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MOLECULAR DISORDER AT PHASE TRANSITIONS OF *n*-ALKANES

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The homologous series of *n*-alkanes, with solid-to-solid phase transitions following fusion, are considered. By means of available experimental data, the total fusion entropy is resolved into its volume and disorder contributions. Their dependences on the number of carbon atoms per molecule are compared with that recently evaluated for those even *n*-alkanes, which reach their final crystal form immediately after solidification. Thus, an insight into changes of molecular disorder, both at fusion and solid transition, is presented.

1. Introduction

The disorder and volume contributions to the fusion entropy $S_f = S_d + S_v$ of *n*-alkanes $C_n H_{2n+2}$, for even-numbered members with $6 < n < 20$, have been recently evaluated and their dependences on the number $(n - 3)$ of effective C-C bonds defined[1]. Both contributions have been divided into basic (inter-molecular) and conformational (intra-molecular) terms S_0 and S_c, respectively, leading to the relatively simple correlation

$$S_f = S_{do} + (n - 3)\, S'_{dc} + S_{vo} + (n - 3)\, S'_{vc} = S_0 + (n - 3)\, S'_c. \qquad (1)$$

In Eq. (1), S'_c is conformational, disorder (S'_{dc}) and volume (S'_{vc}), entropy contribution per monomer, equal at the same time to entropy increment ΔS_c per additional C-C bond. Using the value of ΔS_{dc} which follows from the most accurate

experimental fusion data[1], a basic disorder entropy S_{do} of about 5.7 e. u. has been evaluated (e. u. being 4.184 J/mole K). This value with its ± 0.1 e. u. and ± 0.6 e. u. rms and maximum error, respectively, is in acceptable agreement with theoretically expected value equal to $R \ln 6 \simeq 5.5$ e. u., which has been introduced earlier[2] (R being the gas constant). Namely, the general form of this entropy term, associated only with inter-molecular disorder

$$S_{do} = R \ln (1 + t)(1 + r) \tag{2}$$

includes t and r as the numbers of translational and rotational degrees of freedom of a molecule, associated to kinds of motion which may be modified at fusion[2]. The assumption of maximum possible dynamical disorder in the liquid state, and the disorder completely disappearing after solidification, leads to $t = r = 3$[2,3].

Therefore, the group of even-alkanes, further denoted as C_n^o, has been chosen because their fusion is a single phase transition to a final crystal form stable down to low temperatures. The expected value of $R \ln 16$ has been confirmed experimentally for that group[1]. Analogous results have also been obtained for several compounds with generally-shaped rigid molecules using fusion data under high pressure[3,4].

Here, a similar procedure is extended to odd- and even-numbered n-alkanes up to $n = 19$ and $n = 32$, respectively, with solid-to-solid (s—s) transitions following fusion, further denoted as C_n^s. The crystal phase, between s—s transition and melting, has been often described as a simple rotational one[5,6], with hexagonal unit cell, in which molecules rotate about their long chain axes[7]. However, according to more recent experimental investigation on particular n-alkanes, especially on n-nonadecane (C_{19}) by means of X-ray and electron difraction[8], NMR[9-11], IR and Raman spectroscopy[12], some combinations of hindered roto-translational motions appear to be possible in this *rotator phase* accompanied moreover by certain kind of restricted conformations[9-13], or without them[14]. Indeed, the nature of the molecular motions in the high temperature solid phases of n-alkanes has been a continuing subject for speculation and study in the last fifty years since such a phase was first characterized[5-17].

The various modern techniques cited above, together with small angle X-ray[16] and incoherent quasi-elastic neutron scattering[17] (as for example in the study of molecular motions even in four modifications of solid n-tritriacontane) have been used to introduce reasonable models of molecular motions. It is interesting to note, that in spite of all these studies, an investigation considering volume and entropy changes at all phase transitions for successive members of this homologous series, has not been done. But an evaluation of disorder entropy terms at fusion can also give an experimental insight into the type of molecular motions in crystal before melting. Namely, if a similar correlation as given by Eq. (1) were again obtained and if the basic disorder term were smaller than $R \ln 16$, then it would suggest certain premelting activation of rotational and/or translational inter-molecular motions. At the same time, taking into account the conclusions of other investigations[9-17], it would provide a further test of the validity of Eq. (2)[2]. If the second term in Eq. (1) were also smaller, than that obtained previously for C_n^o alkanes, then premelting activation of certain intra-molecular conformational motions would also be suggested.

The main purpose of this paper is to test such statements, correlating all kinds of contributions to the fusion entropy with those previously evaluated[1-3], in accordance with recent results obtained by the other methods[11-13].

2. Experimental data

It is possible to extract the volume contribution to the fusion entropy from data under high pressure[3,4]. But for *n*-alkanes, such types of fusion and *s*—*s* transition data are scanty and not systematic. Restricted data in this field are rather old, and were taken by Nelson and coworkers[18]. Using results of their measurements, correlations of relative volume change with fusion entropy for several longer members of the series are presented in Fig. 1. The specific volume changes $\Delta V'/\mathrm{cm}^3/\mathrm{g}$ have been directly measured at the fusion temperature T_f and pressure P_f for C_9, C_{12}, C_{13}, C_{15}, C_{18} and C_{24}, while relative volume changes $\Delta V/V_s$ (V_s being the volume of solid at T_f) under increased pressure could be deduced only for three of them: C_{12}, C_{15} and C_{18}. For these three, liquid-phase specific volumes $V_l'/\mathrm{cm}^3/\mathrm{g}$ at fusion have been obtained by the extrapolation of compressibility data far from fusion to the freezing points[18]. For longer *n*-alkanes V_l' approach approximately constant value. A nearly linear decrease of V_l' at a rate smaller than 0.05% per additional monomer can be recognized at $n > 18$[19,20]. By taking into account that this decrement is approximately doubled at higher pressure (up to $6.5 \cdot 10^8$ Pa)[18], V_l' is extrapolated also, as a function of pressure, for C_{24}. Associated values of $\Delta V/V_s$ are calculated and introduced in Fig. 1. This procedure can not be exactly followed for shorter *n*-nonane and *n*-tridecane, because they are in the region where the even-odd effect of *n*-alkanes is still pronounced. This effect is characterized by an oscillating increase of T_f with n[18,19], as well as in analogous decrease of V_l' with n at normal[19,20] and also at high pressures[18]. These oscillations of parameters in even and odd numbered *n*-alkanes practically vanish for n greater than about 20[7,18,19].

$P-T$ phase diagrams (up to even $40 \cdot 10^8$ Pa) have been reported for five longer C_n^s members (from C_{21} to C_{32})[21], but unfortunately without associated volume measurements. Similarly, the lack od directly measured volume data appears in otherwise rather comprehensive $P-T$ studies at relatively lower pressures (to $3 \cdot 10^8$ Pa) for 29 *n*-alkanes up to C_{44}[20].

Thus, relative volume-to-entropy curves for C_n^s members are deduced in an acceptable manner only for C_{15} and C_{24}. The curves have similar behaviour as those for C_{12} and C_{18}, discussed previously[1], only at relatively higher pressures (above 1 to $2 \cdot 10^8$ Pa), when all of them have fusion as a single phase transition (C_n^o). Fusion data for lower pressures, beginning atmospheric pressure, exibit a rather smaller entropy and volume changes (C_n^s), than those for lower numbered even *n*-alkanes. It should be caused by partially consuming these changes in the *s*—*s* transitions which follow solidification in that region of pressure. However, with increasing pressure, the fusion process evidently varies continuously, resulting in an immediate transition to a final low temperature crystal form without any *s*—*s* transition, at some critical pressure[18,20]. This form is orthorhombic or monoclinic one for odd or even members, respectively[21]. One may introduce a hypothe-

tical total fusion process under lower pressures also. Entropy and relative volume changes at both the real fusion and the $s-s$ transition should be summed. This summation is approximate, of course, because measurements have been done neither at the same values of pressure nor with a sufficient density of points[18]. Such a procedure for C_{15}, as an example, results in the straight line with nearly the same slope as for the real single fusion at higher pressures as can be seen in Fig. 1. The line is translated to lower values of entropies by only about 5%. This

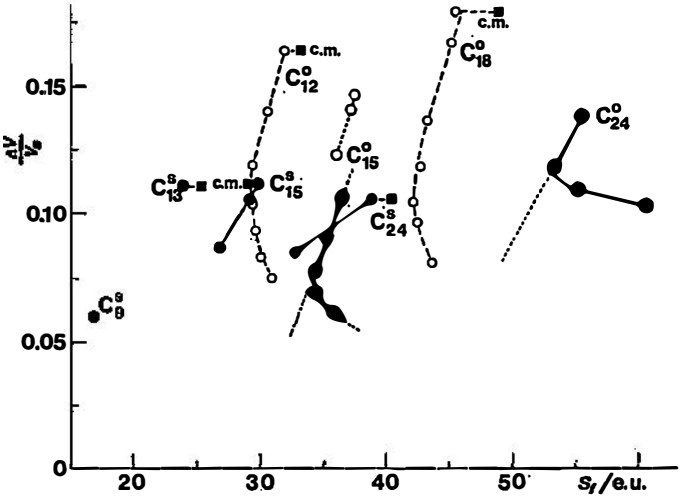

Fig. 1. Correlation between relative volume change $\Delta V/V_s$ and fusion entropy for several n-alkanes ($C_n \equiv C_n H_{2n+2}$) at normal and high pressures — C^s_n denoted by • and C^o_n by ○ and ● (Values of S_f were obtained by means of Clausius-Clapeyron equation, or by calorimetric methods — denoted by c. m.).

discrepancy may be taken as an inaccuracy of the evaluation. It is known that heats of fusion evaluated by means of Clausius-Clapeyron equation (further denoted as C.-C. Eq.) from T_f, P_f and ΔV data, reach the maximum error (at normal pressure), of about 3 to 8% of correspoding values obtained by calorimetric methods[18].

The straight line parts of the curves considered in Fig. 1, for real or hypothetical fusion, without $s-s$ transition (under higher or lower pressures, respectively) may be described by[2]

$$S_f = S_d + b\,\Delta V/V_s \tag{3}$$

as a general from of Eq. (1). The volume contribution to the fusion entropy thus can be defined. Relevant slopes of the curves evidently indicate an increase of the volume coefficient b with n. Coefficient b is close to 33 R and 43 R for C_{15} and C_{24}, respectively, as compared to those previously defined to be about 29 R and 33 R for C_{12} and C_{18}, respectively[1,4]. However, the increase of b with n, which differs for C^s_n and C^o_n members, represents more a qualitative, rather than a quantitative statement, due to the lack of adequate fusion data under high pressure for

all members of the series. One may combine (dT/dP) data by Wurflinger and Schneider[20] with recent volume data up to $5 \cdot 10^8$ Pa by Dollhopf et al.[22]. However, values of ΔV at fusion and s—s transition deduced from available presentation of $V = f(T, P)$ for n-nonadecane[22] are within an uncertainty of about ten percent, while the others are declared with an inaccuracy of only few promilles[18,23]. Nevertheless, the fusion of C_{19} at lower pressures, with S_f calculated by means of C. - C. Eq.[20,22], would appear, in diagram of Fig. 1, in proper order of magnitude (between C^s_{15} and C^s_{24}), but more as a broken line, than a continuous curve. Moreover, pairs of ($S_f - \Delta V/V_s$) values would appear as unconsistent points in this diagram, even at normal pressure, depending whether both values are directly measured (35.88 e. u.[7] — 0.102[23]; 0.114[22]), or one of them is calculated from C. - C. Eq., i.e. ΔV (35.88[7] — 0.122[7,20]), or S_f (33.88[20,22] — 0.114[22]), (30.6[20,23] — 0.102[23]). Discrepancies are rather pronounced. Using $P - T$[20] — — V[22] data under increased pressure, initial entropy-to-volume *line* of hypothetical fusion (obtained anologously as for C^0_{15}) may be constructed. Its slope could then be deduced, but inside too large limits of $34 < b < 54\,R$. For real fusion, as a single phase transition, at higher pressures (above $2 \cdot 10^8$ Pa)[22] no dT/dP values are given[20], and S_f associated to known ΔV values cannot be determined, so neither coefficient b. Thus, the only two points of b values, based on data of the same authors[18], remain as representatives of both groups of n-alkanes (C^o_n and C^s_n in Fig. 1). They are, of course, insufficient for the functional dependence of S_v with n to be determined.

Therefore, another approach, analogous to that used for C^o_n n-alkanes[1], should be applied. Instead of the coefficient b, the thermal pressure coefficient γ, the slope of P—T isochores in liquid at fusion, is evaluated. Using Maxwell's equality

$$\gamma = (\partial P/\partial T)_V = (\partial S/\partial V)_T$$

it follows[1] that

$$S_v \simeq \gamma_f \Delta V. \tag{4}$$

γ_f is determined by extrapolation of experimental data under high pressure[23] and/or at elevated temperatures[24] to the fusion point at normal pressure. It has been done for n equal to 7, 11, 13, 15, 17, 19, 22 and 32. As can be seen in Fig. 2 a slow nearly exponential decrease of γ_f with n is obtained. It enables one to give a reasonable interpolations of γ_f values for longer n-alkanes, with n equal to 24 and 28, whose isochores have not been investigated. An interpolation for shorter n--nonane, being in region of rather steeper variation of γ_f with n, results, of course, in a greater uncertainty. This interpolation is hampered by the uncertain γ_f value of the neighbouring, still shorter odd member, n-heptane, for which rather high temperature extrapolation is done. Namely, its γ (T) has been deduced in the room temperature region[24], while its fusion temperature is about 100 K lower[7].

The situation considering experimental data of volume changes at fusion, even at normal pressure, is also unfavourable, especially for longer n-alkanes[19,20]. However, more recent precise values of specific volume changes presented in Fig. 3[18,23] (measured with a probable error of less than 0.001 cm^3/g) suggest a reasonable assumption, that these changes are then approximately independent on n and equal to about 0.12 cm^3/g, of course, within an uncertainty of a few per cent.

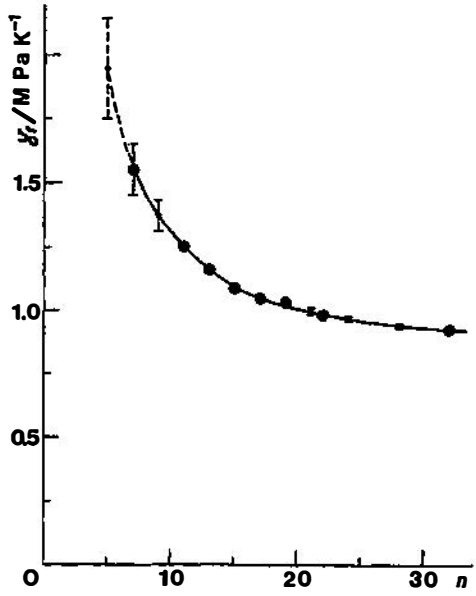

Fig. 2. Thermal pressure coefficient γ_f in dependence on the number of carbon atoms per molecule of *n*-alkanes.

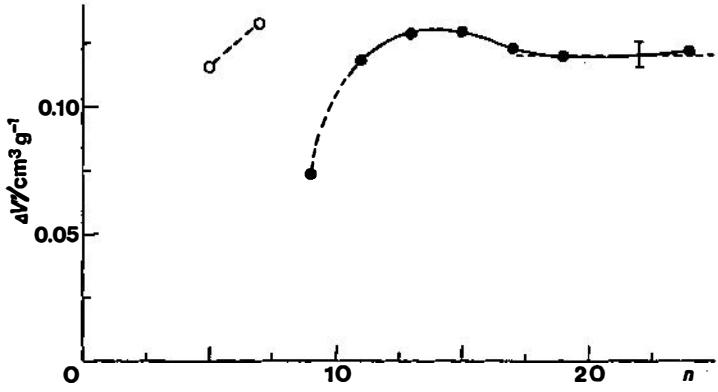

Fig. 3. Specific volume change $\Delta V'$ at fusion of *n*-alkanes with *s*—*s* transition up to $n = 24$ C_n^s denoted by • and C_n^o by ○.

Namely, older data of relative volume changes are somewhat smaller (for n up to 28)[25] and also somewhat higher (up to $n = 34$)[19,20], than more recent ones[18,23]. As an example, $\Delta V/V_s$ for C_{24} has been stated to be 9.5%[25] and 11.2%[19], respectively, as compared to accepted value of 10.5%[18,20].

Otherwise, ΔV values calculated from C.-C. Eq. based on S_f[7] and $P-T$ data are mostly about 10% (but also even 20%) higher[20], than directly measured values[18,19,22,23,25]. Thus, they cannot be taken into account.

n-nonane with its too small $\Delta V'$ of about 0.074 cm^3/g[18] is rather out of line with the others, as can be seen in Fig. 3. This value is actually nearly half of $\Delta V'$ for its neighbour *n*-heptane[19,20], which, however, has no *s*—*s* transition. Thus the *s*—*s* transition in C_9 should be especially *effective* in the sense of an approach to melting of the crystal. Indeed, it has been noted that inelastic neutron scattering observed from its high temperature solid state phase resembles that from liquid more closely, than that from the low temperature phase[14].

On the other hand ΔV deduced by means of C.-C- Eq. from S_f[7] and T—P data is about 50% higher[20], than that directly measured[18]. However, P—T fusion curves also differ; *s*—*s* transition has been detected up to $0.5 \cdot 10^8$ Pa[20] instead at about $5 \cdot 10^8$ Pa[18]. Thus, *n*-nonane needs further investigations.

Altogether, the necessary data, either directly measured, or inter- and/or extra-polated, as presented in Figs. 2 and 3 may be considered as satisfactorily collected for a reasonable calculation of the volume entropy contribution according to Eq. (4).

3. *Contributions to fusion entropy*

3.1. *Volume contribution*

The volume entropy contributions S_v, calculated with the above procedures, and their dependence on the number of carbon atoms *n* per molecule are presented in Fig. 4. As for C_n^o even *n*-alkanes[1], a nearly linear dependence of S_v on *n* can

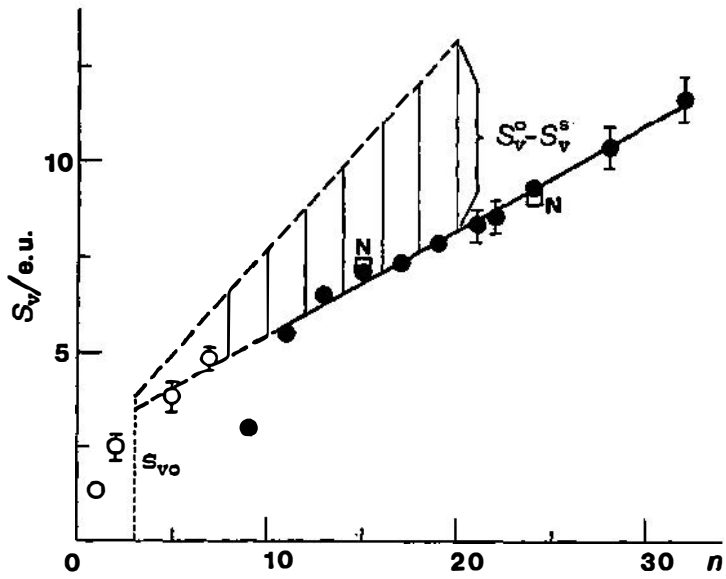

Fig. 4. Dependence of volume contribution S_v^s to fusion entropy on the number *n* of C atoms of *n*-alkanes with *s*—*s* transitions (denoted by ●) in comparison with analogous dependence $S_v^o - n$ for members without transitions. (Values of S_v based on data under high pressure[18] are denoted by N).

be recognized in this diagram, of course, within experimental errors, and excluding n-nonane. It is interesting to note that approximate S_v values for still shorter odd members, such as heptane and pentane (no data exist for volume change for propane), without $s-s$ transition, may also be included in line with the others. However, it may be an accidental agreement. Namely, these shorter n-alkanes have structures different from the normal triclinic one, of the longer even n-alkanes without $s-s$ transition and hence should not be expected to follow the same pattern in their behaviour[7].

Volume entropy contributions, previously evaluated for C_n^o members[1] and here reproduced by a dashed line in Fig. 4, are evidently higher, than for C_n^s members. Bearing in mind, that internal rotations (of about $\pm 120^o$) around the end C—C bonds remain for a molecule of n-alkanes in an unchanged conformation[2,3], only $(n-3)$ bonds appear to be effective[4,2,3]. Thus, one may assume the correlation

$$S_v = S_{vo} + (n-3)\, S'_{vc} \tag{5}$$

for lower straight line in Fig. 4, as well as for the higher one[1]. The least squares $(l-s)$ method gives about 3.5 e. u. and 0.28 e. u. for S_{vo} and S'_{vc}, respectively, for lower line and about 3.8 e. u. and 0.55 e. u., respectively, for higher line[1]. Both volume contributions, for C_{15} and C_{24}, evaluated from fusion data under high pressure[18] (Fig. 1) using Eq. (3), are in good agreement, within 2.5%, with values following from data at normal pressure[2,3,24] (Figs. 2 and 3) using Eq. (4). Of course, adequate P-V-T fusion data under high pressure for all considered members would be useful for better intercomparison, and the confirmation of Eq. (5).

Alternatively, the volume coefficient b may be extracted from data in Fig. 2, using Eqs. (3) and (4) from which follows $b = \gamma_f V_s$. Values of b can be evaluated also directly from the diagram in Fig. 4 by means of $b = S_v V_s / \Delta V$. Analogous, nearly linear, dependence on n is obtained i. e.

$$b = b_o + (n-3)\, b'. \tag{6}$$

The $l-s$ method gives somewhat higher values of constants $b_o = 16.40\, R$ and $b' = 1.36\, R$ for C_n^s members, than for C_n^o ($16.25\, R$ and $1.17\, R$, respectively)[1]. This result, the ratio $(b_n^o/b_n^s) < 1$, contrary to the ratio $(S_v^o/S_v^s) > 1$ is somewhat surprising. It has been previously remarked that the volume coefficient b rises as the geometry of the molecules becomes more complex[1,2]. So, the first member of the series, methane, belonging to the separate group of substances with spherical-like molecules has the smallest value of b about $8\, R$[4], within expected values of $(7 \pm 2)\, R$ for that simplest group[2]. Similarly for substances with linear-like molecules, ethane has b equal to $(10.5 \pm 1.5)\, R$, about 50% higher[2]. These values are rather smaller than those which would follow from Eq. (6). Associated volume entropy contributions for these two members are also relatively smaller and thus out of both lines in Fig. 4. Considering further members of n-alkanes, the complexity of molecules surely rises with their length, as b does[1], according to Eq. (6). But it is difficult to understand why members with $s-s$ transition odd- and even-numbered, seem to be *more complex*, in this aspect, than even members of the same length but without transitions whose $b_n^o < b_n^s$. Probably this difference

in values of b constants should be somehow correlated to the variety of n-alkane crystal structures after solidification. Nevertheless, in spite of these deviations, relative volume changes at fusion of C_n^o members are sufficiently higher than those for C_n^s ones, resulting thus in an analogous correlation of S_v^o and S_v^s values, as expected and confirmed by diagrams in Fig. 4.

3.2. Disorder contribution

Difference between experimentally determined fusion entropy S_f and its volume contribution S_v is just the disorder entropy contribution S_d. It cannot be measured directly, but only evaluated as $S_d = S_f - b\,\Delta V/V_s = S_f - \gamma_f \Delta V$, according to Eqs. (3) and (4).

Fusion entropies are based on values for temperatures and heats of fusion systematized by Broadhurst[7]. They have been determined in such a manner, that an overall consistency with total accumulation of various published data has been achieved[25]. Thus, S_f can be considered to be accurate inside 1% for shorter n-alkanes, but up to a few percent for longer ones[7,27]. Together with an uncertainty of S_v values, the inaccuracy of S_d evaluation may be doubled. Nevertheless, within these approximations, S_d appears to be also in nearly linear dependence on n, but with a discontinuity at $n = 20$, resulting in two straight lines as can be seen in Fig. 5. The correlations of S_d with n may be expressed analogously as for volume contribution, given by Eq. (5), i. e. with[1]

$$S_d = S_{do} + (n - 3)\, S'_{dc}. \tag{7}$$

Both lines are situated lower than lines of C_n^o n-alkanes[1], reproduced in the same figure (dashed line). Thus, by the analogous procedure using the $l - s$ method, rather smaller specific entropies S'_{dc} per monomer follow for C_n^s members, being about 1.5 e. u. (for $n < 19$) and 1.3. e. u. (for $n > 20$) instead of about 2.1 e. u. for C_n^o ones[1].

The basic disorder entropy S_{do} evaluated for $n = 3$ of about 3.7 e.u. ($n < 19$) and 4.6 e. u. ($n > 20$) are also smaller than 5.7 e. u., obtained for C_n^o members[1]. These values, based on too small a number of uncertain experimentally evaluated points (presented in Fig. 5), may be taken, of course, only as approximate ones. However, one may combine Eqs. (5) and (7) in the resultant form of Eq. (1), superposing mean values of all entropy terms evaluated here. Such a superposition fits real fusion entropy rather well, within its experimental accuracy of $\pm 1\%$. Moreover, if entropy changes, both at fusion and s—s transition[7], are combined, resultant total entropies (not shown here) again fit the form of Eq. (1), without any discontinuity for odd members (up to C_{33}). Then the basic entropy term corresponding to real fusion entropy of propane at $n = 3$, is approximately the same as for C_n members. The entropy contribution per additional monomer in such a hypothetical fusion for C_n members is about 10% smaller for odd ones, but only few per cent smaller for even ones, as compared to C_n^0 members. Of course, it is not possible to recognize whether the minor differences of these contributions correspond only to final differences of conformations between liquid and solid state. The different mutual interaction between molecular chains[26], resulting in different crystal structures[7,15], may also introduce certain entropy contribu-

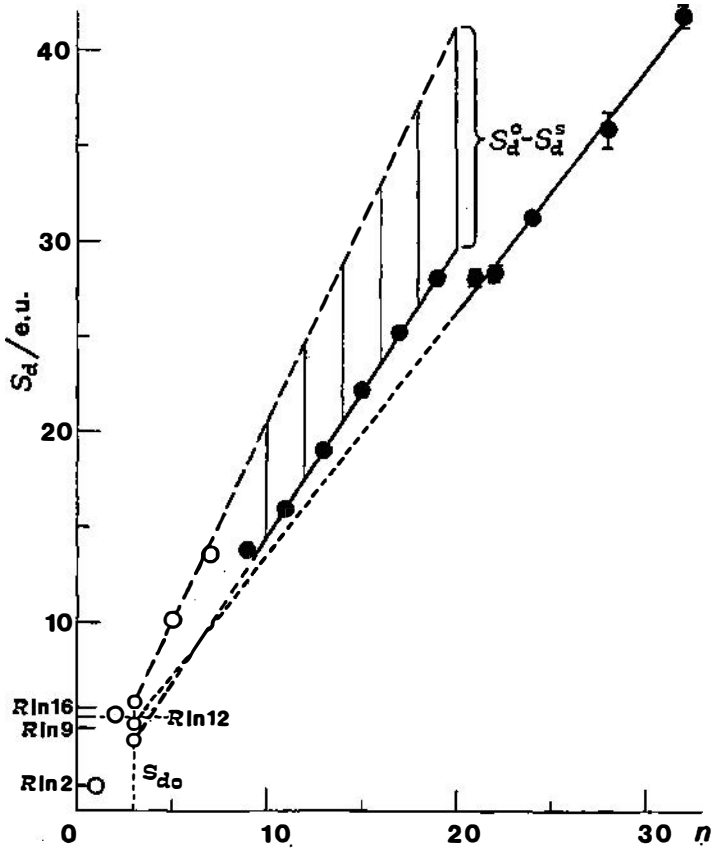

Fig. 5. Dependence of disorder contribution S_d^s to fusion entropy on the number of C atoms of n-alkanes with $s-s$ transitions (denoted by ●) in comparison with analogous dependence $S_d^o - n$ for members without transitions.

tions. Nevertheless, the regularity of total entropy change may be accepted as support to the assertion that definite differences of relevant disorder entropy terms really exist between C_n^o and C_n^1 members. They are evidently more pronounced than possible experimental uncertainties, as indicated in Fig. 5.

4. *Discussion*

Both, the disorder contribution to the fusion entropy and the total entropy of *hypothetical* fusion of n-alkanes with $s-s$ transitions in correlation to those without such transitions, suggest, that decrease of inter- as well as intra-molecular disorder should be lower at fusion of former, than of latter ones. Thus, one may consider the process of crystallization as not to be finished, until $s-s$ transition are also included. Such an approach of *prolonged freezing*, through one or more $s-s$ tran-

sitions, may then give an insight in various high temperature crystal phases of *n*-alkanes. They are realized mostly in relatively narrow temperature interval below the real fusion[7].

As many as four modifications, more and more ordered ones, exist in C_{33}[16,17]. Moreover, for two shorter members, C_{23} and C_{25}, initially thought to have only two modifications[7], an additional weak first-order transition was recently detected[28], closer to the melting point. The more highly ordered phase of C_{25}, for example, is analogous to the third one (at cooling) of C_{33}, as shown by *X*-ray diffraction and explained by Ungar[29], who clarified earlier ideas of *rotator phases*[8,28]. On the other hand four modifications have been revealed by calorimetric (*DSC*) measurements on C_{25}, C_{27} and C_{29}, supported by associated *IR* spectra[13]. It would be nice to include all of these *n*-alkanes as well as further odd and even members up to C_{43} and C_{38}, respectively, which are the last to have $s-s$ transitions[7,20]. Unfortunately, there exist almost no volume data for relevant entropy evaluations (as defined in Sec. 2), which would enable the molecular disorder in particular phases to be resolved.

Thus, in principal, one can deduce only approximately, the rest of molecular disorder after crystallization, which should be consumed in all following $s-s$ transitions down to a final low temperature crystal phase. Of course, comparing the contributions to fusion entropy of considered C_n^0 and C_n^1 members, in this respect, one must take care about their different final crystal structure. The former are triclinic and the latter orthorhombic or monoclinic ones for odd ($n > 9$) or even-numbered C_n^1 members ($24 < n < 32$), respectively, (C_{22} and C_{24} being still triclinic)[7,15]. Associated different packing densities of these structures[7], could also influence entropy contributions and thus obscure difference between them because of conformations alone. Therefore, it would be better to correlate odd *n*-alkanes with hypothetical members obtained as an extrapolation of longer ones with $n > 43$[30], crystallizing in the same orthorhombic structure, but without $s-s$ transition. However, more details about that with an extension up to polyethylene will be reported in full elsewhere.

It is almost impossible to compare contributions to fusion entropy per monomer of *n*-alkane having $s-s$ transition with theory, because a general one does not exist[22,31]. There is no theory also for volume entropy contributions, excluding approximate approaches for the most simple substances with spherical-like molecules[32,2]. Considering a pure disorder approach, activation of conformational changes in solid state are also neglected[14,23]. Even conformations in liquid state are mostly also idealized, assuming that influence of two contrary effects: the solvent effect[33] and the one due to the excluded volume[34,35] are mutually cancelled[26]. Such an oversimplification in liquid and solid near melting point[23,26,34] cannot result in relevant theoretical values of disorder entropy contributions for comparison with values evaluated by ourselves or others[23] from experimental data.

Further, at the present state of entropy investigations, we are not able to determine quantitatively neither the contribution of non-planar molecules among planar ones, nor the number and positions of gauche bonds along the molecular chains, like some other methods do[9-13]. So, Zerbi and coworkers, using *IR* and Raman spectra in comparison with calculated densities of vibrational states[12,36], have been able to give a definite information: a considerable fraction of molecules

with a few gauche bonds near the chain ends, accompanied by translational jumps with length of 2 to 3 CH_2 units, appear in the solid state of *n*-nonadecane[12]. For longer *n*-alkanes some gauche bonds may be realized also in the chain interior[10,13].

Although entropy considerations cannot give such a detail insight, they may confirm an appearance of different solid state conformations as a general property of *n*-alkanes with *s—s* transitions.

5. *Conclusion*

Disorder entropy contribution per additional monomer, although different for odd and even C_n^s *n*-alkanes, being 1.5 e. u. and 1.3 e. u., respectively, are both considerably smaller than 2.1. e. u. evaluated for C_n^0 members[1], Thus, they undoubtedly indicate certain activation of different conformations in the solid before melting. Moreover, due to a decrease of S'_{dc} for C_n^s members in respect to that for C_n^0 ones, more than 25%, these conformations surely cannot be ignored, like some others assumed[23]. Disorder entropy contributions for considered group (see Fig. 5) lead to conclusion that intra-molecular changes are regularly retained in solid after fusion in all *n*-alkanes with *s—s* transitions. Special details of these changes, mentioned in Sec. 4, cannot be resolved, but they are surely not restricted only to particular members investigated recently by methods of *NMR, IR* and Raman spectroscopy[9-13].

Moreover, from the discontinuity of $S_d - n$ diagram in Fig. 5, it is evident that so called *rotator phase* of *n*-alkanes[6,14,28] should not be the same for two groups of C_n^s members ($11 \leqslant n < 19$ and $n > 20$) considered here. It may be recognized that higher solid state molecular disorder per monomer should be associated to this phase for longer *n*-alkanes than for shorter ones. This phase is more or less close to, but not yet truly of hexagonal symmetry for shorter members[28,29] as was at first assumed[5-7]. It was even recently the subject of a continuous study by a number of experimental techniques, as well as theoretically[12,13,17,28,29]. Pecularities of various *rotator phases* are still under discussion, and remain open for future quantitatively more detailed investigations.

The uniform volume contribution per monomer, S'_{vc}, being also smaller, even about 50% for C_n^s members, than for C_n^0 ones (see Sec. 3.1.), supports the conslusion emphasized here of solid-state conformations for all members having any *s—s* transition. It is worthy to note that although important, this contribution is not dominant, but rather smaller than the disorder ones (see Sec. 3.2.) as has been stated previously[1], contrary to some earlier opinions[19].

An exact, general or particular calculation of S'_{dc}, as well as S'_{vc}, is an enormously difficult problem still to be solved and therefore no correlation with theory may be presented here.

Considering the basic disorder entropy term at fusion of non-simple liquids with flexible molecules, the situation is also undefined. Rejecting the old and controversial term of so called *communal entropy* S_{com}[19,37], no other theoretical quantity remains, except our recent simple one[2,3], according to Eq. (2).

Both, the values of S_{do} evaluated here (in Sec. 3.2.) are, of course, higher than $S_{com} \simeq R \simeq 2$ e. u., but smaller than $R \ln 16 \simeq 5.5$. e.u. The last value corres-

ponds to substances with generally shaped rigid molecules[2,3], and also to even n-alkanes ($6 < n \leq 20$)[1], as representatives of substances with flexible molecules. Moreover, both values of S_{do} for C_n^s members are even smaller than $R \ln 12 \simeq 5$ e. u. This value has been associated to substances with linear-like molecules, having the possibility to modify at fusion three translational but only two rotational degrees of freedom, including $t = 3$ and $r = 2$ in Eq. (2). The same value has been evaluated for benzene (from data under high pressure)[3], indicating a possibility of molecular rotation around molecular axis normal to the molecular plane already in the solid state. An assumption, that for C_n^s members, a hindered translation along the long chain axis is possible, in addition to more or less hindered rotations around it[14], before melting, requires $t = r = 2$ and consequently $S_{do}^s = R \ln 9 \simeq$ $\simeq 4.4$ e. u. This value is just between those experimentally evaluated (in Sec. 3.2.) of about 4.6 e. u. and 3.7 e. u. as approximate ones for considered even and odd C_n^s members, respectively.

Thus, the simple entropy investigations presented here, in correlation with those previously done[1], by resolving of fusion entropy into its particular terms according to Eq. (1), present an additional confirmation of the following statement: some kind of roto-translational molecular motions including certain intra-molecular changes are preserved also in solid after fusion down to s—s transition of n-alkanes, as suggested recently by methods already cited[9-17].

On the other hand, inter-molecular solid state disorder, indicated by the method mentioned, in accordance with numbers of translational and rotational degrees of freedom modified at fusion itself, which fits Eq. (2), confirms this simple relation[2,3] once more. Extracted values of basic disorder term fill up the gap between boundary values of $R \ln 2$ and $R \ln 12$, corresponding to substances with rigid molecules, sperically- and linearly-shaped, respectively. Namely, possible combinations of t and r values are rather restricted for rigid molecules[2,3] while more combinations may appear for non-rigid molecules, where partial intra-molecular changes may stipulate intermolecular motions[10,12].

Of course, the poorness of data under high pressure[18], as well as the approximations made necessary in the evaluations by the scarcity of data even at normal pressure[7,19-25], make details of above conclusions somewhat risky and tentative. To improve the entropy considerations introduced, and to fortify the associated conclusions, more complete and more accurate data of relevant parameters (like ΔV, V_t, γ_J or b defined in Sec. 2) for included as well as for omitted members with an extension to longer n-alkanes, still having s—s transitions, should be available.

Nevertheless, it may be already stated now, that inter- as well as intra-molecular disorder, like the rest of more pronounced different types of molecular motions in liquid, should be partially retained after solidification.

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MOLEKULARNO NEUREĐENJE NA FAZNIM PRIJELAZIMA *n*-ALKANA

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Razmatran je niz *n*-alkana, koji imaju fazne prijelaze čvrsto-čvrsto. Pomoću postojećih eksperimentalnih podataka ukupna entropija taljenja razlučena je na volumni doprinos i doprinos neuređenja. Zavisnost tih doprinosa o broju ugljikovih atoma po molekuli uspoređena je sa sličnom ovisnošću za parne *n*-alkane, bez faznih prijelaza prije taljenja. Na taj način dobiven je uvid u molekularno neuređenje kako na taljenju, tako i na faznim predprijelazima.