Conditions of Superfluidity in Molecular Hydrogen

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1. INTRODUCTION

Over the last few decades, there has been a search for bose-condensed systems. Until a little over one year ago, liquid helium below 2 K was the only elemental system which was observed to be Bose-Einstein condensed. Elsewhere we have heard about the successes in seeing BEC in atomic vapors and the attempts to cool spin-polarized atomic hydrogen to sufficiently low temperatures to BEC. [1]

Molecular hydrogen H_2 is a natural candidate for superfluidity since it is composed of two pairs of fermions (electrons and protons) in singlet bound states (in para-hydrogen). (This is different than the system Silvera discussed: spin polarized *atomic* hydrogen.) A hydrogen molecule has half the mass of helium, hence the ideal bose condensation temperature would be double that of helium. Hydrogen is a spherical molecule, stable and commonly found, possessing an internal structure (para/ortho hydrogen)that is easily accessible to experiment. At low temperatures and pressures the density of the triplet state, (ortho-hydrogen) is very low in equilibrium. Because of the light mass, one might expect that exchange effects in hydrogen would be more important than in helium. However nature is not so accommodating. Because a hydrogen molecule is more polarizable than helium, the attractive Van der Walls interactions between two molecules are stronger. Its attractive well depth is 37K instead of 10K between helium atoms. As a consequence, the zero pressure density is somewhat higher in hydrogen (0.026 Å^{-3}) than in helium (0.022 Å^{-3}). In helium, when one compresses by this much, one forms a solid at 25 bars. Unfortunately, from the point of view of superfluidity, this has already happened in hydrogen at zero pressure. To make molecular hydrogen into a superfluid all one needs to do is to lower the density by a small amount (10% to 20%.)

Maris[2] tried to form supercooled droplets of liquid hydrogen since the interior of a droplet would be at a negative pressure. One might hope that there would be a barrier to the nucleation of the solid phase as a droplet cools by evaporation. However, both liquid and solid hydrogen are highly mobile, so that if there is a tendency for

solidification, it is likely that solid hydrogen would form quickly. Several groups[3] initially reported superfluid-like signals of hydrogen in vycor, a substance with a porous fractal geometry. While it is plausible that disorder might favor the liquid over the solid, the temperature where the anomalous signals were seen was well above the expected temperature for BEC. The experiments have now been explained as due to movement of hydrogen in and out of the vycor as the temperature is changed.

We have simulated molecular hydrogen in clusters[4] and found that in clusters of fewer than 20 molecules the superfluid density is high. We have also simulated bare hydrogen surfaces and found surface melting of two layers down to 5.5K and delocalization of the topmost layer at even lower temperatures. Simulations of systems with an incomplete topmost layer are superfluid but incomplete layers are not thermodynamically stable. We see thermally activated vacancies in the top layer below the melting temperature, but too few to Bose condense. Vacancy motion is however responsible for relaxation of hydrogen surfaces.

We speculate that in certain "dirty" hydrogen films, the tendency for solidification might be suppressed enough for the film to undergo a Kosterlitz-Thouless transition at low temperatures. Recent simulations[5] of 2D hydrogen with repulsive potassium impurities support this idea, exhibiting superfluid properties at 1K.

2. PATH INTEGRAL MONTE CARLO METHOD

The method of choice for investigating superfluidity of bosonic systems is Path Integral Monte Carlo (PIMC). For bosonic systems, PIMC is an exact numerical method and computers and methods are fast enough that one can begin to "design" the superfluid. (By that, all that is meant is that one can quickly investigate the effect of changing some of the parameters in the model with enough reliability that an experimentalist might try to see the effect.) Only PIMC is capable of accurately predicting the two transitions in condensed ^{4}He: the transition to the superfluid state below 2.2K and the transition to a localized solid above 25 bars pressure. Thus we can use it with confidence to predict what would happen to molecular hydrogen in various situations.

Feynman[6] introduced imaginary time path integrals. Each molecule is mapped into a "polymer", the molecules trace a path in imaginary time which returns to its starting position. Bose statistics corresponds to exchange of polymers where different molecules end up in exchanged positions. Superfluidity corresponds to a macroscopic exchange.

There are several classic manifestations of superfluidity which can be calculated with PIMC. The first effect to be observed and explained by Feynman was the peak in the specific heat resulting from the enlarged phase space of the permuting paths. The second effect, the non-zero superfluidity density is defined in terms of the response of the system to moving the boundaries. This is calculated in PIMC as the mean squared winding number in periodic boundary conditions, or the mean squared area in a cluster. The third effect is a momentum condensation, where a non-zero fraction of the atoms has precisely zero momentum. This is observed by inelastic neutron scattering as discussed by Silver. The momentum distribution is a delta function in 3D and has an algebraic singularity in 2D, resulting from the Kosterlitz-Thouless transition. The momentum distribution is calculated in PIMC by cutting open a

polymer and seeing if the two ends separate or remain bound. The theory and numerical methods of PIMC are discussed in detail in ref [7].

The calculations reviewed here treat the hydrogen molecule as a spherical particle, which is a good approximation for para-hydrogen at low pressures and temperatures. This is because two interacting molecules, both in the J=0 state, are rotating quickly enough that they appear spherical. We have used the semi-empirical Silvera-Goldman[8] potential. Comparisons to experimental data have errors on the order of a few degrees (K) per molecule.

The only unusual feature of our calculation is the special care that needs to be taken at the boundaries for a surface or cluster. Clusters were enclosed in a spherical cavity (radius about 20 Å) to keep molecules from evaporating. Surfaces were modeled with an external potential in the z direction and periodic boundary conditions in the x and y directions. Typical simulation boxes are roughly cubical, 20Åon a side, containing on the order of one hundred molecules. The external potential is constructed so that the particles are attracted to one wall with precisely the force exerted by a semi-infinite slab of hydrogen at the equilibrium density. In some calculations a "frozen" layer of hydrogen was inserted next to the attracting wall to better model the underlying layers. More details are given in refs. [9-11].

Once the Hamiltonian is specified, the exact pair action of two molecules is calculated, so that long imaginary-time steps can be used. Tests have established that we need an imaginary-time step $\tau \leq 0.025K^{-1}$ so that the time-step error is much smaller that the statistical error and the error from the assumed potential energy. This means that we need 20 "time-slices" to achieve a physical temperature of 2 K. Use of the primitive action would require hundreds of time steps for equivalent accuracy. A generalized Metropolis procedure is used to sample the combined path and permutation space. Statistics are gathered on properties such as energy, density, structure factor, exchange probability and superfluid density. We have used the MPI (message passing interface) language to speed up the calculations by doing several runs in parallel[11]. One can go directly from the Hamiltonian to physical properties with a run of less than 1 day on workstations; less for thermodynamic properties, more for the superfluid density. PIMC is unique as a numerical technique in its accuracy, ability to deal with complex situations, and efficient use of the powerful computers that are available.

3. THE SURFACE OF SOLID HYDROGEN

Molecular hydrogen is unique among the elements in having an interface between a highly quantum solid and a vacuum at low temperature. Scaling from simulations of classical liquids would give a triple point temperature of about 26K; in fact the freezing temperature is 13.8K. Because of the effects of quantum motion, the sublimation energy (*i. e.* the chemical potential) depends very strongly on the isotopic mass. It changes from 95 K for H_2 to 140 K for D_2. We calculate an energy of 87 K for H_2 with PIMC, thus verifying that our potential is reasonably accurate. Errors come from the assumed potential not the path integral method.

The breakdown between kinetic and potential energy is interesting. The kinetic energy is 69 K at low temperatures, showing that quantum effects are very large and explaining the large isotope effect in the sublimation energy. We estimate[9]

the Lindeman's ratio (rms deviation from lattice site divided by nearest neighbor separation) in the bulk as 0.21, in agreement with the experimental estimate of 0.18. Also, the equilibrium solid density is calculated correctly. We calculate a surface tension of 3.4 KÅas compared to extrapolation of measurements in the liquid phase of 5.3 KÅ.

From our PIMC studies[9], it is clear that bare H_2 surfaces are very different from bulk solid because of delocalization and, below $\approx$ 1K, bose statistics. We find the top layer of solid hydrogen to be very fluffy: the rms displacement of the atoms on the surface in the normal direction is almost twice what it is deep inside the sample. This fluffiness is greatly reduced[10] if helium atoms are on top; even though the helium atoms sit well above the hydrogen surface they serve to pack it down and increase the localization of the hydrogen: thus helium poisons any hydrogen superfluidity.

Surface melting is the formation of a stable liquid layer at the solid/vapor interface below the bulk melting temperature. Most bulk materials are believed to be wet by a film of their own melt, a few atomic or molecular layers thick at temperatures very near the melting temperature. For a single molecular H_2 layer, a solidification temperature of 5.74K has been seen in experiment[12]. This is more than a factor of two below the bulk melting temperature, but is still too high to expect that liquid H_2 will become superfluid. The question arises whether quantum surface melting is qualitatively or only quantitatively different than that of classical surface melting.

Figure 1 shows a rough "phase diagram" of the surface layers of solid hydrogen as determined with PIMC[11]. Depending on the surface density and temperature, a layer of hydrogen can be either in a 2D gas, 2D liquid or solid or coexistence between those three phases. We defined the phase of a layer with simple structural criteria. They are not necessarily rigorous (but could be made so.)

1. The spatial extent of a *layer* is identified by the minima in the vertical density. A molecule belongs to that layer if its centroid is between those minima.
2. A *solid* has large peaks in the transverse structure factor. Normally these are commensurate with the underlying solid hydrogen lattice but near melting we see evidence of other incommensurate solid structures.
3. We identify a *liquid* as a layer with a smooth transverse structure function.
4. A *superfluid* has many non-trivial exchanges and windings around the periodic boundaries. The number of superfluid atoms is proportional to the mean squared winding number.
5. A *liquid /gas coexistence* has a very large compressibility, as computed by the structure factor extrapolated to zero wave vector.

Using these definitions of liquid and solid, we find[11] that the top layer remains liquid down to about 6K, in agreement with experiments[12]. We examined the liquid-gas coexistence by doing simulations with a half-filled top layer. That top half layer never froze but below the liquid/gas critical point the resulting superfluid formed a 2D drop. This phase is however not stable in the thermodynamic limit. For a large enough system, the density of the droplet would become large enough for it to solidify. The molecules near a surface step are delocalized even at low temperatures, but it is unlikely that they can connect up with other steps in such a way as to propagate the phase of the wavefunction (the order parameter) across a macroscopic distance.

Figure 1. The dependence of layer density on temperature. 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. The solid line at 0.0804 $\mathring{A}^{-2}$ is the coverage deep inside the solid. The line at 13.8K is the bulk melting temperature. If the system remains a liquid to sufficiently low temperature it will become superfluid as marked.

There is one way in which a solid can become a superfluid: if vacancies in the solid were numerous enough they could bose condense. This is called a "supersolid": a system with a spontaneously broken translational order and momentum condensation. In our simulation we see that top layer expand before it melts. Hence, it must contain vacancies but the question is whether there will there be enough of them to become superfluid. We find[11] that the vacancies are thermally activated. Their concentration is given by:

$$c(T) = D_0 \exp(-\Delta E/(k_B T)) \quad . \tag{1}$$

Bose condensation occurs when a bosonic exchange percolates through the sample. To find the transition temperature one needs a relationship between exchange and the density. The two dimensional superfluid transition (Kosterlitz-Thouless) transition occurs at a temperature when :

$$T_c = 1.8c(T)\sigma_0\hbar^2/m^* \quad , \tag{2}$$

where m^* is the effective mass of the vacancy and the coefficient in front has been determined for 2D ^{4}He by Ceperley and Pollock[13]. The precise value of these two parameters will not matter. The question is whether these two equations have a solution for T_c. They do iff:

$$E_l \leq [1.8D_l\sigma^*\hbar^2]/[m^*\epsilon] \quad . \tag{3}$$

Putting in rough estimates for $m^* \approx 2m$ and D_l for the first layer the LHS of the inequality 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.

Even though vacancies do not Bose condense on the surface of hydrogen, apparently, they are responsible for mass transport at the surface. Classen et al.[14] recently described measurements of surface acoustic waves on hydrogen surfaces at low temperature. They prepared a thick homogeneous layer of hydrogen on silver. Upon raising the temperature the film forms bulk crystallites because the bulk has a lower chemical potential; this is called dewetting. However, the process of dewetting is diffusion-limited and can be sensitively observed by monitoring the changing signature of the surface waves. By varying the temperature, one can determine that the mass diffusion is thermally activated with an energy of 23 ± 2 K. It is plausible that the mechanism for surface diffusion of hydrogen films is thermally activated vacancies since the creation energy of the vacancy that we estimated matches what is measured. We are currently calculating of vacancy energies for the other hydrogen isotopes to further compare with experiment.

4. DIRTY HYDROGEN SURFACES

We have seen that hydrogen at a surface has a tendency to become a superfluid[10]. However, if hydrogen is placed on top of another solid layer of hydrogen, the situation favors too much the solid and the top layer freezes at 6K. One must modify, in some way, the substrate on which a layer of hydrogen sits.

The basic idea of our most recent simulations is to favor the liquid state by putting down an array of impurities, incommensurate with the solid hydrogen structure. This lowers the density and the melting point by lowering the free energy of the liquid phase, relative to the solid phase. To simplify the problem, to date, we have only considered a two dimensional model where the hydrogen molecules were restricted to lie in a plane. In that plane, we placed a number of static impurities. We have varied the density and type of impurities to try to favor the liquid state as much as possible. Figure 2 shows a representation of our best superfluid 2D hydrogen. It is composed of a square lattice of impurities, spaced about 10Åapart. We have yet

Figure 2. A typical path of hydrogen molecules in the superfluid state. The nine large circles represent the K impurities: the small circles are the positions of the hydrogen molecules at a single time slice. The imaginary time trajectory of the particles has been Fourier smoothed for clarity. A single unit cell of the simulation box is shown as the dashed rectangle. One can see that the path winds around the periodic boundary conditions in the x direction, thus it is superfluid.

to examine other ways of putting down the impurities, we have only varied their spacing. We have found that large impurities which repel the hydrogen molecules work best. Attractive impurities form a skin of solid hydrogen around them and "seed" a localized, non-superfluid, glassy hydrogen phase.

Figure 4 shows the energy versus coverage of the clean system (no impurities) and the dirty (impurity) system. The effect of the impurities is to lower the binding energy, but it also lowers the density at the minimum. The system at the minimum is a liquid (solid in the clean system) as evidenced by the structure factor. The superfluid density, calculated from the mean-squared winding number, versus coverage is shown in figure 3. The minimum in the energy corresponds to a maximum of the superfluid response. One half of the atoms are superfluid at temperatures below 1K, the other atoms make a normal liquid skin around the impurities. We predict a superfluid transition at about 1.2K.

Figure 3. The superfluid fraction versus hydrogen coverage (in molecules per Å^{-2}) at 1K for the 2D system with potassium impurities present. At the optimal coverage, roughly half of the molecules participate in superfluid flow. At higher coverages the system becomes localized.

We have examined the spacing between the impurities and determined that if they are closer together the superfluid cannot propagate between the cracks. If they are further apart, small hydrogen crystallites can form in the area between the impurities. A spacing of roughly 10 Å is optimal for stabilizing the liquid.

We are now studying the 3D models as we did with pure hydrogen surfaces. Once the Hamiltonian is constructed the calculations are relatively routine, though potentially time consuming because of the large number of substrate/impurity combinations. An important physical consideration to take into account in looking for an appropriate substrate is that hydrogen must wet the surface at low temperature: hydrogen must prefer to absorb on the surface, rather than form a pure crystal. The chemical potential of bulk hydrogen at low temperature is around 90K and we see that the binding within the 2D layer with impurities present is about 10K. Thus the binding energy of a single molecule to the substrate should be more than 80K. If it is much greater than 80K the hydrogen molecules will be trapped into pockets on the surface and unable to move around and exchange. Amongst the rare gas substrates, Neon has close to this value of binding. However, it is not clear how one would be

Figure 4. The energy/molecule versus the coverage for the "clean" (translationally invariant) systems (lower points and curve) and system with potassium impurities (upper points and curve) at a temperature of 1K. Because of the repulsive interaction of the impurities, the zero pressure coverage is lowered and fluid at all temperatures, while the "clean system" is solid for the lowest energy coverage.

able to place impurities on a neon surface.

5. CONCLUSION

PIMC for systems of bosons is an exact numerical method and is now to the point that we can use it to explore novel systems for superfluidity or other quantum properties. PIMC is past the point where one is simply reproducing the results of experiment but instead we are trying to make predictions that will guide experimentalists. This progress has come about because of the development of accurate robust numerical many-body techniques, and of ever faster computers. The methodology has grown synergestically with other many-body methods. Of course, experiments are crucial to verify the predictions.

We are using the same code to study hydrogen in a completely different regime: at much high temperatures and pressures, to study what happens as the atoms and

molecules become ionized and dissociated. Full details of these and other calculations are on our WWW page: *www.ncsa.uiuc.edu/Apps.CMP/index.html*

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