2D and 3D quantum rotors in a crystal field: critical points, metastability, and reentrance

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July 9, 2009

Abstract

An overview of results of models of coupled quantum rotors is presented. We focus on rotors with dipolar and quadrupolar potentials in two and three dimensions, potentials which correspond to approximate descriptions of real molecules adsorbed on surfaces and in the solid phase. Particular emphasis is placed on the anomalous reentrant phase transition which occurs in both two and three-dimensional systems. The anomalous behaviour of the entropy, which accompanies the reentrant phase transition, is also analyzed and is shown to be present regardless if a phase transition is present or not. Finally, the effects of the crystal field on the phase diagrams are also investigated. In two-dimensions the crystal field causes the disappearance of the phase transition, and ordering takes place via a continuous increase in the value of the order parameter. This is also true in three dimensions for the dipolar potential. For the quadrupolar potential in three dimensions turning on the crystal field leads to the appearance of critical points where the phase transition ceases, and ordering occurs via
a continuous increase in the order parameter. As the crystal field is increased the range of the coupling constant over which metastable states are found decreases.

1 Introduction

In molecular solids the energy scales of translation, rotation, and vibration can be expected to be of different orders of magnitude. In the solid hydrogens [1, 2, 3], the rotational lines are clearly distinct from the spectral signatures of the translations and rotations. For a large pressure interval in such systems models of coupled rigid rotors are sufficient to understand the general features of phase transitions in particular those of the orientational kind. In this work we refer to such systems as orientational crystals.

There exist systems in both two and three dimensions which can be thought of as orientational crystals. Two dimensional examples are physisorbed molecules on inert surfaces, such as N$_2$ or H$_2$ and its isotopes on graphite or boron-nitride. The former can be approximated by a model of planar rotors, known as the anisotropic planar rotor (APR) model [4, 5, 6, 7]. This model exhibits an orientational order-disorder phase transition from an orientationally disordered state to the orientationally ordered herringbone structure. In N$_2$ on a graphite surface this transition takes place at 30 K [8, 9], well below the liquid-solid ordering temperature of 47 K [10]. While the classical APR model accounts for the orientational ordering, a more quantitative description of the system necessitates the inclusion of quantum effects [11]. Also, models of coupled quantum planar rotors are useful in describing other systems, such as granular superconductors [12, 13, 14, 15, 16, 17] and more recently the bosonic Hubbard model [18, 19].

Three-dimensional examples are the solid phases of the hydrogens and different isotopes. The behavior of the hydrogens is generally made more complex by the fact that ortho-para conversion times are slow on the timescale of rotations (in the pressure ranges considered here $\leq 100$ GPa) [20], hence it is a reasonable approximation to take the ortho-para ratio to be a fixed parameter [21]. The existence of ortho and para species is due to the coupling of nuclear spins and the rotational quantum numbers characterizing a particular molecule. For the H$_2$ molecule a rotation of angle $\pi$ corresponds to an exchange of the constituent atoms, hence the wavefunction has to be anti-symmetric in such a rotation. Since the H atoms are of spin $\frac{1}{2}$, the
possible spin states of the molecule as a whole are three symmetric and one anti-symmetric spin state. To preserve the overall antisymmetry of the wavefunction the symmetric spin states couple with anti-symmetric spatial states (odd angular momentum or odd-$J$) and the anti-symmetric spin states couple with symmetric spatial states (even-$J$). In HD, where the atoms are indistinguishable all angular momentum states are allowed (all-$J$). In $\text{D}_2$ the constituent atoms are bosons, hence the wavefunction has to be symmetric. However this leads to a qualitatively similar situation: here symmetric(anti-symmetric) spin-states are even-$J$(odd-$J$).

The orientational ordering properties of odd-$J$, even-$J$, and all-$J$ systems show striking differences. Odd-$J$ systems show orientational ordering in the ground state, whereas even-$J$ systems order at higher pressures. At low pressures and low temperatures the even-$J$ systems can be thought of as spheres. An interesting anomalous feature that was first predicted for all-$J$ systems is the reentrant phase diagram. Upon cooling, in certain pressure ranges, the system orders orientationally due to a decrease in thermal fluctuations. In the reentrant region, the orientationally ordered phase is destroyed by quantum fluctuations (also known as quantum melting). This effect was first predicted in the mean-field phase diagram of the all-$J$ hydrogen system (HD) \cite{22, 23}, and experimentally verified thereafter \cite{24}.

For the quantum generalization of the APR model (QAPR) the system corresponding to the all-$J$ case also shows reentrance. This was first predicted by mean-field theory \cite{25}, and then verified via quantum Monte Carlo calculations \cite{26} as well as quantum Monte Carlo calculations analyzed via finite size scaling \cite{27, 28}. Reentrance was also found in the corresponding model of granular superconductors \cite{16, 17}.

Recently a set of studies \cite{29, 30, 31} have suggested that if the thermal equilibrium distribution of the ortho-para ratio is reached then reentrance can occur in the homonuclear systems $\text{H}_2$ and $\text{D}_2$. This conclusion is supported by experimental evidence \cite{32}.

In this paper we give an overview of the mean-field theory of phase transitions in coupled rotors with particular attention to the issues of reentrance, other quantum anomalies, and meta-stability. We comparatively analyze coupled planar rotors (two-dimensional model) and coupled linear rotors (three-dimensional). We show that the dipolar potential does not exhibit the reentrance anomaly, whereas the quadrupolar one does. The phase transition turns out to be second order in all cases except for the linear rotors in a quadrupolar potential where it is first order. We also investigate the effects
of the crystal field: in the case of the linear rotor model with quadrupolar potentials the crystal field causes the appearance of critical points which separate lines of the phase diagram where the transition is first order from regions where there is no phase transition, but simply a continuous change of the order parameter \[33\]. We show that the range over which metastable states (which accompany a first-order phase transition) depends on the crystal field: as it is increased this region becomes smaller, and disappears when the phase transition itself disappears. We also analyze the behaviour of the entropy in all cases.

2 Coupled rotors in two dimensions

The model we study in this section is described by the Hamiltonian

\[
H = -B \sum_{i=1}^{N} \frac{\partial^2}{\partial \phi_i^2} - \frac{U}{2} \sum_{\langle i,j \rangle} \cos(X \phi_i)\cos(X \phi_j) - U_1 \sum_{i=1}^{N} \cos(X \phi_i),
\]

where \(B, U,\) and \(U_1\) denote the rotational constant, the coupling constant, and the strength of the crystal field respectively, and where the sum \(\langle i, j \rangle\) runs over nearest neighbors. The parameter \(m\) specifies the periodicity of the potential. In this work we will investigate the cases \(X = 1, 2,\) which show...
qualitatively different behaviour. As a unit of energy and temperature we choose the rotational constant $B$ in all of the subsequent cases.

Applying the mean-field approximation to this Hamiltonian results in

$$H_{MF} = -B \sum_{i=1}^{N} \frac{\partial^2}{\partial \phi_i^2} - (U_0 \gamma + U_1) \sum_{i=1}^{N} \cos(X \phi_i) + \frac{U_0 N}{2} \gamma^2;$$

where $\gamma$ denotes the order parameter, and $U_0 = U_z$ with $z$ denoting the coordination number. We note that had we used the dipole-dipole (quadrupole-quadrupole) potential in Eq. (1) the resulting approximate Hamiltonian can be shown to be the same as the one in Eq. (2) with $X = 1(X = 2)$ with a modified coupling constant.

![Figure 2: Order parameter as a function of temperature for the $X = 2$ system at $U_0 = 3.50$. The curves with negative values indicate a metastable state in the case of finite crystal field.](image)

The mean-field phase diagrams without crystal field for $X = 1, 2$ are shown in Figure 1. The phase diagrams separate the orientationally disordered phase (at lower values of the coupling constant) from the orientationally ordered phase. The two striking differences between the two curves are the quantitative difference between the onset of order and the shape of the phase diagram. The former can be attributed to the width of the barrier through which the quantum systems tunnel. The $X = 1$ system has a wider barrier than the $X = 2$ system. The reentrance has been found in the related QAPR...
model via quantum Monte Carlo [20, 27, 28] and is known to be due to the ordering tendency of higher energy states (the states with angular momentum zero are disordered as they are of polar symmetry, the first odd angular momentum states are ordered). In both cases we have found the transition to be of second order.

Figure 3: Entropy calculations for a system without crystal field. The comparison is for the entropy of the actual system (solution of the mean-field equations) and for fixed order parameter ($\gamma = 0.00, 0.25, 0.50, 0.75, 1.00$).

Calculations for the order parameter are presented in Fig. 2 for a system with $X = 2$ ($U_0 = 3.50$ reentrant region). In the case of no crystal field both transitions are manifestly second-order. As the temperature is increased the order parameter is zero until $T \approx 0.27$, it increases up to $T \approx .5$, then the slope switches sign and decreases until $T \approx .86$. Subsequently the order parameter is zero. The effect of the crystal field is also shown in Fig. 2. The order parameter for the system with crystal field shows no discontinuous change in the slope of the order parameter, however a change in sign of the slope occurs at $T \approx .5$ as in the case of no crystal field. Another feature of the crystal field is the appearance of a metastable state with negative order parameter as shown in Fig. 2.

The behaviour of the entropy for the system with $X = 2$ without crystal field is shown in Figure 3. As has been shown for the three dimensional case [30], the entropy displays an anomaly in the case of the reentrant phase.
diagram. The entropy curves for the fixed order parameter show qualitatively
different behavior above and below $T = 0.5$, where the slope of the order
parameter switches sign (Fig. 2). The entropy of the disordered state ($\gamma = 0$)
is the lowest below the temperature $T = 0.5$, and the entropy increases as
the system orders. This behaviour is unexpected from a classical point of
view. Above $T = 0.5$ the entropy of the ordered state is the lowest, and it
increases upon disordering, as expected based on the classical view.

Figure 4: Entropy calculations for a system with crystal field ($U_1 = 0.01$).
The comparison is for the entropy of the actual system (solution of the mean-
field equations), the meta-stable solution, and for fixed order parameter ($\gamma =
0.00, 0.25, 0.50, 0.75, 1.00$). The coupling constant is $U_0 = 3.5$

This unusual feature can be understood from considering the expression
of the entropy for the quantum mechanical system $S = - \sum_i P_i \ln P_i$, where
$P_i$ denote the probability for a particular state. In the quantum mechanical
system the states are obtained after diagonalizing the Hamiltonian (in the
corresponding classical system the sum in the expression for the entropy is
an integral over the angles, and the probability is a function of the angles
as well). As the lowest state, which dominates the behaviour of the sys-
tem at low temperatures (i.e. has the highest probability), corresponds to
a disordered state, it is not surprising that the entropy decreases and that
simultaneously the system disorders. In the state-space to which the prob-
abilities in the entropy expression refer the number of possible states does
in fact decrease (i.e. in that sense the system orders), however the states themselves are disordered in real space. In some sense this picture is similar to Bose-Einstein condensation [34], where the single lowest state becomes populated (and which corresponds to a state that is spatially disordered), with the important difference that here the state is not a collective state.

\[ \begin{align*}
V & \cos(2\phi) \\
\end{align*} \]

Figure 5: Energy levels for a system with potential \( V \cos(2\phi) \).

We also note that the entropy of the solution of the mean-field equations corresponds to the disordered case below and above the phase transition points. At the phase transition points the slope of the entropy is discontinuous.

The effect of the crystal field on the entropy is shown in Fig. 4 (\( U_1 = 0.01 \)). The same behavior is observed with regard to the ordering pattern as in Fig. 3. Below the turning point of the slope of the order parameter (Fig. 2) the entropy of the ordered state is higher than that of the disordered state. Here the slope of the entropy does not change discontinuously as a function of temperature, as no phase transitions are experienced.

The entropy anomaly can also be understood in terms of the local energy spectrum. The eigenvalues of a planar rotor with potential \( V \cos(2\phi) \) are shown in Fig. 5 as a function of \( V \). At \( V = 0 \) (disordered state) the ground state is a singlet and the first excited state is doubly degenerate. As \( V \) is increased the degeneracy of the first excited state is split, and the lower energy state becomes degenerate with the ground state adding a factor of \( R \ln 2 \) to the entropy at low temperatures.
Figure 6: Phase diagram for linear rotors, $X = 1$ and $X = 2$, with several values of the crystal field in the case of the latter.

3 Coupled rotors in three dimensions

In this section we calculate the mean-field phase diagram of a system of coupled three-dimensional rotors under a crystal field.

$$H = B \sum_{i=1}^{N} \hat{L}_i^2 - \frac{U}{2} \sum_{(i,j)} P_{Xm}(\Omega_i)P_{Xm}(\Omega_j) - U_1 \sum_{i=1}^{N} P_{X0}(\Omega_i),$$  \hspace{1cm} (3)

where $P_{X0}(\Omega_i) = \sqrt{4\pi/(2X + 1)}Y_{00}(\Omega_i)$. The mean-field approximation to the Hamiltonian in Eq. (3) results in

$$H_{MF} = B \sum_{i=1}^{N} \hat{L}_i^2 - (U_0\gamma + U_1) \sum_{i=1}^{N} P_{X0}(\Omega_i) + \frac{U_0N}{2} \gamma^2.$$  \hspace{1cm} (4)

The phase diagrams for the two cases $X = 1$ and $X = 2$, and for several crystal fields in the case of the latter, are shown in Figure 6. For the systems without crystal field, the two features identified in the previous section in the case of the planar rotors, namely the stronger ordering tendency in the $X = 1$ case, and the reentrant phase transition in the $X = 2$ case are present in the case of linear rotors as well. An important difference is that the $X = 2$ case exhibits a first order phase transition. An unusual feature develops upon
turning on the crystal field. As shown before [33] the crystal field gives rise to critical points which separate regions in the phase diagram where the transition is first order from regions where no phase transition occurs, rather a continuous increase in the order parameter (the exact quantitative features of the phase diagram are explained in Ref. [33]).

Figure 7: Order parameter for different values of the crystal field as a function of the coupling constant $U_0$ at a temperature of $T = 0.75$ The of the crystal field from left to right are $U_1 = 0.012, 0.008, 0.004, 0.000$. The dotted lines indicate the value of the order parameter for metastable states.

In Figure 7 we show the order parameter as a function of the coupling constant at a temperature of $T = 0.75$ (approximately where the reentrant turning point occurs) for the $X = 2$ system. The calculations are presented for different values of the crystal field $U_1 = 0.012, 0.008, 0.004, 0.000$. The dotted lines indicate the meta-stable states. As usual in first-order phase transitions, as the parameter $U_0$ is varied a meta-stable state develops before the phase transition, which becomes the stable state upon crossing the phase transition point. Simultaneously the stable state becomes meta-stable. When no crystal field is present we found that as $U_0$ is increased from the left, the ordered meta-stable phase first appears at $U_0 \approx 11.2$ and becomes the stable state at $U_0 = 11.38$. Subsequently the disordered phase $\gamma = 0$ becomes metastable. As the crystal field is turned on the range where metastability is encountered decreases. For $U_1 = 0.004$, as $U_0$ is increased from the left we find evidence for a meta-stable phase at $U_0 \approx 11.0$, the phase transition is
encountered at $U_0 = 11.14$, but the less ordered phase (which was stable at $U_0 \leq 11.14$ persists as a meta-stable phase until $U_0 \approx 11.4$. For $U_1 = 0.008$ the phase transition is found at $U_0 = 10.88$ and meta-stability is encountered only in a range $\approx .04$ around the phase-transition point. For $U_1 = 0.012$ no phase transition is encountered, only a continuous increase in the order parameter.

Figure 8: Entropy of the ordered state and at fixed values of the order parameter for the system of linear rotors with $X = 2$ at no crystal field, $U_0 = 12.50$.

The entropy curves verify the general tendency shown in the case of linear rotors in the previous section. In Figures 8 and 9 the value of the entropy corresponding to the solution are shown as well as the value of the entropy at fixed order parameter for the case without crystal field ($U_0 = 12.50$) and with a crystal field of $U_1 = 0.018$ ($U_0 = 12.00$). The inset shows the value of the order parameter at $U_1 = 0.018$ as a function of temperature: as the temperature is decreased the order parameter increases, it experiences a turning point at $T = 0.75$ and then begins to decrease. This happens continuously, without any phase transition. The entropy of the ordered state, as was the case for the planar rotors, is higher at low temperature ($T \leq 0.75$) than that of the disordered state. Thus the reversal of ordering as the temperature is cooled appears to be correlated with the entropy anomaly, however, whether the disordering occurs as a result of a phase transition is not. In the absence of the crystal field the quantum melting phase transition
is second order for planar rotors, first order for linear rotors. When a crystal field is turned on the phase transition is absent for planar rotors, whereas a more complicated situation develops for linear rotors (see Figures 6 and 7 and Ref. [30]), but if the crystal field is large enough the ordering and disordering also happens continuously. The entropy anomaly accompanies all of these ordering patterns.

Figure 9: Entropy of the ordered state and at fixed values of the order parameter for the system of linear rotors with $X = 2$ at a crystal field of $U_1 = 0.018$, $U_0 = 12.00$. The inset shows the order parameter.

The energy levels for the linear rotors in an external potential of $VY_{20}(\Omega)$ are shown in Fig. 10. As in the case of the planar rotors increase of $V$ from zero causes one state to move down and approach the ground state causing an increase of $\approx R\ln 2$ in the entropy.

4 Conclusions

We have presented a comparative review of the mean-field theory of different types of coupled rotors. We have considered planar and linear rotors in dipolar and quadrupolar potentials. These models have corresponding physical realizations: diatomic molecules (heteronuclear in the dipolar case, homonuclear in the quadrupolar case) physisorbed on surfaces (two dimensional system) or in the solid phase (three dimensional system). The dipolar
potentials in both cases lead to a usual phase diagram where above a particular value of the coupling constant the temperature vs. coupling constant phase diagram increases with coupling constant. The quadrupolar potentials lead to reentrant phase diagrams in both cases: at low temperatures, for some values of the coupling constant, quantum melting takes place. The phase transition for the planar rotors is always second order. For the linear rotors the dipolar potential leads to a second-order phase transition, in the quadrupolar potential the phase transition is first order.

We have also shown the different effects found when the systems are subjected to a crystal field. For the dipolar potentials the crystal field causes a disappearance of the phase transition line, as temperature is decreased, and as the coupling constant is increased only a continuous increase in the order parameter is found. As the ordering increases a metastable state is also found with a negative order parameter. We have also found this for the planar rotors coupled via a quadrupolar potential. For the linear rotors the situation is more complicated. As previously found\[30\] increasing the crystal field causes the appearance of critical points which separate the phase diagram into lines where the phase transition is first order from regions where no phase transition, but a continuous change in the order parameter occurs. An interesting accompanying feature is that where there is a phase transition, the range in which a metastable state is found decreases with the strength of the crystal field.

Figure 10: Energy levels for a system with potential $V Y_{20}(\Omega)$. 
The reentrance in the case of the quadrupolar systems is accompanied by an entropy anomaly: if the order parameter is held fixed the entropy of the ordered state is higher at low temperatures than that of the disordered state. The situation reverses when the temperature is increased. This entropy anomaly is present in all the systems which exhibit quantum melting, irrespective whether the melting takes place via a phase transition (either first or second order), or via a continuous change in the order parameter. Calculation of the spectrum of the mean-field potentials shows that the entropy anomaly can be explained in terms of the change in the degeneracies of states as a function of the coupling constant, as the ground state becomes doubly degenerate. It can also be argued that the entropy anomaly is a natural consequence of quantum mechanics: the entropy decreases with temperature, as a single state begins to dominate, but this single state is a delocalized one (zero angular momentum state), hence it is disordered.

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