Mean-field theory of orientational ordering in rigid rotor models with identical atoms: spin conversion and thermal equilibration

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In coupled rotor models which describe identical rotating nuclei the nuclear spin states restrict the possible angular momenta of each molecule. There are two mean-field approaches to determining the orientational phase diagrams in such systems. In one the nuclear spin conversion times are assumed to be instantaneous in the other infinite. In this paper the intermediate case, when the spin conversion times are significantly slower than those of rotational time scales, but are not infinite on the time-scale of the experiment, is investigated. Via incorporation of the configurational degeneracy it is shown that in the thermodynamic limit the mean-field approach in the intermediate case is identical to the instantaneous spin conversion time approximation. The total entropy can be split into configurational and rotational terms. The mean-field phase diagram of a model of coupled rotors of three-fold symmetry is also calculated in the two approximations. It is shown that the configurational entropy has a maximum as a function of temperature which shifts to lower temperatures with increasing order.

1. Introduction

Molecules in crystal phases often exhibit quantum orientational ordering. A well-known example is solid hydrogen [1,2], where the phase diagrams are strongly dependent on the nuclear spin of the molecules. At low pressure the free rotor angular momentum quantum numbers can still be considered good. The symmetry requirement of the molecular wave function imposes constraints on the allowed angular momentum quantum numbers for a molecule of a given nuclear spin configuration. In the case of H_2 molecules in the triplet (singlet) nuclear spin state are coupled to odd (even) angular momentum levels. In D_2 the situation is similar, the degeneracies, however, are different: even (odd) angular momentum states are sixfold (threefold) degenerate [3]. In H_2 the pure para system orders only at high pressures, $\approx 100\,\mathrm{GPa}$ (see Fig. 1,*b* of Ref. 4), whereas the ground state of ortho-H_2 is ordered at finite pressure. When both even and odd angular momenta are accessible, as is the case in the heteronuclear species

HD [5–9], or when the ortho-para distribution in H_2 is thermally equilibrated [10–12], then the phase diagram is reentrant. Very similar patterns of phase diagrams are also found [13–15] in the quantum anisotropic planar rotor model [16], in which uniaxial rotors corresponding to diatomic molecules are coupled, and in similar models [17–19]. Other examples of systems where models of coupled rotors have played a role in elucidating the physics are inclusion compounds [20–23] containing ammonia, Hoffmann clathrates [24–26], and crystals containing methyl groups [27,28]. Regarding these systems the issue of how nuclear spin effects ordering has not been thoroughly studied up to now.

The mean-field approach has been used to understand the orientational ordering in coupled rotor systems. In solid H_2 the mean-field approach predicts the correct qualitative behaviour for systems of pure para or ortho species, and of HD, where nuclear spin is not coupled to angular momentum, hence the angular momentum distribution is allowed to thermally equilibrate instantaneously. In solid H_2 it is

known that the spin conversion times are long compared to rotational time-scales, hence thermal equilibrium is not instantaneous on rotational time-scales at low pressures. This is also thought to be the case in ammonia or methyl containing crystals [29]. In ammonia or methyl containing crystals the effects of nuclear spin on orientational ordering have not been investigated.

Mean-field studies of hydrogen assume that the nuclear spin conversion times are either infinite or instantaneous on rotational time-scales [11]. In this work the intermediate case, where nuclear spin relaxation is long on the time-scale of rotation but allowed to equilibrate on the experimental time-scale is investigated. It is shown that in the thermodynamic limit the mean-field results for such a case are equivalent to the zero relaxation time approximation. The total entropy is also shown to consist of two contributions, one configurational and one rotational.

The mean-field phase diagram of a model of three-fold symmetric coupled rotors is also presented. Here the nuclear spin states can be of three types which couple to three different manifolds of angular momentum (A, E_a, and E_b), of which two (E_a and E_b) are equivalent, they display the same ordering properties. The thermal mixture displays a reentrant phase transition (as predicted prior [30]). The reentrant phase transition is known to be accompanied by an entropy anomaly [11]. At low temperatures the entropy in the ordered state is larger than in the disordered state. In this study the two components of the entropy (configurational and rotational) are calculated and it is shown that both display similar anomalous behaviour in the reentrant region. The maximum of the configurational entropy shifts to smaller values of temperature as the order parameter is increased.

This paper is organized as follows. In Sec. 2 mean-field the theory of coupled rotors and its relation to nuclear spin is addressed. Subsequently the model studied here that of coupled three-fold symmetric uniaxial rotors, is presented. In Sec. 4 the results are presented and in Sec. 5 conclusions are drawn.

2. Mean-field theory for systems with nuclear spin

In the following a model of coupled rigid rotors in which the nuclear spin configurations are coupled to angular momentum states as is the situation in systems with identical rotating atoms is considered. Let the model consist of N rotors whose centers of mass are fixed. Let there be σ different manifold of angular momentum states coupled to a particular manifold of spin states of degeneracy G_σ. For example in solid hydrogen (H_2) $\sigma = 2$, as there is the ortho and para variety, and the degeneracies are $G_1 = 1$ (singlet) and $G_2 = 3$ (triplet).

To calculate the phase diagram a Hamiltonian of the following form is considered

$$H = -B\sum_i \frac{\partial^2}{\partial \phi_i^2} - J\sum_{\langle i,j\rangle} \cos(n\phi_i)\cos(n\phi_j), \quad (1)$$

where B denotes the rotational constant, and J denotes the coupling between rotors, ϕ_i denotes the angular coordinate of rotor at site i, and $\langle i,j\rangle$ denotes summation over nearest neighbors. In this work we apply a mean-field type approximation to the Hamiltonian in Eq. (1), e.g.

$$H_{MF} = -B\frac{\partial^2}{\partial \phi^2} - J\Gamma\cos(n\phi) + J\frac{\Gamma^2}{2}. \quad (2)$$

The coordination number has been absorbed into the coupling constant J. This is a model of coupled uniaxial rotors, but the conclusions in this section are valid for rotors in any number of dimensions. The model (Eq. (1)) includes a simplified potential sensitive only to orientation and the molecular symmetry. While the crystal structure and phonons may also effect orientational ordering, the point of view taken here is that orientation and molecular symmetry are the most important. This point of view is corroborated by the mean-field results of previous studies on hydrogen [5–7,10,11]. Moreover, as models of coupled rotors are used to describe other physical phenomena (granular superconductors [17–19]) the behavior of the model itself is of interest.

2.1. The cases of infinite and zero spin conversion time

There are two common approaches to systems with coupled rotors corresponding to homonuclear molecules with nuclear spin coupled to angular momenta. The zero relaxation time limit corresponds to averaging the partition functions over the spin configurations. The one-particle partition function can be written in this case as

$$Q_{\text{tot}} = \sum_i G_i Q_i, \quad (3)$$

where G_i denotes the degeneracy of angular momentum states corresponding to a particular spin configuration, and Q_i denotes the partition function in which the states which enter are the ones that are coupled to the same spin configuration, i.e.

$$Q_i = \text{Tr}_i\{\exp(-\beta H_{MF})\}, \quad (4)$$

where Tr_i denotes tracing over a particular manifold of angular momentum states. In this case the distribution of states depends on the parameters, i.e. temperature, coupling constant. Minimizing the free energy corresponding to Eq. (3) results in

$$\Gamma = \langle\cos(n\phi)\rangle, \quad (5)$$

and the fraction of a particular species at thermal equilibrium is given by

$$X_i = \frac{G_i Q_i}{\sum_j G_j Q_j}. \quad (6)$$

The fraction of a particular species will in general be a function of the parameters defining the system (temperature, coupling and rotational constant).

The infinite relaxation time limit in the mean-field approximation corresponds to writing the partition function as a product

$$Q_{\text{tot}} = \prod_i Q_i^{X_i}, \tag{7}$$

with the fraction of species i defined as $X_i = N_i / N$. Here Q_i again denotes a partition function into which the angular momentum states that enter are the ones corresponding to a particular spin configuration. This way of writing the partition function is only possible in mean-field theory, where the many-body Hamiltonian separates into a sum of additive single-rotor Hamiltonians. From Eq. (7) it follows that the expression for the free energy is

$$F_{\text{tot}} = \sum_i X_i F_i, \tag{8}$$

where F_i denote the free energies of molecules belonging to a particular manifold of angular momentum states. The free energy is minimized if

$$\Gamma = \sum_i X_i \Gamma_i, \tag{9}$$

where

$$\Gamma_i = \langle \cos (n\phi) \rangle_i, \tag{10}$$

where $\langle \rangle_i$ denotes averaging over a particular manifold of angular momentum states.

2.2. The case of slow but finite spin conversion

In the following the mean-field theory of systems where spin conversion is slow but finite will be considered. The equilibration of the rotors is instantaneous, but the system finds its equilibrium proportion of different spin configurations on a longer time-scale. The starting point is Eq. (8) but the issue is the optimal proportion of different spin configurations (i.e. N_i). The probability of a particular set of N_is is given by

$$P(\{N_i\}) = \frac{C(\{N_i\}) \prod_i Q_i^{N_i}}{Z}, \tag{11}$$

i.e. the partition function of Eq. (7) multiplied by $C(\{N_i\})$ the number of ways such a configuration can occur. Z is the normalization constant

$$Z = \sum_{\{N_i\}} P(\{N_i\}). \tag{12}$$

$C(\{N_i\})$ is a combinatorial factor which can be written as

$$C(\{N_i\}) = \frac{N!}{\prod_i \left[(N_i / G_i)! \right]^{G_i}}. \tag{13}$$

Note that here the number of rotors are taken to be evenly distributed between the different degenerate nuclear spin states within an angular momentum manifold. Such a distribution corresponds to maximizing the entropy, and in the thermodynamic limit it can be expected that one configuration dominates. In the absence of fields which break the

degeneracy this assumption can be expected to be correct.

In the thermodynamic limit Stirling's formula can be applied to the combinatorial factor $C(\{N_i\})$ and obtain

$$C(\{N_i\}) = \exp\left[-N \left\{ \sum_i X_i \ln (X_i / G_i) \right\} \right], \tag{14}$$

where $X_i = N_i / N$. Hence the overall probability of a particular configuration becomes

$$P(\{N_i\}) = \exp\left[-N \left\{ \sum_i X_i \ln \left(\frac{X_i}{G_i Q_i} \right) \right\} \right]. \tag{15}$$

Clearly, in the thermodynamic limit, one set of values of $\{X_i\}$ will dominate, so the exponent of Eq. (15) can be optimized under the normalization constraint. The resulting condition is

$$\ln \left(\frac{X_i}{G_i Q_i} \right) + \left(1 - \frac{X_i}{Q_i} \frac{\partial Q_i}{\partial X_i} \right) + \lambda = 0, \tag{16}$$

where λ denotes the Lagrange multiplier corresponding to the normalization. The second Q_i dependent term in Eq. (16) can be evaluated as

$$\frac{\partial \ln Q_i^{X_i}}{\partial X_i} = \beta \Gamma_i (\langle \cos (n\phi) \rangle_i - \Gamma_i), \tag{17}$$

which evaluates to zero as the Γ_i's in this case are also fixed by the mean-field condition (Eq. (10)). Hence Eq. (16) gives

$$X_i = \frac{G_i Q_i}{\sum_j G_j Q_j}, \tag{18}$$

which is the distribution in the zero relaxation time limit. Substituting the expression for X_i from Eq. (18) into Eq. (15) gives the partition function for the zero spin conversion limit as expected.

An interesting result of the above analysis is that the entropy of the system in which spin conversion times are long but allowed to equilibrate can be broken up into two pieces: a configurational entropy arising from the combinatorial prefactor counting the configurations $C(\{N_i\})$ and one arising from the product of single particle partition functions which here will be called the rotational entropy. The total entropy per molecule calculated from Eq. (15) can be written

$$S = S_{\text{conf}} + S_{\text{rot}}, \tag{19}$$

where

$$S_{\text{conf}} = -\sum_i X_i \ln \left(\frac{X_i}{G_i} \right) \tag{20}$$

and

$$S_{\text{rot}} = \sum_i X_i S_i, \tag{21}$$

with

$$S_i = \ln Q_i - \beta \frac{\partial \ln Q_i}{\partial \beta}. \qquad (22)$$

Equation (22) is a weighted sum over the entropy per molecule associated with the rotational states coupled to a particular spin configuration.

3. Nuclear spin in three-fold symmetric uniaxial rotors

The model studied here is one of three-fold symmetric rotors performing uniaxial rotation. The Hamiltonian is of the form given in Eq. (2), with $n = 3$. As this model can correspond to compounds containing ammonia or methyl groups, where identical atoms are performing the rotation, nuclear spin can be expected to influence properties such as orientational ordering.

The issue of nuclear spin in the case of uniaxial three-fold symmetric rotors is qualitatively different from that in the two-fold symmetric case. In the latter it is the fermionic or bosonic character of the constituent atoms that determine which nuclear spin functions couple to odd or even angular momenta. The effects of nuclear spin in the three-fold symmetric case follow from the fact that a rotation of $2\pi/3$ or $-2\pi/3$ correspond to two permutation exchanges of nuclei, hence no change in the overall wave function occurs either for fermions or bosons [27].

For free uniaxial rotors wave functions which remain unaltered when rotated by $2\pi/3$ can be constructed as follows. The molecular wave function can be written as a product,

$$\Psi_{s,m_s}(\phi) = \frac{1}{\sqrt{2\pi}} \exp(im\phi)\, \Sigma_{s,m_s} , \qquad (23)$$

where ϕ indicates the coordinate of the rotor, and s, m_s indicate the spin quantum numbers of the three nuclei in the coupled angular momentum representation, and Σ_{s,m_s} denotes the spin part of the wave function. Rotating by $2\pi/3$ gives

$$\hat{R}\left(\frac{2\pi}{3}\right)\Psi_{s,m_s}(\phi) = \frac{1}{\sqrt{2\pi}}\exp\left\{im\left(\phi + \frac{2\pi}{3}\right)\right\}\hat{R}\left(\frac{2\pi}{3}\right)\Sigma_{s,m_s}. \qquad (24)$$

It can be shown [27] that the spin eigenfunctions in the coupled representation are eigenfunctions of the rotation operator $\hat{R}(2\pi/3)$ with possible eigenvalues $1, \exp\left(i\frac{2\pi}{3}\right), \exp\left(-i\frac{2\pi}{3}\right)$. It follows that a given spin-eigenfunction can have only certain angular momentum states, so that the requirement that a rotation by $2\pi/3$ causes no change in the wave function is satisfied. In particular spin eigenfunctions with eigenvalues $1, \exp\left(i\frac{2\pi}{3}\right), \exp\left(-i\frac{2\pi}{3}\right)$ couple to angular momentum states $m = 3n, 3n-1, 3n+1$ respectively, where n is an integer.

The ammonia molecules in inclusion compounds consist of nearly freely rotating NH_3 and ND_3 molecules. In the case of an NH_3 group, where the rotating atoms are of spin $1/2$, it can be shown that the $s = 3/2$ states are $m = 3n$, whereas one group of the $s = 1/2$ states are of the $m = 3n-1$ the other of the $= 3n+1$ variety. In ND_3 the $s = 3$, $s = 0$, and one of the three $s = 1$ states are $m = 3n$, one of the $s = 2$ and $s = 1$ states are $m = 3n-1$, the remaining $s = 2$ and $s = 1$ being $m = 3n+1$. In group theoretical terms the $m = 3n$ states form the one-dimensional representation A of the group C_3, the states $m = 3n+1$ and $m = 3n-1$ form the representations E_a and E_b. In the following the rotating atoms are assumed to be of spin-$1/2$.

In Refs. 10, 15 an extension of mean-field theory was developed in which it was assumed that each lattice site is of a particular spin state, but the rotational degrees of freedom were solved using coupled mean-field equations. This method was used to study solid hydrogen. The ratio of ortho versus para species was approximated as that of the free rotor system and the phase boundary was determined. The result that the mean-field theory of equilibrated spin conversion in the case of long spin conversion times is equivalent to the case when spin conversion times are instantaneous lends support to the validity of the approximation used in Refs. 10, 15.

4. Results

In Figs. 1 and 2 the mean-field phase diagrams are shown. The thermally equilibrated species shows a reentrant phase diagram (a result also found previously by Freiman and Tretyak [30]). This phenomenon is common in models of coupled rotors [5–7,9–11,13–15,18,19], and is caused by the fact that the rotational state that lies higher in energy has a stronger ordering tendency. This idea is cor-
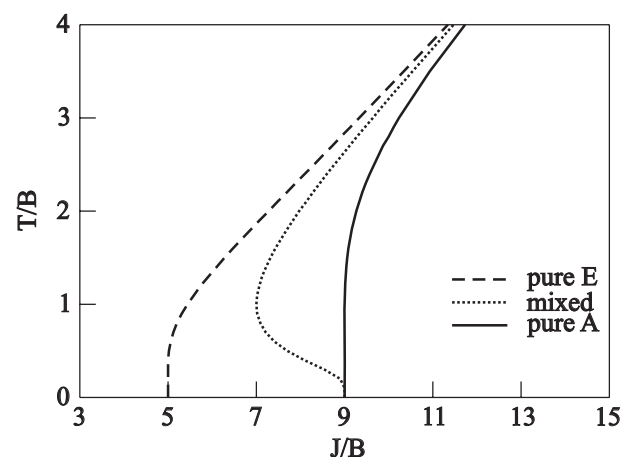

Fig. 1. Phase diagrams calculated via mean-field theory. Systems with pure A and pure E species, and with the thermal equilibrium distribution are shown. The thermal equilibrium phase diagram corresponds to the zero spin conversion time limit, as well as the case of thermally equilibrated rotors with long spin conversion times on the time scale of rotations.
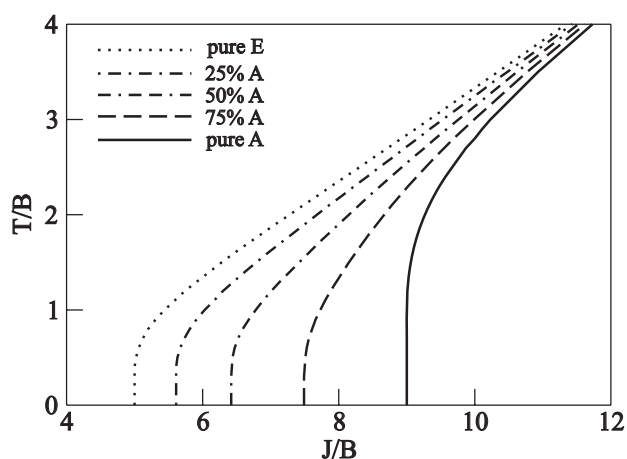
Fig. 2. Phase diagrams calculated via mean-field theory. Comparisons are shown for different proportions of A and E species. All phase diagrams calculated in the infinite spin conversion time approximation. The tendency to order increases with the proportion of E molecules.

roborated by the results in Fig. 1: the pure E system orders at a lower coupling constant than the pure A system, hence it has a stronger tendency to order. As the temperature of the thermally mixed system increases more rotors can access E states hence the system orders. The results for the infinite spin conversion time limit (2) show progressively stronger tendency to order as the proportion of E species is increased. Note that the behaviour found here for three-fold symmetric rotors is qualitatively different from hydrogen, where the ortho species has an ordered ground state for finite coupling constant, and for any small fraction of the ortho species [10,11,15].

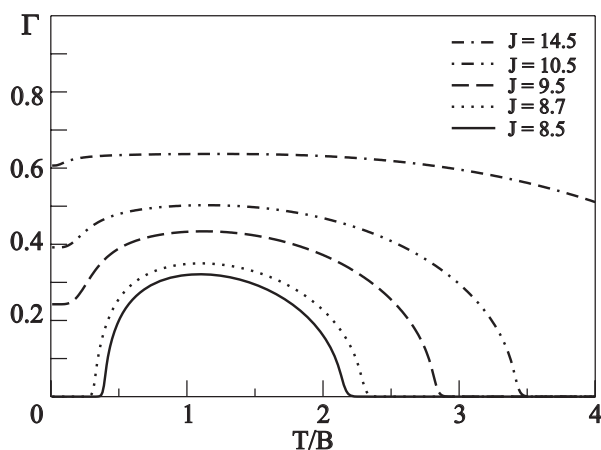In Fig. 3 the order parameter Γ is shown as a function

of temperature at different coupling constants. In the reentrant regime ($J = 8.5$ and $J = 8.7$) the two phase transitions, the high temperature one caused by thermal excitations, and the low temperature one caused by quantum fluctuations are clearly visible. For higher values of the coupling constant J ($J > 9.5$) one still sees increased ordering as the temperature is increased from zero. This tendency is suppressed as the classical limit is approached. The ordering tendency can be understood in all cases in terms of the distribution of the various spin nuclear states shown in Fig. 4. The thick line shows the distribution in the $J = 0$ case, where the system is disordered. In the regime where ordering occurs the deviation of the curves corresponding to $J = 8.5$ and $J = 8.7$ coincide with the range of nonzero order parameter. For higher J values the point where the order parameter begins to increase as a function of temperature corresponds to where the distribution functions begins to deviate from the free rotor case.

It has been argued that the reentrance is driven by anomalous behavior of the entropy [11]. Freiman et al. have shown that if the order parameter is held fixed the entropy is higher in the ordered state at low temperatures, and the situation reverses as the temperature increases. In Fig. 5 the entropy and its components (rotational and configurational, see Eq. (20)) are shown for fixed order parameters, as well as the entropy of the thermally equilibrated solution for $J = 8.5$. Both the rotational and configurational entropies show the entropy anomaly described by Freiman et al. However the behavior of the configurational and rotational entropies is qualitatively different. The configurational entropy displays a maximum which shifts to smaller values of temperature for the states which are more ordered. At large temperature the configurational
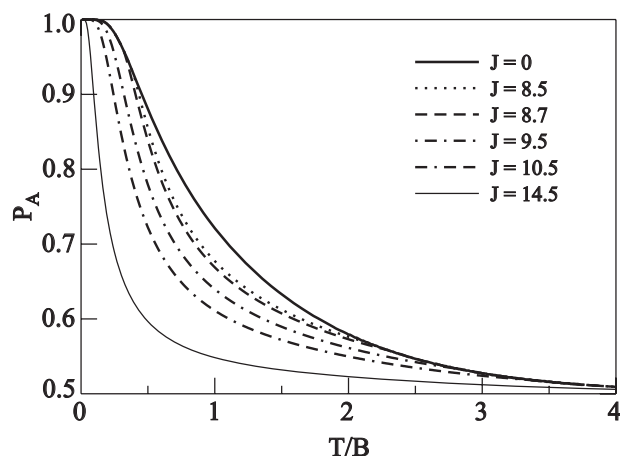

Fig. 3. Order parameter as a function of temperature for different coupling constants. The coupling constants $J = 8.5$ and $J = 8.7$ correspond to the reentrant regime of the phase diagram. $J = 9.5$ and $J = 10.5$ is in the ordered regime, but shows qualitatively similar behavior to the reentrant ordering, the order parameter increases at low temperatures. This tendency is suppressed in the classical limit ($J = 14.5$).

Fig. 4. Proportion of A species as a function of temperature for different coupling constants. For $J = 8.5$ and $J = 8.7$ the regimes of finite order parameter (Fig. 3) correspond to where the distribution deviates from the $J = 0$ case. For the couplings $J = 9.5$ and $J = 10.5$ the increase in order parameter as a function of temperature coincides with where the distribution function deviates from the $J = 0$ case. Hence ordering is correlated with an increase in the proportion of E species.
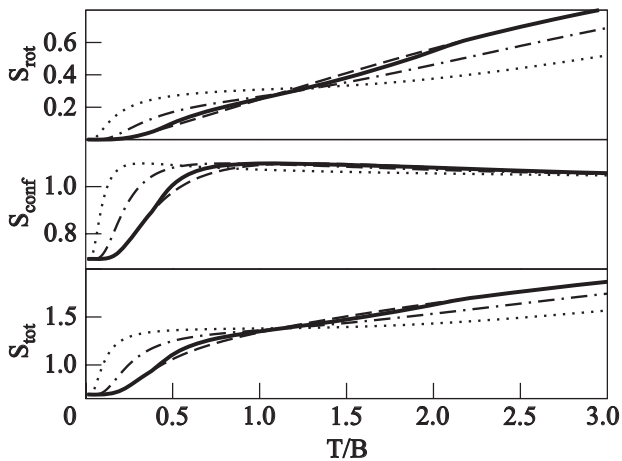
Fig. 5. Rotational, configurational, and total entropy for a thermally equilibrated system at $J = 8.5$. The thick line shows the results with the order parameter which minimizes the free energy. The other curves show results at fixed order parameter: dashed line $\Gamma = 0.0$, dot-dashed line $\Gamma = 0.5$, dotted line $\Gamma = 1.0$. All three graphs show that the ordered state has higher entropy at low temperature than the disordered state, and this situation reverses at higher temperatures. The configurational entropy (middle panel) shows a shift in the maximum to the left as the ordering is increased.

entropies converge. For the configurational entropy the tendency of the entropy to increase with order at low temperatures is very pronounced, whereas at higher temperatures, the opposite tendency is significantly weaker. From Fig. 5 one can argue that the low temperature reentrance anomaly is driven by both the configurational and rotational entropies.

5. Conclusions

In this study the mean-field theory of coupled quantum rotors was investigated. Particular attention was devoted to rotor systems which correspond to molecules where identical atoms rotate. In such systems the nuclear spin states couple to angular momentum states, and thereby effect orientational ordering. As the spin conversion times in such systems tend to be slow, experiments can be performed at fixed ratios of different spin states or at thermal equilibrium.

The mean-field approach to such systems is usually based on two strategies: in one case the spin conversion is assumed to be instantaneous on the time scale of rotation, in the other infinite. In the former case all angular momentum states are allowed for each molecule. In the latter a particular molecule is allowed only one manifold of angular momentum states fixed by the symmetry of the overall wave function. In this study the case of long but finite spin conversion times was considered, i.e., when spin conversion times greatly exceed rotational time-scales, but the experiment is carried out such that the distribution of

molecules in different nuclear spin states is allowed to equilibrate. It was shown that in the mean-field approximation such an approach yields the same results as the instantaneous spin conversion time limit, provided that the system is in the thermodynamic limit. Another outcome of the formalism is that the entropy becomes a sum of a configurational and a rotational contribution.

Calculations were also performed to determine the phase diagram of coupled threefold symmetric rotors. In this case the nuclear spin causes each molecule to be either of three types, A, E_a, and E_b, of which E_a and E_b are energetically equivalent and show the same ordering, hence A and E. Pure A systems show a weaker tendency to order than pure E systems. Zero spin conversion time and thermal equilibration leads to a reentrant phase transition confirming previous results [30]. It was also shown that the entropy anomaly known to exist in reentrant systems [11] is present in both the configurational and the rotational contributions. At low temperatures the ordered state has higher entropy than the disordered state in both cases. The configurational entropy displays a maximum which shifts to lower temperatures with increasing order.

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