ORIENTATIONAL PHASE TRANSITION IN SOLID $C_{60}$: BIFURCATION APPROACH
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A simple model for the angular dependent interaction between $C_{60}$ molecules on the face-centered cubic lattice is proposed. The bifurcations of the solutions of the nonlinear integral equations for orientational distribution functions in the mean field approximation are analyzed and the orientational phase transition in solid $C_{60}$ is described. The quantitative results for the orientational phase transition are in accordance with experimental data.

1. As is well known the mean–field approach often brings one to the formulation of the broken space symmetry problem in terms of the bifurcation of solutions of nonlinear integral equations for distribution functions or order parameters (see, e.g., the review [1]). In particular, the bifurcation approach was fruitfully used in the case of orientational phase transitions in molecular crystals where the intermolecular interaction depends not only on the distance between particles but on the molecule orientations, too. When the temperature decreases the free rotation of molecules fixed on the crystal lattice sites is replaced by rotations about local frozen axes, probably different in different sublattices. These orientational transitions can be conveniently described by changes in the $n$-particle orientational distribution functions $f_n(\omega_1, ..., \omega_n)$. This kind of problems was treated by use of bifurcation approach, for example, in the papers [2, 3, 4, 5, 6]. Here we will follow our papers [2, 3, 6]. Let us describe briefly the main steps of the method.

In the mean–field approximation from the first equation of the Bogoliubov hierarchy [7] for the equilibrium orientational distribution functions or by minimizing the orientational free energy one can obtain the following nonlinear integral equation [2]:

$$g_i(\omega_i) + \frac{1}{6} \sum_{i \neq j} G_j \int d\omega_j \Phi_{ij}(\omega_i, \omega_j) e^{g_i(\omega_j)} = 0; \quad (1)$$

here $\omega_i$ are the angles describing the orientation of the molecule, e.g. Euler angles, $g_i(\omega_i) = \ln\frac{f_i(\omega_i)}{G_i}$, $f_i(\omega_i)$ – is the one-particle orientational distribution function for the molecule on the site $i$, the constants $G_i$ are the normalization constants. If we consider molecules fixed on the rigid lattice sites then

$$\Phi_{ij}(\omega_i, \omega_j) = \sum_{\nu, \tau} \Phi_{\nu, \tau}(\omega_R) u_{\nu}(\omega_i) u_{\tau}(\omega_j), \quad (2)$$

where $u(\omega)$ – is a full system of functions corresponding to the symmetry of the problem. In the case of multipole-multipole electrostatic interaction, usually responsible for orientational ordering in molecular crystals, we can write in the nearest neighbor approximation

$$\Phi_{ij}(\omega_i, \omega_j) = \frac{I^2}{R^{2l+1}} \sum_{\nu, \tau} C_{\nu, \tau}(\omega_{ij}) u_{\nu}(\omega_i) u_{\tau}(\omega_j), \quad (3)$$

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are the components of the molecule multipole momentum, the coefficients \( C_{\nu,\tau}(\omega_{ij}) \) are determined by the configuration of the nearest environment, \( R \) is the nearest neighbor distance.

Assuming that the order is different in not more than \( k \) sublattices \( (k \leq z) \), \( z \) being the number of the nearest neighbors, we will obtain from (1) the system of \( k \) nonlinear integral equations for the functions \( g_i(\omega_i) \), \( i = 1, \ldots, k \):

\[
g_i(\omega) + \lambda \sum_{j=1}^{z} G_j \int d\omega' e^{g_j(\omega')} \sum_{\nu,\tau} C_{\nu,\tau}(\omega_{ij}) u_{\nu}(\omega) u_{\tau}(\omega') = 0; \quad (4)
\]

\[
\lambda = \frac{1}{kT} \frac{I_l^2}{R^{2l+1}}.
\]

These equations differ from the well known Hammerstein equations \([8]\) only by the presence of the factor \( G_i \) depending on \( g_i \).

In the case of finite domain of integration when the fixed point principle is valid there exists detailed theory for such equations (see \([9]\)). We will use the standard methods (see e.g. \([10]\)). In the high temperature region the system \((4)\) has only trivial solution \( g_i(\omega) = 0 \), corresponding to the orientationally disordered phase. At the bifurcation points \( \lambda_\alpha > 0 \) new solutions with broken symmetry appear. Real temperatures are described by \( \lambda_\alpha \). For \( \lambda = \lambda_\alpha + \mu \) the functions \( g^\alpha_i(\omega_i) \) can be written as series in integer or fractional powers of \( \mu \). These powers are defined by the bifurcation equation corresponding to the system \((4)\) or, finally, by the fact whether the integrals \( \int d\omega u_{\nu} u_{\tau} u_{\eta} \) are zero or nonzero.

The bifurcation points are the eigenvalues of the system of linear integral equations of the main order:

\[
h_i(\omega) + \lambda \sum_{j=1}^{z} G_j^0 \int d\omega' \sum_{\nu,\tau} C_{\nu,\tau}(\omega_{ij}) u_{\nu}(\omega) u_{\tau}(\omega') h_j(\omega') = 0. \quad (5)
\]

Here \( h_i(\omega) \) are the main terms in the expansion of \( g_i(\omega) \) in powers of \( \mu \). If \( \int d\omega' \Phi_{ij}(\omega, \omega') = 0 \), the equations of the main approximation do not depend on the powers of \( \mu \) entering the expansion of \( g_i(\omega) \). It is easy to see that \( h_i(\omega) = \sum_{\nu} h^\nu_i u_{\nu}(\omega) \), so that the definite system of nonzero coefficients \( h^\nu_i \) and, consequently, the definite symmetry of the new phase corresponds to each value \( \alpha \).

Following this way we can obtain in principle all possible broken symmetry phases and points of transitions. In fact this program was realized in rather simple cases of hydrogen, methane and others.

However, in the treatise of the complicated problem of the orientational order in fullerite we simplify the program from the very beginning. Now our aim is to describe the real orientational order seen in the experiments, and to obtain (without using of fitting parameters) the transition temperature and the quantitative characteristics of the low temperature ordered phase. Our choice of the simplified model interaction is based on the maximum utilization of the symmetry properties of the problem and on the exploit of the numerical calculations for the energy of the pair of \( C_60 \) molecules with different mutual orientations, performed by other authors.
2. First of all, let us recall that the molecule $C_{60}$ is the result of cutting off the vertices of icosahedron. As result of this cutting off the 20 triangles – the icosahedron faces – are transformed into 20 hexagons and 12 (cutted) vertices with 5 outgoing edges – in 12 pentagons. The edges of the resulting body are of two types: 30 remaining parts of the initial icosahedron edges (the $a$ type) and $5 \times 12 = 60$ new pentagon edges (type $b$). The detailed calculation of the ground state of an isolated $C_{60}$ molecule shows (see, e.g. [24]) that the hexagons are benzol-type rings with double bonds (and the excess of charge) placed on the $a$-type edges, while the deficiency of charge occurs to appear in the centers of hexagons and pentagons.

The orientational ordering in solid $C_{60}$ has been a subject of extensive current experimental investigations (see, e.g., [16, 11, 12, 14]); some theoretical researches were performed, too [17, 18, 19, 20, 21, 22, 23, 28, 29]. At ambient temperature the molecules $C_{60}$ rotate almost freely with centers on the face-centered-cubic (fcc) lattice sites (the space group is $Fm\bar{3}m$).

![Figure 1: The sublattices in fcc $C_{60}$.](image)

When the temperature decreases to $T_s \approx 260K$ the first order orientational phase transition takes place: the sites of the initial fcc lattice become divided between four simple cubic sublattices (see fig.1) with own preferable molecular orientation in each sublattice (the space group is $Pa\bar{3}$). Moreover, the experiments [11, 13, 15] have shown that in the ordered state the electron–rich regions (the interpentagon double bonds) face the electron–deficient regions of the neighboring $C_{60}$ molecule: the centers of pentagons or the centers of hexagons. It was shown that the ratio of the number of molecules in those two states is about $\rho_P : \rho_H = 60 : 40$ at the phase transition temperature and increases when the temperature decreases. This remaining two–level orientational disorder is usually believed to cause the orientational glass transition at $T_G \approx 90K$ now confirmed by various experimental technics (see, e.g., [24]).

These two minima of the intermolecular angle dependent energy were in fact obtained through numerical calculations and were shown to be much lower than the energies of other mutual orientations of the pair of molecules (see, e.g., [18, 22]). In those calculations the previously obtained charge distribution for the isolated $C_{60}$ molecule [24] was taken into account. Usually recent calculations use the intermolecular potential of Sprik et al. [27]: a sum of 6-12 and Coulomb interactions between
60 atoms $C$ and 30 double–bond centers $D$ and between each other:

$$
\Phi(C_{60}(1), C_{60}(2)) = \sum_{k \in C(1)} \sum_{k' \in C(2)} 4\epsilon \left\{ \left( \frac{\sigma_{CC}}{R_{kk'}} \right)^6 - \left( \frac{\sigma_{CC}}{R_{kk'}} \right)^{12} \right\} 
+ \sum_{k \neq k', k, k' \in C, D} 4\epsilon \left\{ \left( \frac{\sigma_{CD}}{R_{kk'}} \right)^6 - \left( \frac{\sigma_{CD}}{R_{kk'}} \right)^{12} \right\} 
+ \sum_{k \in D(1)} \sum_{k' \in D(2)} 4\epsilon \left\{ \left( \frac{\sigma_{DD}}{R_{kk'}} \right)^6 - \left( \frac{\sigma_{DD}}{R_{kk'}} \right)^{12} \right\} 
+ \sum_{k, k' \in C, D} q_k q_{k'} R_{kk'}.
$$

(6)

Here $\epsilon = 1.293meV, \sigma_{CC} = 3.4\text{Å}, \sigma_{CD} = 3.5\text{Å}, \sigma_{DD} = 3.6\text{Å}, q_D = -0.35e, q_C = -q_D/2$.

Rigorously speaking to write the equation (1) in our case we are interested in the angular part of this complicated interaction represented in terms of multipole–multipole interaction of point–like multipoles on the sites of rigid fcc lattice with coefficients to be calculated from (6). The general form of this angular part is:

$$
\Phi_{ij}(\omega_i, \omega_j) = \sum_{l, \nu, \tau} C^i_{l, \nu, \tau}(\omega_i) u_{l, \nu}(\omega_i) u_{l, \tau}(\omega_j)
$$

(7)

with $l = 6, 10, 12, 16, 18, ...$ due to the icosahedral molecular symmetry $I_h$ (see, e.g., [20]).

However, we will not use the multipole series per se, but will simplify the problem and develop a model orientational interaction exploiting the symmetry properties to maximal extend. We will follow the main ideas of the papers [11, 21] and use the restricted number of allowed orientations instead of free continuous rotations. Let us note that a kind of more general discrete model was proposed in Ref. [29]. Let us take into account in the energy (7) only the orientations with pentagons, hexagons or double bonds directed towards 12 nearest neighbors in fcc lattice. It is important that the $C_{60}$ molecule is constructed in such a way that if 6 of its 12 pentagons (or 6 of its 20 hexagons) face 6 nearest neighbors double bonds ($P$ and $H$ states of Lapinskas et al. [21]), then 6 of its 30 interpentagon double bonds (type $a$) face the remaining 6 nearest neighbors.

Now the energy matrix elements can take only three values: $J_0$ – the energy of the general mutual position, $J_P$ – pentagon versus double bond and $J_H$ – hexagon versus double bond. These energies in our model can be compared with those calculated in [18, 19, 23, 25] as functions of the angular displacements of the molecule at (0,0,0). Following [21], and putting $J_0 = 0$ we obtain from the fig.2(b) of the paper [18] $J_P = -300K$ and $J_H = -110K$.

The energy matrix elements $J_P$ and $J_H$ connect the states of molecules only in the allowed orientations. So, only allowed linear combinations of $u_{l, \nu}$ enter the energy. The theoretical curve in [18] makes no difference between the number $l$ of harmonics and describes the effect of all of them. So, in the framework of our model calculation it is possible to build up the allowed functions using only the harmonics with $l = 6$: we need only their transformation properties. We restrict ourselves to $l = 6$, however the coefficients $J_P$ and $J_H$ are not some of $C^6_{l, \nu, \tau}$ given in (2) but effectively take into account higher order terms.
Let us construct the functions \( P_i(\omega) \) and \( H_i(\omega) \) explicitly in terms of cubic harmonics \( K_m \equiv K_{6,m}, m = 1, 2, ..., 13 \). The states \( P_i(H_i) \) have 6 pentagons (hexagons) and 6 double bonds directed towards 12 nearest neighbors along different [100] axes. All functions \( P_i \) and \( H_i \) are the sums of \( K_m \), invariant under the icosahedral symmetry of the molecule (i.e. belonging to the \( A_{1g} \) representation of the icosahedral group \( I_h \)) if icosahedrons are naturally oriented in one of 8 properly chosen coordinate systems. If we choose the \( z \)-axis along the fifthfold icosahedral axis, the the function \( A_1(\omega) \) can be written as \([3]\):

\[
A_1(\omega) = a_0 [Y_{6,0}(\omega) + a_5 (Y_{6,5}(\omega) - Y_{6,-5}(\omega))],
\]

with \( a_0 = -\sqrt{11}/5, a_5 = -\sqrt{7}/\sqrt{11}, Y_{lm}(\omega) \) – spherical harmonics (taken as in \([3]\)). After rotating the icosahedron clockwise about \( y \)-axis by the angle \( \phi = 58.28253 \) it occurs in the position with its three twofold axes parallel to Cartesian axes. This is the so called standard \( B \)-orientation (following \([23]\)). \( P_1(\omega) \) describes the molecule rotated from the standard orientation \( B \) about [111] axis through the angle \( \psi = 97.76125^\circ \) (clockwise). After the rotation three fifthfold icosahedron axes occur to be directed (almost) precisely along \([\pm 1,0,\mp 1], [0,\mp 1,\mp 1], [\mp 1,\mp 1,0] \), that is in the directions of 6 nearest neighbors. The functions \( P_2(\omega), P_3(\omega) \) and \( P_4(\omega) \) are obtained from \( P_1(\omega) \) by subsequent counter–clockwise rotations of the molecule by 90° around \( z \) axes. In analogous way one can obtain the functions \( H_i(\omega) \), with the only difference that now \( \psi' = 37.76125^\circ \).

If written in the "standard" coordinate frame with Cartesian axes along the cube sides these functions have the following explicit form:

\[
\begin{align*}
P_1(\omega) &= \alpha_P K_1(\omega) + \beta_P [K_8(\omega) + K_9(\omega) + K_{10}(\omega)] + \gamma_P [K_{11}(\omega) + K_{12}(\omega) + K_{13}(\omega)], \\
P_2(\omega) &= \alpha_P K_1(\omega) + \beta_P [-K_8(\omega) + K_9(\omega) - K_{10}(\omega)] + \gamma_P [-K_{11}(\omega) + K_{12}(\omega) - K_{13}(\omega)], \\
P_3(\omega) &= \alpha_P K_1(\omega) + \beta_P [K_8(\omega) - K_9(\omega) - K_{10}(\omega)] + \gamma_P [K_{11}(\omega) - K_{12}(\omega) - K_{13}(\omega)], \\
P_4(\omega) &= \alpha_P K_1(\omega) + \beta_P [-K_8(\omega) - K_9(\omega) + K_{10}(\omega)] + \gamma_P [-K_{11}(\omega) - K_{12}(\omega) + K_{13}(\omega)], \\
H_1(\omega) &= \alpha_H K_1(\omega) + \beta_H [K_8(\omega) + K_9(\omega) + K_{10}(\omega)] + \gamma_H [K_{11}(\omega) + K_{12}(\omega) + K_{13}(\omega)], \\
H_2(\omega) &= \alpha_H K_1(\omega) + \beta_H [-K_8(\omega) + K_9(\omega) - K_{10}(\omega)] + \gamma_H [-K_{11}(\omega) + K_{12}(\omega) - K_{13}(\omega)], \\
H_3(\omega) &= \alpha_H K_1(\omega) + \beta_H [K_8(\omega) - K_9(\omega) - K_{10}(\omega)] + \gamma_H [K_{11}(\omega) - K_{12}(\omega) - K_{13}(\omega)], \\
H_4(\omega) &= \alpha_H K_1(\omega) + \beta_H [-K_8(\omega) - K_9(\omega) + K_{10}(\omega)] + \gamma_H [-K_{11}(\omega) - K_{12}(\omega) + K_{13}(\omega)],
\end{align*}
\]

with \( \alpha_P = -0.38866; \beta_P = 0.31486; \gamma_P = -0.42877; \alpha_H = 0.46588; \beta_H = 0.37740; \gamma_H = 0.34432 \). The functions are normalized to unity. We use the notations for cubic harmonics from \([20]\) (see Appendix).

So, we suppose in the spirit of the papers \([14, 27]\) that instead of free rotations only discrete jumps between restricted number of orientations is allowed even in the high temperature phase. Let us remind that the number of these allowed rotations is rather large one: the molecule has 20 hexagons, 12 pentagons and 30 double bonds.

4. Let us write now the equations \( \{4\} \) for our model in the case of four sublattices of experimentally determined \( Pa\bar{3} \) structure (see fig.1):
to the

and the system (9) is equivalent to the following system of linear algebraic equations:

\[ h_1(\omega) + \frac{\lambda}{4\pi} \int d\omega'[B(\omega, \omega')h_2(\omega') + A(\omega, \omega')h_3(\omega') + D(\omega, \omega')h_4(\omega')] = 0, \]

\[ h_2(\omega) + \frac{\lambda}{4\pi} \int d\omega'[B(\omega, \omega')h_1(\omega') + A(\omega, \omega')h_4(\omega') + D(\omega, \omega')h_3(\omega')] = 0, \]

\[ h_3(\omega) + \frac{\lambda}{4\pi} \int d\omega'[B(\omega, \omega')h_4(\omega') + A(\omega, \omega')h_1(\omega') + D(\omega, \omega')h_2(\omega')] = 0, \]

\[ h_4(\omega) + \frac{\lambda}{4\pi} \int d\omega'[B(\omega, \omega')h_3(\omega') + A(\omega, \omega')h_2(\omega') + D(\omega, \omega')h_1(\omega')] = 0. \] (9)

Here \( \lambda = 1/T \) (\( J_P \) and \( J_H \) are taken in Kelvin) and \( A(\omega, \omega'), B(\omega, \omega'), D(\omega, \omega') \) are the sums of interactions over nearest neighbors of the central molecule in the sublattices \( A, B \) and \( D \) (see fig.1), respectively. For example, the sum in the plain perpendicular to the \( x \) axis (the sites \( D \) in fig.1) can be written explicitly in the form:

\[
D(\omega, \omega') = \]

\[
= 2\{(P_1(\omega) + P_4(\omega))J_P + (H_1(\omega) + H_4(\omega))J_H \}
\]

\[
\times \{[P_2(\omega') + P_3(\omega') + H_2(\omega') + H_3(\omega')]\}
\]

\[
+ \{[P_2(\omega') + P_3(\omega') + H_2(\omega') + H_3(\omega')]\}
\]

\[
\times \{[P_1(\omega') + P_4(\omega') + H_1(\omega') + H_4(\omega')]\}
\]

\[
+ \{[P_1(\omega') + P_4(\omega') + H_1(\omega') + H_4(\omega')]\}
\]

\[
\times \{[P_2(\omega') + P_3(\omega')]\}
\] (10)

The bifurcation points for the solutions of initial system are the eigenvalues of the system (9) while the nontrivial solutions of (9) define the symmetry character of the new phase.

It is easy to see that the solutions of the system (9) can be written as linear combinations

\[ h_i(\omega) = \sum_{\nu} h_i^{\nu} K_{\nu}(\omega), \]

and the system (9) is equivalent to the following system of linear algebraic equations:

\[ h_1^{\nu} + \frac{\lambda}{4\pi} \sum_{\tau=1}^{13} [A_{\tau\nu} h_{\tau}^{\nu} + B_{\tau\nu} h_{\tau}^{\nu} + D_{\tau\nu} h_{\tau}^{\nu}] = 0, \]

\[ h_2^{\nu} + \frac{\lambda}{4\pi} \sum_{\tau=1}^{13} [A_{\tau\nu} h_{\tau}^{\nu} + B_{\tau\nu} h_{\tau}^{\nu} + D_{\tau\nu} h_{\tau}^{\nu}] = 0, \]

\[ h_3^{\nu} + \frac{\lambda}{4\pi} \sum_{\tau=1}^{13} [A_{\tau\nu} h_{\tau}^{\nu} + B_{\tau\nu} h_{\tau}^{\nu} + D_{\tau\nu} h_{\tau}^{\nu}] = 0, \]

\[ h_4^{\nu} + \frac{\lambda}{4\pi} \sum_{\tau=1}^{13} [A_{\tau\nu} h_{\tau}^{\nu} + B_{\tau\nu} h_{\tau}^{\nu} + D_{\tau\nu} h_{\tau}^{\nu}] = 0, \] (11)
\[ \nu = 1, 8, 9, \ldots, 13. \]

Using the explicit form of the matrices \( A, B, D \) it is easy to obtain the only nonzero elements:

\[
\begin{align*}
A_{1,1} & = B_{1,1} = D_{1,1} \equiv u, \\
A_{8,8} & = B_{9,9} = D_{10,10} \equiv v, \\
A_{11,11} & = B_{12,12} = D_{13,13} \equiv z, \\
A_{8,11} & = A_{11,8} = B_{9,12} = B_{12,9} = D_{10,13} = D_{13,10} \equiv w.
\end{align*}
\]

One can write the elements \( u, v, z \) and \( w \) in terms of the coefficients \( \alpha_P, \beta_P, \gamma_P, \alpha_H, \beta_H, \gamma_H \) and energies \( J_P, J_H \) and obtain the following values: \( u = 32 \cdot 5.046, v = 32 \cdot 94.127, z = 32 \cdot 7.665, w = -32 \cdot 37.155. \) The determinant of the algebraic system is factorized in \( 2 \times 2 \) determinants, so that the eigenvalues \( \lambda_\alpha \) can be easily obtained. Among the values \( \lambda_\alpha \) there are two positive values. The first one \( \lambda_1 = 4\pi/u \) corresponds to the solution proportional to \( K_1 \) and is of no interest now. The second \( \lambda = \lambda_b \) is the positive solution of the equation

\[ 1 - \frac{\lambda}{4\pi}(v + z) + \frac{\lambda^2}{(4\pi)^2}(vz - w^2) = 0, \quad (12) \]

namely \( \lambda_b = 0.00364K^{-1} \) or \( T_b = 275K \). The corresponding nontrivial eigenfunctions have \( h_i^1 = 0 \), and

\[
\begin{align*}
h_1^{11} - h_3^{11} & = Q(h_1^8 - h_3^8) \neq 0; \\
h_2^{11} - h_4^{11} & = Q(h_2^8 - h_4^8) \neq 0; \\
h_1^{13} - h_4^{13} & = Q(h_1^{10} - h_4^{10}) \neq 0; \\
h_2^{13} - h_3^{13} & = Q(h_2^{10} - h_3^{10}) \neq 0; \\
h_1^{12} - h_2^{12} & = Q(h_1^9 - h_2^9) \neq 0; \quad h_3^{12} - h_4^{12} = Q(h_3^9 - h_4^9) \neq 0;
\end{align*}
\]

where

\[ Q = \frac{4\pi - v\lambda_b}{\lambda_b w}, \]

and

\[
\begin{align*}
h_1^{11} + h_3^{11} & = h_1^8 + h_3^8 = h_2^{11} + h_4^{11} = h_2^8 + h_4^8 = \\
h_1^{13} + h_4^{13} & = h_1^{10} + h_4^{10} = h_2^{13} + h_3^{13} = h_2^{10} + h_3^{10} = \\
h_1^{12} + h_2^{12} & = h_1^9 + h_2^9 = h_3^{12} + h_4^{12} = h_3^9 + h_4^9 = 0.
\end{align*}
\]

If we add the condition for the functions \( h_i(\omega) \) to transform one into another under the action of the cubic group rotation elements which leave the fcc lattice invariant, then only three of the coefficients remain to be independent and the functions \( h_i \) can be written in the following form:

\[
\begin{align*}
h_1(\omega) & = aP_1(\omega) + bH_1(\omega) + cK_1(\omega), \\
h_2(\omega) & = aP_3(\omega) + bH_3(\omega) + cK_1(\omega), \\
h_3(\omega) & = aP_4(\omega) + bH_4(\omega) + cK_1(\omega), \\
h_4(\omega) & = aP_2(\omega) + bH_2(\omega) + cK_1(\omega),
\end{align*}
\]

(13) \hfill (14) \hfill (15)
while

$$a \alpha_P + b \alpha_H + c = 0. \quad (16)$$

Now

$$h_1(\omega) = r(K_8(\omega) + K_9(\omega) + K_{10}(\omega)) + s(K_{11}(\omega) + K_{12}(\omega) + K_{13}(\omega)),
\quad h_2(\omega) = r(-K_8(\omega) + K_9(\omega) - K_{10}(\omega)) + s(-K_{11}(\omega) + K_{12}(\omega) - K_{13}(\omega)),
\quad h_3(\omega) = r(K_8(\omega) - K_9(\omega) - K_{10}(\omega)) + s(K_{11}(\omega) - K_{12}(\omega) - K_{13}(\omega)),
\quad h_4(\omega) = r(-K_8(\omega) - K_9(\omega) + K_{10}(\omega)) + s(-K_{11}(\omega) - K_{12}(\omega) + K_{13}(\omega)),
\quad (17)$$

where

$$r = a \beta_P + b \beta_H, \quad s = a \gamma_P + b \gamma_H,$$

$$s = Qr. \quad (18)$$

Using the numerical values given above we obtain immediately $Q = -0.3707$, so that $b : a$. We see now that the bifurcation temperature and the ratio of the number of molecules in $P$ and $H$ states occur to coincide with the experimental data [11, 13, 15]:

$$\rho_P = \frac{a}{a + b} = 0.608; \quad \rho_H = \frac{b}{a + b} = 0.392. \quad (19)$$

5. To obtain the remaining unknown coefficient we use the equations of the second order in $\mu$. As usually, we will calculate this coefficient from the condition of solvability of these equations, i.e., from the condition on right hand sides to be orthogonal to the solutions of the homogeneous integral equations. The second order equations have the form (let us remind that $g_i(\omega) = \mu h_i(\omega) + \mu^2 x_i(\omega) + \ldots; \lambda = \lambda_b(1 + \mu)$):

$$x_1(\omega) + \frac{\lambda_b}{4\pi} \int d\omega'[A(\omega, \omega') x_3(\omega') + B(\omega, \omega') x_2(\omega') + D(\omega, \omega') x_4(\omega')] = R_1;
\quad x_2(\omega) + \frac{\lambda_b}{4\pi} \int d\omega'[A(\omega, \omega') x_4(\omega') + B(\omega, \omega') x_1(\omega') + D(\omega, \omega') x_3(\omega')] = R_2;
\quad x_3(\omega) + \frac{\lambda_b}{4\pi} \int d\omega'[A(\omega, \omega') x_1(\omega') + B(\omega, \omega') x_4(\omega') + D(\omega, \omega') x_2(\omega')] = R_3;
\quad x_4(\omega) + \frac{\lambda_b}{4\pi} \int d\omega'[A(\omega, \omega') x_2(\omega') + B(\omega, \omega') x_3(\omega') + D(\omega, \omega') x_1(\omega')] = R_4; \quad (20)$$

where

$$R_1 = h_1(\omega) - \frac{\lambda_b}{8\pi} \int d\omega'[A(\omega, \omega')(h_3)^2 + B(\omega, \omega')(h_2)^2 + D(\omega, \omega')(h_4)^2];$$
$$R_2 = h_2(\omega) - \frac{\lambda_b}{8\pi} \int d\omega'[A(\omega, \omega')(h_4)^2 + B(\omega, \omega')(h_1)^2 + D(\omega, \omega')(h_3)^2];$$
$$R_3 = h_3(\omega) - \frac{\lambda_b}{8\pi} \int d\omega'[A(\omega, \omega')(h_1)^2 + B(\omega, \omega')(h_4)^2 + D(\omega, \omega')(h_2)^2];$$
$$R_4 = h_4(\omega) - \frac{\lambda_b}{8\pi} \int d\omega'[A(\omega, \omega')(h_2)^2 + B(\omega, \omega')(h_3)^2 + D(\omega, \omega')(h_1)^2]. \quad (21)$$
The system of nonlinear inhomogeneous equations (20) has nontrivial solutions for \( x_i \) if the right hand sides (21) of the system are orthogonal to the solutions of the homogeneous equations. In terms of inhomogeneous linear algebraic equations for the coefficients \( x^\mu_i \) in the series for \( x_i \) in spherical harmonics the analogous condition reads that the rank of the system determinant is equal to the rank of the determinant of the system examined above. All 16 equations

\[
\int d\omega R_i(\omega) h_j(\omega) = 0
\]

are identical and give the following equation for the coefficients \( s, r \):

\[
s^2 + r^2 + \frac{\lambda}{4\pi} \{ r^3(M_1v + M_3w) + r^2 s[2(M_3v + M_2w) + (M_1w + M_3z)] + \\
rs^2[2(M_3w + M_2z) + (M_2v + M_4w)] + s^3(M_2w + M_4z) \} = 0.
\]

Here

\[
M_1 = <8, 9, 10> = 0.027; M_2 = <8, 12, 13> = <11, 9, 13> = <11, 12, 10> = 0.093;
\]

\[
M_3 = <8, 9, 13> = <8, 12, 10> = <11, 9, 10> = -0.012; M_4 = <11, 12, 13> = -0.011
\]

- are the nonzero integrals

\[
<k, m, n> = \int d\omega K_k(\omega) K_m(\omega) K_n(\omega).
\]

Solving equations (16), (18) and (23) simultaneously, we obtain finally \( a = -25.7; b = -16.6; c = -2.27 \). The main term in \( g_i(\omega) \) near the bifurcation point has the form:

\[
g(\omega) = -\tau[aP(\omega) + bH(\omega) + cK_1(\omega)],
\]

\[
\tau = \frac{T - T_b}{T_b}.
\]

6. With this analytical solution near the bifurcation point it is easy to find numerical solution of the initial nonlinear integral equations in wider region of temperatures. The solution is of the form (17) with the coefficients \( r(T) \) and \( s(T) \) depending on the temperature and goes in both directions from the bifurcation point (see fig.2). The solution has the turning point at \( T_t = 290K \). The calculation of the orientational part of the free energy of the system

\[
F = \sum_{i<j} \int d\omega_i \int d\omega_j \Phi_{i,j}(\omega_i, \omega_j) g_i(\omega_i) g_j(\omega_j) + kT \sum_i \int d\omega_i g_i(\omega_i) \ln[4\pi g_i(\omega_i)]
\]

was performed for the obtained solutions and the lowest state was identified. The solid curves in fig.2 correspond to the stable solution and the dotted curves - to the unstable one. At the temperature \( T_c = 288.4K \) the first order phase transition takes place with the jump of the order parameter. The disordered phase \( g_i(\omega_i) = 0 \) is stable at higher temperature. The ratio of the coefficients \( r(T) \) and \( s(T) \) slightly depends
on the temperature. The relative fractions of molecules in the states $P$ and $H$ in the ordered phase at the transition point are:

$$\rho_P(T_c) = \frac{a}{a+b} = 0.606; \quad \rho_H(T_c) = \frac{b}{a+b} = 0.394.$$  \hspace{1cm} (24)

These values as well as the value of $T_c$ are in very good agreement with the experimental data [11, 13, 15].

7. To conclude, we developed a simple model for angle dependent interaction for $C_{60}$ molecules in the fcc cubic lattice. We used rigorous analytic approach based on the Lyapunov–Schmidt theory of bifurcation of solutions of nonlinear integral equations to treat this model and found the first order orientational phase transition. The results for the transition temperature and the characteristics of the ordered phase are in quantitative agreement with the experimental data.

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Appendix.

We use the expressions for cubic harmonics from [20]. Let us write them explicitly.

$$K_1 = \frac{\sqrt{13}}{2\sqrt{2\pi}}\left[\frac{1}{2}(x^6+y^6+z^6) - \frac{15}{4}(x^4y^2+x^4z^2+y^4z^2+y^4x^2+z^4x^2+z^4y^2) + 45x^2y^2z^2\right],$$

$$K_8 = \frac{\sqrt{13}}{16\sqrt{2\pi}}\sqrt{105}xy(1 - 18z^2 + 33z^4),$$

$$K_{11} = \frac{\sqrt{13}}{16\sqrt{2\pi}}\sqrt{231}xy[3(1-z^2)^2 - 16x^2y^2],$$
The functions $K_9$, $K_{10}$ and $K_{12}$, $K_{13}$ can be obtained by cyclic permutations of the coordinates from $K_8$ and $K_{11}$, respectively.

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