===== **POLYMERS** =====

Habit of Long-Chain Molecular Crystals

V. M. Egorov* and V. A. Marikhin

Ioffe Institute, Russian Academy of Sciences,
Politekhnicheskaya ul. 26, St. Petersburg, 194021 Russia
*e-mail: victor_egorov1@inbox.ru
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Abstract—The quantitative analysis of the temperature dependence of the heat capacity of molecular crystals with chains of different lengths was performed using the theory of diffuse first-order phase transitions. The same chemical structure of the "core" of molecular crystals of $\{CH_3(CH_2)_nCH_3\}$ normal paraffins, $\{COH(CH_2)_nCOH\}$ diols, $\{CH_3(CH_2)_nCOH\}$ normal alcohols, and $\{CH_3(CH_2)_nCOOH\}$ saturated carboxylic and $\{COOH(CH_2)_nCOOH\}$ dicarboxylic acids enabled the comparative analysis of phase transition parameters.

Long-chain molecular crystals are convenient model objects for the solution of such discussion problems as the effect of the length of a chain and the type of terminal groups on the feature of structure formation in the process of crystallization and the conformation transformations during phase transitions due to their monodispersion and the absence of chemical defects. Studies on long-chain molecular crystals become especially important in comparison with convenient polydisperse and chemically defective polymers for the establishment of quantitative generalizing regularities in the relation between structure and properties. This work continues the series of papers devoted to studying the effect of the type of terminal groups on the structure and properties of molecular crystals.

The structure and properties of long-chain molecular crystals have been studied to a different extent. The simplest long-chain molecular crystals are *n*-paraffins. The structure and many properties of *n*-paraffins depend on the number *n* of $-CH_2-$ groups in the methylene chain. In particular, the dependences on an even or odd value of *n* is typical for them [1−7]. The structure and properties are not as well studied for long-chain alcohols and diols as for *n*-paraffins [8−13], and much worse studied for carboxylic and dicarboxylic acids [14, 15]. It has been established that the above listed molecular crystals have the same lamellar supramolecular structure with an orthorhombic or monoclinic crystal unit cell for odd or even *n*, respectively.

Since the "core" of molecular crystals is formed by methylene chains of the same repeating $-CH_2-$ groups, these compounds are of interest due to the possibility of clarifying the effect of terminal groups on the structure and properties of crystals, as they imple-ment a certain order of strengthening in the interaction between terminal groups from van der Waals interaction forces ($-CH_3$ groups of paraffins and alcohols) to the so-called "specific" interaction with the formation of ordinary and double hydrogen bonds ($-COH$ groups for alcohols and diols and $-COOH$ groups for carboxylic acids). Terminal hydroxyl groups are located on the basal planes of lamellar crystals to form two-dimensional layers and extended "polymeric" chains of hydrogen bonds. This leads to a considerable increase in the frontal surface energy of these crystals and, as a consequence, to a change in their thermophysical characteristics. At the same time, these molecular crystals must lose their individual properties and evolve into polyethylene upon the quantitative multiplication of repeating $-CH_2-$ groups.

It is known that thin films and fine particles of inorganic materials are observed to exhibit the so-called phase size effect, i.e., the dependence of thermophysical characteristics on the thickness of a film of the characteristic size of particles [16−18]. Distinctions in the phase states of fine particles are due to different intrinsic causes, between which a certain interrelation exists. The formation and stabilization of phases, which are not observed at all in particles of large sizes, can occur in some cases. In particular, the size effect can be exhibited as a shift in the temperatures of phase transitions, including melting. This temperature shift (ΔT) depends on several factors and is determined in the general form as $\Delta T/T_0 = \gamma K/\Delta H \rho R$, where γ is the surface energy, ρ is the crystal density, ΔH is the transition enthalpy, R is the characteristic size of a fine particle or the thickness of a thin film, K is the shape coefficient, and $\Delta T = T_0 - T_m$,
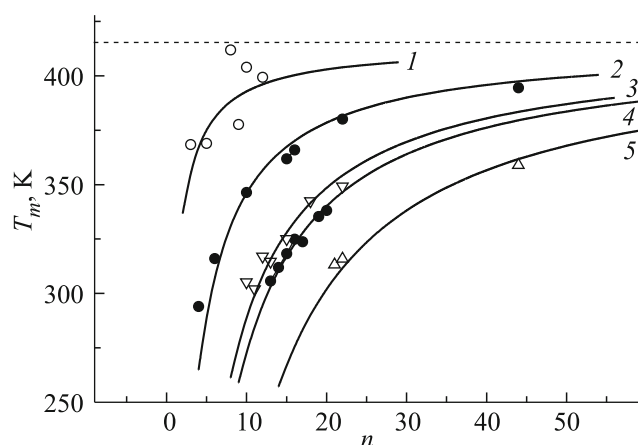
Fig. 1. Melting temperature T_m versus number n of methylene $-CH_2-$ groups for (*1*) dicarboxylic acids, (*2*) diols, (*3*) carboxylic acids, (*4*) alcohols, and (*5*) paraffins.

where T_0 and T_m are the temperature of a phase transition in a bulk material and a fine particle, respectively.

A similar relationship

$$T_m = T_0[1 - 2\gamma_1/\Delta H_0 \rho L_0], \qquad (1)$$

called the Thomson−Gibbs equation was introduced in [19, 20] and is widely used to study the melting and crystallization of lamellar polymeric crystals, in particular, polyethylene. In this case, the lamella thickness (L_0), the frontal surface energy (γ_1), and the melting enthalpy and temperature (ΔH_0 and T_0, respectively) of an equilibrium infinite crystal are used as a size parameter. For polyethylene, $\Delta H_0 = 290$ J/g and $T_0 = 414.5$ K [21]. The side surface energy (γ_2) is neglected here, as the frontal surface area is much larger than the side surface area at rather great transverse sizes of a lamella.

Molecular crystals straddle the features of both fine particles, for which the phase size effect is observed, and a "polymeric" supramolecular structure with a nanosized thickness of lamellae. As can be seen from Fig. 1, the melting temperatures of different molecular crystals based on a methylene $-CH_2-$ chain can satisfactorily be fitted by the curves $T_m = 414.5(1 - A/L)$. Here, L_0 is the thickness of an individual lamella and equal to $0.1273n$, where n is the number of carbon atoms in a molecular chain, and 0.1273 nm is the value of C−C bond projection onto the axis of a molecule [22−30]. The dimensionless parameter A is 0.95 for dicarboxylic acids, 2.25 for diols, 4.15 for carboxylic acids, 4.68 for alcohols, and 7.3 for paraffins. From the Thomson−Gibbs equation, a common nature of molecular crystal cores ($\Delta H_0 \sim$ const $= 290$ J/g), and a close densities ($\rho \sim 1$ g/cm³) it follows that the surface energy (γ) is the parameter, which has an effect on the melting temperature of molecular crystals with comparable lengths. However, it can be seen from the data obtained for the parameter A that an apparent decrease

in the surface energy of molecular crystals with comparable lengths occurs instead of an expected increase in the surface energy with an increase in the interaction between terminal groups from van der Waals interaction forces to the so-called "specific" interaction with the formation of ordinary and double hydrogen bonds. This conclusion follows from the hypothesis that the crystal structure of molecular crystals is formed by individual lamellae. If lamellae overlap each other to retain a long-range crystal order and form a macrocrystal, the observed effect can be explained by a discrepancy between the individual lamella thickness L_0 used to perform the calculation by the Thomson−Gibbs equation and construct the plot in Fig. 1 and the actual macrocrystal thickness $L*$, which exceeds L_0 by several times. In this case, the relative change of $L*$ in the series of molecular crystals of paraffins (L_1^*), alcohols (L_2^*), carboxylic acids (L_3^*), diols (L_4^*), and dicarboxylic acids (L_5^*), which are arranged in the order of increasing cohesion energy of their terminal groups, will be inversely proportional to the parameter A. Taking the minimum surface energy from this series as unit, we obtain the following order of $L*$ values: $L_1^* = 1$, $L_2^* > 1.5$, $L_3^* > 1.7$, $L_4^* > 3.0$, and $L_5^* > 6.9$. Hence, the use of the Thomson−Gibbs equation for molecular crystals requires the real thicknesses $L*$ of effective macrocrystals representing stacks of lamellae to be estimated in addition to the surface energy.

It has been mentioned above that the formation and stabilization of phases, which are not observed at all in bulk materials, can be observed in fine particles in some cases. Really, when considering lamellar formations of molecular crystals based on a methylene $-CH_2-$ chain as fine particles and high-molecular polyethylene as a related, but bulk material, they can be revealed to exhibit a distinction in the phase transition from a crystalline state to a melt. As follows from the data [22−30], melting in molecular crystals represents in many cases a two-stage process incorporating the first-order solid-phase structural transition from an orthorhombic structure to a pseudohexagonal liquid-crystal structure, which sustains a second-order order−disorder phase transition under heating in a certain temperature interval and turns into a melt. The existence of an intermediate phase within a temperature range $T_{max1}-T_{max2}$ between the first-order solid-phase transition and melting itself is comprehensively illustrated by curves *1−3* in Fig. 2. At the same time, polyethylene melting is calorimetrically detected as a single unsymmetric peak with a rather smeared low-temperature shoulder (curve *4*). The existence of a low-temperature shoulder for partially crystalline polyethylene is explained by the unfreezing of mobility in the amorphous regions of polymer. As the degree of crystallinity grows, e.g., upon orienta-
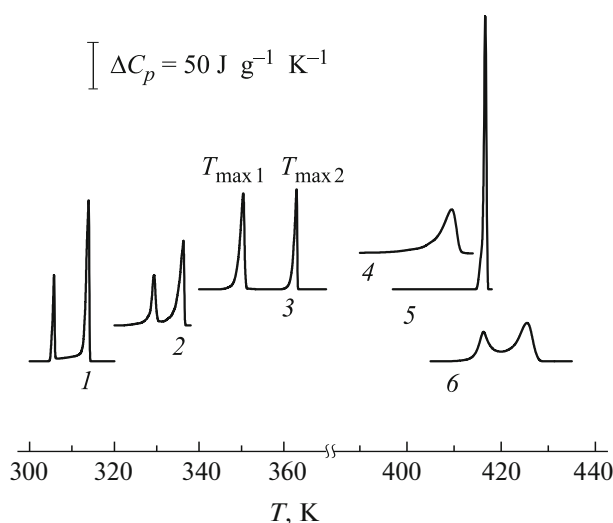
Fig. 2. DSC curves obtained under heating (1.25 K/min) within a melting temperature range of the samples of (*1*) paraffin ($n = 21$), (*2*) alcohol ($n = 19$), (*3*) diol ($n = 15$), (*4*) polyethylene with a lamellar supramolecular structure, (*5*) polyethylene fibers (stretching degree $\lambda \sim 100$), and (*6*) polyethylene fibers with fixed ends.

Fig. 3. Elementary volume ω versus the number n of carbon atoms in a chain for (*1*) paraffins, (*2*) alcohols, (*3*) diols, and (*4*) acids.

tion, the low-temperature shoulder becomes less smeared, and the melting peak takes a more symmetric shape (curve *5*). As a rule, no fine structure of the peak can be observed, even in a superoriented state of polymer, without external effects, though it is stated [31] that two thermodynamic potential minima and, correspondingly, two stable states, each of which is thermodynamically stable, exist in the transition region. The peak can be observed to split only under an external effect, when a sample of strongly oriented fibers is heated with fixed ends (Fig. 2, curve *6*).

The existence of a first-order solid-phase structural transition in molecular crystals as a melting component enables the analysis of the formation of new phase "nuclei." Such an analysis has been performed in [22–30] using the self-consistent field theory as a basis. The main idea of this theory consists in that the localization of fluctuations in the volume of an old phase occurs upon phase transition in the form of stable new phase nuclei. The volume of a new phase increases by small portions. As a transition develops, elementary volumes of new phase nuclei, i.e., so-called elementary transition volumes (ω), are sequentially added to the new phase at interphase boundaries. It seems that this must occur in interphase boundary regions with the lowest surface energy, and such regions in the case of molecular crystals are the side surface of lamellae. If an elementary volume is localized within a single lamella, the phase transition in a crystal will more easily occur via the addition of new volumes inside this lamella. When an elementary volume contains molecules from several lamellae, the phase transition in a crystal will more easily occur via
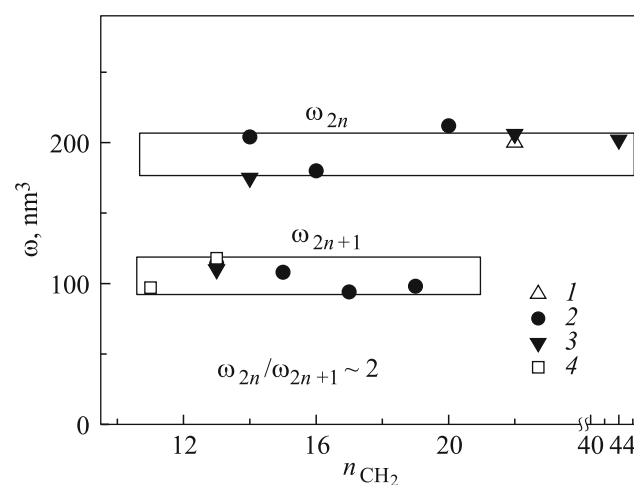
the addition of new volumes inside these several lamellae. Hence, the geometric parameters or habit of a "nucleus" will govern to a considerable extent the thickness of an effective macrocrystal, i.e., a stack of lamellae.

The data [22–30] on the elementary transition volumes (ω) of different molecular crystals as a function of the number of carbon atoms in a chain n are plotted in Fig. 3. It has turned out that the values of ω for a rather wide variation range of $n \sim 8$–40 fall into two volume value regions of 100 and 200 nm^3, which correspond to odd and even values of n. The comparison of the obtained values of ω with the volume occupied by a single molecular crystal molecule [32] shows that the elementary transition volumes in the first-order transition region contain ~400 and ~200 molecules, i.e., the transition region covers a rather broad domain.

The revealed dependence on even-odd n seems to be due to different structure of a unit cell, which is orthorhombic with arrangement of molecules along the axis of a macrocrystal at odd n and monoclinic with inclined arrangement of molecules with respect to the axis of a macrocrystal at even n. In the latter case, the axes of molecules change their positions upon the overlapping of lamellae and the formation of a macrocrystal to constitute an angle repeated on the two following lamellae, i.e., the elementary volume of a "brick" composing a macrocrystal is doubled (the unit cell of a macrocrystal is transformed in this case in a more complicated fashion) [7].

To determine the geometric parameters or habit of a "nucleus," let us consider the simpler case with odd n. The generally accepted habits of crystals of the same volume are schematized in Fig. 4 [32]. The equilib-
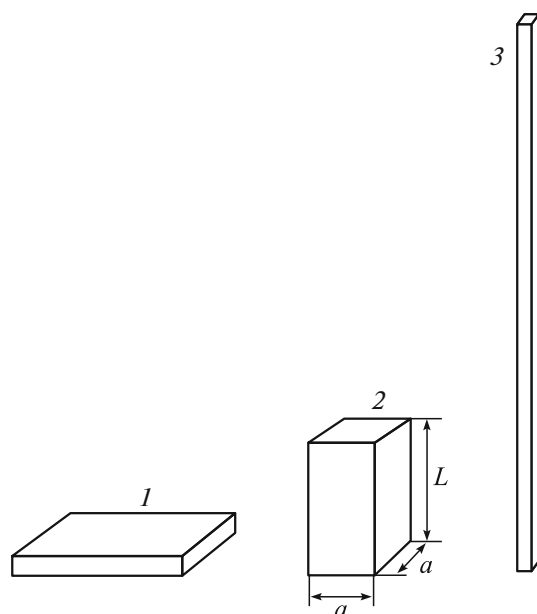
Fig. 4. Crystal habit: (*1*) lamellar, (*2*) prismatic, and (*3*) fibrillar [32].

rium shape of a crystal can be determined from the Gibbs equation

$$\sum \gamma_i S_i = 2a^2 \gamma_1 + 4aL\gamma_2, \qquad (2)$$

where each individual face has its own index *i*, S_i is the surface area of this face, and γ_i is its surface energy. Summation is performed over all the faces of a crystal. It should be noted that the side surface energies in the case of an orthorhombic crystal lattice coincide only for two opposite faces. However, the surface energy is proportional to the bond energy [33], and the latter in molecular crystals represents a part of the cohesion energy of repeating $-CH_2-$ groups building all the side surfaces. For this case, it is possible to consider γ_i as equal for all the side surfaces in the first approximation and further use only the frontal (γ_1) and side (γ_2) surface energies.

The surface energy of a crystal in a stable state must be minimal and, for this reason, differentiating Eq. (2) with respect to the parameter *a* or *L* and setting the derivative to zero, we obtain the relationship

$$L = \omega^{1/3}(\gamma_1/\gamma_2)^{2/3}, \qquad (3)$$

where $\omega = a^2 L$ is the elementary transition volume.

From Eq. (3) it follows that the parameter *L* depends on the ratio between the frontal and side surface energies, i.e., the ratio γ_1/γ_2 determines the shape of habit of a new phase "nucleus." A further increase in the volume of a new phase, as mentioned above, will more easily occur via the addition of new volumes to a side surface. This growth will occur until the appearance or accumulation of hindrances on the side surface with an increase in the side surface energy to such

a level that the growth through the frontal surface will be more profitable.

To perform the quantitative estimation of the parameter *L*, it is necessary to calculate the ratio γ_1/γ_2. As mentioned above, the surface energy is proportional to the energy of bonds between structural units [33], and such bonds in the case of molecular crystals are intermolecular interaction forces (IMFs). They are the forces of van der Waals interaction between $-CH_2-$ groups for the side surfaces of an elementary volume of all the considered molecular crystals. These forces also represent van der Waals interaction forces for the frontal surfaces of paraffins and alcohols ($-CH_3$ groups) and the forces of so-called "specific" interaction with the formation of ordinary and double hydrogen bonds for alcohols and diols ($-COH$ groups) and carboxylic and dicarboxylic acids ($-COOH$ groups). The quantitative measure of IMFs is the cohesion energy E_c defined as the energy required for the destruction of intermolecular contacts and the transition of a solid through a liquid state into a gas phase. A decrease in the intermolecular interaction energy during a phase transition occurs due to a partial decrease in the cohesion energy ΔE_c. The experimental estimation of this decrease for the compounds consisting of multiatomic molecules is difficult. ΔE_c can be compared with the potential barrier of the motion of a molecule in local liquid-like acts of motion in a solid. The value of this barrier determined experimentally for glassy liquids and solid oligomers, which radically differ from each other by the character of IMFs, the structure and shape of molecules, including compounds with a developed network of hydrogen bonds, attains ~$0.4E_c$ [34].

The parameter E_c can experimentally be determined only for low-molecular bodies able to exist in a gas phase. For the majority of oligomers, polymers, and molecular crystals, vaporization follows the destruction process, so the cohesion energy is determined for them in an indirect way or calculated [34, 35]. The cohesion energies given in the monography [35] for the contributions from $-CH_2-$groups $E_{c1} = 3.6$ kJ/mol, $-CH_3$ groups $E_{c2} = 4.14$ kJ/mol, the hydrogen bond of $-COH$ groups $E_{c3} = 13.4$ kJ/mol, and the double hydrogen bond of $-COOH$ groups $E_{c4} = 26.8$ kJ/mol are used in this work.

The dependence between the surface energy and the cohesion energy change enables Eq. (3) to be written in the following form:

$$L = \omega^{1/3}(E_{cn}/E_{c1})^{2/3}, \qquad (4)$$

where E_{c1} and E_{cn} are the cohesion energies of a methylene group and terminal groups, respectively. The calculation of the parameter *L* for paraffins (L_1), diols (L_2), and dicarboxylic acids (L_3) gives the following relationships: $L_1 = 1.1\omega^{1/3}$, $L_2 = 2.4\omega^{1/3}$, and $L_3 = 3.8\omega^{1/3}$. Using these relationships, it is possible to

determine the number of lamellae participating in the formation of an elementary volume. Thus, this gives 2 lamellae for a paraffin ($n = 21$), 6 lamellae for a diol ($n = 15$), and 15 lamella for a dicarboxylic acid ($n = 9$). When comparing the ratio $L_1/L_2/L_3 = 1/3/7.5$ with the ratio $L_1^* = 1$, $L_4^* > 3.0$, $L_5^* > 6.9$ obtained above from the Thomson−Gibbs equation, it can be seen that the habit of an elementary transition volume determined the thickness of a macrocrystal.

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