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Another approach to the Gibbs–Thomson equation and the melting point of polymers and oligomers

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Abstract

The common Gibbs–Thomson equation, widely used to explain the melting temperature of lamella crystals, is based on a given heat of fusion and a given surface free energy and the size (thickness) of the crystal. With this equation it is not possible to explain the, compared to the thickness of the crystals, very high melting temperature of cyclic alkanes and ultra-high molar mass polyethylene (UHMMPE). Another thermodynamic approach to the Gibbs–Thomson equation, starting from an incremental composition of enthalpy and entropy of the chain molecule, is presented. This describes the melting temperature of (lamella) crystals of linear, folded and cyclic alkanes as well as UHMMPE, all forming crystals of the same lattice type, with only one set of parameters. The essential variable turns out to be the number of CH_2-groups of the respective molecule, incorporated into the crystallite, rather than its thickness. This may be explained if we assume the melting process caused by conformation dynamics which are more restricting the greater number of CH_2-groups that are involved in the chain movement. In a lamella crystal of a certain thickness, a cyclic alkane 'feels' longer than an *n*-alkane, as well as a linear molecule with adjacent or tight folds feels longer than one with randomly distributed chains and large loops in the amorphous. This approach helps to understand the melting behavior of polymers forming folded-chain crystals. It enables the cyclic and folded ultra-long alkanes to serve as model substances for the folded-chain crystals of polyethylene without further assumptions concerning the surface energy and fits all findings smoothly into one picture. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Melting of a solid is described in different ways. The mostly used approach is the thermodynamic one with the temperature of a first-order transition defined as the intersection of the Gibbs free energy $G(T)$ of the solid and liquid state, respectively. The first-order transition is 'sharp', i.e. the enthalpy, entropy, volume and other quantities change discontinuously (step-like) and the transition temperature is fixed as long as both phases coexist. But this is, strictly speaking, only true if we consider equilibrium conditions and if the size of both the involved phases is infinite. For polymers this premise is not fulfilled, there is no equilibrium, the crystallization is not total and the crystal size is not infinite. Many semi-crystalline polymers, in particular polyethylene (PE), crystallized from the melt as well as from solutions, form lamellae crystals which are 10–30 nm thick and at least one order of magnitude larger in the lateral direction. It was experimentally found that the melting transition is not sharp, as expected for a pure one-component system, but covers a certain temperature range and that the (maximum) melting temperature correlates with the thickness of the lamellae.

To describe this finding quantitatively the Thomson–Gibbs Eq. (2) has widely been used. From the thermodynamic point of view, there is a decrease of the melting temperature on changing from infinite crystal sizes to finite ones. Small crystals are less stable, the reason is the more and more dominant surface energy, which reduces the cohesion energy of the molecules and shifts the temperature of breakdown of the lattice to lower values. Originally Gibbs and Thomson derived their formula considering the phase in question as homogeneous and isotropic with a spherical boundary. In other words, they compared the transition temperature of a 'bulky' phase with that after crushing it to a fine powder with a lot of surface energy.[1]

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[1] Thomson himself, however, based his formula on a liquid phase and formulated the dependence of the vapor pressure on the radius of a spherical (droplet) liquid.

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The effect is, however, small and becomes only measurable for 'grain' sizes well below 1 μm. The respective formula of Thomson [1], derived from the laws of classical thermodynamics reads

$$\frac{T_{\mathrm{fus}}^{\infty} - T_{\mathrm{fus}}^{r}}{T_{\mathrm{fus}}^{\infty}} = \frac{2\sigma}{r q_{\mathrm{fus}} \rho} \tag{1}$$

where $T_{\mathrm{fus}}^{\infty}$ is the melting temperature of infinite crystal and T_{fus}^{r}, the melting temperature of a spherical 'aggregate' of radius r, σ, the specific (Gibbs) free energy of the crystal-melt phase boundary, q_{fus}, the specific heat of fusion and ρ is the density of solid.

It can easily been shown, that the right-hand side, except a constant factor, is the ratio of the total surface energy and the total heat of fusion of the crystal. For spherical samples with given specific energies this fraction is proportional to $1/r$. In the case of a lamella crystals, being much larger in the lateral dimensions, the right-hand side scales with $1/d$, with d, the thickness of the lamella, and the equation can be rewritten as:

$$\frac{T_{\mathrm{fus}}^{\infty} - T_{\mathrm{fus}}^{r}}{T_{\mathrm{fus}}^{\infty}} = \frac{2\sigma}{q_{\mathrm{fus}} \rho} \frac{1}{d} \tag{2}$$

This so-called Gibbs–Thomson equation has been proved experimentally [2] and describes the melting temperature of polyethylene (PE) lamellae crystals very well and has therefore often been used in the literature.

Another approach starts from the melting point of linear alkanes—the oligomers of linear PE—crystallizing in stacks of lamellae, and extrapolates the melting point of those alkanes forming the same lattice type (orthorhombic) to infinite chain length. The formula of Broadhurst [3], even presented by Flory and Vrij in their fundamental paper on linear-chain homologs [4] is based on the calculation of Huggins [5] which goes back to a linear increase with chain length of the enthalpy and entropy of fusion

$$T_{\mathrm{fus}}^{n} = T_{\mathrm{fus}}^{\infty} \frac{a+n}{b+n} \tag{3}$$

where n is the number of C-atoms in the alkane, $T_{\mathrm{fus}}^{\infty} = 414.3$, $a = -1.5$ and $b = 5.0$. This equation has been used as well to calculate the melting temperature of PE crystals [2]. For $n > 150$ the calculated temperatures coincide with those from Eq. (2) within 0.1 K if one takes $d = l_c n$ (with $l_c = 0.1273$ nm the orthorhombic C–C lattice distance in c-direction) and $2\sigma/(q_{\mathrm{fus}}\rho) = 0.8$ nm (see Fig. 3 in Ref. [2]).

Nevertheless there are problems arising: for some types of polyethylene (e.g. nascent as well as gel-crystallized ultra-high molecular weight PE (UHMWPE)), though containing small lamella like crystals as well, the measured melting temperature is much too high compared to the expected one from the well known crystal size [6] and there is a controversial discussion about the reasons for the high melting point [7]. Obviously the Flory–Huggins Eq. (2) is not valid in these cases without further assumptions concerning the parameter values.

Another problem arises from the melting behavior of oligomers, the alkanes (linear as well as cyclic, chain-extended as well as chain-folded) which have been synthesized with a n up to several hundred of C-atoms [8] to serve as model substances for PE: generally their melting points depend on the number of C-atoms (Eq. (3)) of the respective alkane rather than on the thickness of the respective stacked lamella crystal (Eq. (2)) (the crystal size of melt-crystallized alkanes is known to be large and the crystals are nearly perfect). Only in the case of linear n-alkanes both equations are able to describe the melting point quantitatively and the number of C-atoms within one lamella and the thickness of it are equivalent quantities where the lattice properties define the relation. Why does the almost perfect, large stacked and laterally very extended n-alkanes crystals formally follow the Gibbs–Thomson equation, although the surface energy does not play a role for these large crystals? And why in the case of cyclic alkanes and ultra-long n-alkanes forming folded-chain crystals, this equation does not hold anymore but yield a too low melting temperature (see below), although the crystals are of the same type: stacked large lamella crystals with the same lattice and thus almost the same interaction energy?

It may be helpful to leave thermodynamics for a moment and look on the dynamic approach to describe the melting process. As early as 1910, Lindemann defined the melting temperature that temperature, where the vibration amplitude becomes so large, that the atom 'bounces' against the neighbored one. Of course this idea is rather primitive from our point of view, but for metals and other small molecules it worked well and shows that melting (on an atomic level) is a dynamic process. To day it is known that atoms are in fact not fixed on their original position in the lattice and for metals the idea is accepted, that on rising the temperature there is an continuous increase of the number of very mobile lattice defects (e.g. dislocations) within the crystal. If the number of defects becomes too large, the long-range order is lost and the lattice breaks down (melts) loosing the position order. There is no doubt that the respective total (positional) entropy increase can be calculated as the number of atoms times the contribution of each atom, which for large crystals has only one value (Richards rule [9] even tells us, that it is 7–14 J K^{-1} mol^{-1}, the same for all spherical molecules!). For non-spherical molecules in addition rotational degrees of freedom are involved and on melting the much larger orientational entropy (20–50 J K^{-1} mol^{-1}) plays a dominant role. For chain molecules (and polymers) a third component, the conformational entropy (7–12 J K^{-1} mol^{-1}), must be taken into consideration [10]. Of course the dynamics of the respective molecular motion is involved in the melting process too. Obviously the type and the size (number of repeating units) of the molecule must be taken into consideration for quantitative description of the melting process and the calculation of the fusion temperature.

Having that in mind, we tried to describe the melting temperature of PE as well as all types of alkanes with one and the same formula. We had succeeded with a thermodynamic formulation which starts from an incremental (by the number of repeating units of the molecule) composition of the enthalpy and entropy of fusion similar to Huggins early linear approach [5]. This will lead to a formula which looks very like that of Thomson and Gibbs (Eq. (2)) but contains Eq. (3) as well. The difference against Eq. (2) is, that the melting temperature now depends on the size of the molecule (i.e. the number of repeating units (monomers) of the molecule which are incorporated into the crystal) rather than the dimension (thickness) of the crystal. With this formula the melting behavior of *n*-alkanes as well as cyclic alkanes can be described quantitatively with the same set of parameters. Even the melting point of different thick polyethylene lamella crystals can be explained this way without the necessity of certain surface energies. Of course the influence of the surface energy cannot be neglected for small crystallites, it causes a melting point decrease which follows the original Gibbs–Thomson formula (Eq. (1)), but this effect is normally much smaller than expected and does not play any role in the case of alkanes, which form rather large crystals. An additional advantage of our approach is, that it takes not only the thermodynamics but even the dynamics of melting into account, which in the case of chain molecules should depend on the number of units connected together.

In what follows we try to describe our basic ideas and prove the validity with known data from linear as well as cyclic alkanes including ultra-long paraffin which form folded-chain crystals as PE does. We want to explain how this approach could help to interpret the deviations of certain materials from the expected melting point, calculated with the common Gibbs–Thomson Eq. (2), including the unusual high melting point of some ultra-high molecular mass PEs.

2. Another approach to the Gibbs–Thomson formula

The basic idea is that the molar enthalpy $\Delta_{\text{fus}}H_{\text{mol}}$ and entropy $\Delta_{\text{fus}}S_{\text{mol}}$ of fusion of chain molecules (oligomers), each containing n repeating units (r.u.) in crystals of the same lattice type,[2] is incrementally composed. This is reasonable both from the thermodynamic (extensive quantities!) and dynamic (chain mobility!) point of view:

$$\Delta_{\text{fus}}H^{n}_{\text{mol}} = n\Delta_{\text{fus}}H^{\infty}_{\text{r.u.}} + \Delta_{\text{fus}}H_{\text{e}} \tag{4}$$

$$\Delta_{\text{fus}}S^{n}_{\text{mol}} = n\Delta_{\text{fus}}S^{\infty}_{\text{r.u.}} + \Delta_{\text{fus}}S_{\text{e}} \tag{5}$$

The infinite sign refers to the value for an infinite long chain, the second term on the right-hand side then contains the excess quantities, i.e. all differences compared to the ideal infinite crystal: it contains the contribution from the end groups of the chain, which are different from the internal repeating units, the difference in chain interaction energy of the marginal (compared to the central) monomer units of the chain (i.e. the surface energy of the lamella crystal), the interface energy between two lamellae (for stacked lamella crystals), etc. Of course we are aware that we have 'forgotten' the entropy of 'unpairing' [4] the molecular ends of the originally parallel chains on melting which leads to an additional term $R\ \ln(n)$ on the right-hand side of Eq. (5) and we discuss this point later.

For a first-order transition (e.g. the melting) the change in Gibbs free energy is zero: $\Delta_{\text{tr}}G = \Delta_{\text{tr}}H - T_{\text{tr}}\Delta_{\text{tr}}S = 0$. From that follows with Eqs. (4) and (5):

$$\frac{1}{T^{n}_{\text{fus}}} = \frac{\Delta_{\text{fus}}S^{n}_{\text{mol}}}{\Delta_{\text{fus}}H^{n}_{\text{mol}}} = \frac{\Delta_{\text{fus}}S^{\infty}_{\text{r.u.}} + \dfrac{\Delta_{\text{fus}}S_{\text{e}}}{n}}{\Delta_{\text{fus}}H^{\infty}_{\text{r.u.}} + \dfrac{\Delta_{\text{fus}}H_{\text{e}}}{n}} \tag{6}$$

The right-hand side of this equation can be expanded as a Taylor series around $1/n = 0$:

$$\frac{1}{T^{n}_{\text{fus}}} = \frac{\Delta_{\text{fus}}S^{\infty}_{\text{r.u.}}}{\Delta_{\text{fus}}H^{\infty}_{\text{r.u.}}} - \frac{\Delta_{\text{fus}}S^{\infty}_{\text{r.u.}}\Delta_{\text{fus}}H_{\text{e}} - \Delta_{\text{fus}}H^{\infty}_{\text{r.u.}}\Delta_{\text{fus}}S_{\text{e}}}{(\Delta_{\text{fus}}H^{\infty}_{\text{r.u.}})^{2}n} + \frac{(\Delta_{\text{fus}}S^{\infty}_{\text{r.u.}}\Delta_{\text{fus}}H_{\text{e}} - \Delta_{\text{fus}}H^{\infty}_{\text{r.u.}}\Delta_{\text{fus}}S_{\text{e}})\Delta_{\text{fus}}H_{\text{e}}}{(\Delta_{\text{fus}}H^{\infty}_{\text{r.u.}})^{3}n^{2}} - \cdots \tag{7}$$

For large n the first approximation is sufficiently precise:

$$\frac{1}{T^{n}_{\text{fus}}} \approx \frac{\Delta_{\text{fus}}S^{\infty}_{\text{r.u.}}}{\Delta_{\text{fus}}H^{\infty}_{\text{r.u.}}} - \frac{\Delta_{\text{fus}}S^{\infty}_{\text{r.u.}}\Delta_{\text{fus}}H_{\text{e}} - \Delta_{\text{fus}}H^{\infty}_{\text{r.u.}}\Delta_{\text{fus}}S_{\text{e}}}{(\Delta_{\text{fus}}H^{\infty}_{\text{r.u.}})^{2}n} \approx \frac{\Delta_{\text{fus}}S^{\infty}_{\text{r.u.}}}{\Delta_{\text{fus}}H^{\infty}_{\text{r.u.}}} \times\left(1 - \frac{1}{\Delta_{\text{fus}}H^{\infty}_{\text{r.u.}}n}\left(\Delta_{\text{fus}}H_{\text{e}} - \frac{\Delta_{\text{fus}}H^{\infty}_{\text{r.u.}}}{\Delta_{\text{fus}}S^{\infty}_{\text{r.u.}}}\Delta_{\text{fus}}S_{\text{e}}\right)\right) \tag{8}$$

This can also be written as

$$\frac{1}{T^{n}_{\text{fus}}} = \frac{1}{T^{\infty}_{\text{fus}}}\left(1 - \frac{\Delta_{\text{fus}}H_{\text{e}} - T^{\infty}_{\text{fus}}\Delta_{\text{fus}}S_{\text{e}}}{\Delta_{\text{fus}}H^{\infty}_{\text{r.u.}}n}\right) \approx \frac{1}{T^{\infty}_{\text{fus}}} - \frac{\Delta_{\text{fus}}G_{\text{e}}}{T^{\infty}_{\text{fus}}\Delta_{\text{fus}}H^{\infty}_{\text{r.u.}}}\,\frac{1}{n} \tag{9}$$

with

$$\Delta_{\text{fus}}G_{\text{e}} = \Delta_{\text{fus}}H_{\text{e}} - T_{\text{fus}}\Delta_{\text{fus}}S_{\text{e}} \approx \Delta_{\text{fus}}H_{\text{e}} - T^{\infty}_{\text{fus}}\Delta_{\text{fus}}S_{\text{e}}$$

and $T^{\infty}_{\text{fus}} = \Delta_{\text{fus}}H^{\infty}_{\text{r.u.}}/\Delta_{\text{fus}}S^{\infty}_{\text{r.u.}}$.

Formula (9) looks formally like the Gibbs–Thomson Eq. (1) (and we shall still call it so) but it contains the number n of repeating units of the chain molecule rather than a size measure (r or d) and a quantity which is the total excess (Gibbs) free energy (considering $T^{\infty}_{\text{fus}} \approx T_{\text{fus}}$) rather than only the surface free energy which is only a part of it.

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[2] Or at least the same interaction energy between the chains inside the crystal.

Remark. To be precise, Eq. (9) is equivalent to the reciprocal temperature described by the Gibbs–Thomson equation. If we would expand the reciprocal of Eq. (6) in a similar way we would get an equation which directly has the form of Eq. (1). However, we prefer the expansion of the reciprocal temperature, because it converges somewhat better.

From the linear approach of Eq. (6) a formula like Eq. (3), originally derived by Huggins [5] and later presented by Broadhurst [3] as well as by Flory and Vrij [4], can easily be calculated too. It should be emphasized, that the quantities on the right-hand side of Eq. (9) are, of course, temperature dependent and, that the entropy of unpairing of the chain ends has been forgotten as mentioned above. As shall be shown in what follows, Eq. (9) describes the melting behavior of different alkanes and PE very well, so obviously the temperature dependence of the right-hand side is almost compensated by ignoring the unpairing entropy term (see even Ref. [2] concerning this problem).

Anyhow, the validity of Eq. (9) should be proved with experimental data. If we plot $1/T_{\rm fus}$ against $1/n$ ('Gibbs–Thomson plot') for different oligomers and the polymer composed of the same repeating unit, we should get a straight line.

3. Verification of the approach

3.1. Literature data

In what follows we shall apply Eq. (9) to polyethylene and its oligomers, the alkanes, and rewrite it for this purpose:

$$\frac{1}{T^{n}_{\rm fus}} = \frac{1}{T^{\infty}_{\rm fus}} - \frac{\Delta_{\rm fus}G_{\rm e}}{T^{\infty}_{\rm fus}\Delta_{\rm fus}H^{\infty}_{\rm CH_2}}\,\frac{1}{n} \tag{10}$$

To prove this formula we have collected all available fusion data of linear and cyclic alkanes from literature [8]. From the (total) molar enthalpy (and entropy) of fusion of the alkanes plotted against n, the number of CH_2 groups in the respective molecule, we found a linear relation for all alkanes with $n > 10$ (Fig. 1) Even and odd numbered linear and cyclic alkanes crystallize in different lattices, this yields of course different enthalpy values. The linear behavior is, however, clearly verified for each lattice type. The slopes are almost the same for the linear ($\Delta_{\rm fus}H^{\infty}_{\rm CH_2} = 3.4$ kJ mol^{-1}) as well as cyclic alkanes ($\Delta_{\rm fus}H^{\infty}_{\rm CH_2} = 3.5$ kJ mol^{-1}). In other words the incremental fusion enthalpy and entropy do not differ very much, obviously the chains are packed in a similar way and the internal interaction inside the crystal is quite the same though the lattice type may differ (there exist even some X-ray data in literature supporting this finding [11]). From the interception with the y-axis, on the other hand, we get the respective excess enthalpies which are quite different for the orthorhombic linear ($\Delta_{\rm fus}H_{\rm e} = -3$ kJ mol^{-1}) and the cyclic ($\Delta_{\rm fus}H_{\rm e} = -35$ kJ mol^{-1}) alkanes. This seems reasonable because, on the one hand, different lattices should give different contributions to the surface energy and, for cyclic alkanes on the other hand, the chains are twisted in the neighborhood of the folds and fit badly into the preferred (orthorhombic) packing, leading to a loss in interaction energy between the chains in that region of the crystal resulting in a reduction of the total enthalpy. Similar results can be obtained for the total entropy of transition. This supports the idea of incremental composition of the total enthalpy and entropy of fusion (Eqs. (4) and (5)) at least for this class of compounds.

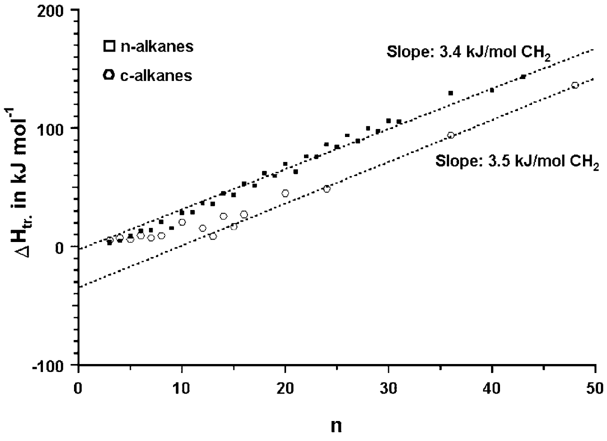

Fig. 1. The total enthalpy of fusion of different alkanes [3,8]. The dotted lines mark the best fit for odd linear and even cyclic alkanes with more than 20 CH_2 groups.

The Gibbs–Thomson plot ($1/T_{\rm fus}$ against $1/n$) of all available alkane data is shown in Fig. 2. The dotted line represents the best fit for linear alkanes of medium size ($n = 30–100$), for which the most reliable data exist:

$$\frac{1}{T^{n}_{\rm fus}} = 2.413 \times 10^{-3} + 0.0162\frac{1}{n} \tag{11}$$

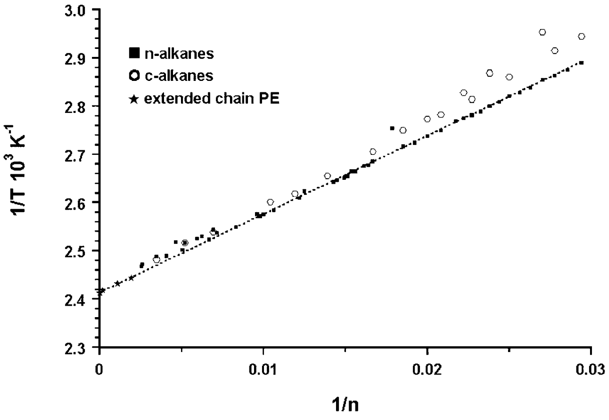

Fig. 2. Gibbs–Thomson plot of melting temperature of alkanes (most data from Ref. [8]) and chain-extended PE [2]. The dotted line represents the best fit for medium sized n-alkanes ($T^{\infty}_{\rm fus}$: 414.4 K, slope: 0.0162 K^{-1}, Eq. (11)).

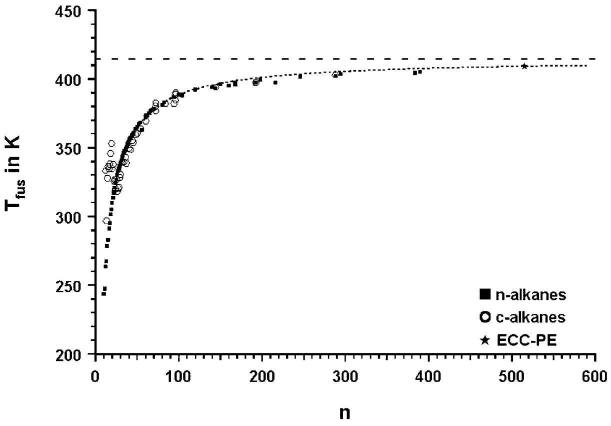

Fig. 3. Data from Fig. 2, but plotted in conventional manner. The dotted line marks the fit function, the dashed line marks the melting temperature of infinite chains (414.4 K).

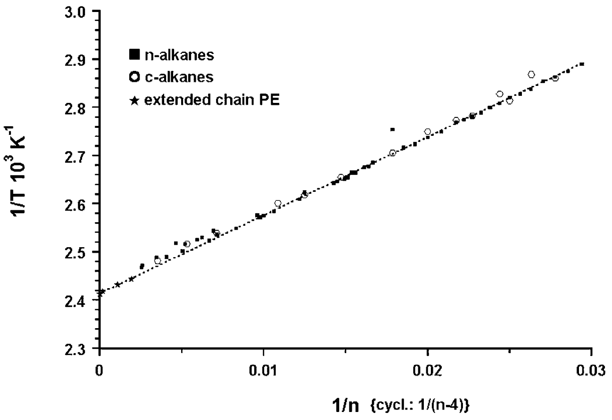

Fig. 4. Gibbs–Thomson plot as in Fig. 1, but for the cyclic alkanes n is reduced by 4 CH_2 groups (see text).

The different lattices [11] were disregarded in this case, the differences in melting point are smaller than the uncertainty of the temperature values from different sources. Obviously the influence of different lattice types on the melting point is rather low. From Fig. 2 it follows that Eq. (7) is generally valid for both types of alkanes. But some divergent details are of interest: (i) the melting points of the ultra-long n-alkanes ($n > 140$) deviate from the dotted line and there is a larger scattering, and (ii) the fusion temperatures of the cyclic alkanes are all somewhat too low whereas the slope is a little higher than for n-alkanes (to elucidate a T_{fus} versus n plot has been added, see Fig. 3).

3.2. Discussion of the findings

How can the latter be understood? The excess Gibbs free energy G_e is always a negative quantity (i.e. the total enthalpy is reduced) because the parts of the molecule at the surface of the lamella are not bound as strong as the inner parts are. This is in particular true for the chains of cyclic alkanes around the folds, they are somewhat twisted and do not fit well into the lattice. For these alkanes we know the structure of the crystals [11,12], the main parts of the chains are parallel to one another and there are two tight folds with 4 CH_2 groups in each of the (lateral) surfaces of the lamella (see Fig. 6b and Refs. [11–13]). Two of these four CH_2 groups are almost part of the stems and two are perpendicular to them in the surface of the lamella. The former do and the latter do not contribute to the total enthalpy of the lamella crystal and we should subtract $2 \times 2 = 4$ from the total number of CH_2 groups to get the true number n of CH_2-groups which are really inside the molecule stems of the crystal and thus contribute to the total crystal enthalpy. If we use the corrected (reduced by 4) number n, the (reciprocal) fusion temperature of the even numbered cyclic alkanes fits much better to the Gibbs–Thomson line of linear alkanes (Fig. 4), but the fusion temperatures of some odd numbered cyclic alkanes are still too low. This can be explained by the non-symmetric ring, causing a more disturbed lattice in the neighborhood of the folds. This in turn causes a reduced interaction energy in this region, formally leading to a decreased number of those CH_2 groups which contribute to the fusion enthalpy, and therefore to a larger excess enthalpy and a reduced fusion temperature for these alkanes.

The other deviation from the Gibbs–Thomson line concerns the alkanes with $n > 140$. They almost show a too low fusion temperature compared to the expected one (Figs. 2–4). As the intersection point of this line (at 2.4125×10^{-3}) corresponding to 414.5 K is well proved experimentally—it is the melting point of the infinite n-alkane and that of fully chain-extended linear polyethylene crystals [2]—and as the melting temperatures of other chain-extended PEs fit well again, we assume this line should describe the true melting temperatures. A possible explanation of the somewhat too low measured temperatures of most of the ultra-long alkanes could be some unavoidable 'impurities' from the complex synthesis resulting in a product containing some alkanes of different length. This would reduce the melting point of the main component. Another possible explanation could be the different laminar habit of the ultra-long alkanes (e.g. 36° tilted stems)[3] and thus a different enthalpy per CH_2 unit compared to that of smaller alkanes.

Anyhow, as a result we can realize: (i) the modified Gibbs–Thomson Eq. (10) is valid for linear as well as cyclic alkanes with almost the same parameters (Eq. (11)), (ii) the fusion temperature is determined by the number of CH_2 units in the stems of the molecule which are fitted into the crystal and (iii) for cyclic alkanes, having the same melting point as the linear alkanes, the thickness of the lamellae in the stack is only about half of that of the linear alkanes. On the other hand, if we would use the common

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[3] Referee remark, which is thankfully acknowledged. However, a possible tilt angle may influence the thickness and the surface energy of the lamella, but does not play a role in our approach if the chain distance and thus the interaction energy between the chains is not changed very much.

Gibbs–Thomson approach (with the lamella thickness as variable) the relatively high melting point of cyclic alkanes could only be explained with a distinctly reduced surface free energy and/or higher enthalpy of fusion. Both assumptions are in contradiction to the experimental findings showing a higher excess free energy and a lower enthalpy of melting for cyclic alkanes than for linear ones. For the melting behavior of cyclic alkanes, the lamella thickness is, obviously, not the main quantity. In our approach, however, the number of CH_2 units of the molecule stems incorporated in the crystal determines the right melting temperature regardless whether we consider linear or cyclic alkanes. This is in line with the dynamic explanation of the melting process, where the mobility of the molecule is the dominant factor for the break down of the lattice, and the mobility, of course, depends on the number of repeating units within the chain molecule.

Linear alkanes have since many years successfully served as model substances for polyethylene and we have to ask the question whether our approach is specific for the oligomers (alkanes) only, or whether it could be helpful as well to explain the melting of the polymers (polyethylene and its copolymers) as well.

4. The melting of polyethylenes

4.1. Normal melting behavior

For partial crystalline linear polyethylene the close connection between the lamellae thickness and the melting point is well known and has been proven by X-ray and IR measurements. Numerous papers on this topic exist in literature and there is no doubt about the validity of the traditional Gibbs–Thomson equation (containing the lamella thickness l). Wunderlich [2] published the following equation for PE data collected by Illers and Hendus [14]

$$T_{\text{fus}} = 414.2\left(1 - \frac{0.627}{l}\right) \pm 0.8\ \text{K} \tag{12}$$

where l is given in nm. We first calculate an equivalent formula from our Eq. (11) by substituting n, the number of CH_2 groups inside the crystal lamella with $l/l_{\text{C–C}}$ with $l_{\text{C–C}} = 0.1273$ nm, the C–C distance in direction of the c-axis of the orthorhombic lattice[4]:

$$\frac{1}{T^n_{\text{fus}}} = 2.413 \times 10^{-3} + 0.0162\frac{0.1273}{l} = 2.413 \times 10^{-3}\left(1 + \frac{0.855}{l}\right) \tag{13}$$

The reciprocal of this equation yields approximately:

$$T^n_{\text{fus}} = 414.4\left(1 - \frac{0.855}{l}\right) \tag{14}$$

Eq. (14), calculated from the alkane data fit of Eq. (11), is almost equal to Eq. (12) fitted to PE data. As one would expect, the (extrapolated) melting point of the infinite large lamella is the same for both formulas, but the slope is somewhat different because the excess free energy involved differ for PE lamellae crystals and for alkanes. As a result the new approach holds even for PE lamella crystals, but there are no really new aspects so far, beside the fact that we can calculate the melting point of polyethylene crystals as well as linear and cyclic alkanes with one and the same formula and one, almost unchanged, set of parameters. This way the alkanes can serve as model substances for PE.

4.2. Unusual melting behavior

However, for some types of polyethylene the melting point cannot be calculated from the lamella thickness. An interesting example is ‘gel crystallized’ ultra-high molecular weight polyethylene (UHMWPE). This material contains rather thin stacked lamellae with a thickness of 12.5 nm (125 Å) and a narrow thickness distribution, as measured by SAXS [15,16]. On heating this material, in the temperature region of 110–120 °C a doubling of the lamella thickness takes place, which then remains almost unchanged until melting occurs. The measured melting temperature (133.5 °C, see Fig. 5) is, however, significantly higher than the calculated value using Eq. (12) or (14) and a thickness of 25 nm, namely 130.6 or 127.0 °C, respectively. Furthermore, the lamellae doubling process is not at all visible in the DSC curve (Fig. 5) though any real melting of the thin and crystallization of the thick lamella should be somehow visible. Obviously the enthalpy is identical for both types of lamellae (no net heat exchanged) and melting and

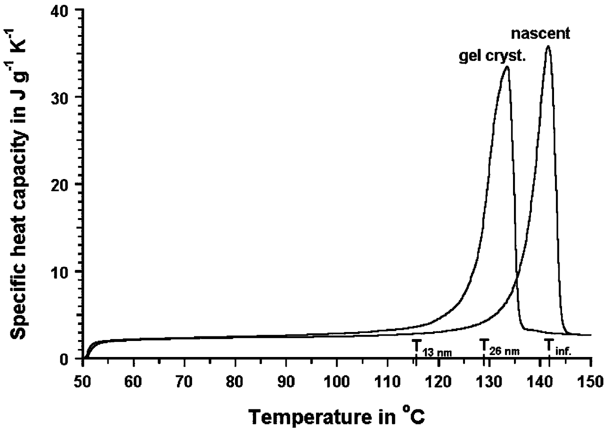

Fig. 5. Normalized DSC curve of gel crystallized (mass: 2.2 mg, heating rate: 10 K min^{-1}) and nascent (mass: 2.7 mg, heating rate: 10 K min^{-1}) UHMWPE, the expected melting temperatures for certain lamellae, calculated with Eq. (12), are marked.

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[4] A possible tilting angle of 35° [11] would, of course, result in a somewhat different factor.

crystallization are taking place simultaneously in a continuous process well below the real melting point of the resulting lamellae and without changing the degree of crystallinity. This is an unusual behavior, normally the start of melting of smaller lamellae is clearly visible in DSC, e.g. in the case of low density PE.

Another example of unusual melting has been reported from 'nascent' (i.e. virgin material from the catalyst) ultra-high molecular mass PE (UHMMPE) [7,17]. The original small crystals (13 nm, measured by X-ray and TEM [6]) thicken on annealing at 120 °C to maximum 25 nm (without any visible effect in the DSC curve, see Fig. 5) but melts at 140.9 °C, a temperature which is normally found for high pressure crystallized 'chain-extended' PE with very thick (>1 μm) lamellae [2]. From Eq. (12) the melting temperature of the nascent UHMWPE should on heating change from 121 °C (nascent crystal size) to 131 °C (25 nm maximum final size), but nothing is visible in this temperature region (Fig. 5). Very interesting in this context is the finding of Phillips that the melting temperature after etching the nascent material with fuming nitric acid drops from 142 to 130 °C, whereas the 'coarse particle macromorphology remains relatively unchanged' [7]. If we assume that the etching cuts the PE chains along the surface (e.g. the folds) and leaves the lamellae unchanged the resulting material should melt in the temperature region of the respective *n*-alkane lamella (in the oxidized form, to be precise). From the measured melting temperature of the etched sample (130 °C [7]) we can calculate a lamella thickness l somewhat lower than 25 nm in nice agreement with the X-ray results of the unetched sample. Obviously the folds, existing in nascent UHMMPE, cause an increase of the melting point as is the case with cyclic alkanes, having narrow folds, compared to linear alkanes with free ends.

As a result, the melting point of these special PEs cannot be explained from the crystal thickness within the frame of the common Thomson equation. In what follows we try to show, that our approach containing the melt dynamics—via the length of the crystallized part of the chain—may be more helpful.

5. Discussion of the new approach to the Gibbs–Thomson equation

The essential outcome from the application of our approach on alkanes was that the melting temperature of linear as well as cyclic alkanes can be calculated with the same formula, if we take the number of repeating units (CH_2 groups) from the molecule stems which are incorporated in the crystal as determining parameter.[5] Here the question arises how can the molecule 'knows' this number and feels its length inside the crystallite. The answer comes from the picture of melting dynamics presented in Section 1: there is a high mobility of the repeating units as well as of the total molecule already well below the melting point, at least in the case of hydrocarbons. This is supported by the above-mentioned findings of lamella thickening (doubling) below the real melting point. For chain molecules not only the positional and orientation but also the conformational entropy increases on melting. The dynamics of conformations imply a high mobility even inside the crystal. A conformational defect inside the crystal can only be generated by moving the complete molecule somehow. This dynamics and the distinct increase of conformational defects in the pre-melting region enable the molecule to feel its length.

Of course, the mobility of a large molecule incorporated in a crystallite is more constraint than that of a small molecule. In the case of linear alkanes every molecule feels its own length (the number of CH_2 units) because they must move cooperatively to produce conformations. In the case of cyclic alkanes, a movement of one of the two parallel chains in the crystal is only possible when the adjacent other chain moves with it (see arrows in Fig. 6b). Again the total molecule (the complete ring) has to move cooperatively to produce conformational defects and it feels its total length. This way the generation of conformational distortions requires the mobility of the molecule in crystallized part. The mobility of a cyclic alkane (in a thinner lamella crystal) is then almost the same as the mobility of a linear alkane with the same number of repeating units but in a much thicker lamella. From the dynamic picture of melting the melting point of molecules in a crystal is linked to its mobility and we can understand the melting behavior of the two types of alkanes in this way.

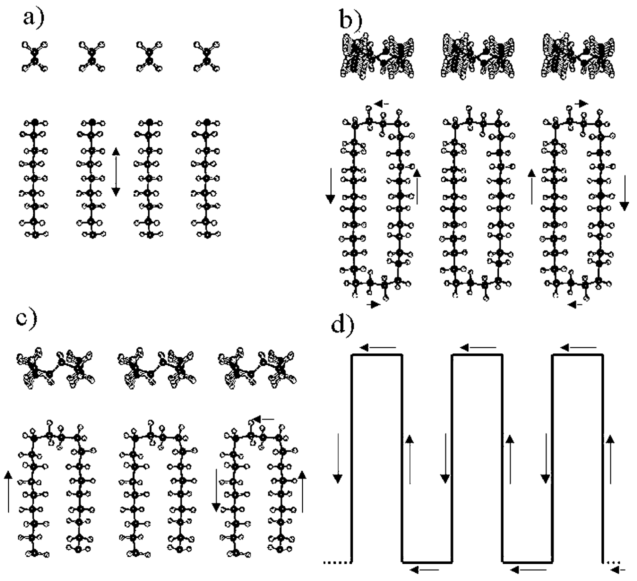

Fig. 6. Scheme of structure (from X-ray analysis and molecular modeling) of alkane and PE chain molecules. Projections into and perpendicular to the fold plane of (a) *n*-alkanes, (b) cyclic alkanes, (c) once folded long alkanes, (d) tightly folded PE (arrows: cooperative movement of chain segments).

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[5] Remark: Broadhurst's formula (3) gives the same approach but only for linear alkanes.

So far so good, but how can the unexpected high melting point of UHMMPE be explained in this picture? The lamellae of normal linear PE (crystallized from the melt) normally contain parallel chains with randomly arranged loose loops and inter-crystal molecules within the amorphous layer. There are only a very low number of adjacent narrow folds like those in cyclic alkanes. There are no serious mobility constraints outside the crystal lamella and the conformation dynamics let the molecule feels only that part of it which is inside the crystal. Whether there is a CH_3 end-group in the surface as in *n*-alkanes, or a loose loop hanging there seems to lead to the same feeling. But if tight or adjacent folds (like in cyclic alkanes) exist in the lamella, the respective part of the chain feels longer, because incorporating a conformation into one part of the chain in the crystal implies not only the movement of that part but also the tightly connected part of the molecule (see arrows in Fig. 6). In other words a lamella which contains tight or adjacent folds should melt at a higher temperature than that without such folds, because the dynamics is more constraint. To be honest this is a speculation not jet proved for PE crystals, but it is true in the case of lamellae crystals of cyclic alkanes compared to those of linear ones.

For the gel crystallized UHMMPE, mentioned above, the too high melting point could be explained with our picture, if we assume a corresponding amount of adjacent folds in the lamella. (The existence of such folds is also a precondition for the lamella doubling process to occur [15].) And the well proved doubling process [16], for its part, is an indisputable proof for the chain dynamics inside the crystal.

The other unexpected example, the very high melting point of the above-mentioned nascent UHMMPE powder, can be explained if we assume that the crystallite formed in the reactor contains only a very little amount of inter-crystal chains (or tie-molecules) and very little entanglements. This nascent UHMMPE is synthesized in solution at rather low temperatures, the chain, ‘shooting’ out of the active center of the catalyst, is immediately attached to the crystal grain. The virgin crystal aggregate is obviously rather disordered, with large loops in the amorphous layers, but there are a lot of adjacent folds and only little number of entanglements. On heating, the huge chain mobility, even inside the crystallite, tightens the chains. The loose loops are lost and the resulting crystal contains only adjacent folds and chains in the amorphous layers which are pulled tight. For conformation dynamics many chains (if not all) have to move cooperatively in such a crystal (Fig. 6d). Consequently the molecule feels very long and the melting point should equal to that of a very large *n*-alkane approaching that of the infinite alkane (which for its part equals that of high pressure crystallized, chain-extended PE). As a result, such a crystal should melt at the same temperature as the chain-extended one, what is found experimentally.

During discussions on different crystallization meetings it was, however, argued that experiences with ultra-long *n*-alkanes contradict our ideas and support the common Gibbs–Thomson approach [18]. To check this objection we collected all available literature on the melting behavior of large *n*-alkanes. Unfortunately there are only very few DSC results published, but what we found is presented in Section 6.

6. The proof with ultra-long *n*-alkanes

Linear alkanes with more than 150 CH_2 groups can form both extended chain (ECC) as well as folded-chain crystals (FCC). It has been shown, that, depending on the chain length, 1–3 tight folds are possible. The respective lamella thickness has been measured with X-ray and the number of all-*trans* CH_2 groups by Raman spectroscopic methods (LAM).

Table 1 contains the available experimental data [19–22] on melting temperatures of those ultra-long alkanes which exist in ECC as well as FCC form. In Table 2, on the other hand, the expected melting temperatures of those alkanes are listed. We used Eq. (11), which describes the melting behavior of *n*-alkanes very precisely, together with the measured n_l (from LAM), i.e. the number of effective $-CH_2$ groups in the all-*trans* chain stems $n_l = (n-2)/2$—to calculate these values.

Table 1
Measured fusion temperatures and of ultra-long *n*-alkanes [11,19–22]

n	$T_{\text{fus ECC}}$ (K)	$T_{\text{fus FCC}}$ (K)	$n_{l\ \text{FCC}}$ (from LAM)	$T_{\text{fus ECC}} - T_{\text{fus FCC}}$ (K)	Impurity correction[a] (K)	$T_{\text{fus FCC}}$ (K) (corrected)	$n_{\text{eff FCC}}$ with Eq. (11)	n_{eff} from Fig. 7
168	397.5	395.1	92	2.4	1.0	396.1	145	
198	399.8	391.2	97	7.6	1.0	392.2	119	118
216	401.5	397.2	111	4.3	0.4	397.6	159	
246	401.8	395.7	124	6.1	1.6	397.3	156	154
288	?	402.0	151		?			
294	403.6	398.8	153	4.8	1.6	400.4	192	191
384	?	404.5	–		?			
390	405.2	402.2	?	3.0	2.2	404.4	270	262

[a] For impurity correction the difference between the expected and the measured ECC melting point has been used.

Table 2
Calculated fusion temperatures of long n-alkanes (using Eq. (11))

n	$T_{\text{fus ECC}}$ (K)	$n_l = (n-2)/2$ (FCC)	$T_{\text{fus FCC}}$ (K)	$T_{\text{fus ECC}} - T_{\text{fus FCC}}$ (K)	n_{eff}/n_l	n_{eff}/n
168	398.5	83	383.4	15.1	1.7	0.86
198	400.8	98	387.9	12.1	1.2	0.61
216	401.9	107	390.0	11.9	1.5	0.74
246	403.4	122	392.8	10.6	1.3	0.63
288	405.0	143	395.8	9.2		
294	405.2	146	396.2	9.0	1.3	0.65
384	407.3	191	400.3	7.0		
390	407.4	194	400.6	6.8	1.4	0.69

Checking the unfolded crystals first, one find the measured fusion temperatures of the alkanes in the ECC state always somewhat lower as calculated. This is probably caused by impurities or by different lamellar habit, as already mentioned in Section 3 (see even Figs. 2 and 4). Assuming the same influence (reduction of the melting point) even for the folded-chain state, we used these differences (Table 1) to correct the measured fusion temperatures of FCC properly. This correction is reasonable because the lowering of the melting point should be same for ECC and FCC, either we use the one or the other explanation for the melting point depression, because the impurities are the same in both cases and the lamellar habit as well.

These results lead to remarkable findings. (i) The measured melting temperatures of the FCC are significantly higher than the calculated ones. That is even more pronounced for the (impurity-)corrected values. (ii) The measured differences between the melting points of the ECC and FCC crystals (Table 1) are much smaller than the calculated ones (Table 2). As these quantities should not be influenced by possible impurities or other influences, we have to draw the conclusion that the measured melting point of the FCC is much higher than the respective lamella thickness predict.

This reminds us of the finding with cyclic alkanes (Section 3). To put it into the picture of our approach, there are again more CH_2 groups involved in the melting dynamics as calculated from the lamella thickness ($n_l = l/0.1273$ nm). On the other hand: from the measured FCC fusion temperatures (the corrected ones!), the effective number n_{eff} of CH_2 groups which the molecule feels via the melting dynamics can be calculated using our approach and the alkane fit of Eq. (11) (Table 1). This number is considerably higher than the number n_l calculated from the lamella size or from the FCC morphology (with $n_l = (n-2)/2$, assuming two CH_2 groups of the fold outside the lamella stems, see Fig. 6). The quotient of these two quantities is, however, almost the same for all n-alkanes (at least if we compare the results from the same author, see Table 2). Obviously neither the lamellae thickness (n_{l}) nor the total number of CH_2 groups determines the melting point of the FCC but a certain n_{eff} which is somehow in between n_{l} and n. In Fig. 7 the relations are demonstrated. It contains the melting points of some ultra-long alkanes in the ECC as well as FCC states. For FCC crystals the possible positions using n, n_l and n_{eff}, respectively, are included for the measured temperature in question.

Taking the picture of melting dynamics into account, this finding can be explained. As mentioned in Section 3 the chain molecule of cyclic alkanes feels the total ring length because of the constraints from the two tight folds which enforce a cooperative movement of all CH_2 groups to produce a conformation in the crystal. In the case of once folded long n-alkane molecules in the FCC, we can draw the conclusion, that the movements of either chain (with conformation changes) is hindered in a different manner, depending on the direction of the movement. A movement toward the fold (see left-hand side of Fig. 6c) should be minor constraint, the chain only feels the free end of the molecule, whereas the movement in the other direction, away from the fold (see right-hand side of Fig. 6c) is only possible if the total molecule follows. As a result the melt dynamics enables the molecule to feel a length which is a compromise between the total (n) and half of the length (n_l).

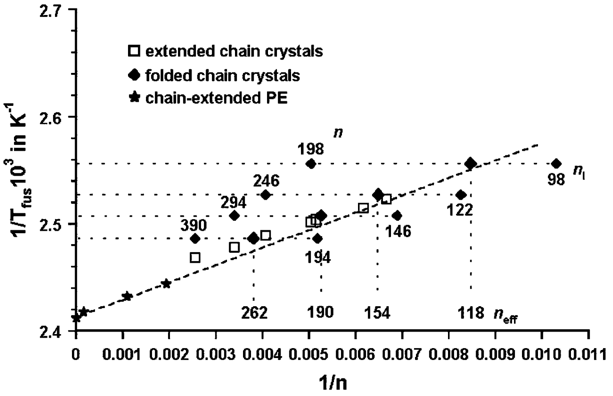

Fig. 7. Gibbs–Thomson plot of measured DSC melting points [11,19–22] for some of the very large n-alkanes forming ECC as well as FCC crystals. The horizontal dotted lines represent the measured melting temperatures of FCCs. Neither the total number (n) nor $n_l = (n-2)/2$, defining the lamella, fits to the expected value (dashed line from Eq. (11)). But a number n_{eff} (marked with vertical dotted lines) in-between the two numbers leads to the right value. All temperatures are somewhat too low (i.e. above the dashed line) because of unknown reasons (impurities?) not corrected for. Some data of chain-extended PE [2] are included.

The effective value depends on the probability of the different movements. It seems reasonable, that the minor constraint movements are more probable than the other. A probability ratio of 70:30 for the toward and away the fold movement would result in a number ratio $n_{\mathrm{eff}}/n = 0.65$ which fits to the values of Table 2. We would get the same ratio if we estimate the Boltzman factor for the movement probability of chain segments of length n and n_l, respectively, taking the activation energy proportional to the number of CH_2 groups involved. To be honest these argumentation is highly speculative so far but could be a possible explanation for the experimental findings and fits smoothly into the new approach to the melting behavior.

To summarize, irrespective of the speculations of the last paragraph, the ultra-long alkane data, as far as available from literature, support our approach rather than the arguments of the critics. The melting point is mainly determined by the number of CH_2 units which the molecule feels dynamically than by the size (lamella thickness) and the surface energy.

7. Conclusions

The thermodynamic approach to the Gibbs–Thomson equation via an incremental composition of the melting enthalpy and entropy leads to a formula which formally equals the common Gibbs–Thomson equation, but contains the number of repeating units in the chain molecule rather than the thickness of the lamella crystal. The idea is not new, it has been used by Huggins [5] and Broadhurst [3] before, but only in the case of linear alkanes. We have shown that this approach holds for cyclic alkanes as well, and that the melting point of all types of hydrocarbons, which crystallize in the same type of lattice, can be calculated with almost the same set of parameters. This way cyclic alkanes can serve as model substances for PE crystals with adjacent or tight folds, whereas linear alkanes already before proved to model melt crystallized PE very well.

The idea to deduce the melting point of PE and its oligomers from the number of CH_2 groups involved in the melting dynamics rather than from the thickness of the lamella and the surface energy, enables us to explain the melting behavior of all types of polyethylene with one and the same (modified) Gibbs–Thomson equation (containing the number of repeating units instead of the lamella thickness). With this approach it is possible to describe the melting behavior of linear, cyclic and folded alkanes with the same set of parameters as well as all types of polyethylene. In particular the unusual high melting point of gel crystallized and nascent PE can be explained this way if we assume a large number of tight folds in the respective crystals. This view is supported by (i) the melting behavior of alkanes, namely the fact, that the melting points of linear alkanes equal those of cyclic alkanes with the same number of CH_2 groups and (ii) the melting behavior of ultra-long alkanes which crystallize in extended chain as well as folded-chain form. In both cases an almost equivalent crystal structure is assumed, with about the same melting enthalpy per CH_2 group. This seems to be the case, at least for the longer alkanes ($n > 40$) and enables us to get some more insight into the crystallization and melting procedures of all types of polyethylene as well. There are still some open questions in particular concerning the explanation of the melting points of alkanes and PE with adjacent folds. It would be very helpful if precise measurements of the melting points of ultra-long alkanes in ECC and FCC could be done in future. These measurements could serve to prove the presented approach to the Thomson equation and help to understand the unusual high melting temperature and the melting dynamics of certain polyethylenes.

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