

## Calculation of the Orientational Phase Transition Temperature in Solid C<sub>60</sub>

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*A method is developed to describe the orientational phase transition in solid C<sub>60</sub>, considering both Lennard-Jones atomic pair potentials and Coulombic forces. We obtained the active mode while the transition occurs, and the calculated transition temperature agrees with experiments.*

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C<sub>60</sub> has attracted wide interests due to both its elegant molecular symmetry and the intriguing structural, dynamic, and electronic properties of its solid phase and doped derivatives.<sup>1</sup> Solid C<sub>60</sub> forms a face-centered-cubic (fcc) structure at room temperature, in which the molecules exhibit dynamic orientational disorder. At 249 K the molecules develop an orientational order via a first ordered phase transition, lowering the space group symmetry to Pa $\bar{3}$  in simple cubic lattice.<sup>2,3</sup> Michel *et al.*<sup>4-6</sup> has developed a microscopic theory to calculate the transition temperature. With only Lennard-Jones (LJ) potentials, they found  $T_c$  is far below experimental results. Group of Lu<sup>7</sup> pointed out that Pa $\bar{3}$  structure is stabilized by both LJ potentials and Coulombic forces. In this paper, we developed a method to calculate the orientational phase transition temperature with rotator function, and found LJ and Coulombic potentials play different roles in crystal field and in multipolar interactions.

An ideal C<sub>60</sub> is a truncated icosahedron. The 6-5 and 6-6 edges are inequivalent and are not in the same length,<sup>8</sup> causing a small amount of charge transfer. Thus, a simple model was proposed with charges  $q$  and  $-2q$  on the centers of single and double bonds, respectively. The position of the  $\mu$ -th charge or atom is given by spherical polar coordinate  $(r_\mu, \theta_\mu, \phi_\mu)$ . Then the angular-dependent distributions of atoms and charges on a C<sub>60</sub> molecule surface can be described by expanding in terms of spherical harmonics

$$\sum_{\mu} \delta(\Omega - \Omega_{\mu}) = \sum_{l,m} c_l^m Y_l^m(\Omega), \quad (1)$$

where  $-l \leq m \leq +l$  and  $c_l^m = \sum Y_l^m(\Omega_{\mu})$ . The sum  $\mu$  is performed over 60, 60 and 30 for atom, positive charge and negative charge distributions, respectively. As their distributions have high symmetry  $I_h$ , only certain values, such as  $l = 0, 6, 10, 12$  etc. occur. In addition, the coefficients  $c_l^m$  are real numbers. The molecular symmetry-adapted function is defined by

$$S_{l(I_h)}^1 \equiv \sum_{l,m} \alpha_{l(I_h)}^{m1} Y_l^m(\Omega), \quad (2)$$

where  $\alpha_{i(I_h)}^{m1} = c_i^m / \sigma_i$ , with  $\sigma_i^2 = \sum (c_i^m)^2$ . The indices 1 refer to the identity representation of  $I_h$  group. Here, we remind that for three kinds of distributions, MSAFs are either the same or only different in sign, due to the symmetry.

$C_{60}$  molecules form a fcc lattice with  $O_h$  group. The site-symmetry-adapted function (SSAF) needs considering

$$S_{i(O_h)}^\tau(\Omega) \equiv \sum_{m=-l}^{+l} Y_l^m(\Omega) \alpha_{i(O_h)}^{m\tau}, \quad (3)$$

where  $\tau$  stands for the irreducible representation of  $O_h$  group. The coefficients  $\alpha_{i(O_h)}^{m\tau}$  are tabulated by Ref. 9. An arbitrary orientation  $\Omega'_\mu$  can be obtained through a rotation  $\omega = (\alpha, \beta, \gamma)$  from the standard position  $\Omega_\mu$ , i. e.  $\Omega'_\mu = R(\omega)\Omega_\mu$ . When applying  $R(\omega)$  to SSAF and summing over all atoms or charges, we obtain the rotator function (RF)  $U$ :

$$\sum_{\mu} S_{i(O_h)}^\tau(\Omega'_\mu) = g_i^1 U_{i(O_h)}^{1\tau} = g_i^1 \sum_{n,m=-l}^{+l} \alpha_{i(I_h)}^{n1} D_l^{nm}(\omega) \alpha_{i(O_h)}^{m\tau}, \quad (4)$$

where,  $g \equiv \sum S_{i(I_h)}^1$  is named molecular form factor, and  $D_l^{nm}(\omega)$  is Wigner matrix.<sup>9</sup> Obviously, both the molecular symmetry and the crystal site symmetry are taken into account in the RF. For  $l = 6, 10$  and considering relation between the coefficients, we have  $U_6^a = U_6^+ = -U_6^-$ ;  $U_{10}^a = U_{10}^+ = U_{10}^-$ .

Total potential of the system performs by summing up all the atom-atom interactions and all the charge-charge interactions on different  $C_{60}$ :

$$V_{\text{total}} = \frac{1}{2} \sum_{nn'} \left[ \sum_{\mu\mu'}^{60} V^{aa} + \sum_{\mu\mu'}^{60} V^{++} + \sum_{\mu\mu'}^{30} V^{--} + \sum_{\mu\mu'}^{60,30} V^{+-} + \sum_{\mu\mu'}^{30,60} V^{-+} \right]. \quad (5)$$

We notice there are 11700 terms in the square bracket per pair of molecules. For conventional sake, we expend each term, separately, in their own RFs in reciprocal space. That is

$$V_{\text{total}} = \frac{1}{2} \sum_{\mathbf{q}} \sum_{ll'} \sum_{\tau\tau'} \sum_{AA'} J_{ll'}^{\tau A, \tau' A'}(\mathbf{q}) U_l^{\tau A}(\mathbf{q}) U_{l'}^{\tau' A'}(-\mathbf{q}), \quad (6)$$

where  $A, A' \in \{a, +, -\}$ ,  $\tau, \tau'$  are representations of  $O_h$  group,  $J(\mathbf{q}) = \sum_{\mathbf{k}}^{12} J(\mathbf{k}) \cdot \cos[\mathbf{q} \cdot X(\mathbf{k})]$ , due to twelve nearest neighbors per  $C_{60}$  molecule, and  $J_{ll'}^{ij}(\mathbf{k}) = \sum_{AA'} g_i^A g_{l'}^{A'} v_{ll'}^{iA, jA'}$

$$v_{ll'}^{iA, jA'}(\mathbf{n} - \mathbf{n}') = \int d\Omega_{\mu'} \int d\Omega_{\mu} V^{A, A'}(\mathbf{n}, \mu; \mathbf{n}', \mu') S_{i(O_h)}^{iA}(\Omega) S_{l'(O_h)}^{jA'}(\Omega_{\mu'}), \quad (7)$$

here,  $V = V_{\text{LJ}}, V_{\text{cl}}$  for LJ and Coulomb potentials, respectively. Using Eq. (7) to calculate the interaction matrix, we found Coulomb terms dominate in mode  $T_{2g}^{(3)}$  of  $l=10$ .

The crystal field is defined as the field experienced by a center molecule when its neighbors are taken into spherical approximation. The center molecule is described by unity representation, and the neighbors by  $A_{1g}$  symmetry of  $O_h$  group, i. e.

$$V^{\text{CF}}(\mathbf{n}) = \sum_{\kappa}^{12} \sum_{\sigma} \sum_{\sigma'} J_{0l}^{1A, \sigma}(\kappa) U^{A, \sigma}(\mathbf{n}). \quad (8)$$

Firstly, we know that Coulomb interactions should not be influent to the mean field because  $C_{60}$  is a charge-neutral molecule. Secondly, comprising  $l=6$  and  $l=10$  for LJ potentials, we find  $l=6$  is dominant, and  $l=10$  can be neglected.

With Eqs. (6)–(8), we calculate the phase transition temperature. In molecular field approximation the free energy for an orientationally disordered is expended in terms of powers of the orientational order parameter. Then the second term of the free energy is given<sup>5</sup> by

$$F^{(2)} = \frac{1}{2} \sum_{\mathbf{q}} \sum_{i'j'} \sum_{ij} \left[ T \left( \chi_i^{(2)} \right)^{-1} \delta_{i'j'} \delta_{ij} + J_{i'j'}^{ij}(\mathbf{q}) \right] U_i^i(\mathbf{q}) U_{i'}^{j'}(-\mathbf{q}). \quad (9)$$

The energy is mainly from the coupling of orientation-orientation of neighbour molecules. After we get the coupling between the same orientational modes on different  $C_{60}$ , and average it under the crystal field, we obtain

$$\chi^{(2)} = \left\langle [U_{10}^i]^2 \right\rangle_{\text{CF}} \equiv (Z^{-1}) \int d\Omega [U_{10}^i]^2 \exp(-V^{\text{CF}}/T), \quad (10)$$

where  $Z = \int d\omega \exp(-V^{\text{CF}}/T)$ . The orientational transition occurs when  $F^{(2)}$  vanishes:

$$T_c = -J^{ii} \chi^{(2)}(T_c). \quad (11)$$

By graphic solution of the equation, we obtain  $T_c = 243$  K (see Fig. 1), which is very close to the experimental result.<sup>8</sup>

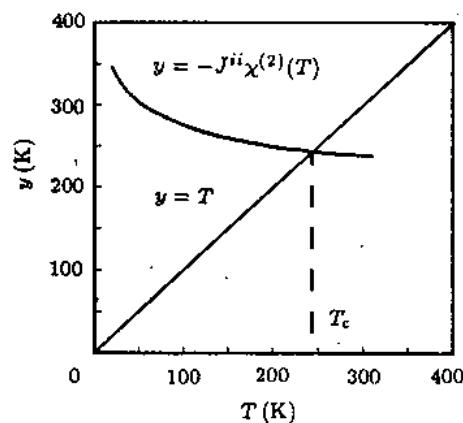


Fig. 1. Graphic solution of the equation  $T_c = -J^{ii} \chi^{(2)}(T)$ .

Recently, studies on orientational transition have been stimulated since the discovery of condensed  $C_{60}$ -based materials. This paper deals with orientational phase transition in pristine solid  $C_{60}$ . As conclusions and discussions we have:

(1) The interactions between molecules in molecular crystals can be generally modeled by van der Waals potentials, but it is not sufficient in  $C_{60}$ -based systems. The shortest distance of two atoms on neighbor  $C_{60}$  is almost the same as radius of  $C_{60}$  cage, so Coulomb interactions rise, and become dominant in orientational transition.

(2) For pristine solid C<sub>60</sub>, we found  $T_{2g}^{(3)}$  of  $l=10$  manifold of  $O_h$  group is active mode when the transition occurs. Disappearing of the coupling between them results in the order-disorder transition. This mode is mainly driven by Coulomb interactions, it is different to that only LJ potential involved, and the transition temperature is closer to experiments.

(3) The calculation error is mainly from the ignorance of deformation of molecule and distortion of fcc lattice when mean field was considered, also from neglecting of orientational coupling between  $l=6$  and  $l=10$  in calculation of free energy.

(4) It is suggested that RF be suitable for description of orientational transitions in C<sub>60</sub>-based materials. RFs can be used to express crystal field and orientational coupling. This method is expected to deal with alkali-doped C<sub>60</sub> and other fullerenes.

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