Orientational Phases of Hydrogen Molecules on a Triangular Lattice

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Abstract
A mean-field theory for the ordering of hydrogen molecules on a triangular net is derived in terms of the quadrupole coupling constant $\Gamma$, the crystal field $V_c$, and the temperature $T$. The phase diagram consists of six regions, separated by first- and second-order transitions. For almost all values of $V_c/\Gamma$ for which ordering occurs, the disordered to ordered phase transition is continuous. At $T=0$ K, all phases have energy gaps except for a ferrorotational phase which behaves like an XY model.

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Orientational Phases of Hydrogen Molecules on a Triangular Lattice

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A mean-field theory for the ordering of hydrogen molecules on a triangular net is derived in terms of the quadrupole coupling constant $\Gamma$, the crystal field $V$, and the temperature $T$. The phase diagram consists of six regions, separated by first- and second-order transitions. For almost all values of $V/\Gamma$ for which ordering occurs, the disordered to ordered phase transition is continuous. At $T=0$, all phases have energy gaps except for a ferromagnetic phase which behaves like an $XY$ model.

In this Letter we present the results of an analysis, based on mean-field theory, for the phase diagram of ($J=1$) hydrogen molecules (ortho-H$_2$, or para-D$_2$) on a two-dimensional triangular lattice. In the model we treat, the centers of mass of the molecules are fixed at their lattice sites whereas the orientations of the molecules, specified by their occupation of three $m_J$ levels within the $J=1$ manifold, are determined by the electrostatic quadrupole-quadrupole (EQQ) interaction between molecules and the crystal field of the substrate. This model describes monolayers of ortho-H$_2$ or para-D$_2$ on graphite (or Grafoil) in the phases where the centers of mass of the molecules are in registry with the substrate. Our conclusions form the basis for better treatments of the cooperative orientational ordering and, as will be seen, give rise to a rich variety of phases. Among these is a phase having the same symmetry as the widely studied two-dimensional Heisenberg model for planar spins, the $XY$ model.

It is well established that in the solid the EQQ interaction is dominant. On Grafoil one expects an additional orientation-dependent interaction due to the field of the substrate. This crystal field will have the form

$$H_c = V_c \sum_i [J^z(i) - 1/2],$$

where $i$ is summed over all hydrogen molecules, $J^z(i)$ is the angular momentum of molecule $i$, and the $z$ axis is chosen perpendicular to the substrate. The EQQ interaction has the form

$$H_{EQQ} = (16\pi\Gamma/45)\sqrt{70\pi} \sum_{i,j} C(i,j) Y^m_{j}(i) Y^m_{j}(j) Y^{m+N}_{j}(\Omega_{ij}),$$

where $i$ is the nearest-neighbor EQQ coupling constant, $C(i,j)$ is a Clebsch-Gordan coefficient, and $\Omega_{ij}$ specifies the direction of the vector joining molecules $i$ and $j$ which are nearest neighbors. The operators $Y^m_{j}$ are given by $Y^0_{j} = (5/16\pi)^{1/2} (3J_z - 2)$, $Y^{21}_{j} = (15/32\pi)^{1/2} (J_z J_x + J_x J_z)$, and $Y^{22}_{j} = (15/32\pi)^{1/2} J_z^2$. In the disordered or pararotational ($"para"$) phase, the molecules mainly feel the crystal field which tends to align them parallel (for $V_c>0$) or perpendicular (for $V_c<0$) to $z$. As this order builds up, the alignment is opposed by the EQQ interaction which classically would cause a pair of molecules to orient perpendicular to each other in a "$T$" configuration. Thus in mean-field theory for the para phase, there is an effective temperature-dependent gap between the $m_J=0$ and $m_J=\pm 1$ states

$$\Delta(T) = V_c - \frac{32}{9} \sigma_0 \Gamma,$$

where $\langle \cdots \rangle$ is a thermal average over $m_J=0, \pm 1$. Clear evidence for a temperature-dependent gap has been obtained from recent measurements of the NMR spectrum of ($J=1$) D$_2$ on Grafoil by Kubik and Hardy, who first attributed it to the EQQ mechanism described above and whose observations led us to consider the problem of the possible low-temperature ordered states.

To investigate these ordered phases we calculate the free energy

$$F = \text{Tr} [\rho H + k T \ln \rho],$$

where $\rho$ is the density matrix.
where the density matrix $\rho$ is chosen to minimize $F$ subject to the condition $\text{Tr}\rho = 1$. Within mean-field theory $\rho$ is restricted to be a product of single-particle density matrices, $\rho_i$. We work in a coordinate system in which the $z$ axis is normal to the layer and the $x$ axis connects the molecule at the origin to one of its nearest neighbors. In the absence of magnetic interactions the most general form for $\rho_i$ is

$$
\rho_i = \begin{bmatrix}
(1 - \sigma_i)/3 & -\mu_i^-/\sqrt{2} & -\eta_i^-/2 \\
-\mu_i^+/\sqrt{2} & (1 + 2\sigma_i)/3 & \mu_i^+/\sqrt{2} \\
-\eta_i^+/2 & \mu_i^+/\sqrt{2} & (1 - \sigma_i)/3
\end{bmatrix}
$$

in the $m_j$ representation. We will also use the notation $v_i \pm iv_j = \nu^\pm$, where $\nu = \mu$ or $\eta$, and $v_x$ and $v_y$ are real. In terms of these order parameters, $\langle x^2 \rangle = - (5/4\pi)\delta o$, $\langle x^4 \rangle = (15/32\pi)\delta \mu^2$, and $\langle x^2 y \rangle = (15/32\pi)\delta \eta^2$ where $\langle \cdots \rangle = \text{Tr}(\rho \cdots)$.

Three equivalent techniques were used to explore the mean-field phase diagram. These are (1) the Landau expansion, (2) a self-consistent-field method of the type developed by James for solid hydrogen, and (3) analytic formulas. The Landau expansion, in terms of the parameters $\eta_i$, $\mu_i$, and $(\sigma_i - \bar{\sigma})$, where $\bar{\sigma}$ is the average of $\sigma_i$ over all molecules, was only useful close to the disordered phase where these parameters are small. This method is quite powerful, however, since it does not necessitate the assumption of a particular sublattice structure. The self-consistent-field method requires a computer calculation for an $N \times N$ array of molecules with periodic boundary conditions. This method is useful for locating first-order transitions. Analytic formulas were obtained for the free energies of each of the phases which were studied. These formulas allowed us to check the accuracy of the computer calculations and provided alternative derivations of the Landau expansions.

Our results are summarized in the phase diagram in Fig. 1, in which the coordinate axes are the dimensionless variables $V_2/\Gamma = \bar{V}_x$ and $T/\Gamma = \tau$. Five different ordered regions are seen to occur. For large negative crystal fields at low temperature, the stable structure is the two-sub-
lattice phase shown in Fig. 2(a) with $\varphi = 45^\circ$. In this phase the molecular wave functions are in the plane of the substrate ($\mu = 0$), and hence it is labelled “2-in”. A similar structure has been proposed by Fuselier, Gillis, and Raich for $N_2$ on Grafoil.

Just above the 2-in phase there is a small region labeled “2-out” in which the molecules begin to tip up out of the plane ($|\mu| > 0$). As the crystal field is increased (at $V_c = -2.80$ for $\tau = 0$) there is a first-order transition from the 2-out phase to a four-sublattice phase (labeled “4”). The structure of this phase is illustrated in Fig. 2(b). It is characterized by $\mu = 0$ for all sublattices, $\eta = 0$ for sublattice 1, and $\sigma_+ = \sigma_2 = \sigma_3 = \sigma_4$. If we write $\eta_0 = (\eta_0 \cos 2\chi_0, \eta_0 \sin 2\chi_0)$ for $i = 2, 3, 4$, then $\chi_0 = \chi_2 + 60^\circ, \chi_0 = 120^\circ$ and

$$\cos 2\chi_0 = (\sigma_+ - \sigma_3) / \eta_0.$$  

(6)

Close to the pararotational phase $\sigma_+ - \sigma_3$ goes to zero like $\eta_0^2$, and hence $\chi_0$ goes to $45^\circ$ at this boundary.

For $V_c > 5.07$ at $\tau = 0$ the 2-out phase reappears. As $V_c$ increases, this phase evolves continuously into a one-sublattice ferrototational (“ferro”) phase. [For $\tau = 0$ the angle $\varphi$ in Fig. 2(a) goes continuously to zero at $V_c = 19$.] The ferro phase is characterized by $\mu = (\mu_0 \cos \chi, \mu_0 \sin \chi)$, $\eta = (\eta_0 \cos 2\chi, \eta_0 \sin 2\chi)$ with $\chi$ arbitrary and $\sigma > 0$. For $V_c > 5/2$ there is no cooperative ordering. The only nonzero order parameter is $\eta_0$ whose temperature dependence is determined by Eqs. (3).

Using the Landau expansion, the phase transition from the para phase, if it is second order,7 is signaled by the occurrence of a zero eigenvalue of the matrix $\theta F / \delta q_i \delta q_j$ for $i$ and $j$ label molecules and $q_i, q_j (\alpha = 1, \ldots, 5)$ is one of the five fluctuating order parameters $\mu_1, \mu_2, \mu_3, \eta_1, \eta_2, \eta_3$, or $(\sigma_+ - \sigma_3)$. The matrix is reduced to block diagonal form by a spatial Fourier transform. For $10.43 < V_c < 15$, the eigenvalue which goes soft at the highest temperature is a $Q = 0$ mode for which the associated eigenvector is an arbitrary linear combination of $\mu_2, \mu_3$ corresponding to $\bar{\mu} = (\mu_0 \cos \chi, \mu_0 \sin \chi)$ which describes the ferro phase. Within mean-field theory the degeneracy with respect to $\chi$ persists to all orders in the Landau expansion since the entropy is independent of $\chi$. Near the order-disorder transition $\eta_0$ is proportional to $\mu_0^2$.

For $V_c < 10.43$ the eigenvectors which first have a zero eigenvalue as $\tau$ is lowered are

$$X_A = \sum_i \eta_0 \exp (iQ_A \cdot r_i),$$  

(7a)

$$X_B = i \sum_i [\sqrt{3} \eta_0 - \eta_0] \exp (iQ_B \cdot r_i),$$  

(7b)

$$X_C = i \sum_i [\sqrt{3} \eta_0 - \eta_0] \exp (iQ_C \cdot r_i).$$  

(7c)

where $Q_A = (2\pi/a\sqrt{3}) \vec{f}, Q_B = -(\pi/a) \vec{f} - (\pi/a\sqrt{3}) \vec{f}, Q_C = -Q_A - Q_B, a$ is the lattice constant. As Landau pointed out, one must look at higher-order terms to decide what phase actually occurs. There are no terms in the free energy which are of odd order in the $\chi$'s. At the temperature at which the zero eigenvalues first develop, the fourth-order term in the free energy has the form

$$F^{(4)} = \alpha(X_A^2 + X_B^2 + X_C^2)^2 + \beta(X_A X_B + X_A X_C + X_B X_C)^2,$$  

(8)

where $\alpha > 0$. For $V_c < 2.34$, $\beta$ is positive and the ordered state is one in which only one of $X_A$, $X_B$, or $X_C$ is nonzero. This is the two-sublattice structure 2-in. For $2.34 < V_c < 9.82, \beta$ is negative but $\alpha + \beta/3$ is positive. Then the ordered state is one in which $X_A = X_B = X_C$ which corresponds to the four-sublattice state with $\chi_0 = 45^\circ$. [Cf. the discussion below Eq. (6).] As long as $F^{(4)}$ is positive, the transition temperature $\tau_0$ is simply determined by the vanishing of the smallest eigenvalue and the transition is continuous. We find that

$$\tau_0 = 73(1 - \sigma_0) / 12,$$  

(9)

where $\sigma_0$ is determined by Eq. (3).

At $V_c = 9.82$, $\tau_0 = 3.50, \alpha + \beta/3$ (and hence $F^{(4)}$) passes through zero. For $V_c > V_c$, the transition from the para to the four-sublattice phase is first order. The point $(V_c, \tau)$ is a tricritical point, and the critical exponent for the appearance of the order parameter $\eta_0$ at this point is 1/4 instead of 1/2 which is its value elsewhere on the second-order line given by Eq. (9). The details of the phase boundaries near the tricritical point (in particular for $9.82 < V_c < 10.43$) are not represented in Fig. 1.

What is the outlook for this problem? Experiments on hydrogen on Grafoil will continue and it will be interesting to see whether $V_c$ can be varied in order to map out the phase diagram. At present, NMR experiments seem to show that for $D_3$ on Grafoil $|V_c| = 4$, but that there is no phase transition for $\tau > 2$. This suggests that a more complete and realistic treatment of this problem, not based on mean-field theory, is es-
Ultrasonic Observation of a Strong Pretransitional Anomaly near a Nematic–Smectic-A Phase Transition

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Strong anomalies in the velocity and attenuation of longitudinal ultrasound in the megahertz range were observed for the first time in the vicinity of the nematic–smectic-A phase transition in a liquid crystal (terephthal-bis-p-p′-butylaniline). Results are in strong contradiction with theoretical predictions and are qualitatively consistent with a picture involving both critical fluctuations and relaxations of the smectic order parameter, similar to that observed near the \( \lambda \) transition in liquid helium.

In recent years the nematic–smectic-A phase transition in liquid crystals has undergone extensive studies, both theoretical and experimental. The possibility of a second-order transition (either mean-field-like\(^{1}\) or \( \lambda \)-like\(^{2} \)) was predicted theoretically. Experimental evidence, though somewhat contradictory in nature, has been obtained on the pretransitional behavior of the

Frank elastic constants, twist viscosity, etc., in \( N-p \)-cyanobenzylidene-\( p \)-octyloxyaniline (hereafter referred to as CBOOA) which is known to have an almost second-order nematic–smectic-A phase transition.\(^{3} \) Sound propagation in CBOOA in the megahertz range of frequency, however, did not exhibit any anomaly near the transition.\(^{4} \) Experiments performed at lower frequencies\(^{5} \)

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