

THE MECHANISM OF MELTING OF LAMELLAR CRYSTALS WITH BRANCHED CHAINS

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A model of a lamellar crystal with branched chains, which contains specific defects, namely supervacancies, has been proposed. The latter are voids, the longitudinal size of which is equal to the chain length, and the transverse one to the interchain distance. An expression for the free energy of the crystal has been obtained in the framework of this model. Melting was considered as a result of the growth of the number of supervacancies. A conclusion about the emergence of a mesomorphic phase in the course of melting has been drawn. Melting has been shown to include the “crystal-mesomorphic phase” and “mesomorphic phase-melt” stages.

1. Introduction

Lamellar crystals are known to belong to a class of molecular crystals. Their name derives from a Latin word “lamella”, which is translated as a “plate”, the latter being an element of those objects’ structure. A lamella is a crystalline plate, where chain molecules are aligned in parallel to one another. The axes of chains are directed perpendicularly to both surfaces of the plate. The chains, which the chain molecules of lamellar crystals are composed of, can be branched and nonbranched. The structure of a lamellar crystal with nonbranched chains is depicted in Fig. 1.

Generally speaking, the concept of a chain has been borrowed from the graph theory. From the viewpoint of

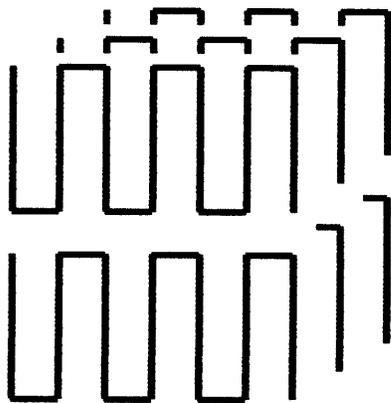


Fig. 1. Structure of a lamellar crystal with nonbranched chains

this theory, the graph of a nonbranched chain molecule with N links includes two vertices with degree one and $N - 2$ vertices with degree two. Chain branching corresponds to the emergence of vertices with degree three, four, and so on. We examine a simple branched chain that contains one vertex with degree three. In this case, the chain is a union of three branches. Suppose that each branch contains the same number of links. The graph of such a branched chain is displayed in Fig. 2.

What space form has a branched chain in a crystal lattice? A possible variant of such a formation is shown in Fig. 3. Here, two branches are on one side of the branch point and one branch on the other. It is also to be noted that the axes of the branches are parallel to the crystallographic axis. Earlier we have proposed the mechanism of melting of lamellar crystals with nonbranched chains [1, 2]. In this work, we consider the variant of this mechanism for lamellar crystals with branched chains.

2. Supervacancies in a Lamellar Crystal with Branched Chains

According to works [1, 2], lamellar crystals have to include specific defects, supervacancies. The term “supervacancy” was introduced in work [3], according to which a supervacancy is an empty cell of the lattice [5].

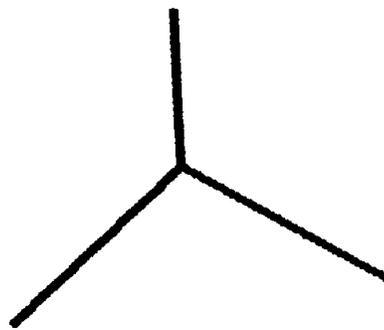


Fig. 2. Graph of a simple branched chain

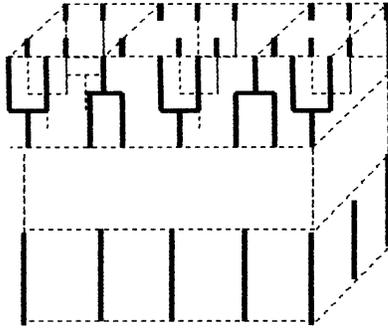


Fig. 3. Spatial arrangement of branched chains in the lattice

A supervacancy in a crystal with branched chains is shown in Fig. 4.

It is evident from the figure that a supervacancy is a void, the longitudinal and transverse dimensions of which are equal to the longitudinal and transverse dimensions, respectively, of the branched molecule in the lattice. The longitudinal dimension of a molecule amounts to several tens of Angströms.

3. Theoretical Calculation of the Supervacancy Concentration in a Lamellar Crystal with Branched Chains

We call traditionally a group of atoms that form a force center as a particle. In our case, such a force center is a chain link. The spatial region occupied by a link is commonly named a subcell.

Consider the process of melting in the system at a constant temperature T and a variable volume V . Let V_0 denote the volume of the system as the temperature tends to zero. The state of the system that corresponds to the value V_0 will be referred to as the undeformed one. Let θ designate the relative variation of the volume that is determined by the formula

$$\theta = \frac{V - V_0}{V_0}. \quad (1)$$

Owing to a large rigidity of the system along the chains, we assume no deformation in a longitudinal direction. Let λ designate a degree of stretching that is determined by the relation

$$\lambda = r / r_0, \quad (2)$$

where r and r_0 are the distances between particles, i.e. links, in the transverse direction in the deformed and undeformed states, respectively.

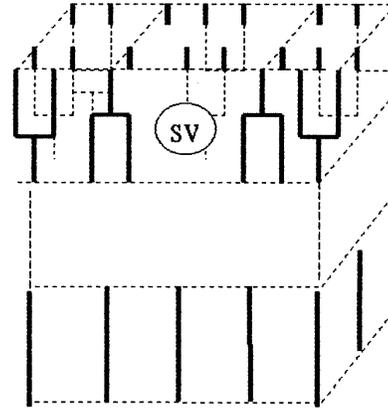


Fig. 4. Supervacancy in the crystal with branched chains

According to formula (2), the degree of stretching can be written down as

$$\lambda = (v/v_0)^{1/3}, \quad (3)$$

where v and v_0 are the volumes of a subcell in the deformed and undeformed states, respectively.

Let us designate the number of empty subcells within a supervacancy through $\mu = L/c_1$, where L is the thickness of a lamella and c_1 is the interparticle distance along the chain. For a lamellar crystal with branched chains, the thickness of a lamella is much greater than the distance between particles-links ($\mu \gg 1$).

The bulk concentration of supervacancies is equal to $c = n\mu/N$, where n is the number of supervacancies in the system and N the number of particles.

If n supervacancies have been appeared in the system, the volume of a subcell becomes equal to

$$v = V/N + n\mu \quad (4)$$

in the deformed state and to

$$v_0 = V_0/N. \quad (5)$$

in an undeformed one. Substituting Eqs. (4) and (5) into Eq. (3), we obtain

$$\lambda = \left(\frac{l + \theta}{l + c} \right)^{1/2}. \quad (6)$$

We calculated the free energy of a nonequilibrium state (according to Leontovich)

$$F = F(V, T, c) \quad (7)$$

which is a function of the concentration c , the volume V , and the temperature T . The expression for the free

energy F is a sum of the potential energy U calculated at $T \rightarrow 0$, the energy of free oscillations F_V , and the entropy of mixing S (with the inverse sign) times the temperature T .

The value of S was represented as a sum of two terms, the first of which, S_1 , is defined by the ability of supervacancies to occupy various sites of the superlattice and the second, S_2 , is related to an opportunity for chains, which surround a supervacancy, to change the configuration. Really, a chain, which is located near to a supervacancy, may acquire, in addition to the rectilinear form, various configurations with one, two, and so on ledges, thus penetrating into the volume occupied by a supervacancy. The opportunity for chains to penetrate partially into the volume occupied by a supervacancy is the main feature of such defects, because it affects the mechanism of melting of lamellar crystals with branched chains substantially.

The value of S_2 was calculated by the formula obtained in our previous work [1],

$$S_2 = k_B n \mu \xi_2, \quad (8)$$

with the factor $\xi_2 = 1.3$.

Since the appearance of a supervacancy results in that $n\mu$ links become broken, the potential energy can be written down as

$$U = \frac{Nq}{2}(1 - 2c)u(\lambda), \quad (9)$$

where $u(\lambda)$ is the Lennard—Jones potential of interparticle interaction.

The energy of free oscillations was calculated in work [4] and is determined by the formula

$$F_V = F_{0V} - k_B T \xi_1 n \mu, \quad (10)$$

where $\xi_1 = 0.1$ and F_{0V} is the energy of free oscillations of a lamellar crystal with branched chains that does not contain defects of the supervacancy type. In order to calculate F_{0V} , we used the textbook formula of solid state physics [5]

$$F_{0V} = k_B T \sum_j \ln \frac{\hbar \omega_{0j}}{k_B T}, \quad (11)$$

where ω_{0j} is the eigenfrequency.

Differentiating the free energy, we received the expression

$$\frac{l}{NkT} \frac{\partial F}{\partial c} = \frac{q\varepsilon}{2kT} \lambda^{-12} (2\lambda^6 - 1) + \frac{l-c}{l+c} (-6\lambda^6 + 6) +$$

$$+ \frac{Y}{l+c} \frac{182 - 56\lambda^6}{(13 - 7\lambda^6)^{0.75} \lambda^{3.5}} - \gamma + \ln c / \mu, \quad (12)$$

where ε is the energy of breaking of the interchain coupling, q is the number of the nearest chains, and $\mu = 54$ is the number of links in a molecule. For the numerical calculation of the function $\partial F(\theta, c)/\partial c$, we used the values of the coefficients q and ε typical of the considered crystal, namely, $q = 4$ and $\varepsilon = 3.7 \times 10^{-21}$ J, as well as $Y = 0.05$ and $\gamma = 1.4$. The temperature was assumed equal to 273 K. The results of this calculation for various values of θ are shown in Fig. 5, *a*. Fig. 5, *b* illustrates the initial sections of the relevant curves scaled-up.

From this figure, one can see that the curve $\partial F/\partial c$ crosses the c -axis at a certain point c_E , thus changing the sign from minus to plus. This means that the function $F(c)$ has a minimum at this point, i.e. the point c_E is the equilibrium value of the supervacancy concentration. The dependence $c_E(\theta)$ is shown in Fig. 6.

In accordance with Fig. 5, the function $F(c)$ always has a minimum at any θ value. However, according to Fig. 6, there exists such a value θ_0 that if $\theta < \theta_0$, the corresponding equilibrium concentration is practically equal to zero. If this value is exceeded, c_E grows abruptly, as is seen from the figure, reaching the values of about several volume percent.

4. Role of Supervacancies in a Destruction of Crystals with Branched Chains

In order to obtain an increment of the free energy at the equilibrium concentration c_E caused by the appearance of supervacancies, it is necessary to integrate the dependence $\partial F(c)/\partial c$ from zero up to c_E . As is seen from Fig. 5, *a*, the value of $\partial F(c)/\partial c$ is negative at $c < c_E$. Therefore, the integration would result in a negative increment of the free energy $F(c)$. From the thermodynamical point of view, this means that it is beneficial for the crystal to have vacancies in its lattice. However, as is seen from Fig. 6, there exists such a value θ_0 that the crystal almost does not contain vacancies if $\theta < \theta_0$ this state is a perfect crystal. This state will be referred to as “crystal” or “phase *A*”. The state at $\theta < \theta_0$ will be called as “phase *B*”. As has already been mentioned, the chains that surround a supervacancy can penetrate into the volume occupied by the latter. In fact, the supervacancy is the region of a disordered material, as is shown in Fig. 7.

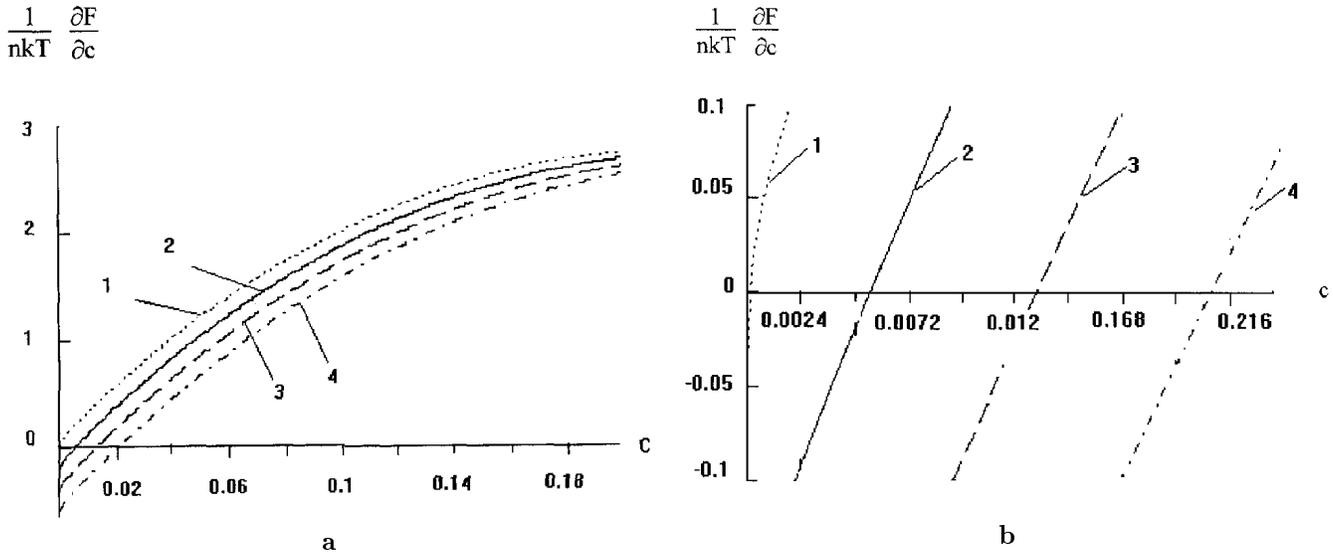


Fig. 5. Dependences of the function $\frac{1}{nkT} \frac{\partial F}{\partial c}$ for various values θ : 0.1 (1); 0.11 (2); 0.12 (3); and 0.13 (4)

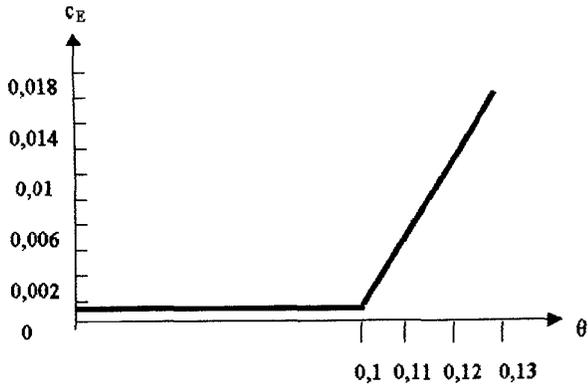


Fig. 6. Dependence $c_E(\theta)$

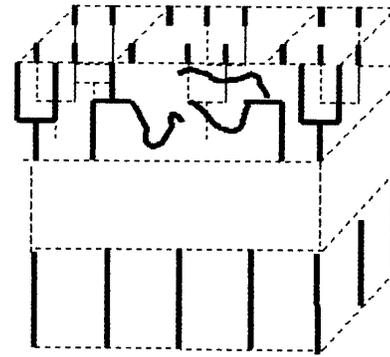


Fig. 7. Penetration of chains into the volume of a supervacancy

Thus, an increase of the number of supervacancies in the system means an increase of the number of disordered regions in it. Since every supervacancy is surrounded by four molecules, the formation of one supervacancy means, in fact, the disordering of a material within the volume of five molecules. Therefore, at the relative concentration of supervacancies of 0.2, all material becomes disordered. Such a state of the system will be referred to as “phase C”. A characteristic feature of this phase is that it, as well as phase A, consists of lamellae. However, contrary to the “crystal” case, there is no lattice in these lamellae, as is shown in Fig. 8. So, phase C preserves some elements of the ordering in the form of lamellae.

The calculation, carried out by us, showed that, as the volume increases and θ exceeds some critical value θ_0 , the perfect crystal must become transformed into a

disordered material, i.e. phase C. In the framework of the approximation adopted here, where the availability of vacancies at $\theta < \theta_0$ is neglected, one can talk about the start of the $A \rightarrow C$ phase transition at $\theta > \theta_0$. Let us calculate the specific heat of melting of this transition. As was indicated above, the difference between phase entropies is determined mainly by the value of S_2 . Using expression (8) for S_2 , we obtain the estimation

$$H \sim nk_B T c / v \rho, \tag{13}$$

where ρ is the density, so that, using the literature data [2], $v = 2 \times 10^{-19} \text{ m}^3$. As has already been mentioned, the complete transition into phase C occurs at a supervacancy concentration of about 0.2. Adopting the values $c = 0.2$ and $\rho = 10^3 \text{ kg/m}^3$, we obtain $H \approx 40 \text{ kJ/kg}$.

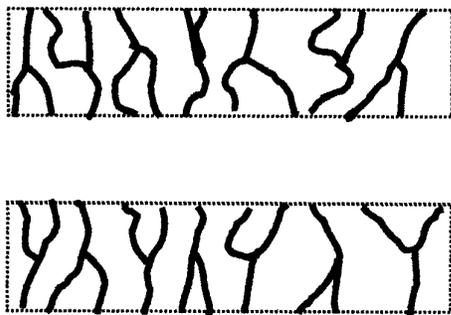
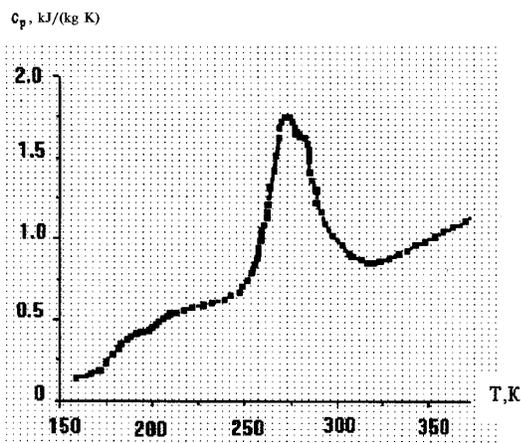
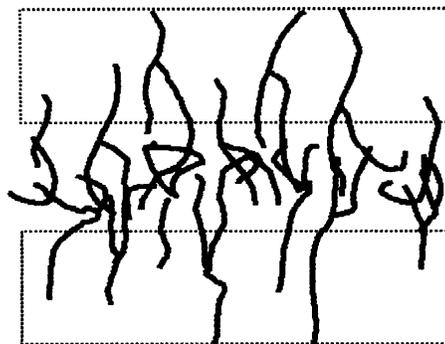
Fig. 8. Schematic image of phase *C*

Fig. 9. Dependence of the specific heat on the temperature

5. Experiment and its Discussion

Triacylglycerides may serve as representatives of the class of lamellar crystals with branched chains. So they were selected as objects for experimental researches. The studies were carried out using a dynamic calorimeter operating at a heating rate of 4 K/min. The experimental dependence of the specific heat on the temperature is shown in Fig. 9. It is evident that, within the temperature interval 250–310 K, there is a phase transition accompanied by the appearance of a maximum of the heat capacity. The specific heat of the transition was calculated as the area under the $c_p(T)$ curve and amounted to (33 ± 3) kJ/(kg K).

The agreement between the theoretical and experimental values of the transition heat makes it possible to assert that the transition that was observed in the experiment was nothing else than a transition of the $A \rightarrow C$ type, which was an essential point of our theoretical calculations. So, it is possible to state that melting is a consequence of the growth of the number of supervacancies.

Fig. 10. Schematic image of phase *D*

The figure testifies to that the experimental dependence $c_p(T)$ can be considered as a result of the overlapping of two dependences, each of which possessing its own maximum. In our opinion, the existence of such two maxima can be explained as follows. The formation of phase *C* does not mean that the process of disordering of the system comes to the end. The further destruction of lamellae, which is accompanied by the entangling of chains (Fig. 10), is profitable for the system, because it results in an increase of the entropy of mixing.

A structure with entangled chains will be referred to as “phase *D*”. Actually, it is this phase that is a melt. As concerning phase *C*, it plays the role of a mesomorphic (intermediate) phase. Therefore, the process of disordering of a crystal is a sequence of two transitions: $A \rightarrow C$ and $C \rightarrow D$. The first process induces the occurrence of a low-temperature maximum and the second of a high-temperature one on the curve $c_p(T)$.

6. Conclusions

As follows from our researches, the process of melting of lamellar crystals with branched chains develops in two stages. At the first stage, due to an increase of the number of supervacancies, the transition of a perfect crystal into some mesomorphic phase takes place. This phase contains remnants of the elements of ordering in the form of lamellae. However, contrary to the crystalline phase, the chains in a lamella do not form a lattice.

At the second stage, the transition “mesomorphic phase—melt” takes place. The melt differs from the mesomorphic phase in that there are no lamellae in the former and that its chains are entangled with one another.

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МЕХАНІЗМ ПЛАВЛЕННЯ ЛАМЕЛЯРНИХ КРИСТАЛІВ З РОЗГАЛУЖЕНИМИ ЛАНЦЮГАМИ

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Резюме

Запропоновано модель ламелярного кристала з розгалуженими ланцюгами, що містить специфічні дефекти — супервакансії. Останні являють собою порожнечні порожнини, поздовжній розмір яких дорівнює довжині ланцюга, а поперечні розміри — відстані між ланцюгами. Отримано вираз для вільної енергії кристала за такою моделлю. Процес плавлення в рамках моделі розглядається як наслідок зростання кількості супервакансій. Зроблено висновок про виникнення у процесі плавлення мезоморфної фази. Показано, що плавлення протікає в два етапи: “кристал — мезоморфна фаза” та “мезоморфна фаза — розплав”.