Orientational Phases of Hydrogen Molecules on a Triangular Lattice

A. J. Berlinsky
Department of Physics, University of British Columbia, Vancouver, British Columbia V6T 1W5, Canada

and

A. B. Harris
Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104
(Received 27 March 1978)

A mean-field theory for the ordering of hydrogen molecules on a triangular net is derived in terms of the quadrupole coupling constant Γ, 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/Γ 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.

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 which 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.[1] 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.[2]

It is well established that in the solid the EQQ interaction is dominant.[3] On Grafoil one expects an additional orientation-dependent interaction due to the field of the substrate. This crystal field will have the form

$$H_c = V_c \sum\nolimits_i [J_z(i)^2 - \tfrac{2}{3}], \tag{1}$$

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

$$H_{\text{EQQ}} = (16\pi\Gamma/45)\sqrt{70\pi}\sum_{i,j}\sum_{M,N} C(224;M,N)\mathcal{T}_2^{M}(i)\mathcal{T}_2^{N}(j)Y_4^{M+N}(\Omega_{ij}), \tag{2}$$

where Γ is the nearest-neighbor EQQ coupling constant,[4] $C(224;M,N)$ is a Clebsch-Gordan coefficient,[5] $Y_4^M(\Omega_{ij})$ is a spherical harmonic,[5] and Ω_{ij} specifies the direction of the vector joining molecules i and j which are nearest neighbors. The operators $\mathcal{T}_2^M$ are given by $\mathcal{T}_2^0 = (5/16\pi)^{1/2}(3J_z^2 - 2)$, $\mathcal{T}_2^{\pm1} = \mp(15/32\pi)^{1/2}(J_\pm J_z + J_z J_\pm)$, and $\mathcal{T}_2^{\pm2} = (15/32\pi)^{1/2}J_\pm^2$.

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 $m_J=\pm1$ states

$$\Delta(T) = V_c - \tfrac{27}{2}\sigma_0\Gamma, \tag{3a}$$

$$\sigma_0 = \langle 1 - \tfrac{3}{2}J_z^2\rangle, \tag{3b}$$

where $\langle\cdots\rangle$ is a thermal average over $m_J = 0, \pm1$. 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,[6] 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

$$F = \text{Tr}[\rho H + kT\rho\ln\rho], \tag{4}$$

where the density matrix ρ is chosen to minimize F subject to the condition $\mathrm{Tr}\rho = 1$. Within mean-field theory ρ is restricted to be a product of single-particle density matrices, ρ_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 ρ_i is

$$\rho_i = \begin{bmatrix} (1-\sigma_i)/3 & -\mu_i^-/\sqrt{2} & -\eta_i^-/2 \\ -\mu_i^+/\sqrt{2} & (1+2\sigma_i)/3 & \mu_i^-/\sqrt{2} \\ -\eta_i^+/2 & \mu_i^+/\sqrt{2} & (1-\sigma_i)/3 \end{bmatrix} \qquad (5)$$

in the m_J representation. We will also use the notation $v_x \pm i v_y \equiv v^\pm$, where $v = \mu$ or η, and v_x and v_y are real. In terms of these order parameters, $\langle\langle \mathcal{T}_2{}^0 \rangle\rangle = -(5/4\pi)^{1/2}\sigma$, $\langle\langle \mathcal{T}_2{}^{\pm 1} \rangle\rangle = \pm(15/32\pi)^{1/2}\mu^\pm$, and $\langle\langle \mathcal{T}_2{}^{\pm 2} \rangle\rangle = -(15/32\pi)^{1/2}\eta^\pm$ where $\langle\langle \cdots \rangle\rangle \equiv \mathrm{Tr}(\rho \cdots)$.

Three equivalent techniques were used to explore the mean-field phase diagram. These are (1) the Landau expansion,[7] (2) a self-consistent-field method of the type developed by James[8] for solid hydrogen, and (3) analytic formulas. The Landau expansion, in terms of the parameters $\vec{\eta}_i$, $\vec{\mu}_i$, and $(\sigma_i - \sigma_0)$, where σ_0 is the average of σ_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 $V_c/\Gamma \equiv \hat{V}_c$ and $T/\Gamma \equiv \tau$. Five different ordered regions are seen to occur. For large negative crystal fields at low temperature, the stable structure is the two-sub-

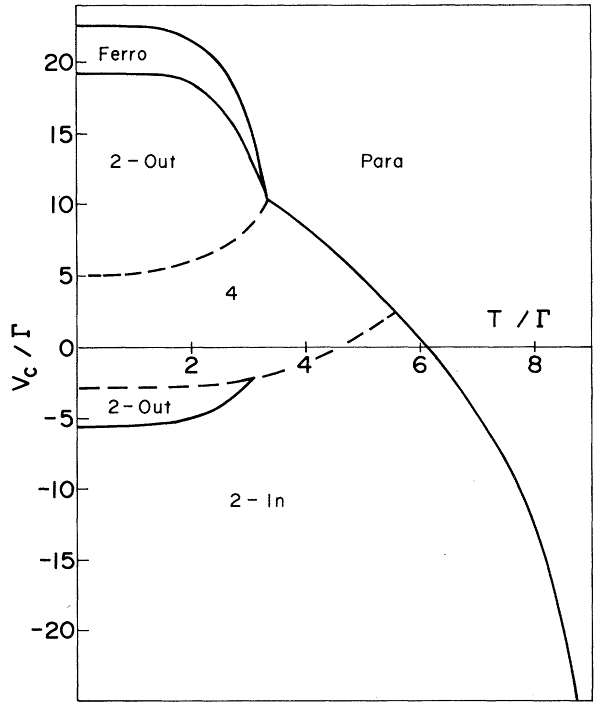

FIG. 1. Phase diagram for hydrogen molecules on a triangular lattice. V_c is the crystal field, T is the temperature, and Γ is the EQQ coupling constant. The various orientational phases, 2-in, 2-out, 4, ferro, and para, are described in the text. Dashed (solid) lines represent first- (second-) order transitions.

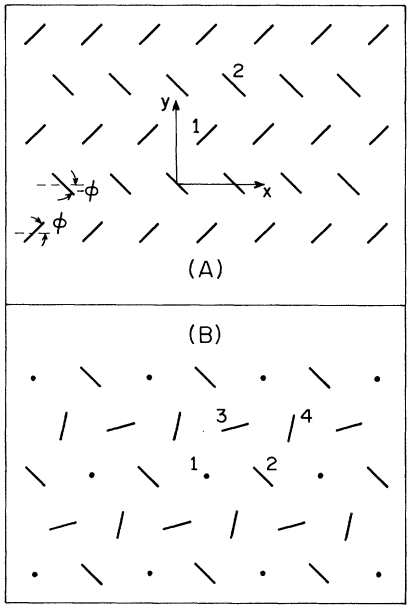

FIG. 2. Possible ordered structures for hydrogen molecules on a triangular net. (a) The projection onto the xy plane of the two-sublattice structure. When the molecular wave functions lie in the plane, φ is 45°. For the "2-out" phases, φ is a function of $\hat{V}_c$. (b) The four-sublattice structure. The average orientation of molecules on sublattice 1 is along z. Molecules on sublattices 2, 3, and 4 are equivalent to each other and lie in the xy plane.

lattice phase shown in Fig. 2(a) with $\varphi = 45°$. In this phase the molecular wave functions are in the plane of the substrate ($\vec{\mu} = 0$), and hence it is labelled "2-in". A similar structure has been proposed by Fuselier, Gillis, and Raich[9] 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 ($|\vec{\mu}| > 0$). As the crystal field is increased (at $\hat{V}_c = -2.80$ for $\tau = 0$) there is a first-order transition from the 2-out phase to a four-sublattice phase (labeled "4").[10] The structure of this phase is illustrated in Fig. 2(b). It is characterized by $\vec{\mu} = 0$ for all sublattices, $\vec{\eta} = 0$ for sublattice 1, and $\sigma_1 \geq \sigma_2 = \sigma_3 = \sigma_4$. If we write $\vec{\eta}_i = (\eta_0 \cos 2\chi_i, \eta_0 \sin 2\chi_i)$ for $i = 2, 3, 4$, then $\chi_3 = \chi_2 + 60°$, $\chi_2 + 120°$ and

$$\cos 2\chi_2 = (\sigma_1 - \sigma_2)/7\eta_0. \tag{6}$$

Close to the pararotational phase $\sigma_1 - \sigma_2$ goes to zero like η_0^2, and hence χ_2 goes to 45° at this boundary.

For $\hat{V}_c > 5.07$ at $\tau = 0$ the 2-out phase reappears. As $\hat{V}_c$ increases, this phase evolves continuously into a one-sublattice ferrorotational ("ferro") phase. [For $\tau = 0$ the angle φ in Fig. 2(a) goes continuously to zero at $\hat{V}_c = 19$.] The ferro phase is characterized by $\vec{\mu} = (\mu_0 \cos\chi, \mu_0 \sin\chi)$, $\vec{\eta} = (\eta_0 \times \cos 2\chi, \eta_0 \sin 2\chi)$ with χ arbitrary and $\sigma > 0$. For $\hat{V}_c > \frac{45}{2}$ there is no cooperative ordering. The only nonzero order parameter is σ_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 $\partial^2 F/\partial q_{i\alpha}\partial q_{j\beta}$ where i and j label molecules and $q_{i\alpha}(\alpha = 1, \ldots, 5)$ is one of the five fluctuating order parameters μ_{ix}, μ_{iy}, η_{ix}, η_{iy}, or $(\sigma_i - \sigma_0)$. The matrix is reduced to block diagonal form by a spatial Fourier transform. For $10.43 < \hat{V}_c < \frac{45}{2}$, the eigenvalue which goes soft at the highest temperature is a $\vec{Q} = 0$ mode for which the associated eigenvector is an arbitrary linear combination of μ_x and μ_y corresponding to $\vec{\mu} = (\mu_0 \cos\chi, \mu_0 \sin\chi)$ which describes the ferro phase. Within mean-field theory the degeneracy with respect to χ persists to all orders in the Landau expansion since the entropy is independent of χ. Near the order-disorder transition η_0 is proportional to μ_0^2.

For $\hat{V}_c < 10.43$ the eigenvectors which first have a zero eigenvalue as τ is lowered are

$$X_A = \sum_i \eta_{iy} \exp(i\vec{Q}_A \cdot \vec{r}_i), \tag{7a}$$

$$X_B = \tfrac{1}{2}\sum_i [\sqrt{3}\eta_{ix} - \eta_{iy}] \exp(i\vec{Q}_B \cdot \vec{r}_i), \tag{7b}$$

$$X_C = \tfrac{1}{2}\sum_i [-\sqrt{3}\eta_{ix} - \eta_{iy}] \exp(i\vec{Q}_C \cdot \vec{r}), \tag{7c}$$

where $\vec{Q}_A = (2\pi/a\sqrt{3})\hat{j}$, $\vec{Q}_B = -(\pi/a)\hat{i} - (\pi/a\sqrt{3})\hat{j}$, $\vec{Q}_C = -\vec{Q}_A - \vec{Q}_B$, and a is the lattice constant. As Landau pointed out,[7] 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 X's. At the temperature at which the zero eigenvalues first develop, the fourth-order term in the free energy has the form

$$F^{(4)} = \alpha(X_A^2 + X_B^2 + X_C^2)^2 + \beta(X_A^2 X_B^2 + X_A^2 X_C^2 + X_B^2 X_C^2), \tag{8}$$

with $\alpha > 0$. For $\hat{V}_c < 2.34$, β 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 $2.34 < V_c < 9.82$, β is negative but $\alpha + \beta/3$ is positive. Then the ordered state is one in which $X_A^2 = X_B^2 + X_C^2$ which corresponds to the four-sublattice state with $\chi_2 = 45°$. [Cf. the discussion below Eq. (6).] As long as $F^{(4)}$ is positive, the transition temperature τ_c is simply determined by the vanishing of the smallest eigenvalue and the transition is continuous. We find that

$$\tau_c = 73(1 - \sigma_0)/12, \tag{9}$$

where σ_0 is determined by Eq. (3).

At $\hat{V}_c{}^T = 9.82$, $\tau_T = 3.50$, $\alpha + \beta/3$ (and hence $F^{(4)}$) passes through zero. For $\hat{V}_3 > \hat{V}_c{}^T$ the transition from the para to the four-sublattice phase is first order. The point $(V_c{}^T, \tau_T)$ is a tricritical point, and the critical exponent for the appearance of the order parameter η_0 at this point is $\frac{1}{4}$ instead of $\frac{1}{2}$ which is its value elsewhere on the second-order line given by Eq. (9). The details of the phase boundaries near the tricritcal point (in particular for $9.82 < \hat{V}_c < 10.43$) 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 $\hat{V}_c$ can be varied in order to map out the phase diagram. At present, NMR experiments[6] seem to show that for D_2 on Grafoil $|\hat{V}_c| \approx 4$, but that there is no phase transition for $\tau \gtrsim 2$. This suggests that a more complete and realistic treatment of this problem, not based on mean-field theory, is essential.[11]

A fuller report of this work is being submitted for publication elsewhere. The authors would like to thank T. C. Lubensky for several comments on the general aspects of this work, P. Kubik and W. N. Hardy for many useful discussions and for allowing us to quote their experimental results prior to publication, and W. Opechowski for helpful comments on the manuscript. This work was supported in part by the National Science Foundation under Grant No. DMR76-21703 and Material Research Laboratory Grant No. DMR76-00678 and by the U. S. Office of Naval Research under Grant No. N00014-76-C-0106.

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Ultrasonic Observation of a Strong Pretransitional Anomaly near a Nematic–Smectic-*A* Phase Transition

S. Bhattacharya[a]
Department of Physics and Astronomy, and Materials Research Center, Northwestern University, Evanston, Illinois 60201

and

B. K. Sarma
Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60201

and

J. B. Ketterson
Department of Physics and Astronomy, and Materials Research Center, Northwestern University, Evanston, Illinois 60201, and Argonne National Laboratory, Argonne, Illinois 60439
(Received 20 March 1978)

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 relaxation of the smectic order parameter, similar to that observed near the λ 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 λ-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]