Superfluidity in H$_2$ Films

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Path integral Monte Carlo calculations were used to study a 2D system of H$_2$ molecules. The ground state on a flat substrate is a triangular lattice, a localized solid. We find that the introduction of some weakly attractive impurities (specifically alkali metal atoms) in the right concentration ($\sim$0.01 Å^{-2}) stabilizes a *liquid* hydrogen phase of concentration 0.04 Å^{-2} which undergoes a Kosterlitz-Thouless superfluid transition below approximately 1.2 K.   [S0031-9007(97)04345-7]

Since hydrogen molecules are relatively light, quantum effects are important at low temperatures. In fact, because a para-H$_2$ molecule is a boson and very similar to a ^{4}He atom, it has been proposed that condensed molecular hydrogen at low temperature could become superfluid as helium does. Unfortunately, the H$_2$-H$_2$ interaction is more than 3 times as attractive as the He-He interaction, so that pure bulk hydrogen is solid at temperatures below 13.8 K. This temperature is too high to observe superfluidity in the liquid phase.

One can reduce the tendency for hydrogen to be localized by decreasing the average number of neighbors of a H$_2$ molecule. Monte Carlo simulations of H$_2$ clusters with 13 and 18 particles [1] show that there is indeed a tendency for the system to be superfluid below 1 K. Much work has been devoted to studying experimentally and theoretically the behavior of H$_2$ films in a variety of substrates, such as Vycor glass [2–6], MgO [7], or graphite [8,9], employing different techniques. Unfortunately, the triple point temperature for the top layer of solid H$_2$ is 5.74 K [9], still not low enough to produce a superfluid.

Here we report path integral Monte Carlo (PIMC) calculations in a 2D system of p-H$_2$ molecules to predict the conditions under which it could be superfluid. We found that at low temperature, the stable state for a 2D H$_2$ surface is a solid, but we can stabilize a liquid phase by introducing certain impurities (alkali metal atoms) in the right concentration. As a result the hydrogen undergoes a Kosterlitz-Thouless (K-T) superfluid transition at $\sim$1 K.

PIMC is an exact simulation method, able to calculate thermodynamic properties of nonrelativistic bosonic systems directly from the assumed interaction potential. Essentially it is a numerical method for performing expectations of the many-body thermal density matrix using Monte Carlo sampling. The method has been extensively used to calculate properties of superfluid and solid helium and hydrogen at low temperatures [10].

In the simulations reported here, we assume that the H$_2$ molecules can be represented as spherical particles interacting with semiempirical potentials. For the H$_2$-H$_2$ interaction, we chose the semiempirical form given by Silvera and Goldman [11], a reliable potential for simulations at low temperatures and pressures, and successfully used for studies of H$_2$ clusters [1] and surfaces. For example, it was found [12,13] that the melting temperature for a single monolayer of H$_2$ molecules resting on several layers of solid H$_2$ was about 6 K, in good agreement with experimental measurements [9].

The H$_2$-alkali atom interactions were modeled by a 12:6 Lennard-Jones potential. To our knowledge, there are not values for σ or ϵ in the literature, so we deduced them as follows. σ was determined so that the minimum of the potential would correspond to the average of the molecular radius of H$_2$ (determined from the density of the molecular solid) and the radius of an alkali atom. ϵ was determined by the potential well felt by a H$_2$ molecule on a alkali metal surface [14]. We used $\sigma_{H_2-K} = 3.75$ Å, $\epsilon_{H_2-K} = 9.54$ K and $\sigma_{H_2-Cs} = 4.06$ Å, $\epsilon_{H_2-Cs} = 5.67$ K. Our structural results depend little on the exact value of these parameters. We believe that a hard-sphere interaction would yield similar results since the attraction is weak.

Our simulations were carried out in the canonical ensemble, i.e., in each run we input the temperature, the total number of particles, and the area of the simulation cell. We used an imaginary time step $\tau = \beta/M = 0.025$ K, where $\beta = 1/k_B T$ and M is the number of time slices, good enough for accurate quantitative predictions. The maximum number of H$_2$ molecules used in our simulations was 30. This is enough to distinguish between a 2D liquid and a solid but not for properties near the critical temperature. For systems of pure hydrogen, we kept the number of molecules constant and modified the cell size to vary the density. However, when impurities were included, we kept the cell size constant and varied the number of H$_2$ particles. In the latter case, two different cells were used, depending on the assumed arrangement of the alkali atoms. First, we used a "supercell" with dimensions 18.9 Å $\times$ 19.7 Å, with periodic boundary conditions. This corresponds to a complete monolayer of 30 H$_2$ molecules of bulk hydrogen. In our simulations with this cell, we used from 1–4 K or Cs atoms on a rectangular lattice. Second, we used a supercell with 4 K atoms on a triangular lattice

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with dimensions 17.32 Å × 20.0 Å with a K-K distance of 10 Å. The maximum CPU time for one of these calculations was 150 CPU hours in a Convex Exemplar SPP-1200.

One might expect the introduction of some impurities could reduce the freezing temperature of the film, and produce a stable liquid phase. However, it is necessary to choose carefully the type and concentration of impurities to obtain the desired effect. For example, classical noble gases are not good candidates because their interaction with an H_2 molecule is stronger than between H_2 molecules. We have verified that the H_2 molecules coat the noble gas, reducing their mobility and increasing the coverage of minimum energy.

On the contrary, an alkali metal atom achieves the purpose of lowering the density of the stable state. The attraction between an alkali metal atom and an H_2 molecule is one of the weakest known [14,15] so that H_2 molecules will not stick to the impurity. To achieve a stable liquid it is necessary to have a large enough concentration of impurities. The introduction of a single impurity per simulation cell hardly changed the equilibrium coverage. With two impurities per unit cell, the density of the stable state is changed, but the shift is not enough to create a liquid. However, for a $\sigma_K = 0.01$ Å^{-2} (4 K atoms per cell) the number of impurities is enough to have a low temperature liquid.

In Fig. 1 we show the total energy per H_2 molecule, E_{H_2}, as a function of the hydrogen coverage at 1 K. That temperature is low enough to observe exchange, since the thermal de Broglie wavelength is larger than the intermolecular distance. On the other hand, 1 K is much lower than the kinetic energy in the solid phase (∼20 K) and the

melting temperature in 2D (6 K) [13]. As a result, the solid is essentially in the ground state. The lower curve shows the energy of the pure H_2 film versus coverage, while the other three curves display the coverage dependence when potassium atoms are present. The minimum energy coverage (corresponding to the structure with the lowest homogeneous coverage) varies with the number of impurities; for a pure H_2 film it is 0.064 Å^{-2}, while for a system with four impurities on a rectangular lattice it is 0.04 Å^{-2}. If the concentration of impurities is 2 per cell, the equilibrium coverage increases to 0.053 Å^{-2}. Calculations with Cs impurities (not shown for reasons of space), give the same equilibrium coverage as potassium. A system with the impurities located on a triangular lattice has a lower equilibrium coverage (0.038 Å^{-2}) as compared to a rectangular lattice for the same concentration of impurities.

In order to determine the phase of the different systems, we calculated their structure factors, $S(\mathbf{k})$, as shown in Fig. 2. The pure H_2 film at the minimum coverage has a solid structure factor with one sharp peak at 1.7 Å^{-1} corresponding to a triangular lattice. The same figure shows also the $S(\mathbf{k})$ of a pure H_2 system at half of a monolayer coverage, which is liquidlike [12,13]. However, a layer with this density will be unstable and separate into a complete monolayer and a very low density gas. Analysis of the structure factors for different coverages allows us to say that for $\sigma < 0.059$ Å^{-2}, a pure film of H_2 molecules is a fluid. However, as one can see from Fig. 1, those liquids are unstable in comparison to a solid.
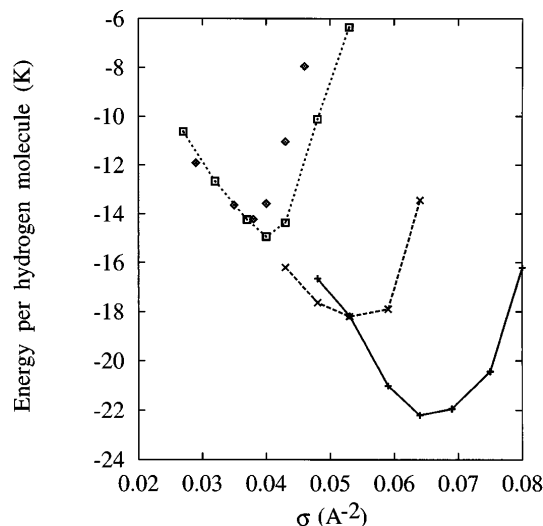

FIG. 1. Energy vs H_2 coverage for four different impurity densities at 1 K: a 2D film of pure H_2 (lower solid curve, plusses); 2 K atoms per simulation cell (dashed curve and ×'s); 4 K atoms on a rectangular lattice (squares and dotted curve), and 4 K atoms in a triangular lattice (diamonds).
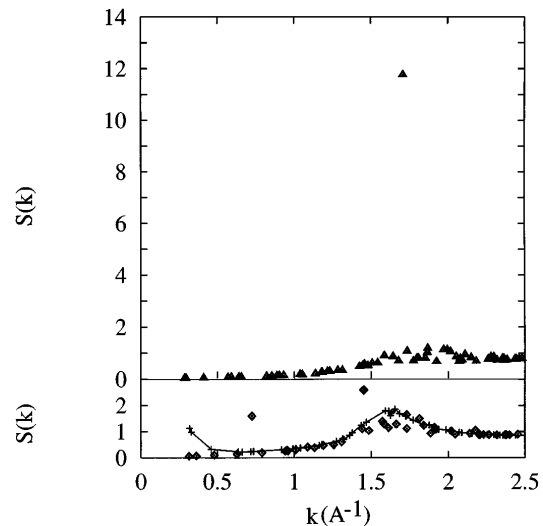

FIG. 2. Structure factor, $S(k)$, for three different hydrogen films at 1 K. The upper panel is for a solid 2D film of pure H_2 at $\sigma_{H_2} = 0.064$ Å^{-2}. The other two $S(k)$'s in the lower panel are liquids: a pure 2D H_2 film at 2 K with coverage 0.04 Å^{-2} (full line + crosses), and a H_2 film with 4 K atoms per simulation cell arranged in a triangular lattice with $\sigma_{H_2} = 0.04$ Å^{-2} (diamonds).

One can see that a system with impurities located 10 Å apart is indeed a liquid by means of Fig. 2: the $S(\mathbf{k})$ for it is similar to that of a half layer of pure hydrogen at 2 K. The main differences appear for k corresponding to the periodicity imposed by the impurity atoms (peaks at 0.75 and 1.5 Å^{-1}). In particular, scattering peaks corresponding to a solid or glassy phase do not appear.

Once we have established that the minimum energy structure is liquidlike we now determine whether the molecules are delocalized enough to exchange between the cells bounded by the impurities and behave as a superfluid. The superfluid coverage σ_s of a liquid can be calculated from the mean squared winding number: the flux of paths across the simulation cell [10]. Figure 3 shows the superfluid fraction, (σ_s/σ_{H_2}), versus H_2 coverage. For different impurity structures, the superfluid fraction has a maximum near the equilibrium coverage and drops to zero for $\sigma_{H_2} > 0.05$ Å^{-2}. The fact that σ_s/σ_{H_2} reaches its maximum value at about half a monolayer is consistent with the results of Ref. [12]. We can see also that a triangular lattice of impurities has a lower superfluid coverage.

The dependence of the superfluid fraction on temperature is given in Fig. 4 for the case of K impurities at the equilibrium H_2 coverage. It reaches a plateau for $T < 1.1$ K. For a translationally invariant single-component Bose liquid the superfluid fraction would approach unity at low temperature. Impurities lower the maximum superflow since it must go around them and the molecules have fewer atoms with which to exchange. Superfluidity drops to zero at high temperature. However one does not see the sharp jump characteristic of the K-T transition because of the finite system size [16]. Preliminary calculations support the idea that the scaling behavior for this very inhomogeneous superfluid is similar to the scaling seen in homogeneous ^{4}He films [16]. In particular, the low temperature superfluid density is changed little by size effects.

The specific heat as a function of temperature, shown in Fig. 5, was obtained by numerically differentiating the E_{H_2} vs T. From the maxima in C_v we estimate that the transition temperature for the 4 K hydrogen films would be 1.2 ± 0.2 K for the rectangular case, and 1.1 ± 0.2 K when the K atoms are located on a triangular lattice. (In the K-T transition the peak occurs at a temperature higher than T_c [16].)

The question that now arises is how to make such a system in the laboratory. First, a monolayer of H_2 must be absorbed on the substrate at low temperatures, i.e., the binding energy to the substrate should be comparable to the energy of solid H_2 (-90 K/molecule). It is also desirable to have a relatively smooth (and incommensurate) substrate to allow the H_2 molecules free movement in the transverse direction. We estimate that the weakly attractive impurities must be approximately equally spaced at distances between about 8 to 12 Å apart. If they are too close together, it will be impossible to form the appropriate exchange paths, and if they are too far apart, a glassy state will form in between the impurities.

Remarkably, there exists a possible experimentally accessible manifestation of this system. It is possible to absorb fractions of a monolayer of alkali metal atoms (Rb, Cs, and K) onto a Ag(111) surface [17]. Depending on the alkali metal coverage, the alkali atoms have been observed to form regular lattices with lattice constants between 2.9 and 10 Å. These lattices are stabilized by the interaction with the substrate and by the repulsive dipolar interactions
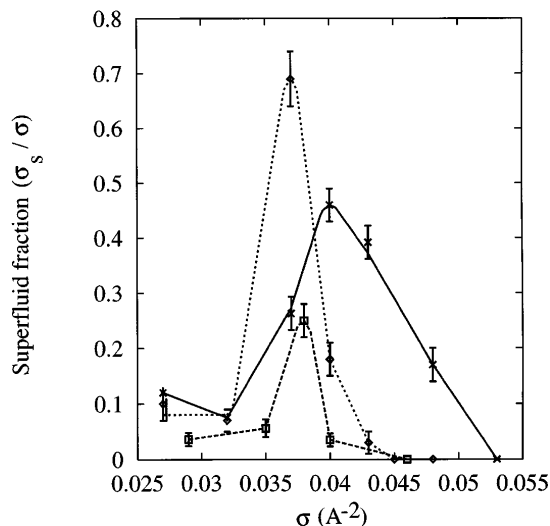

FIG. 3. Superfluid fraction as a function of coverage for three different systems at 1 K: 4 K atoms per cell, rectangular lattice (×'s and solid line); the same number of K atoms on a triangular lattice (squares and dashed line), and 4 Cs impurities per cell (diamonds and dotted line).
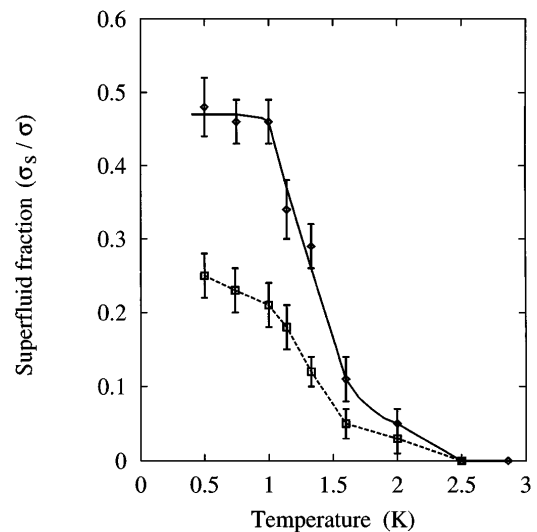

FIG. 4. Temperature dependence of the superfluid fraction for a system with 4 K impurities on a rectangular lattice with $\sigma_{H_2} = 0.04$ Å^{-2} (diamonds and solid curve). The squares (dashed line) are for K impurities on a triangular lattice with $\sigma_{H_2} = 0.038$ Å^{-2}.
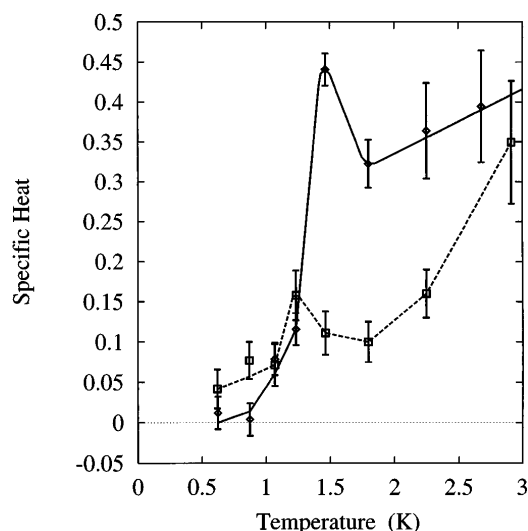
FIG. 5. Specific heat for the same systems as in Fig. 4 (the symbols have the same meaning).

between the alkali metal atoms. For example, Rb and Cs form a triangular lattice (lattice constant 10 Å) at temperatures below 40 K. The alkali metal atoms sit about 2.8–3.0 Å above the top layer of the silver atoms. Hydrogen molecules are observed to absorb onto Ag(111) without significantly modifying their molecular properties [18].

We made several simulations with 3D models to verify that our 2D model was realistic. We placed four alkali metal atoms on the sites of a $2\sqrt{3} \times 2\sqrt{3}$ lattice above the Ag(111) plane. The Ag surface was modeled in two different ways, giving similar results: as a Ag plane interacting with the H_2 molecules along the z coordinate [19], and as three layers of Ag atoms interacting with the H_2 film. We obtained the same value of the minimum energy coverage as for our 2D model of 0.038 Å^{-2}. The mean distance of the hydrogen molecules to the Ag plane was 2.4 with an rms (zero-point) fluctuation of 0.3 Å^2 and a binding energy of -304.4 ± 0.1 K. Since the hydrogen motion is so constrained relative to the Ag surface and the H_2-alkali metal interaction so weak, we expect the 2D model to be accurate. The in-plane structure factors confirm the hydrogen is liquid at the equilibrium coverage. Therefore, we are confident that the proposed mechanism is robust enough that hydrogen superfluidity will be observed under conditions similar to the model presented here.

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