Theoretical evidence for a reentrant phase diagram in \textit{ortho-para} mixtures of solid H$_2$

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We develop a multi order parameter mean-field formalism for systems of coupled quantum rotors. The scheme is developed to account for systems where \textit{ortho-para} distinction is valid. We apply our formalism to solid H$_2$ and D$_2$. We find an anomalous reentrant orientational phase transition for both systems at thermal equilibrium. The correlation functions of the order parameter indicate short-range order at low temperatures. As temperature is increased the correlation increases along the phase boundary. We also find that even extremely small \textit{odd-J} concentrations (1\%) can trigger short-range orientational ordering.

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Quantum effects dominate the low temperature ($T < 200\,\text{K}$) phase diagram of solid molecular hydrogen in a wide range of pressures from ambient up to $\sim 100\,\text{GPa}$\footnote{See HD in Fig. 1.} In this regime the coupling between molecules is smaller than the molecular rotational constant, so quantum effects are generally described by means of weakly coupled quantum-rotor models\footnote{See HD in Fig. 1.}. Homonuclear molecules (H$_2$ and D$_2$) can assume only even or odd values of the rotational quantum number \textit{J}, depending on the parity of the nuclear spin. Important differences exist in the phase diagrams of even-\textit{J} (\textit{para}-H$_2$ and \textit{ortho}-D$_2$), odd-\textit{J} (\textit{ortho}-H$_2$ and \textit{para}-D$_2$) and all-\textit{J} (HD) species.\footnote{See HD in Fig. 1.} At low pressure or high temperature, even-\textit{J} species are found in a rotationally disordered free-rotor state (phase I). Increasing pressure causes an increase of the intermolecular coupling, and eventually leads to an orientationally ordered state (phase II). Odd-\textit{J} systems on the other hand are orientationally ordered at low temperature and ambient pressure and remain ordered as pressure is increased. The stronger tendency of \textit{ortho}-H$_2$ to order can be traced to the fact that its \textit{J} = 1 lowest rotational state allows for a spherically asymmetric ground state, unlike the \textit{J} = 0 ground state of even-\textit{J} species. The pressure-temperature phase diagram of HD exhibits a peculiar \textit{reentrant} shape\footnote{See HD in Fig. 1.}. Reentrance refers to phase diagrams where in some range of pressure the system reenters the disordered phase at ultra-low temperatures (see HD in Fig. 1). The zero-temperature orientationally disordered phase is characterized by an energy gap against \textit{J} = 1 excitations. When this gap is sufficiently small and the temperature is finite, the thermally generated \textit{J} = 1 excitations suffice to induce ordering, which is then reentrant, as also shown by mean-field theory\footnote{See HD in Fig. 1.}. Reentrance is also found in models of two-dimensional rotors\footnote{See HD in Fig. 1.}, such as the quantum anisotropic planar rotor (QAPR) model\footnote{See HD in Fig. 1.}.

High pressure experiments have focused mainly on the behavior of pure species. While understanding the orientational transition in \textit{ortho-para} mixtures of quantum rotors in two and three dimensions is a problem of long-standing theoretical and experimental interest\footnote{See HD in Fig. 1.}, less attention has been given at establishing the effects of \textit{ortho-para} distinction. Exceptions\footnote{See HD in Fig. 1.} are the investigation of vibrons in \textit{ortho-para} mixtures by Feldman et al.\footnote{See HD in Fig. 1.} and a recent work by Goncharov et al.\footnote{See HD in Fig. 1.}, where \textit{ortho}-D$_2$ mixed with small amounts of \textit{para}-D$_2$ indicated that the possibility of an orientationally frustrated phase between phases I and II (phase II'). Phase II' persisted for a narrow pressure range ($\sim 2\,\text{GPa}$) for a thermally equilibrated \textit{ortho-para} mixture.

At ambient pressure hydrogen is known to enter gradually a phase of short-range order (orientational glass)\footnote{See HD in Fig. 1.}.
the rate of interconversion between species with fixed concentration are possible because Ambient pressure experiments on pure species as well as a decrease of the minimum concentration of para species is extremely slow at low pressure. Samples with ortho-para, as stated above. Ambient pressure experiments on pure species as well as on samples with fixed concentration are possible because the rate of interconversion between para and ortho H\textsubscript{2} species is extremely slow at low pressure. Samples with fixed ortho-para concentration are prepared by letting the system thermalize at the corresponding temperature for very long times and experiments are then performed at any other temperature by rapid heating or quench (rapid on the time scale of interconversion). At high pressures however the interconversion rate rises steeply. At 58 GPa, the highest pressures where the conversion rate has been measured, interconversion takes place in the time scale of seconds. While interconversion is still orders of magnitude slower than molecular rotation, the ortho-para distribution in this range of pressure is likely to be determined by thermal equilibrium. On the other hand ortho-para distinction is still valid.

Previous theoretical studies addressing quantum effects in compressed hydrogen (mean-field \textsuperscript{23} \textsuperscript{24} \textsuperscript{25} \textsuperscript{26} or quantum Monte Carlo \textsuperscript{22} \textsuperscript{24} \textsuperscript{25} \textsuperscript{26} \textsuperscript{27} \textsuperscript{28} studies) have in most cases neglected the distinction between even-J and odd-J species \textsuperscript{22} \textsuperscript{24} \textsuperscript{25} \textsuperscript{26}, and in those cases where the distinction was explicitly considered, the analysis was restricted to pure even-J or odd-J species \textsuperscript{24} \textsuperscript{25} \textsuperscript{26} \textsuperscript{27} \textsuperscript{28}. On the other hand, theoretical modeling of mixed ortho-para systems \textsuperscript{13} \textsuperscript{17} \textsuperscript{20} at low pressure is generally limited to \textit{J} = 0/\textit{J} = 1 states. \textsuperscript{17} \textsuperscript{20} This is not an accurate model for compressed H\textsubscript{2}, as pressure and temperature cause a non-negligible admixture of rotational states with higher \textit{J’s} in the ground state of both ortho and para species. A binary alloy model \textsuperscript{13} was also used to analyze the low-pressure vibrons in ortho-para mixtures.

In order to calculate the phase diagram of ortho-para mixtures of hydrogen in the solid phase we develop a multi order parameter (MOP) mean-field theory which accounts explicitly for ortho-para distinction in systems of coupled rotors. Our formalism enables us to treat a system of \textsim 3000 molecules, which would be extremely computationally intensive with quantum Monte Carlo. Our formalism also includes correlations due to ortho-para distinction, a feature that is absent in standard mean-field theory. We apply the formalism to a system of coupled quadrupolar rotors whose centers of mass form a face-centered cubic lattice. We find that the phase line separating the orientationally disordered state (phase-I) from the orientationally ordered state is reentrant in the case of thermally equilibrated ortho-para mixtures for both H\textsubscript{2} and D\textsubscript{2}. We also find that orientational order is short-ranged at low temperatures. The validity of our conclusion is supported by the fact that for the two-dimensional model mean-field theory \textsuperscript{3} \textsuperscript{10} is in agreement with quantum Monte Carlo \textsuperscript{11} \textsuperscript{12} simulations on the overall shape of the phase diagram.

The Hamiltonian of a system of \textit{N} coupled quadrupolar quantum rotors interacting through a quadrupole-quadrupole potential can be written in the form

\begin{equation}
H = B \sum_{i=1}^{N} \hat{L}_{i}^{2} + K \sum_{i<j}^{N} \left( \frac{R_{0}}{R_{ij}} \right)^{5} \sum_{m,n} C(224; mn) Y_{2m}(\Omega_{i}) Y_{2n}(\Omega_{j}) Y_{2m+n}^{*}(\Omega_{ij}),
\end{equation}

where \textit{B} is the molecular rotational constant, \textit{K} is the coupling strength, \textit{C}(224; \textit{mn}) are Clebsch-Gordan coefficients, \textit{\Omega}_{i} denote the coordinates of rotor \textit{i}, and \textit{\Omega}_{ij} denote the direction of the vector connecting rotors \textit{i} and \textit{j}. We define \textit{R}_{0} to be the nearest neighbor distance, \textit{R}_{ij} is the distance between molecules \textit{i} and \textit{j}. Our MOP mean-field theory is based on the trial Hamiltonian

\begin{equation}
H_{0} = B \sum_{i=1}^{N} \hat{L}_{i}^{2} + K \sum_{i<j}^{N} \left( \frac{R_{0}}{R_{ij}} \right)^{5} \textit{C}(224; 00) Y_{20}(\Omega_{i}) Y_{20}^{*}(\Omega_{ij}),
\end{equation}

where \textit{\gamma}_{i} are parameters. Variation of the free-energy leads to the self-consistent expression

\begin{equation}
\textit{\gamma}_{i} = \langle Y_{20}(\Omega_{i}) \rangle_{\text{U}}.
\end{equation}

Since the trial Hamiltonian in Eq. \textsuperscript{40} is a sum of single-rotor Hamiltonians, it follows that for each \textit{\gamma}_{i} in Eq. \textsuperscript{40}
the average needs to be performed over the corresponding coordinate $\Omega_i$ only. Ortho-para distinction can be implemented by restricting a particular average to be over odd-$J$ or even-$J$ states.

Since in this study we are only interested in the phase diagram we expand to first-order in the potential $\Phi$. Such an expansion is expected to be valid here, since the transition between the long-range ordered state and the disordered state is only weakly first-order. Furthermore the transition between the short-range ordered state and the disordered state is known to be continuous at ambient pressure. The resulting expression can be written

$$\gamma_i = K3\sqrt{\frac{2}{35}}\sum_j \gamma_j \left(\frac{R_0}{R_{ij}}\right)^5 Y_{40}(\Omega_{ij}),$$

(4)

where $\Phi_i$ is the phase correlator defined as $\Phi_i = \int_0^\beta d\tau \langle Y_2(0(\Omega(\tau))) Y_{20}(\Omega(0)) \rangle_{free,i}$. The averaging is to be performed over a free rotor at inverse temperature $\beta$, and ortho-para distinction can be invoked by restricting the average as described above. Thus, for a given temperature and rotational constant, $\Phi_i$ can take on two values depending on whether rotor $i$ is odd-$J$ or even-$J$. Order will be signalled by non-zero solutions for $\gamma_i$, disorder by solutions in which all $\gamma_i$ are identically zero. The standard mean-field theory is automatically recovered for pure systems.

We calculated the phase diagrams for systems of fixed odd-$J$ fraction, as well as at the thermal equilibrium distribution, taking account of nuclear spin degeneracy. D$_2$ and H$_2$ differ by the values of the rotational constants (2B$_{D_2} = B_{H_2}$) and in the degeneracies of states. Ortho(para) H$_2$ is restricted to be odd-$J$(even-$J$) angular momentum and in D$_2$ the reverse. In our calculations for mixed systems, configurations of 2916 molecules on a face-centered cubic lattice were used. For a given odd-$J$ fraction 20 configurations are generated. A cutoff distance of 2.65 times the lattice constant is used, thus 134 nearest neighbors are included in the interaction calculation. The phase transition point is obtained by diagonalizing Eq. (4) (which is a matrix equation) and finding the lowest coupling constant for which a nonzero solution exists.

In Fig. 4 we present the results of standard mean-field theory phase diagrams of pure odd-$J$/even-$J$ of H$_2$ and D$_2$, and HD, all in excellent qualitative agreement with the experimental results (see Fig. 1b of reference 4). The energy scale is defined to be the rotational constant of the H$_2$ molecule. The main difference between the phase diagrams of odd-$J$ and even-$J$ systems is accurately captured, namely that at low pressures odd-$J$ systems are always ordered, whereas even-$J$ systems order at finite pressures. As expected from experiment odd-$J$ D$_2$ orders at a lower coupling strength than odd-$J$ H$_2$, and the reentrant phase transition in HD is also well reproduced by mean-field theory.

In Fig. 2 the results of the formalism presented above are shown for solid H$_2$. As the ortho concentration is decreased the system tends towards disorder entering the ordered state at higher coupling constants for a given temperature. A noteworthy result of our calculations is that even at an ortho concentration of 1% the system enters an ordered state at coupling constants quite different from that of pure para hydrogen, and that for any ortho concentration the ground state is always ordered. The 50% ortho system is very close to the pure ortho one. Our results are consistent with the phase diagram shown in Fig. 1 of Ref. 13 in which the pure para-H$_2$ phase transition occurs at $\sim 110$ GPa, and ortho containing samples show ordering at lower pressures.

In order to assess the nature of the ordering we calcu-
lated correlation functions of the local order parameters \( \{\gamma_i\} \). This is an advantage of our multi order parameter formalism over the standard mean-field theory, since in single-site mean-field theory only phases of complete order or disorder are possible. In particular we have calculated

\[
G(r) = \langle (\gamma(0)\gamma(r))^2 \rangle. \tag{5}
\]

The results along the phase line of the 10% ortho system of hydrogen are shown in Fig. 3. The correlation increases along the phase boundary with increasing temperature indicating the onset of long-range order. The onset of long range order is due to the fact that ortho-para distinction ceases as temperature and coupling constant (pressure) are increased.

The orientational ordering of the system with ortho-para concentrations at thermal equilibrium is shown in Fig. 4 along with the phase diagrams of the pure systems (also shown in Fig. 1) for comparison. For H\(_2\) and D\(_2\) we calculated the phase diagrams via the multi order parameter mean-field theory presented here, and via the standard mean-field theory. The resulting phase diagrams indicate reentrance in both D\(_2\) and H\(_2\). Reentrance is also seen \[27\] in the corresponding 2D model \[10\]. Reentrance is stronger in the case of H\(_2\), due to higher relative weight of odd-J contribution (nuclear spin degeneracy), and higher rotational constant (stronger quantum effects). The correlation functions for different temperatures along the reentrant phase diagram are shown for H\(_2\) in Fig. 5. As the temperature increases correlation increases along the phase boundary. At high temperatures \( T > 1 \) the order is definitely long-range. We conclude that short-range order may be present up to \( T = 0.75 \). In the case of D\(_2\) reentrance is less severe.

In summary we calculated the phase diagrams of solid hydrogen and its isotopes. We found that the I-II phase line is interspersed by another phase, likely to be orientationally frustrated, as suggested by the experiments of Goncharov et al. \[14\]. For a thermal distribution of ortho-para rotors we find a reentrant phase diagram for both H\(_2\) and D\(_2\). At low temperatures the order is short-ranged. Most experimental signatures of the long-range ordered phase are well known. \[1, 2\] the short-range ordered phase may be seen by probing the distribution of the local order parameter. While nuclear magnetic resonance \[17\] is a useful probe, it may be difficult to apply at high pressure. The II\(^+\) phase was found \[14\] by investigating the Raman vibronic shift and it is known to be sensitive in ortho-para mixtures \[13\]. Rotational Raman lines are also sensitive to local order. Experimental studies to resolve the issues raised here would be helpful.

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FIG. 5: Correlation functions along the phase boundary of the of solid H\(_2\) at thermal equilibrium.