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Calorimetry on small systems—a thermodynamic contribution

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Abstract

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 polyethylenes (PEs) of different type with only one set of parameters. The essential variable turns out to be the number of repeat units (r.u.) ("beads") of the respective molecule, incorporated into the crystallite, rather than the crystallite size. The finding supports the melting being a dynamic process which starts at the surface (interface) of the crystallite. The approach helps to understand the melting behavior of semi-crystalline polymers, it enables the cyclic and normal alkanes to serve as model substances for polymer crystals although their crystals are nearly perfect and large by contrast to the situation in semi-crystalline polymers.

Keywords: Thomson equation; Melting; Small crystals; Polymer; Surface melting

1. Introduction

Conventional thermodynamics starts from large systems and does not take surface energies into consideration. For small systems, sized in micro- and nano-meter range, the surface energy cannot be neglected and the respective equations have to be modified. No less than W. Thomson (Lord Kelvin) and J.W. Gibbs introduced the surface energy to describe the thermodynamic behavior of small systems. With the surface area as an additional variable the total differential of the Gibbs free energy then reads:

$$\mathrm{d}G = \left(\frac{\partial G}{\partial T}\right)_{p,A} \mathrm{d}T + \left(\frac{\partial G}{\partial p}\right)_{T,A} \mathrm{d}p + \left(\frac{\partial G}{\partial A}\right)_{p,T} \mathrm{d}A$$

with T temperature, p pressure and A surface area. With well known relations for the three partial derivatives of G the following differential equation results for the thermodynamic potential function:

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \sigma\,\mathrm{d}A \qquad (1)$$

with S entropy, V volume and σ (Gibbs) surface energy per unit area.

These are the basic equations to understand the phase transition behavior of small systems from the thermodynamic point of view: inclusion of the surface energy increases the Gibbs energy of a system, or, in other words, the G-function is shifted upwards in the G–T-diagram. The (equilibrium) temperature of transition between two phases is determined by the point of intersection of the respective G-functions (where $\mathrm{d}G = 0$). As $G(T)$ is always a monotonic decreasing function of temperature, the phase transition temperature of a smaller system is shifted toward lower

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temperatures if we consider the high temperature phase as a large one (with only little surface energy involved) or, at least, with almost the same G. This assumption is reasonable for the melting process, the liquid melt is normally one large phase with, compared to small crystals, a low surface energy. A powder of small crystals melts together to one bulky phase. The same is true if we consider the evaporation of small droplets: there is always only one vapor phase, much larger in size than the original droplets have been. As a result, the melting point of smaller crystals is lower than that of larger crystals and the boiling point of a small droplet is lower than that of a whole pan of the liquid.

The latter follows immediately from the fact that the surface molecules of the droplet are less bound than inner molecules of the liquid phase; the weaker the binding the higher the vapor pressure and the lower the boiling point. It's obvious why a smaller droplet has a higher vapor pressure: the smaller the radius, the lower the binding forces. In 1871, W. Thomson [1] derived a formula for the vapor pressure of small spherical droplets:

$$RT\ln\frac{p_r}{p_\infty} = \frac{2\sigma}{r}V_\mathrm{l} \tag{2}$$

with r the radius of the droplet, σ the liquid–vapor interface energy per unit area, p_r the vapor pressure of a droplet of radius r, p_∞ the (equilibrium) vapor pressure of the infinite large liquid phase and V_l the molar volume of the liquid.

Smaller droplets have a higher vapor pressure than larger droplets. From this, it follows that a system of different sized droplets is unstable because the smaller droplets evaporate molecules to increase the vapor pressure to the proper value, whereas the larger droplets at the same time absorb molecules to decrease the pressure to a value proper to their size. As a consequence there is a stream of molecules from the smaller to the larger droplets via the gas phase until all smaller ones disappeared and only one large remains, which now coexist in equilibrium with its gas phase of proper pressure. Only a system of droplets with exactly the same size would exist for a moment until an accidental fluctuation would destroy the balance.

Analogous circumstances exist for the dissolution of small crystals as well as the transition from solid to liquid (melting): the small crystals dissolve in a saturated solution at a certain concentration and larger crystals grow in the same moment. The same happens in the melting region: small crystals melt at lower temperatures than large crystals do. At a medium temperature small crystals disappear and larger crystals grow at the same time, a behavior well known from polymers. To describe the melting of small crystals, Thomson [2] modified the equation of J.J. Thomson modified Eq. (2) of W. Thomson in 1888

$$\frac{T_\mathrm{fus}^\infty - T_\mathrm{fus}^r}{T_\mathrm{fus}^\infty} = \frac{2\sigma}{rq_\mathrm{fus}\rho} \tag{3}$$

with T_fus^∞ melting temperature of infinite crystal, T_fus^r melting temperature of a spherical "aggregate" of radius r, σ (Gibbs) free energy per unit area of the crystal–melt interface, q_fus specific heat of fusion, ρ the density of solid. Of course, this is an approximation only, crystals are never spherical and different crystal faces have normally different interface energies, but the equation connects the melting point with size of the crystallite at a given average interface energy. A more detailed formula must contain all different crystal faces together with the size in that direction and the respective interface energy.

However, Eq. (3) forms the thermodynamic basis of the Gibbs–Thomson equation (often called so in polymer literature), used to describe the melting behavior of small crystals present in partial crystallized polymers. In literature it is normally found in two forms:

$$\begin{aligned} T_\mathrm{fus}^r &= T_\mathrm{fus}^\infty\left(1 - \frac{2\sigma}{q_\mathrm{fus}\rho}\frac{1}{r}\right)\\ \frac{1}{T_\mathrm{fus}^r} &= \frac{1}{T_\mathrm{fus}^\infty}\left(1 + \frac{2\sigma}{q_\mathrm{fus}\rho}\frac{1}{r}\right)\end{aligned} \tag{4}$$

These equations are not only used for theoretical purposes but even in practice. Small crystals play a dominant role in material sciences, they influence the properties of metal alloys and in particular in polymer science to describe the melting behavior of semi-crystalline materials.

However, the original thermodynamic approach starts from systems of small spherical particles (atoms) with isotropic interaction forces and a droplet-like shape of crystallites. Metals and alloys meet these conditions rather well, beside the always non-spherical shape of the crystallites formed by different flat crystal faces with corners and edges, whereas polymers are made up of large chain molecules (where only the respective repeat units (r.u.) may meet the requirement of smallness) which are clearly anisotropic both from the size and from the interaction energy point of view. Nevertheless, Eq. (4) have successfully been used to describe the melting behavior of semi-crystalline polymers forming lamellae crystals (see e.g. [3]), although they normally are far away from being droplet like and small. The reason for the success is, that a lamella-like crystallite has been considered as small in one direction (r in this case the thickness) and infinite in the other two dimensions. This way only two faces of the crystallite are considered and the lateral faces are ignored. The melting point depression of such crystallites is thus considered to be caused by the Gibbs surface/interface energy of the two main lamella faces. But, as we see it, the success is only a formal one because the main problem of thermodynamics with chain molecules, what is the "particle" in the thermodynamic system and what are the number of modes (degrees of freedom) in this context, has not been solved and the formulation must be considered as empirical. A simple transfer of the thermodynamic formulas derived for systems of atoms and small sized molecules to macromolecular systems is in our opinion not allowed. As we shall show below the respective formulas coincide formally by chance.

Anyway, some qualitative conclusions, valid even for polymer crystals, can be drawn from Eq. (3): crystal faces with different surface energy are different stable and corners and edges of the crystal melt earlier than large flat faces of the crystal because of the smaller effective radius. We shall come back to this point later again.

So far we have moved within the framework of classical thermodynamics, but melting can also been described via a dynamic approach. To clarify, let us consider a droplet of a liquid surrounded of an atmosphere of its own vapor. Obviously, only surface molecules can evaporate, inner molecules have to diffuse to the surface first, and the evaporation rate will be the larger the smaller the radius of the droplet and thus the interaction energy to the other molecules in the liquid phase. The tendency of the surface molecules to evaporate is mirrored in the respective vapor pressure of the droplet. At normal temperatures, there is a high dynamics in the liquid droplet as well as in the surrounding gas. Molecules evaporate from the surface into the gas and other molecules from the gas phase condense on the surface of the droplet. The residence time of the molecules at the surface is the larger the larger the interaction energy. In steady state (at equilibrium vapor pressure, see Eq. (2)), the evaporation rate is, however, equal to the condensation rate and the numbers of molecules in both phases remains constant. The evaporation rate from a given surface area depends on the binding forces of the surface atoms at the given temperature, whereas the condensation rate depends on the density of molecules in the gas phase, i.e. on the vapor pressure. Of course, the molecules have a broad energy distribution and the relevant variables show large fluctuations, the system is highly dynamic, only the time average values of the variables remain constant in steady state.

As a consequence, such a system can not be stable, even if we start with an ideal system of droplets of total equal size, the unavoidable fluctuations cause small differences in the radius of the droplets and immediately the higher evaporation rate of the smaller droplets together with the lower evaporation rate of the larger droplets causes a mass transfer from the smaller to the larger droplets leading to a increasing in-homogeneity of the droplet distribution. At the very end the small droplets disappear and only one large droplet, in dynamic equilibrium with its vapor pressure, remains.

The situation is similar if we consider small crystals instead of droplets, there is only a subtle difference: the surface energy is not the same at all positions on the surface, but depends on the respective crystal plane, the binding force of a surface molecule is different on different facets of the crystallite. However, if we consider the solid crystallites in vacuum, there will be a certain evaporation of surface atoms leading to an increase of the vapor pressure until again a dynamic equilibrium (steady state) is reached.

We come to an analogous situation if we consider the crystallite surrounded by a solvent. In this case, the surface energy has to be replaced by the interface energy and the vapor pressure by the concentration of the molecules in the surrounding solution, but the observed phenomena are the same: the small crystallites disappear and one larger crystal remains in dynamic equilibrium with the surrounding solution or gas phase.

Of course, this dynamic picture of sublimation and solubility cannot directly be applied to polymer systems or other large molecules, but it is clear, that even in this case the dynamics of those parts of the chain molecule, which are located in the surface (or interface) region is much more pronounced than inside the crystallite because of the much lower binding forces.

Now the question arises, what happens on melting then? The phenomenon of melting can be considered in different ways (see for instance, Cahn's article in [4]): beside the thermodynamic view described above, there is the approach of a sudden cooperative collapse of the lattice, "when the root-mean-square amplitude reaches a critical fraction of the interatomic distance" (Lindeman criterion from 1910 [5]). Other approaches starts from the assumption that "catastrophic defect (dislocation) generation" (Cotterill [6]) or a certain concentration of vacancies (Cahn [4]) is the crucial factor. The common outcome of all these approaches is that, at least for small particles, the melting is a surface-initiated process. It has been proven, that the mean square amplitude of vibration is up to two times larger in the surface layer than in the bulk (Goodman and Somorgai [7]), the same is true for the number of defects (dislocations, defects, voids). Within the scope of all of these models it follows, that the surface layer of a crystal "melts" much earlier than the bulk. In every case, the molecules in this layer are not fixed, they are much more mobile than the molecules in the bulk. As a consequence small crystals are surrounded by a liquid, with properties similar to those of a melt, already at temperatures well below the melting point.

Such a system has to be considered as a two-phase system, though the liquid phase is very small: crystallites are in contact with a surrounding liquid and melting becomes a phenomenon, similar to a dissolution process. There is no sudden break-down of the lattice at a certain point but a continuous process of transform from solid to liquid state. However, even in this dynamic picture, the melting point of small crystals is lowered and melting starts from the surface layer and proceeds more and more into the solid. Consequently, the melting process is not "sharp", there is no melting "point" but a region with a continuous phase transform for every crystallite. In addition, there will be a more ore minor broad distribution of melting points which corresponds to the unavoidable distribution of crystal sizes (see Eq. (4)) and we get an even broader melting region.

What we have outlined so far concerns systems made up of small spherical molecules. This is of course an approximation, true in the case of metals and alloys, and the model must be extended if we want to consider other systems. Interesting and important materials in this context are the semi-crystalline polymers. These systems are in line with the above mentioned models concerning the size of the small crystals (from 20 nm to some micrometers) which normally are in contact to an amorphous (liquid) phase surrounding them, on the other hand, they break the rules, because the respective molecules are, for sure, not small and, and for typical chain molecules, the interaction field is far a way from to be isotropic (spherical). Nevertheless, Eq. (4) has been used successfully to describe the melting behavior of semi-crystalline polymers, in particular those which form thin lamella crystals like polyethylene (PE) [3]. The parameter r was in this case equated with the thickness d of the lamellae and the two other dimensions were considered much larger (infinite) and there influence was neglected.

But the thermodynamic prerequisites for the historical Gibbs–Thomson equation are too different from the properties of polymers and, as we see it, the applicability of the Thomson equation to polymer systems was only quite by chance successful. As we shall show in what follows, it is possible to derive a formula from thermodynamics, which is able to describe the melting behavior of oligomers and semi-crystalline polymers quantitatively. This formula looks similar the Thomson equation (Eq. (4)), but is based on more realistic prerequisites, it starts from chain molecules instead of spheres and takes the anisotropy into account. It should, however, be emphasized once more that all small sized systems are in principle unstable and melting of small crystallites of small molecules as well as polymers is thus a non-equilibrium process.

2. Gibbs–Thomson equation for polymers

Polymers consist of macromolecules with a large number of subunits which repeat themselves along the chain. Therefore, a macromolecule can be modeled as a chain of identical "beads" where the bead consists of the r.u. and the "thread" consists of the (covalent) bond between the r.u. For many polymers the r.u. itself is a "small" molecule in the sense mentioned in the introduction and has, approximately, a spherical size, in every case it can serve as “particle” in a thermodynamic approach.

Furthermore, it is well known, that polymers normally crystallize so that all chains run parallel to each other. The crystal can be considered as a bundle of rigid “rods” (“stems”) or rather as a chain of “beads” with a backbone like, stiff “thread”. In this picture, the crystal consists of a “stack” of identical layers of “beads” which normally lay perpendicular to the chain direction. In such crystals the extension of the “stack” in chain direction is normally much smaller, than in the lateral direction. However, the binding energy between the “beads” within a layer as well as between the layers can be considered as identical, if the “beads” are identical and the crystal lattice the same and undistorted. Only in the outer parts of the crystal there are deviations because of the surface and/or interface energy. In terms of a thermodynamic approach the system is considered as divided into subsystems and the same is true for the macromolecule as “particle” which is divided into sub-particles, the “beads”.

The basic idea of such an approach is that the total (molar) enthalpy $\Delta_{\text{fus}}H_{\text{mol}}$ and entropy $\Delta_{\text{fus}}S_{\text{mol}}$ of fusion of chain molecules (oligomers), each consisting of n r.u. in crystals of the same lattice type,[1] is incrementally composed of the respective values from the subunits.

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

$$\Delta_{\text{fus}}S^{n}_{\text{mol}} = n\,\Delta_{\text{fus}}S^{\infty}_{\text{r.u.}} + \Delta_{\text{fus}}S_{\text{e}} \tag{6}$$

The infinite sign refers to the respective value for a crystal formed of infinite long chains, the second term on the right 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 molecule, 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” [8] the molecular ends of the originally parallel chains on melting, when the rigid rods transforms to a coiled state. This would lead to an additional term $R\ln(n)$ on the right side of Eq. (6) which we shall come back to later.

As mentioned above, 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. (5) and (6):

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

The right side of this equation can be expanded as a Taylor series around $1/n = 0$, this results, after some calculations, in the following formula (for details, see [9]):

$$\frac{1}{T^{n}_{\text{fus}}} \approx \frac{1}{T^{\infty}_{\text{fus}}}\left(1 - \frac{\Delta_{\text{fus}}G_{\text{e}}}{\Delta_{\text{fus}}H^{\infty}_{\text{r.u.}}}\,\frac{1}{n}\right) \tag{8}$$

which formally looks like the Gibbs–Thomson equation (Eq. (4)) (and we shall still call it so) but it contains the *number* n of r.u. (“beads”) of the chain molecule rather than a *size* measure (r or l) 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. In addition it explains why the classical equation (Eq. (4)) can be successfully used for polymer systems: usually the number n of “beads” of the chain is unambiguously connected with the thickness of the respective lamella crystal via the well defined distance between two r.u. in the chain and the possible tilt angle of the chains inside the crystal. However, Eq. (8) starts from more realistic conditions than the classical Gibbs–Thomson equation does and offers further advantages as we shall show later. But first we have to prove the validity of this approach.

Remark. It should be emphasized, that the quantities on the right side of Eq. (8) 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, this equation describes the melting behavior of different alkanes and PE very well, so obviously the temperature dependence of the right side is almost compensated by ignoring the “unpairing” entropy term (see even [3] concerning this problem) and/or the temperature dependences of the Gibbs free excess energy (numerator) and enthalpy of fusion (denominator) are almost

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[1] Or at least the same interaction energy between the chains within a layer inside the crystal.

the same, so that the quotient becomes independent from temperature.

To prove the validity and the power of the approach we chose a system where a lot of literature data exist and which has been successfully used as model system before, namely PE and its oligomers, the alkanes. For these chain molecules, the r.u. is the CH_2-group. To prove the formula we have collected all available fusion data of linear and cyclic alkanes from literature (see [10]).

From the total (including the existing solid–solid phase transitions) molar enthalpy (and entropy) of fusion of the alkanes plotted against n, the number of CH_2-groups in the respective molecule, we found an almost linear relation for all alkanes with $n > 10$ (see 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 ($\Delta_{\text{fus}} H^{\infty}_{\text{CH}_2} = 3.4\,\text{kJ}\,\text{mol}^{-1}$) as well as cyclic alkanes ($\Delta_{\text{fus}} H^{\infty}_{\text{CH}_2} = 3.5\,\text{kJ}\,\text{mol}^{-1}$). 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 both negative and quite different for the orthorhombic linear ($\Delta_{\text{fus}} H_{\text{e}} = -3\,\text{kJ}\,\text{mol}^{-1}$) and the cyclic ($\Delta_{\text{fus}} H_{\text{e}} = -35\,\text{kJ}\,\text{mol}^{-1}$) alkanes. The reason for that results from the formulation (Eqs. (5) and (6)), where n is the total number of “beads” including those which are part of the chain end (linear alkanes) or folds (cyclic alkanes). Of course, the enthalpy contribution of these “beads” is lower than that of the beads from the core of the crystal, in other words, the excess enthalpy should be negative. Different lattices should give different contributions to the surface energy as well and, for cyclic alkanes, the chains are somewhat twisted in the neighborhood of the folds and fit only badly into the preferred (orthorhombic) packing, which results in a loss in interaction energy between the chains in that region of the crystal and thus in a larger reduction of the total enthalpy.

Similar results can be got for the total entropy of transition, but will not be shown here. However, the idea of incremental composition of the total enthalpy and entropy of fusion (Eqs. (5) and (6)) is supported this way, at least for this class of compounds.

The “Gibbs–Thomson plot” ($1/T_{\text{fus}}$ against $1/n$) of all available alkane and some PE 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

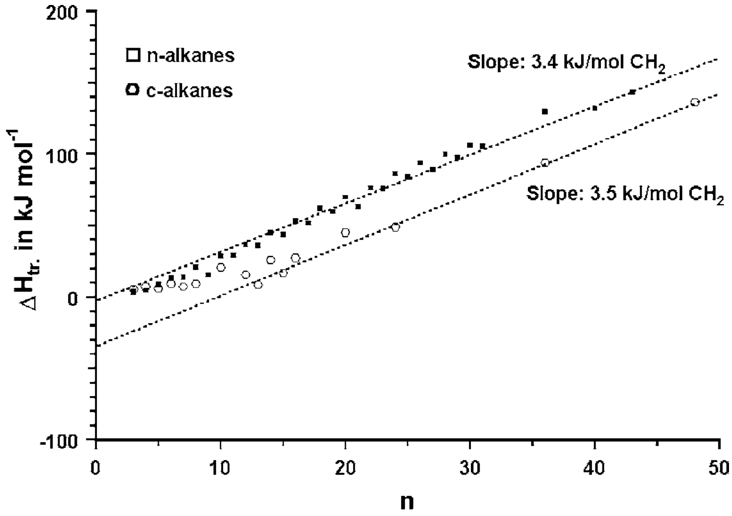

Fig. 1. The total enthalpy of fusion of different alkanes [10]. The dotted lines mark the best fit for odd linear and even cyclic alkanes with more than 20 CH_2-groups, respectively.

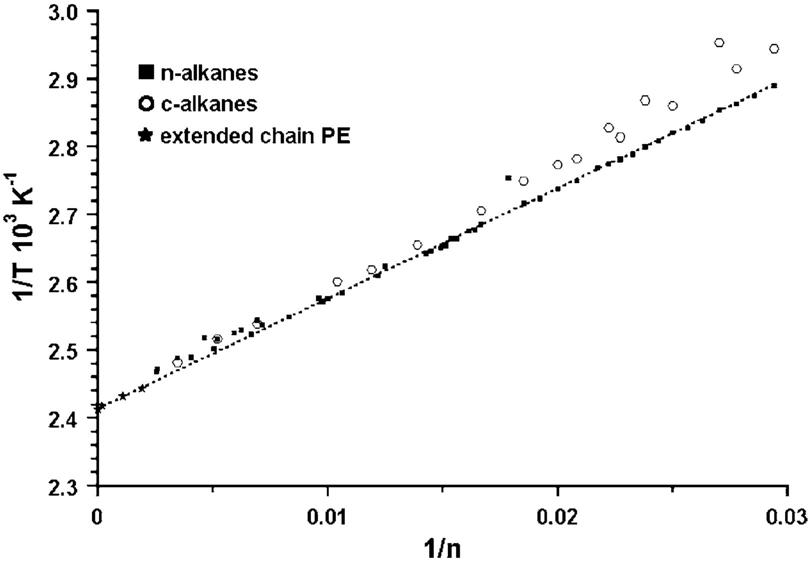

Fig. 2. Gibbs–Thomson plot of melting temperature of alkanes (most data from [10]) and some chain-extended PE [3]. The dotted line represents the best fit for medium sized n-alkanes ($T_{\mathrm{fus}}^{\infty}$: 414.4 K, slope: 0.0162 K^{-1}, Eq. (9)).

most reliable data exist):

$$\frac{1}{T_{\mathrm{fus}}^{n}} = 2.413 \times 10^{-3} + \frac{0.0162}{n} \tag{9}$$

The different lattices of the linear and cyclic alkanes [12] were disregarded in this case, because the respective differences in melting points 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 follows that Eq. (8) 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 (i.e. $1/T$ is too high) whereas the slope is a little higher than for n-alkanes.

Let us start with the latter finding: if we compare Eqs. (8) and (9), we have to draw the conclusion that for alkanes the excess Gibbs free energy G_e is a negative quantity[2] (i.e. the negative excess enthalpy predominates) This is in particular true for cyclic alkanes, in the region of the folds, the chains are somewhat twisted and do not fit well into the lattice, the interaction energy of the "beads" is reduced in this region and the excess enthalpy thus more negative (see Fig. 1). As a consequence, the slope in Fig. 2 is steeper for the cyclic alkanes than for the linear ones. This is also supported by the following argumentation: we know the structure of the crystals of cyclic alkanes [11,12], the main parts of the chains are parallel to one another and there are two tight folds with four $\mathrm{CH_2}$-groups in each of the (lateral) surfaces of the lamella (see [11–13]). Two of these four $\mathrm{CH_2}$-groups are almost part of the "stems" and two are perpendicular to them in the surface of the lamella. Within the picture of layers of "beads" we can assume that the former do and the latter do not contribute to the total enthalpy of the lamella crystal. Consequently, we should subtract $2 \times 2 = 4$ from the total number of $\mathrm{CH_2}$-groups to get the "true" number n of $\mathrm{CH_2}$-groups ("beads") which really contribute to the enthalpy of the crystal layers. 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 (see Fig. 3). Now the slope is almost the same for both types of alkanes (because the (negative) excess enthalpy is, of course, reduced if we don't

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[2] The *excess* Gibbs free energy must not be mixed up with the *surface* Gibbs free energy, which is only part of it.

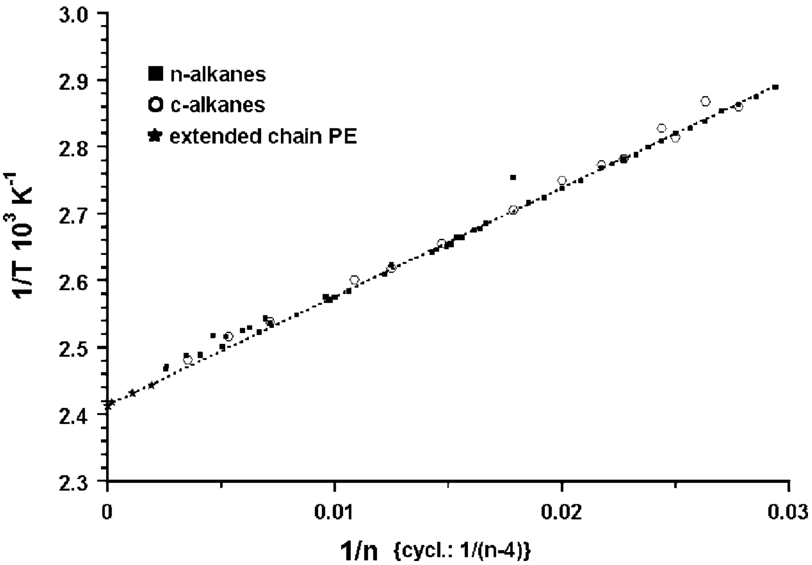

Fig. 3. Gibbs–Thomson plot as in Fig. 2, but here for the cyclic alkanes n is reduced by 4 (for details, see text).

count those “beads” of the alkanes which do not contribute to the total enthalpy anymore) and the melting point of all alkanes can be described with one equation. However, the fusion temperatures of some odd numbered cyclic alkanes are still too low, but this can be explained by the, in this case, non-symmetric ring, which causes a more disturbed lattice in the neighborhood of the folds and thus a more negative excess enthalpy than for even numbered cyclic alkanes.

The other systematic deviation from the Gibbs–Thomson line in Fig. 2 concerns the alkanes with $n > 140$. They almost show a too low fusion temperature compared to the expected one (see Figs. 2 and 3). As the intersection point of this line (at 2.4125×10^{-3}, corresponding to 414.5 K, the melting point of the infinite n-alkane and that of fully chain-extended linear PE crystals [3]) is well proved experimentally and as the melting temperatures of other chain-extended PEs fit well again to this line, we assume it the right line to describe the true melting temperatures. A possible explanation for the deviation of the experimental melting points from this line could be (beside possible “impurities” from the complex synthesis resulting in a reduced melting temperature) the different laminar habit of the ultra-long alkanes (e.g. 36° tilted stems [12]) 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 equation (Eq. (8)) is valid for linear as well as cyclic alkanes and some chain-extended PEs with almost the same set of parameters (Eq. (9)),

(ii) the fusion temperature is determined by the *number* of r.u. (“beads”) in the stems (rods) of the molecule which are part of the crystal,

(iii) the melting point of linear and cyclic alkanes is almost the same if we take the number of CH_2-groups of the “stems” of the respective molecule into consideration. This is correctly reproduced by Eq. (8) whereas Eq. (4) fails, as the thickness of the lamellae of cyclic alkanes is only about half of that of the linear alkanes and the Gibbs free interface energy of cyclic alkanes is for sure not only half of that of linear alkanes, it’s rather larger,

(iv) the surface energy, which is the determining factor in the classical approach of Thomson, does in this case obviously not play an essential role, because all alkanes form nearly ideal large crystals with a negligible surface energy, the internal interface energy between the stacked lamellae plays, of course, a role but this is only a part of the excess Gibbs free energy in Eq. (8),

(v) the melting temperature is mainly determined by the size of the *molecule* (number ob "beads"), the larger the molecule, the higher the melting point, regardless whether we consider linear or cyclic alkanes.

Although we have derived the formula from thermodynamic laws, the results from alkanes are in line with the different dynamic models of the melting process as well. For these approaches, the dynamics of the molecule is the dominant factor for the break down of the lattice. The dynamics of a molecule depends, of course, on the number and mass of the r.u. of the chain molecule rather than on the surface energy and thickness of the respective lamella. We shall discuss that in detail in a moment.

First 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 polymers (PE and its copolymers). For partial crystalline linear PE, 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 and Czornyj [3] published the following equation for PE data collected by Illers and Hendus [14]:

$$T_{\mathrm{fus}}\,(\mathrm{K}) = 414.2\left(1 - \frac{0.627}{l}\right) \pm 0.8 \qquad (10)$$

where l is given in nm. We transform this formula (to be better comparable to our Eq. (9)) by substituting l, the thickness of the crystal lamella with $nl_{\mathrm{C–C}}$ (where $l_{\mathrm{C–C}} = 0.1273\,\mathrm{nm}$ the C–C distance in direction of the c-axis of the orthorhombic lattice, n the number of CH_2 units) and a transition to the reciprocal:

$$\frac{1}{T_{\mathrm{fus}}} = \frac{1}{414.2}\left(1 - \frac{0.627}{0.1273n}\right)^{-1} = 2.414 \times 10^{-3} + \frac{0.0119}{n} \qquad (11)$$

This result must be compared with our fit line from the alkanes (Eq. (9)). As one would expect, the (extrapolated) melting point of the infinite large lamella is almost the same for both formulas, but the slope is somewhat different because the excess Gibbs free energy (the numerator of the slope coefficient, see Eq. (8)) for PE lamellae crystals and for alkanes is different because of the different interface. In case of alkanes there are CH_3-groups or C_2H_4 folds, respectively, and in case of PE there are free (non-crystallized) chain segments leading to a lower interface energy. However, as it looks like our approach (see Eq. (9)) holds generally even for polymer lamella crystals.

3. Discussion

The essential outcome from the application of our approach to 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 ("beads") from the molecule stems, which are part of the crystal, as determining parameter. Here, the question arises how can the molecule "know" this number and "feel" its length inside the crystallite.

The answer comes from the picture of melting dynamics presented in Section 1: the mobility and the dynamics of the total molecule depends, of course, on the number and mass of the "beads" involved. For chain molecules, the "beads" cannot move independently of the other "beads" because of the stiff covalent bonds. This is in particular true for the "beads" of the "stems" inside the crystal. In the case of linear alkanes, the total molecule forms one stem (rod) inside the crystal, for cyclic alkanes there are two stems (of about half the length) but tied together with two tight folds. The mobility of a cyclic alkane (in a thinner lamella crystal) is thus almost the same as the mobility of a linear alkane with the same number of r.u. 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 why the melting point of the two types of alkanes is the same though the lamellae are different thick.

In the case of partial crystalline polymers, the crystallized part forms one stem which on both sides of the lamella crystal is only loosely (i.e. with more degrees of freedom) connected to the amorphous (random coiled) region. From the dynamics the molecule only "feels" as long as the crystallized "stem" is. In the case of folded-chain crystals, we have to distinguish between those with loose loops which can be compared to the case above and those with tight folds were the molecule "feels" longer than the thickness of the lamella predict because of the restricted mobility (similar to the case of cyclic alkanes) and the melting point is higher.

So far so good, but now the question arises why the crystals of a semi-crystalline polymer, like PE, follow the same melting law as the respective oligomers, the alkanes, though the systems actually are quite different: alkanes form large nearly perfect crystals and crystallize completely whereas PE forms small crystals and crystallize only partially. In the first case, we have perfect pure crystals, i.e. one single phase, in the second case, we have a two-phase system: small crystals in contact with an amorphous phase, the melt, which act as a solvent as well. From the classical thermodynamic point of view one-component-one-phase and one-component-two-phase systems must be described different, and it can not be assumed that they follow the same law, or, in other words, that they show the same Gibbs free energy. How can that be then?

The fact, that for small particles the melting is a surface-initiated process, is, as we see it, the common ground on which to base the similar melting behavior of these obviously different systems. The interface (or surface) layer disorders first and becomes highly mobile and enriched with defects and dislocations, in other words, a thin layer around the crystallites can be considered as in liquid state already below the melting point. For semi-crystalline polymers, this is obvious, the small lamella-like crystals are always surrounded with an amorphous phase, which is in the liquid state (above the glass transition temperature). In the case of oligomers, this is not so clear, but at least from alkanes we know, that they form large stacked crystals with layers of well ordered alkane molecules. If we consider one such alkane layer as the actual crystallite, we have a stacked system of lamella-like crystals which, at least in chain direction, are small in size. The respective interface contains the end-groups (or folds) of the chain molecule, which are always different from the r.u. ("beads") in the "stem" and therefore should have a different interaction energy. It is this interface that becomes mobile first and plays the role of the liquid surrounding of the crystallites. For linear alkanes, it is well known, that the so-called (hexagonal) "rotator phase", formed some degrees below the melting point and endothermic in character, has a structure where the CH_3-groups are tilted against the all-*trans* stem of the chain. This shows the higher mobility of the interface layer, which (in this state) contains significant more entropy. For cyclic alkanes, it is obvious from the crystal structure, that the respective interface is distorted and initiate a so-called conformational disordered (CONDIS) mesophase, in some cases even at atmospheric pressure (see [15]). This supports the melting of the oligomers as a surface-initiated process as well as the dislocation (conformation) model of melting and it explains why the crystals of a semi-crystalline polymer, like PE, follow the same melting law as the respective oligomers, the alkanes.

However, at this point, it should be emphasized once more, that a semi-crystalline polymer as well as a small crystallite is not in an equilibrium state, it is never stable and will change toward a more stable state if the fixing constraints come loose. The crystallite will expand and the melting point will increase. This will always run parallel to the behavior mentioned above and one has to be careful in interpretation of the experimental findings.

4. Conclusions

The phenomenon of melting as an surface initiated process (see even [16]) can be taken as the real reason why we are able to describe the melting of such different systems, as perfect oligomeric crystals on the one hand and semi-crystalline polymers with small crystallites on the other hand with one and the same Eq. (8) and almost the same parameter set.

The success of our approach in the case of PE and different alkanes give us the courage to generalize the findings to other polymers. Of course, this needs a lot more experiments. However, the essential points of the approach are the following:

(i) the thermodynamic "particle" is not the total molecule, but the r.u. (the "bead"),
(ii) the total melting enthalpy and entropy is incrementally compound of the r.u. contributions,
(iii) the melting temperature is determined by the dynamic size of the molecule, i.e. by the number of r.u. ("beads") in the crystallized stems of

the macromolecule, which have to move cooperatively when the dynamics becomes critical,

(iv) a thin surface/interface layer of the small crystallites transforms into a liquid (mobile and disordered) state well below the real melting point, i.e. melting is a surface initiated process and its progress differs, of course, for different crystal faces,

(v) from the thermodynamic point of view, the crystallite in the melting region should be considered as a two-phase system (solid in contact with liquid) with a certain *temperature region* of coexistence rather than with a sharp transition *point* which is found for large crystals of small molecules from classical thermodynamics,

(vi) melting starts in that surface/interface with the largest interface energy and proceeds continuously through the crystal on temperature increase, there is no sudden break down of the lattice,

(vii) small crystals are generally unstable and should disappear (or thicken) on temperature rise, they can only exist if there are constraints which prevent the approach to the equilibrium state.

The last three points need some more words: in chain molecules there are natural constraints, the “beads” are not free but connected via covalent bonds and therefore such molecules, as a rule, form anisotropic lamella-like crystals. The chains are parallel and often perpendicular (but even somewhat tilted) to the lamella. Therefore, we have to distinguish between two different types of interfaces. The vertical (often stacked) interfaces contain the end-groups of the chains (oligomers) and tight folds as well as loosely packed (liquid) chain segments and cilia sticking out of the interface almost vertically. Whereas in the lateral interfaces, disordered (liquid) as well, the chains are positioned within the interface/surface (in parallel). Of course the chain dynamics and the melting progress will be different in these different interfaces. The dynamics of the vertical (stacked) interfaces is determined by the mobility of the r.u. (“beads”) which is restricted by the rigid “stems” whereas at the lateral interfaces larger parts than only some “beads” of the chain can move from the liquid to the solid state dynamically and diffuse within the interface layer. Correspondingly, two types of melting should exist for such polymer crystals: interface initiated melting from the stacked lamellae in chain direction (the reversal of lamella thickening) and lateral melting (the reversal of crystal growth). Depending on the constraints involved in the different processes (e.g. from the rigid amorphous fraction) and the respective surface energy one or the other of these processes should play the dominant role. We expect the lateral melting to be slower and having a dynamics with a higher energy barrier (activation energy). Recently, experimental findings have been published which support this view, but we refrain from presenting these details here, this would go beyond the scope of this paper.

To sum up, the new approach to the Gibbs–Thomson equation, although founded on thermodynamic laws, support the dynamic picture of melting rather than the classical thermodynamic view. It tells us furthermore, that small crystals only can exist, if there are constraints which stabilize the non-equilibrium system. For chain molecules, the covalent bond is such a constraint which dominates the system and makes a semi-crystalline state with small crystallites possible. The melting of such systems is a complex process which needs both thermodynamic and dynamic models for a successful description.

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References

[1] W. Thomson, Phil. Mag. 42 (1871) 448.
[2] J.J. Thomson, Applications of Dynamics, London, 1888.
[3] B. Wunderlich, G. Czornyj, Macromolecules 10 (1977) 906.
[4] R.W. Cahn, Nature 323 (1986) 668.
[5] F.A. Lindemann, Z. Phys. 11 (1910) 609.
[6] R.M.J. Cotterill, J. Cryst. Growth 48 (1980) 582.
[7] R.M. Goodman, R.M. Somorgai, J. Chem. Phys. 52 (1970) 6326.
[8] P.J. Flory, A. Vrij, J. Am. Chem. Soc. 85 (1963) 3548.
[9] G.W.H. Höhne, Polymer 43 (2002) 4689.

[10] M. Rothe, I. Rothe, J. Brandrup, E.H. Immergut (Eds.), Polymer Handbook, 3rd edition, Wiley, New York, 1989 (Chapter IV).
[11] H. Drotloff, D. Emeis, R.F. Waldron, M. Möller, Polymer 28 (1987) 1200.
[12] G. Ungar, X. Zeng, Chem. Rev. 101 (2001) 4157.
[13] S.P. Chum, Macromolecules 27 (1994) 656.
[14] K.-H. Illers, H. Hendus, Makromol. Chem. 113 (1968) 1.
[15] H.-P. Grossmann, Polym. Bull. 5 (1981) 137.
[16] B. Wunderlich, Macromolecular Physics, vol. 3, Academic Press, New York, 1980.