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Discussion of problems of nonequilibrium thermodynamics of polymers as presented in the paper by Sommer and Reiter☆,☆☆

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Abstract

A number of discussion points are raised concerning the nonequilibrium melting and crystallization as described in the paper by Sommer and Reiter.[1]

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1. Introduction

In the discussions during the 8th Lähnwitz Seminar [1] it was pointed out that nonequilibrium thermodynamics of macromolecules needs to be discussed in the light of research as it developed in the past. This discussion was then and is now offered in the spirit of the Lähnwitz Seminar to advance the calorimetry and thermal analysis of macromolecules which must go in the direction from equilibrium thermodynamics to nonequilibrium thermodynamics [2]. The former has been used almost exclusively in the past and has long reached the limit of usefulness. The latter explain the importance of the paper of Sommer and Reiter in [3] who present a link of coarse-grained simulation of nonequilibrium processes by the Monte-Carlo method to irreversible thermodynamics. The development of the ideas about the influence of the surface on the nonequilibrium thermodynamics of the melting and glass transition of thin films and fibers has also been summarized in Ref. [4]. In the following sections, several points are raised for discussion. They are given in the sequence as they arise in the first half of Ref. [3].

2. High conformational entropy

The statement that “high conformational entropy which is the basis of the understanding of many universal features of polymeric systems and plays an important role for the understanding of material properties of soft matter ([3], Section I, para 1)” is actually the basis of the tripartition of all molecules (small molecules, flexible macromolecules, and rigid macromolecules) [5] and should, perhaps, be expanded to include enthalpy effect as is explained in the following summary: The liquid phase of small molecules is characterized by molecular translation, rotation, and if sufficiently large, additionally some internal rotation, also called conformational motion. These three types of molecular motion are of large amplitude. To this large-amplitude of motion molecules of more than one

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☆ J.-U. Sommer and G. Reiter, “Crystallization in ultra-thin polymer films morphogenesis and thermodynamical aspects.” Thermochim. Acta, elsewhere in this issue.

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atom add small-amplitude vibrations. For larger molecules this vibrational motion becomes the main type of motion and contributes most to the integral thermodynamic quantities of enthalpy and entropy. Small molecules show the highest entropies of fusion of any material (per mole of atoms). Flexible macromolecules may also form a liquid phase and show then practically only conformational motion with a considerably lower entropy of fusion than found for an equivalent mass of smaller molecules [6]. As an example, one can take the entropy of fusion of normal paraffins, $H{-}(CH_2{-})_xH$, and extend this homologous series to polyethylene. The molar conformational entropy increases with chain-length, x, but never quite reaches the translational and rotational entropy contributions of the shortest members of the series. For $x = 1$, methane, a molecule showing on melting only a change of three vibrational degrees of freedom to translation, causing positional disorder, the entropy of fusion is $10.3\,J\,K^{-1}\,mol^{-1}$ (Richards' rule suggests $7–14\,J\,K^{-1}\,mol^{-1}$ for this type of fusion). Propane, the smallest rigid n-paraffin with $x = 3$, shows in the melt three degrees of freedom of rotation (orientational disorder) in addition to positional disorder, but no conformational degrees of freedom. Its entropy of fusion is $38.5\,J\,K^{-1}mol^{-1}$ (Walden's rule, $20–60\,J\,K^{-1}\,mol^{-1}$, independent of molecular size). On fusion of longer paraffin chains, an increasing number of torsional vibrations about the C–C-bonds are changed to internal rotations, resulting in conformational disorder. The increment for conformational disorder is typically $7–12\,J\,K^{-1}\,mol^{-1}$ for each flexible bond [6]. Polyethylene, $(CH_2{-})_n$, has an equilibrium entropy of fusion of $n \times 9.91\,J\,K^{-1}\,mol^{-1}$ resulting from conformational disorder alone. The translational and rotational entropy are negligible in polyethylene since it is similar in value to that of a propane molecule. The entropy of fusion for dodecane ($x = 12$) is $11.6\,J\,K^{-1}$ (mol of C)$^{-1}$, i.e., is similar, but slightly larger than for polyethylene, but it represents a compound of much different properties.

Completing the list of possible compounds, one finds that more rigid macromolecules develop increasingly less conformational disorder on fusion, i.e., their melting temperatures increase ($T_m{}^\circ = \Delta H_f/\Delta S_f$). Finally, the molecules cannot melt without decomposition, i.e., the entropy of fusion without decomposition approaches zero. This scheme illustrates that the properties of soft matter are governed by *both*, the entropy and enthalpy of fusion, as fixed by molecular bonding and structure [5]. The conformational entropy of linear polymers is only one parameter determining the melting temperature. The change of intermolecular forces on melting is the other.

3. Suggestion of single-molecule systems for soft-matter, flexible polymers

A single macromolecule can certainly be "*considered to be a small thermodynamic system*" as expressed in ([3] Section 1, para 1). This was proven by experimentation in Ref. [7], but in the case considered in [3], the total mass consists of a solution of several or many large molecules, then this assignment should not be made since then the molecules act as components of the system which is the solution of many large molecules. Additional complications in the descriptions of macrolmolecules arise from decoupling of parts of the molecules to multiple components, for example, due to effects on the crystal surface or entanglements. These effects are at the root of broadening of the glass transition, rigid-amorphous fractions, reversible melting, and even chain folding [8].

4. Surface free energy and surface tension

The statement "*the surface free energy of the fold surfaces (top and bottom surfaces of the lamella) is much higher than that of the lateral surface*" in ([3] Section 1, para 1) is in need of an explanation why in melting of lamellar crystals surface free energy is not identical to surface tension, an oversight illustrated in the description of Eq. (2) of [3]. The surface tension with the dimension $N\,m^{-1}$ is identical to surface free energy with the dimension $J\,m^{-2}$, yielding for both the dimension $[kg\,s^{-2}]$. When measuring surface tension from the contact angle with a suitable liquid on the different surfaces of a polymer crystal, quite similar values are expected for the surface tension since the cohesive energy densities of both are similar. The fold-surface free energy, in contrast, is about 10–20 times larger. One, thus, must use the surface free energy as defined by Gibbs [9], being the excess quantity over what the free energy would be if the two phases would extend unchanged to a suitably chosen interface. The strain energy introduced by chain folds and by other features in the surface are also part of the surface free energy, but would have no, or only little influence on the surface tension. For a general discussion, see pp. 22–28 in Ref. [10].

5. Extended-chain crystals and equilibrium melting

This topic needs to be discussed in more detail to understand Fig. 1 in Ref. [3] and it would be advantageous to improve on the references cited. It is important to notice that it was shown recently that a melting-crystallization equilibrium (reversibility) can be obtained for n-paraffins only up to about $C_{70}H_{142}$, (planar zig-zag length 9 nm) [11,12]. The extended-chain crystals "*for short n-alkanes up to a length of about 150 CH_2-units*" in ([3] Section 1, para 1), are probably also grown irreversibly and extended after an initial folded-chain crystal growth! The history of growing of extended-chain crystals goes back to research on polytetrafluoroethylene crystals grown from the melt at atmospheric pressure by Bunn in 1958 [13], an observation largely overlooked. This was followed by the initial work on polyethylene grown at elevated pressures in 1964 [14,15]. The next progress involved the observation of Bassett [16] that a hexagonal phase exists for polyethylene at these high pressures which causes enhanced sliding diffusion, as suggested by Hikosaka [17], explaining the mechanism proposed before solely based on the morphology of the crystal growth-faces [18]. The hexagonal polyethylene was later identified to be a mesophase, due to its conformational disorder (condis-crystalline), and was first summarized in [19].

6. Phase equilibrium for semicrystalline polymers

The imagined "*phase-equilibrium between an extended chain crystal and the corresponding melt*" ([3] Section 1, para 2) has actually been determined quantitatively for polyethylene. The lowest possible temperature for melting occurs for a given metastable or stable crystal at the condition of zero-entropy-production, while crystallization needs usually a certain amount of supercooling (although for polyethylene, it is much less than for other polymers like polypropylene). A zero-entropy-production melting temperature is possible *either* at the equilibrium melting temperature, *or* at the non-equilibrium temperature where the metastable crystals and the resulting melt have the same degree of metastability ($\Delta G_{\mathrm{melting}} = 0$). The second point has been overlooked when discussing Eq. (2) in Ref. [3 (at the end of the para containing the equation)]. This well-known concept of irreversible thermodynamics represents the basis of the nonequilibrium melting described by the Gibbs-Thomson equation [20,21] (see also [4]). The equilibrium melting temperature is available for polyethylene due to the easy production of extended-chain crystals at elevated pressures. With slow dilatometry, to avoid superheating, the equilibrium melting temperature could be measured to be 414.6 ± 0.5 K [22] and linked within experimental error to the empirical extrapolations from paraffin melting temperatures, and to predictions based on Flory's entropy calculations, all summarized in [23]. Finally, multi-component phase diagrams for polyethylenes with broad molar mass distributions were established [24].

These facts illustrate that Fig. 2 in [3] is thermodynamically not fully correct. Points A and B cannot be different states which can be reached by crystallization followed by fast heating, they must be the same state! The value of T_m is then the variable that describes the zero-entropy-production melting of a crystal grown at T_c. The trace of the change to T_m with decreasing heating rates or increasing annealing temperatures should be the curve *B–C*. Where curve A–C correct, in order to agree in shape with Fig. 3, the fast melting temperature would have to be close to T_c. Note, however, that isothermal crystallization creates more than one crystal with different melting characteristics, as documented for PEEK [25] and for polyethylene [10 (Figs. VI.24 and VI 26)]. Fig. 3 implies the same for crystals with different annealing histories, but of the same thickness.

7. Shapes of equilibrium crystals

The drawing of morphological changes in Fig. 4 of [3] is oversimplified. Spheres of isotropic matter have the lowest surface free energy, but this statement applies to the melt, so that the disordered phase at the bottom of the figure should be spherical! Crystals are always anisotropic and their equilibrium shape is fixed by the so-called Wulff construction [26] which determines the morphology as a function of all possible surfaces and always represents a regular polyhedron (see also page 182 of [27]). The intermediate lamella of thicker and thinner segments would be not as stable as the starting crystal. Contrary to what is said in the legend of Fig. 4 of [3], the melting temperature under zero-entropy-production conditions *is* determined by the overall surface free energy of the crystal morphology. If the zero-entropy-production condition is not satisfied, the Gibbs-Thomson equation is not valid. This, naturally, applies only as long as internal crystal defects are negligible and the crystals melt into a large volume of a liquid or disorder into a mesophase.

8. The mechanism of crystallization

The description of the growth of monatomic and polymeric crystals in Fig. 5 of ([3], Section 2 para 1)] should be clarified. The role of internal chain disorder must be connected to the discussion offered in Section 2, above. Even molecules as simple as butane or tetraethylammonium iodide lose conformational degrees of freedom on crystallization, i.e., their internal state is not invariant. Also, the *external and internal degrees of freedom* are not well defined. Note, degrees of freedom are never *lost*, they just *change* from one type to the other. In particular, on crystallization, the large-amplitude motion changes to small-amplitude vibrational degrees of freedom. At low temperature, these vibrational degrees of freedom collect in their zero-point energy level and then do not contribute to the heat capacity (but are still there). All molecules lose entropy on crystallization (but not as much as is implied in Ref. [3], polyethylene, one of the most-flexible polymers, loses only about 1/5 of its total entropy on crystallization, as much as the melt loses on cooling by 100 K). The difference in going from a small molecule to a macromolecule is that on crystallization, the macromolecule loses practically conformational entropy only, the rotational and translational entropies, referring to the molecule as a whole, are negligible. Small, molecules, in contrast, may have a non-negligible amount of rotational and translational entropy of fusion. This change in internal entropy of fusion is very gradual and actually not very suited to distinguish between large and small molecules. It can be seen when looking quantitatively at the percentage of conformational entropy of fusion of paraffins: Methane 0%, decane: 30%, hexacontane (longest molecule without molecular nucleation, i.e., crystallizing reversibly): 7%, $C_{150}H_{302}$ (cited in [3] to be the upper limit of extended-chain crystallization): 3%, polyethylene (of molar mass 280,000 Da): 0.02%.

9. Crystallization in ultra-thin films

It must be pointed out that the term ultra-thin film is not commonly used as in ([3], Section III). In the thinnest possible films (which should, perhaps, bear the name ultra-thin?), crystallization occurs usually with the polymer chain oriented within the surface layer. A large number of epitaxial growths, heterogeneously nucleated, with a chain-orientation parallel to the surface of the substrate have been documented in pp. 266–283 of [27]. In order to create chain orientation as shown in Fig. 6 of [3], a vertical surface element must exist, possible only if the films are not ultra-thin, but are created as outlined in Fig. 7 in [3] with a thicker rim. Ultra-thin (monomolecular) films have been produced recently by Magonov and coworkers [28]. These crystalline, truly ultra-thin films are stable even above the equilibrium melting temperature due to interaction energy (not entropy effects!) and present an explanation for the crystal growth of polyethylene without nucleation when in contact with a suitable support. The same was observed on growth of a thin layer of a melt on extended-chain crystals (see [18], or, for example, described also on pp. 267–271 in [27]). Going to single-molecule droplets of the melt, in contrast, the original film is not ultra-thin but closer to a hemisphere and on crystallization of poly(oxyethylene) [7,29] and isotactic polystyrene [7,30] these droplets grew into single crystals with their chains normal to the substrate, as assumed in Fig. 6 of [3], and simulated in the second half of [3].

10. Conclusions

The above points have illustrated that an extensive body of information on the nonequilibrium thermodynamics exists and should be used as the basis for further development of this most important theoretical support of thermal analysis [2]. The work on the coarse-grained simulation of crystal growth, presented in [3], is an important step in bridging the microscopic fluctuations about equilibrium to macroscopic descriptions using irreversible thermodynamics. This work, however, will only reach maximum impact and value for the development of thermal analysis if it is solidly grounded in prior work. It is an impediment for calorimetry that in the past most work on irreversible thermodynamics and the achieved progress of the description of polymer processes has been neglected [31,32] in favor of the simpler, more popular, but for the processes on hand the often incorrect, equilibrium thermodynamics.

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