Orientational Ordering of *ortho–para* Mixtures of Crystals of Homonuclear Diatomic Molecules: Theoretical Evidence for Reentrance

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We have developed a theoretical formalism to calculate the orientational phase diagram of ortho–para (or odd-J/even-J) mixtures of homonuclear diatomic molecules in the low-pressure solid phases. In particular, our formalism allows for the explicit disorder present in such mixtrues. While the formalism is general, here we apply it to the quantum anisotropic planar rotor model, a two-dimensional model of coupled rotors. Our calculated phase diagram, separating phases of disorder and short-range order is reentrant, *when an equilibrium mixture of odd-J/even-J species is considered. A reentrant phase diagram separating states of disorder and long-range order is known to exist in all-J species in both two and three dimensions. The phase diagram we find for the thermal mixture of odd-J/even-J species exhibits reentrance over a wider range of coupling constants than the corresponding all-J species. We also investigate systems where the odd-J fraction is fixed as a function of temperature. We find that even 1% odd-J mixture exhibits a phase diagram different from the pure even-J case, indicating that the even-J molecules play important role in orientational ordering.*

1. INTRODUCTION

Understanding the orientational glass transition in mixtures of *ortho–para* hydrogen and its isotopes in two and three dimensions is a problem of long-standing theoretical and experimental interest.[1–13] It has been known for a long time, mainly from NMR measurements, that at low pressures and

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ortho fractions of $x < 0.53$ [1,2,4] solid H_2 *gradually* enters a phase of short-range order. This phenomenon can be understood from the symmetry of the orbitals of *ortho* and *para* species, respectively. In the case of H_2 *ortho* (*para*) molecules are antisymmetric (symmetric) with respect to intramolecular exchange (rotation by π), therefore the *ortho*-species has a stronger tendency to order. The antisymmetry (symmetry) corresponds to odd (even) angular momentum states (J). Solid *para*-H_2 exhibits orientational ordering at $\sim 110\,\text{GPa}$, whereas *ortho*-H_2 is thought to be always ordered at zero temperature.[14,15] A random mixture of *ortho–para* (odd-J/even-J) species thus introduces orientational frustration, which in the absence of *ortho–para* interconversion can lead to short-range ordered (orientational glass) state.

The pressure dependence of the phase diagram is complicated by the increasing rate of *ortho–para* interconversion.[16] In extremely high pressure phases ($> 150\,\text{GPa}$ in H_2) *ortho–para* interconversion is some orders of magnitude faster than that at zero pressure. In the phases at pressures lower than $150\,\text{GPa}$, the effects of *ortho–para* distinction is a subject of debate.[17] In mixed systems there is also evidence for an orientationally frustrated phase between the orientationally ordered and disordered phases (phase II$'$ in Ref. 3).

The theoretical modeling of mixed *ortho–para* systems is generally based on random-site models, and quantum effects are taken into account impicitly, for example by substituting an empty site (or a $J = 0$ state) for the species symmetric in π.[1,8–10] In this case the temperature dependence is inaccurate, since states of higher angular momentum can be expected to mix with the ground state for both odd-J and even-J species.

In this study we develop a formalism in which quantum effects are explicitly taken into account. While the system under scrutiny here is the quantum anisotropic planar rotor (QAPR)[18–20] model, the ideas are easily extendable to models of coupled rotors in three dimensions, and will be carried out in future work. Furthermore, the qualitative features of the ordering phase transitions of the QAPR model are essentially the same as that of models of coupled quadrupolar rotors: the charateristic reentrant phase transition is found in the mean-field theory of both 2D[18,26] and 3D[22,23] models, and is also seen experimentally in the corresponding system.[24] In QAPR, computer simulation studies have also given evidence for reentrance.[19,20] We emphasize that the reentrant phase transition was found experimentally and theoretically in *all-J systems*.

Our solution of QAPR is based on writing a separable trial Hamiltonian and minimizing the trial free-energy.[25] In the trial Hamiltonian we use, each rotor present in the system is represented by a single parameter, allowing for the explicit treatment of disorder in odd-J/even-J mixtures (in mean-

field theory one parameter represents the average of all rotors). In order to arrive at an expression easily solvable for a large lattice of rotors, we expand it in the potential energy as was done by Šimánek.[26] An advantage of our formalism is that the disorder due to the symmetry properties of the different molecules is explicitly considered.

In the following section we describe QAPR. Subsequently, we describe our formalism that includes explicit *ortho–para* disorder. In section 4. we give the mean-field equations. In section 5. results of our formalism and mean-field theory are presented and compared. In section 6. we conclude our work.

2.   THE QAPR MODEL

The quantum anisotropic planar rotor (QAPR) model[31,18] is the quantum generalization of the classical APR model,[28–30,32] which was originally developed to study the orientational ordering of nitrogen on a graphite surface. Nitrogen on graphite is known to order classically into a "herringbone" structure. In APR and QAPR a set of uniaxial rotors on a two-dimensional triangular lattice are coupled *via* the anisotropic part of the electrostatic quadrupole–quadrupole potential. Both the classical[28–30,32] and the quantum[31,18–20] models have been studied extensively.

The QAPR Hamiltonian can be written as

$$\mathcal{H} = -B \sum_{i=1}^{N} \frac{\partial^2}{\partial \phi_i^2} + K \sum_{\langle i,j \rangle} \cos(2\phi_i + 2\phi_j - 4\Phi_{ij}), \tag{1}$$

where N is the number of rotors, ϕ_i is the coordinate of rotor i, B is the rotational constant, and K is the coupling constant. The summation $\langle i,j \rangle$ indicates sums over interacting pairs, in this study we assume nearest neighbor coupling. The phase angle Φ_{ij} is the angle which the line between rotors i and j makes with some arbitrary axis. The exact form of the herringbone order parameter are given elsewhere.[18–20,31] In this study we will set the energy scale to be the rotational constant B.

3.   FORMALISM WITH EXPLICIT
ODD-*J* / EVEN-*J* DISORDER

Our aim is to calculate the phase diagram for the system described by Hamiltonian given in (1) in the case where a given molecule or rotor can have

only even or odd angular momentum states. To this end we introduce a trial Hamiltonian of the form

$$\mathcal{H}_t = -\sum_{i=1}^{N} B \frac{\partial^2}{\partial \phi_i^2} + K \sum_i \cos(2\phi_i) \sum_j^{(i)} \gamma_j \cos(4\Phi_{ij}) , \tag{2}$$

where the γ_i are a set of parameters to be optimized. The summation $\sum_j^{(i)}$ indicates summing over nearest neighbors of rotor i.

The trial Hamitonian in (2) is separable in ϕ_i. Thus we can write

$$\mathcal{H}_t = \sum_i H_{t,i}, \tag{3}$$

where the trial Hamiltonian for a particular rotor i can be written as

$$\mathcal{H}_{t,i} = -B \frac{\partial^2}{\partial \phi_i^2} + K \cos(2\phi_i) \sum_j^{(i)} \gamma_j \cos(4\Phi_{ij}) . \tag{4}$$

In order to derive a set of equations for the parameters γ_i we use the well-known identity:[25]

$$F \leq F_t + \langle S - S_t \rangle_t , \tag{5}$$

where $F(S)$ is the free energy (action) of the true QAPR system, $F_t(S_t)$ is the free energy (action) of the system described by the trial Hamiltonian in (2), and $\langle \rangle_t$ indicates evaluating the thermal average using the trial Hamiltonian. The trial free energy to be minimized is the right-hand side of (5). Minimization in the parameters γ_i leads to a set of coupled equations for γ_i

$$\gamma_i = \big\langle \cos(2\phi_i) \big\rangle_{t,i} . \tag{6}$$

Note that a particular γ_i is coupled to its nearest neighbors, $\{\gamma_j\}^{(i)}$. Furthermore, in evaluating the average on the right hand side of (6), it is possible to restrict the symmetry of the states over which the average for a particular γ_i is performed. Thus we are able to explicitly implement the disorder in odd-J/even-J mixtures.

In order to further simplify (6), we expand to first order in the potential energy (as was done by Šimánek[26]), and obtain the simple matrix equations

$$\gamma_i = K \widetilde{\Phi}_i \sum_j^{(i)} \gamma_j \cos(4\Phi_{ij}) , \tag{7}$$

where $\widetilde{\Phi}_i$ is the phase correlator defined as

$$\widetilde{\Phi}_i = \int_0^\beta d\tau \Big\langle \cos\big(2\phi_i(0)\big) \cos\big(2\phi_i(\tau)\big) \Big\rangle_{f,i} , \tag{8}$$

where $\langle\rangle_{f,i}$ indicates averaging over the free rotor Hamiltonian of rotor i. Note the index i is kept because the phase correlator, being the integral of the imaginary time correlation function of the free rotor, is dependent on whether rotor i is odd-J or even-J. Equation (7) can be written in the form

$$\gamma_i = \sum_j \Gamma_{ij}\gamma_j \ , \tag{9}$$

where $\Gamma_{ij} = K\,\Phi_i \cos(4\Phi_{ij})$ if rotor i and j are nearest neighbors, and zero otherwise.

By solving (9) one can determine the phase diagram of an odd-J/even-J mixture. One solution of (9) is the trivial one (with all $\gamma_i = 0$), indicating a disordered state. At a given temperature T, we solve for the smallest K that gives an eigenvalue of Γ_{ij} that is unity. The K thus obtained separates (K_c) the phase of complete disorder and a phase characterized by a set of γ's that are, in general, finite. While the magnitude of $\{\gamma_i\}$ is not known in our formalism, we can calculate normalized correlation functions in order to characterize the nature of the ordered state.

The expansion in the potential (7) implicitly assumes a continuous phase transition. A first-order phase transition would lead to an instability in (9) expected to give the same K_c with different ordering characteristics.

In our calculations, where the formalism developed in this section was used, we generated 20 configurations with the required odd-J/even-J ratio and have determined the phase diagram for each one separately. The results shown below are averages over the twenty configurations.

4.   MEAN-FIELD THEORY

For purposes of comparison we also present results based on standard mean-field theory. In the following theories, the phase diagram for an order–disorder transition is determined. For systems that are purely even, odd, or thermally distributed, the mean-field expression for the phase-diagram obtained by Šimánek[26] reads as

$$\gamma = Kn\widetilde{\Phi}\gamma \ , \tag{10}$$

where n denotes the number of nearest neighbors, $\widetilde{\Phi}$ is the phase correlator as defined in (8). The phase correlator is restricted in angular momentum states in the case of purely even or odd systems. Note that one solution of (10) is $\gamma = 0$, i.e. the disordered state. The order–disorder transition occurs for combinations of K, T where a non-trivial solution of (10) is found.
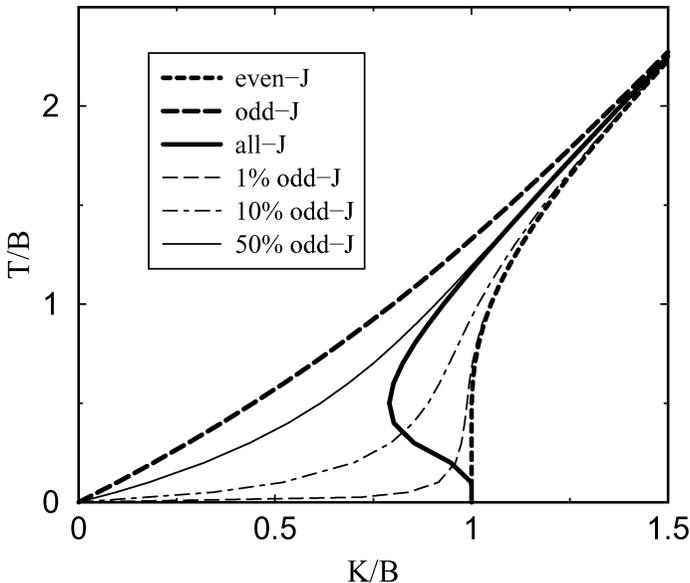
Fig. 1. Mean-field phase diagrams for the quantum anisotropic planar rotor model.

A mean-field theory for a mixture of even and odd rotors (with fraction of odd rotors P_o) can be obtained by writing the phase correlator as a weighted average of odd and even ones as

$$\widetilde{\Phi} = [P_o\widetilde{\Phi}_o + (1 - P_o)\widetilde{\Phi}_e]\,, \tag{11}$$

and solving (10).

5.   RESULTS

In Figure 1 we present the mean-field results for the K *vs* T phase diagram of QAPR. The thick lines represent the purely odd-J, even-J, and all-J rotors. The thin lines represent the mean-field results for various ratios of odd-J/even-J. In the thermally equilibrated mean-field result one sees the *reentrant* phase diagram as has been shown by various methods previously.[18–20,22,23] The purely odd-J system is always ordered at zero temperature, the purely even-J one has a phase transition at $J = 1$ and exhibits no reentrance. It is not surprising that the mean-field treatment of various ratios of odd-J/even-J rotors exhibits an ordered ground state, since in this case odd rotors are coupled as in the purely odd case, albeit with a smaller effective mean-field coupling constant. As the odd fraction is increased,
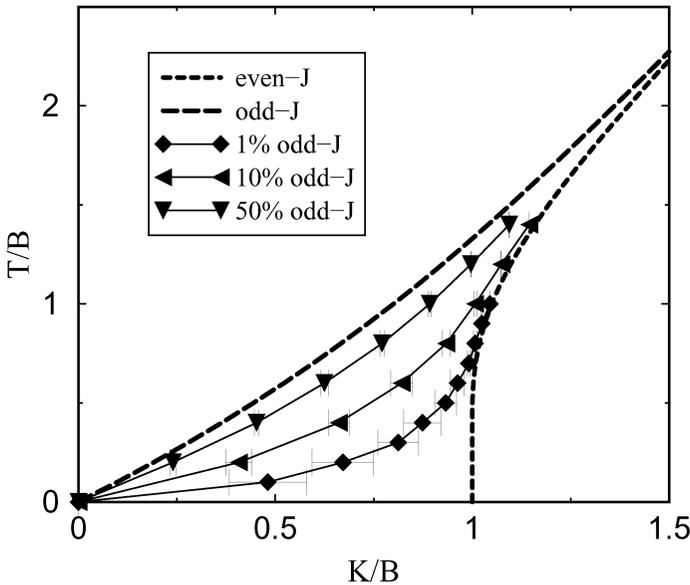
Fig. 2. Phase diagrams for the quantum anisotropic planar rotor model calculated with explicit *ortho–para* disorder.

the phase diagram approaches that of the purely odd system. Since the normalized correlation functions in mean-field theory are trivially unity, the phase diagrams presented in Fig. 1 separate phases of complete disorder and long-range order.

In Figure 2 the phase diagram for the same systems as in Fig. 1 calculated using the formalism developed in Section 3. are shown. In the case of pure odd-J or pure even-J systems, the phase diagrams correspond exactly to mean-field theory. The 1%, 10%, and 50% systems show phase diagrams similar to the ones obtained from mean-field theory, except that ordering occurs at lower pressures for a given temperature (an explicit comparison for 1% and 10% is given in Fig. 3). We have also calculated the correlation functions of the order parameter (not shown) and have found that the order is short range. The correlation lengths increase along the phase diagram with increasing temperature. The fact that at 1% odd-J fraction the ground state is always ordered is not as straightforward as in the mean-field case. This result indicates that short-range ordering is not caused solely by the odd-J rotors present, but is mediated by even-J rotors, most likely by mixing with angular momentum states $J > 0$.

In Figure 4 we compare the phase diagrams for thermal equilibrium distribution of odd-J/even-J rotors calculated using explicit disorder with
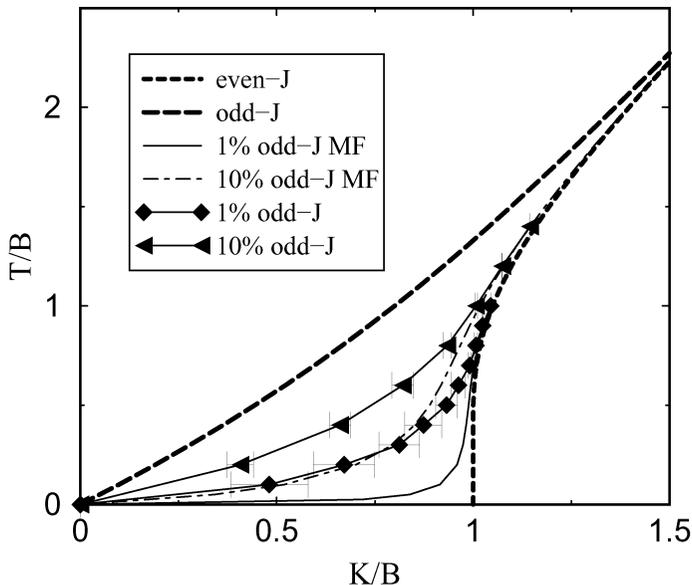
Fig. 3. Comparison of the mean-field phase diagrams with the ones calculated with explicit *ortho–para* disorder for 1% and 10% odd-J.

the mean-field result for the all-J system. (A mean-field treatment with thermal equilibrium distribution would correspond to an all-J system.) Both phase diagrams are reentrant. The one with explicit disorder is more strongly reentrant than the all-J one, as can be expected from the results shown in Fig. 3. From the correlation functions along the phase boundary (Fig. 5) it can be concluded that at low temperatures the order is short range. The correlation length increases along the phase boundary with temperature.

The results presented here would be strongly dependent on the time-scales of *ortho–para* interconversion.[16,17] While this issue is a subject of debate, we can state the following. What is essential is the difference between the time-scales of rotation and *ortho–para* interconversion. If the interconversion is significantly slower than molecular rotation, the formalism including explicit disorder is expected to be valid. When the interconversion time-scales approach the time-scales of molecular rotation, the standard mean-field theory is expected to be valid. Thus reentrance would be present in both cases. Also experiments conducted at thermal equilibrium *ortho–para* ratios (and, in general, at fixed *ortho–para* ratios could give insight into the nature and relative time-scales of the interconversion.
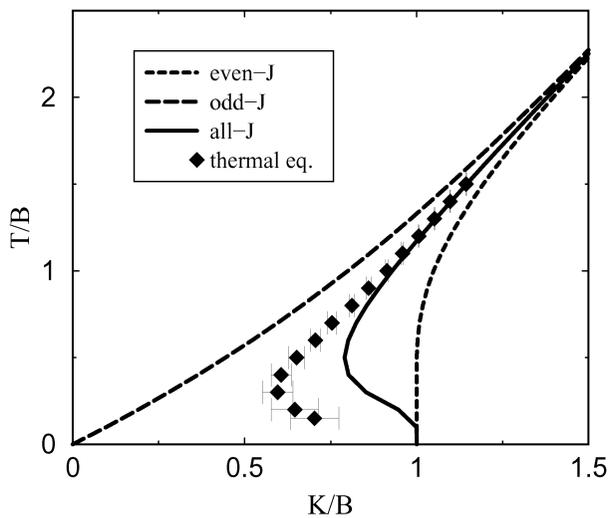
Fig. 4. Mean-field and explicit *ortho–para* disorder phase diagrams at thermal equilibrium.
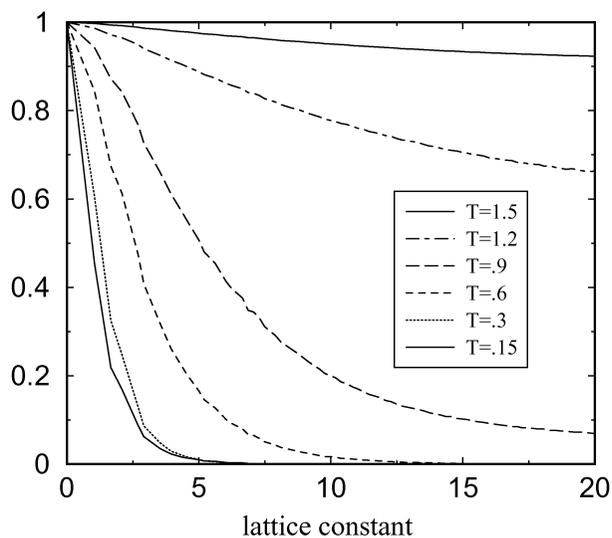

Fig. 5. Normalized correlation functions of the order-parameter as a function of temperature along the reentrant phase diagram.

As stated before, however, in the pressure ranges corresponding to the range of coupling constants presented here, the *ortho–para* interconversion is expected to be an order of magnitude slower than molecular rotation. In light of this, our calculations would correspond to a strongly reentrant phase diagram (diamonds in Fig. 4), possibly exhibiting a dynamic equilibrium phase of short-range order.

6.   CONCLUSION

We have developed a formalism to study the phase diagram of coupled homonuclear diatomic molecules. In particular, our formalism is useful in studying the nature of *ortho–para* (or odd-J/even-J) mixtures, since the disorder due to the molecules being either odd-J or even-J is implemented explicitly, allowing for the study of short-range ordered states. Our model system is the QAPR model, a model of coupled rotors in two-dimensions. We found that short-range order occurs at coupling constants much lower than in case where standard mean-field theory predicts the occurrence of long-range order. Even very low concentrations (1%) give rise to a phase transition from disorder into short-range order, indicating that mediation by molecules of even angular momentum symmetry cannot be neglected. For systems at thermal equlibrium our formalism predicts a strongly reentrant phase transition. The reentrance is stronger than in the case of all-J systems (found experimentally in HD[24]).

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