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Orientational ordering in molecular crystals

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The general phenomenon of orientational ordering in molecular crystals is reviewed. Some of the basic physical questions which arise in connection with orientational ordering in molecular crystals are enumerated and experimental techniques used to address them are described. The description of orientational ordering in terms of order parameters and the resulting form of the Landau expansion is discussed for several typical cases. The relation to the modern theory of critical phenomena and notions of elementary excitations are also discussed. Analogous theories of dynamics are briefly mentioned.

1. Introduction

One of the oldest problems in molecular crystals concerns the ordering transition that occurs when molecules (or molecular groups) cooperatively develop long range orientational order. Perhaps the most celebrated example is solid ortho-hydrogen (o-H_2) in which molecular ordering was discussed as long ago as the 1930's by Pauling [1]. In both solid H_2 and solid N_2 there is a critical temperature (~ 4 K for o-H_2 and ~ 35 K for N_2) above which the orientations of molecules are essentially random and below which long lange orientational order appears discontinuously. In the orientationally ordered phase the fcc lattice of molecules consists of four simple cubic orientational sublattices, within each of which all molecules are preferentially oriented along one particular [111] direction, as listed in Table 1. This structure, which occurs in several contexts, is an interesting [2] cubic space group, $Pa\bar{3}$. The purpose of this paper is to review the phenomenon of orientational ordering. Theoretical descriptions of this ordering and experimental techniques to investigate such systems will be described. Readers wishing further details may usefully refer to a number of reviews [3–8].

Table 1

Data for the two possible realizations of the $Pa\bar{3}$ structure

Site	Molecular orientations along 3-fold axes	
0,0,0	[1,1,1]	[1,1,1]
$a/2,a/2,0$	$[\bar{1},1,1]$	$[1,\bar{1},1]$
$a/2,0,a/2$	$[1,1,\bar{1}]$	$[\bar{1},1,1]$
$0,a/2,a/2$	$[1,\bar{1},1]$	$[1,1,\bar{1}]$

Two equivalent realizations of this structure are shown in columns 2 and 3.

2. Basic phenomena

2.1. Fundamental theoretical concepts

It is useful to enumerate the most fundamental questions which arise in connection with orientational ordering phase transitions. These are

A) What kind of order parameter is required to describe orientational ordering? Clearly, different systems may require different types of order parameters.

B) What is the form of the Landau expansion of the free energy in terms of the aforementioned order parameters? The most obvious consequence of such a theory will be to predict (or explain) whether the transition is continuous or discontinuous.

C) What is the nature of the symmetry operation which takes one orientational ground state into another? In particular, if this symmetry operation is continuous (e.g., uniform rotation in the case of an isotropic ferromagnet), one expects the elementary excitations to be gapless. In contrast, for discrete symmetry (such as for the Ising model) there will be no low energy elementary excitations.

D) In the case of continuous transitions, one would like to determine the universality class of the transition. In particular, this will enable one to say something about the values of the critical exponents that characterize the transition.

E) Coupling between the so-called critical order parameters and the non-critical (or nonordering) fields can lead to interesting effects. In the case of continuous transitions such coupling when suitably increased can lead to a tricritical point where the transition first becomes discontinuous. When the non-critical fields are lattice distortions, anomalies in elastic properties may become significant.

F) The problem of determining what molecular arrangements are consistent with a given crystal symmetry can become quite subtle when the molecular

symmetry is nontrivial (as in the case of the icosahedral molecule, C_{60}).

G) The description of the dynamics at the level of mean field theory is especially interesting when the transition is either continuous or weakly discontinuous. We will not review such calculations [9] here.

2.2. Fundamental experiments

Here we briefly review the major experimental techniques that have been used to address the conceptual issues enumerated in the preceeding subsection.

A) Structure determination via diffraction. To identify a structural or orientational ordering transition the most straightforward technique is that of powder diffraction of either x-rays (using the relatively recently available high flux synchrotron sources) or neutrons. The latter has a slight conceptual advantage in that for nonmagnetic materials neutrons are scattered by nuclei and therefore give direct structural information, whereas x-ray are scattered by electrons and thus, in principle, need a model to yield structural information. (Usually the model assumes an electronic form factor for spherical atoms.) If hundreds of reflections are obtained, quite sensitive structural information can be deduced from the diffraction intensities. Solid hydrogen is a difficult case because it has only a few electrons (to scatter x-rays) and the proton has a large spin-dependent cross section for neutron scattering leading to a large incoherent scattering. The determination of the orientational structure of C_{60} was a particularly interesting case [10–12]. We reproduce the structural analysis of Ref. 11 in Fig. 1.

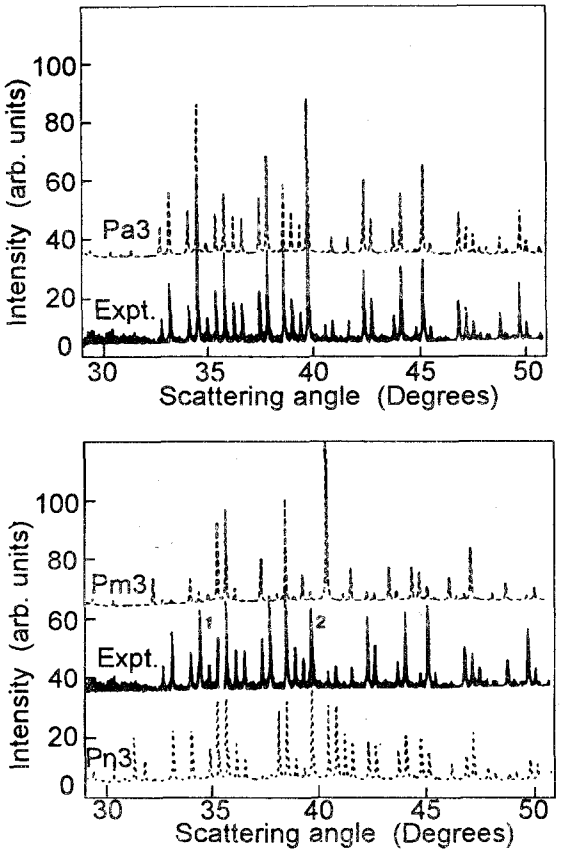

Fig. 1. Comparison of experimental and theoretical powder x-ray diffraction vs scattering angle. Top: comparison with *Pa*3. Bottom: comparison with *Pm*3 and *Pn*3. In the comparison with the *Pm*3 and *Pn*3 structures, the experimental peaks labeled 1 and 2 are truncated, but can be seen on the other panel. As shown in Ref. 11, these are the only space groups which are consistent with a four sublattice structure of oriented icosahedra. (as W. I. F. David has pointed out, for a special value of the setting angle the *Pn*3 structure actually becomes that of space group $Pn\bar{3}m$.) The setting angle was optimized for the *Pa*3 structure to be 21.5° and for the *Pn*3 structure to be 21.6°. The calculations were done by D. E. Cox and the data are from P. A. Heiney et al. The setting angle φ is given in the convention that the two equivalent orientations occur at 0 and 47°. The setting angle is the angle through which the molecules are rotated away from the standard orientation (See Ref. 11).

B) Inelastic scattering. Inelastic light scattering, known as Raman scattering, can provide accurate information on the frequency and sometimes the width of zero wave vector modes. When orientational ordering is accompanied by an enlargement of the unit cell

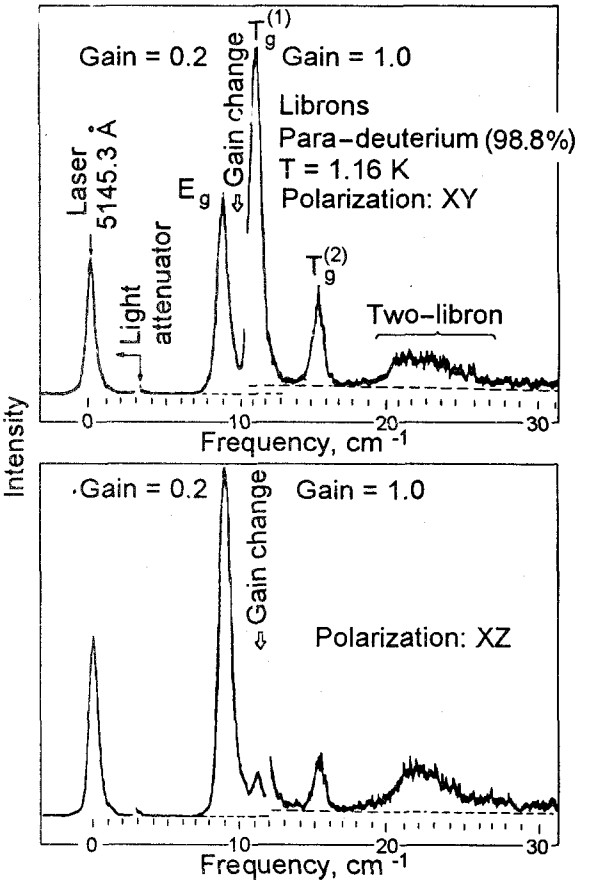

Fig. 2. Raman scattering intensity for para-D_2 as a function of frequency for two different polarizations. The incident and scattered photons propagate along the *z* and *x*-axes, respectively. The polarization gives the coordinate axis of linear polarization (along which the electric field of the photon is aligned).

(i.e. when the ordered phase consists of more than one orientational sublattice), one can observe optical phonons and librational modes. The symmetry properties of the libron modes with respect to polarizations provide a very sensitive way to test any proposed structure. This technique was very useful in the case of solid o-H_2 and Fig. 2 shows the data of Hardy et al. [13] which can be well understood on the basis of anharmonic lattice dynamics [14]. The presence of orientational sublattices can also be detected via infra-red absorption. The absorption intensity of optical modes is then usually proportional to the square of the orientational order parameter [15] (because when the ordering disappears the unit cell reverts to an orientationally disordered Bravais lattice.

C) Nuclear magnetic resonance and relaxation. A common case is that of a molecule which contains more than one nuclear spin with a magnetic moment. Perhaps the best example of this is solid hydrogen in its various isotopic variants. In the orientational disordered phase the nuclear magnetic resonance (NMR) line is very narrow because the orientation fluctuations are effective in completely averaging out the dipolar interactions between the two protons (or two deuterons) in the molecule. But in the ordered phase the orientations of the molecule are preferentially directed along the cubic body diagonals. Then, the dipolar contribution to the local field depends on the angle between the molecular axis and the externally applied magnetic field. In most experiments one deals with a powder sample, in which case one observes the famous Pake line shape first observed in solid o-H_2 by Reif and Purcell [16] and later extensively studied by Meyer and collaborators, whose data [17] we show in Fig. 3.

Observation of the nuclear spin-lattice relaxation time, T_1, also provides information on orientational ordering because, qualitatively speaking, a typical result for T_1 due to orientational fluctuations is of the form [18]

$$T_1^{-1} = \frac{V^2\tau}{1+\omega^2\tau^2}\,, \qquad (1)$$

where τ is the orientational correlation time; ω is the NMR frequency; and V is the magnitude of the fluctuating magnetic field, h. In most diatomics h is the dipole field created by one nucleus which acts on the other nucleus. For C_{60} the field h is due to the chemical shift tensor, whose axes fluctuate in orientation as the molecule rotates. In principle, one could vary ω and determine τ (at any given temperature) by finding the minimum in T_1 (which occurs when $\omega\tau \approx 1$). More usually, one varies the temperature and passes

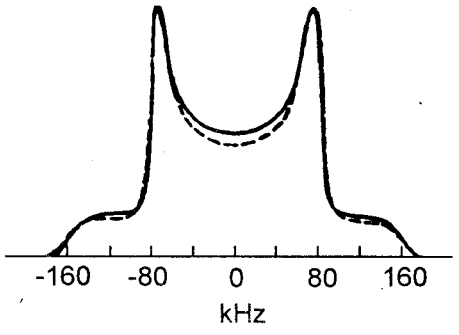

Fig. 3. Solid curve: NMR lineshape of solid 65% o-H_2 at temperature 0.5 K (in the orientationally ordered phase). The dashed curve is the theoretical curve for a powdered sample, taking into account dipolar broadening.

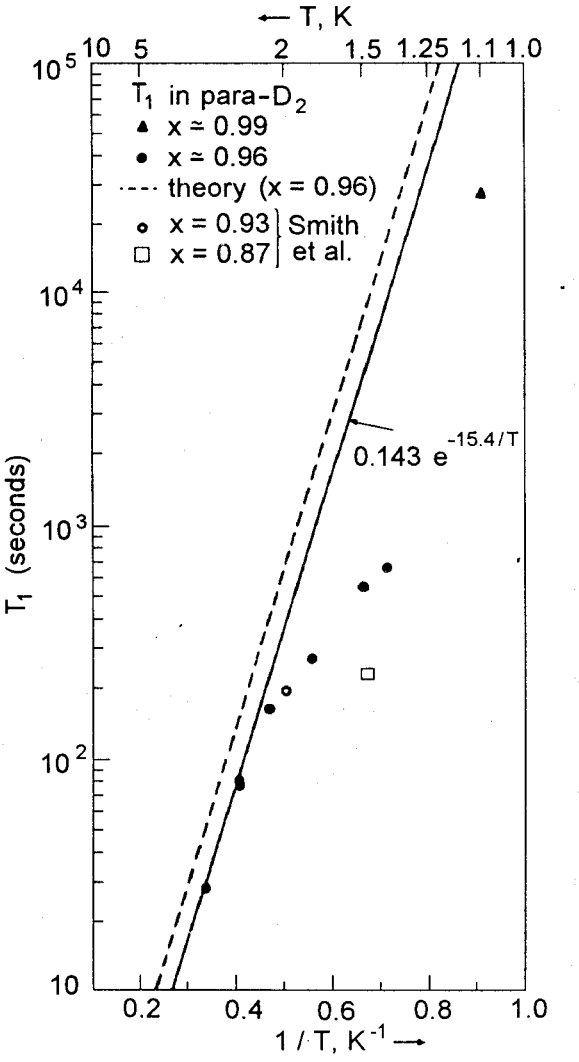

Fig. 4. The nuclear spin-lattice relaxation time of nearly pure ortho-D_2 as a function of temperature. (All data are for the orientationally ordered phase.) The fit to a formula similar to Eq. (2) yields a libron energy, $\Delta E/k_B$, of about 15.4 K. For more precise experimental details, see Ref. 19.

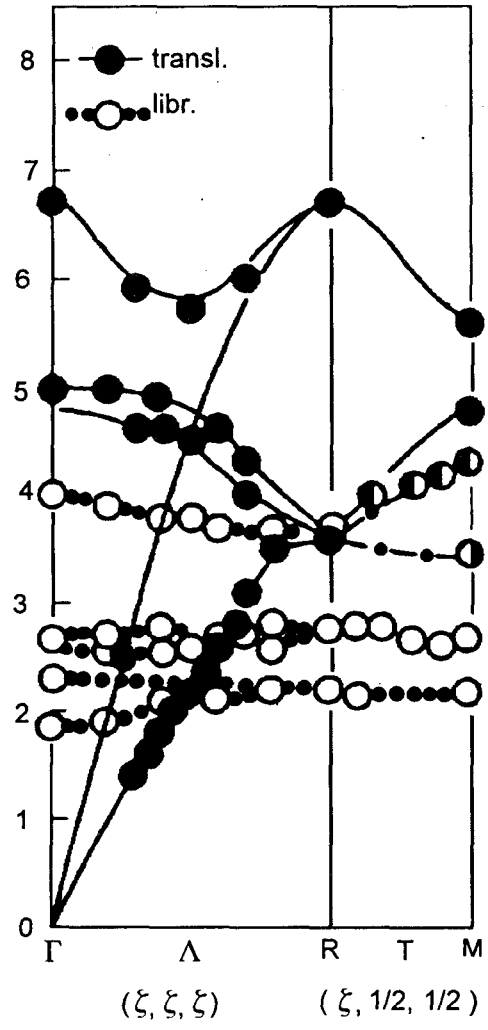

Fig. 5. Libron and phonon dispersion curves for the ordered C_{60} from inelastic neutron scattering (taken from Ref. 22).

from the limit $\omega\tau << 1$ at high temperatures to the reverse case when the orientational ordering has developed. In the orientationally ordered phase, T_1 depends on the number of thermal orientational excitations and therefore shows activated temperature dependence:

$$T_1 \propto \exp(\Delta E/k_B T) , \qquad (2)$$

where ΔE is the energy needed to create a libron and $k_B T$ is the thermal energy. Figure 4 shows data of this type from Hardy and Berlinsky [19].

It is quite common to observe diffusional motion this way, in which case a result like Eq. (2) holds. Data of this type [20] indicate that orientational diffusion in the orientationally ordered phase of C_{60} requires surmounting a barrier of the order of 250 meV between successive minima in the orientational potential. This barrier can also be obtained from studies of how equilibration depends on cooling rate [21].

D) Other techniques. An extremely powerful probe is of course inelastic neutron scattering, when it is experimentally feasible. Obviously, for such experiments it is desirable to have single crystals. There are some experiments of this type for C_{60} [22]. The interpretation of such experiments is not trivial because there are several (12) libron modes and the details of their crossing or near crossing are not easy to follow without taking an extraordinary amount of data. We show data of Pintschovius et al. [22] in Fig. 5.

E) Monte Carlo simulations. We should also mention the «experiment» of theorists, namely Monte Carlo simulations [23]. These have their good and bad sides. The bad one is that they require a knowledge of the intermolecular potential which for complicated molecules like the C_{60} and C_{70} fullerenes is not known in great detail. The good one is that numerical work, if done in great detail, avoids the limitations of the analytic approximations. Note that for C_{70} neither experiment [24] nor simulations have really determined the low temperature ordered phase. In the case of experiment the complicated monoclinic structure will probably require single crystal diffraction data. In the case of simulations the complicated structure obviously depends sensitively on the presently unknown details of the orientational potential.

3. Orientational order parameters

In this Section we turn to the description of orientational ordering in molecular crystals using order parameters. The simplest way to introduce an order parameter is through a trial free energy. What one invokes is an analog of the variational principle for quantum wave functions, but here the variational idea is applied to the free energy. This principle says that the true free energy is the minimum (with respect to variations of the density matrix ρ) of

$$F_{\text{trial}} = \text{Tr}\,[\rho H + T\rho \ln \rho] , \qquad (3)$$

where ρ, the trial density matrix, is normalized by $\text{Tr}\,\rho = 1$, we set $k_B = 1$, and H is the Hamiltonian of the system. Mean field theory is obtained by looking for the best trial density matrix which is a product of single particle density matrices. That is, we set

$$\rho = \prod_i \rho_i , \qquad (4)$$

in which case

$$F_{\text{trial}} = \frac{1}{2}\sum_{i,j} \text{Tr}\,\rho_i \rho_j H_{ij} + T\sum_i \text{Tr}\,\rho_i \ln \rho_i . \qquad (5)$$

Here we assumed that the Hamiltonian is a sum of pairwise interactions:

$$H = \frac{1}{2}\sum_{ij} H_{ij} \,. \tag{6}$$

In Eq. (5) one may interpret the first term as the energy and the second term as $-TS$, the entropic contribution to the free energy. With such a density matrix, each molecule finds the optimal state in the average field of its neighbors. No correlations between the orientations of different molecules are contained in this ansatz.

3.1. Wavevector selection

To get the flavor of this approach, consider an Ising model whose Hamiltonian is

$$H = -J \sum_{\langle i,j\rangle} s_i s_j \,, \tag{7}$$

where each s_i assumes the values $+1$ and -1 and $\langle i,j\rangle$ indicates a sum over pairs of nearest neighbors on (say) a simple cubic lattice. Since experience tells us that we can expect spin ordering in this model, we take a trial density matrix for the i-th site in the form

$$\rho_i = \frac{1}{2}[1 + \sigma_i s_i] \,. \tag{8}$$

We see that

$$\langle s_i \rangle \equiv \mathrm{Tr}\, s_i \rho_i = \sigma_i \,, \tag{9}$$

so that the order parameter σ_i is the thermal averaged value of the spin at site i. Now we evaluate the trial energy as

$$F_{\text{trial}} = -\frac{1}{2} J \sum_{i,j} \sigma_i \sigma_j - T \sum_i S(\sigma_i) \,, \tag{10}$$

where the entropy $S(\sigma)$ is given by

$$-S(\sigma) = \left[\frac{1+\sigma}{2}\ln\frac{1+\sigma}{2} + \frac{1-\sigma}{2}\ln\frac{1-\sigma}{2}\right] \sim$$

$$\sim \frac{1}{2}\sigma^2 + O(\sigma^4) \,. \tag{11}$$

To minimize the free energy, it is convenient to simply check the stability of the term in the trial free energy which is quadratic in the order parameter. To do that we introduce the Fourier transformed order parameter:

$$\sigma(\mathbf{q}) = \frac{1}{\sqrt{N}} \sum_i \sigma_i \exp(i\mathbf{q}\mathbf{r}_i) \,, \tag{12}$$

where $\mathbf{r}_i$ is the position of the i-th spin (or later molecule); $\mathbf{q}$ is the wave vector, and N is the total number of sites in the system. Then up to quadratic order in $\sigma(\mathbf{q})$ one has

$$F_{\text{trial}} = \frac{1}{2}\sum_{\mathbf{q}} [-J\gamma(\mathbf{q}) + T]\,\sigma(\mathbf{q})\sigma(-\mathbf{q}) \equiv$$

$$\equiv \frac{1}{2}\sum_{\mathbf{q}} \chi^{-1}(\mathbf{q})\sigma(\mathbf{q})\sigma(-\mathbf{q}) \,. \tag{13}$$

The last line is the definition of the susceptibility $\chi(\mathbf{q})$. Here $\gamma(\mathbf{q})$ is the form factor for the interaction:

$$\gamma(\mathbf{q}) = \sum_{\vec{\delta}} \exp(i\mathbf{q}\vec{\delta}) \,, \tag{14}$$

where $\vec{\delta}$ is now summed over all nearest nieghbor vectors. For a simple cubic lattice,

$$\gamma(\mathbf{q}) = 2\cos(q_x a) + 2\cos(q_y a) + 2\cos(q_z a) \,,$$

where a is the lattice constant.

Now we must minimize F_{trial} with respect to the σ's. This minimization will yield the actual thermal equilibrium value of the order parameters, of course, within the approximation of the mean field theory. First suppose that J is positive, so that we are dealing with a ferromagnet. We refer to Fig. 6, where we give a plot of χ^{-1} versus $\mathbf{q}$ for two temperatures.

The plot of $\chi^{-1}(\mathbf{q})$ indicates that for high temperatures this quantity is always positive. Thus, at high temperatures the minimal free energy occurs when $\sigma(\mathbf{q}) = 0$ for all $\mathbf{q}$. As the temperature is lowered, the whole curve shifts downward and when $T = J\gamma(q=0) = 6J$, then $\chi(\mathbf{q}=0)$ becomes zero. The vanishing of the coefficient of the quadratic term $\sigma^2(q=0)$ indicates that the disordered phase is unstable with respect to the formation of order for $q = 0$. This means what we knew all along: the instability of the disordered phase occurs with respect to a zero wave vector condensation. That is so because J was positive and we were dealing with a ferromagnet.

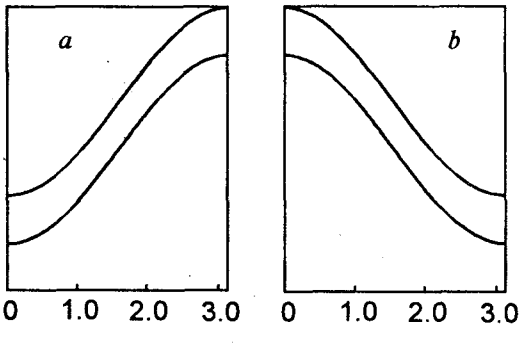

Fig. 6. Plot of χ^{-1} versus $a\,\mathbf{q}$ for positive J (*a*) and negative J (*b*). Here the upper curve is for $T = T_1$ and lower curve for $T = T_2$ with $T_1 > T_2$.

When J is negative, the curve has its instability at $q = \pi/a$, as indicated in Fig. 6. This is obviously the correct result for an antiferromagnet. The lesson is that if we introduce position-dependent order parameters, the q dependence of the inverse susceptibility will tell us which wave vector becomes unstable. For a model with competing interactions, say, having nearest and next nearest neighbor interactions, both antiferromagnetic, the instability can come at an incommensurate value of q determined by the ratio between the competing interactions.

In summary, by introducing position-dependent order parameters, we allow mean field theory to tell us the wave vector at which order will occur. This is what one might call «wavevector selection». This principle is an essential one when there is a possibility of sublattice formation and we do not know beforehand what the sublattice structure actually is. In general there are three cases. In the first case the instability comes at zero wave vector. (This point is usually called the Γ point of the zone, to use group theoretical labelling.) In the second case, the instability comes at a wave vector which is a special high-symmetry point in reciprocal space. (In the case of the antiferromagnet, the instability occurs at the corner of the first Brillouin zone, and does not depend in detail on the exact values of the second-neighbor interaction.) The third case is one which we will not consider in detail here. In this case, the instability comes at an incommensurate wavevector whose exact value will depend on the coupling constants. In the first two cases the ordered phase is described by a relatively small unit cell. In the third case, the incommensurate wavevector will depend on all the parameters, including the temperature. In cases two and three, it is important to realize that if there is an instability at a wavevector $\mathbf{q}_0$, there is an equivalent instability at all wave vectors equivalent by symmetry to $\mathbf{q}_0$. (In the case of the antiferromagnet, the set of equivalent wave vectors contains only a single member.)

For a given sublattice structure, it is easy to determine the wave vectors needed to build up the structure. Consider, for instance, the $Pa\bar{3}$ structure, described in Table 1. Take linear combinations of the waves having wavevectors 0, $\mathbf{Q}_x \equiv (2\pi/a)\hat{i}$, $\mathbf{Q}_y \equiv (2\pi/a)\hat{j}$, $\mathbf{Q}_z \equiv (2\pi/a)\hat{k}$, where $\hat{i}$, $\hat{j}$, and $\hat{k}$ are unit vectors along the x, y and z coordinate directions, respectively. Let the respective amplitudes be A_0, A_x, A_y, and A_z. Then the amplitude on the sublattice at the origin is $A_0 + A_x + A_y + A_z$, the amplitude on the sublattice at $(a/2, a/2, 0)$ is $A_0 - A_x - A_y + A_z$, and so forth. By adjusting these amplitudes A_i, we have arbitrary amplitudes on each of the sublattices. That implies that a four-sublattice order requires condensation at these four wave vectors. However, we see that if we had an instability only at zero wave vector, we would have a uniform system. So, sublattice formation requires critical fluctuations at the wavevectors $\mathbf{Q}_x$, $\mathbf{Q}_y$, $\mathbf{Q}_z$. As we will see in a moment, the fluctuations at zero wave vector are noncritical. They may be viewed as nonordering order parameter which are induced by the critical order parameters.

3.2. Orientational order parameters

Finally, we discuss the order parameters which describe orientational ordering of a single molecule. Consider a diatomic molecule like N_2. (In this paper «diatomic» always means «homonuclear diatomic».) In general its density matrix will be of the form

$$\rho(\theta, \varphi) = \frac{1}{4\pi}\left[1 + \sum_{L,M} C_L^M Y_L^M(\theta, \varphi)^*\right], \quad (15)$$

where we have introduced a full set of order parameters C_L^M. (For such a classical situation, «trace» should be interpreted to mean «integration over all angular coordinates».) Since rotating the molecule through 180 degrees leaves it unchanged, C_L^M must vanish for odd L. Although an accurate description would require keeping higher C_L^M's, we can get a qualitatively correct theory, i.e. a theory that at least has the correct symmetry, by keeping only the terms with $L = 2$. In general, we should keep all $L = 2$ terms. In many contexts one expects the probability distribution to be uniaxial, i.e. to have cylindrical symmetry about a preferred axis. However, it does not hurt to allow for the possibility of biaxiality. (Biaxiality means that, say, the maximal probability would be to point along the z-axis, but the x and y-axes would have lesser, but unequal probabilities.) To interpret the C_L^M's we note that (for $L \neq 0$)

$$\langle Y_L^M \rangle = \int d\Omega\, Y_L^M(\theta, \varphi)\rho(\theta, \varphi) = C_L^M. \quad (16)$$

Thus, the ordering of a diatomic molecule is described by the five components of a second rank tensor, $\langle Y_2^M \rangle$. One can see that in general five parameters are required: if the probability distribution is biaxial, it takes three Euler angles to specify the coordinate system for the principal axes of the distribution. Given the principal axes, it takes two order parameters to specify the three probabilities for a biaxial distribution (in which the three probabilities add up to unity). Alternatively, and perhaps, more intutively, instead of the C_L^M's one can choose as the order parameter the symmetric traceless second-rank tensor Q, defined by

$$Q_{\alpha,\beta} \equiv \langle n_\alpha n_\beta - \tfrac{1}{3}\delta_{\alpha,\beta} \rangle, \quad (17)$$

where δ is the Kronecker delta, α and β label Cartesian coordinates, and $\hat{n}$ is a unit vector along the molecular axis. This order parameter is the one usually chosen to describe liquid crystals. If the molecule is preferentially aligned along, say, the x-axis in a uniaxial distribution, then

$$Q_{yy} = Q_{zz} = -Q_{xx}/2 < 0 \; ; \qquad Q_{xy} = Q_{xz} = Q_{yz} = 0 \; . \tag{18}$$

On the other hand, if the molecules preferentially point along one of the crystal [111] directions (which is a trigonal axis), then

$$Q_{xx} = Q_{yy} = Q_{zz} = 0 \; ; \qquad Q_{xy}^2 = Q_{xz}^2 = Q_{yz}^2 \; , \tag{19}$$

where the signs of the off-diagonal Q's depend on which [111] direction is associated with the order. Here we see the simplest case of the principle that all order parameters of the type $\langle Y_L^M(\theta, \varphi)\rangle$ will vanish identically if the molecule has sufficient symmetry that

$$\sum_a r_a^L Y_L^M(\theta_a, \varphi_a) = 0 \; , \tag{20}$$

where the sum, is over all atoms in the molecule. The simplest example of this idea is that a homonuclear diatomic molecule cannot have a dipole moment.

How are we to describe molecules that have even higher symmetry than diatomics as, for instance, C_{60} molecules? A convenient rule is the following: take the most general interaction between molecules I and J of the form

$$V(I, J) = \sum_{i \in I; j \in J} \Phi(\mathbf{R} + \mathbf{r}_i - \mathbf{r}_j) \; , \tag{21}$$

where $i \in I$ denotes atom i in molecule I. Here $\mathbf{R}$ is the vector displacement between molecules I and J and $\mathbf{r}_i$ ($\mathbf{r}_j$) is the location of atom i (j) relative to the center of gravity of molecule I (J). Now expand the atom-atom potential Φ in a multipole moment series. Take as dominant order parameters

$$\sigma_L^M(I) = \sum_{i \in I} r_i^L Y_L^M(\theta_i, \varphi_i) \; , \tag{22}$$

for the lowest value of L which can be nonzero for the given symmetry of the molecule [25]. These quantities, analogs of the mass multipole moments, are implicit functions of the three Euler angles which would be needed to specify the orientation of the molecule. As mentioned before, for a full description one should take *all* multipole moments allowed by the molecular symmetry. However, the correct symmetry of the Landau expansion can be obtained by the simplified procedure outlined here. In actual calculation, for instance for C_{60}, it is convenient to take symmetry adapted linear combinations of the order parameters given here. To see that this results in a simplification consider the following situation. Suppose we have a diatomic molecule placed on a site having a threefold (trigonal) axis. Then biaxiality is impossible: it is not consistent with trigonal site symmetry. So in the order parameter description we should only allow order parameters $\langle Y_2^M\rangle$ consistent with the local site symmetry. In principle, even if we allowed such order parameters to be nonzero, they would turn out to be zero, consistent with the local site symmetry. One should also point out that although taking the lowest L value for order parameters $\langle Y_L^M\rangle$ does give the correct symmetry of the Landau free energy, it may not be adequate for quantitative calculations, as has been shown for the case of C_{60} [26]. Finally, this discussion also implicitly assumes that the molecule is not distorted when placed at a particular site in the crystal. That, of course, is not strictly true. The molecule will suffer a distortion consistent with the local symmetry. Thus, when the icosahedral C_{60} molecule is put into the site in the $Pa\bar{3}$ structure which has S_6 (three fold with inversion) symmetry, we can expect a corresponding uniaxial distortion, such that $\langle Y_2^0\rangle$ will be nonzero, where the z axis is taken to coincide with the local trigonal axis. Such distortions will be small to the extent that the solid is really a molecular solid in which the intramolecular interactions dominate the intermolecular ones. Thus, strictly speaking, the C_{60} molecule will have a quadrupolar distortion and it will have a nonzero anisotropy of its polarizability tensor. (Such an anisotropy would not be permitted for a true icosahedron.) Physically, this anisotropy could give rise to a nonzero intensity for the Raman activity of the libron modes [27].

3.3. Examples

Monolayers of diatomics. In this subsection we now give some examples of the use of mean field theory to describe orientation ordering. One simple case concerns the ordering of N_2 or H_2 molecules on a graphite substrate. We focus on the registered phase in which the molecules form a monolayer consisting of a triangular lattice. We follow Refs. 28 and 29. For o-H_2 molecules, the fact that their orientational ground state has angular momentum $J = 1$, dictates that the averages $\langle Y_L^M\rangle$ with $L > 2$ vanish. Thus for H_2, and also as an approximation for N_2, one may truncate Eq. (15) to contain only the terms with $L = 2$. It is assumed that the molecules interact via quadrupolar interactions between nearest neighbors on a triangular lattice and that there is a potential

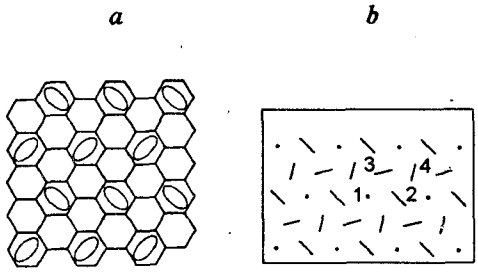

Fig. 7. The HB phase (*a*). The axis of each molecule makes an angle of 45 degrees with respect to the horizontal (x) axis. The PW phase (*b*). In this phase molecule 1 tends to be perpendicular to the substrate and has no ordering in the plane of the substrate. Just below the ordering temperature, the other three molecules in the unit cell each assume one of the HB orientations. As the temperature is decreased the PW angles will vary.

$$V_c = -(5/6)V_0 \sum_i (3\cos^2\theta_i - 1)$$

due to the interaction of each molecule with the substrate. The phase diagram of this model is a rather rich one, but the most important phases are the so-called «herringbone» (HB) and «pin-wheel» (PW) phases, shown in Fig. 7. To describe the nature of the order parameter in these two phases, it is convenient to take the z-axis to be perpendicular to the graphite plane. For these two phases the order parameters which are nonzero are $\sigma_2^{\pm 2}(i)$ and $\sigma_2^0(i)$. To avoid the cumbersome prefactors of spherical harmonics, we introduce the order parameters $u_1(i) \equiv \eta_x(i)$, $u_2(i) \equiv \eta_y(i)$, and $u_3(i) \equiv \sigma(i) - \sigma_{eq}(i)$ by

$$\langle \sin^2\theta(i) \exp(\pm 2i\varphi(i)) \rangle \equiv \eta_x(i) \pm i\eta_y(i) \qquad (23)$$

and

$$\langle 3\cos^2\theta(i) - 1 \rangle / 2 \equiv \sigma(i) \ . \qquad (24)$$

To see the significance of these order parameters, note that if $\sigma(i) = 1$, then the molecule is oriented out of the plane, whereas if $\sigma(i) = -1/2$, the molecule is oriented in the plane. Intermediate values indicate intermediate ordering. If the molecule is not oriented precisely out of the plane, then the molecule will assume a preferential orientation within the $x-y$ plane along an axis which makes an angle ψ with the crystal x-axis, where

$$\tan 2\psi = \eta_y(i)/\eta_x(i) \ . \qquad (25)$$

Notice that whatever η_α is, ψ and $\psi + 180°$ are equivalent, as they must be for a diatomic molecule.

One must now evaluate the trial free energy according to Eq. (3). When $\eta_\alpha(i) = 0$, the equilibrium value of σ_i, is given by

$$\frac{1 - \sigma_{eq}}{1 + 2\sigma_{eq}} = \exp\left[-(V_0 - 27\,\Gamma\sigma_0/2)/T\right] \ , \qquad (26)$$

where Γ is the coupling constant which scales the quadrupolar interactions. Notice that even at very high temperatures this order parameter is nonzero. This order parameter express the average alignment, either perpendicular or parallel to the substrate, depending on the sign of V_0. Clearly, the nonzero value of this order parameter does not indicate cooperative ordering. Now we look at quadratic fluctuations relative to this equilibrium in the substrate «crystal field». As mentioned, the important fluctuations are those involving the quantities $u_\alpha(i)$ for $\alpha = 1, 2, 3$. Because the equilibrium value of $\sigma(i)$ is determined so as to minimize the free energy when $\eta_\alpha(i) = 0$, there are no terms linear in any of the order parameters. Therefore the free energy at quadratic order in the u's is of the form

$$F = F(\sigma_{eq}) + \frac{1}{2}\sum_{\mathbf{q}} \sum_{\alpha\beta} u_\alpha(\mathbf{q})[\chi^{-1}(\mathbf{q})]_{\alpha\beta} u_\beta(\mathbf{q}) \ , \qquad (27)$$

where now the susceptibility is a matrix, because the order parameter is no longer a scalar, as for the Ising model, but has five components (or in fact only the three u's that matter) in the present case. It is known that for quadrupolar interactions, the molecules prefer to be approximately perpendicular to one another. This explains why it is found that the eigenvalue of χ^{-1} which first becomes zero is the one associated with the wavevector $\mathbf{Q}_1 = q_0 \hat{j}$, where the x axis is horizontal in Fig. 7 and $q_0 = 2\pi/(a\sqrt{3})$, where a is the separation between molecules. Of course, we will have equivalent instabilities at the equivalent wavevectors $\mathbf{Q}_2$ and $\mathbf{Q}_3$, where

$$\mathbf{Q}_2 = q_0(\sqrt{3}\,\hat{i} - \hat{j})/2 \qquad (28)$$

and

$$\mathbf{Q}_3 = q_0(-\sqrt{3}\,\hat{i} - \hat{j})/2 \ . \qquad (29)$$

Although we have discovered which wavevectors are selected, the type of order is not yet apparent. What we need to know is the nature of the eigenvector associated with the eigenvalue of the stability matrix χ^{-1} which first becomes zero. For $\mathbf{Q}_1$ the eigenvalue is $u_2 = \eta_y$. What kind of order does the molecule have if $\eta_x = 0$ but η_y is nonzero? As we have said, if η_y positive such a molecule is aligned along an axis whose orientation is given by Eq. (25). In this case $\varphi = 45°$. But for the wavevector $\mathbf{Q}_1$, as we move from one row parallel to x to the next such row, the wavevector dependence causes the order parameter to oscillate in sign. This oscillation causes the angle ψ of each row to

oscillate between the two values +45° and −45°. Such a structure is obviously the HB structure. On can perform a similar analysis for the other wavevectors Q_2 and Q_3. By symmetry we know what we will get: these instabilities correspond to the development of order in a phase in which the rows and orientations are rotated through 120° from the one shown in Fig. 7.

If we call these critical fluctuation coordinates y_1 (associated with Q_1) and so forth, then the free energy is of the form

$$F = F(\sigma_{eq}) + \frac{1}{2}(T - T_0)\sum_{\alpha=1}^{3} y_\alpha^2 +$$

$$+ A(y_1^2 + y_2^2 + y_3^2)^2 + B(y_1^2 y_2^2 + y_2^2 y_3^2 + y_1^2 y_3^2) + \ldots , \quad (30)$$

where the reader is referred to the original reference for an explanation of the symmetry of the higher-than-quadratic terms. If we stopped here, we would conclude that, since A and B are positive, the transition is always continuous, at least within mean field theory. However, it turns out that these critical degrees of freedom have nonlinear coupling to other noncritical degrees of freedom. Such coupling must obey all the symmetries of the system, and in particular, will have to conserve wavevector. If z_i is such a noncritical fluctuation, there are interaction terms of the type

$$y_\alpha y_\beta z_\gamma \cdot \quad (31)$$

Because the z's are noncritical, their susceptibility is finite and therefore their quadratic free energy is definitely stable. So the part of the free energy depending on z will be of the form

$$\delta F = \frac{1}{2}\sum_\alpha \chi_{z\alpha}^{-1} z_\alpha^2 + \sum_{\alpha\beta\gamma} y_\alpha y_\beta z_\gamma \cdot \quad (32)$$

(This equation is a bit schematic — for details see the original reference.) Now, minimizing with respect to z one sees that $z \sim y^2$ and this term gives rise to an additional fourth-order interaction in terms of the critical order parameters y_α. In other words, the coupling to noncritical degrees of freedom leads to a renormalization of the parameters A and B in Eq. (30) so that they decrease remaining positive. In fact, now it is found that for appropriate values of the parameters there is a critical point at which B changes sign, and then eventually one where the entire fourth-order term changes sign, leading to a first order transition at a tricritical point.

It is amusing to see what happens when the anisotropy B in Eq. (30) changes sign. When B is positive, the directions in order parameter (y) space for which only a single y is nonzero are favored. In contrast, when B is negative, it is favorable for all three y to simultaneously condense. That means that the system condenses into a superposition of three HB phases. By suitably adding the amplitudes in the local order parameters $\eta_\alpha(i)$, one can show that a 2×2 structure forms in which one of the four molecules in the unit cell has out of plane ordering. In fact, this superposition leads to the PW structure.

One can also deduce other properties of the ordered state. Because the orientations of the molecules cannot be continuously modified within the HB or PW phases, we expect that librational waves will have a nonzero energy gap, even at zero wavevector. One might want to consider how domains of the ordered phase might arrange themselves. For the HB phase, one sees that there are six equivalent ground states: there are three choices of wavevectors, and for each wavevectors we may adjust the phase of the ordering so as to tell whether a given row is «up» or «down».

This case does illustrate the fact that wavevector selection tells you what the allowed sizes of the unit cell are. But to get detailed information on the nature of the orientational ordering, one must keep track of the components of Y_L^M which are associated with the instability.

Fullerene C_{70}. In this subsection we review the mean field treatment of the orientational ordering in solid C_{70} as given by Sachidanandam and Harris [30] and more completely by Callebaut and Michel [31]. We start with the observation that the C_{70} molecule is essentially an ellipsoid of revolution. In the orientationally disordered phase the crystal structure is very similar to that of C_{60} : namely the molecules form an fcc lattice with no long-range orientational correlations. The orientational ordering transition we seek to describe here is that in which the ellipsoids pack with their long axis parallel to one of the cubic [111] directions. Of course, once ordering of this type occurs, there will be an associated lattice distortion, so that the actual orientationally ordered structure is trigonal. Thus we must consider both orientational and strain degrees of freedom [30]. In this phase, the molecule still can spin about their long axis. At somewhat lower temperature there is another phase transition below which spinning stops and complete order is achieved [24]. However, the structure of this phase is not currently known with any precision. We will only consider the higher temperature transition which involves alignment of ellipsoids.

As we mentioned before, if these ellipsoidal molecules favor alignment along a [111] direction we can characterize their order parameter, $Q_{\alpha\beta}$, by

$$Q_{\alpha,\alpha} = 0 \quad (33)$$

and for $\alpha \neq \beta$:

$$Q_{\alpha\beta} = Q\varepsilon_\alpha \varepsilon_\beta \ , \qquad (34)$$

where Q describes the magnitude of the ordering and the epsilons $|\hat{\varepsilon}_\alpha| = 1$) indicate which of the [111] directions is the axis of alignment. (There are only four inequivalent choices for the ε's because changing the signs of all of them does not change the physical state.)

From the above discussion we conclude that the ordering transition is the one in which only the order parameters of Eq. (34) are important. Instead of constructing the free energy from an assumed Hamiltonian, we can construct its form, merely by requiring that it have the correct symmetry. The fluctuations in the disordered phase must be governed by a free energy whose symmetry is that of the fcc lattice. Thereby we conclude that the free energy (which we denote by F_Q to indicate that this is the part of the free energy that depends only on the orientational degrees of freedom) is of the form

$$F_Q = \frac{1}{2}(T - T_0)[Q_{xy}^2 + Q_{yz}^2 + Q_{xz}^2] + wQ_{xy}\,Q_{yz}\,Q_{xz} + \\ + v\,[Q_{xy}^2 + Q_{yz}^2 + Q_{xz}^2]^2 + u\,[Q_{xy}^4 + Q_{yz}^4 + Q_{xz}^4] + \ldots . \qquad (35)$$

Note that in contrast to the previous example, we have a third order term in the free energy. This guarantees that the transition will be discontinuous. We see that indeed the free energy of Eq. (35) can condense into four equivalent minima in each of which the Q's have the same magnitude but the signs are chosen as in Eq. (34).

Next we wish to include the elastic degrees of freedom. For this purpose we introduce strains in the usual way. If u(r) is the local displacement u at position r, we have

$$\varepsilon_{\alpha\beta} = \frac{1}{2}\left[\frac{\partial u_\alpha}{\partial r_\beta} + \frac{\partial u_\beta}{\partial r_\alpha}\right] . \qquad (36)$$

Note that $\varepsilon_{\alpha\alpha}$ indicates an elongation in the α direction, whereas $\varepsilon_{\alpha\beta}$ $(\alpha \neq \beta)$ is a shear which we may visualize as a distortion in which a square in the α–β plane becomes a rhombus. One may also note that the combination of three equal shears $\varepsilon_{\alpha\beta}$ corresponds to pulling the unit cube along a body diagonal. (It is obvious that this last distortion is the one we hope to encounter.) It is now necessary to formulate an analog of Eq. (32) where the strains play the role of the noncriticial fluctuations. The part of the free energy (per unit volume) that depends only on the strains assumes a form familiar for a cubic crystal, namely:

$$F_{\rm el} = \frac{1}{2}c_{11}\,[\varepsilon_{xx}^2 + \varepsilon_{yy}^2 + \varepsilon_{zz}^2] + \\ + c_{12}\,[\varepsilon_{xx}\,\varepsilon_{yy} + \varepsilon_{yy}\,\varepsilon_{zz} + \varepsilon_{xx}\,\varepsilon_{zz}] + \\ + \frac{1}{2}c_{44}\,[\varepsilon_{xy}^2 + \varepsilon_{yz}^2 + \varepsilon_{xz}^2] . \qquad (37)$$

Likewise the free energy due to the coupling between the orientational and elastic degrees of freedom must (by symmetry) be of the form

$$F_{\rm inter} = -E[Q_{xy}\,\varepsilon_{xy} + Q_{yz}\,\varepsilon_{yz} + Q_{xz}\,\varepsilon_{xz}] + \\ + G[Q_{xy}^2 + Q_{yz}^2 + Q_{xz}^2][\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}] . \qquad (38)$$

Now we have to minimize the total free energy, which is the sum of F_Q, $F_{\rm el}$, and $F_{\rm inter}$. To see what the result is, let us assume that Q assumes the value which minimizes the total free energy and which is not much different from that value of Q which minimizes F_Q. So doing we find that

$$\frac{\varepsilon_{xy}}{Q_{xy}} = \frac{\varepsilon_{yz}}{Q_{yz}} = \frac{\varepsilon_{xz}}{Q_{xz}} . \qquad (39)$$

This result shows that the distortion is correctly correlated with the axis along which ordering occurs.

IV. Summary

In this paper I have tried to illustrate some general feature of mean field theory. Similar work is described elsewhere [32].

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