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Mean-Field Theory for C$_{70}$

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Abstract

Orientational ordering transitions in C$_{70}$ are studied by constructing a Landau free energy in terms of order parameters describing long-range orientational order. This theory predicts that the transition from the orientationally disordered state into a partially ordered state, where the long axes of the molecules are parallel to one another, is discontinuous with an elastic distortion. Order parameters describing the lower temperature transition, where spinning about the long axis becomes hindered, are also discussed.

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Mean-field theory for C_{70}

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Orientational ordering transitions in C_{70} are studied by constructing a Landau free energy in terms of order parameters describing long-range orientational order. This theory predicts that the transition from the orientationally disordered state into a partially ordered state, where the long axes of the molecules are parallel to one another, is discontinuous with an elastic distortion. Order parameters describing the lower temperature transition, where spinning about the long axis becomes hindered, are also discussed.

I. INTRODUCTION

In two very interesting papers Vaughan et al.[1,2] studied the structure of solid C_{70} at various temperatures using x-ray scattering from powder samples. They determined that at high temperatures the lattice is face centered cubic (fcc), belonging to the space group $Fm\bar{3}m$.[3] In this phase each site is occupied by a crystallographically equivalent orientationally disordered molecule. As the temperature is lowered through $T_> \approx 340$ K, the lattice becomes rhombohedral with all molecules still spinning about their fivefold axis but with all fivefold axes aligned parallel to one another along one of the (1,1,1) directions of the original cubic lattice.[4] The transition from the $Fm\bar{3}m$ to this $R\bar{3}m$ structure is accompanied by a trigonal lattice distortion. At a lower temperature $T_< \approx 280$ K, the lattice undergoes another transition and becomes monoclinic,[2,4] at which point it is believed that the molecules no longer spin freely. The existence of these phase transitions and the evidence that they are first order have also been obtained from specific heat and differential-scanning-calorimetry measurements.[5] The prupose of this paper is to analyze the symmetry of these transitions and to thereby predict the relationship between orientational ordering and elastic distortion.

Molecular dynamics simulations have been carried out[6] and with proper parameters they give results in qualitative agreement with the experimental results for the $T_>$ transition. A disadvantage of this method is that the results are model dependent, as can be seen from the fact that it does not reproduce the observed[2] structure for $T < T_<$. In contrast, mean-field theory provides qualitatively accurate model-independent information based only on symmetry considerations. We develop a Landau expansion[7] for the transition at $T_>$. Since this expansion contains terms which are third order in the order parameter, it predicts that this transition is a first order one. For temperature $T_> > T > T_<$ the molecules have their long axes aligned parallel to one another but are still spinning about this axis. To describe the transition at $T_<$ it is necessary to introduce order parameters which

become nonzero when the molecules can no longer spin freely about their long axis. Although the symmetry of the phase for $T < T_<$ is not yet known and therefore we cannot yet treat this transition by a Landau theory, we are able to identify the order parameters which must characterize this transition.

This paper is organized as follows. We first discuss the molecular geometry and the models that have been proposed for the different phases on the basis of x-ray scattering data. We then determine order parameters for the $T > T_>$ phase and form the Landau free energy using invariants constructed from these order parameters. The existence of a cubic invariant indicates that the transition at $T = T_>$ is a discontinuous one. An important result of our Landau analysis is that it predicts the dependence of the discontinuities in the strains to that in the order parameter. Lastly, we discuss order parameters for the $T < T_<$ phase.

II. THE C_{70} MOLECULE

As shown in Fig. 1, the C_{70} molecule is made up of 70 carbon atoms in the shape of an ellipsoid. As we shall see, the symmetry of this molecule leads to the existence of the two orientational ordering transitions mentioned above. We may describe the structure of the C_{70} molecule as follows. It has a fivefold axis. If we call this the z axis and take the origin to be at the center of mass, then the xy and the yz planes are mirror planes if the x and y axes are chosen as in Fig. 1. The molecule can be built up by stacking four pentagons and five decagons of carbon atoms in planes perpendicular to the z axis. The z coordinate and radius of these geometric figures (taken to be the radius of the circumscribed circle) are given in Table I.

We define the 2^L-pole moments of the mass distribution in the molecule by the sum

$$\sigma_L^M = \sum_{i=1}^{70} \langle r_i^L Y_L^M(\hat{r}_i) \rangle , \tag{1}$$
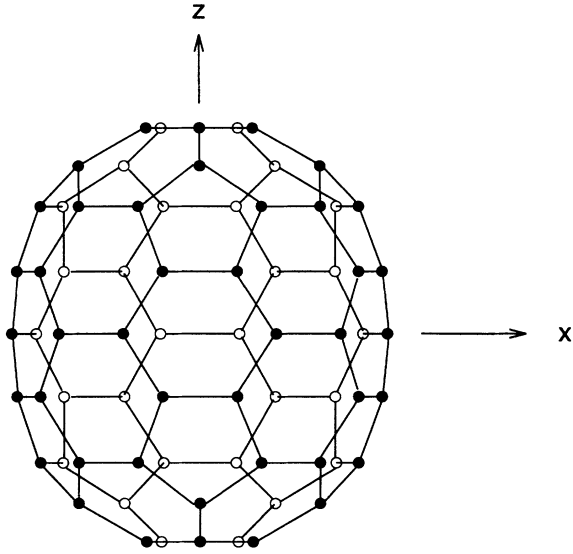
FIG. 1. The C$_{70}$ molecule. Open circles represent atoms whose y coordinates are negative, i.e., behind the plane of the page.

where M ranges from $-L$ to L, $\langle \ \rangle$ indicates an average over the distribution function for molecular orientations, the angular coordinates $\hat{r}_i$ are measured with respect to axes fixed in the crystal, and the spherical harmonics Y_L^M are defined as in Ref. 9.

A natural question is, what moments are nonzero when the fivefold axis is fixed to lie along the z axis? Once we answer this question, the values of the moments relative to the crystal axes can be obtained by suitable rotation of coordinates. Since we take the origin to be at the center of mass, the lowest possible L is 2. Under a reflection about the xy plane $Y_L^M \to (-1)^{L+M} Y_L^M$. Thus the xy mirror plane ensures that the moment σ_L^M is nonzero only if $L + M$ is even. The fivefold axis ensures that only $M = 5n$, where n is an integer, are allowed. The first few allowed combinations are given below in Table II. Also note that if the molecule spins about its fivefold axis, the $M = 0$ moments do not change but the moments for nonzero M vanish.

III. ORIENTATIONAL ORDER PARAMETERS

Now we define order parameters σ_L^M which are zero in the disordered phase but which become nonzero for $T < T_>$. In view of the structure of the rhombohedral

TABLE I. Structural parameters for C$_{70}$ (from Ref. 8).

	Height (Å)	Radius (Å)
Pentagon 1	± 3.983	1.243
Pentagon 2	± 3.235	2.401
Decagon 1	± 2.449	3.005
Decagon 2	± 1.197	3.461
Decagon 3	0	3.565

TABLE II. Values of L and M for which σ_L^M can be nonzero.

L	2	4	5	5	6
M	0	0	5	-5	0

phase, it is clear that the lowest suitable value of L is $L = 2$. At the transition to the monoclinic structure, it is believed[4,2] that the molecules can no longer spin freely, in which case the crystal can no longer have a threefold axis. As we have seen in Table II, when the molecule stops spinning, order parameters with $M \neq 0$ can become nonzero. The lowest such moment which is permitted is $\sigma_L^{\pm 5}$. These order parameters are zero in the $R\bar{3}m$ phase but are nonzero in the monoclinic phase.

Orientational ordering is the driving force in these transitions. Orientational order will induce lattice distortions. In the $R\bar{3}m$ phase the distortion is a trigonal one. In the monoclinic phase it may be more complicated, involving a monoclinic angle being distorted away from 90°. In any case, we wish to relate the distortions of the crystal to order parameters by interaction terms whose form is dictated by symmetry.

As in the case of liquid crystals,[12] it is convenient to introduce the order parameters corresponding to σ_2^M written in Cartesian coordinates. There one defines

$$Q_{\alpha\beta} = \sum_{\text{atoms}} \langle (3r_\alpha r_\beta - \delta_{\alpha\beta} r^2) \rangle_T , \qquad (2)$$

where α and β assume the values x, y, or z, the sum is over all atoms in a given molecule, and $\langle \ \rangle_T$ indicates a thermodynamic average at temperature T. When an ellipsoid of revolution is aligned with its symmetry axis along the z axis, then only the $M = 0$ moment is nonvanishing. In Cartesian language we have $Q_{zz} = 2Q_0$ and $Q_{xx} = Q_{yy} = -Q_0$ and the rest of the components vanish. Note that positive Q_0 corresponds to a prolate ellipsoid (i.e., an egg-shaped object) whereas negative Q_0 corresponds to an oblate ellipsoid (i.e., a pancake-shaped object). If we align the symmetry axis of the ellipsoid with any of the threefold axes in the cube, then the quadrupole tensor has $Q_{\alpha\alpha} = 0$ and off-diagonal components as listed in Table III.

When electrostatically interacting molecules with quadrupolar charge distributions are placed on a fcc lattice, the structure is $Pa\bar{3}$, as happens for solid hydrogen.[11] But here the analogous problem is that of the nematic liquid crystal ordering and the mean-field theory we develop has close parallels in that problem.[12] Here, however, we are in a cubic lattice, which introduces

TABLE III. Nonzero components of the quadrupole tensor when the molecule is aligned with its fivefold axis along n.

n	Q_{xy}	Q_{yz}	Q_{zx}
111	Q_0	Q_0	Q_0
$1\bar{1}\bar{1}$	$-Q_0$	Q_0	$-Q_0$
$\bar{1}\bar{1}1$	Q_0	$-Q_0$	$-Q_0$
$\bar{1}1\bar{1}$	$-Q_0$	$-Q_0$	Q_0

further splitting of the invariants into groups of invariants. The physical reason why here the ellipsoids order parallel to one another, whereas in solid hydrogen they order nearly perpendicular to one another, is that in C_{70} steric forces (which tend to align molecules parallel to one another) dominate whereas in solid hydrogen electrostatic quadrupolar forces (which tend to align molecules perpendicular to one another[13]) dominate. This difference is explained by the fact that the ratio of the distance between nearest neighboring molecules to the diameter of the molecule is large (≈ 5) in the case of hydrogen and small (≈ 1.2) in the case of C_{70}. Since in C_{70} there is no formation of sublattices at $T = T_>$, the fluctuations which condense at this transition must be associated with zero wave vector.

IV. THE LANDAU FREE ENERGY NEAR $T = T_>$

In a cubic environment, the $L = 2$ representation of the rotation group is split into a threefold, t_g, and a twofold, e_g, irreducible representation. The threefold t_g is made up of Q_{xy}, Q_{yz}, and Q_{zx} and the twofold e_g of $(Q_{xx} - Q_{yy})/\sqrt{2}$ and $(2Q_{zz} - Q_{xx} - Q_{yy})/\sqrt{6}$.[10] From the form of $Q_{\alpha\beta}$ given in Table III, we see that the three t_g order parameters are the only ones which become nonzero as the temperature is reduced through $T_>$.

The Landau free energy (per unit volume) is constructed to be a polynomial function of the order parameters which is invariant under symmetry operations of the disordered phase. The Landau expansion in powers of Q_{xy}, Q_{yz}, and Q_{zx} (up to Q^4) is of the form

$$
\begin{aligned}
F(Q) = &\, A_0(T - T^*)(Q_{xy}^2 + Q_{yz}^2 + Q_{zx}^2) \\
&- B(T)(Q_{xy}Q_{yz}Q_{zx}) \\
&+ C(T)(Q_{xy}^2 + Q_{yz}^2 + Q_{zx}^2)^2 \\
&+ D(T)(Q_{xy}^2 Q_{yz}^2 + Q_{yz}^2 Q_{zx}^2 + Q_{zx}^2 Q_{xy}^2)
\end{aligned}
\tag{3}
$$

for temperature T near T^*, which is also near $T_>$, providing the ordering transition is not strongly first order. (For T near T^* one can also neglect the temperature dependence of B, C, and D.) For T less than some temperature $T_>$ (which depends on the numerical constants that are used in the expression above), $F(Q)$ is a minimum when $|Q_{xy}| = |Q_{yz}| = |Q_{zx}| = Q_0$ and either all these components are positive or any two of them are negative. Later we will comment on the fact that this form of free energy gives rise to four symmetry-related minima. [Recall that Q_0 in Table III is positive for a prolate ellipsoid, so that $B(T_>)$ must be positive.] For $T > T_>$, $F(Q)$ is minimal when Q_0 is zero. We thus have a discontinuous transition at $T_>$.

V. THE TRIGONAL STRAIN

We know that there is a trigonal strain which distorts the cubic lattice into a rhombohedral one at $T = T_>$. So we now analyze the way strains couple to the order parameter. The strain tensor is like the quadrupole tensor

but is not traceless, being defined as

$$
\epsilon_{\alpha\beta} = \frac{1}{2}\left(\frac{\partial u_\alpha}{\partial R_\beta} + \frac{\partial u_\beta}{\partial R_\alpha}\right) ,
\tag{4}
$$

where $\mathbf{u}$ is the displacement of a molecule and $\mathbf{R}$ is the position of a molecule in the solid whose components are denoted u_α and R_α, respectively, where α ranges over x, y, and z. In addition to the t_g components [similar to those of $Q_{\alpha\beta}$], the strain tensor has the invariant (under cubic symmetry) $(\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}) \equiv \epsilon_0$, which describes a uniform compression or expansion.

We analyze the coupling of strains to order parameters only to linear order in the strains. We form invariants which couple strains to $Q_{\alpha\beta}$ by combining ϵ_0 with an invariant of the Q's, or by forming scalar products of t_g functions of Q with similar t_g functions of ϵ. Thereby we find the elastic free energy per unit volume, F_{el}, to be of the form

$$
\begin{aligned}
F_{\mathrm{el}} = &\, -E(\epsilon_{xy}Q_{xy} + \epsilon_{yz}Q_{yz} \\
&+ \epsilon_{zx}Q_{zx}) + H(\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz})(Q_{xy}^2 + Q_{yz}^2 + Q_{zx}^2) \\
&+ \frac{1}{2}c_{44}(\epsilon_{xy}^2 + \epsilon_{yz}^2 + \epsilon_{zx}^2) + \frac{1}{2}c_{11}(\epsilon_{xx}^2 + \epsilon_{yy}^2 + \epsilon_{zz}^2) \\
&+ c_{12}(\epsilon_{xx}\epsilon_{yy} + \epsilon_{yy}\epsilon_{zz} + \epsilon_{zz}\epsilon_{xx}) .
\end{aligned}
\tag{5}
$$

The free energy is minimized when $\epsilon_{\alpha\beta} = EQ_{\alpha\beta}/c_{44}$, for $\alpha \neq \beta$. Since, as we have seen, for $T < T_>$ all the off-diagonal terms in the quadrupole tensor are equal in magnitude, this result shows that all the off-diagonal terms in the strain tensor are equal in magnitude. Also, their signs are such that the axis of the trigonal strain coincides with the axis along which the ellipsoidal molecules are aligned. The effect of the second term in Eq. (5) leads to minimal F_{el} when $\epsilon_{xx} = \epsilon_{yy} = \epsilon_{zz} = -H(Q_{xy}^2 + Q_{yz}^2 + Q_{zx}^2)/(c_{11} + 2c_{12})$. So there will be a discontinuous uniform compression or expansion at the transition depending on whether H is positive or negative. Note that the magnitude of this jump is proportional to the square of the jump in the orientational order parameter. In contrast, the jump in $|\epsilon_{\alpha\beta}|$ with $\alpha \neq \beta$ is linearly proportional to the jump in the order parameter. These results suggest that the transition at $T_>$ should be studied as a function of a noncritical field, such as pressure. Then our results could be tested by correlating the pressure dependence of the jump in the orientational order parameter with the discontinuitites in the strain components.

As mentioned previously, there are four equivalent equilibrium states for $T_< < T < T_>$. This is consistent with the fact that the ratio of the number of equivalent sites in the high-symmetry state to that in the low-symmetry state is the number of possible ground states in the new phase.[14,15] $Fm\bar{3}m$ has 48 sites (we have to use a basis with the same number of units per lattice cell) while $R\bar{3}m$ has 12 equivalent sites and hence the ratio, 4, is the predicted number of equivalent ground states in agreement with physical intuition and the Landau free energy result.

VI. THE LOW TEMPERATURE PHASE

Below $T_<$ the crystal is monoclinic. The exact details of this structure are not known but it is believed that the C_{70} molecules no longer spin freely and effectively take up definite orientations. This means that the threefold axis of the rhombohedral phase is lost (it is impossible to have the fivefold axis of the molecule coincide with a threefold axis of the crystal). Consequently, we no longer expect all the molecules to point in the same direction as in the $R\bar{3}m$ phase. If the tipping of these molecules away from this axis is small, we can use the $L = 5, M = 5, -5$ moments as the order parameters. We could then proceed to describe the phase transition in terms of a spontaneous reduction of symmetry from that of the $R\bar{3}m$ phase to the lowest-temperature phase. But from what we have said, we do know that this theory will involve critical order parameters $\sigma_5^{\pm 5}$.

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