

# Phase Transitions in Molecular Crystals of the Paraffin Series: Heneicosane and Docosane

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

*Ioffe Institute, Russian Academy of Sciences, St. Petersburg, 194021 Russia*

\*e-mail: victor\_egorov1@inbox.ru

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**Abstract**—Comparative analysis of phase transition in normal paraffins, heneicosane ( $C_{21}H_{44}$ ) and docosane ( $C_{22}H_{46}$ ), was performed using differential scanning calorimetry. Elimination of methodical inaccuracies allowed obtaining proper values of the thermodynamic parameters of the phase transitions and revealing their nature. Quantitative analysis of the heat capacity steps was made based on the theory of blurred first-order phase transitions and Landau's theory for second-order phase transitions.

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## INTRODUCTION

Revealing the nature and evolution of phase transitions (PTs) in solids, including polymers and long-chain molecular crystals, is one of the most important fields of solid state physics. However, a substantial dispersion of characteristics of polymers on the molecular level and on different hierarchical levels of supra-molecular organization leads to a noticeable blurring of parameters characterizing PTs. This makes it difficult to reveal the nature of a PT and to find dependences of PTs on the polymer structure; therefore, analysis of experimental data based on present theories of first- and second-order phase transitions is impossible.

Studying PTs in crystals composed of chain molecules gives new possibilities for finding general quantitative laws of the correlation between structure and thermodynamic properties, since today the studies can be conducted with monodisperse homologous series of high-purity molecular crystals of different chemical nature. Homologous series of aliphatic hydrocarbons and their derivatives, including normal paraffins ( $C_nH_{2n+2}$ ), attract great interest.

Differential scanning calorimetry (DSC) is an effective method for investigating PTs that is widely used in studying molecular crystals of various types, including paraffins [1–5]. However, in most published works, methodical inaccuracies that arise due to the temperature lag in DSC measurements and can lead to significant distortions in the values of thermodynamic characteristics of the studied molecular crystals were not eliminated. Furthermore, DSC studies following heating–cooling cycles were usually not carried out and not analyzed. It is shown in this paper that these studies can reveal the nature of phase transitions

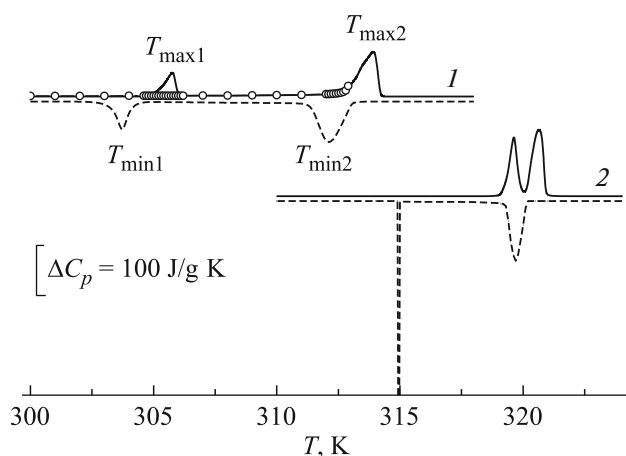
and obtain true profiles of endo- and exothermal peaks on the thermograms. The latter circumstance is very important for analysis of experimental data based on recently developed theories of blurred first-order phase transitions [6, 7] and second-order phase transitions [8].

## EXPERIMENTAL

Samples of heneicosane and docosane were purchased from Sigma. Thermal properties were investigated on a Perkin–Elmer DSC-2 calorimeter in the nitrogen atmosphere with the heating and cooling rates varied in the range from 5 to 0.3 K/min. The temperature scale was calibrated using the ice and indium melting points (273.1 and 429.7 K); the heat flow scale was calibrated using the heat capacity of leucosapphire. Measurements were carried out in the temperature range of 250–400 K. A small amount of a sample, 1–3 mg, provided the minimal thermal resistance of the calorimetric cell and diminished the methodical inaccuracies.

## RESULTS AND DISCUSSION

Figure 1 shows the DSC curves obtained by heating and cooling the samples of heneicosane and docosane. Evidently, the crystal-to-melt transition upon heating for both paraffins takes two stages: there is a doublet on the DSC curves with the maxima temperatures of  $T_{\max 1}$  and  $T_{\max 2}$ . The inverse process of changing the phase state from the melt back to the crystal upon cooling occurs also in two steps (the temperatures of minima of corresponding exothermal peaks are  $T_{\min 1}$  and  $T_{\min 2}$ ). Note that the shape of the



**Fig. 1.** DSC curves obtained upon heating (solid lines) and cooling (dashed lines) of (1) heneicosane and (2) docosane samples. Circles represent the dependence calculated by Eq. (1) (see text). The scanning rate is  $V = 1.25$  K/min.

endothermal peak of the transition from the crystal to the melt has its own peculiarities for both of the studied materials.

This behavior generally agrees with the results reported in published papers, and thus we can expect that the endothermal peak at  $T_{\max 1}$  upon heating is probably related to a phase transition in the solid state ( $T_{s-s}$ ), which is followed by melting at the temperature  $T_{\max 2}$ . An inverse pattern is observed upon cooling of the melt: crystallization at  $T_{\min 2}$  and solid-phase transition at  $T_{\min 1}$ .

To understand the physical nature of the transitions observed on the thermograms, the mismatch of the peaks should be explained: the relative positions of the endo- and exothermal peaks on the DSC curves in the heating and cooling cycles are shifted ( $T_{\max 1} - T_{\min 1}$  and  $T_{\max 2} - T_{\min 2}$ ). These shifts (hysteresis) turned out to have its own reason for each of the peaks in the doublet, which involve both methodical and physical reasons. It is known that methodical inaccuracies (shifts of the peaks) take place in DSC measurements due to the heat resistance of the studied sample in the calorimetric cell, which depends strongly on the sample mass and scanning rate [9]. The following method of eliminating this inaccuracy is proposed in [10]: experimental data obtained at varied scanning rates  $V$  (upon heating or cooling) are used to build the dependences  $T_{\max, \min} = f(V^{1/2})$ , which should be linear provided that no structural transformations occur. Extrapolation of the linear dependences to  $V \rightarrow 0$  allows obtaining proper transition temperatures that are not biased by an erroneous method.

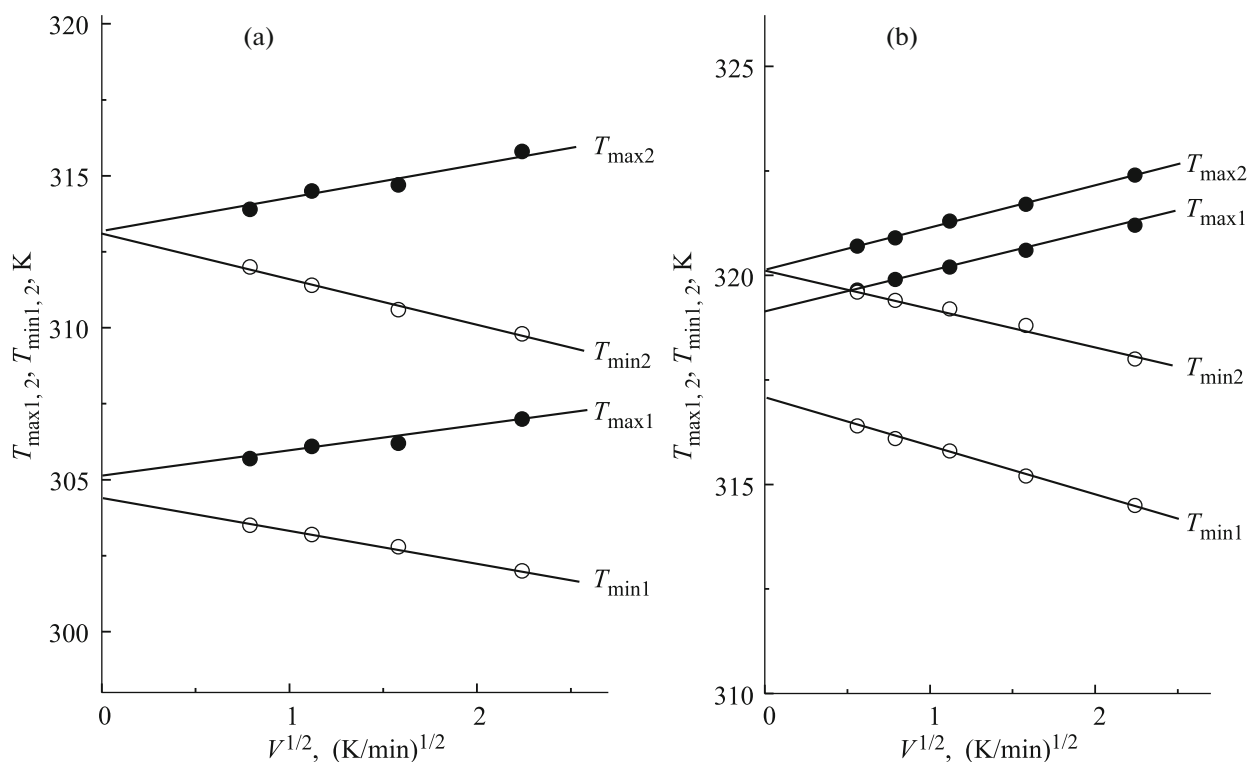
Figure 2 shows the dependences obtained by this algorithm for the studied samples of (a) heneicosane and (b) docosane in the heating–cooling cycles. The extrapolated (true) phase transition points derived

from these dependences are as follows: for heneicosane,  $T_{\max 1}^r = 305.1$  K,  $T_{\max 2}^r = 313.1$  K,  $T_{\min 1}^r = 304.6$  K, and  $T_{\min 2}^r = 313.1$  K; for docosane,  $T_{\max 1}^r = 319.4$  K,  $T_{\max 2}^r = 320.1$  K,  $T_{\min 1}^r = 317.0$  K, and  $T_{\min 2}^r = 320.1$  K. These data allow concluding that there is no hysteresis for the second extremums for the samples of heneicosane and docosane in the heating–cooling cycles; the observed difference in their positions on the experimental DSC curves is due to methodical reasons. At the same time, a hysteresis loop is revealed for the low-temperature transition from the extrapolated dependences that are free from the methodical inaccuracy.

Enthalpy  $\Delta H$  and entropy  $\Delta S$  in the DSC method are independent of the scanning rate and are defined by the expressions  $\Delta H_{\text{exp}} = \int C_p(T) dT$  and  $\Delta S_{\text{exp}} = \int C_p(T) d(\ln T)$ . The summary values of the enthalpy  $\Delta H_{\text{sum}}$  and entropy  $\Delta S_{\text{sum}}$  for the transitions in heneicosane were found to be 242 J/g and 0.781 J/g K; for docosane, 234 J/g and 0.794 J/g K.

Presence or absence of a temperature hysteresis in some physical property (including the peaks on the temperature dependence of the heat capacity) is known to be one of the criteria of first- and second-order phase transitions, respectively. Therefore, the absence of hysteresis for the second extremums points to the fact that the high-temperature peaks in the doublets correspond to the second-order transitions. If extrapolated dependence  $T_{\max, \min} = f(V^{1/2})$  were not used, and only data obtained at a single temperature scanning rate were used (Fig. 1), the high-temperature peaks would be erroneously ascribed also to the first-order phase transitions. On the other hand, the presence of a true hysteresis for the low-temperature DSC peaks allows ascribing this transformation to a solid-state (structural) first-order transition, connected with a change in the crystal symmetry type. It was shown earlier by X-ray diffraction [2, 11–13] that a symmetry change indeed occurs in the temperature range corresponding to the heat capacity peak at  $T_{\max 1}$ : the orthorhombic unit subcell is transformed into a hexagonal one in crystalline cores of lamellae.

Figure 1 shows that the exo-peaks of  $C_p$  for heneicosane and docosane, corresponding to the first- and second-order phase transitions, are distinctly separated on the temperature scale in the cooling cycle (transition from the melt to the crystal). On the other hand, in the heating cycle (transition from the crystal to the melt) corresponding endo-peaks can be either separated (heneicosane) or partially overlap (docosane), which noticeably limits accurate analysis in the latter case. If the first- and second-order peaks are separated on the temperature scale, then the solid-phase transition can be analyzed independently from the second-order transition. We developed an



**Fig. 2.** Dependence of the phase transition temperatures on the scanning rates for (a) heneicosane and (b) docosane. Dark circles correspond to heating; empty, cooling.

approach allowing experimental separating of overlapping peaks. To do this, we used the property of first-order transitions—temperature hysteresis, i.e., the difference between the true transition temperatures upon heating and cooling,  $\Delta T = T_{\max}^r - T_{\min}^r$ .

To separate the peaks for docosane, the experimental procedure presented in Fig. 3 was employed: the sample was heated to melt at  $T = 323$  K (curve 1), and then it was cooled passing through the exothermal peak at  $T_{\min 2}$  down to 316 K (curve 3). Thus an intermediate phase state was achieved, in which the first-order solid-state phase transition had not yet occurred, but the ordering due to the second-order transition had taken place. Heating from 316 K to the melt temperature (curve 2) in this case shows the “pure” second-order transition. The difference between the peaks on the first and second heating curves allows observing endothermal effects corresponding solely to the first-order phase transitions.

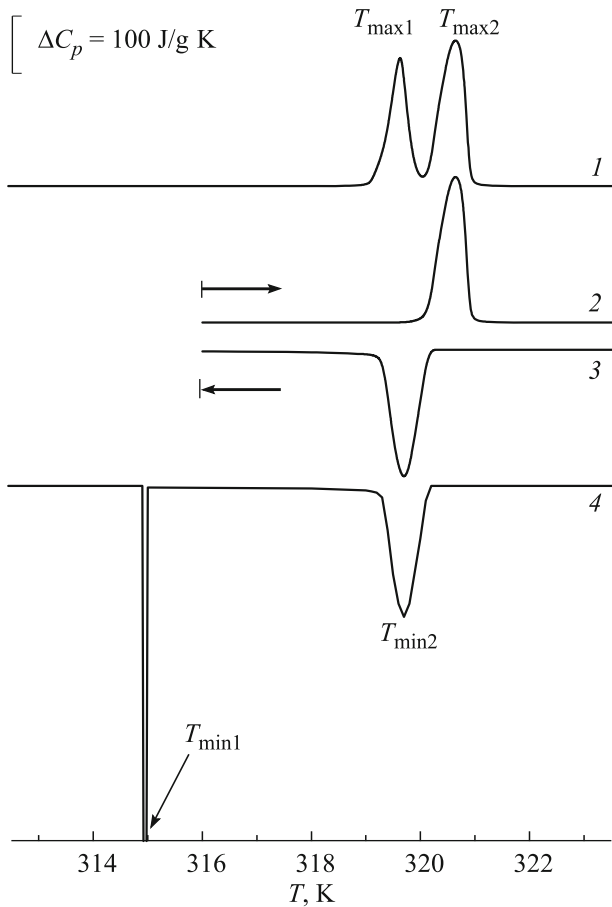
It was shown by Landau [8] that the peak of  $C_p$  for second-order PTs should have the shape of the Greek letter  $\lambda$ . This peak shape together with the abovementioned absence of the hysteresis effect is the specific feature of second-order transitions. The dependence of the heat capacity  $C_p(T)$  at  $T < T_{\max}$  should, in this case, be expressed by a power function of the type

$$C_p(T) = D(T_0 - T)^{-\alpha}, \quad (1)$$

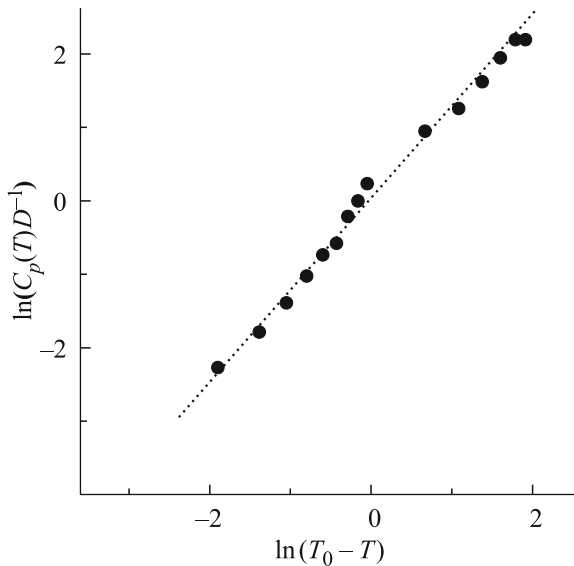
where  $D$ ,  $T_0$ , and  $\alpha$  are constants, and  $T_0$  is the proper temperature of the second-order PT.

The simplest way to check the agreement between experimental data and correlation (1) is building a plot in double logarithmic scale  $\ln(C_p D^{-1}) - \ln(T_0 - T)$ ; a linear dependence should result with the slope giving the value of the power  $\alpha$ . Figure 4 shows that experimental data for heneicosane correspond to a line with the slope of  $\alpha = 0.5$  with a high level of accuracy. In addition, circles on curve 1 in Fig. 1 represent the behavior of  $C_p$  calculated using Eq. (1) for the low-temperature part of the peak  $T_{\max 2}$ ; the best agreement is achieved with the parameters  $D = 9.5$ ,  $\alpha = 0.5$ , and  $T_0 = 313.0$  K. Since the calculated power dependence can be extended to the temperature range corresponding to the first-order phase transition, the peak shape of this PT can be clarified by subtracting the calculated dependence of  $C_p$  in the vicinity of  $T_{\max 1}$  from the experimental data.

Endothermal peaks corresponding to first-order structural phase transitions were thus reconstructed (Fig. 5). For docosane, this peak was found to be symmetrical, resembling a so-called  $\Lambda$ -shaped peak (Fig. 5b). For heneicosane, however, the peak was asymmetrical (Fig. 5a), which allows suggesting that it consists of at least two components. These peculiarities of the peak shapes are considered below.



**Fig. 3.** DSC curves for docosane samples obtained upon heating (1, 2) and cooling (3, 4).

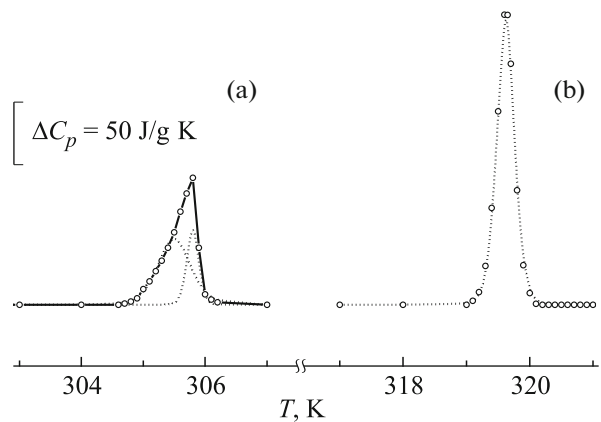


**Fig. 4.** Dependence  $C_p(T)$  for heneicosane in double logarithmic scale.

Analysis of peaks obtained by the abovementioned approach was conducted according to the thermodynamic theory of self-consistent field [6, 7, 14] applied to blurred  $\Lambda$ -shaped first-order phase transitions. The fact that the transition is blurred means that the phase state transformation occurs not suddenly but smoothly, within a certain temperature range. The theory analyzes the change in the phase state of a system of interacting particles of different phases, including nucleation and subsequent growth of stable nuclei of the new phase in the matrix of the initial phase. The nucleation mechanism is a heterogeneous one; the nuclei of the new phase appear at different defects in the crystals leading to appearing of an interface that is a characteristic property of the first-order PT. The basic idea of the theory is that multiple fluctuations are localized in a limited volume of the initial phase, which are stable nuclei of the new phase, so-called elementary transition volumes  $\omega$ . As the transformation develops, the interface moves by successive additions of the nuclei with the volume  $\omega$  to the arisen interface. Formation of the nuclei domains requires changing the temperature by a small value which depends on the energy necessary for appearing of these regions. This is what leads to the temperature blurring of the transition. For example, it was shown that elementary transition units in ferroelectrics have a size on the order of the so-called Kenzig areas ( $\sim 10^{-18} - 10^{-17} \text{ cm}^3$ ) and belong to the mesoscopic level [15, 16].

It turned out that the sizes of stable nuclei  $\omega$  can be determined from the shape of the  $C_p$  peaks corresponding to the first-order transitions. The temperature dependence of the heat capacity at a blurred phase transition was obtained in [17] in the following form:

$$\Delta C_p(T) = 4\Delta C_m \exp[B(T - T_o)/T_o] \times \{1 + \exp[B(T - T_o)/T_o]\}^{-2}, \quad (2)$$



**Fig. 5.** Endothermic peaks corresponding to solid-phase transitions in (a) heneicosane and (b) docosane. Circles show experimental data; lines, calculations according to Eq. (2).

where  $T_o$  is the temperature of the first-order PT,  $\Delta C_m$  is the maximal value of the heat capacity at  $T = T_o$ , and  $B$  is an athermic parameter.

Calculation of the heat capacity using Eq. (2) for docosane was made based on the peak with parameters  $T_o = 319.5$  K and  $\Delta C_{\max} = 240$  J/g K corresponding to the position and maximal value of the peak. The asymmetrical peak of heneicosane was divided into two symmetrical  $\Lambda$ -shaped peaks with the condition that the enthalpy of the experimental peak should equal the sum of enthalpies of the two symmetrical peaks. By varying the parameters  $T_o$ ,  $\Delta C_{\max}$  and  $B$  for each of the symmetrical peaks, coincidence with either the right (high-temperature) or left (low-temperature) peak shoulder could be achieved. The best approximation for the experimental dependence of  $\Delta C_p$  by the sum of two peaks was found when the left (low-temperature) shoulder of the  $\Delta C_p$  peak coincided with the low-temperature shoulder of one of the symmetrical peaks. These features of the  $\Delta C_p$  peaks are considered below.

Results of calculation of the  $\Lambda$ -shaped peaks from Eq. (2) and the experimental dependences of the heat capacity  $\Delta C_p(T)$  are shown in Fig. 5. The best fit of the theoretical and experimental dependences is achieved with the following parameters: for docosane,  $B = 3600$ ; for each of the two peaks of heneicosane,  $B_1 = 1750$ ,  $T_{o1} = 305.5$  K,  $\Delta C_{m1} = 55$  J/g K,  $B_2 = 6000$ ,  $T_{o2} = 305.8$  K, and  $\Delta C_{m2} = 75$  J/g K.

The parameter  $B$  in the correlation (2) contains the most interesting information on the physical nature of the PT, since it is related to the value of the heat capacity peak value  $\Delta C_m$ :

$$\Delta C_m = q_o B / 4T_o, \quad (3)$$

where  $q_o$  is the heat of transformation [17], and the elementary transition unit volume  $\omega$ :

$$B = \omega \rho q_o / k T_o, \quad (4)$$

where  $k$  is the Boltzmann's constant and  $\rho$  is the density. The parameter  $B$  is structure-dependent, because it determines the volumes of new phase nuclei in materials with blurred phase transitions [7]. Equation (3) allows finding the specific heat (enthalpy) of the transformation, and Eq. (4) gives the elementary unit  $\omega$  (the density of the paraffin crystals can be assumed  $\rho \sim 0.8$  g cm<sup>-3</sup> in the first approximation [1]). Calculation results are: for docosane,  $q_o = 86$  J/g and  $\omega \cong 230$  nm<sup>3</sup>; for heneicosane,  $q_{o1} = 39$  J/g,  $\omega_1 \cong 240$  nm<sup>3</sup>,  $q_{o2} = 15$  J/g, and  $\omega_2 \cong 2000$  nm<sup>3</sup>.

Estimation of the number of molecules participating in formation of a new phase nucleus in docosane and in the first stage of the PT in heneicosane shows that there are about 450–500 molecules in the elementary first-order transition volumes  $\omega \sim 230$ –240 nm<sup>3</sup>; that is, this transition region encloses quite a big domain. Even larger number of molecules ( $\sim 4000$ )

takes place in formation of the nuclei in the second stage of the PT in heneicosane.

Consider possible local places of appearing of new phase nuclei. Shape and position of the domain or nucleus is defined by the ratio of the volume and surface energies of the supramolecular structure consisting of the stacks of lamellae (crystalline cores) and the interlamellar layers. The central part of the lamellae is formed by dense-packed rods of long-chain molecules that are bound by the so-called universal (van der Waals) interaction between methylene groups. Interlamellar layers in paraffins consist of the terminal CH<sub>3</sub> groups. Based on the idea of minimizing the internal energy, it is reasonable to suggest that the nucleus may locate within one lamella. Second, the phase interface cannot pass through a molecule, i.e., through the strongest chemical bonds in the methylene part of the molecule (C–C and C–H); apparently, it crosses relatively weak van der Waals bonds between methylene groups of adjacent molecules and between terminal methyl groups CH<sub>3</sub>. Thus, a domain can be described as a parallelepiped made of parallel-packed rods having 400–500 methylene chains in its basis.

The presence of the second stage of transition in heneicosane with  $\omega_2 \cong 2000$  nm<sup>3</sup> can be explained as follows. On the first stage, precipitation of a large number of the new phase domains with the volume of  $\sim 240$  nm<sup>3</sup> each occurs and the phase transition involves the most volume of the crystal. This is proved by the ratio of the transition heats  $q_{o1}/q_{o2} \sim 2.5$ . Accumulation of numerous domains of the new phase leads to an increase in their influence, a kind of cumulative effect. This effect arises due to a change in the ratio of the volume and surface energies in the remaining part of the crystal that has not experienced the PT. It seems likely that to maintain the balance between the volume and surface energies, the fraction of the higher energy of the frontal side of the lamella (and hence the domain volume) should increase.

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