

Macromolecular conformational volume and thermodynamics of crystal melting

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Conformational parts of the thermodynamical function change on melting, in particular the conformational volume ΔV_{conf} , the conformational entropy ΔS_{conf} and the pressure variation of the latter are analysed for an ideal polymer crystal. These quantities can be calculated from the data for low molecular compounds combined with the three-state rotational isomer model (with adjacent *gauche* states of opposite sign forbidden). The assumption of intramolecular dominance in the Gibbs energy difference between conformers in a polymethylene chain results in a negative value for ΔV_{conf} and a positive value for the quotient $(\partial \Delta S_{\text{conf}} / \partial P)_T$ which contradicts the available experimental data for polyethylene crystal fusion. The disagreement might be reconciled by the postulation of intermolecular contribution to the Gibbs energy difference between conformers favouring the existence of *trans* sequences of bonds in the chain and the correlation of molecular orientations in neighbouring chains.

(Keywords: polymethylene melting; conformational entropy; configurational statistics; orientational correlations; van der Waals volume; packing in liquids)

INTRODUCTION

Melting of polymer crystals is usually thermodynamically treated as a process consisting of two steps: firstly an isochoric fusion of an ideal crystal with formation of the melt at high pressure, followed by an expansion of the melt to atmospheric pressure. Using this simplified picture the change of thermodynamic functions on melting can be divided into at least two contributions. This can be exemplified on the separation of the melting entropy ΔS_m into the entropy change at constant volume of the crystalline phase $(\Delta S_m)_{V^c}$ and an entropy contribution due to the volume expansion ΔS_{ve} .

$$\Delta S_m = (\Delta S_m)_{V^c} + \Delta S_{ve} \quad (1)$$

The first term on the right-hand side of equation (1) is often identified with the change in intramolecular conformational entropy of chains when passing from the crystalline to the molten amorphous state, ΔS_{conf} , and the volume expansion term can be found from the measurement of the thermal pressure coefficient γ , hence

$$\Delta S_m = \Delta S_{\text{conf}} + \int_{V^c}^{V^l} \gamma dV \quad (2)$$

where integration proceeds from V^c to V^l , i.e. from the volume of crystal to the volume of liquid at the melting point temperature T_m . Assuming melting of an ideal crystal possessing a perfect conformational order S_{conf}^c is zero and ΔS_{conf} equals S_{conf}^l .

The conformational entropy in equation (2) can be determined as a difference of two other experimentally accessible terms in equation (2). However, using the configurational statistics method based on the rotational isomeric state model of a polymer, the average conformational entropy of a chain in the unperturbed state \bar{S}_{conf} can be calculated¹⁻³ and its value identified with the conformational entropy of the collection of chains in the melt, S_{conf}^l . Values of ΔS_{conf} experimentally derived via

equation (2) and calculated theoretically are usually in relatively good accord for various polymers.

In spite of its popularity the foundation of the method of the conformational entropy determination is still actively discussed⁴⁻⁸. The main criticisms are e.g. correctness of the entire entropy-separation concept according to equation (1); the existence of an additional term in equation (1) accounting for the 'communal entropy' of a liquid; the assumptions of unperturbed chain parameters in the calculation of S_{conf}^l or of perfect conformational order in the crystal, etc. The whole procedure of comparison of ΔS_{conf} determined via two paths suffers from the insensitivity of the results to an arbitrary selection of input data and from the possibility of a fortuitous compensation of errors. The independence of the conformational entropy of melting on the volume or pressure which is implicitly involved in equating $(\Delta S_m)_{V^c}$ with S_{conf}^l or S_{conf}^c is somewhat controversial.

Determination of the conformational part of ΔS_m (and similar parts of the other thermodynamical functions on melting) depends critically on the role of intermolecular forces played in establishing a conformational equilibrium of chains in the polymer melt. Two types of models are presently assumed for the organization of macromolecules in the condensed state⁹⁻¹¹ with contradictory views concerning the role of intermolecular forces. In the 'coil model', a minimum influence of intermolecular interactions of the surrounding chains on the local distribution of conformers in the chain is assumed and the average dimensions of coils in the melt are about the same as those in theta solution. On the other hand, various 'bundle models' or 'meander models' of macromolecular organization presume the enhanced local parallel ordering of neighbour chain segments.

The intermolecular effect on the chain conformation undoubtedly increases at higher pressure and, simultaneously, in this case also the changes in the inherent volume of chains with conformation become important.

Theoretical and experimental results for the low molecular weight compounds indicate a several percent difference in the molecular volume between rotational isomers¹²⁻¹⁵. Both the abovementioned effects, namely the variation of conformational volume and the pressure (intermolecular) influence on conformational equilibria, are taken into account in the analysis of polymer crystal melting presented in this paper. On the basis of semi-empirical calculations, the conformational volume of melting ΔV_{conf} and the pressure changes of ΔS_{conf} are estimated for an ideal polymethylene crystal. Correlation of molecular orientations between the chain segments in liquid polymethylene is invoked in order to achieve some accord between the experimental and theoretical values.

RESULTS AND DISCUSSION

Partition of the volume of melting

In a similar way to the melting entropy, other thermodynamical functions can also be divided into several terms. For example, the conformational part can be separated from the total enthalpy of melting ΔH_m ^{16,17}. However, the volume change at melting ΔV_m is traditionally viewed (with one notable exception⁶) merely as the result of thermal expansion of the polymer melt with respect to the crystal. In fact, this quantity can also involve a conformational contribution due to the possibility of change of the inherent (e.g. van der Waals) chain volume with rotation. Since this effect has already been proven in low molecular compounds including alkanes, it should be expected that this effect would also operate in the polymer systems. Accordingly, the change of volume at melting of the polymer crystal can be divided as follows

$$\Delta V_m = \Delta V_{\text{unocc}} + \Delta V_{\text{conf}} \quad (3)$$

where ΔV_{conf} represents the difference between the inherent volume of chains in the crystal and in the melt (if intermolecular effects on the conformational equilibrium are neglected, *vide infra*). When the volume of the chain is expressed as a sum of van der Waals volume contributions of constituent atoms the unoccupied volume difference ΔV_{unocc} in equation (3) represents a change of an 'empty' volume between the crystal and the melt.

Calculation of the melting conformational terms

Conformational parts of the thermodynamical functions at polymer crystal melting ΔX_{conf} (where X is S , H or V) can be approximately estimated from knowledge of the conformational energetics of individual chains in the melt. Generally, the difference between the Gibbs energy of two conformers, Δg , is expressed as a sum of isolated molecule contribution and an environmental term

$$\Delta g = \Delta g_{\text{isol}} + \Delta g_{\text{env}} \quad (4)$$

and analogous relations apply to the enthalpy and entropy differences. The environmental term is indispensable in a description of the solvent effect on conformational equilibria of polar molecules and usually involves^{18,19} the expressions for dispersion and electrostatic solute-solvent interactions Δg_{dis} and Δg_{els} and the cavity term accounting for the Gibbs energy of the accommodation of solute in solvent. Recently, it has been shown that, due to the differences in inherent volume and solvent packing requirements between rotational isomers,

the term Δg_{env} might not be negligible for nonpolar solutes also^{13,20}.

Differentiation of equation (4) with respect to pressure yields an expression for the volume difference of two conformers Δv given as a sum of intramolecular and environmental contributions²¹

$$(\partial \Delta g / \partial P)_T = \Delta v = \Delta v_{\text{isol}} + \Delta v_{\text{env}} \quad (5)$$

The first term on the right-hand side of equation (5) corresponds to the difference in 'inherent' volume of two stable conformers and the second term accounts for the volume difference due to electrostriction, packing and other intermolecular factors.

In order to obtain the average conformational quantity for a chain molecule, it is necessary to find a proper mean value of Δg (and similarly for Δh , Δs and Δv) averaged over all possible conformational isomers in the chain. Flory's matrix method of configurational statistics²² represents the most appropriate method of averaging for linear chain molecules. However, since pressure-volume relationships are neglected in the present version of the latter method, we restrict our treatment to the simplified model of a chain with mutually interdependent rotational potentials. A three-state model with *trans* and two equienergetic *gauche* states (G^+ and G^-) is assumed with the exclusion of the pair of *gauche* states with opposite signs ('pentane interference'). Miller has shown⁶ that the following simple partition function represents an adequate approximation:

$$Q = 1 + \sqrt{2} \exp(-\Delta g/RT) \quad (6)$$

where Δg is the Gibbs energy difference between *gauche* and *trans* isomers. Fraction of bonds in the *gauche* states, f , is given by

$$f = (Q - 1)/Q \quad (7)$$

From the standard thermodynamic relations the expressions follow for the average conformational quantities of the chain. Conformational energy of chain \bar{E}_{conf} , conformational entropy \bar{S}_{conf} and its pressure derivative are:

$$\bar{E}_{\text{conf}} = f\Delta g \quad (8)$$

$$\bar{S}_{\text{conf}} = R \ln Q + f\Delta g/T \quad (9)$$

and

$$-(\partial \bar{S}_{\text{conf}} / \partial P)_T = (\Delta g/RT^2)(f/Q)(\partial \Delta g / \partial P)_T \quad (10)$$

Next, we assume that the total conformational volume change of the chain \bar{V}_{conf} is proportional to the number of *gauche* states in the chain:

$$\bar{V}_{\text{conf}} = f\Delta v \quad (11)$$

where Δv is the *gauche-trans* volume difference. The experimental results for polyethylene⁶ substantiate this assumption. Within the simple statistical model both average chain conformational energy and volume are related by the additive way to the single *trans* to *gauche* isomerization. If Δv is temperature independent, the variation of conformational volume of the chain \bar{V}_{conf} with temperature will be determined by the change of *gauche* fraction f with temperature. Hence,

$$(\partial \bar{V}_{\text{conf}} / \partial T)_P = (\Delta g/QR^2T^2)\bar{V}_{\text{conf}} \quad (12)$$

From the average conformational Gibbs energy of the chain expressed as a total differential:

$$d\bar{G}_{\text{conf}} = -\bar{V}_{\text{conf}} dP + \bar{S}_{\text{conf}} dT$$

a Maxwell relation will follow:

$$(\partial \bar{S}_{\text{conf}} / \partial P)_T = -(\partial \bar{V}_{\text{conf}} / \partial T)_P \quad (13)$$

Rearrangement of equation (10) using relations (5) and (11) and comparison with equation (12) confirms that equation (13) is satisfied.

Relations (8)–(13) provide the average conformational quantities and their derivatives for a model linear chain. If the Δg and Δv differences are known, the computed results can then be identified with the conformational terms appropriate for the set of chains in the melt state and compared with the conformational terms derived experimentally, similarly, as shown in the Introduction for the melting entropy.

Application to ideal polymethylene crystal

For polymethylene (PM) both conformational entropy and enthalpy calculated for the model polymer chain have already been compared with data derived from crystal fusion experiments^{1–3,6–8}. In the present work we concentrate on the estimation of conformational volume at melting and pressure variation of conformational entropy in PM. Therefore, reliable appraisal of the Δv difference appropriate for the molten PM is required.

Organic stereochemistry provides a great deal of examples on the existence of molecular volume changes with conformation. Apart from experimental works, convincing arguments concerning the existence of a conformational volume effect in linear chain molecules are furnished by theoretical calculations. Using the simple geometrical model we have calculated¹⁴ the magnitude of the mutual overlap of methylene groups in the *gauche* position of the PM chain. A sphere with a centre on each atom in the chain with the van der Waals radius was assumed and the surface (and volume) of a geometrical body formed by interlocking the spheres have been computed. The model computation for linear chain alkanes resulted in a value of about $-2.5 \text{ cm}^3 \text{ mol}^{-1}$ for Δv_w , the change of van der Waals chain volume at transition from the *trans* to *gauche* conformation. However, the computations are based on an approximation of rigid bond lengths and bond angles in molecule. There are indications in the literature that the latter condition is too restrictive; the bond angles can be slightly enlarged in the *gauche* conformation in order to accommodate the increase in repulsion energy due to the steric overlap of methylene groups. Accordingly, the calculations based on the rigid internal parameters could slightly overestimate the van der Waals volume differences Δv_w as can also be seen from Table 1 where all available data on the conformational volume changes in n-alkanes are summarized.

It should be pointed out that all data in Table 1 confirm the decrease in volume of the alkane molecule in going from the *trans* to the *gauche* conformation. The environmental term Δv_{env} in the molecular volume difference seems to be of less importance and the overall change Δv can be roughly estimated from the calculation of the van der Waals volume. The best present estimate of the *gauche*–*trans* volume difference in linear alkanes seems to be about $-1.5 \text{ cm}^3 \text{ mol}^{-1}$ of *gauche* bond and this value should certainly depend on the temperature and pressure of the system. The mentioned figure should be valid for the solutions of linear alkanes in quasi-spherical solvents (of the CCl_4 type) and for neat liquid short-chain

Table 1 *Gauche*–*trans* molecular and van der Waals volume difference for n-alkanes (in $\text{cm}^3 \text{ mol}^{-1}$)

Method of determination	$-\Delta v$	$-\Delta v_w$	Refs.
Raman spectroscopy			
Butane	1.0		23
Hexane	1.1		24
Heptane	1.8		12, 15
Statistical mechanical calculation for butane			
In CCl_4	4.7		
Neat	2.0		20
Monte Carlo simulation of liquid butane	0.4		25
Overlapping spheres calculation for n-alkanes		2.5	14
Correlation of liquid characteristic parameters		1.02	26
Correlation of partial molar volumes of n-alkanes in CCl_4		1.54 ^a	27

^a After recalculation from the partial molar volume data, see ref. 14

alkanes, at least. We should mention, however, that in recent Raman spectra measurements²⁸, no evidence was found for pressure induced change in the conformer population in liquid alkanes which implied the zero value Δv . As follows from Table 1, little is known still about the conformational volume changes of alkanes in rod-like solvents and, generally, about long chain alkane liquids.

Using the above estimation of Δv and equation (11) one can tentatively separate the conformational part of the melting volume ΔV_{conf} of an ideal PM crystal at the melting temperature 414 K. The generally accepted value²² of the *gauche*–*trans* Gibbs energy difference Δg , appropriate for chains in the ‘unperturbed state’, in the PM melt is about 2.1 kJ mol^{-1} . That corresponds to the fraction of CH_2 group in the *gauche* positions with $f \sim 0.43$. For comparison, the same quantity is about 0.405 (ref. 22) when computed using the more rigorous model of a chain with the interdependent rotational potentials in PM chain. The combination of the former value of f with $\Delta v = -1.5 \text{ cm}^3 \text{ mol}^{-1}$ of *gauche* bonds yields $-0.64 \text{ cm}^3 \text{ mol}^{-1}$ for \bar{V}_{conf} .

Identification of the calculated value V_{conf} with the term ΔV_{conf} in equation (3) results in an unconventional picture of volume changes during PM melting. Since the conformational volume change at melting is negative, the change of unoccupied volume in equation (3) should be higher than the experimentally observed total volume of melting⁷ ($3.28 \text{ cm}^3 \text{ mol}^{-1}$ of CH_2 groups). This means that during the melting process the average effective interchain distances should enlarge not only due to the thermal expansion on melting but also due to the ‘shrinkage’ of the volume occupied by the chains.

Since the population of *gauche* bonds in the PM chain is increasing with the rising temperature, \bar{V}_{conf} should become more negative with the increase in temperature, i.e. $(\partial \bar{V}_{\text{conf}} / \partial T)_P < 0$ as can be seen also from equation (12). From equation (13) it follows $(\partial \bar{S}_{\text{conf}} / \partial P)_T > 0$; which indicates an increase in conformational disorder in the melt with rising pressure. This quantity can be evaluated from equation (10) using the same parameters as above and it reads $5.4 \times 10^{-4} \text{ cm}^3 \text{ K}^{-1} \text{ mol}^{-1}$. Indeed, the spectroscopical measurements for short chain alkanes¹² suggest an increase in *gauche* bonds in the alkane liquids with rising pressure.

A few available experimental data for long-chain polymethylenes are completely at variance with the

foregoing findings derived from the experimental and computational data for short-chain alkanes. The only existing 'experimental' estimation of the conformational volume ΔV_{conf} for PM was derived⁶ from the pressure–volume–temperature properties of a polymer liquid combined with the three-state conformational model specified by equation (6) (using $\Delta g \sim 5.9 \text{ kJ mol}^{-1}$) reads $1.0 \text{ cm}^3 \text{ mol}^{-1}$ of *gauche* bonds, i.e. about 30% of the total volume change ΔV_m during the PM crystal melting. In contrast to the data from Table 1 this result suggests an increase in chain volume of about $4.31 \text{ cm}^3 \text{ mol}^{-1}$ of *gauche* bonds in the isomerization process from the *trans* to the *gauche* state.

Similarly, the observed pressure dependence of conformational entropy disagrees with the foregoing (positive) computed value. Indeed, large differences have been found^{7,29} between conformational entropy ΔS_{conf} and entropy of fusion at constant volume (ΔS_m)_{v^c} which may invalidate the entropy partition concept given by equation (2). However, the compression (pressure) necessary to maintain the melting at constant crystal volume seems to decrease the conformational entropy of the melt, i.e. the derivative $(\partial \Delta S_{\text{conf}} / \partial P)_T$ has a negative sign. Robertson estimated²⁹ that $(\Delta S_m)_{v^c}$ represents only about 75% of the conformational entropy existing in the melt at atmospheric pressure which is about $7.49 \text{ J K}^{-1} \text{ mol}^{-1}$ of CH_2 group. In other words approximately 25% of this value is lost on compressing the melt from the volume of the melt to the volume of the crystal. At a molecular level this observation corresponds to an increase in the *trans* bond population in the PM chain with increasing pressure. An analogous pressure-induced decrease in ΔS_{conf} has recently been found also for *trans*-polyisoprene melting⁵.

Due to the limited data available concerning the pressure (volume) conformational terms in PM it is difficult to decide what importance should be assigned to the disagreement between the experimental and the calculated results. The origin of disagreement is not connected with the application of the simple statistical model in the calculation. In the simple model, similarly as in more elaborate models²², the sign of terms \bar{V}_{conf} and $(\partial \bar{S}_{\text{conf}} / \partial P)_T$ is determined by the sign of Δv . The only difference is that in the latter case the simple additive relation, equation (11), is no more valid since the *gauche* bonds in the chain will not contribute independently to the total volume \bar{V}_{conf} . In fact, the latest experimental results for liquid n-hexane²⁴ indicate the interdependence of *gauche* interconversions on molecular volume changes.

From a comparison of experimental results for PM and Table 1 it seems that there may exist a difference in the pressure (volume) conformational properties of short-chain alkanes and long-chain PM analogues. According to a recent study³⁰ this may be evidence that conformational properties of short and very long alkanes cannot be described by the same model. Traditionally, however, the similarity in n-alkane behaviour is assumed, regardless of chain length, and a different rationalization should be sought to account for this discord.

Correlation of molecular orientation in PM







If the difference in sign of the terms \bar{V}_{conf} and ΔV_{conf} or $(\partial \bar{S}_{\text{conf}} / \partial P)_T$ and $(\partial \Delta S_{\text{conf}} / \partial P)_T$ for short and long alkanes is real, a tentative explanation emphasizing the role of intermolecular interactions can be suggested. The con-

tribution of van der Waals volume changes ought to be similar (and negative) in both cases. Therefore, the difference is connected with the Δv_{env} term in equation (5) and may be assigned to the existence of the correlation of molecular orientations (CMO) in long-chain alkanes. Depolarization of Rayleigh light scattering, calorimetric and other techniques confirm the small preference in the alignment of neighbouring segments in long chain alkanes^{9,10,31,32}. The molecular correlation is of the short-range order with the correlation length less than 1 nm or about 8–9 bonds in all *trans* sequence which may be in a parallel orientation with the similar chain segment in the near vicinity¹⁰. Since the tendency to CMO influences only the local segment population, the overall chain conformational equilibrium is only slightly perturbed in comparison with the dilute solution in the theta state.

So far all evidence for the existence of CMO in long alkanes was inferred from the experimental measurements. Recently, we have performed molecular-mechanics calculations³³ of internal rotation in clusters of hexane molecules which provide some energetical parameters concerning CMO. The *gauche*–*trans* energy difference Δe was determined for the rotation around the central bond in all-*trans* hexane with one or two additional extended hexane molecules in the near vicinity. The position of one or two neighbouring extended hexane and all internal parameters have been optimized for each value of the torsional angle. A more elaborate description of the method, the model and the computational details can be found in ref. 33. Here we wish to point out some implications of the calculations for CMO. From the computation it follows that the additional molecules in the vicinity influence the Δe value of an isolated molecule and the effect is sensitive to the mutual orientation of the zig-zag backbone in hexanes. The intermolecular contribution to the *gauche*–*trans* energy difference, Δe_{env} , is listed in Table 2. It can be seen that in most cases the presence of a rod-like molecule or molecules in the vicinity induces the chain stiffening of the central molecule resembling the notion of CMO. The all-*trans* segments which are translationally completely free prefer the aligned positions and induce an additional preference for the *trans* state in the segments with internal rotation. Surprisingly, the computation also predicts the opposite effect, namely an increase in chain flexibility due to the presence of a rod-like molecule in its vicinity when the molecules are in the sandwich configuration AA.

Neglecting the differences between Δe_{env} and Δg_{env} we can conclude that, locally, in the regions with CMO the *gauche*–*trans* Gibbs energy difference Δg can be much higher than the recommended effective mean value for the chain which is about 2.1 kJ mol^{-1} (ref. 21). Since the extent of CMO is pressure sensitive it may also influence the *gauche*–*trans* volume difference Δv through the Δv_{env} term. It depends on the sign of the derivative $(\partial \Delta g_{\text{env}} / \partial P)_T$ whether Δv_{env} will follow the same tendency as Δv_{isol} or, on the contrary, it will compensate the latter negative value. Unlike the situation covered in Table 1, packing forces in long-chain alkanes may bring about the situation where both mentioned terms are equally important parts of the total Δv . At present it is difficult to evaluate the value of $(\partial \Delta g_{\text{env}} / \partial P)_T$ for PM quantitatively on the mere basis of theory because of the lack of data concerning the variation of the intermolecular interaction of the aligned

Table 2 *Gauche-trans* potential energy difference Δe and its environmental contribution Δe_{env} in isolated n-hexane and various configurations of the pairs and a triad of hexane molecules (in kJ mol^{-1})

Configurations ^a						
	isolated molecule	AA	AA'	BB	AC	BBB
Δe	2.8	1.2	4.3	3.7	4.9	6.3
Δe_{env}		-1.6	1.5	0.9	2.1	3.5

^a Zig-zag backbone is projected along the long molecular axis with the full circles representing the carbon atoms closer to the observer

molecules with pressure. However, it was observed experimentally that the higher the pressure (the closer the molecules are packed together) the stronger is CMO³² and, therefore, the corresponding Δg_{env} or Δe_{env} terms in Table 2 would be larger. The enhanced rod-like character of the chain with pressure, due to the greater preference of the *trans* position, results in a positive volume term Δv_{env} and a negative quotient $(\partial \Delta S_{\text{conf}} / \partial P)_T$. Schoen *et al.*¹² interpreted the experimentally found positive value of the latter term in heptane using the virial coefficient analysis for spherocylinders. However, they noted the problems in generalization of their results to the long chains due to the complete neglect of short-range orientational correlations. If the Δv_{env} term is larger (in absolute value) than the $-1.5 \text{ cm}^3 \text{ mol}^{-1}$ value used for Δv_{isol} , the total *gauche-trans* difference Δv might even be positive in PM in accord with the result of ref. 6. But the question still remains whether the *gauche-trans* volume difference in the presence of CMO, Δv_{CMO} , (presumably positive) represents an effective mean value of Δv for the whole PM chain. Further experimental and theoretical data are needed to clarify the disharmony in the conformational volume results between short alkanes and PM, and to decide whether the CMO concept is really indispensable in the interpretation of this inconsistency.

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