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Determination of the Equilibrium Melting Temperature of Polymer Crystals: Linear and Nonlinear Hoffman−Weeks Extrapolations

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ABSTRACT: The applicability of the Hoffman−Weeks (HW) linear extrapolation for the determination of equilibrium melting temperatures of polymers is critically reviewed. In the first paper of this series, it is shown that the linear extrapolation of observed melting temperatures cannot, in general, provide a reliable estimate of the equilibrium melting temperature. A combination of the experimentally observed undercooling dependence of the initial lamellar thickness, $l^* = C_1/\Delta T + C_2$, and the finite lamellar thickness dependent melting temperature depression, as described by the Gibbs−Thomson treatment, provides a venue to the general relationship between the crystallization and observed melting temperatures. It is further shown that, for a constant thickening coefficient, the observed melting temperature must vary nonlinearly with the crystallization temperature. The origin of this nonlinearity lies in the term C_2, which is neglected in the classical HW treatment. The principal implications of this study in the context of the Lauritzen−Hoffman theory are the following: (1) the linear extrapolation, when carried out for lamellar crystals exhibiting a constant thickening coefficient, invariably underestimates the equilibrium melting temperature; (2) the extent of the underestimation increases with a decrease in the lamellar thickening coefficient, with an increase in the magnitude of C_2 and with an increase in the range of undercoolings where the crystals are formed; (3) the linear extrapolation always leads to an overestimation of the lamellar thickening coefficient. Finally, a more accurate method is proposed for the determination of equilibrium melting temperatures in cases where the thickening coefficient can be assumed constant.

Introduction

The equilibrium melting temperature, T_m, of a polymer crystal is defined as the melting temperature of an infinite stack of extended chain crystals, large in directions perpendicular to the chain axis and where the chain ends have established an equilibrium state of pairing. This quantity is one of the most important thermodynamic properties of crystallizable chain polymers, as it is the reference temperature from which the driving force for crystallization is defined. Within the current paradigm of crystallization theories,[1−4] knowledge of this quantity is essential for a proper understanding of the temperature dependence of bulk crystallization and lineal crystal growth rates. More importantly, a precise determination of this thermodynamic quantity is necessary for the evaluation and comparison of crystallization theories. Crystallization processes in polymers are generally thought to occur through a sequence of primary nucleation and crystal growth mechanisms, the rates of which, at a temperature T_x, are a function of the undercooling $\Delta T = T_m - T_x$, where T_m is the equilibrium melting temperature. When the temperature dependence of crystal or spherulitic growth rates is analyzed in the context of the Lauritzen−Hoffman secondary nucleation (LH) theory,[1,2] even small variations in the choice of the equilibrium melting temperature can lead to significant changes in the magnitude of the calculated nucleation constant K_g, and surface free energy product $\sigma\sigma_e$. More importantly, it can lead to the artificial creation or disappearance of regime transitions when the raw spherulitic growth rate data are presented in a LH plot.[5]

Since the morphology of semicrystalline polymers is controlled by kinetic factors rather than by thermodynamic ones, practitioners in this field are faced with the unfortunate fact that equilibrium crystals of even low-to-intermediate molecular weight polymers cannot be obtained experimentally.[6,7] The equilibrium melting temperature for the crystalline form of a polymer can therefore only be obtained through extrapolative procedures. Four general methods have been devised for the assessment of equilibrium melting temperatures of semicrystalline polymers: the Gibbs−Thomson[1−3,8,9] and the Flory−Vrij approaches,[10−12] the Hoffman−Weeks procedure,[13] and the fitting of growth rate data at a sufficiently low undercooling with the classical theory of lamellar crystal growth.[14,15] The applicability of the latter two methods relies on the assumption of a specific crystal growth model. The former two methods are based solely on thermodynamic arguments and should be a priori more reliable, although they have limitations of their own.

The Flory−Vrij formalism was developed to determine the equilibrium melting temperature of polyethylene in the long-chain limit and is based on the availability of equilibrium melting temperature data for a series of pure short-chain paraffins, which are homologues of polyethylene. The equilibrium melting temperature of an extended chain crystal of linear polyethylene having n CH_2 groups and two methyl end groups can then be calculated from the latent heat and entropy of fusion per methylene group, the methyl end groups contribution to the enthalpy and entropy of fusion, and the localization entropy associated with the pairing of chain

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ends. These thermodynamic input parameters are obtained through refinement of paraffin melting and heat capacity data. As this approach requires the availability of a homologous series of strictly monodisperse materials and an inordinate amount of thermodynamic data, it has not been widely applied to other semicrystalline polymers.[12]

The Gibbs–Thomson approach is based on the thermodynamic argument that the melting temperature of a crystal of finite size is depressed below that of an infinite size crystal, the result of an increase in the free energy of the crystal with a decrease in its dimensions. In the case of polymer lamellar crystals, it is generally but not universally observed that the lamellar thickness is much smaller than the other two dimensions, in which case, the melting temperature depression is proportional to the ratio of the crystal basal surface free energy to the theoretical enthalpy of fusion (i.e., to the reciprocal of the lamellar thickness; see below). Limitations of this thermodynamic treatment have been discussed in the literature[3,16] and are not of particular concern for relatively high molecular weight flexible linear polymers, for which the equilibrium melting temperature becomes approximately independent of the chain length. A plot of the observed melting temperature as a function of the reciprocal of the lamellar thickness, if linear, would therefore yield the equilibrium melting temperature as the intercept. This method, which appears at first sight very straightforward, is only suitable if a number of experimental conditions are satisfied. First, lamellar crystals should be large enough along directions parallel to their basal plane for the lateral surface free energy contribution to the melting point depression to be negligible. Second, the crystal lamellar thickness should be measured just prior to the onset of its melting. If the crystal thickness is recorded at the crystallization temperature or at ambient conditions, the crystals may reorganize, melt, and recrystallize or thicken during the heating scan required to record their melting temperature.[9] In most instances, the lamellar thickness is actually determined at room temperature from either small-angle X-ray scattering (SAXS) measurements, electron microscopy observations, or the longitudinal acoustic modes (LAM) observed by Raman spectroscopy. It must be emphasized that in the case of Raman LAM studies the correction for chain tilt with respect to the normal of the basal crystal planes must be carried out to determine the actual lamellar thickness. Furthermore, as a result of the finite crystal-melt interfacial thickness at the crystal basal plane, it is anticipated that both the SAXS and the LAM analyses lead to a slight overestimation of the core lamellar thickness. In the SAXS analysis this arises from the equal apportionment of the interphase thickness to the crystal and amorphous phases. In the Raman LAM analysis of polyethylene, overestimation results from the variable persistence of trans sequences into the interfacial region. In any case, for linear polyethylene, estimates of the interfacial thickness through SAXS and Raman spectroscopy suggest that this overestimation should be of a magnitude ca. 5 Å per interphase. Unless the above issues are rigorously addressed, one should not expect the Gibbs–Thomson method to provide an accurate estimate of the equilibrium melting temperature.

The authors believe that the best possible approach may consist of following simultaneously the evolution of the SAXS and WAXD (wide-angle X-ray diffraction) patterns of a semicrystalline polymer during heating using a synchrotron radiation source.[17] The latter assertion obviously assumes that the semicrystalline polymer morphology can be reasonably approximated by the lamellar stack model, so that the correlation or interface distribution function approach can be reliably used to determine the length scales associated with spatially periodic electron density fluctuations.[18,19] It is therefore doubtful that such a technique could be rigorously applied to polymers such as poly(ethylene terephthalate) (PET), poly(ether ether ketone) (PEEK), or poly(phenylene sulfide) (PPS), since morphological studies carried out by transmission electron microscopy (TEM) have unambiguously revealed that, over most of their practical crystallization temperature range, these polymers display thin lamellae of relatively narrow width.[20-22]

The determination of an equilibrium melting temperature through the analysis of the temperature dependence of spherulitic growth rates was discussed in two previous manuscripts[14,15] and will be addressed further in the subsequent paper of this series for the case of isotactic polypropylene.

The Hoffman–Weeks (HW) method involves the extrapolation of a linear regression of experimentally observed melting temperatures, T_m', for various crystallization temperatures, T_x, to the equilibrium line $T_m' = T_x$. The associated HW equation results from a combination of the Gibbs–Thomson equation and an expression derived from the LH secondary nucleation theory,[1,2] which relates the initial stem length to the undercooling. It is also based on the assumption that the difference between crystallization and observed melting temperatures is solely due to the thickening of lamellae formed at the crystallization temperature. The thickening coefficient, γ_{HW}, which is calculated as the reciprocal of the slope of the T_m' versus T_x regression line, should account, in principle, for the thickening process occurring during isothermal crystallization.[13] Because of its straightforward experimental implementation and its analytical simplicity, this method has been widely used for the determination of the equilibrium melting temperatures of semicrystalline polymers. It should be noted, however, that this procedure was not developed to provide the best estimate of equilibrium melting temperatures, but merely to explain the observed increase in the melting temperature with the crystallization temperature.[2,5] It has been reported that in some cases this approach fails as a result of enhanced lamellar thickening for samples crystallized at the lowest undercoolings.[2,23] It is also commonly but incorrectly accepted (see below) that the observation of a linear T_m' versus T_x behavior is an indication that the lamellar thickening coefficient is constant. At this stage, it is important to realize that a necessary prerequisite for the isothermal lamellar thickening process is the existence of some molecular mechanism for segmental motion within the lamellar crystal. It is generally agreed that the observation of a crystalline α-relaxation (through dielectric, dynamic mechanical and NMR spectroscopic measurements) provides compelling evidence for the existence of segmental motion within the lamellar crystals.[24] However, one should note that the existence of such a relaxation is a necessary, but not sufficient, prerequisite for the lamellar thickening process. Other factors such as the

Table 1. Thermodynamic Constants for High-Molecular-Weight Linear Polyethylene

T_m (°C)	145.5[a]
ΔH_f (J·cm^{-3})	283[b]
$\sigma_{em} = \sigma_e^1$ (mJ/m^2)	90.4[c]
C_2 (Å)	43.25[c]

[a] Flory−Vrij extrapolation (see ref 2). [b] Calculated using a density of 0.968 g·cm^{-3} at 145.5 °C (ref 45). [c] Reference 2.

presence of noncrystallizable units along the polymer backbone (branches, comonomer, etc.), a high entanglement density in the interlamellar regions, and the nature of the lamellar morphology (for example, the crosshatched morphology[19,25,26] in isotactic polypropylene) may affect the kinetics of this process in such a way that lamellae do not thicken considerably after their formation. Furthermore, a number of polymers such as PEEK, PPS, PET, nylons, it-PS, and so forth show no sign of a distinct crystalline α-relaxation in the temperature range where their crystallization/melting behavior has been investigated.[24] These materials are therefore not expected to exhibit lamellar thickening under isothermal crystallization conditions. Time-resolved SAXS studies have actually suggested that, for this latter class of materials, the average lamellar thickness does not increase during primary or secondary crystallization but appears to decrease, most likely the result of secondary crystallization.[27−30] In light of the above discussion, it is rather puzzling to note that the linear HW analysis almost invariably yields thickening coefficients between 2 and 3, regardless of the polymer under consideration, its molecular weight, and the existence or absence of a crystalline α-relaxation.

The goals of this paper are then to examine the assumptions involved in the linear HW extrapolation and to investigate the applicability of this method to the determination of the equilibrium melting temperature and thickening coefficient of a given polymer crystal. We first recall the general relationship between observed melting and crystallization temperatures, expected on the basis of the LH theory, and discuss the validity of the various approximations involved in the HW linear extrapolation. We examine the conditions under which the linear extrapolation is expected to provide a reliable estimate of the equilibrium melting temperature and investigate the effect of lamellar thickening and that of the temperature range where experimental data is accessible. We carry out a number of model calculations using different values of the thickening coefficient ($\gamma = 1$ and 2). The case $\gamma = 1$ is elaborated upon to provide insight into the behavior of polymers whose crystals do not exhibit isothermal lamellar thickening or for which the melting temperature of nonthickened crystals can be either recorded experimentally or inferred from experimental data. We consider throughout this manuscript the case of a hypothetical linear polyethylene material of sufficiently high molecular weight that the equilibrium melting temperature is independent of the chain length. The choice of this polymer is dictated by the a priori reliable estimate of its equilibrium melting temperature (upper bound) through the Flory−Vrij or Broadhurst treatments, and by the availability of thermodynamic and crystallographic parameters.[2,23,31] Pertinent molecular characteristics and thermodynamic properties for this material are listed in Table 1.

Hoffman−Weeks Treatment. The HW approach assumes that the initial lamellar thickness, l^*, of a polymer crystal growing under isothermal and quiescent conditions is appropriately described by the LH secondary nucleation theory. It is also assumed that the Gibbs−Thomson equation, in its standard form, provides an accurate estimate of the melting temperature depression associated with the finite thickness of lamellar crystals. This latter assertion has been rigorously verified for polymers in the long-chain length limit.[2,16] We recall that a rigorous use of the Gibbs−Thomson equation requires recording both the melting temperature and the lamellar thickness for the same crystals (minimize reorganization, premelting, or thickening of the crystals during heating or measure the lamellar thickness just before the onset of melting). According to the LH theory, the average initial lamellar thickness observed at the temperature of crystallization, T_x, is given by

$$l^* = \frac{2\sigma_{ex}}{\Delta G_{fx}} + \delta l_x \tag{1}$$

where σ_{ex} and ΔG_{fx} are, respectively, the basal plane crystal/melt interfacial free energy and the bulk free energy of fusion at T_x and δl_x is the thickness increment above the minimum lamellar thickness, which enables the secondary surface nucleus to enter a region of thermodynamic stability at the fastest rate at T_x.[1,2] The importance of δl_x is generally recognized by noting that it prevents a crystal formed at T_x to melt at its own crystallization temperature. In the $\psi = 0$ version of this theory,[2] δl_x is expressed by

$$\delta l_x = \left(\frac{kT_x}{2b_0\sigma_x}\right)\left(\frac{4\sigma_x + a_0\Delta G_{fx}}{2\sigma_x + a_0\Delta G_{fx}}\right) \tag{2}$$

where σ_x is the lateral crystal/melt interfacial free energy at the crystallization temperature, k is the Boltzmann constant, b_0 is the thickness of the secondary nucleus in the direction normal to the growth front, and a_0 is the width of the stem in the direction parallel to the long dimension of the growth plane. It should be noted that eq 1 has been criticized as being invalid for some polymers (such as isotactic polystyrene[32]) at large undercoolings, where apparently the lamellar thickness becomes independent of the crystallization temperature. However, inspection of this earlier experimental study indicates that it is the long spacing and not the actual lamellar thickness which becomes independent of T_x. This criticism is not rigorously warranted for flexible chain polymers with small repeat units, as the LH theory only addresses isothermal growth rates and stem lengths of isolated crystals and cannot provide any information on the thickness of the interlamellar amorphous region, except, however, for low molecular weight polymers, where chain folds and cilia are the only amorphous constituents of these regions.[2] For other polymers, such as polyamides,[33] the maximization of interchain hydrogen-bonded interactions may prevent the lamellar thickness to vary smoothly with the crystallization temperature. Such specific cases need to be recognized but are beyond the focus of this work and will not be discussed here.

The bulk free energy of fusion at the crystallization temperature can be expressed in terms of the undercooling, ($\Delta T = T_m - T_x$), the latent heat of fusion at the equilibrium melting temperature, ΔH_f, and a correction factor, f_x, accounting for the temperature dependence of both the latent heat and entropy of fusion.

$$\Delta G_{\mathrm{fx}} = \frac{f_x \Delta H_{\mathrm{f}}(T_{\mathrm{m}} - T_x)}{T_{\mathrm{m}}} \tag{3}$$

The term f_x can be rigorously determined by carrying out a Taylor series expansion of the Gibbs free energy of fusion around T_{m}.[10-12]

Let us consider a lamellar crystal of thickness l with lateral dimensions X and Y. Setting the free energy of fusion of the finite size crystal at the observed melting temperature, T_{m}', to be zero, we obtain

$$XYl\Delta G_{\mathrm{fm'}} - 2XY\sigma_{\mathrm{em'}} - 2l(X+Y)\sigma_{\mathrm{m'}} = 0 \tag{4}$$

where $\Delta G_{\mathrm{fm'}}$, $\sigma_{\mathrm{em'}}$, and $\sigma_{\mathrm{m'}}$ are the bulk free energy of fusion and the basal and lateral interfacial free energies at the observed melting temperature T_{m}', respectively. Expressing $\Delta G_{\mathrm{fm'}}$ in terms of the melting temperature depression $T_{\mathrm{m}} - T_{\mathrm{m}}'$ in a manner similar to that shown in eq 3 leads to the classical Gibbs–Thomson equation:

$$T_{\mathrm{m}}' = T_{\mathrm{m}}\left(1 - \frac{2\sigma_{\mathrm{em'}}}{l f_{\mathrm{m'}} \Delta H_{\mathrm{f}}}\right) \tag{5}$$

when the conditions $\sigma_{\mathrm{m'}}/X$ and $\sigma_{\mathrm{m'}}/Y \ll \sigma_{\mathrm{em'}}/l$ are satisfied.

Since a number of polymer crystals thicken[34] either isothermally at T_x or upon heating to the melting temperature, the lamellar thickness at the time of melting, l, may be greater than the initial lamellar thickness, l^*. An average thickening coefficient, $\gamma_{x\mathrm{m}}$, is introduced and defined by

$$\gamma_{x\mathrm{m}} = \frac{l}{l^*} \tag{6}$$

It should be noted that $\gamma_{x\mathrm{m}}$ is generally a function of the crystallization temperature, time, and possibly heating conditions up to the melting temperature.[23,34,35]

At this juncture, we can combine eqs 1, 3, 5, and 6 to obtain the general form of the relation between the observed melting temperature and crystallization temperature.[23,36]

$$T_{\mathrm{m}}' = T_{\mathrm{m}}\left[1 - \frac{1}{\gamma_{x\mathrm{m}}}\left(\frac{T_{\mathrm{m}} - T_x}{T_{\mathrm{m}}}\right)\left(\frac{\sigma_{\mathrm{em'}}}{\sigma_{\mathrm{ex}}}\right)\left(\frac{f_x}{f_{\mathrm{m'}}}\right)\left(\frac{1}{1 + \dfrac{\delta l_x \Delta H_{\mathrm{f}} f_x (T_{\mathrm{m}} - T_x)}{2\sigma_{\mathrm{ex}} T_{\mathrm{m}}}}\right)\right] \tag{7}$$

A number of approximations are generally made to render this approach tractable. First, it is assumed that both the ratio of the fold surface free energies and that of the f_{T} terms are close to unity. Under these conditions, the expression relating T_{m}' and T_x becomes

$$T_{\mathrm{m}}' = T_{\mathrm{m}}\left(1 - \frac{\Theta_x}{\gamma_{x\mathrm{m}}}\right) + T_x\frac{\Theta_x}{\gamma_{x\mathrm{m}}} \tag{8}$$

where

$$\Theta_x = \frac{1}{1 + \dfrac{\delta l_x \Delta H_{\mathrm{f}} f_x (T_{\mathrm{m}} - T_x)}{2\sigma_{ex} T_{\mathrm{m}}}} \tag{9}$$

Second, if we consider crystallization processes carried out at low undercoolings, such that the term $\delta l_x \Delta H_{\mathrm{f}} f_x (T_{\mathrm{m}} - T_x)$ is significantly smaller than $2\sigma_{ex}T_{\mathrm{m}}$, then we may neglect the contribution from the δl_x containing term to the melting depression below the equilibrium melting temperature and assume that Θ_x is unity. This consideration, combined with the assumption that the thickening coefficient $\gamma_{x\mathrm{m}}$ is constant, constitutes the various approximations which are at the origin of the classic linear Hoffman–Weeks approach.[13] This approach, therefore, implicitly assumes that T_{m}' is greater than T_x solely due to crystal thickening effects and yields a linear relationship between observed melting and crystallization temperatures:

$$T_{\mathrm{m}}' = T_{\mathrm{m}}^{\mathrm{HW}}\left(1 - \frac{1}{\gamma_{\mathrm{HW}}}\right) + \frac{T_x}{\gamma_{\mathrm{HW}}} \tag{10}$$

where $T_{\mathrm{m}}^{\mathrm{HW}}$ and γ_{HW} are the "equilibrium melting temperature" and the thickening coefficient calculated from the intercept with the equilibrium line and the slope of the T_{m}' versus T_x regression line, respectively. One of the goals of this manuscript is therefore concerned with the determination of the conditions under which $T_{\mathrm{m}}^{\mathrm{HW}} = T_{\mathrm{m}}$ and $\gamma_{\mathrm{HW}} = \gamma$.

It is apparent in the conventional HW treatment that the δl_x term, which is of prime importance when considering the rate of substrate completion,[2] plays no role in relating the melting temperature to the crystallization conditions. On cursory examination, this assumption seems justified in the case of polyethylene and a few additional polymers such as PEO (poly(ethylene oxide)), which display relatively large lamellar thicknesses ($l \gg 100$ Å). Indeed, the δl_x value, calculated from eq 2 to be 13 ± 1 Å for polyethylene in the practical isothermal crystallization range, would make a negligible contribution to l, especially at a low undercooling.

Rather than assuming the initial lamellar thickness to be given by eq 1, a prediction of the LH theory, it appears safer to express l^* by

$$l^* = \frac{C_1}{\Delta T} + C_2 \tag{11}$$

where C_1 and C_2 are constants, obtained experimentally. It has, on one hand, been previously suggested for polyethylene[2,17,31] that the quantity C_1 is approximately equal to $2\sigma_{\mathrm{em}}T_{\mathrm{m}}/\Delta H_{\mathrm{fm}}$. On the other hand, C_2 is found to be ca. 43 Å, which is about 3–4 times larger than the δl_x value calculated from eq 2. The origin of this discrepancy between the magnitude of C_2 and δl_x is discussed below. Since large values of C_2 are also found for other semicrystalline polymers,[37] it would follow that the approximation $C_2 \ll l^*$ is generally unjustified. Furthermore, if we exclude polyethylene and poly(ethylene oxide), which can crystallize fairly rapidly at a low undercooling to yield thick lamellae, most polymers crystallize sufficiently rapidly under isothermal conditions only at fairly large undercoolings. Under these conditions, their lamellar thickness is expected to be much lower than that observed for PEO or even PE (i.e., $l < 100$ Å). Consequently, the above approximation ($C_2 \ll l^*$) will be more inaccurate for these polymers than for PE and PEO.

Another important consequence of the above approximation is that the linear HW treatment, in the conventional form (eq 10), cannot describe the melting of polymer crystals which do not thicken isothermally or upon heating ($\gamma_{xm} = 1$), as this yields the erroneous conclusion that $T_m' = T_x$. This case is discussed in more detail in subsequent papers. If lamellar crystals formed at a crystallization temperature, T_x, melt, and recrystallize into thicker crystals during the heating process, the basic premise of the HW treatment that we can correlate the crystallization temperature to the resulting observed melting temperature is not satisfied and this treatment should not be used without further modification.

A More Rigorous Relationship between Observed Melting and Crystallization Temperatures

We noted in the previous section a discrepancy between the magnitude of C_2 and δl_x. This discrepancy can be qualitatively accounted for on the basis of stem length fluctuations during the chain-folding process. Lauritzen and Passaglia[38] proposed a stem length fluctuation model in which they computed the "kinetic" fold surface energy, σ_{ex}, accounting for the extra lateral surface energy due to fold protrusion and for the mixing entropy associated with stems of different lengths. The kinetic roughening of the fold surface leads to an increase in the basal plane interfacial free energy with increasing undercooling, which is approximated by

$$\sigma_{ex} = \sigma_e^1(1 + y\Delta T) \tag{12}$$

where y is a small positive constant and σ_e^1 is the fold surface free energy estimated from the slope of l^* versus $1/\Delta T$.[1,2] Under these conditions, the undercooling dependence of the initial lamellar thickness can be recast as

$$l^* = \frac{2\sigma_e^1 T_m}{\Delta H_f \Delta T} + \frac{2\sigma_e^1 y T_m}{\Delta H_f} + \delta l_x \tag{13}$$

The sum of the last two terms on the right-hand side of eq 13 can be taken as constant, (i.e., independent of undercooling), which we associate with the term C_2. The constant y has been evaluated[1,2,39−41] from the experimental value of C_2 and the estimate of δl_x defined by eq 2 has been quoted in the range from 0.0025 to 0.05 K^{-1}. We will however not indulge here in such calculations, which we feel are unlikely to shed new light on this problem, as (1) the quantity δl_x given in eq 2 actually depends on the magnitude of ψ,[1] which although thought to be small, is not known accurately and may differ for substrate completion and first-stem deposition processes;[42] (2) the exact temperature dependence of σ_{ex} is unlikely to be rigorously linear.[1,38] In any case, examination of a number of studies lends supports to the applicability of eq 11 and to the need to account for the temperature dependence of the kinetic fold surface free energy. In recent treatments,[1,2] it has been implicitly assumed that the fold surface free energy, σ_e^1 which appears in the term C_1 is approximately equal to that appearing in the Gibbs−Thomson equation. Although one should expect the quantities σ_e^1 and σ_{em} to be slightly different,[38,39] experimental results in the literature are not accurate enough to allow us to differentiate these quantities. The linearity, universally observed in Gibbs−Thomson plots, indeed suggests that σ_{em} can be assumed constant, in agreement with the prediction that the equilibrium roughness of the fold surface is only very weakly temperature-dependent.[38,39] The use of σ_{em} rather than σ_{ex} in the Gibbs−Thomson equation implies that either after the folding process at T_x or during heating to the melting temperature, the fold surface has enough mobility to reach a state of equilibrium roughness. If we nevertheless assume, for the sake of completeness, that the magnitude of σ_e^1 and σ_{em} may differ slightly, a combination of eqs 5, 6, and 11−13 leads to the following relationship between T_m' and T_x:

$$T_m' = T_m\left(1 - \frac{1}{\gamma_{xm}}\left(\frac{T_m - T_x}{T_m}\right)\left(\frac{f_x}{f_{m'}}\right)\left(\frac{\sigma_{em}}{\sigma_e^1}\right)\left(\frac{1}{1 + \frac{C_2\Delta H_f}{2\sigma_e^1}\frac{(T_m - T_x)}{T_m}}\right)\right) \tag{14}$$

We note that eq 14 differs from similar relationships given in the literature in two respects. First, and most significantly, δl_x has been replaced by C_2, which, as will be shown below, renders the approximation $\Theta(T_x) = 1$ very inaccurate. Second, a new term (σ_{em}/σ_e^1) is introduced in the T_m' versus T_x relation, which may or may not be significant, but whose value should be obtained experimentally for a more rigorous estimation of T_m.

When Is the Linear Extrapolation Rigorously Valid?

Focusing on polymer crystals which may exhibit isothermal lamellar thickening and/or lamellar thickening during heating, without melting−recrystallization, we investigate the conditions under which the $C_2 = 0$ approximation is justified. To do so, we calculate the difference between the observed melting temperature predicted by the linear HW equation, eq 10, and that derived from the more general relation (eq 14) and determine the conditions under which this difference is less than some fixed error, ϵ. This procedure allows us to define a range of undercoolings up to which the linear extrapolation is a good approximation of the nonlinear one. As justifed above, we emphasize that, from here on, we describe the undercooling dependence of the initial lamellar thickness using the term C_2 rather than δl_x. Subtracting eq 10 from eq 14 and setting the absolute value of the difference to be less than ϵ leads to

$$\left|\left(\frac{T_m - T_x}{\gamma_{xm}}\right)\left(1 - \frac{1}{1 + \frac{C_2\Delta H_f(T_m - T_x)}{2\sigma_e^1 T_m}}\right)\right| \le \epsilon \tag{15}$$

which, assuming γ_{xm} to be constant and σ_e^1 to be equal to σ_{em}, is recast as

$$a(T_m - T_x)^2 - a\epsilon\gamma_{xm}(T_m - T_x) - \epsilon\gamma_{xm}T_m \le 0 \tag{16}$$

where a is defined as

Table 2. Undercooling ΔT_{max} up to Which the Linear (Equation 10) and the Nonlinear (Equation 14) Expressions of $T_m' = f(T_x)$ Differ by Less Than ϵ for $\gamma_{xm} = 1$ and 2

ϵ (°C)	$\gamma_{xm} = 1$ ΔT_{max} (°C)	$\gamma_{xm} = 2$ ΔT_{max} (°C)
0.1	2.5	3.6
0.5	5.8	8.4
1	8.4	12.1
2	12.1	17.8
5	20.2	30.3

$$a = \frac{C_2 \Delta H_f}{2\sigma_e^1} \qquad (17)$$

The only physically meaningful solution of eq 16 is

$$T_m - T_x \le \frac{\epsilon\gamma_{xm}}{2}\left(1 + \sqrt{1 + \frac{8\sigma_e^1 T_m}{\epsilon\gamma_{xm} C_2 \Delta H_f}}\right) \qquad (18)$$

This derivation implies that for a given set of T_m, σ_e^1, ΔH_f, γ_{xm}, and C_2 values, the observed melting temperature predicted by the HW equation, eq 10, differs by at most ϵ from the melting temperature predicted by the more rigorous approach (eq 14), if the undercooling is less than that given by eq 18. In Table 2, these maximum undercoolings are given for various choices of the thickening coefficient and of the allowable error, ϵ, in the case of polyethylene. The input material parameters for polyethylene are given in Table 1. Considering the results shown in Table 2, it is immediately apparent that the linear extrapolation is only valid at very small undercoolings, where crystallization would not occur on any practical time scale. These calculations also indicate that for a larger but constant thickening coefficient, there is a larger temperature range below the equilibrium melting temperature where the linear extrapolation is accurate. Recalling that, among all known polymers, polyethylene exhibits one of the highest crystallization rates at a given undercooling, one can conclude that other polymers will generally crystallize at a finite rate only at larger undercoolings. Thus, their observed melting temperature will be more significantly depressed below the equilibrium melting temperature than that for the case of polyethylene and systematic deviations between the linear approximation and the nonlinear form of $T_m' = f(T_x)$ will become more significant. This simple calculation therefore indicates that if the linear extrapolation is used, accurate values of the equilibrium melting temperature should not be expected in general.

Practical Consequences of the Linear T_m' vs T_x Extrapolation

To examine the implications of using the linear LH treatment in a temperature range where it is not rigorously applicable, we first generate a set of T_m' versus T_x data using eq 14, assuming a constant thickening coefficient. To generate these data for polyethylene, we make use of the thermodynamic constants listed in Table 1. Theoretical plots of T_m' versus T_x for different values of the thickening coefficient ($\gamma_{xm} = 1$ and 2) are then constructed using eq 14 where, as indicated above, we assume $\sigma_{em} = \sigma_e^1$, take f_T to be unity, and take γ_{xm} to be independent of temperature. The latter approximations are of no consequence here. The results of these calculations are shown in Figure 1, where predicted melting temperatures are plotted as a function of the crystallization temperature for $\gamma_{xm} = 1$ and 2. It is clear that these plots exhibit significant curvature in the hypothetical crystallization temperature range between 100 and 140 °C. Linear extrapolations carried out from different data sets selected over a 10 °C crystallization temperature interval lead to different intercepts with the $T_m' = T_x$ line, the worst case being when the extrapolation is carried out far from the true equilibrium melting temperature and the thickening coefficient is low. We now apply the HW procedure to the T_m' versus T_x generated data for the experimental range of crystallization temperatures that is appropriate for linear polyethylene (i.e., T_x = 120−130 °C). Below 120 °C, isothermal crystallization may not be achieved with bulk samples, as primary nucleation and the growth process could occur during cooling. Above 130 °C, isothermal thickening becomes very significant, leading unavoidably to a nonconstant thickening factor.[23,37] Linear regressions of the predicted melting points in the 120−130 °C crystallization temperature range for the cases $\gamma_{xm} = 1$ and 2 are also shown in Figure 1. Intersection of these linear extrapolations with the $T_m' = T_x$ line leads to apparent equilibrium melting temperatures of 136.9 and 142.9 °C for $\gamma_{xm} = 1$ and 2, respectively. These values are 8.6 and 2.6 °C lower than the Flory−Vrij estimate (T_m = 145.5 °C), which was used to generate the theoretical T_m' versus T_x data.

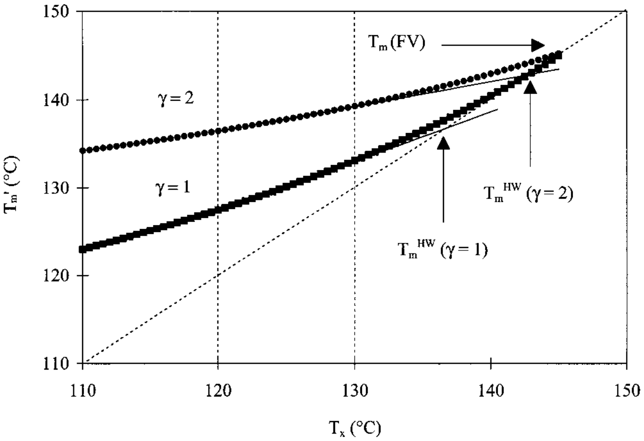

Figure 1. Dependence of observed melting temperature on the crystallization temperature as calculated from eq 14 for $\gamma_{xm} = 1$ (■) and 2 (●). The full lines are the corresponding HW linear regressions and extrapolations from the 120−130 °C crystallization temperature range. T_m (FV) is the equilibrium melting temperature calculated from the Flory−Vrij equation. T_m^{HW} ($\gamma = 1$) and T_m^{HW} ($\gamma = 2$) are the "equilibrium melting temperatures" determined by the linear HW extrapolation for the indicated thickening coefficients.

It is also worth noting that the apparent thickening coefficient, which is calculated from the slope of the HW linear extrapolation, overestimates the value chosen in the calculation of the T_m' versus T_x data. The data generated with $\gamma_{xm} = 1$, when fitted by a straight line in the T_x range from 120 to 130 °C, leads to an apparent thickening coefficient of $\gamma_{HW} = 1.77$. For the data generated with $\gamma_{xm} = 2$, γ_{HW} is equal to 3.54. The results of HW extrapolations carried out over various temperature intervals in the 100−140 °C range are shown in Table 3.

This exercise allows us to draw a number of conclusions. First, the linear extrapolation is not justified on

Table 3. Hoffman−Weeks Analysis of Theoretical T_m' vs T_x Data Generated Using $C_2 = 43.25$ Å, $\sigma_e^1 = 90.4$ mJ/m², $T_m = 145.5$ °C, for $\gamma = 1$ and $\gamma = 2$ (The H−W Linear Extrapolation Is Carried Out Over Different Temperature Ranges from 100 to 140 °C)

	temperature range considered			
	100−110 °C	110−120 °C	120−130 °C	130−140 °C
	$\gamma = 1$			
T_m (HW) (°C)	130.3	133.4	136.9	141.1
γ_{HW}	2.74	2.23	1.77	1.36
	$\gamma = 2$			
T_m (HW) (°C)	139.6	141.2	142.9	144.6
γ_{HW}	5.48	4.46	3.54	2.73

theoretical grounds, as it is shown to hold only at exceedingly low undercoolings, which are not experimentally accessible. Second, the linear extrapolation leads to an underestimation of the equilibrium melting temperature and an overestimation of the thickening coefficient. The extent of this underestimation decreases as the thickening coefficient increases, but could become extremely significant if the range of undercoolings, over which the linear extrapolation is carried out, is far removed from the equilibrium melting temperature. We assert that the principal reason for the inaccuracy of the HW procedure lies in the neglect of the C_2 contribution to the difference between observed melting and crystallization temperatures. It is noted that the linear extrapolation does not appear to lead to a large error in the case of PE, since this polymer crystallizes at relatively low undercoolings. However, the constant thickening coefficient assumption made here in the analysis of $T_m' - T_x$ is not appropriate, as was clearly pointed by Alamo et al.[23] These authors clearly showed that, as a result of the temperature dependence of the lamellar thickening coefficient, it is actually very difficult to define rigorously a temperature region over which to carry out the extrapolation. These authors furthermore demonstrated that linear extrapolations lead to different “equilibrium melting temperatures” when carried out with a series of samples exhibiting different degrees of crystallinity. Similar results were obtained by Hoffman and Weeks for poly(chlorotrifluoroethylene).[13] The origin of such discrepancies can now be understood as arising from (1) the fact that linear extrapolations are not justifiable even for samples crystallized at different temperatures but exhibiting the same lamellar thickening coefficient and (2) isothermal crystallization at different temperatures to the same level of crystallinity invariably leads to systematic variations in the lamellar thickening coefficient.

The above exercise also suggests that one should anticipate even larger errors for slower “crystallizers”, such as isotactic poly(propylene) (it-PP), where the practical range of crystallization temperatures is further removed from the equilibrium melting temperature, and where, consequently, the average lamellar thicknesses are smaller than those for PE. The case of it-PP is discussed in detail in the second paper of this series.[43] Finally, polymers such as it-PS, PEEK, and PPS, whose crystals do not exhibit any isothermal lamellar thickening, deserve particular attention, as in this case, the difference between observed melting and crystallization temperatures cannot be accounted for by the magnitude of γ_{xm}, since it must be unity. If the use of the LH theory is still justified for these semiflexible chain polymers, and if melting−recrystallization−remelting effects can be ignored, one would have to face the fact that the simple application of the HW procedure would lead to a very significant underestimation of their equilibrium melting temperature (tens of degrees). For these materials, the assumption that the melting temperature depression is only associated with the thickness of the crystals and not with their width (Gibbs−Thomson equation) may not even be valid, except possibly at the highest crystallization temperatures. This specific issue will be the subject of the third paper of this series.

New Data Analysis of Experimental $T_m' - T_x$ Data

We now consider another method for the analysis of experimental T_m' versus T_x data. Defining the quantities M and X (scaled melting and crystallization temperatures) by $M = T_m/(T_m - T_m')$ and $X = T_m/(T_m - T_x)$, respectively, and using the definition of the term a given in eq 17, we can rearrange eq 14 as

$$M = \gamma_{xm}\frac{\sigma_e^1}{\sigma_{em}}(X + a) \tag{19}$$

This simple equation seems to provide a means to assess whether the thickening coefficient, γ_{xm} , is constant or not. On the basis of linearity of a M versus X plot, one may be tempted to conclude that the quantities γ_{xm} and a are independent of temperature and can be obtained in a straightforward manner from the slope and intercept. In principle, this procedure provides access to the quantity C_2, if σ_e^1, σ_{em}, and ΔH_f are known from independent measurements (in the absence of l^* versus ΔT data, we noted earlier that $\sigma_e^1 = \sigma_{em}$ may be a good approximation). Conversely, for a polymer crystal of unknown T_m, if the magnitude of γ_{xm} can be determined experimentally (e.g., SAXS, LAM Raman), then varying the equilibrium melting temperature until the correct value of γ_{xm} is obtained would enable the determination of the equilibrium melting temperature. It is important to note that an observed nonlinearity in a M versus X plot can arise for a variety of reasons, such as a significant but unrecognized temperature dependence of γ_{xm} or simply an inadequate choice of T_m. It should be recalled, in contrast, that the linearity in a T_m' versus T_x plot is not expected on theoretical grounds, nor should its observation prove γ_{xm} to be constant. Let us consider again the T_m' versus T_x data (shown in Figure 1), where we chose γ_{xm} to be either 1 or 2. Recalling that T_m' was calculated using the Flory−Vrij estimate of T_m (145.5 °C), we can plot M versus X for different choices of T_m and attempt to infer from the linearity of these plots whether the appropriate value of T_m was selected. Such plots are shown in Figure 2a,b for T_m values of 138, 145.5, and 150 °C for the cases $\gamma_{xm} = 1$ and 2, respectively.

For the case $\gamma_{xm} = 2$, it is clear that, except when the correct equilibrium melting temperature is used, the plots M versus X are no longer linear and the apparent slopes differ from the initially chosen γ_{xm} values.

In the case $\gamma_{xm} = 1$, these theoretical plots exhibit only minor curvature. This curvature would most likely not be observed due to data scatter, if experimental, instead of theoretical, values of the observed melting temperature were used. In this case, the artificial observation of linearity in the M X plot cannot guarantee that the

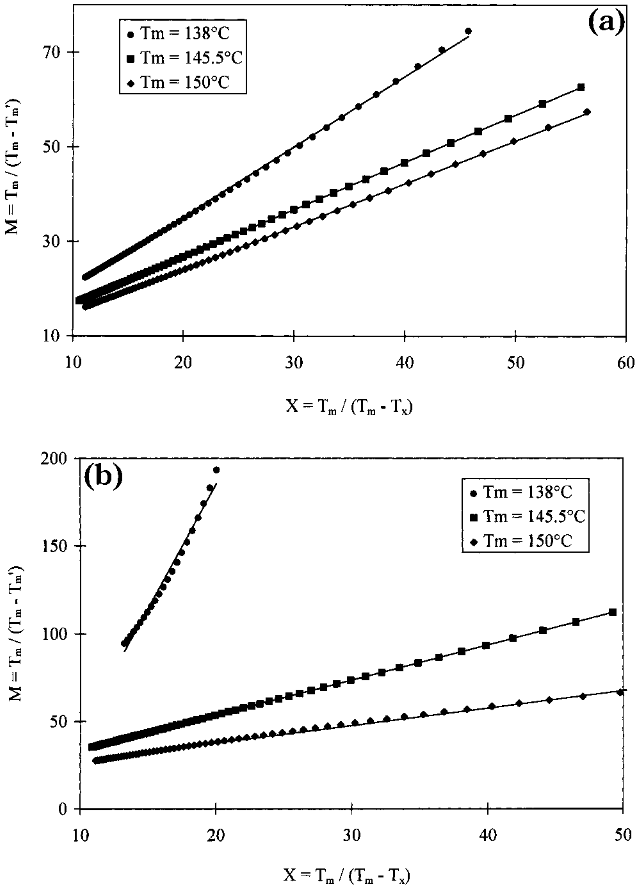

Figure 2. M vs X plot assuming $T_m = 138$ (●), 145.5 (■), or 150 °C (◆). T_m' was calculated for each T_x using thermodynamic data in Table 1. Regression lines are shown to highlight the departure from linearity when T_m differs from the Flory–Vrij value used to calculate T_m' for each T_x. M and X were calculated using the above values of T_m. (a) $\gamma_{xm} = 1$; (b) $\gamma_{xm} = 2$.

correct equilibrium melting temperature was used. Recalling that the curvature in a M versus X plot increases with the magnitude of the thickening coefficient, we can state that an equilibrium melting temperature determination will be most accurate for crystals that exhibit large but constant thickening coefficients! This result is obviously discouraging as it is difficult, if not impossible, to crystallize samples at different temperatures with a priori the same lamellar thickening coefficient. Historical considerations of the widespread use of the HW approach lead us to believe that one might be tempted to apply "blindly" the M versus X procedure to determine the equilibrium melting temperature for any polymer. We therefore want to impress on the reader that scatter in the data and slight but unrecognized variations of γ_{xm} with temperature may prevent the optimum equilibrium melting temperature to be determined by this simple procedure, unless further assumptions are made, as will be discussed below.

Practical Use and Limitations of the *M*−*X* Method

Having noted in the previous section that the temperature dependence of the lamellar thickening coefficient prevents an accurate determination of the equilibrium melting temperature through an optimization of an M versus X regression, we consider the case where the thickening coefficient is assumed to be constant and a priori known and where the experimental data exhibit a certain amount of random scatter. This is equivalent to treating the case where polymer crystals formed at different temperatures exhibit slight and random variations in the thickening coefficient about a known average. We first generate a set of theoretical T_x, T_m' data points in the T_x range from 120 to 130 °C using the thermodynamic input parameters in Table 1 and an a priori thickening coefficient γ. We then impart a certain amount of random scatter to the various T_m' values (maximum scatter was ± 0.3 °C, which is considered an absolute upper bound rarely encountered by a careful experimentalist). Since we attempt to deal with practical situations, we only consider the analysis of a rather small number of data points. However, we "chose" the random scatter in such a way that the sum of the deviations between theoretical observed melting temperatures, T_m', and scattered observed melting temperatures, $T_{m\ scatt}'$, is small (ca. 0.03 °C). We then assume an equilibrium melting temperature T_m and calculate for this choice of T_m the magnitude of X and M associated with each T_x and $T_{m\ scatt}'$. A linear regression of the M versus X generated data allows us to derive values of a_{fit} and γ_{fit}. From these two values, we can calculate the fitted values of M, denoted M_{fit}, and the fitted observed melting temperature, $T_{m.fit}'$. The sum of the squares of the deviations between the fitted observed melting temperatures and the scattered observed melting temperatures is then calculated and denoted by the quantity S^2. The process is repeated for different choices of the equilibrium melting temperature. These calculations are carried out for a number of initial sets of scattered observed melting temperatures. Typical results are shown in Figures 3 and 4 for the case $\gamma = 1$ and in Figures 5 and 6 for the case $\gamma = 2$. Focusing first on Figure 3, we note that the equilibrium melting temperature estimated from the first minimum in the variance S^2 for $\gamma = 1$ is 138.1 °C, which is significantly lower than the expected value of 145.5 °C. Furthermore, if this value of 138.1 °C is chosen for

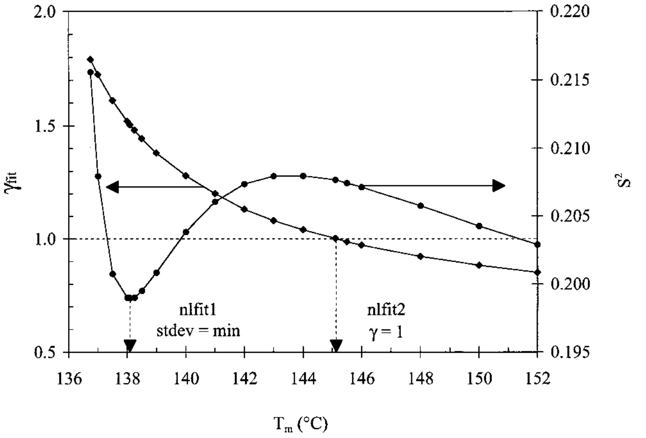

Figure 3. Dependence of the thickening coeffficient, γ_{fit}, and of the variance, S^2, on the choice of the equilibrium melting temperature, T_m, used to generate the M vs X plot. γ_{fit} is the slope of the M vs X plot and S^2 is the sum of the squares of the deviations between the observed melting temperatures ($T_{m.scatt}'$) and the fitted observed melting temperatures ($T_{m.fit}'$). $T_{m.scatt}'$ values are obtained by adding a random scatter of maximum amplitude equal to ±0.3 °C to the theoretical observed melting temperature calculated using eq 14, input parameters in Table 1 and $\gamma = 1$. $T_{m.fit}'$ values are calculated from the linear regression of M vs X data for a given choice of T_m.

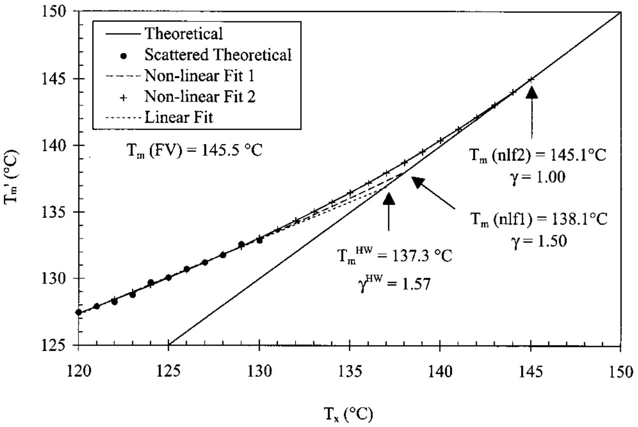

Figure 4. Variation of T_m' with T_x: theoretical (eq 14, full curve). Scattered theoretical in the 120−130 °C temperature range (●). Nonlinear fit 1 (T_m defined by the minimum of S^2, long dashed curve). Nonlinear fit 2 (T_m defined by $\gamma = 1$, +). HW linear regression and extrapolation (eq 10, short dashed line). Case $\gamma = 1$.

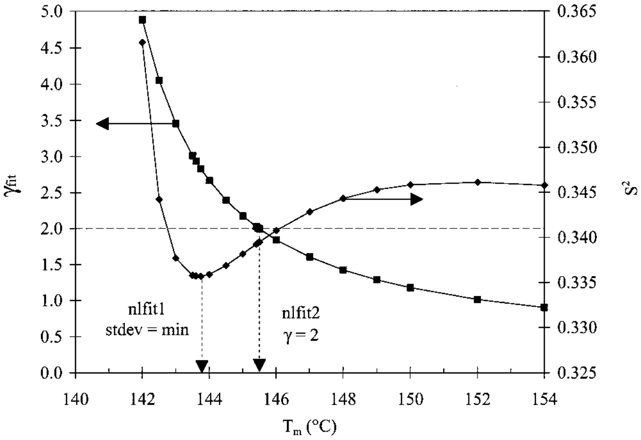

Figure 5. Dependence of the thickening coeffficient, γ_{fit}, and of the variance, S^2, on the choice of the equilibrium melting temperature, T_m, used to generate the M vs X plot. γ_{fit} is the slope of the M vs X plot and S^2 is the sum of the squares of the deviations between the observed melting temperatures ($T_{m.scatt}'$) and the fitted observed melting temperatures ($T_{m.fit}'$). $T_{m.scatt}'$ values are obtained by adding a random scatter of maximum amplitude equal to ±0.3 °C to the theoretical observed melting temperature calculated using eq 14, input parameters in Table 1, and $\gamma = 2$. $T_{m.fit}'$ values are calculated from the linear regression of M vs X data for a given choice of T_m.

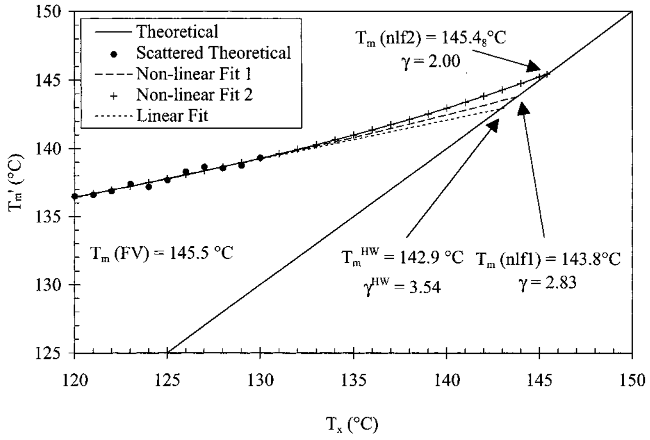

Figure 6. Variation of T_m' with T_x: theoretical (eq 14, full curve), Scattered theoretical in the 120−130 °C temperature range (●). Nonlinear fit 1 (T_m defined by the minimum of S^2, long dashed curve). Nonlinear fit 2 (T_m defined by $\gamma = 2$, +). HW linear regression and extrapolation (eq 10, short dashed line). Case $\gamma = 2$.

the equilibrium melting temperature of polyethylene, the thickening coefficient derived from this analysis is estimated to be $\gamma_{fit} = 1.5$ as opposed to the expected value of 1.0. Similarly, the C_2 value inferred from the quantitiy a_{fit} is estimated to be 17.6 Å instead of the expected 43.3 Å. If, on the other hand, we assume a priori knowledge of the thickening coefficient (in this case $\gamma = \gamma_{fit} = 1$), we infer from the plot shown in Figure 3 that the equilibrium melting temperature is 145.1 °C, which is an acceptable estimate of the theoretical equilibrium melting temperature (145.5 °C). Under these conditions, the C_2 value inferred from the quantity a_{fit} is estimated to be 44.8 Å instead of the expected 43.3 Å. On Figure 4, we show the theoretical variation of T_m' with T_x, the variation of $T_{m.scatt}'$ with T_x, the linear HW extrapolation of the scattered data, and the nonlinear extrapolations of $T_{m.scatt}'$ versus T_x for cases where T_m is chosen as 138.1 °C (nlf1) or where γ is chosen as 1.0 (nlf2). Note that the nonlinear fit nlf2 ($\gamma = 1.0$) cannot be discerned from the theoretical data and that the HW linear extrapolation significantly underestimates the equilibrium melting temperature and overestimates the thickening coefficient. Similar results are obtained for the case where we initially calculate T_m' from T_x for $\gamma = 2$. Minimization of the variance through changes of T_m leads to a more accurate estimation of the equilibrium melting temperature in the case $\gamma = 2$ than for $\gamma = 1$ ($T_m = 143.8$ °C for $\gamma = 2$ nlfit1 in Figure 5). Again, assuming a priori knowledge that $\gamma = 2$ leads to a further increase in the accuracy of the estimation of the equilibrium melting temperature ($T_m = 144.48$ °C for nlfit2 in Figure 5). In this case, C_2 is estimated to be 43.2 Å. In Figure 6, we show the theoretical variation of T_m' with T_x, the variation of $T_{m.scatt}'$ with T_x, the HW linear extrapolation of the scattered data, and the nonlinear extrapolations of $T_{m.scatt}'$ versus T_x for cases where T_m is chosen as 143.8 °C (nlf1) or where γ is chosen as 2.0 (nlf2). Note again that the nonlinear fit nlf2 ($\gamma = 2.0$) cannot be discerned from the theoretical data and that the HW linear extrapolation underestimates the equilibrium melting temperature and overestimates the thickening coefficient. These results allow us to conclude that the M versus X approach can only provide an accurate estimation of the equilibrium melting temperature in two situations: (1) when the thickening coefficient is constant and much larger than unity, in which case an a priori knowledge of the thickening constant is not required and an acceptable estimate (within a few degrees) of the equilibrium melting temperature can be obtained by minimizing the variance of the fit (see above) and (2) when the thickening coefficient is known to be unity and the equilibrium melting temperature is determined using the constraint $\gamma = 1$. It is worth pointing out that the latter method appears to be significantly more accurate. We will show in the following paper[43] that the melting temperature of unthickened lamellar crystals ($\gamma = 1$) can indeed be inferred, at least for it-PP, by extrapolation of the melting behavior of samples isothermally crystallized for different times.

In connection with the former method, it is noted that when γ is constant, two minima are generally observed in plots of the variance versus the equilibrium melting temperature (a hint for the existence of a second minimum at higher T_m values is apparent upon examination of Figures 3 and 5). This should be expected on the basis of the relationship between T_m' and T_x. Using eq 14 and assuming $\sigma_{em} = \sigma_e^1$, we can express the quantity $T_m' - T_x$ as a function of T_x.

$$T_m' - T_x = (T_m - T_x) - \left(\frac{T_m}{\gamma}\right)\left(\frac{T_m - T_x}{T_m + a(T_m - T_x)}\right) \quad (20)$$

The function $T_m' - T_x = f(T_x) = 0$ has two roots, T_m and $T_m(1 + (1/a)(1 - 1/\gamma))$. At each of these values, the theoretical $T_m' = f(T_x)$ curve crosses the $T_m' = T_x$ line. Obviously, the equilibrium melting temperature should correspond to the smaller of these two solutions since the quantity a must be positive and γ must be larger or equal to unity. Note that for $\gamma = 1$, the two roots are equal to each other and the theoretical $T_m' = f(T_x)$ curve is tangential to the $T_m' = T_x$ line at the equilibrium melting temperature. It is therefore important when using the above M versus X approach for large and constant γ to ensure that the nonlinear regression analysis only yields the melting temperature associated with the first minimum of the variance versus the temperature plot. Cases can be encountered where the lowest value of the standard deviation is obtained for the highest (unphysical) root.

Conclusions

We have shown through an examination of the various assumptions inherent to the Hoffman–Weeks linear extrapolation that the increase in the melting temperature with the crystallization temperature cannot be solely attributed to the existence of lamellar thickening during crystallization or upon heating to the melting temperature. A significant contribution to the difference between melting and crystallization temperatures arises from the C_2 term which, in the LP secondary nucleation theory, accounts for both the temperature dependence of the fold surface free energy and the thickness increment δl above the minimum (thermodynamic) lamellar thickness. When the value chosen for C_2 for polyethylene is appropriately taken from experimental LAM or SAXS data ($C_2 = 43.3$ Å), it makes a significant contribution to the elevation of the melting temperature above the crystallization temperature. The contribution of the term C_2 leads to a nonlinear relationship between the observed melting temperature and crystallization temperature. Not accounting for this term (HW approach) leads to an underestimation of the equilibrium melting temperature and overestimation of the thickening coefficient. The inaccuracy of the HW extrapolation was shown to worsen for polymer crystals which do not thicken and have a relatively large value of C_2 and when it is carried out far from the true equilibrium melting temperature. The experimental observation of a linear $T_m' = f(T_x)$ behavior is shown to be inconsistent with a constant thickening coefficient. Finally, a new method is proposed for a more accurate estimation of equilibrium melting temperatures. This method should only be used to analyze $T_m' = f(T_x)$ data, when T_m' values refer to real or hypotethical lamellar crystals exhibiting a temperature-independent lamellar thickening coefficient. It is important to note that this new approach relies on a specific relationship between the initial lamellar thickness and undercooling. This method is applied in the following paper of this series to the case of isotactic polypropylene, where it is shown that the use of the linear HW extrapolation leads to an underestimation of the equilibrium melting temperature by as much as 25–30 °C. The nonlinear M versus X approach, when applied to the melting of unthickened crystals ($\gamma = 1$), yields an estimate of the equilibrium melting temperature which is consistent with that obtained from the analysis of the temperature dependence of spherulitic growth rate data.[43,44]

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