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Simulation of solid molecular hydrogen - a new twist to an old problem

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Abstract

Solid molecular orthohydrogen exhibits orientational order at low temperatures. The ortho-hydrogen molecules, which are quadrupoles, order in the Pa_3 structure. We have simulated this ordering, and explored the behaviour under dilution by spherical parahydrogen molecules.

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1. Introduction

Solid molecular hydrogen is a fascinating material, even though some may consider it to be less exotic than solid atomic hydrogen. It was intensively explored in the seventies and eighties, both in the laboratory and as theoretical/computational models. For some states, the hydrogen molecules behave like quadrupoles which preferentially orient perpendicular to each other, leading to an orientational ordering. Hydrogen has great relevance to many aspects of clean energy generation. Interactions between hydrogen and nanotubes/fullerenes are receiving special attention nowadays, due to their relevance to issues of nanotechnology.

Studying solid molecular hydrogen involves understanding the interaction between hydrogen molecules under compression. Such an understanding is also important when modelling hydrogen storage. The motivation for this project was viewing visualizations of hydrogen molecules inside amorphous and fullerene carbon structures, observing their tendency to be perpendicular to each other and wishing to explore possible connections between this effect and the orientationally ordered phases.

Two aspects of hydrogen must be reviewed before we can continue:

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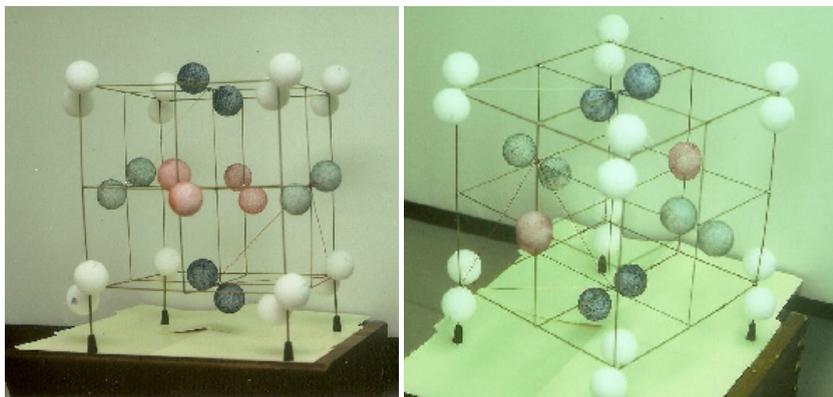


Figure 1: Pictures of a model that illustrates the Pa_3 structure by using two styrofoam balls for each quadrupole. Image at left is a side view and image at right shows how the quadrupoles make a pin-wheel like rotation when viewed from above

(i) hydrogen has three isotopes, hydrogen (sometimes called protium), deuterium and tritium, with zero, one and two neutrons respectively.

(ii) hydrogen molecules take two forms with different relative nuclear spins. When these are parallel, as for orthohydrogen, they take an elongated triplet state. When antiparallel, as in parahydrogen, they form a spherical singlet state. For deuterium this is reversed.

A discussion of the molecular solid and some theoretical results will be given in the next section and a description of our recent simulations will be presented in the following one. Some conclusions will be made in the final section.

2. The Molecular Solid

An excellent review of early results for molecular hydrogen is given by Silvera,[1]. The basis for the solid molecular hydrogen structures is the following: parahydrogen molecules are spherical, but orthohydrogen is an elongated quadrupole. Quadrupoles like to be perpendicular to each other but when they sit on an fcc or hcp lattice and have 12 neighbours there is a shortage of possible perpendicular directions and they must compromise. The compromise is the Pa_3 structure, see Figure 1. This structure was first deduced by Felsteiner, [2], in 1967 within the mean-field approximation. The solid structures are complicated by an HCP-FCC lattice transition that occurs near the orientational ordering transition temperature

If the orthohydrogens are diluted by parahydrogen molecules then (analogously to a dilute magnet) the order will be lost for some dilution value. However, unlike the case of usual Ising magnets, where spins are either up or down and so just one piece of information has to be transmitted, this loss of order does not occur near the percolation threshold, but substantially above it. The concentration of ordered species needed to maintain Pa_3 order must be such that information about several directions to which the molecules must be perpendicular to have to be transmitted. This concentration is nearer to 50 percent (~ 0.53 in experiments, [1]) than to the 20 percent that is typical of three dimensional percolation thresholds. At one point in time, there was speculation

that this was a quantum effect, but, a similar threshold is seen for loss of order in paradeuterium diluted by orthodeuterium. Deuterium has less quantum nature than hydrogen, and therefore it was concluded that the raised threshold effect is geometrical rather than quantum mechanical. The zero temperature situation under dilution was studied by Adler et al[3], who found a lower bound of 0.3 and an upper bound of 0.83 from considerations of bootstrap percolation.

In the region near the 50 percent threshold, claims have been made of a quadrupolar glass (analogous to a spin glass) at finite temperature since there is freezing into a phase with short range order, but a lack of long range order. Computational exploration of this region was hampered in the eighties by the limited system sizes that could be modeled for reasonable times. An impressive set of simulations searching for quadrupolar glasses was carried out by the late M. A. Klenin [4], but the results were inconclusive. Twenty years later, computers have improved “just a little” and so the present project was begun with the aim of returning to such explorations.

3. Our simulations

These simulations were made in a class project in a Computational Physics course. We use a simplified classical model where we place quadrupoles at each lattice point, and although the code allows these to move off-lattice, the results presented below are from runs where the quadrupoles were constrained to be on site. We also considered the dilute case where the absence of a quadrupole represents dilution by parahydrogen. In order to reach equilibrium simulated annealing is performed. We have studied cases with nearest neighbours only and with both nearest and next-nearest neighbour interactions. We do not consider HCP-FCC transitions (yet), exploring both lattices independently. The program has two versions - an interactive C code with X11 graphics and a batch code that uses AViz[5] for visualization. Both can be downloaded [6]. The cylindrical objects used for the quadrupoles have been an option in the AViz code has from its beginning although the atom and spin options have been more heavily used in practice. For this project a modification to AViz was made [7] to enable continual updating of the sample temperature in the images.

Each run is made either for the FCC or the HCP lattice. Since it is known that order only occurs on the FCC lattice we do not discuss the HCP case further here, beyond noting that no orientational order was observed, as expected. In the initial pure orthohydrogen simulations, two groundstates were seen: a planar one and the expected Pa_3 . Addition of a small second neighbour term resulted in stabilization of the Pa_3 state, explaining why the planar state has not been observed in experiment. A tiny amount of dilution also often led to a Pa_3 state.

Four images are shown in Figures 3 and 4, each pair of images being taken from the same viewing angle. First, a pure disordered state is shown, and then an orientationally ordered state is shown, both viewed from an angle where the quadrupoles would appear to take a pinwheel state if ordered. (The pinwheel viewpoint was also shown on the left in Figure 1.) Two images of diluted systems are shown in Figure 4. The case of 10 percent retains the orientational order quite nicely. However for 45 percent of dilution long range order is clearly lost at 0.2K. This point is close to the expected phase boundary between order and disorder and for these small samples we would expect most realizations to be disordered.

4. Conclusions and summary

These simulations, made on personal computers and laptops, not surprisingly match and exceed the sample sizes and statistics of the older simulations. We do not report in detail on

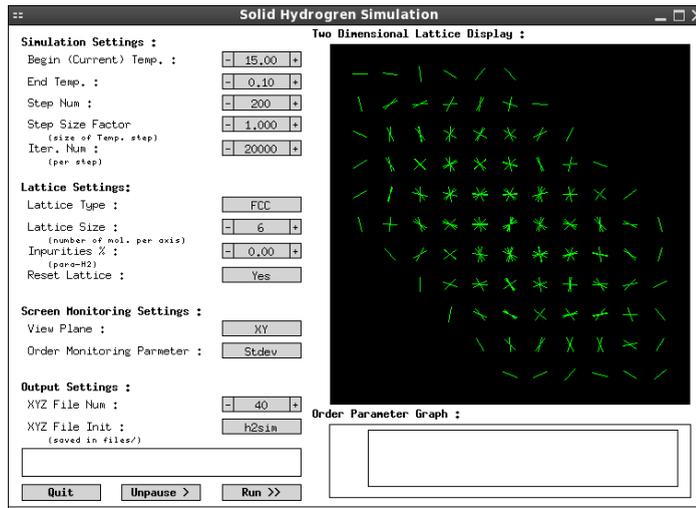


Figure 2: Image of the interface of the X11 version of the code. Buttons enable choice of temperature, dilution, and all the parameters needed to steer the simulation and control the monitoring process by changing the viewing direction. The window showing the state is two dimensional, but .xyz files are prepared to make three dimensional visualizations of desired states as needed

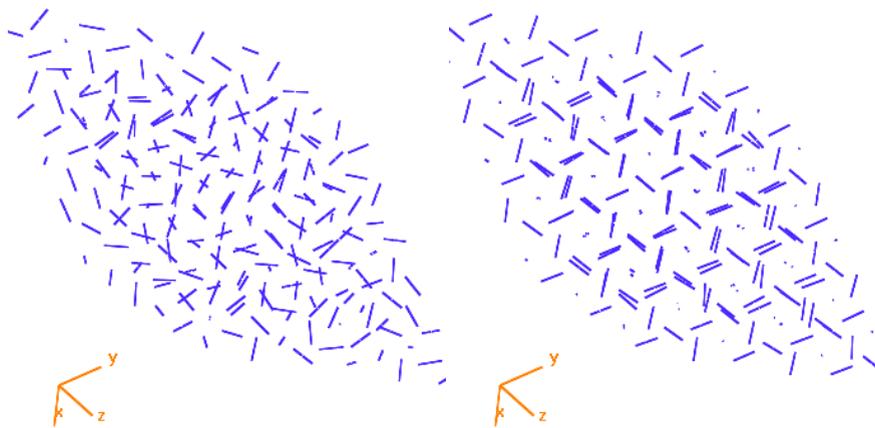


Figure 3: An initial disordered state is shown on the left, and an ordered state from a viewpoint where the pinwheel is clearly seen is shown on the right

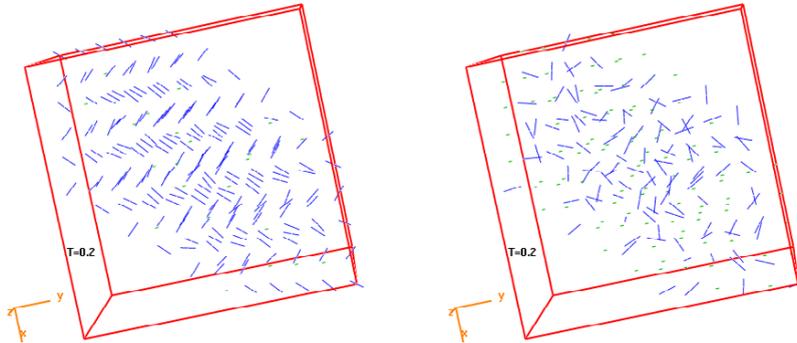


Figure 4: Low temperature (0.2K) states for two cases of dilution, 10 percent on the left and 45 percent on the right

the statistics of runs calculating order parameters, because these still need to be repeated with allowance for finite size scaling. The movement of the quadrupoles off lattice also remains to be explored. The effect of inclusion of second neighbour terms stabilising the Pa_3 order, is, to the best of our knowledge, new, as is the possibility of steering the simulation with the interactive interface which will be used for further explorations towards deducing the nature of the shortrange ordered phase. This study confirms previous results for the pure case, and is consistent with the 50 percent value of dilution for loss of longrange order.

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