lindemann’s ratio of 0.18 at zero temperature$^1$. In the case of the free H$_2$ surface, $\Gamma$ is more than 50% larger than the bulk value, indicated by the right upper arrow in Fig. (4). The right lower arrow is the
experimental bulk value at zero temperature\textsuperscript{1}. Obviously, at least the two top H\textsubscript{2} layers have much more zero point motion than the molecules deep inside the solid. This is displayed in more detail in Fig. (4), where $\Gamma$ and its components perpendicular ($z$-direction) and parallel to the surface are shown. As one might expect, the fluctuation perpendicular to the free surface is significantly larger than parallel to it. The horizontal axis of Fig. (4) shows the coverage of $^4$He adsorbed on the hydrogen surface, as discussed in the companion paper\textsuperscript{20}. The compression of the hydrogen due to the adsorbed helium is visible, even in the second H\textsubscript{2} layer. Thus, the free H\textsubscript{2} surface is “fluffed up” compared to bulk H\textsubscript{2}.

The zero point motion of the H\textsubscript{2} molecules depends sensitively on the underlying substrate. As an illustration we have used various combinations of model, frozen and dynamic substrates. The $\Gamma$ component values lying on the curves were calculated from a slab of four dynamic H\textsubscript{2} layers, stabilized against buckling by an external potential, but there was no frozen layer underneath. To see effect of a frozen substrate layer on the zero point motion of adsorbed layers, we include in Fig. (4) the parallel and perpendicular $\Gamma$ components of two top dynamic H\textsubscript{2} layers, resting on a frozen layer. Since there is no $^4$He adsorbate in that case, one should compare these values, indicated by the four left arrows in Fig. (4), to the plot symbols on the curves for $\sigma = 0$. The two top left arrows refer to the top dynamic layer, which should be compared to the triangles, and the two bottom left arrows refer to the second dynamic layer, which should be compared to the squares. The top layer is obviously not much affected by whether the third layer is dynamic or frozen, but for the second layer, which rests on the frozen layer, the effect is drastic. The $z$-component of the H\textsubscript{2} layer resting on the frozen layer, shown as the second left arrow from the bottom, is noticeably lower the empty square representing a H\textsubscript{2} second layer on a dynamic third layer. Conversely, the parallel component of the dynamic layer on the frozen one, shown as the lowest left arrow,
exceeds the corresponding value of the H₂ layer on a dynamic third layer, as shown by the filled square at \( \sigma = 0 \). It is interesting to note that the 3D value of \( \Gamma \) of the layer next to a frozen layer (not shown) is within the plot symbols unchanged by whether the neighboring layer is frozen or dynamic. This implies that the zero point kinetic energy is unchanged, although the component perpendicular is diminished and the parallel component enhanced. Therefore, to compute zero point motion in a layer reliably, it is not sufficient to have a correct substrate potential. One should include at least one extra dynamic layer.

C. Hydrogen Surface: Partial Top Layer

Based on electron localization measurements, Edel’man and Faley\(^3\) have suggested that the free H₂ surface may have a terrace structure for temperatures lower then \( \approx 5K \), with step widths on the order of 1000 Å and step heights between 10 Å and 100 Å. This is in accord with Klitsner and Pohl\(^4\), who conclude from phonon scattering experiments of H₂ surfaces grown on silicon that hydrogen has a characteristic surface roughness length of about 200 Å. Leiderer and Albrecht\(^2\) observe high surface diffusion in H₂ films on Ag between 2.6 and 2.8 K and suggest, that crystallites on the order of light wave length form. If these observations indicate a roughening transition, then it would be hard to understand why it would occur so far below the triple point (13.8 K), because at least in classical surfaces, roughening transitions are entropy driven, so that the solid surface would be roughest near the freezing temperature, but get smoother with decreasing temperature. Clearly, these experimental observations motivate the theoretical study of incomplete H₂ surface layers. Moreover, close to a surface step, the H₂ molecules should be less localized parallel to the surface than in a complete top layer. The boundary of the terraces could be liquid like, and
possibly bose condense.

We have carried out simulations of hydrogen adlayers for coverages from 1/6 of a H\textsubscript{2} monolayer (ML) to one ML (\(\sigma = 0.0804\text{Å}^{-2}\)) for temperatures between 0.5K and 1.33K. The substrate is simulated by two explicit layers and an infinite number of model layers of H\textsubscript{2}. The top filled layer is dynamic, and can respond to the adsorbed H\textsubscript{2} molecules, and can exchange with the partial adlayer. The second filled H\textsubscript{2} layer is frozen and rests on model layers. Before the H\textsubscript{2} molecules in the second layer were frozen, the system was equilibrated, so that the top layer of H\textsubscript{2}, upon which partially filled H\textsubscript{2} layers of various coverages will be adsorbed, has a realistic bulk substrate. This approach is preferable to letting the dynamic layer rest either on a perfect crystal, or on a hard wall. The frozen and the dynamic filled H\textsubscript{2} layer have 5 \times 6 H\textsubscript{2} molecules each. Periodic boundary conditions are used parallel to the surface to simulate an infinite system, but of course, the minimum box side in the \(x\)-\(y\) plane of \(\approx 19\text{Å}\) limits the largest surface inhomogeneities in our simulation. The H\textsubscript{2} density profiles obtained from simulations with partially filled adlayers for coverages from zero to 0.080\text{Å}^{-2} in increments of 0.013\text{Å}^{-2}, corresponding to zero to one monolayer in increments of 1/6 monolayer, are shown in Fig. (5). The dynamic substrate layer gets visibly compressed by the adsorbed layer.

Shown in Fig. (6) is the binding energy of the adlayer as a function of adlayer coverage at \(T=0.5\text{K}\). The binding energy of a completed layer should be \(N \times e_o \approx 2610\text{K}\). This is shown as the “bulk-line” in Fig. (6). Our simulations have a slightly higher energy for ML completion of \(-2350\text{K}\) or an excess of 8.3K/molecule. We attribute this 5\% excess to the neglect of relaxation of the underlying frozen and model layers. As shown in Fig. (4) for the case of \(^4\text{He}\) adsorption\textsuperscript{20} the compression of H\textsubscript{2} layers near the surface due to surface adsorption continues beyond two dynamic layers. This compression changes the substrate
density near the surface, which we do not fully recover with only two explicit hydrogen layers. Therefore, the total energy per H\textsubscript{2} is different for two and three explicit layers. This can be avoided by including more dynamic layers, but at the price of more computer time.

We are interested in how the binding energy per H\textsubscript{2} molecule in a partial adlayer depends on the areal density \( \sigma \) of that layer, since it determines whether an adlayer of a density less than complete filling would spread out homogeneously, giving rise to the possibility of a liquid layer at density \( \sigma \), or whether a crystalline terrace at a density higher than \( \sigma \) would form, leaving part of the substrate free, i.e. a two-phase coexistence. To calculate the binding energy for a fractional layer we subtracted out a “base-line” of \( \tilde{\varepsilon}_0 \times N \) where \( \tilde{\varepsilon}_0 \) has been adjusted to compensate for the lack of responsive surface, \( \tilde{\varepsilon}_0 \approx 78.3 \text{K} \). We expect the missing substrate response to be linear in adlayer coverage. The result is shown in Fig. (7). The strongest binding occurs in complete surface layers, suggesting that the hydrogen surface should not exhibit steps or islands. One can directly see in our simulations the tendency of the H\textsubscript{2} molecules in a partially filled layer to clump together. This apparent contradiction to experiment can be resolved because the observed surface structures\textsuperscript{3,4,2} have a length scale of several hundred Angstroms whereas our current simulation setup imposes an upper limit of 19\( \text{Å} \). Therefore, our results implies that the experimentally observed terraces are smooth on a length scale of at least our simulation box size.

One can estimate the line tension from the binding energy change per H\textsubscript{2} molecule in the partially filled adlayer and the length of the terrace or droplet. From density plots in the \( x\cdot y \) plane, we can directly read off the circumference, and obtain the line tension of H\textsubscript{2} droplets at \( T=0.5 \text{K} \) as \( \sim 13 \text{K}/\text{Å} \). However, we caution that this is no more than an estimate, because our droplets are so small (10 molecules).

To find out if the partial H\textsubscript{2} adlayer is in fact liquid for some temperatures and coverages,
we compute the static structure factor within that layer, defined as

\[ S(\vec{k}) \equiv \frac{1}{N} \left\langle \rho_{\vec{k}} \rho_{-\vec{k}} \right\rangle , \]  

with

\[ \rho_{\vec{k}} = \sum_{j=1}^{N} e^{i \vec{k} \cdot \vec{r}_j} , \]

and \{\vec{k}\} parallel to the interface plane. Results for several coverages at \( T=0.5\text{K} \) are shown in Fig. (8). The peaks at \( k \approx 1.6\text{\AA}^{-1} \) in the structure factors are remnants of the crystalline initial conditions of the simulation, and kept shrinking during throughout the simulation, even though in some cases the cpu time per coverage and temperature exceeded 400 hours on an IBM RS6000/530 work station. It is likely, that we are not fully in equilibrium. However, we started the simulation from crystal sites, and the layers melted, suggesting that the equilibrium state for the coverages shown are liquid. The fact that for coverages less than about half filling \( S(k) \) bends upward again as \( k \to 0 \), see Fig. (8), indicates the formation of a droplet on the length scale of our simulation box, i.e. we observe a phase separation. At the three lowest coverages the simulation broke the symmetry between \( x \) and \( y \). At \( \sigma = 0.013\text{\AA}^{-2} \) (plus symbols in Fig. (8)), an oval shaped droplet formed. At the second coverage, \( \sigma = 0.027\text{\AA}^{-2} \) (triangles) a liquid stripe formed, and at the third lowest coverage, \( 0.040\text{\AA}^{-2} \) (squares) an oval shaped area on the substrate stayed empty. This is consistent with the above discussion of the binding energy of partial adlayers shown in Fig. (7), according to which complete top layers are preferable.

A direct picture of the paths provides convincing evidence that the partial adlayer is a bose liquid droplet. Fig. (1.a) shows the completely filled crystalline top layer of the bare \( \text{H}_2 \) substrate at \( T=0.5\text{K} \) of a simulation with 56 molecules. The first time slice of each polymer has been marked with a filled circle. Straight lines are drawn to connect the positions at
consecutive time slices. The extent of the polymers shows the zero point motion, and the center of mass of each polymer is at the sites of the triangular lattice. Fig. (1.b) shows the half filled ($\sigma = 0.040\,\text{Å}^{-2}$) liquid H$_2$ layer adsorbed on top of the crystalline substrate. The polymers are clearly more spread out and irregularly shaped than in the crystal layer and are involved in macroscopic exchanges. Furthermore, the free area in the liquid partial adlayer is a signature of the gas-liquid coexistence. Notice also, that the average density in the liquid is lower than in the crystal, because approximately three quarters of the area are covered with liquid hydrogen, but the total density is only half that of the crystal.

Given the liquidity of partial hydrogen layers for some densities at such low temperatures, the large zero point motion, and the fact, that H$_2$ molecules are bosons, raises immediately the question about the relevance of quantum exchange.

**VI. QUANTUM EXCHANGE IN THE HYDROGEN SURFACE**

One fascinating aspect of bare H$_2$ surfaces is that they might exhibit superfluidity in a thin surface layer. Non-interacting bosons at the density of H$_2$, with the H$_2$ mass, would Bose-Einstein condense (BEC) at $\approx 7$K. However, the triple point of para H$_2$ lies at 13.8K$^{18}$, far above temperatures where it could become superfluid. Maris et al.$^{21}$ argue, that it should be possible to supercool liquid H$_2$ sufficiently to get into the temperature range of BEC, but this has not yet been achieved experimentally. Finite superfluid densities have been computed by Sindzingre et al.$^{16}$ with PIMC in clusters of 13 and 18 molecules. A cluster of 33 H$_2$ was already large enough that the total potential energy caused too much localization for the H$_2$ to remain superfluid. Much better chances for the experimental observation of superfluid H$_2$ should exist in atomically thin films, simply because the molecules are more weakly bound
in a film. If the ratio of kinetic to potential energy is high enough to delocalize the H$_2$ molecules then they can quantum exchange. If this happens in a liquid and surface layer then superfluidity should be present. Ceperley and Pollock$^{22}$ obtained for a $^4$He film on a flat substrate with coverage 0.0432Å$^{-2}$ a superfluid transition temperature of $T_c = 0.72 \pm 0.02$K. To estimate for H$_2$ films what $T_c$ we might expect, if it exists, we substitute the H$_2$ mass for the $^4$He mass in

$$k_B T_c^- = \pi \frac{\hbar^2}{2m} \sigma_s(T_c^-)$$

(17)

at the same density, and obtain $T_c = 1.43$K. The presence of a substrate with potential corrugations may lower $T_c$. Liu et al.$^8$ may have experimentally observed a lowered triple point temperature of an H$_2$ layer on D$_2$ preplated graphite as low as $T_3 = 5.74$K, taking advantage of the incommensurable lattice constants of D$_2$ and H$_2$ to frustrate the crystallization of the latter. Unfortunately, this is still far to high to observe superfluidity.

Superfluidity is by definition the phenomenon of irrotational and frictionless flow past a wall. In PIMC, superfluidity corresponds to large ring polymers winding around the simulation cell in periodic boundary conditions$^{13}$ as permuting particles connect. Pollock and Ceperley$^{13}$ derived in the PIMC formalism an expression for the effect of moving boundary walls on the many-body density matrix. The superfluid coverage is computed as:

$$\sigma_s = \frac{m}{\hbar^2} \frac{\langle \vec{W}^2 \rangle}{2A \beta} ,$$

(18)

where $\vec{W}$ is the winding number of all paths, which is a multiple of the box length, and $A$ the surface area. For further details on the computation of superfluid densities see Refs. [22,13].

We did a “coverage scan”, shown in Fig. (9), and a “temperature scan”, Fig. (10), to bracket the region of significant quantum exchange in $\sigma$ and $T$. The most promising coverages are between 1/6 and 5/6 of a layer, the best temperatures between 0.4K and 1K. The highest
occurrence of exchange was found at 1/2 layer and 0.66K. Roughly half of the H$_2$ molecules in the partial adlayer participated in exchanges. The solid line in Fig. (10) is the jump in superfluid coverage as a function of critical temperature given the the KT relation, Eq.(17). Based on this, we estimate $T_c^-$ $\approx$ 0.8K and $\sigma_s(T_c^-)$ $\approx$ 0.021\AA$^{-2}$ at half filling. However, given the long equilibration and correlation times of the winding number, the numerical values should be considered a guideline rather than the last word on this matter. For example the zero values of $\sigma_s$ at 0.013\AA$^{-2}$ and 0.027\AA$^{-2}$ in Fig. (9) are probably due to insufficient equilibration, because we find a finite $\sigma_s$ at 0.020\AA$^{-2}$ (circle in Fig. (9)) and at 0.040\AA$^{-2}$. What we can state, however, is that there would be superfluidity of molecular hydrogen in the region given above, provided the film is liquid.

As discussed in the context of the Lindemann’s ratio, the proximity of a frozen second layer diminishes the zero point motion perpendicular to the layers, and concomitantly reduces the outward relaxation and density decrease of the surface layer. Thus, a frozen layer will decrease quantum exchange in nearby dynamic layers. To study the effect of the frozen layer on the superfluid density we also did some checks with different setups. In a simulation at T=0.5K of four layers of 16 H$_2$ molecules each with another 4 H$_2$ on each side of the four layers, constituting a quarter filled top layer, or $\sigma = 0.02\AA^{-2}$, we obtained the superfluid coverage $\sigma_s = 0.011 \pm 0.001\AA^{-2}$, as shown as a circle in Fig. (9). Exchanges between the partial layers and the next full layer were observed. Hence we believe our results with the frozen layer are reliable.

In our calculations, the completely filled top layer of H$_2$ at T=0.5K was always crystalline and we never observed quantum exchanges. However, for simulations with quarter and half filled top layers of H$_2$, that ‘partial’ layer stayed liquid and superfluid. But to date, no experimental observation of a liquid surface layer of H$_2$ at T=0.5K has been documented.
Because of the small size of our sample the question remains whether H$_2$ could possibly be superfluid in a thin surface layer, or whether we found a finite $\sigma_s$ merely due to finite size effects. If we are below the critical temperature of the KT transition, then the issue of surface superfluidity of H$_2$ is equivalent to that of the existence of a macroscopic liquid H$_2$ film.

We note that there is experimental evidence of hydrogen surface terraces. The terraces have a width of several hundred Angstroms but our calculations show they are smooth on length scales of at least 20 Å, and have a liquid perimeter of at least 10 Å, i.e. we find the surface of the terraces melted. This roughness will promote quantum exchanges. In the perimeter quantum exchange takes place, but superfluidity will not be observed experimentally unless these liquid stripes around the islands/steps are connected on a macroscopic scale in a 2D network. We have not yet simulated surface steps of more than one layer, even though these have been experimentally observed$^{3}$ and can therefore not comment on what effect they might have.

Finally, motivated by third sound experiments of $^4$He film adsorption on H$_2$ surfaces by Chen, Roesler, and Mochel$^{23}$, we adsorbed an additional $\sigma = 0.02\text{Å}^{-2}$ of $^4$He on a dynamic substrate, but the effect on the hydrogen superfluidity was a decrease of the hydrogen superfluid coverage from $\sigma_s(H_2) = 0.011 \pm 0.001\text{Å}^{-2}$ without $^4$He present to $\sigma_s(H_2) = 0.003 \pm 0.001\text{Å}^{-2}$ with $^4$He adsorbed. The $^4$He-H$_2$ system is studied in the companion paper$^{20}$. 


VII. CONCLUSIONS

We have introduced a way of treating arbitrary layered surfaces and used this to perform PIMC simulations of the H$_2$ surface. At least two layers of the H$_2$ (1,1,1) surface are "fluffy", i.e. have lower density and more zero point motion than bulk. Completely filled H$_2$ surface layers are solid. However, partially filled H$_2$ surface layers are liquid for coverages less than \( \approx 0.040 \text{Å}^{-2} \), corresponding to half layer filling. We observe quantum exchange in the liquid partial adlayers for temperatures 0.5K to 1K, some involving H$_2$ molecules in the underlying H$_2$ substrate. Yet, for a completely filled top layer, we did not see exchanges. Motivated by the experimental discovery of two coexisting sound modes in the $^4$He on H$_2$ system by Chen, Roesler, and Mochel$^{23}$, we looked for superfluid H$_2$ films as a possible source for a new third sound mode. But in spite of the observed liquid partial H$_2$ layers and quantum exchange, we can not yet confirm the existence of superfluid hydrogen films, because the binding energy of H$_2$ in the partial adlayer to the bulk substrate indicates that crystalline terraces are preferred to liquid layers in macroscopic systems, in agreement with experiment. Our liquid partial adlayers for less that half filling indicate that these terraces have a liquid shore line at least 10Å wide, where quantum exchange occurs.
Acknowledgements

We wish thank Ming-Tang Chen and Jack M. Mochel for stimulating discussions about their experimental finding of two coexisting sound modes in $^4$He on H$_2$, which motivated us to take a closer look at the surface, and for the communication of their results prior to publication. This work was done at the National Center for Supercomputing Applications in Urbana, Illinois. The computations were performed using NCSA’s Cray Y-MP and IBM RS6000/530 work stations. We gratefully acknowledge funding through NSF grant No. DMR–91–17822, and the support of the Department of Physics of the University of Illinois at Urbana-Champaign.
REFERENCES

1 I. F. Silvera, Rev. Mod. Phys. 52, 393 (1980).


5 V. L. Ginzburg and A. A. Sobyanin, JETP Lett. 15, 242 (1972).


FIGURE CAPTIONS

Fig. 1. Paths of H\textsubscript{2} molecules at T=0.5K, projected on the x-y plane. Straight lines are drawn connecting the positions of the H\textsubscript{2} molecules at consecutive time slices. The first of the 80 times slices of each particle’s path is marked by a filled circle. (1.a) 56 H\textsubscript{2} molecules in a close packed crystal layer at monolayer density 0.080\AA\textsuperscript{2}. (1.b) 28 H\textsubscript{2} molecules in a liquid layer at half filling 0.040\AA\textsuperscript{2}.

Fig. 2. Density profiles of partially filled H\textsubscript{2} adlayers on a H\textsubscript{2} (1,1,1) surface at T=0.5 K for adlayer coverages from 0.027\AA\textsuperscript{2} to 0.067\AA\textsuperscript{2} in increments of 0.013\AA\textsuperscript{2} overlayed with the Gaussian fits. The bare substrate is represented by one dynamic and one frozen layer of H\textsubscript{2}, neither of which are shown.

Fig. 3. H\textsubscript{2}-H\textsubscript{2} pair potential [K] vs. interparticle distance [\AA], Ref. [15].

Fig. 4. Lindemann’s ratio for H\textsubscript{2} molecules vs. coverage [\AA\textsuperscript{2}] of adsorbed \textsuperscript{4}He on a H\textsubscript{2} substrate of four dynamic H\textsubscript{2} layers, as discussed in the companion paper Ref. [20]. All lines are to guide the eye only. Top pair of curves: empty circles: top layer; filled circles: second layer. Middle pair of dashed curves are components \textit{perpendicular} to the surface: empty triangles: top layer; filled triangles: second layer. Bottom pair of curves are components \textit{parallel} to the surface: Empty squares: top layer; filled squares: second layer. The right arrows are 3D H\textsubscript{2} bulk values; right upper arrow: T=0.5 K, this work; right lower arrow: T=0K, experiment, Ref. [1]. The left four arrows refer to a simulation of two dynamic H\textsubscript{2} layers directly on a frozen layer without any adsorbate. Top two left arrows: top layer;
bottom two left arrows: second layer. Open arrows are \textit{perpendicular} components, filled
arrows are \textit{parallel} components.

Fig. 5. Density profiles of partially filled H\textsubscript{2} adlayers on a H\textsubscript{2} (1,1,1) surface at T=0.5K for
seven adlayer coverages from 0 to 0.080\AA\textsuperscript{-2} in increments of 0.013\AA\textsuperscript{-2}. The bare substrate
is represented by one frozen layer and one dynamic layer of H\textsubscript{2}. Left peak: frozen layer;
middle set of peaks: dynamic layer; right set of peaks: adlayers.

Fig. 6. Total energy difference [K] of the H\textsubscript{2} substrate with and without the H\textsubscript{2} adlayer vs.
adlayer coverage [\AA\textsuperscript{-2}] at T=0.5K. The maximum $\sigma$ shown corresponds to layer completion
of the adlayer. The error bars are within the squares, and the solid ”base-line” connects the
energies for completion of the surface top layer (bare substrate) and the adlayer. The dashed
line shows the bulk energy according to our calculations of 87K per H\textsubscript{2} molecule, denoted
”bulk-line”. The difference between the ”base-line” and the ”bulk-line” is attributed to the
neglect of relaxation of underlying layers.

Fig. 7. Binding energy [K] per H\textsubscript{2} molecule in a partial H\textsubscript{2} layer to a H\textsubscript{2} surface in (1,1,1)
direction at T=0.5K vs. coverage [\AA\textsuperscript{-2}] with the ”base-line” subtracted out.

Fig. 8. The structure factor of partial H\textsubscript{2} adlayer at constant temperature 0.5K for \textbf{k} par-
allel to the surface for coverages: $\sigma = 0.013\AA^{-2}$ (plusses), 0.027\AA\textsuperscript{-2} (triangles), 0.040\AA\textsuperscript{-2}
(squares), 0.054\AA\textsuperscript{-2} (circles). Note that at the lowest \textbf{k} vector, there are two symbols for
each coverage – they represent $S(k_x)$ and $S(k_y)$ for $k_i = 2\pi/L_i$. One triangle (not shown) is
off scale \( S(3) = 3.5 \).

Fig. 9. Superfluid coverage \( [\tilde{A}^{-2}] \) of \( \text{H}_2 \) at constant temperature 0.5K \( v.s. \) coverage \( [\tilde{A}^{-2}] \) of adlayer. The circle is from a simulation with four filled dynamic layers, the squares are with one filled dynamic layer and one filled frozen layer.

Fig. 10. Superfluid coverage \( [\tilde{A}^{-2}] \) of \( \text{H}_2 \) at constant \( \sigma = 0.040 \tilde{A}^{-2} \) (half filling) \( v.s. \) temperature. The solid line is the critical coverage \( v.s. \) critical temperature given by the KT relation, Eq.(17).