

PATH INTEGRAL MONTE CARLO SIMULATIONS OF THE MELTING OF MOLECULAR
HYDROGEN SURFACES

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Abstract

We have used Path Integral Monte Carlo to study the surface melting of molecular hydrogen. Density profiles perpendicular and parallel to the bare H_2 surface are computed showing the formation of a liquid adlayer at 6K, less than half the bulk melting temperature of para-hydrogen, 13.8K. To estimate the onset temperature and depth of H_2 surface melting we determine the static structure factor within the individual H_2 -layers for wave vectors in the plane and find no crystalline order down to 3K in a partially filled H_2 adlayer at the free surface. We find quantum effects amplify the melting point depression at the free H_2 surface compared to bulk by a factor of five over classical Lennard-Jones solids and find that the zero-point fluctuations of molecules at the surface are much enhanced over their bulk fluctuations. We see vacancy formation in the solid before melting.

1 Introduction

Surface melting is the formation of a stable liquid layer at the solid/vapor interface below the bulk melting temperature, T_{3M} . Excellent reviews on the surface melting of classical solids are available, see e.g. van der Veen *et al.* [1], Dash [2], Tosatti [3], and Nelson [4]. Most bulk materials are believed to be wet by a film of their own melt, a few atomic or molecular layers thick [2] at temperatures near the melting temperature.

Molecular hydrogen is unique among the elements in having an interface between a highly quantum solid and a near vacuum at low temperature. Our initial motivation to study the surface of molecular hydrogen in detail was the experimental discovery of an additional third sound mode in atomically thin superfluid ^4He films adsorbed on H_2 [5, 6]. As discussed in Ref. [7], the second mode is still not understood in detail. We speculated that a thin superfluid H_2 surface could cause this new sound mode. Ginzburg and Sobyenin [8] proposed molecular hydrogen as a candidate for a new bulk bose superfluid. Yet, experiments investigating that avenue have so far not succeeded [9, 10, 11]. Our own work discussed in Ref. [12] found quantum exchange in partially filled liquid H_2 surface layers between 0.5 and 1K, but we expect those partially filled layers to be unstable with respect to filled layers in the thermodynamic limit. We saw no “superfluid” behavior of solid layers.

From our PIMC studies it became clear that down to 0.5K, terraces on the bare H_2 surfaces are very different in structure from bulk solid because of delocalization and, below $\approx 1\text{K}$, bose statistics. Because of these studies, the question arises whether quantum surface melting is qualitatively or only quantitatively different than that of classical surface melting. To get more information, in this paper, we report results of simulations of a thicker substrate slab than in our earlier work, and a wider range of temperatures between 3K and 20K (our earlier work was between 0.5K and 2K).

There have been some experiments relevant to surface melting of hydrogen. Brewer *et al.* measured the heat capacity of para-H₂ in Vycor glass, and interpreted their data as showing that not all hydrogen solidified at temperatures as low as 4K [13]. Recently de Kinder *et al.* [14] conclude from Raman scattering measurements that the H₂ in Vycor is neither in a bulk liquid state nor in a simple lattice. For a mono-molecular H₂ layer, a solidification temperature of 5.74K has been verified by experiment [15], spectacular since this is more than a factor of two below the bulk melting temperature, but still too high to expect that liquid H₂ will become superfluid.

Even without that immediate hope, however, the melting transition of the H₂ surface will prove a worthwhile object of study, because experimental data show that the H₂ surface changes its structure significantly below the bulk melting point [16]. We hope that our simulations will be useful in constructing a more complete microscopic picture of the free H₂ surface.

In the next section we briefly review our computational methodology. In section 3 we discuss the implications of our density profiles perpendicular to the substrate/vapor interface, to establish the layers' position prior to elaborating on their properties. In section 4 the change from crystalline layers to a liquid film through the surface melting transition, monitored with the static structure factor, $S(\vec{k})$, for wavevectors parallel to the surface. Consistent with the experimental observation [17] of large surface diffusivity at 2.3K in H₂ films on Ag and with our earlier work [12] we find liquid behavior in the partially filled top layer on the H₂ surface down to 3K. Density profiles parallel to the interface are presented in section 5 to complement the perpendicular densities from section 3. Looking down on the substrate provides a very intuitive understanding for the lateral localization of H₂ molecules and for the difference between a crystalline layer and a quasi-liquid layer. Moreover, slightly below the melting temperature of a H₂ layer we compute the vacancy concentration. The change in energy with temperature is discussed in section 7. We discuss the rms particle fluctuations both parallel and perpendicular to the substrate surface in section 8. It turns out that the deviation

is a much finer measure of structural change within layers with temperature and of compression from surface adsorption than the density profiles are. Finally, section 9 summarizes what we have learned from these simulations.

2 Computational Method and Model

The results discussed here were obtained with Path Integral Monte Carlo (PIMC) [18, 19, 20], a computational method for quantum many-body properties at finite temperatures, based on Feynman’s [21, 22, 23, 24] imaginary time path integrals. PIMC is an exact mapping of the thermal density matrix of a quantum system onto a classical system making numerical quantum statistics calculations as feasible as classical equilibrium thermodynamics, at least for particles obeying Boltzmann or Bose statistics. Each quantum particle is mapped onto a particular type of ring polymer, each monomer of which corresponds to a hydrogen molecule for a given value of imaginary time. The path integral method can calculate exact thermodynamic properties at arbitrary finite temperatures, such as is needed in the study of phase transitions. We do not calculate real time properties. For details on PIMC we refer to a recent review, Ref. [20].

The quantities we report are obtained as averages over “paths” or “configurations”. By a path, we mean the real-space coordinates, R , of N particles at M time-slices, sampled from the many-body density matrix. On each path, N particles traverse M positions each, $\{R_0, R_1, R_2, \dots, R_{M-1}, R_0\}$. These paths are sampled by PIMC from the product of density matrices:

$$Z^{-1} \rho(R_0, R_1; \tau) \rho(R_1, R_2; \tau) \cdots \rho(R_{M-1}, R_0; \tau) , \quad (1)$$

where the “time-step”, τ , defined by $\beta \equiv M \tau$, results from the break up of the density matrix into M density matrices at the “high” temperature τ^{-1} . Thus, for fixed τ , more time-slices mean

longer polymers and lower temperatures, where β is always the inverse of the (actual) temperature of the physical system. We used $\tau = 1/120\text{K}$ in this work. Hence, one can start at temperature $1/\tau$, high enough to accurately calculate a “high-temperature” many-body density matrix, and then apply Eq. (1), to obtain the desired many-body density matrix at the “low-temperature” of the physical system, $T \equiv 1/\beta$. The lowest simulated temperature discussed here is 3K, according to our experience [12] not low enough for H_2 molecules to make quantum exchange significant. Therefore, we need to use only Boltzmann statistics in the present work.

In this work, the calculations are done at fixed temperature, volume, and number of particles. The latter is a major limitation in the study of surface phase transitions, for which it is more appropriate to work at fixed chemical potential. Our fixed-N results must be interpreted with caution whenever we may be in a coexistence region of two phases. There is no theoretical reason why path integral Monte Carlo cannot be done at fixed chemical potential. One would have to introduce steps in which entire paths are added or deleted from the system. This is difficult at low temperatures where the paths are delocalized and overlapping with other paths, but there is no reason in principle why it could not be done.

The investigation of a phase transition on a parallel computer system with independent processors, in our case Thinking Machines Connection Machine CM-5, is much facilitated by Parameter Space Scanning (PSS) [25]. The basic concept of PSS is to interpret the axes of a phase diagram as spanning a parameter space in which one can lay out a grid of parameter points. If, e.g., the axes are N and T , then each parameter point in that space corresponds to the same type of physical system, differing only in the number of particles and temperature. Thus, PSS allows us to simulate a phase transition efficiently on a parallel computer by distributing user-defined parameter points over independent processors. Moreover, ensemble averaging within a single parameter point is naturally implemented by cloning a physical system over several processors. Depending on the simulated

temperature and number of particles, each PIMC run may take 100 CPU hours for a 150 particle system on a SPARC processor. We typically ran between four and 16 clones of each parameter point, equilibrated from slightly different initial conditions, on as many processors in parallel, generating a total of about 2000 statistically independent particle configurations per parameter point.

We represent the H₂ molecules by spherical particles, interacting with a semi-empirical pair-potential [26]. In the temperature and density range we consider, the molecules are predominantly in their rotational ground state ($J=0$), *i.e.* para-hydrogen. The first excited state of a free para-hydrogen molecule ($J=2$) has an energy 510 K higher than the ground state. For the highest temperature we investigate, 20K, the first excited state of para-H₂, has an occupation probability of only about $(2J + 1) e^{-E_J/T} \approx 4 \times 10^{-11}$. Therefore, we need not be concerned with para-H₂ excitations or with higher multipole terms in the interaction of two H₂ molecules. The pair-potential of Silvera and Goldman (SG) [26] for the interaction between two H₂ molecules has been used for various simulation studies [27, 28, 29, 30, 12, 31]. Our choice of the SG potential is further validated by comparison between several potentials that Norman, Watts, and Buck (NWB) [32] did with the variational MC method on bulk solid molecular hydrogen. Despite NWB's [32] discussion favoring the potential by Buck *et al.* [33], we read their tabulated data as showing the SG potential to reproduce best the experimental values of pressure and total energy in the low pressure regime, crucial for our investigation. Moreover, using the SG potential Scharf *et al.* [34] simulated bulk fluid para-hydrogen between 14 and 25K with PIMC, and obtained good agreement with experiment for the density and the total energy per H₂-molecule.

Our rectangular simulation box is of fixed size $L_x \times L_y \times L_z = 18.95\text{\AA} \times 19.69\text{\AA} \times 60\text{\AA}$ with periodic boundary conditions in the x - y plane, taken parallel to the substrate/vapor interface. Hence, 30 H₂ molecules correspond to a mono-layer (ML) at solid bulk density, 0.0804\AA^{-2} . To avoid an unphysical change of sign in the gradient of the pair potential at the cut-off radius, $r_c \lesssim L_x/2$,

all pair potentials are shifted upwards to vanish outside of r_c . At the end of the simulation, we add this shift to the potential energy.

Since we start our simulations from crystalline particle coordinates, we designate our systems as the “five”, “5.5”, and “seven layer” systems, containing 150, 165, and 210 molecules respectively. Of course, the term “layer” loses its meaning as the temperature approaches the surface melting transition and the layer densities re-adjust. As we shall see, even slightly below the H_2 surface melting temperature the H_2 density is smaller than in the zero temperature bulk so that fewer than 30 molecules per box area will fill a single layer. For the seven layer system we use a repulsive potential as a lid at high z to prevent H_2 molecules from evaporating from the simulation box at high temperatures. This lid is short-ranged and does not influence the substrate layers.

We use the following terminology in the discussion of layering: An explicit layer is explicitly represented by the coordinates of its constituting particles. A model layer is represented by the mean particle density (assumed to be Gaussian), and never changes during any given simulation run. The model layers’ density contributes to an external potential which the explicit layers see. Model layers are useful to represent the deep substrate interior whose long-range potential is crucial for binding energies in surface adsorption. The densities of the model layers are taken from previous bulk simulations. Model layers offer the benefit of costing no CPU time during the simulation, independent of their number, but of course they do not relax under surface adsorption. To describe the substrate response with sufficient accuracy for the simulation of adsorption, we found it necessary [12, 7] to include at least one explicit layer in addition to the surface layer upon which adatoms are adsorbed. The zero point motion and the density profiles, are not reliable for the explicit layer adjacent to the model layers, as we shall see below.

The present work examines the five, 5.5, and seven layer system, at the temperatures listed in Table *I*. Our previous work [12] considered lower temperatures.

We simulated the seven layer system to test how much our results are affected by the number of layers, verifying that the five layer system is thick enough to compute the onset of H₂ surface melting reliably. Moreover, in the five layer system, we observe the formation of a new top layer, which we name the “zeroth” layer, at temperatures above 5.5K. Simulations with the seven layer system confirm this result. The additional temperature point of 5.45K allows us to bracket the onset of H₂ surface melting more precisely. We did a simulation at 20K, well above the bulk melting point of 13.8K, to see the effect of the model layers on liquid hydrogen.

3 Perpendicular Density Profiles

In this section we discuss our density profiles that are shown in Fig. 1 as a function of temperature. The upper panel shows the 5.5 layer system; the lower the 5 layer system. The layers’ peak positions change very little with increasing temperatures while the maximum densities diminish; the layer structure becomes less well defined and eventually disappears as one approaches the bulk melting temperature. We find that the movement of particles out of a solid layer into the vapor or liquid above is a precursor of the melting of that solid layer. Thus the perpendicular density profiles provide a way of monitoring surface melting.

First let us define that we mean by “layer” a region, parallel to the substrate/vapor interface, that contains a density maximum bracketed by density minima. We will discuss more direct melting criteria in following sections. Our naming convention is to count full layers downward from the free surface, “1” being the filled layer at the substrate/vapor interface. The “0”-th layer is a partially filled ad-layer above layer “1”, existing either from the initial configuration in the 5.5 layer system, or formed during the simulation when H₂ molecules move upwards as vacancies appear in the first

layer and the surface melts.

We count a given particle as being in layer l if its centroid has a z coordinate between the l^{th} and $(l + 1)^{th}$ minimum of the perpendicular density profile. We will use this definition in the later sections, in defining the layer structure factor, the vacancy concentration, and the in-plane density distribution. Figure. 2 compares the density distribution to the centroid distribution. The centroid distribution is much more strongly peaked than the density itself, so the centroid coordinate is a less ambiguous way of identifying to which layer a particle belongs. In the centroid coordinate instantaneous, out-of-layer fluctuations due to zero point motion are averaged out to some extent. The definition of a layer is less meaningful when a genuine 3D liquid forms on the surface. This happens to the zeroth and first layer above 12K.

With this definition of layers, the zeroth, first and second moments of the layer density, give important information about the change in the surface with temperature. The zeroth moment is the layer density σ_l . The first moment is its mean position z_l . The second moment is the average zero-point fluctuations with respect to its mean position. We will discuss these fluctuations in Section (8).

Table *II* compares the layer spacing and the layers' density maxima between the five and the seven layer system.

We see consistency from the five to the seven layer systems. At 7.5K the “0”-th layer on the five layer system has a higher maximum density and also a larger integrated coverage than in the seven layer system, whereas the converse holds when comparing layers “1” and “2” of both systems. This suggests that the seven layer system is not perfectly equilibrated.

Figure 3 shows how the layer density depends on temperature and the depth below the surface. The open and filled circles, to the left represent the “0”-th layer for the five and 5.5 layer system, respectively. Notice that the five layer system's “0”-th layer disappears below 6K as it is

absorbed into the first layer. The first layer (squares) has a density of around 0.065\AA^{-2} and then compresses at 6.5K to a higher density upon freezing. Similarly for the second layer (triangles) though its compression happens near 8K.

Our results for $\rho(z)$ show the formation of a partially filled layer on the five layer system at 6K. In Fig. 4 we show the formation of this next layer in more detail, overlaying only the layers “1” and “0” at 5, 6, 6.67, and 7.5K. We observe that the density profile has a much enhanced tail at 6K and above and that a minimum in the density between layer “0” and layer “1” exists at 7.5K and above.

The temperature dependence of the compression of the bulk surface due to the half filled top layer can be seen when comparing profiles shown in the upper and lower panel of Fig. 1. Whereas at 6K only layer “1” nearest to the free surface gets visibly compressed by the half full top layer, already at 7.5K the compression caused by that partial adlayer propagates down to the second lowest full layer, “4”. At 10K, even layer “5” is affected by the adsorption of the half full adlayer, “0”. We need to caution that layer “5”, the lowest explicit one in these two systems, rests against a flat and unresponsive model layer. We shall see in section 8, the density is not the most sensitive indicator of how deep into the bulk material the compression due to adlayer adsorption at the free surface has an effect.

We find that at 15K, where the layer structure at the free surface is almost entirely molten, the H_2 density at the liquid/vapor interface is $\approx 0.019\text{\AA}^{-3}$, somewhat below the bulk liquid triple point density of 0.023\AA^{-3} [35]. (The experimental bulk liquid density is almost unchanged between 13.8K and 15K, decreasing to 0.0228\AA^{-3} .) Both entropic forces and the zero point motion of the H_2 molecules could cause this expansion of the liquid at the liquid/vapor interface.

The H_2 vapor density is very small below $T=12\text{K}$. However, already at 12K we observe a nonzero H_2 density above the surface. See Fig. 1. (The triple point of H_2 is 13.8K and 7030 Pa [35].)

In Fig. 5 we have overlaid the perpendicular density profiles for 15 and 20K of the seven layer system, and at 15K for the five layer system. To check if the H₂ vapor densities we obtain at 15K and 20K are reasonable we make the following estimate: The saturated H₂ vapor pressure (Souers, Ref. [35]) in Pa is:

$$\log P = 15.46688 - \frac{101.3378}{T} + 5.432005 \times 10^{-2}T - 1.105632 \times 10^{-4}T^2 . \quad (2)$$

According to Eq. (2) SVP is 13372 Pa at 15K and 93169 Pa at 20K. Substituting this into the ideal gas equation yields at 15K, 0.12 ideal gas particles in the gas volume above the five and the 5.5 layer system and 0.07 ideal gas particles above the seven layer system. We count H₂-molecules in the gas phase by integrating the particle density between $z = 25\text{\AA}$ and 28.5\AA to avoid including liquid particles at the lower bound, and a possibly artificially high gas density at the upper bound, due to the proximity effect of the short-range repulsive potential used as a lid at 30\AA . The corresponding average values we obtain for 15K are 0.30 and 0.27 H₂ molecules above the surface in the five and the 5.5 layer system, and 0.14 H₂'s in the seven layer system. At 20K we find 1.76 H₂ molecules vaporized over the seven layer system, more than four times the 0.37 ideal gas particles one would have at the SVP of H₂. Thus, we have two to 2.5 times as many H₂ molecules in the gas phase. But there is some ambiguity in specifying the gas volume, it is not clear where the liquid ends and the gas phase begins, and we may have included molecules that are really zero-point excursions from the solid. Given the crudeness of this estimate the agreement is reasonable.

Comparing the profiles of the five and the seven layer system overlaid in Fig. 5 (we have translated them so their maxima match) for 15K shows that the three lowest layers of both systems are very similar in maximum density, widths, and spacing. For temperatures lower than the surface melting transition we find that the properties we compute for the H₂ substrate/vapor interface are insensitive to whether we use five or seven layers. In solid layers, the proximity of the model layers

biases only the density of the explicit layer adjacent to the model layers. Above 15K, on the other hand, the layering we see in the perpendicular density profiles is an artifact caused by the model layers. A two sided slab geometry would be more appropriate to study the interface between liquid H₂ and its vapor.

4 Static Structure Factor

The static structure factor gives a clear signal of long-range order and hence of melting. We will use it in this section to identify the phase of a layer. We have already defined how we classify which layer a given path is in. The *generalized* static structure factor between layers A and B is defined as:

$$S_{A,B}(\vec{k}) \equiv \left\langle \frac{\rho_{\vec{k}}^A \rho_{-\vec{k}}^B}{\sqrt{N_A N_B}} \right\rangle, \text{ with } \rho_{\vec{k}}^A \equiv \sum_{j=1}^{N_A} e^{i\vec{k} \cdot \vec{r}_j}. \quad (3)$$

N_A and N_B are the number of molecules in layers A and B . If $A \neq B$ we refer to $S_{A,B}$ as off-diagonal, otherwise it is the diagonal structure factor. The latter is the conventional definition of the 2D static structure factor. We will use the off-diagonal structure factor to discuss commensuration between adjacent layers.

By looking at various features of the diagonal structure factor we can characterize the phase of a layer as being either a (2D) solid, liquid, or gas or a coexistence between these phases. There are two main features of $S(\vec{k})$ that we look at: the peak height at the reciprocal lattice vector of a triangular lattice and the compressibility at long wavevectors.

For a perfect crystal, the peak value of $S(\vec{k})$ will equal the number of molecules in a layer which is thirty for our systems. Because of zero-point motion (the Debye-Waller factor) the peak height is reduced by 55% to a value of 16.5. On the other hand, in a quantum liquid the peak

height is between one and two. Figure 6 shows typical examples of our calculated diagonal structure factors. The peak height provides a good indication of the amount of ordering in a layer. The maximum value of $S(\vec{k})$ is shown in Fig. 7 for each layer and for both the five and 5.5 layer systems. The curve for each of the layers has three regions: a high plateau value, a low value and a transition region. We identify these as a solid, liquid and liquid/solid coexistence. Only layers “0” and “1” do not cleanly fit into this classification. The zeroth layer always remains a liquid and the first layer never quite makes a good crystal even for the five layer system.

The second important feature is the value at $k = 0$. Note the developing minima in the low k region of the structure factor shown in Fig. 6b. This is an indication of separation of a layer into high-coverage and low-coverage regions. For layers in a liquid state, we fit $S(k)$ in the range $0.4\text{\AA}^{-1} \leq k \leq 1.4^{-1}$, with a quadratic polynomial and extrapolated to $k = 0$. If the resulting $S(0)$ is larger than unity, we denote that as a liquid-gas phase separated layer. In fact this is usually the case.

With the above characterization we have identified four conditions of a layer:

- A. Solid:

We characterize a solid as a layer having $S_{max} > 12$. We will discuss later the vacancy distribution in the solid layers.

- B. Solid/Liquid:

As one can observe on figure 7, the difference between the melting and freezing temperature is on the order of 2K or larger. We characterize the solid/liquid coexistence as a layer having $3 < S_{max} < 12$. We cannot investigate in detail what happens in these layers because the small size of our simulation cell distorts the transition. We note that surface melting differs from bulk melting in that long-range order is always present, since the underlying bulk layers

provide a corrugated potential for the molecules to sit in. On the one hand, this means that a solid can only lower its density by either creating vacancies or by a transition to another commensurate structure. We will discuss evidence for the first mechanism later.

There is some evidence that layers in this intermediate density regime are attempting to find a different commensurate structure – note the extra peaks in Fig. 6b. This speculation is consistent with Vilches’ heat capacity measurements [15], showing a peak at 9.3K between the top two hydrogen layers. The fact that we find this transition at lower temperature can be due to the differences in bulk substrates, deuterium preplated graphite in Vilches’ [15] case *vs.* H_2 .

- C. Liquid:

We take our working definition of a 2D liquid as having a relatively smooth structure factor with a maximum peak height of less than 3. The static structure factors in the two layers nearest to the free surface, are shown in Fig. 6b. Its overall shape is very similar to a 2D quantum liquid such as helium. One can observe slight modulations due to the underlying solid layers. We note from figure 7, that a layer does not complete its melting until its underlayer has at least begun to melt, except for layer “0” which never freezes.

- D. Liquid/Gas:

We define the liquid/gas coexistence as a liquid with a compressibility greater than that of a free gas: $S(0) > 1$. To definitively establish the phase boundaries would require simulations of larger systems. However, this criterion can roughly indicate whether phase separation is likely. We find that the half filled top layer of the 5.5 layer system is liquid down to 0.5K [12]. But the large compressibility indicates that the true phase is filled solid layer.

Figure 8 summarizes our classification of states. The axes and *location* of symbols are the same as in Fig. 3. We have marked where a liquid would be superfluid. This is based on scaling our

2D ^4He simulations of the Kosterlitz-Thouless transition, *cf.* Ceperley and Pollock [36].

Wiechert [37] has drawn a very similar phase diagram using heat capacity measurements of H_2 adsorbed on graphite. He finds a triple point of the second layer above graphite at 5.96 K, and a 2D liquid-vapor critical temperature of about 10K. He verified the solid order of the uppermost layer at lower temperatures (2K) with neutron scattering.

Using our estimates that we discussed above for the melting and freezing temperatures of a layer let us define the mean melting temperature as the average of the freezing and melting temperature. It is shown in Fig. 9. The partially filled H_2 layer at the free surface, and the “0”-th layer never solidifies, so it is not shown. The left arrow in Fig. 9 indicates Vilches’ [15] estimate of the top layer freezing on top of $\text{H}_2/\text{H}_2/\text{graphite}$ and $\text{H}_2/\text{D}_2/\text{graphite}$. The right arrow shows the bulk melting temperature where the number of melted layers diverges. The additional 1/2 layer of the 5.5 layer system increases the melting temperature of the underlying layers as expected.

It is interesting to compare the ratio of surface to bulk melting temperature, between solid H_2 and classical Lennard-Jones solids. Broughton and Gilmer have determined that the melting of a Lennard-Jones classical surface depends on the layer as:

$$d/d_0 = \ln \left[\frac{\delta}{1 - T/T_m} \right] , \quad (4)$$

where T_m is the triple point temperature, $\delta \approx 0.28$, and $d_0 \approx 1$ layer. Substituting the results computed by Broughton and Gilmer [38] with Molecular Dynamics for the first layer melting of classical Lennard-Jones solids gives $1 - T/T_m \simeq 0.11$. However, for the solid H_2 the ratio of top layer melting to bulk melting is $1 - 6\text{K}/13.8\text{K} \simeq 0.57 \pm 0.04$. Clearly, the surface melting transition of solid H_2 is dominated by quantum effects. Hence the melting point depression in the quantum system a factor five times lower in the first layer than in a classical Lennard-Jones solid. Using the data of melting temperature versus layer, we roughly estimate that both d_0 and δ are strongly

modified by quantum effects: $d_0 \approx 4$ layers and $\delta \approx 0.7$ for solid H_2 .

Now, we investigate the static structure correlation and commensuration between the first and second layers. The top panel of Fig. 10 shows the “off-diagonal” static structure factor of the 5.5 layer system for temperatures from 5K to 7.5K. The nearest neighbor anti-correlation comes about because the H_2 molecules in the zeroth layer avoid the atoms in the underlying solid layer. When that layer melts the anti-correlation decreases. The anti-correlation between layer “0” and layer “1” of the 5.5 layer system for $T \leq 6\text{K}$ is most pronounced at $k \approx 1.9\text{\AA}^{-1}$, but there is also anticorrelation for $k \gtrsim 1.6\text{\AA}^{-1}$ indicating a significant fraction of configurations with a different commensuration. For the 5.5 layer system, we also observe for temperatures $\leq 6\text{K}$ a positive correlation at the second neighbor position in the plane, $k \simeq 3.3\text{\AA}^{-1}$.

5 Parallel Density Profiles and Vacancies

To get a better idea of the order in each layer, we compute the H_2 density of a single layer in the directions parallel to the surface. Specifically, by “looking down” we gain an intuitive picture of the layers as it changes from solid to liquid.

The 2D density, $\sigma_l(x, y)$, in layer l , is defined as the average over particles within layer l :

$$\sigma_l(x, y) = \left\langle \frac{1}{A} \sum_{j=1}^{N_l} \delta(x_j - x) \delta(y_j - y) \right\rangle, \quad (5)$$

where A is the area of the box and the average is over several hundred Monte Carlo path updates. We have typically averaged over 500 paths (snapshots of the physical system) for the five layer system, 600 for the 5.5 layer system, and 400 for the seven layer system. If one averages for too long, translation symmetry would wash out many of the interesting features. We reduce the statistical noise by fourier smoothing the density [12]. Shown in the panels of figure 11 are contour plots with

typical densities, for the five layer system. From left to right, the columns of Fig. 11 correspond to the H₂ surface at 6K, 7.5K, and 10K, whereas lower rows correspond to lower layers, *i.e.* layers “0”, “1”, and “2”. The top row of panels of Fig. 11 shows, from left to right, how layer “0” forms with increasing temperature. Some phases can be recognized in figure 11:

- A. solid. In the middle panel of the third row, layer “2” at 7.5K, we see a solid with a vacancy in the upper right corner. The vacancy causes a large rearrangement of density in the neighborhood.
- B. liquid/solid. In the left column middle panel we see a layer which has localized molecules , but the solid order is not the same as the initial condition.
- C. liquid. In the middle row of the right column is shown as liquid layer. Less than 1/2 of the molecules are localized during the PIMC simulation. The triangular pattern imposed by the underlying layers is hardly present.
- D. liquid/gas. It is seen in the middle panel of the top row that the molecules in a partially filled layer clump together to form a liquid-like droplet on the surface.

6 Vacancies

In the previous sections we have seen that the density of a solid layer drops, even before it melts. But since a layer must remain commensurate with underlying layers this implies that vacancies must form. We showed a picture of this in the last section.

We have earlier defined the layer coverage. For a solid layer we define the vacancy concentration $C_l = 1 - \sigma_l/\sigma^*$, where σ^* is the coverage of a layer deep inside the bulk. The vacancy

concentration is plotted in Fig. 12 for the first and second layers. With increasing temperature, the vacancy concentration rapidly rises, the layer begins to melt for concentrations on the order of 5% and is completed when it reaches 10%. The vacancies are evidently thermally activated since the vacancy concentration is well approximated by:

$$C_l = D_l \exp[-E_l/(k_B T)] \quad (6)$$

with $E_1 \approx 25K \pm 2K$ and $E_2 \approx 70K \pm 10K$.

Now let us consider whether vacancies could Bose condense to form a supersolid. This possibility was suggested by Andreev and Lifshitz [39] if the mean separation of the vacancies was comparable to their thermal wavelength. The two dimensional superfluid transition (Kosterlitz-Thouless) transition occurs at a temperature when :

$$T_c = 1.8 C_l \sigma_0 \hbar^2 / m^* \quad (7)$$

where m^* is the effective mass of the vacancy and the coefficient in front has been determined for 2D ^4He by Ceperley and Pollock [36]. (The precise value of these two parameters will not matter).

There is a common solution to Eq. (6) and Eq. (7) only if

$$E_l \leq \frac{1.8 D_l \sigma_0^* \hbar^2}{m^* e} \quad (8)$$

Putting in rough estimates for $m^* \approx 2m$ and D_l from Fig. 12, for the first layer the LHS of the inequality (8) is 25K and the RHS is 2.3K so one never has Bose condensation. The concentration of vacancies drops too fast as the temperature is lowered so that the thermal wavelength (growing as $T^{-1/2}$) never reaches a neighboring vacancy.

7 Energies

Vilches [15] has measured the heat capacity for the same range of temperatures studied here for a H₂ bi-layer on a graphite substrate, and a H₂ mono-layer on D₂ on preplated graphite. He observed two peaks in C_v , the first one associated with top layer melting at 5.96K and 5.74K of H₂/H₂/graphite and H₂/D₂/graphite respectively. The difference in temperatures shows the importance of the substrate. Vilches [15] suggested that the second peak in the both of his systems, occurring at 9.32K and 9.30K, could indicate a transition between a commensurate and an incommensurate phase between the top two hydrogen layers. This suggestion is consistent with the anti-correlation, exhibited by the off-diagonal structure factor between layers “1” and “2”, which we found to persist up to temperatures of 8.57K, shown in the bottom panel of Fig. 10 and to the extensive two-phase region.

However, Wiechert [37] interprets his measurements as showing that for the second layer of H₂ on graphite, there is a coexistence between a solid and gas-phase below approx. 6K, followed by a liquid/gas coexistence up to about 9.3K. Our calculations and identifications of the phases, agree with the locations Wiechert [37] found for the phase boundaries, and with the melting of the topmost surface layer at 6K. We need simulations on larger systems to definitively decide between these two explanations.

The total energy per H₂ molecule is plotted *vs.* temperature for both systems in Fig. 13. In the five layer system, the onset of the formation of layer “0” is barely visible, in contrast to the melting of layer “1”. Using the 5.5 layer system, where the total energy is smoother than in the five layer system (compare Fig. 13) we compute the heat capacity at constant volume by numerically differentiating the energy versus temperature, and plot the result in Fig. 14. To facilitate the comparison with experiment, we also show the heat capacities Vilches [15] measured for two systems of a hydrogen double layer on a graphite substrate, H₂/H₂/*graphite* and H₂/D₂/*graphite*, respectively. To convert Vilches’ units to ours, k_B per H₂ molecule, we used his published [40] H₂

top layer coverage, 0.094\AA^{-2} , and surface area, $47m^2$.

In agreement with Vilches [15] we obtain two peaks in the constant volume heat capacity, but the low lying one is in our case a mere shoulder, much smaller than the experimentally observed peak presumably because of the limited size of our simulation cell. However, in Vilches' case, the major contribution to c_v will have come from the liquid H_2 top layer alone, because the second hydrogen layer, H_2 or D_2 , was clamped to the strongly attractive graphite substrate, and hence solid. The computed heat capacity displayed in Fig. 14, comes from the entire system containing 5.5 layers. However, the heat capacity change of the molecules in the melting layers does contribute significantly to the peaks, while the H_2 molecules in the still solid underlying layers provide a “background”. This explains why the heat capacity signature of surface melting in our simulation, *i.e.* the shoulder at 5.5K in Fig. 14, is of much smaller magnitude than the second peak, in contrast to Vilches' [15] measurements. We note that the slope and, except for the first peak, the heat capacity itself we calculate, is approximately bounded from above and below by Vilches' results for the $H_2/H_2/graphite$ and the $H_2/D_2/graphite$ systems, respectively. The peak at 11K in Fig. 14 can be attributed to the melting of our entire simulated system.

8 Lindemann Ratio

The Lindemann ratio of a particle is its root mean squared deviation with respect to its mean position divided by its crystal lattice nearest neighbor distance. The Lindemann criterion of melting [41] is a widely used empirical rule which states that a classical crystal melts once the Lindemann ratio reaches about 0.14 [42]. However, for a 3D quantum crystal the Lindemann ratio is ≈ 0.26 at melting. Quantum solids can handle a greater amount of zero-point motion. Of course,

once the layer is liquid, the Lindemann ratio is not useful. We generalize the definition of the Lindemann ratio by computing it separately in different layers and in the directions parallel and perpendicular to the surface.

Define z-component of the l^{th} -layer Lindemann's ratio as:

$$\gamma_l^z = \frac{\langle (\bar{z}_i - \langle \bar{z}_i \rangle)^2 \rangle_l^{1/2}}{r_{nn}}, \quad (9)$$

where r_{nn} is the bulk nearest neighbor distance, the average being taken over all atoms i , in layer l . The z-component ratio is well-defined even for a 2D-liquid layer as long as layers are well defined and is proportional to the rms width of a layer. Fig. 15 shows γ_l^z for layers "1" to "5". Missing up to half the near neighbor molecules compared to the bulk interior, the H₂ molecules close to the surface are more weakly bound and spatially less confined, causing their rms position fluctuations to be larger. The H₂ surface is similar to loosely packed snow, the top is much less dense than the underlying layers and much more compressible showing significant changes down to the fifth layer. In fact, the width of the lowest layer, may be too narrow, since it rests on model layers. Notice that γ_l^z for these layers is larger in the five layer system than in the 5.5 one, due to compression of the additional half top layer in the former system. The z-component of Lindemann's ratio is relatively unaffected when a layer melts.

The lateral component of the Lindemann ratio is defined as:

$$\gamma_l^{xy} = \sqrt{(\gamma_l^x)^2 + (\gamma_l^y)^2}, \quad (10)$$

where the x and y components of γ_l have been calculated analogously to γ_l^z . and shown in Fig. 16. The lateral ratio is sensible only if the molecules are localized in the x and y directions. There is a rapid rise in the transverse ratio just before melting. Whitlock and Kalos [43] found a melting of 2D helium with a 2D Lindemann's ratio of 0.254. We find melting occurs (from the previous section) with the 2D ratio beginning at 0.20 and ending at about 0.25. At a level of 0.01, this "melting"

criterion is independent of the layer.

The isotropic Lindemann ratio is: $\gamma_l^2 = (\gamma_l^z)^2 + (\gamma_l^{xy})^2$ and is shown in Fig. 17. In no layer of any of our H₂ simulation systems did we find at any temperature a Lindemann ratio of less than 0.19, well above where classical crystals melt. The Lindemann ratios of our deepest layers are in rough agreement with experimental measurements [44] and become roughly isotropic.

9 Conclusions

Building on our earlier work [12] we carried out a more detailed PIMC study of surface melting of the H₂ bulk surface, computing density profiles perpendicular and parallel to the surface, structure factors, energies, vacancy concentrations and zero point motion. We found the onset temperature of surface melting to be no higher than 6K, in agreement with experiment but we obtained no evidence that a completely filled top layer at the free H₂ surface melts under its own saturated vapor pressure at 5.45K, also consistent with the current experimental evidence. A H₂ substrate layer at the vapor interface at half filling compared to bulk remains liquid-like, or at least amorphous, down to 3K, the lowest temperature simulated in this study. This is in agreement with previous work [12] where a half filled H₂ surface top layer stayed liquid for all temperatures studied, down to 0.5K.

Fig. 9 shows our melting temperatures as a function of distance away from the surface. We find that quantum effects amplified the melting point depression compared to bulk a factor of five more at the H₂ surface than in classical Lennard-Jones systems. Layers begin melting when their 2D rms motion exceed 0.20 or alternatively when they get roughly a 10% vacancy concentration. The free surface of solid H₂ is highly compressible, showing outward relaxation at least four layers deep.

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Figure Captions

Figure 1: H_2 density [\AA^{-3}] perpendicular to the free surface obtained with PIMC. (a) Top panel: 5.5 layer slab; (b) bottom panel: five layer slab. Overlaid are profiles of systems at $T=15, 12, 10, 7.5, 6, 5, 4,$ and 3K . For easier distinction, the profiles at 7.5K are given as plus symbols. Solid arrow indicates bulk liquid triple point density [35].

Figure 2: density [\AA^{-3}] of layers “0” through “3” perpendicular to the free surface of the 5.5 layer system at 6K . Solid line: full paths/density distribution, dashed line: centroid density.

Figure 3: The dependence of layer density on temperature. Closed symbols: five and seven layer systems; open symbols: 5.5 layer system. Circles: “0”-th layer; Triangles: “1”-st layer; Squares: “2”-nd layer; Pentagons: “3”-rd layer. The solid line at 0.0804\AA^{-2} is the coverage deep inside the solid.

Figure 4: H₂ density [\AA^{-3}] perpendicular to the free surface of the seven-layer system: Formation of layer “0”. Lines: thin, continuous: 5K; thick, dashed: 6K; thick, continuous: 6.67K; thin, dashed: 7.5K.

Figure 5: H₂ density [\AA^{-3}] perpendicular to the free surface. Overlaid are profiles of three simulations: The 210 H₂ system at 20K (dotted line), and at 15K (solid line). The 150 H₂ system at 15K (small plus symbols), is shifted by 3.3\AA to best match the maxima near free surface of the 210 H₂ system at 15K. Experimental bulk liquid density [35]: Upper (open) arrow 15K, lower (solid) arrow 20K.

Figure 6: Diagonal static structure factor from Eq. (3) *vs.* \vec{k} in x - y -plane. (a) Top panel: 5.5 layer system, overlaid for 6K: dashed thin line, open triangles: layer “1”; continuous thick line, \times 'es: layer “4”. (b) Bottom panel: five layer system: continuous thick line, filled triangles: layer “0”. 5.5 layer system, layer “1”: continuous thin line, \times 'es: 8.57K; dashed line, circles: 7.5K.

Figure 7: Maximum of diagonal static structure factor of layers, \vec{k} parallel to layer, *vs.* temperature. “0”-th layer is the initially half filled one in the 165 particle system, and the one appearing only for $T \gtrsim 6\text{K}$ in the 150 particle system. *Full* layers counted downward from the interface, beginning with “1”. Lines to guide the eye only. Statistical errors are within the line widths. (a) Top panel, dashed lines, open symbols: 165 H₂ system. (b) Bottom panel, continuous lines, filled symbols: 150 H₂ system. In each panel: Lowest line, no plot symbols: Zeroth H₂ layer at substrate/vapor interface. Triangles: First full layer; Crosses: Second; Circles: Third; Plusses: Fourth; Squares: Fifth. Arrow indicates melting temperature in 3D bulk.

Figure 8: 2D phase diagram. The results of classifying the order of the various layers of solid hydrogen as described in the text. Each point represents the layer density and temperature. The solid circles are identified as a liquid; open circles as the coexistence between a 2D liquid and a 2D gas; solid squares are a 2D solid; the open triangles are a very disordered 2D solid, possibly the coexistence between 2D liquid and 2D solid. If the system remains a liquid to sufficiently low temperature it will become superfluid as marked, (our estimate comes from similar calculations with 2D liquid ⁴He). The vertical line at 0.0804\AA^{-2} is the coverage deep inside the solid and the horizontal line corresponds to the bulk melting temperature.

Figure 9: Melting temperature within H₂ layers, defined as mid temperature between high and low plateaus of the maximum diagonal $S(k)$ in Fig. 7. Molten full layers counted downward, starting at the substrate/vapor interface. Lines drawn to guide the eye only. Continuous line, filled squares: 150 particle system. Dashed line, open squares: 165 particle system. Experiment: left arrow: melting of frustrated H₂ mono-layer, Ref. [15]; right arrow: 3D bulk melting, Ref. [44].

Figure 10: Off-diagonal static structure factor, def. by Eq. (3), applied to adjacent H₂ layers parallel to the free (1,1,1) surface *vs.* \vec{k} parallel to the interface of the 5.5 layer system. Open circles: 8.57K; plusses: 7.5K; \times 'es: 6K; open triangles: 5K. (a) Top panel: $S(k)$ between layer “0” and layer “1”. (b) Bottom panel: $S(k)$ between layer layer “1”, centered near $z = 5.6\text{\AA}$, and layer “2”, near $z = 2.3\text{\AA}$, see Fig. 1.

Figure 11: H₂ density in five layer system *parallel* to the x - y plane. Panel columns correspond to temperatures: Left column: 6K, center: 7.5K, and right: 10K. Panel rows correspond to layers: Top panel row, layer “0” (observed only for $T \geq 6$ K), middle row, layer “1”, and bottom row, layer “2”. All panels, $\sigma_{min} = 0$.

Top row: left column: $\langle \sigma \rangle = 0.003 \pm 0.002 \text{ \AA}^{-2}$, $\sigma_{max} = 0.19 \text{ \AA}^{-2}$. center: $\langle \sigma \rangle = 0.020 \pm 0.0002 \text{ \AA}^{-2}$, $\sigma_{max} = 0.22 \text{ \AA}^{-2}$. right: $\langle \sigma \rangle = 0.041 \pm 0.0003 \text{ \AA}^{-2}$, $\sigma_{max} = 0.018 \text{ \AA}^{-2}$.

Center row: left column: $\langle \sigma \rangle = 0.077 \pm 0.0002 \text{ \AA}^{-2}$, $\sigma_{max} = 0.59 \text{ \AA}^{-2}$. and in *center* of vacancy/defect, $\sigma_{vac} = 0.2 \pm 0.1 \text{ \AA}^{-2}$. center: $\langle \sigma \rangle = 0.065 \pm 0.0002 \text{ \AA}^{-2}$, $\sigma_{max} = 0.41 \text{ \AA}^{-2}$. right: $\langle \sigma \rangle = 0.065 \pm 0.0002 \text{ \AA}^{-2}$, $\sigma_{max} = 0.29 \text{ \AA}^{-2}$.

Bottom row: left column: $\langle \sigma \rangle = 0.080 \pm 0.00002 \text{ \AA}^{-2}$, $\sigma_{max} = 0.58 \text{ \AA}^{-2}$. center: $\langle \sigma \rangle = 0.077 \pm 0.0002 \text{ \AA}^{-2}$, $\sigma_{max} = 0.61 \text{ \AA}^{-2}$. in *center* of vacancy, $\sigma_{vac} = 0.1 \pm 0.06 \text{ \AA}^{-2}$. right: $\langle \sigma \rangle = 0.067 \pm 0.0002 \text{ \AA}^{-2}$, $\sigma_{max} = 0.37 \text{ \AA}^{-2}$.

Figure 12: The vacancy concentration of the first layer (circles) and second layer (triangles) as a function of the inverse temperature. The two lines represent fits to the data giving an activation energy of 25K for the first layer and 70K for the second layer. Results from both the 5 layer and 5.5 layer system are included together.

Figure 13: Total energy in $^{\circ}$ K per H₂ molecule *vs.* temperature, overlaid for five and 5.5 layer system. Solid line and filled plot symbols: five layer system. Dashed line and open plot symbols: 5.5 layer system. Lines to guide the eye only. Statistical errors within plot symbols.

Figure 14: Specific heat at constant volume *vs.* temperature in $k_B \equiv 1$ per H₂ molecule in our 5.5 layer system. Open circles: Computed values, connected by dashed line, to guide the eye only. Statistical error within plot symbols. Overlaid, without adjustments, are Vilches’ [15] heat capacity measurements, sketched by continuous lines: upper curve/plus symbols: H₂ mono layer on D₂ preplated graphite; lower curve/ \times es, two H₂ monolayers on graphite.

Figure 15: Lindemann ratio perpendicular to the free surface, from Eq. (9), within (labeled) H₂ layers *vs.* T [K]. Dashed lines, empty symbols: 5.5 layer system; solid lines, full symbols: five layer system. Lines to guide the eye only. To facilitate layer identification, cf. Fig. 1: Triangles: layer “1”, centered at $z \approx 5.6 \text{ \AA}$; circles: layer “2”, centered at $z \approx 2.3 \text{ \AA}$; squares: layer “3”, centered at $z \approx -1.0 \text{ \AA}$; \times es: layer “4”, centered at $z \approx -4.2 \text{ \AA}$; no plot symbols: layer “5”, centered at $z \approx -7.4 \text{ \AA}$.

Figure 16: Lindemann ratio parallel to the free surface, from Eq. (10), within (labeled) H₂ layers *vs.* T [K]. Dashed lines : 5.5 layer system; solid lines : five layer system. Lines to guide the eye only. To facilitate layer identification, cf. Fig. 1: Triangles: layer “1”, centered at $z \approx 5.6 \text{ \AA}$; circles: layer “2”, centered at $z \approx 2.3 \text{ \AA}$; squares: layer “3”, centered at $z \approx -1.0 \text{ \AA}$; \times es: layer “4”, centered at $z \approx -4.2 \text{ \AA}$; no plot symbols: layer “5”, centered at $z \approx -7.4 \text{ \AA}$. Horizontal lines at 0.20 and 0.25 indicate approximate beginning and ending of surface melting, respectively.

Figure 17: Lindemann ratio, 3D isotropical, within (labeled) H₂ layers *vs.* T [K]. Lines connecting symbols to guide the eye only. Dashed lines, empty symbols: 5.5 layer system; solid lines, full symbols: five layer system. To facilitate layer identification, cf. Fig. 1: Triangles: layer “1”, centered at $z \approx 5.6 \text{ \AA}$; circles: layer “2”, centered at $z \approx 2.3 \text{ \AA}$; squares: layer “3”, centered at $z \approx -1.0 \text{ \AA}$; \times es: layer “4”, centered at $z \approx -4.2 \text{ \AA}$; no plot symbols: layer “5”, centered at $z \approx -7.4 \text{ \AA}$. Horizontal lines at 0.20 and 0.25 indicate approximate beginning and ending of surface melting, respectively.

TABLES

Table <i>I</i>	<i>Temperature [K]</i>											
<i>System</i>	3	4	5	5.45	6	6.67	7.5	8.57	10	12	15	20
five layer	t	t	t		t	t	t	t	t	t	t	
5.5 layer	t	t	t		t	t	t	t	t	t	t	
seven layer			t	t	t	t	t				t	t

Table *I*. Temperatures used here to study the five, 5.5, and seven layer system. The letter, ‘t’, indicates a combination of system and temperature where we have performed simulations.

Table II	<i>five layer system</i>				<i>seven layer system</i>			
T [K]	$z_1 - z_2$	$z_2 - z_3$	ρ_1^{max}	ρ_2^{max}	$z_1 - z_2$	$z_2 - z_3$	ρ_1^{max}	ρ_2^{max}
6	3.30	3.25	0.044	0.058	3.25	3.25	0.044	0.057
6.67	3.35	3.25	0.041	0.056	3.30	3.25	0.040	0.053
7.5	3.30	3.30	0.033	0.045	3.30	3.25	0.037	0.052

Table II. Layer spacing. z_i [\AA], is the location of the density maximum, ρ_i^{max} [\AA^{-3}], of layer i .