Quantum Effects on the Herringbone Ordering of N_2 on Graphite

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The effects of quantum fluctuations on the "2-in" herringbone ordering in a realistic model of 900 N_2 molecules adsorbed in the $(\sqrt{3}\times\sqrt{3})R30°$ structure on graphite are studied via path-integral Monte Carlo (PIMC) simulations. Quasiclassical and quasiharmonic calculations agree for high and low temperatures, respectively, but only PIMC gives satisfactory results over the *entire* temperature range. We can *quantify* the lowering of the transition temperature and the depression of the ground state order to 10% as compared to classical modeling.

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For many years adsorbed layers of N_2 on graphite have served (see, e.g., Refs. [1–9]) as a prototype example to study phase transitions in two dimensions. The phase diagram [1] includes below 50 K a registered phase having a commensurate $(\sqrt{3}\times\sqrt{3})R30°$ structure. The orientations of the molecular axes undergo in this phase an *orientational* phase transition quite independent from coverage (below a coverage of 1.2) at around 27 K to the "2-in" herringbone phase keeping the translationally ordered $\sqrt{3}$ structure of the molecular centers of mass.

This orientationally ordered phase of N_2 on graphite has been studied experimentally [1–3] and theoretically [3–9] under various aspects until very recently. However, all theoretical investigations of the *phase transition* itself were carried out with purely *classical* methods or on the *mean-field* level. We address in this Letter the problem of *quantifying* the effect of *quantum fluctuation* on the orientational ordering in this molecular system. A method suited to study finite-temperature many-body quantum systems is the path-integral Monte Carlo (PIMC) technique; see, e.g., Ref. [10] for an introduction. We have already used such an approach to study phase transitions in a simplified *model* adsorbate with internal quantum states [11]. In the present communication, a very efficient PIMC scheme [12] especially tailored to simulate rotational motion is used for the first time to study a many-body system. This allows us to investigate a *highly realistic* adsorbate composed of as many as 900 quantum N_2 rotators and Trotter dimensions up to 500. Thus, we are able to quantify for the first time the influence of quantum fluctuations on a collective phenomenon in a *molecular* system beyond strongly simplified models or approximations. We compare our benchmark data, which are exact over the whole temperature range of experimental interest, to quasiharmonic results and quasiclassical Feynman-Hibbs effective potential simulations at low and high temperatures, respectively.

The PIMC approach [10] is by now a well established and efficient tool to study quantum effects in many-body systems. However, only recently [12] a first step to simulate directly rotational motion in a *one*-particle problem was done. Now, we successfully generalize this approach to the nontrivial case of *many interacting* rotators. Starting from the N-particle Hamiltonian including an external crystal-field $V^{(1)}$ and the interaction potential $V^{(2)}$, we apply the Trotter theorem [13] to the partition function $Z_N = \mathrm{Tr}\exp(-\beta\sum[\hat{L}_j^2/2I_j + V^{(1)}(\hat{\varphi}_j) + V^{(2)}(\{\hat{\varphi}_j\})])$, where $\hat{L}_j$, $\hat{\varphi}_j$, and $I_j(=\hbar^2/2\Theta_j)$ are angular momentum operator, angle operator, and moment of inertia of the jth molecule. Only after a Poisson transformation to the so-called "winding-number representation" is a numerical stable path-integral representation found. The major difference from Cartesian path integrals is that the circle is a multiply connected space; i.e., the *complete* path integral consists of a usual path integration in each homotopy class and an additional regular summation over all these classes [13]. In the resulting PIMC partition function for the interacting case with Trotter dimension P,

$$Z_N = \lim_{P\to\infty}\left(\frac{IP}{2\pi\hbar^2\beta}\right)^{\frac{NP}{2}}\prod_{j=1}^{N}\left\{\sum_{n_j=-\infty}^{\infty}\int_0^{2\pi}d\varphi_j^{(1)}\prod_{s=2}^{P}\left[\int_{-\infty}^{\infty}d\varphi_j^{(s)}\right]\right\}$$
$$\times\exp-\beta\sum_{j=1}^{N}\sum_{s=1}^{P}\left\{\frac{IP}{2\hbar^2\beta^2}[\varphi_j^{(s)}-\varphi_j^{(s+1)}+2n_j\pi\delta_{s,P}]^2+\frac{1}{P}V^{(1)}(\varphi_j^{(s)})\right\}$$
$$\times\exp-\beta\sum_{\langle j,i\rangle}^{N}\sum_{s=1}^{P}\left\{\frac{1}{P}V^{(2)}(\varphi_j^{(s)},\varphi_i^{(s)})\right\}, \qquad (1)$$

we specified nearest neighbor $\langle j,i\rangle$ interactions. The closed paths or ring polymers [10] are now defined in angle space and the cyclic boundary conditions $\varphi_j^{(P+1)}=\varphi_j^{(1)}$ of the paths have to be understood modulo $2n_j\pi$.

This formulation of the problem does not take into account the consequences of the indistinguishability of the nuclei, but it is an *excellent* approximation for the present case as explicitly demonstrated in Ref. [12]. In the algorithm, we include local and global angle moves supplemented by superglobal winding-number moves, which are in spirit similar to moves in world-line MC [10] or exchange-permutation moves [14]. As tested against exact results for a one-particle case, the algorithm assures the correctly weighted path integration over the homotopy classes; the Trotter dimension was large enough to reach the Trotter limit within the statistical error bars. In addition to these *full* quantum PIMC calculations, we performed quadratic Feynman-Hibbs effective potential calculations; see Ref. [15] for applications, suitably generalized for coordinates with constraints. Following Refs. [16, 17], we used a quasiharmonic quantum theory to approximate the librational motion at low temperatures.

Following our aim, we try to capture as much of the microscopic features of the system as possible, but restricting ourselves at the same time to design a model which is *just tractable* with modern techniques. First of all, we pin the molecular centers of mass on a regular trigonal $\sqrt{3}$ superlattice found experimentally [1–3] and confirmed as an excellent approximation in previous investigations [5]. In addition, it is established by several methods that the molecular axes stay *in* the graphite plane [2, 3, 6, 8] with a very sharp distribution [3, 6] around this favored plane nearby and below the orientational transition. Concerning the N_2-N_2 interactions, the well established [8] $X1$ model [18] consisting of site-site Lennard-Jones and quadrupole interactions was shown to yield a realistic representation; $\Theta_{N_2} = 2.9$ K. Steele's Fourier representation [19] is used to model the N_2-graphite interactions.

The herringbone order parameter [5] (OP) $\Phi = \langle [\sum_{\alpha=1}^{3} \Phi_\alpha^2]^{1/2} \rangle$ possessing the symmetry of the problem is defined with suitably generalized components for PIMC investigations,

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

where $\mathbf{Q}_1 = 2\pi(0, 2/\sqrt{3})/a'$, $\mathbf{Q}_2 = 2\pi(-1, -1/\sqrt{3})/a'$, $\mathbf{Q}_3 = 2\pi(1, -1/\sqrt{3})/a'$ and $\eta_1 = 0$, $\eta_2 = 2\pi/3$, $\eta_3 = 4\pi/3$; $a' = \sqrt{3}a$, and $a = 2.46$ Å. Two alternative definitions of the OP with different ordering of the summations and average were tested, but all of them gave the same values within the statistical error bars. In addition, we present the heat capacity via the fluctuation relation in the classical case and via the temperature derivative of the energy in the quantum case; in the latter case error bars are difficult to assess.

The first signature of the orientational transition can be identified in the anomaly of the heat capacity around 35 K; see Fig. 1. Switching off the N_2-substrate interaction does not change the behavior. Several features distinguish the quantum result from the classical one. As expected, the quantum peak is smeared out and lowered due to quantum fluctuations on top of the thermal ones. In addition, quantum effects lower the transition temperature T_c by nearly 10%. The most striking *qualitative* difference is the decay of the quantum heat capacity to zero upon approaching low temperatures whereas the classical curve merges into the Dulong-Petit value at $T = 0$. The zero-point energy due to librational motion in the potential minima can be quantified to amount to approximately 30 K.

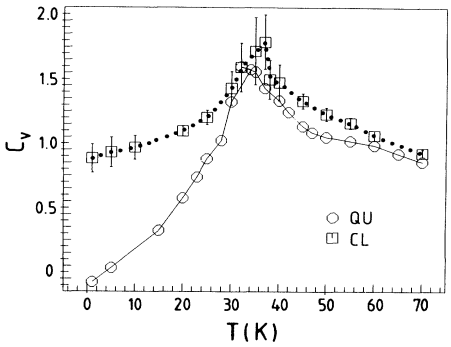

FIG. 1. Heat capacity per molecule (see text) as a function of temperature. Quantum simulation, circles; classical simulation, squares. The lines are linear connections.

The central quantity is the OP as a function of temperature; see Fig. 2. The point of inflection of the classical curve can be located around 38 K. Analogous classical models with rotations and translations in three dimensions yield a similar T_c: 33 K [6] with 96 molecules, 28 K [7] with 64 molecules. The agreement with these classical simulations shows that our model captures the orientational transition of N_2 on graphite extremely well. At high temperatures, the quantum curve of the OP merges on the classical curve, whereas it starts to deviate below T_c. Qualitatively, quantum fluctuations lower the ordering and thus the quantum OP is always smaller than the classical counterpart. This behavior can be visu-

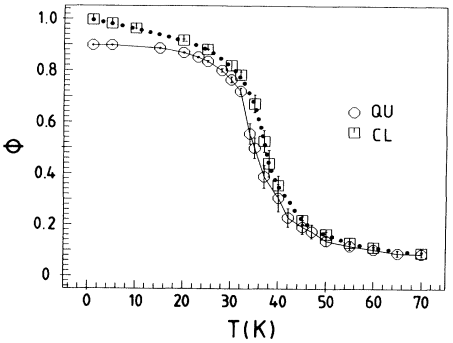

FIG. 2. Herringbone order parameter as a function of temperature; symbols as in Fig. 1.

alized by presenting angle distributions in Fig. 3. Plotted in the direction of a given angle is the probability of finding this angle in the simulation; the maximum diameter is out of scale but the same in all graphs and we show for clarity only a patch of 36 molecules out of the 900. At low temperatures (5 K) the classical distribution in (b) is sharply peaked around the directions corresponding to herringbone ordering. In (a), the same situation is presented but now includes the additional quantum fluctuations. These fluctuations allow one to populate angle configurations that are classically forbidden at a given temperature. One clearly sees a substantial broadening of the distributions due to quantum librations of the molecules in the herringbone potential wells. Near T_c in (c), the herringbone ordering is decreased as indicated by nonzero probabilities for the molecules to stay perpendicular to the preferred directions. In the high temperature limit (200 K) in (d), the rotators are completely free and an isotropic angle distribution without quantum corrections is reached.

The inclusion of quantum effects results in a nearly 10% lowering of T_c; see Fig. 2. Furthermore, we can infer *quantitatively* from our data in Fig. 2 that the quantum system cannot reach the maximum herringbone ordering even at extremely low temperatures: the quantum librations depress the saturation value by 10%; since the OP at 15 K is only 1% lower than at 5 K the ground state OP seems to be safely reached at our lowest temperature. This situation should be compared to the spin-$\frac{1}{2}$ quantum Heisenberg *antiferromagnet* in two dimensions where the ground state staggered magnetization is reduced [20] from its Néel, or classical, value; *no* OP reduction due to quantum fluctuations is observed for the *ferromagnet*. In Fig. 4, we compare in detail OP and total energy as obtained from the full quantum simulation with approximate theories valid for low and high temperatures. One can clearly see how the quasiclassical Feynman-Hibbs curve matches the "exact" quantum data above ≈ 30 K. However, just below the phase transition, this second order approximation in the quantum fluctuations fails and yields *uncontrolled* estimates: just below the point of failure it gives classical values for the OP and the herringbone ordering even *vanishes* below 5 K. On the other hand, the quasiharmonic theory comes from the other end of the temperature axis and yields very accurate data below 5 K. Similar ranges of validity can be based on the heat capacity. In addition to OP and energy, our PIMC technique also allows one to extract an average zero-point libration amplitude (14°) from the "radius of gyration" of the angular ring polymers, which compares favorably to the 0 K data from this approximation (13°) and to the quasiharmonic lattice dynamics [8] (18°) for $X1$ N_2 in three dimensions including translations. Since the range of validity of such approximations is very difficult to estimate *a priori* (see Ref. [21] for a critical and extensive discussion), exact full quantum *reference* simulations as presented here for a specific phase transition are clearly required to control such approximation schemes. This becomes clear when one considers the shift in T_c as obtained from the second order Feynman-Hibbs simulation: it breaks down essentially at the same temperature where the phase transition occurs and a breakdown at a slightly higher temperature would give a wrong result. In addition, one does not know where to match the regimes where different approximations are still valid. The PIMC simulations, however, yield exact results over the *whole* temperature range from the classical to the deep quan-

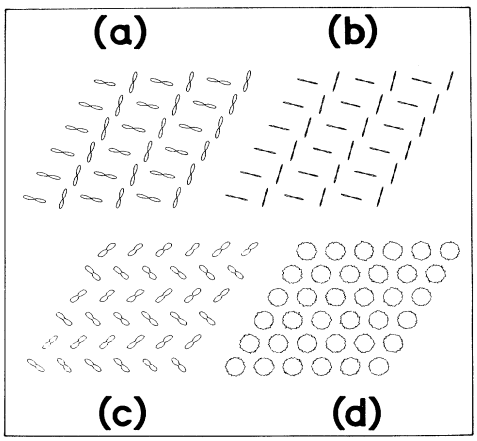

FIG. 3. Angle distributions; see text. (a) 5 K, quantum simulation (QU); (b) 5 K, classical simulation (CL); (c) 35 K, QU; (d) 200 K, CL.

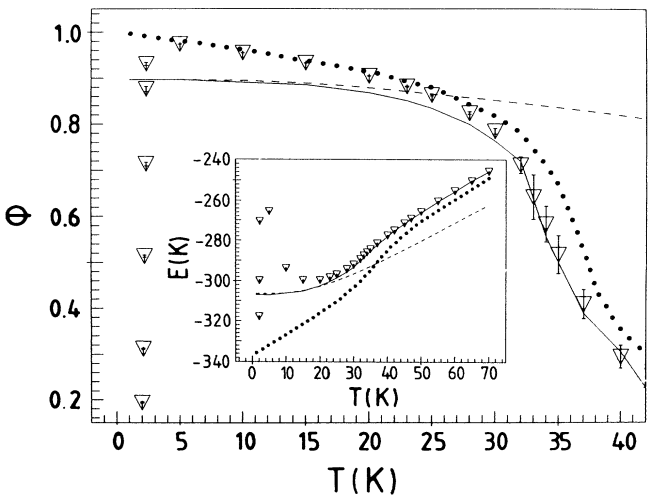

FIG. 4. Herringbone order parameter and total energy (inset) as a function of temperature. Quantum simulation, full line; classical simulation, dotted line; quasiharmonic theory, dashed line; Feynman-Hibbs simulation, triangles. The lines are linear connections of the data.

tum regime.

To sum up, using a novel path-integral Monte Carlo technique optimized for the direct simulation of rotational motion in many-body systems, we investigated quantitatively the role of quantum fluctuations concerning orientational ordering properties in a molecular system, namely, $(\sqrt{3}\times\sqrt{3})R30°$ N_2 monolayers on graphite. A highly realistic model using 900 molecules was designed to capture the essential features of the orientational ordering transition to the "2-in" herringbone phase. The peak shape of heat capacity, which vanishes correctly as $T \to 0$, is strongly distorted at the low temperature wing due to quantum effects. We find a suppression of the orientational transition temperature due to quantum fluctuations of nearly 10%; this is considerably less than previously estimated. In addition, our method yields a decrease of the ground state herringbone ordering of 10%, which is caused by quantum librations of the N_2 molecules in the potential wells. Comparison of our full quantum benchmark data with quasiclassical and quasiharmonic results shows that these approximations account for the high and low temperature properties, which is an *a posteriori* justification of their usefulness for the present system. Since our approach is not restricted to nearly classical systems, techniques similar to those presented here may serve in the future to investigate *quantitatively* quantum effects on such *collective* phenomena in a whole class of *realistic molecular* adsorbates, as, e.g., H_2 layers, where more pronounced quantum effects are expected.

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