

THE MODEL ROTATOR PHASE

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It is shown that the formation of the so-called rotator phase of alkanes (one of the high temperature crystalline phases) might be connected with a partial increase of the conformational flexibility of chains. The conformations with higher number of kinks per chain, which have been neglected till now, are shown to contribute effectively to the conformational partition function. Small probability of these states given by the Boltzmann exponent is compensated by a large number of ways in which they can be distributed along the chain. The deduced features of the rotator phase seem to be in agreement with the experimentally observed properties.

The behaviour of chain molecules and/or chain parts of molecules becomes the subject of primary interest in several fields. We can mention the properties of polymers, condensed phases of alkanes, mesomorphism of thermotropic and lyotropic liquid crystals, etc.¹.

The modelling of the structure and behaviour of chain molecules in condensed phases is a very obscure problem. In addition to the anisotropy of interaction of chains as hard rods, they can, under specific conditions, change their shape due to internal rotation around simple bonds. However, as it has been stressed, this internal rotation differs from the conformational motions of an isolated molecule^{2,3}. The steric and packing effects of condensed surrounding influence the molecular conformational equilibrium.

In the present paper we try to give a qualitative model of one of the high temperature crystalline phases of alkanes known as the rotator phase. The rotator phase, or the D-crystalline modification appears in the phase diagrams of alkanes with the number of segments, $N \in (21; 45)$, as the last crystal-like structure before melting to an isotropic liquid^{4,5}.

Molecular mechanics calculations (MMC) have proved competent for the investigation of flexibility, mobility and interaction of alkanes^{6,7}. This method enables us to obtain correct values of the potential energy barriers for different motions of the chain in a condensed phase. According to MMC simulations the most hindered motion of the chain in condensed surroundings is the internal rotation⁸. The average number of the so-called kink deformations ($g^{\pm}tg^{\mp}$) per chain is not greater than two⁹. Therefore, it has been concluded that a partial increase of the conformational flexi-

lity in the rotator phase does not have any convincing influence on its appearance^{5, 10, 11}.

In the present paper it is shown using a simple model that the increase of the entropy caused by the partial increase of conformational flexibility can be greater than originally thought. At first we investigate qualitatively the shape of the potential energy field of the nearest neighbours acting on the molecule. Then a formula is derived for the calculation of the number of possible ways in which the given conformational defect can be effected. In the last part of the paper the deduced properties of the model rotator phase are confronted with the experimental data. It was found that the increase in the conformational flexibility might be the origin of the creation of the rotator phase.

THEORETICAL

Potential Energy of Molecule in the Field of Nearest Neighbours

For evaluating possibilities of conformational motions in condensed phases it is necessary to know the geometric shape of the field of nearest neighbours which acts on each molecule of the ensemble. In the present work we do not want to know the exact numerical values of this potential in any place. Rather, we try to elucidate how the geometry of this field changes when unit cells of the crystalline structure are expanded. Such an expansion was observed in transitions to high-temperature crystalline phases⁵. Therefore, in this section we use some hypothetical, but qualitatively correct potentials.

Without lengthy numerical calculations, it is clear from Fig. 1 that the interaction of alkanes in configuration **b** is stronger than in configuration **a**. Due to this, it is sufficient to study the influence of the nearest neighbours placed in a two-dimensional lamella. According to experimental data, the individual lamellae in the rotator phase possess a hexagonal symmetry^{5, 6, 9}. This means that each molecule has six nearest neighbours. Thus, the model aggregate we are interested in consists of seven molecules (Fig. 2).

Finally, it is possible to use the last simplification: the molecular pair interaction of all-*trans* alkanes in configuration **b** can be divided by the number of chain segments to obtain the shape of pair interaction field per chain site. A similar approximation was used several years ago by Salem¹¹. Although it is clear that this approximation is not exact, since the interaction between central segments should differ from the interaction of chain-end segments, it is a very useful "first" approximation. Fig. 3 shows the dependence of this "hypothetical" pair potential per segment on molecular separation.

Now, let us analyze the shape of interaction energy of the individual segments in the aggregate. Let the separation between alkanes in the aggregate be equal to

the distance r_m , where the potential in Fig. 3 has its minimum. Fig. 4 shows how it is possible to obtain the potential energy field acting on the segment of the central molecule by adding individual pair interactions from Fig. 3. The potential field

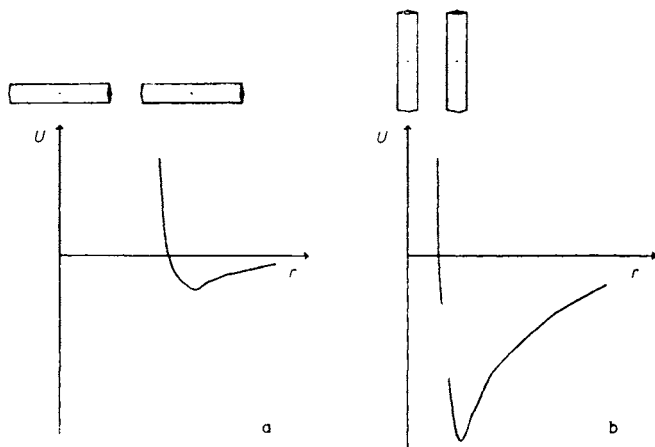


FIG. 1

The shape of molecular pair interaction of parallel hard chains in two basic configurations: a long chain axes are parallel with the axis joining the mass centres; b long chain axes are perpendicular to this axis

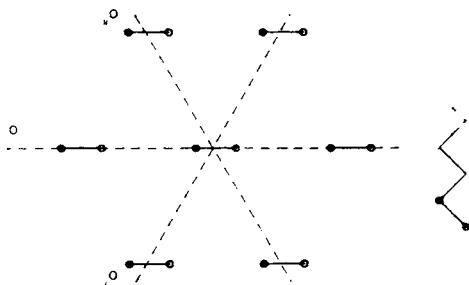


FIG. 2

A typical structure of the nearest surrounding of chains in the lamellae of the rotator phase

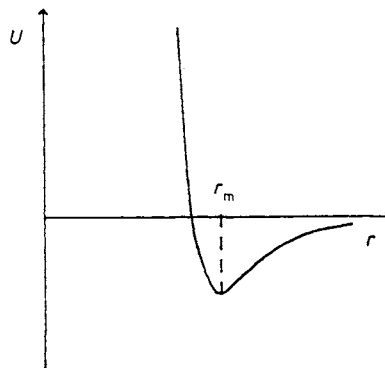


FIG. 3

The shape of the hypothetical pair molecule potential per segment in dependence on the separation between chains in configuration b (see Fig. 1)

along the axes o' and o'' of the hexagon has the same shape. As can be seen, the interaction energy has a sharp minimum in the centre of the hexagon. The equipotential energy lines have approximately the shape of concentric circles. The radius l_0 with the potential energy equal to zero determines the cylinder where the segments are most likely situated.

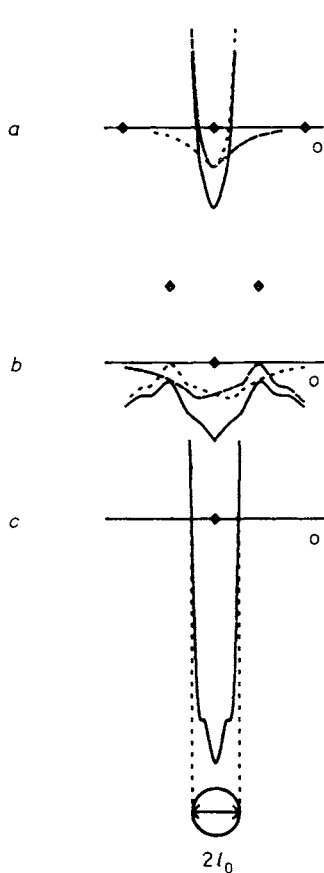


FIG. 4

The resulting shape of the potential of a segment of the central molecule in the hexagon along the axis o , c , is given by the sum of interactions in a and twice the interaction in b . The separation between the molecules in the hexagon is r_m

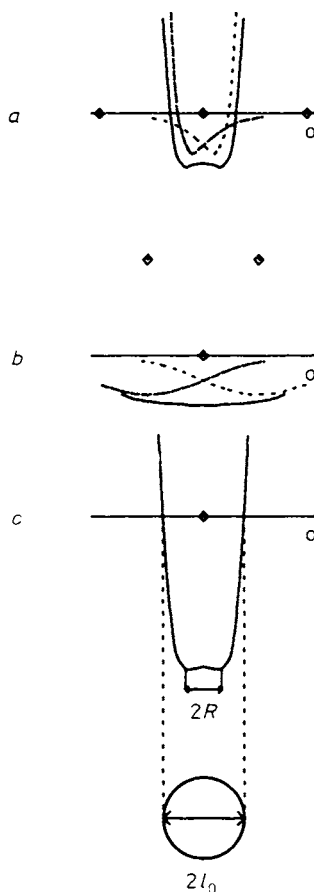


FIG. 5

The same as in Fig. 4 for the expanded hexagon

The changes of the potential energy field after the symmetric expansion of the hexagon are clearly visible from Fig. 5. Instead of a one-point minimum of the interaction, one obtains a closed line (nearly a circle with radius R), where the potential energy reaches its minimum. In the place of the previous minimum in the centre there is a local maximum now. The zero energy radius l_0 also increases with the hexagon expansion.

If the radius of the minimum energy, R , equals zero (most condensed hexagon), any conformational transition of the chain transforms one or more segments beyond the cylinder l_0 . This means that the only possible conformation of the chain is the all-*trans* state. The least disturbing conformation which can be found by the expansion of the hexagon is the so-called kink state ($g^\pm tg^\mp$). To make this conformation possible the diameter of the circle of the zero energy, $L = 2l_0$, should be equal to the distance between the parallel long axes of the two parts of the chain separated by the kink, $d = 0.2$ nm, Fig. 6. In such a cylinder the isolated *gauche* states of the second and third bonds from both ends of the chain are also possible. According to Helfand¹², one can find the isolated *gauche* state in the middle part of the alkane on condition that the neighbour bonds and bond angles are slightly deformed. For the sake of simplicity, however, we consider kinks as the only possible conformational deformation in the hexagon expanded to a distance $(r_m + \Delta l_0)$, where Δl_0 is the difference between the radii of zero energy of the most condensed and expanded hexagons.

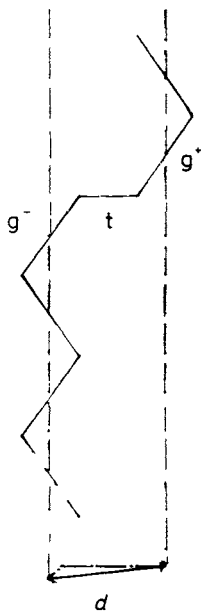


FIG. 6
Schematic view of the chain divided by kink
into two parallel parts

Now it is necessary to confirm whether this expansion corresponds to the known structure of the rotator phase. According to the experimental data, the averaged distance between two alkanes in the lamella of the rotator phase is 0.48 nm (refs^{5,8,13}). We will turn to the previously obtained MMC results¹⁴ to show that the formation of kinks is possible with these dimensions. (The rotation round the central bond of hexane simulates the main features of the creation of kinks.)

The numerical MMC results show that no internal rotation is possible, when the dimension of the hexagon, r , is 0.48 nm (ref.¹⁴). The kinks are no more hindered by r 0.52 nm ($\Delta l_0 = r - r_m = 0.07$ nm) and become even stabilized (i.e. more probable than all-*trans*) by r 0.64 nm ($R = r - r_m = 0.19$ nm). Nevertheless, these results are artefacts of the model of calculation used since one part of the central hexane is always fixed in the centre of the hexagon. In that case the inevitable expansion of the hexagon is such that the radius of the circle, R , is equal to the "kink distance", d . If the position of neither chain part is fixed (the present model), one needs only $R = d/2 \doteq 0.1$ nm. Similarly, for the unhindered kinks it is satisfactory if the hexagon is expanded to the distance 0.485 nm ($r = r_m + \Delta l_0/2 \doteq r_m + 0.35$). This is in good agreement with the experimental data obtained on the rotator phase.

The "geometric" view of the potential energy field explains also why the kinks are even stabilized in comparison to the all-*trans* conformation in the previous model¹⁴: in the all-*trans* state all segments are in the middle of the hexagon, where the potential energy has the local maximum. The translation of segments which are separated by the kink from the centre-fixed part of the hexagon to the region of the minimum of potential energy leads to energy stabilization. This effect has been classified as the "intermolecular" anomeric effect¹⁴. As is clear from present considerations, this effect cannot be observed in the ensembles of real alkanes. In contrast to previous results, each kink should lead to an increase of intermolecular potential by $2 \Delta u$, since the two central segments of the kink are placed in the region where the energy has the local maximum. (Correct only qualitatively since with a change of conformation the energy value per segment also somewhat changes.)

The total value of the energy increase caused by the kink transition is

$$\Delta \mathcal{U} = 2 \Delta u + 2 \Delta U_{\text{gt}}. \quad (1)$$

The term ΔU_{gt} is the internal energy difference between *trans* and *gauche* states of the simple bond in an isolated alkane.

The number of Rotational States of the Chain with a Kinks

We have shown in the previous part that due to the change of the surrounding energy field it is possible to find the chain with one or more kinks in the rotator phase. The presence of a kinks in the chain increases its energy by $a \cdot \Delta \mathcal{U}$. Before

the conformational partition sum is calculated, it is necessary to know the number of possible ways in which a kinks can be placed on the chain consisting of N segments. The recursive formula for the calculation of the number of ways in which a *gauche* states can be distributed along the chain has been derived elsewhere¹⁵. Due to intermolecular forces, however, not all these states are allowed in the condensed phase. In the first part of this section we therefore derive a formula for the calculation of the number of possible distributions of a *gauche* states on condition that the neighbouring bonds ($(i - 1)$ -th and $(i + 1)$ -th) of the i -th bond in the *gauche* state are inevitably in *trans* conformation. In comparison to the previous work¹⁵, the possibility of $g^{\pm}g^{\pm}$ sequence is also neglected.

The number of simple C—C bonds in the alkane consisting of N segments is $(N - 1)$. Since it is not possible, due to the symmetry of $-\text{CH}_3$, to distinguish between g^+ , t , g^- during the rotation of end groups, the actual number of bonds involved in the conformational analysis, N' , is $N - 3$.

Each chain of any length can be in one all-*trans* conformation. The number of possible ways in which one *gauche* state (g^+ or g^-) can be placed on the chain of N segments is

$$n_1 = 2N' . \quad (2)$$

Let us now derive an expression for the number of ways of the appearance of two *gauche* states on the chain. Due to the correlation of the neighbouring bonds the minimal number of bonds, N'_{\min} , at which two *gauche* can be placed, is three (i.e. $N = 3 + 3$). It can be generalized for a *gauche* states

$$(N'_{\min})_a = (2a - 1) . \quad (3)$$

The number of the possible ways of distribution of the two *gauche* states is

$$n_2 = 4 \sum_{i=2}^{N'-1} (N' - i) . \quad (4)$$

If one g state is placed on the first bond, then the second g state can be found on any of the $(N' - 2)$ bonds. If the first g state is on the second bond, there are $(N' - 3)$ free bonds for the second *gauche*, etc. The coefficient $4 = 2^a$; a equal to 2 means that there are two possibilities for each *gauche* state g^+ and g^- .

By analogy with Eq. (4) for the occurrence of three, four and five *gauche* states on the chain, one obtains

$$n_3 = 2^3 \sum_{b_0=4}^{N'-1} (N' - b_0) (b_0 - 3) , \quad (5)$$

$$n_4 = 2^4 \sum_{b_0=6}^{N'-1} \sum_{b_1=4}^{b_0-2} (N' - b_0)(b_0 - 1 - b_1), \quad (6)$$

$$n_5 = 2^5 \sum_{b_0=8}^{N'-1} \sum_{b_1=6}^{b_0-2} (N' - b_0)(b_0 - 1 - b_1)(b_1 - 1 - b_2). \quad (7)$$

The lowest values of b_s in the sums are $b_s = 2(a - s) - 2$; $s = 0, 1, 2$.

Relations (3)–(7) can be generalized for the calculation of the possible ways in which a *gauche* states can be placed on the chain consisting of N' bonds: for even a

$$n_a = 2^a \sum_{b_0} \sum_{b_1} \dots \sum_{b_s} (N' - b_0)(b_0 - 1 - b_1) \dots (b_{s-1} - 1 - b_s), \quad (8a)$$

for odd a

$$n_a = 2^a \sum_{b_0} \sum_{b_1} \dots \sum_{b_s} (N' - b_0)(b_0 - 1 - b_1) \dots (b_s - 1 - b_{s+1}), \quad (8b)$$

where $s = \text{Int}\{a/2\} - 1$ and $b_i = 2(a - i) - 2$. The maximum number of *gauche* states in the considered chain is given by the integer part of $a_m = \text{Int}(N' + 1)/2$.

On the basis of similar considerations one obtains the number of the possible ways of distribution of a kinks ($g^\pm tg^\mp$) in the form

for even a

$$n_a^k = 2^a \sum_{b_0^k} \sum_{b_1^k} \dots \sum_{b_s^k} (N' - b_0^k)(b_0^k - 3 - b_1^k) \dots (b_{s-1}^k - 3 - b_s^k), \quad (9a)$$

for odd a

$$n_a^k = 2^a \sum_{b_0^k} \sum_{b_1^k} \dots \sum_{b_s^k} (N' - b_0^k)(b_0^k - 3 - b_1^k) \dots (b_s^k - 3 - b_{s+1}^k), \quad (9b)$$

with $s = \text{Int}\{a/4\} - 1$ and $b_i^k = 4(a - i) - 2$.

Relations (8) and (9) differ in b_s and b_s^k values. The occurrence of kink determines fixed states of longer chain parts and therefore the number n_a^k is always smaller than n_a for a given chain. In contrast to the recursive formula¹⁵, Eqs (8) and (9) allow to calculate the number of the conformation states with a deformations on the chain of N segments without the knowledge of the number of previous states with $(a - i)$ deformations.

The Conformational Partition Sum

Eq. (9) gives the number of possible ways of distribution of a kinks irrespective of their space orientation. A closer look at Fig. 6 shows that the second kink separated by at least one bond in the *trans* state can put the rest of the chain beyond the cylinder with a radius l_0 (even if the orientation and position of individual chain segments is not fixed in the cylinder). Therefore, in the hard molecule model (the bond lengths,

bond angles and dihedral angles are fixed) the orientation of existing kinks is correlated. Hence, not all the possibilities of the distribution of kinks, n_a^k , are allowed. The new number of ways of distribution of kinks \tilde{n}_a^k should differ in the multiplying factor standing in front of the summation sign of Eq. (9). The orientation of the first kink determines the orientation of all consecutive kinks, i.e. instead of 2^a there should be the factor $2 \cdot 1^a$. The summation itself is not changed, since it is determined only by the position of the kinks along the chain and not by their orientation.

Nevertheless, alkanes are known to possess intramolecular flexibility. The energy needed for slight deformations of dihedral and bond angles, as well as bond lengths, is relatively small, although the change of the resulting molecular shape can be rather large. Therefore, one can consider the orientation of individual kinks along the chain to be quite independent. In this case the number of possible states is given by n_a^k from Eq. (9). All n_a^k states, however, can be observed at higher energy, $W = \Delta\mathcal{U} + U_a$. The term U_a represents the energy needed for intramolecular deformations.

Some years ago Helfand considered the possibility of occurrence of one *gauche* state on the chain in the condensed state. In *gauche* the chain is divided into two parts, long axes of which are not parallel. In the hard molecule model the existence of an isolated *gauche* state is not allowed due to the intermolecular repulsion of the surroundings. However, Helfand showed that the energy of intramolecular deformations (mainly bond lengths and angles) which are needed to make the isolated *gauche* state possible is not greater than that of additional *gauche*, i.e. the energy of one *gauche* in condensed surroundings is approximately equal to the energy of the kink state¹².

Returning to our problem, the long axes of the chain parts separated by kinks are always parallel, irrespectively of the mutual orientation of individual kinks. Therefore, we suppose that the intramolecular deformation energy needed for orientationally independent kinks is not greater than ΔU_{g1} . The a -th contribution to the conformational partition sum is then given by the integral

$$Z(a) = K \int_{\Delta\mathcal{U}}^W \exp(-x/kT) n_a^k(x) dx. \quad (10)$$

The expression under the integral is the product of two functions. The exponential function $\exp(-x/kT)$ decreases in the integration interval. The function $n_a^k(x)$ is equal to \tilde{n}_a^k in the left limit of integration and is equal to n_a^k at least in the right limit. Between these two limits the function $n_a^k(x)$ increases. From the available data it is not possible to evaluate exactly the shape of the function $\exp(-x/kT) \cdot n_a^k(x)$. Therefore, we propose to replace the value of integral (10) by the expression

$$Z_a = \exp(-a \Delta\mathcal{U}/kT) \cdot n_a^k. \quad (11)$$

The conformation partition sum is then given in the form

$$Z_{\text{conf}} = \sum_a \exp(-a \Delta \mathcal{U}/kT) \cdot n_a^k. \quad (12)$$

Eq. (12) represents, according to our opinion, the lower estimate of the actual value of conformational partition function. Even if the function under the integral sign decreases and Z_a is greater than the integral (10), Eq. (12) cannot exceed the conformational contribution since all the conformational states with the exception of the kinks are neglected.

As can be seen, each term of sum (12) is given by the product of two functions of a . With increasing number of kinks the Boltzmann exponent $\exp(-a \Delta U/kT)$ decreases and, in some limits, the number of the rotational states increases. Fig. 7 shows the decrease of the Boltzmann exponent as a function of a for $2\Delta U_{\text{gt}} = 5.8 \text{ kJ/mol}$ and $T = 320 \text{ K}$ (refs^{9,16}). It also shows the shape of functions $\ln(n_a^k)$ depending on a for alkanes of different length N . As can be seen, the functions n_a^k have maxima at \tilde{a} equal to $a_m/2$. For the alkanes $N > 20$ the increase of the function n_a^k in the interval $(0, \tilde{a})$ is comparable, or even more rapid than the decrease of the corresponding Boltzmann exponent.

In all studies published so far, the main attention was concentrated on the dependence of the Boltzmann exponent, which describes the one-molecule averaged

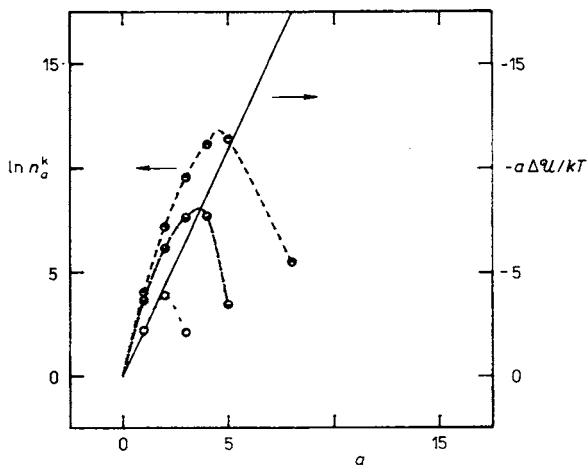


FIG. 7

Dependence of n_a^k on the number of kink defects a on a logarithmic scale for $N = 21$ (\circ), $N = 31$ (\ominus) and $N = 41$ (\bullet) compared with the dependence of the Boltzmann exponent on a on the same scale

probability of the occurrence of a kink defects on the chain. The average number of kinks per chain is accordingly a little lower than two, in agreement with the experiment. On the basis of small probability it was deduced that it is not necessary to consider the conformations with greater number of kinks for a correct description of the phase transition. The resulting computed change of the conformational part of free energy, F , was smaller than the experimentally observed value. One therefore needs mechanisms additional to the conformational flexibility which would cooperate in the phase transition.

For example, Baur¹⁰ has found that one kink contribution to the entropy change during the transition represents about 30% of the experimentally measured change. As is clear from our qualitative analysis for alkanes with $N > 20$, "little" probable states with a greater number of kinks $a > 2$ bring a rather large contribution to the partition sum Z , Fig. 7. We can thus conclude that the origin of the rotator phase might lie in the increase in the conformational entropic part of the free energy¹⁵,

$$S_{\text{conf}} = k \cdot \ln Z_{\text{conf}} + \{\Delta u/kT\}/Z_{\text{conf}} \sum_a a \cdot \exp\{-a \Delta u/kT\} n_a^k, \quad (13)$$

since the whole-molecule rotational and translational motions are partly released in the preceding high-temperature crystalline phases. The numerical estimate performed on the basis of Eq. (13) shows that in comparison to Baur¹⁰ the change of conformational entropy represents about 90% of the increase in the phase transition entropy.

DISCUSSION

In this part we would like to discuss and compare the properties of the rotator phase which can be deduced from the simple qualitative model with experimental data. Using the X-ray diffraction technique, the structure of the crystalline state of different alkanes at different temperatures was ascertained^{5,13,17}. In all cases the dimensions of the crystal unit cell increase with increasing temperature (crystal A → crystal B, crystal B → crystal C). This expansion is approximately symmetric in all directions. The only exception to the symmetric expansion is the phase transition crystal C → crystal D (rotator phase). During this transition, the separation of neighbouring molecules in the lamella is expanded, but the distance between the individual lamellae becomes smaller. This decrease of the interlamellar separation on an assumption that the amplitudes of vibrations of the mass centre increase in all directions is possible only if the effective chain length is shorter. This shortening can exceptionally be caused by a change of the conformational equilibrium structure of chains. By one kink to the chain the projection of the C—C bond on the long molecular axis is shortened by approximately 1.2 times.

Up to now, we have been concerned with the equilibrium structure, where at the average internal energy value there are two kinks per chain. Nevertheless, due to energy fluctuations in the ensemble the states with a greater number of kinks on one chain and with no kinks on the nearest neighbours are also possible. Since with increasing N' the function n_a^k increases more rapidly, the probability of such fluctuations also increases. Therefore, with increasing N' , the difference in the length between the all-*trans*, the averaged and the instantaneous conformations also increase. This means that the dispersion of the length of chains which form the ensemble increases. Too much free space per molecule triggers additional intra- and inter-molecular motions resulting in the break-down of the crystalline structure. On this basis we conclude that there should exist an upper limit N above which the alkanes do not form the rotator phase. According to experimental data, the chains with $N > 45$ really cannot form the rotator phase^{5,9}. The maximum number of kinks in alkanes with $N = 45$ is ten. This means that the all-*trans* conformation and the conformation with the greatest possible number of kinks differ by more than one fourth of the maximal chain length.

Using current NMR and IR spectroscopy, it is possible to measure even the probabilities of *gauche* states for individual chain segments^{1,9,18-21}. According to recent results of Maroncelli et al.⁹, the most probable states in ensembles of alkanes of different length in the rotator phase are the *gauche* states at chain ends. Towards the middle of the chain their occurrence becomes less likely. The authors explain this probability profiles as a result of increasing disorder of the interlamellar structure⁹.

According to our simple model allowing only kink deformations, the probability of the *gauche* state occurrence should be the same for all segments. We will show now that after removing most imprecise approximations of the model, it is possible to explain qualitatively the experimentally observed profiles.

First of all, in our simple model we were limited to kink deformations as the only possibility of conformational transition. Nevertheless, it is clear that in the case of the existence of kinks, creation of isolated *gauche* states of the second and third bonds at both ends of alkanes also becomes possible. This effect increases the measured likeliness of *gauche* states at chain ends. Another reason for the greater probability of *g* states at chain ends is connected with molecular interactions. Division of the whole-molecule interaction by the number of segments makes all $-\text{CH}_2-$ sites equivalent from the point of view of intermolecular forces. However, it was made clear when introducing this approximation that the potential energy of the segment from the central part of the chain should be greater than the energy of the segment from the chain end. This is caused by a greater number of $-\text{CH}_2-$ segments of the neighbouring molecules (interaction sites) which are at the optimal interaction distance. Therefore, for the end segments of the central molecule the term Δu caused by surrounding molecules is the smallest. Towards the chain center

the actual value Δu per segment should increase up to some constant value Δu_m . This maximal value is determined by the geometrical structure of chains which limits the maximal number of the nearest molecular interaction sites. The difference in Δu determines the probability of g states along the chain, in agreement with the experimentally observed profiles.

However, if the mentioned mechanisms are the only ones, then the measured probability profiles for chains of different length should look equally. They should differ only in the length of the central part where the probability value is constant. As this is not in accord with the experimental data, we suppose that in addition to molecular interactions there should exist another mechanism connected with the disorder of interlamellar structure. However, in contrast to Maroncelli et al.⁹, who suppose some additional mechanism of disorder which does not depend on the conformational structure of molecules, in our opinion the interlamellar disorder can be caused by the above mentioned increasing dispersion in the chain length with increasing number of segments, N . The observed probability of g states of end-chain segments therefore increases with increasing number of alkane segments⁹.

CONCLUSIONS

The suggested qualitative model shows that the occurrence of the rotator phase in the phase diagrams of some alkanes might be connected with a partial increase of the conformational flexibility. The resulting increase of entropy is greater than originally thought, since also the "little" probable conformations (which have been neglected) effectively contribute to the conformational partition function. The small probability given by the Boltzmann exponent is compensated by the great number of ways in which these conformational states can be placed on the chain.

On the basis of the present estimate and comparison with experimental data, the partial increase of conformational flexibility can even have a decisive influence on the existence of the rotator phase in alkanes.

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