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Orientational quantum melting of linear rotors pinned onto surfaces

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Abstract. – Ground-state properties of the quantum anisotropic-planar-rotor (QAPR) model, which describes orientational ordering of linear molecules on graphite surfaces, are investigated by means of diffusion Monte Carlo. It is found that a quantum melting of the long-range orientational ordering occurs at a rotational constant $b \approx 0.4$ in units of the quadrupolar coupling constant. This result together with the finite-temperature simulations of Martonak *et al.* (*Phys. Rev. E*, **55** (1997) 2184) shows that the QAPR model exhibits reentrance.

Finite-temperature properties of the two-dimensional anisotropic-planar-rotor (APR) model [1-3] have been studied extensively in order to understand the orientational ordering of physisorbed linear molecules on surfaces, *e.g.*, commensurate N_2 monolayers on graphite, see ref. [3] for a review. In the APR model the center-of-mass coordinates are fixed to an ideal triangular rigid lattice. One-dimensional rotations within the plane parallel to the substrate surface are the only degrees of freedom taken into account. Only first-neighbor interactions via the anisotropic part of a quadrupole-quadrupole potential are considered. The classical APR model is thus described by just one parameter J, the coupling constant. The APR model can be assumed to qualitatively capture all features associated with the transition of an orientationally disordered phase to the so-called herringbone phase. Despite its simplicity, the classical APR model required extensive computational studies in order to determine the phase transition being weak first order [4]. It is therefore a challenging task to investigate the corresponding quantum generalization, the so-called quantum anisotropic-planar-rotor (QAPR) model [5], in which the rotational constant B is an additional parameter. In particular, quantum coherence effects between strongly correlated degrees of freedom may reveal new phenomena that are not only difficult to treat computationally, but also interesting to understand.

On the basis of path integral Monte Carlo (PIMC) simulations, Marx and Nielaba [5] report four distinct transition regimes for the QAPR model as a function of $b = B/J$: i) a quasi-

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classical regime with an ordered ground-state (non-zero order parameter M at temperature $T = 0$ for small values of b) and $\partial M/\partial T \leq 0$ at any temperature. ii) A crossover behavior with residual ground state order but the occurrence of *positive* $\partial M/\partial T$ for intermediate values of b; iii) absence of order in the ground state, thermally induced ordering upon heating, followed by thermally induced reentrance into the disordered phase upon further heating; iv) absence of order at any temperature for large values of b. Thus in regimes iii) and iv), quantum fluctuations are supposed to be strong enough to destroy the long-range orientational order, where in regime iii) (small) additional thermal fluctuations would lead to an ordering of the rotors. In the following, we will call the transition from regime ii) (intermediate b) to regime iii) or regime iv) (larger b) quantum-melting and the thermally induced disorder-order-disorder transition sequence in regime iii) will be called reentrance.

While a recent mean-field treatment by Martonak *et al.* [6] supported the idea of reentrance in the QAPR model, their PIMC simulations did not. In a small region at $b = 0.63$, transition temperatures seemingly drop to zero and for $b > 0.63$ the absence of long-range order at any temperature is presumed. Since PIMC simulations are carried out at finite temperatures it is still questionable where the b driven ground state transition really occurs. Determining the location of the $T = 0$ transition point in addition to the finite-T phase diagram is therefore crucial to disapprove reentrance or helpful to show the existence of reentrance.

For the range of b where a quantum melting transition might possibly occur ($b \lesssim 0.6$), an experimental realization of the model has not been found yet. Of the two possible candidates, N_2 on graphite is close to the classical limit and H_2 (along with its deuterated isotopes) on graphite is close to the quantum-mechanical limit [7]. However, Raman spectroscopy [8] gives experimental evidence that solid HD under pressure undergoes a reentrance transition. The coupling of residual dipole moments of HD does not need to be considered for the experimentally observed transition, because those couplings are so small that they can only become important at much lower temperatures than the observed reentrance temperature. For this case of two-dimensional rotations of linear molecules interacting dominantly via a quadrupolar potential, the possibility of quantum melting and reentrance has first been suggested [9, 10] theoretically. These predictions, however, have been based upon a simple mean-field theory involving uncontrolled approximations. In fact, a model that assumes Gaussian fluctuations around equilibrium positions can be shown to give always smaller upper bounds for the ground state energy for any value $0 < b < \infty$ than a self-consistent treatment, which is analogous to the mean-field approximation [11]. This Gaussian model predicts a non-zero order parameter for any finite value of b. Hence it is not necessarily obvious that there is a quantum melting transition at $T = 0$ at all.

The intention of this letter is to study the $T = 0$ properties of the QAPR model such that the underlying quantum mechanics are not subject to uncontrolled approximations. Conclusions for the existence and the mechanism of reentrance can be drawn based on this study and known finite-temperature results. We consider the free-field N-particle Hamiltonian

$$H_0 = -B \sum_{i=1}^{N} \frac{\partial^2}{\partial \varphi_i^2} + J \sum_{\langle i,j \rangle} \cos\left(2\varphi_i + 2\varphi_j - 4\phi_{i,j}\right), \tag{1}$$

with φ_i the angle of the molecule pinned at site $\underline{R}_i$ of the triangular lattice and $\phi_{i,j}$ the six phase angles that measure the angle between neighboring sites $\underline{R}_i$ and $\underline{R}_j$. The ordering process can be described by a three-component order parameter

$$\phi_\alpha = \frac{1}{N} \sum_{i=1}^{N} \sin(2\phi_i - 2\eta_\alpha) \exp\left[i \underline{Q}_\alpha \cdot \underline{R}_i\right] \tag{2}$$

with $\underline{Q}_1 = 2\pi(0, 2/\sqrt{3}), \underline{Q}_2 = 2\pi(-1, -1/\sqrt{3}), \underline{Q}_3 = 2\pi(1, -1/\sqrt{3})$, and $\eta_1 = 0, \eta_2 = 2\pi/3, \eta_3 = 4\pi/3$. Accordingly, a field-dependent Hamiltonian can be defined as $H = H_0 - h_1\phi_1$.

In the present letter this model is investigated by means of diffusion Monte Carlo (DMC) [12], in principle an exact numerical method to calculate ground state energies. Unlike variational Monte Carlo (VMC) and mean-field approximations, DMC does not suffer from uncontrolled systematic errors. For computational details we refer the reader to the reviews [13, 14] and the original literature [12]. Unfortunately observables other than the ground state energies are difficult to determine for many-particles systems using DMC because the wave function is used as the probability measure and not the probability density. One therefore needs to extract information indirectly, *e.g.*, the kinetic energy expectation value per particle $\langle t_{\mathrm{kin}} \rangle$ can be gained by

$$\langle t_{\mathrm{kin}} \rangle = \frac{1}{N} \frac{\partial \langle H_0 \rangle}{\partial \log B}. \tag{3}$$

Furthermore, the magnetization M_1, which is defined here as the expectation value of ϕ_1, and also the corresponding susceptibility χ_{11}, can be obtained by calculating the ground state energy per particle $\epsilon_0(h)$ and using the small field expansion

$$\epsilon_0(h_1) = \epsilon_0(0) - M_1 h_1 - \frac{1}{2}\chi_{11} h_1^2 + O(h_1^3). \tag{4}$$

Before presenting DMC results we address two approximate treatments, which are found very useful to help in interpreting the quasi-exact results: i) The Gaussian model, which is based on a trial wave function ψ_{G} where the rotors carry out fluctuations around equilibrium angles $\varphi_i^{(\mathrm{eq})}$, and ii) the Jastrow model with a Jastrow wave function ψ_{J} as the trial wave function, *i.e.*

$$\psi_{\mathrm{G}} \propto \prod_{i=1}^{N} \left\{ \sum_{n=-\infty}^{+\infty} \exp\left[-\frac{\left(\varphi_i + n\pi - \varphi_i^{(\mathrm{eq})}\right)^2}{4\Delta\varphi^2} \right] \right\} \tag{5}$$

and

$$\psi_{\mathrm{J}} \propto \exp\left[-\alpha V\right]. \tag{6}$$

Here, $\Delta\varphi^2$ and α are variational parameters to be optimized and V is the total potential energy from eq. (1). It can be shown that the analytically solvable Gaussian model is always ordered, while VMC calculations applied to the Jastrow wave function give a weak first-order $T = 0$-phase transition at a rotational constant $b \approx 0.19$ [11].

Ground state energies for the Gaussian model, the Jastrow model, and from DMC for a system with $N = 900$ are shown in fig. 1, where we express all energies in units of the coupling parameter J. ψ_{J} is used as a guidance wave function in the DMC simulation. It can be seen that the Gaussian model describes ground state energies fairly accurate for $b \lesssim 0.3$, while the Jastrow wave function is accurate in the region $b \gtrsim 0.7$. Since the Gaussian model shows order for any b and the Jastrow model is disordered for $b \gtrsim 0.19$, these approximate treatments of the QAPR model suggest that a quantum melting transition occurs in the intermediate region $0.3 < b < 0.7$.

In order to verify this behavior as well as to locate the phase transition more accurately, we calculate with DMC the dimensionless kinetic energy per particle as a function of b by using eq. (3). Due to the fact that within DMC typically 1000 identical replicas have to be simulated in parallel, we limit the system size to $N = 256$. In fig. 2, a sudden change in the derivative

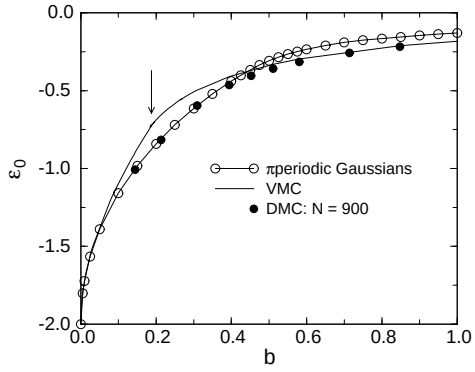

Fig. 1

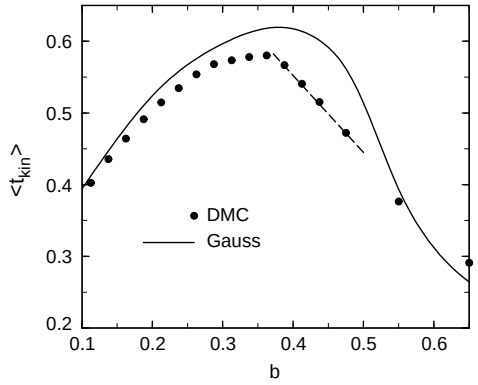

Fig. 2

Fig. 1. – Dimensionless ground state energy ϵ_0 as a function of rotational constant b (circles) for the treatments described in the text. The arrow indicates the order-disorder transition of the Jastrow ansatz. Jastrow ansatz and DMC results were each obtained for $N = 900$.

Fig. 2. – Expectation value of dimensionless kinetic energy per particle $\langle t_{\rm kin}\rangle$ as a function of rotational constant b obtained by DMC for $N = 256$ and by the Gaussian model. A dashed line is drawn to guide the eye.

of $\langle t_{\rm kin}\rangle(b)$ near a maximum at $b \lesssim 0.4$ is striking. In a $N = 64$ study of the functions $\epsilon(b)$ and $\langle t_{\rm kin}\rangle(b)$, the kink in the slope of $\langle t_{\rm kin}\rangle(b)$ is less obvious. However, one can see that the size effect in $\epsilon(b)$ is maximal at $b = 0.4$. Size effects in $\epsilon(b)$ are undetectably small outside the region $0.25 < b < 0.65$. One can certainly expect the transition to be close to the point where size effects are the most striking.

The kinetic energy in the Gaussian model behaves similarly to the one calculated in the DMC simulation. However, there is no discontinuity in the slope. Within the Gaussian effective one-particle picture the maximum of $\langle t_{\rm kin}\rangle$ has a simple interpretation. For small values of b, the harmonic approximation applies so that $\langle t_{\rm kin}\rangle \propto \sqrt{b}$ with corrections due to interwell tunneling of order $\exp[-1/b]$. With increasing b these delocalization corrections tend to exceed the barrier height of the cosine potential, which is of order $1/b$. Then quantum delocalization starts to suppress the tendency to localize within the wells. Consequently, $\langle t_{\rm kin}\rangle$ decreases with further increasing b. The crossover from localization ($\langle t_{\rm kin}\rangle \propto \sqrt{b}$) to delocalization ($\langle t_{\rm kin}\rangle \propto 1/b$) results in a maximum in the intermediate region at $b \approx 0.4$. Although different in detail, we suggest that a similar crossover occurs in the N-particle system. Quantum coherence effects extended over many correlated rotors can moreover change the macroscopic behavior discontinuously indicating a phase transition. Such a discontinuity is observed in the slope of $\langle t_{\rm kin}\rangle$ obtained by DMC at a rotational constant $b_{\rm d} \approx 0.4$, see fig. 2.

Further evidence that there is a phase transition around $b_{\rm d}$ can be obtained by exploiting eq. (4), *i.e.* the response of the system due to an external field $h = h_1$. Calculations of susceptibilities and cumulants require expensive numerical computations, which are plagued by particularly large statistical errors in the transition region. Instead, we investigate the ground state energy per particle $\epsilon_0(h)$ for various b and introduce the crossover field $h_{\rm c}$. $h_{\rm c}$ is the external field at which the slope of $\epsilon_0(h)$ becomes constant with increasing h. See fig. 3a) for a schematic definition of $h_{\rm c}$.

For sufficiently small b, the system is ordered in its thermodynamic limit but for finite N tunneling between the various global ground states is always present. As a consequence, the

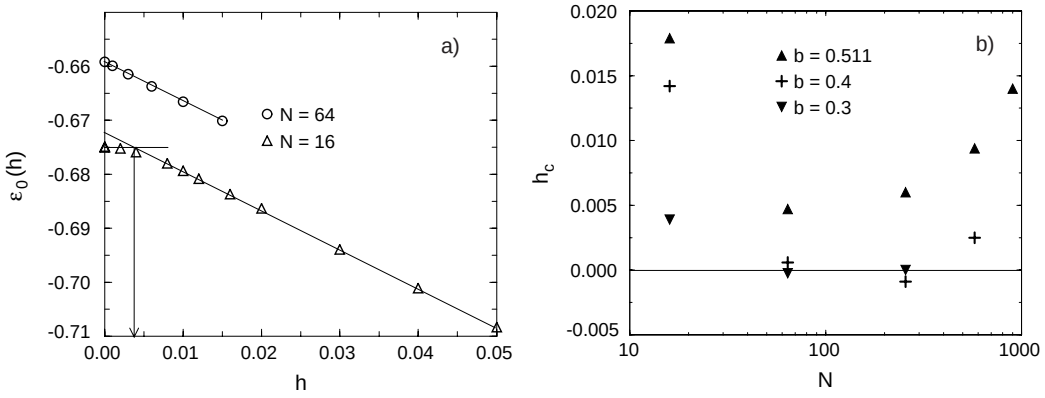

Fig. 3. – a) Ground state energy $\epsilon_0(h)$ as a function of field h for $b = 0.3$ and two system sizes N. For $N = 16$ it is shown schematically how the crossover field h_c, indicated by the arrow, is obtained. b) Crossover field h_c as a function of the system size N and for various rotational constants b. The resolution of the crossover field is about 0.0015.

response of a finite system is never strictly linear as h tends to zero. However, for systems that are ordered in the thermodynamic limit, h_c can, of course, be expected to decrease as N increases. This effect, which can be seen in fig. 3a) for $b = 0.3$, is due to a smaller relative tunneling splitting in the larger system. For a disordered system, h_c must reach a finite limit since the absolute value for the order parameter is bounded from above, namely saturation takes place at $M = 1$. We want to note that in all our studies the used fields were only small perturbations and the responses were always far from saturation. Studies similar to the investigation shown in fig. 3a) have been carried out for various rotational constants. In the regime $0.4 < b < 0.7$, one observes a crossover to a predominant linear response in $\epsilon_0(h)$ where, however, h_c does not tend to zero as $N \to \infty$, see fig. 3b). Instead, h_c increases with increasing N. This behaviour reflects increasing disorder for increasing system sizes. Given the huge size effects (particularly in the susceptibility) of the classical APR model, where several ten thousand rotors were needed to determine the order of the phase transition, large size effects in h_c seem plausible for the quantum model. It would certainly be interesting to see at which system sizes saturation in h_c sets in. Unfortunately, an accurate $T = 0$ quantum simulation for N significantly larger than 256 does not yet seem to be computationally tractable.

From the size-dependent analysis shown in fig. 3b), we conclude that a quantum melting phase transition takes place within the range $0.3 < b_c < 0.511$, presumably $b \lesssim 0.4$. Given this result and the PIMC study by Martonak *et al.* [6], who observed thermally driven phase transitions at $T = 0.3$ and $b = 0.61$, it is clear that the QAPR model shows reentrance. A more precise value for b_c cannot be obtained by a similar size-dependent study due to the enormous numerical effort needed in the transition region. Thus, one can only conjecture that b_c lies nearby the anomaly in $\langle t_{\rm kin} \rangle$ at $b_d \simeq 0.4$ (cf. fig. 2).

In order to understand reentrance we develop the following picture. For b slightly larger than b_c the system is disordered at $T = 0$. There is, however, a large but finite correlation length. As the system is heated, some rotors are excited from their even parity ground state to the first excited state, which has odd parity. Similar as in the case of a double-well potential, the first excited state is more localized in the bottom of the potential wells. This results in a larger quadrupole moment which in turn acts localizing on neighbored rotors. Consequently, the correlation length increases and might even diverge. Such a scenario seems

only possible if there is an energy gap between single-particle even to odd conversions and N-particle excitations without parity conversions, which invoke thermal delocalization. Those N-particle excitations will only be populated at further heating leading to global disorder. This picture is in agreement with the observation that there is reentrance in solid HD but not in solid H_2 and D_2, where spin conversion and thus parity conversion are extremely slow. Mixing particles of paramagnetic species into solid H_2 or D_2 might make reentrance observable on typical experimental time scales.

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