A one-dimensional Ising model for C_{70} molecular ordering in C_{70}-peapods

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Abstract. A description using the Ising model is proposed for the C_{70} molecular orientational ordering in C_{70} one-dimensional crystals formed inside single-wall carbon nanotubes (SWNTs). It is shown that the observed standing and lying alignments can be deduced naturally from the present Ising model where the SWNT diameter effectively changes the 'effective field' acting on C_{70} molecules. The thermal expansion of the C_{70} intermolecular distance is well described by this model. The possibility of antiferro-orientational ordering is also suggested.

It is well known that many kinds of guest atom or molecule can be encapsulated in one-dimensional (1D) cavities of single-wall carbon nanotubes (SWNTs) [1]–[4]. Such materials confined within nanometre-size spaces are expected to show novel properties that cannot be observed in the bulk materials. In the case of C_{70}-peapods where the 1D arrays or crystals of C_{70} molecules are formed inside SWNTs, a previous x-ray diffraction (XRD) study [5] clarified that the molecular orientational order, related to the elongated molecular shape, is gradually destroyed with increasing temperature. This behaviour is quite different from the cases in three-dimensional (3D) C_{70} crystals, where C_{70} orientational transitions [6]–[8] occur successively at 280 and 340 K, and is assigned to the 1D nature of the C_{70} crystals. In the present work, we propose an Ising model for the molecular orientational ordering in C_{70}-peapods.

XRD [5] and electron diffraction [9] measurements on C_{70}-peapods showed that the C_{70} molecules inside SWNTs are dominantly aligned parallel or perpendicular to the tube axis, as illustrated in figure 1. These orientations are called lying or standing, respectively. Therefore, we introduce a variable to describe the orientation of the ith C_{70}; $\sigma_i = 1$ for the standing ones and -1 for the lying ones. The interaction energies of the nearest-neighbour C_{70} pair $\langle i, j \rangle$ are
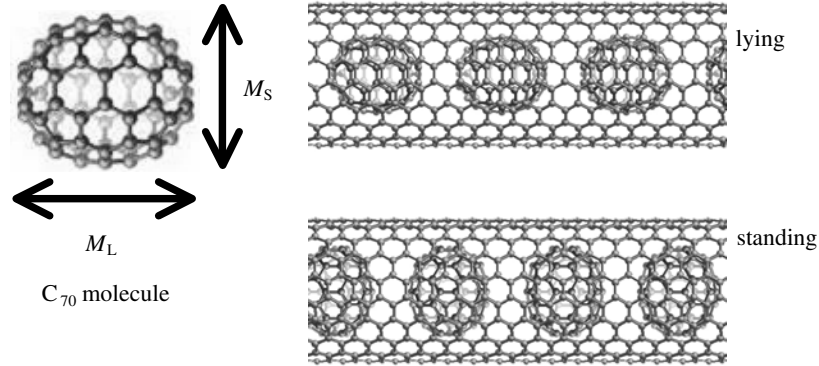
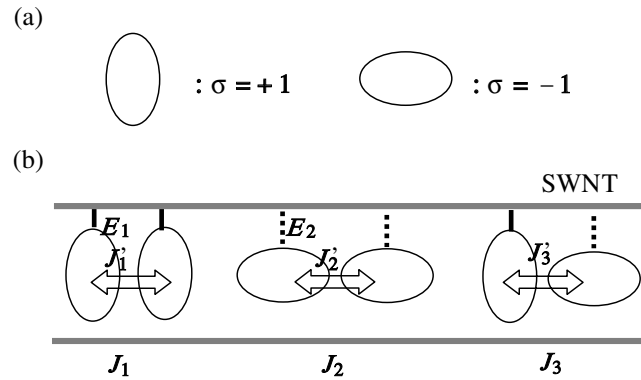**Figure 1.** Schematic illustrations of a C_{70} molecule, and standing and lying C_{70}s inside SWNTs.

Figure 2. 'Definitions' of the orientational variable σ, inter-C_{70} interaction, and C_{70}–SWNT interactions. The ovals represent C_{70} molecules.

defined as in figure 2: J_1' for the standing pair, J_2' for the lying pair, and J_3' for the standing–lying pair. Furthermore, the interaction between the standing (or lying) C_{70} and the wall of the SWNT is given by E_1 (or E_2).

Then, the interaction energy of the nearest-neighbour pair $\langle i, j \rangle$ is written as

$$J_1'\tfrac{1}{4}(\sigma_i + 1)(\sigma_j + 1) + J_2'\tfrac{1}{4}(\sigma_i - 1)(\sigma_j - 1) - J_3'\tfrac{1}{4}(\sigma_i + 1)(\sigma_j - 1) - J_3'\tfrac{1}{4}(\sigma_i - 1)(\sigma_j + 1)$$
$$+ E_1\tfrac{1}{2}(\sigma_i + 1) - E_2\tfrac{1}{2}(\sigma_i - 1) + E_1\tfrac{1}{2}(\sigma_j + 1) - E_2\tfrac{1}{2}(\sigma_j - 1).$$

Summing up all the pair $\langle i, j \rangle$s and defining the effective interaction energies as

$$J_1 = J_1' + E_1, \qquad J_2 = J_2' + E_2, \qquad J_3 = J_3' + (E_1 + E_2)/2,$$

we obtain the total Hamiltonian:

$$H = -\sum_{\langle i,j \rangle} \frac{-(J_1 + J_2 - 2J_3)}{4}\sigma_i\sigma_j + \frac{1}{2}(J_1 - J_2)\sum_i \sigma_i + \frac{J_1 + J_2 + 2J_3}{4}N$$
$$\equiv -J\sum_{\langle i,j \rangle}\sigma_i\sigma_j - H_e\sum_i \sigma_i + \text{constant}, \tag{1}$$

where N is the number of C_{70} molecules in the 1D crystal. This formula is equivalent to that of the Ising model for spin $S = 1/2$ with a coupling constant J in an effective field H_e:
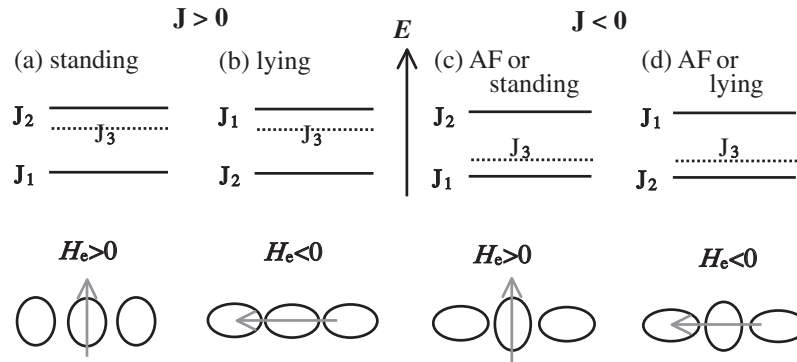
Figure 3. Possible energy scales and ground states. The arrows show the directions that the effective fields tend to align along the long axes of C_{70} molecules.

$$J \equiv \frac{-(J_1 + J_2 - 2J_3)}{4} = \frac{-(J_1' + J_2' - 2J_3')}{4},$$

$$H_e \equiv \frac{(J_2 - J_1)}{2} = \frac{J_2' - J_1' + E_2 - E_1}{2}. \tag{2}$$

From the above equations (1) and (2), we find that there are several cases for the C_{70} ordering, as summarized in figure 3:

(i) For $J > 0$, 'ferro-orientational (FO) ordering' appears at $T = 0$ K, with standing FO ordering for $J_2 > J_1$ and lying FO ordering for $J_2 < J_1$.

(ii) On the other hand, for $J < 0$ antiferro-orientational (AFO) ordering is favourable, but the effective field tends to stabilize the standing or lying orientation.

Here, it should be emphasized that H_e is determined by both the C_{70}–C_{70} interaction and the C_{70}–SWNT interaction, whereas J is primarily determined by the C_{70} intermolecular interaction and independent of the tube diameter within the present model. Therefore, H_e can be changed by changing the tube diameter, keeping J constant. Thus, the standing or lying alignments can be determined by the tube diameter, as observed. Tentatively we assume $J > 0$ and $J_1' < J_2'$, for which the standing FO ordering is energetically favourable. Even in this case, however, the interaction between the C_{70} and the wall of the SWNT can also stabilize the lying FO ordering, as well as the standing ordering. The lying ordering would occur for thin and too thick SWNTs. In these tubes, E_1 may be much higher than E_2, because the potential energy is minimized at the appropriate distance between the C_{70} molecule and the wall of the SWNT. Similar comments are also possible for $J < 0$. However, another interesting situation appears for $H_e \approx 0$ in this case; the 'AFO' state, which has not yet been observed, could be observed.

Now, we discuss the thermal expansion of the C_{70} intermolecular distance in the C_{70} standing alignment. The average lattice expansion Δa is given by

$$\Delta a = \alpha_g T g(0) + (M_L - M_S)N_-/N, \tag{3}$$

where M_S, M_L, and $g(0)$ are the mean lengths of the short and long axes of the molecules, and the intermolecular gap at $T = 0$ K, respectively. The first term describes the thermal expansion
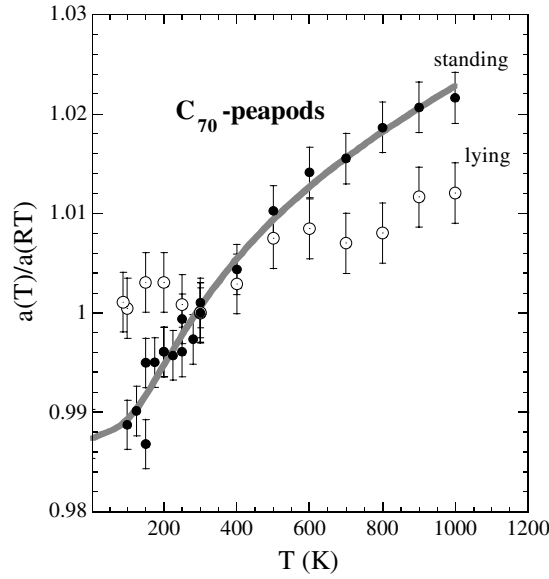
Figure 4. Thermal expansion of the C_{70} intermolecular distance. The solid curve is a fit with equation (5). The data were taken from [5].

of the intermolecular distance and the coefficient α_g is approximated as the value for the solid C_{60}, $\sim 5.4 \times 10^{-5}$ (K^{-1}). N_- is the number of the lying C_{70} molecules, and is given by

$$\frac{N_-}{N} = \frac{1}{2}\left(1 - \frac{\sum \sigma_i}{N}\right). \tag{4}$$

Thus, we have

$$\Delta a = g(0)\alpha_g T + \frac{1}{2}\left(1 - \frac{\sum \sigma_i}{N}\right)(M_L - M_S). \tag{5}$$

For this 1D Ising model the exact solution is well known:

$$\frac{\sum_i \sigma_i}{N} = \frac{e^{2K} \sinh L}{\sqrt{1 + e^{4K} \sinh^2 L}}, \qquad \text{with } K \equiv \frac{J}{k_B T} \quad \text{and} \quad L \equiv \frac{H_e}{k_B T}. \tag{6}$$

Inserting this equation into equation (5), we have the thermal expansion of the C_{70} intermolecular distance. Fitting the equation to the observed lattice expansion [5] makes it possible to estimate the magnitudes of J and H_e. However, equation (5) must be slightly modified before fitting to the observed data; the factor $1/2$ is replaced by $1/3$ in order to explain the high temperature thermal expansion ($T \to \infty$), where N_-/N should be $1/3$. This is due to the limitation of the present Ising model. In the actual system, there are two possible standing directions with respect to the tube axis.

The result of the fitting is fairly good, as demonstrated in figure 4 with the parameters

$$J/k_B = -21 \pm 29 \text{ K} \qquad \text{and} \qquad H_e/k_B = 282 \pm 53 \text{ K}.$$

These parameters imply that the observed standing FO alignment is dominantly stabilized by the effective field H_e. However, because the effective coupling J may be negative, the AFO ordering may be realized by choosing the tube diameter such that $H_e \approx 0$.

Here, we should compare the present fit with the previous one [5] with a phenomenological equation with an activation energy E_0. The results of the two fits are almost identical in spite of the different parameters and functions. This is because the present fitting function is more general than the previous one, and it is reduced to a function similar to the previous one for the parameters obtained. Therefore, the present analysis can be taken as the microscopic grounds for the previous phenomenological treatment.

In summary, it was shown that the 1D Ising model successfully describes the observed behaviours of the C_{70} orientational alignment inside SWNTs. The C_{70} orientational order cannot be realized at finite temperatures owing to the 1D nature of the C_{70} crystals inside SWNTs as experimentally observed, although the 'effective field' tends to stabilize the standing or lying C_{70}. Numerical estimations of the interaction energies from a microscopic point of view and using a more sophisticated treatment taking account of the continuous rotational freedom have not yet been performed. Although these works are left for the future, we believe that the Ising model is the simplest and most useful model to use to extract the essence of the orientational behaviours inside SWNTs. The present method or similar treatments, therefore, can be applied to other interesting systems, such as metal–fullerene peapods where 1D crystals of metal-encapsulating fullerene molecules with magnetic and/or electric dipole moments are formed inside SWNTs.

Acknowledgments

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