Second-Order Reentrant Phase Transition in the Quantum Anisotropic Planar Rotor Model

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(Received 17 May 1999)

The orientational behavior of the quantum anisotropic planar rotor model is studied by means of the path-integral Monte Carlo method combined with finite size scaling. We compare a system where all angular momentum states are allowed, and one where the angular momentum is restricted to have even values. We find that a reentrant phase transition is present in the unrestricted case, where the system reenters a disordered phase upon cooling. Cumulants that are sensitive to the order of the transition indicate that the phase transition is second order. In the parameter range investigated in this paper, the even angular momentum system does not show reentrance.

PACS numbers: 68.35.Rh, 68.45.Da, 82.65.My

The phase diagram of the quantum anisotropic planar rotor (QAPR) model has been studied extensively [1–4], in large part due to the possibility of the anomalous reentrant phase transition. Reentrance refers to a phase transition of the system into an ordered phase at some temperature followed by a phase transition of the same system into a disordered phase at a lower temperature.

The QAPR model is an ideal minimalistic model that was constructed to understand quantum effects on orientational ordering of homonuclear diatomic molecules physisorbed onto inert surfaces. Recent reviews of experiments and simulations relevant to the study presented here can be found in Refs. [5,6]. Even though the full parameter space of the QAPR model cannot (yet) be investigated experimentally, it is an interesting model of statistical mechanics, and there are many systems whose Hamiltonians are similar to the QAPR Hamiltonian (specified below). Recent NMR studies [7] suggest that there is an ordered herringbone structure of H_2 on boron nitride for temperatures $T < 1.2$ K and for ortho-H_2 mole fractions of $x < 0.47$. However, until now the reentrant phase transition in these types of systems has not been experimentally investigated.

In the QAPR model, rotors are pinned onto an ideal two-dimensional triangular lattice. Nearest neighbor rotors are coupled through a quadrupolar potential of strength J. The kinetic energy is treated quantum mechanically with a finite rotational constant B. In the following we will express all energies in units of J such as $B^* = B/J$, reduced temperature $T^* = k_B T/J$, and $J^* = 1$. Thus our reduced Hamiltonian H^* can be written as

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

where ϕ_i denotes the coordinate of rotor i. The phase angles $\phi_{i,j}$ measure the angle of the line connecting nearest neighbors, which in the case of a hexagonal lattice are given by $\phi_{i,j} \in \{0, \pi/3, 2\pi/3, \pi, 4\pi/3, 5\pi/3, 2\pi\}$.

Studies of the phase diagram (B^* vs T^*) of the QAPR model have led to a controversy as to whether or not there is a regime of reduced rotational constants B^* where reentrance is present. In a recent study [3] a mean-field treatment showed reentrance, but this result was not verified by simulation. In another study a critical rotational constant at zero temperature was found [4]. The value of the critical rotational constant was such that in conjunction with the finite temperature results of Ref. [3] it was concluded that reentrance is present [4].

The mean-field analysis of the QAPR model has been carried out in the framework of a model of coupled Josephson junctions consisting of coupled one-dimensional rotors [8,9], as well as in the framework of homonuclear diatomics on an inert surface [3]. In the former case mean-field theory has shown that reentrance is present if the "rotors" are allowed to interconvert between states that are symmetric in 2π and states that are antisymmetric in 2π for a potential that is symmetric in 2π. States symmetric (antisymmetric) in 2π correspond to states with even (odd) angular momenta. When the system was restricted to states that are symmetric in 2π, reentrance was not found. A similar result has been found in the case of solid hydrogen isotopes [10,11]. In the case of homonuclear diatomics [3], a mean-field analysis found reentrance for a system where even and odd angular momentum states were allowed to interconvert.

Path-integral Monte Carlo (PIMC) simulations of the QAPR model at finite temperature [2,3] have given strong evidence that the system does not become ordered for rotational constants $B^* > 0.7$, independent of temperature. It has been suspected [2] that there is a region of rotational constants for $B_c^* < B^* < 0.7$ where reentrance occurs. Extensive PIMC simulations [3] did not show reentrance, although sufficiently low temperatures were not investigated. Although a decrease in the order parameter was found with decreasing temperature, no phase transition could be established by means of an analysis of the order parameter distributions.

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A diffusion Monte Carlo (DMC) simulation [4] found evidence for a rotational constant $B_c^* = 0.4$ above which the system is suspected to be disordered at zero temperature. In conjunction with the finite temperature simulation results of Ref. [3], a critical rotational constant of $B_c^* \approx 0.4$ at zero temperature provides preliminary evidence for reentrance. This result is in agreement with the results of previous mean-field treatments [3,8,9]. However, it is not trivial to obtain information about the order parameter Φ defined below and its moments within a zero-temperature simulation. A finite system tunnels between equivalent macroscopic ground states at $T^* = 0$, resulting in $\lim_{N\to\infty} \lim_{T\to 0} \Phi = 0$. Information about the order was obtained indirectly, and it was not possible to locate the zero-temperature transition precisely and to determine the order of the transition.

Models for granular superconductors mentioned above have been studied by PIMC [12]. The coupling term in that study has the form $\cos(\phi_i - \phi_j)$, giving rise to a Kosterlitz-Thouless transition. The lattice is a two-dimensional simple cubic lattice. Evidence for a first-order reentrance was found, but no proof of the first-order nature was given through a size scaling analysis. However, finite size scaling is extremely important to establish the bare existence of a reentrance transition. Furthermore, the differences between the models do not allow conjectures for the QAPR model.

The purpose of the study presented here is to ascertain if there is a reentrance transition in the QAPR model. We do this by combining efficient path-integral Monte Carlo techniques for one-dimensional rotation with finite size scaling techniques. We investigate the order of both transitions: the reentrance transition and the well studied high-temperature order-disorder transition formerly believed to be a weakly first-order transition [13].

The Hamiltonian used in this study is defined in Eq. (1). The equilibrium behavior of the model is investigated with a version of the PIMC [14,15] method that has been modified to sample paths for uniaxial rotation efficiently [16]. In the PIMC method a quantum system is represented by P replicas of the corresponding classical system coupled by harmonic bonds in a cyclic manner. The version of PIMC put forth by Cao [16] offers a simple way to analyze systems of all (even) angular momentum states by restricting the wave function to be periodic in $2\pi(\pi)$.

We calculate the averages of powers of the order parameter for different system sizes and perform finite size scaling. The forms of the Binder cumulants we use in finite size scaling [17–19] are suited to rule out the first-order nature of a transition [20]. We focus on a range of the rotational constant which is in the region where reentrance has been suspected to occur.

The ground state of our corresponding classical system has been determined to have the "herringbone" structure [21,22]. The order parameter that describes herringbone ordering is a $n = 3$ dimensional vector $\vec{\Phi}$ whose components Φ_α with $\alpha = 1, \ldots, n$ may be written as

$$\Phi_\alpha = \frac{1}{NP} \sum_{j=1}^{N} \sum_{\tau=1}^{P} \sin[2\phi_j(\tau) - 2\eta_\alpha] \exp[i\mathbf{Q}_\alpha \cdot \mathbf{R}_j], \tag{2}$$

where $\mathbf{Q}_1 = \pi(0, 2/\sqrt{3})$, $\eta_1 = 0$, $\mathbf{Q}_2 = \pi(-1, -1/\sqrt{3})$, $\eta_2 = 2\pi/3$, and $\mathbf{Q}_3 = \pi(1, -1/\sqrt{3})$, $\eta_3 = 4\pi/3$. There are $q = 6$ possible realizations of the herringbone structure on a triangular lattice. We calculate moments of the magnitude of the vector given in Eq. (2) and evaluate the cumulant given in Ref. [20], which has the form

$$g_N(T^*) = \frac{n}{2}\left(1 + \frac{2}{n} - \frac{\langle\Phi^4\rangle_N}{\langle\Phi^2\rangle_N^2}\right). \tag{3}$$

Φ denotes the magnitude of the order parameter $\vec{\Phi}$. For reasons of simplicity, we refer to Φ as the order parameter in the following.

It has been shown [20] that $g_N(T^*)$, aside from some negligible correction terms, has a size independent crossing point at the transition temperature with a universal value of $g_N(T_c^*) = 1 - n/2q$ for a first-order phase transition, where T_c^* is the phase transition temperature, and q is the number of ordered states of the system. In our case $g_N(T_c^*) = \frac{3}{4}$. For a second-order phase transition the same cumulant has a size independent crossing point at the critical temperature, but its value is not known.

For our main investigation, a system with a rotational constant of $B^* = 0.6364$ is chosen for which disordering at ultralow temperatures has been suspected [2–4]. In Fig. 1 we show the temperature dependence of the order parameter for three system sizes ($N = 256$, 324, and 400). Upon cooling, the order parameter for all system sizes increases initially. At high temperatures the order parameter is strongly size dependent. In the ordered state (around the maximum of the order parameter where $T^* \approx 0.21$), the size dependence weakens. Subsequently

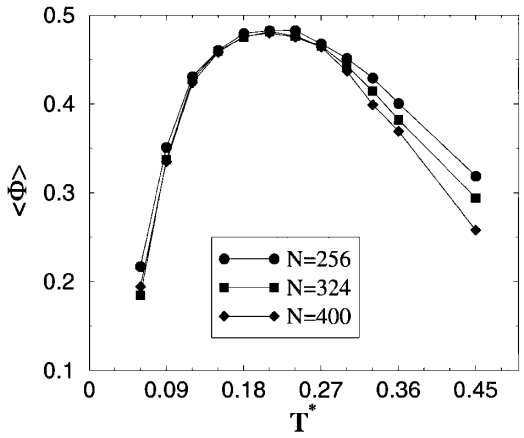

FIG. 1. Order parameter as a function of temperature for systems of rotational constant $B^* = 0.6364$ and sizes $N = 256$, 324, and 400.

there is a sharp drop in the order parameter, in which size dependence for the most part is weak.

Figure 2 shows the temperature dependence of the cumulant $g_N(T^*)$ for the $B^* = 0.6364$ system at the same two system sizes. The cumulants cross twice, at $T^* \approx 0.09$ and at $T^* \approx 0.3$. The two crossing points are an unmistakable indication of reentrance. The value of g_N at both crossing points is certainly different from $\frac{3}{4}$. This is a clear sign that the transitions are second order.

Reentrance is believed to be driven by a competition between kinetic and potential energies [4,12]. This competition is particularly apparent if the symmetry of the first excited states does not correspond to the symmetry of the Hamiltonian, e.g., the first excited state in a double well potential has a different symmetry than the ground state. As the temperature is lowered to the order of the tunneling splitting, the quantum particle in the double well potential delocalizes thereby reducing its kinetic energy and increasing its potential energy. An increasing potential energy with decreasing temperature is therefore quantum mechanically possible in contrast to the classical case. The increasing potential energy is associated with a decreasing quadrupolar polarization. This picture can certainly be generalized from a one-particle double well potential to multiparticle double well potential such as the QAPR model with rotors in mixed angular momentum states. Hence, in a mean-field picture, as fewer and fewer rotors populate the first excited state, the rotors become more delocalized. This weakens the coupling between neighboring rotors and may eventually result in a transition to a disordered phase.

The above mentioned effect of the potential energy that decreases with temperature can be seen in Fig. 3. The potential energy has a dip, while the kinetic energy is a monotonically increasing function of temperature. The temperature regime where the anomaly takes place coincides with the reentrance regime. One may therefore conjecture that local coherence (each individual rotor occupies only even angular momentum states even though odd angular momentum states are accessible) induces global disorder. Of course, there does not have to be a transition into a disordered state when the rotors occupy only even angular momentum. Indeed, DMC finds long range order for $B^* < 0.4$ [4].

In Fig. 4 PIMC results for the kinetic energy $T^*_{\rm kin}$ are shown for a QAPR system of $B^* = 0.6$, where the rotors are constrained to have even angular momenta. The potential energy $V^*_{\rm pot}$ is shown in the inset. Within the error bars of our simulation, the potential energy is constant and the kinetic energy is a monotonically increasing function with temperature, in contrast to the unconstrained system shown in Fig. 3. This behavior can be understood in a mean-field picture if the potential is treated as a perturbation to the free rotors. The difference in energy between $m = 0$ and $m = 2$ (m denoting the angular momentum of a single free rotor) is $\Delta E^* = 4B^*$. The coupling to the potential energy contributes in second-order perturbation theory only. First and second excited states have similar kinetic energies (approximately $4B^*$) but opposite potential energies. Furthermore, the splitting between the first and second excited states can be expected to be smaller than the difference in the ground state and first excited state. Hence, first and second excited states become populated nearly simultaneously. As these two states become populated the kinetic energy increases, but the average potential energy remains constant. Having constant potential energy can be associated with an unchanged local order.

Even though there is no apparent competition between kinetic and potential energies for the $B^* = 0.6$ system with only even angular momentum states, the behaviors of the order parameter and the cumulant, both not shown here, are quite peculiar. Order in the small system ($N = 144$) at intermediate temperature regimes ($T \approx 0.25$) is

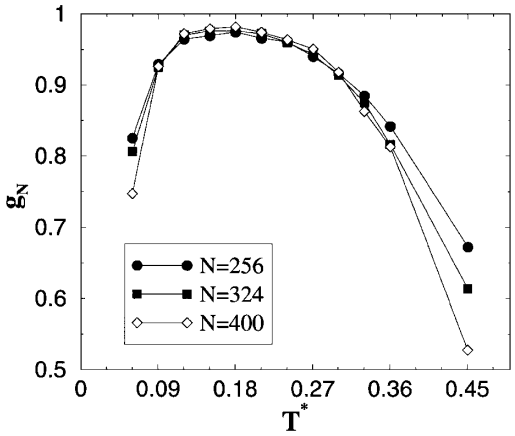

FIG. 2. Cumulant $g_N(T^*)$ as a function of temperature for systems of rotational constant $B^* = 0.6364$ and sizes $N = 256$, 324, and 400.

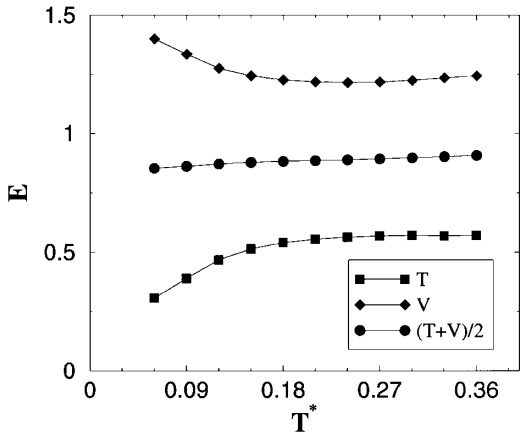

FIG. 3. Kinetic energy $T_{\rm kin}$, potential energy $V_{\rm pot}$, and half of the total energy $(T_{\rm kin} + V_{\rm pot})/2$ as a function of temperature for rotational constant $B^* = 0.6364$ and system size $N = 400$. $V_{\rm pot}$ is shifted by a constant such that the classical ground state corresponds to $V_{\rm pot} = 0$.

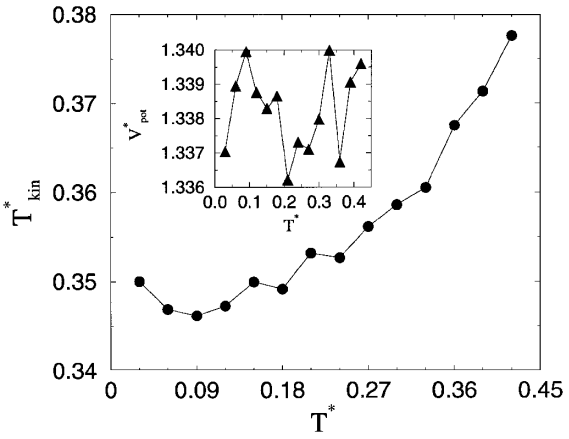

FIG. 4. Potential and kinetic energies are shown for an ensemble 324 rotors with $B^* = 0.6$ as a function of temperature T. All rotors are constrained to even angular momentum. Potential energy V_{pot} is shifted by a constant such that the classical ground state energy is zero.

much stronger than in the large system ($N = 324$). This is due to the periodic image convention that typically induces a larger order parameter for a smaller system. At very low temperatures ($T \leq 0.12$), the effect inverts. The small system becomes much more disordered than the large system. We suspect that tunneling between the various metastable states occurs. The tunneling splitting can be expected to be larger for the small system than for the large system. Hence, care has to be exercised in deciding in which order the limits $\lim_{N\to\infty}$ and $\lim_{T\to 0}$ are taken. Just looking at one system size might have led us to the conclusion that the even angular momentum rotors also show reentrance at a rotational constant $B^* = 0.6$. From our data, we cannot yet disapprove of the existence of reentrance for the even system. However, it is apparent that the phase diagram in this case is strongly distorted with respect to the regular phase diagram, e.g., there does not seem to be an ordered state for the even $B^* = 0.6$ system, while there is a temperature regime for the mixed $B^* = 0.63$ system in which the mixed $B^* = 0.63$ rotors are ordered.

These findings are similar to the experimental findings on solid hydrogen [23] and with computer simulation of three-dimensional hydrogen [24]. Reentrance is observable for solid HD under pressure but not for H_2 and D_2. The computer simulations also showed the absence of reentrance for *parahydrogen* [24]. Unfortunately an equilibrium mixture of *para-ortho* rotors was not considered.

We have presented a study in which the reentrant phase transition of the QAPR model has been simulated for the first time. Both the high-temperature disorder-order and the low-temperature order-disorder transitions are found to be second-order transitions. If the rotors are constrained to be of even angular momentum, we cannot exclude the possibility of reentrance, but the area of the reentrance regime in a (B^*-T^*) phase diagram is certainly reduced.

B. H. would like to thank Professor E. Šimánek for helpful discussions. This work was supported by a grant to B. J. B. from the National Science Foundation. M. H. M. gratefully acknowledges support provided by the Alexander von Humboldt Foundation.

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