

## Frank and Seto model revisited and a comment about a recent paper by Hoffman and Miller (*Polymer*, 1997, 38, 3151)

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### Introduction

In a recent review article Hoffman and Miller (HM)<sup>1</sup> rework the kinetic theory of polymer crystal growth and reactivate its controversy in its application to polymer physics<sup>2</sup>. In this note we first establish (in a new and precise manner) important equations and inequalities related to the Frank and Seto model (FS).<sup>3</sup> Following this we discuss two paradigms of regime theory and show, through careful use of these equations and inequalities, that a two-step analysis rules out previous accepted interpretations assigned to curves giving the thermal dependence of crystal growth rate. Lastly, we offer other interpretations to some of the peculiarities observed in growth rate curves chiefly in systems like polyethylene, poly(ethylene oxide) and poly(pivalolactone). The HM theory is invalid. Our alternative views explain the origin of chain-folding<sup>4</sup> and breaks in growth rate curves<sup>5</sup>.

### Part 1

For sake of brevity, we have used the same symbols and definitions as HM<sup>1</sup>. Let us consider the growth of 2-dimensional crystals by secondary nucleation. According to (FS)<sup>3</sup> nuclei are initiated at a rate of  $i$  on a substrate of length  $L$  that spread laterally at a rate  $g$ . For certain values of  $i$  and  $g$  (see below) the interior of the crystal is composed of strips of thickness  $b$  of mean width  $L_k$  each formed from a single nucleation event. This model was applied to polymer crystallization (*Figure 1*). If  $a$ ,  $b$  and  $l$  are the width, thickness and length of a stem the volume of a developing crystal over a time interval  $\Delta t$  is equal to:

$$V = lLG\Delta t \quad (1)$$

$lL$  is the area of the growing facet and  $G$  its rate of advance.

$$V = 2(L/L_k)(bl)(g\Delta t) \quad (2)$$

$L/L_k$  is the mean number of simultaneous growing nuclei,  $bl$  the area of each of their two lateral facets and  $g$  their rate of advance.

$$V = (blL_k)(iL\Delta t) \quad (3)$$

$iL\Delta t$  is the intervening number of nucleation events and  $blL_k$  the volume of each generated nucleus or strip.

Dividing equation (3) by equation (2) leads to

$$L_k = (2g/i)^{1/2} \quad (4)$$

Dividing (2) by (1) and replacing  $L_k$  by equation (4) leads to the following expression for crystal growth

$$G = b(2gi)^{1/2} \dots \quad (5)$$

These equations were previously obtained by solving differential equations and/or a Klein–Gordon equation<sup>2,6</sup>. In this particular instance they were obtained here by us (and this is a partial justification for writing this note) in a much simpler way without using sophisticated mathematics or physics.

### Part 2

These equations say nothing about the thermal dependence of  $G$ . However, according to HM<sup>1</sup>,  $g$  and  $i$  are proportional to a retardation factor  $\beta$  and  $i$  is proportional to the  $\exp(-4b\sigma\sigma_e/\Delta GkT)$  a thermodynamic property related to the free energy barrier associated with the attachment of the first stem of a nucleus (see *Figure 2* and its legend). Ramifications of equation (5) explain the occurrence of the middle straight segment AB in the classical representation of the thermal dependence on crystal growth rate (shown in *Figure 2* for the case of isotactic polypropylene<sup>7</sup>). If the standard theory of polymer crystallization could accurately describe physical processes then measurement of polymer crystal growth rate would undoubtedly be at best of tremendous benefit. Estimations of numerous physical parameters like  $L_k, \sigma, \sigma_e, \sigma_d, \dots$  could then be afforded with credibility. Further details and examples can be found in the latest offering by HM<sup>1</sup>. The controversy which is central to this communication goes back many years now. The main points which need reiterating are discussed as follows: The considerations given in Part 1 are only valid if  $L_k \gg a$  and  $L_k \ll L$  because  $a$  is the width of a stem and  $L_k$  must accommodate several nuclei. These inequalities explain why in *Figure 2* the segment AB is limited in size and magnitude by points A and B which denote growth at intersection point A as:

$$L_k \approx a \quad (6)$$

and at intersection point B as:

$$L_k \approx L \quad (7)$$

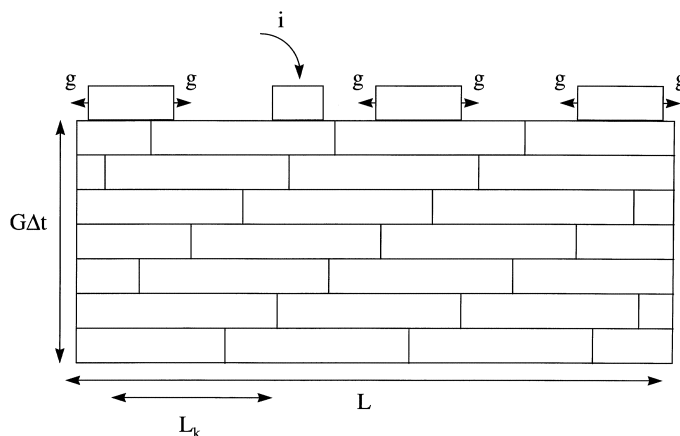
respectively.

By denoting subscript A and B to designate corresponding values of the various involved physical parameters while taking into account that  $g_A/\beta_A > g_B/\beta_B$  we arrive from equations (5) and (7) a very useful inequality

$$L/a < (G_A/\beta_A)/(G_B/\beta_B) \quad (8)$$

Returning to *Figure 2* and to segment AB, it is noted that

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**Figure 1** Frank and Seto model as applied to polymer crystallization. It is analysed here for simple geometric considerations

according to HM<sup>1</sup> theory, the value of this slope (a measure of surface free energy) is limited in range by intersection points A and B. This figure shows that numerical values to the right of inequality (8) are less than 10, unacceptably small to be of any importance. For polyethylene HM proposed a value larger than 100.

This inconsistency derives from the analysis of the experimental data, in particular from expressions  $\beta$  and  $i$  given in Hoffman–Lauritzen (HL) theory (see Ref. 1 for cited works). Note that we have not analysed parts CA and BD of *Figure 2* since it is unnecessary as parts of the curve were constructed from erroneous expressions for  $\beta$ . The reader may find in Ref. [8] of Ref. 1 a list of experimental data that when analysed in the same way yield similar conclusions.

### Part 3

The origin of the artefact which misleads supporters of the HM theory and its application to real polymer systems is clearly seen in the analysis of the experimental data of Phillips *et al.* on *cis*-poly(isoprene).<sup>9</sup> Over the temperature range investigated, Phillips' raw crystal growth rate data suggested neither the correct trend for the thermal dependence of  $\beta$  (it increases as temperature increases) nor the opposite trend for the thermal dependence of  $i$ . Assuming that the variation of one factor compensates more or less that of the other, achieved by dividing  $G$  by  $\beta$ , Phillips has claimed in a recent review<sup>10</sup> that the plot of  $\log G/\beta$  versus  $1/T\Delta T f$  is a paradigm of regime theory. Furthermore, various quantities of  $\beta$  were explored by the authors selecting those values which produced a closer agreement with regime theory. No comment was offered at the time on the much smaller value of  $L/a$ , (as in the case of isotactic polypropylene<sup>7</sup>) a key element in establishing regime transitions.

On the other hand, in the case of polyethylene (the main subject of Ref. [6] of Ref. 1) HM have proposed a value for the effective substrate length of 87.5 nm, correct to within a factor of 1.5. This value is neither too low nor too high. Nevertheless, HL theory cannot be applied to this polymer because from data on low molecular weight fractions, HM derive inconsistent values<sup>11</sup> for  $\sigma_e$ <sup>12</sup> (given in Table 4 of Ref. 1).

### Conclusions

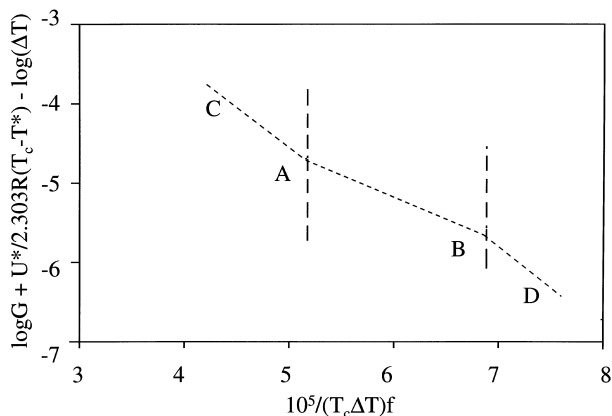
In the 1960s it was assumed by Hoffman and others that

the limiting factor in the kinetics of polymer crystal growth was a free energy barrier and that surface nucleation was dependent upon this barrier. This barrier would later become associated to a "lateral surface free energy of an isolated stem of length  $l$  and thickness  $b$ " (see Fig. 2 of HM<sup>1</sup>). The value of this barrier is a rapid increasing function of  $l$  where crystal thickness is calculated to be nearly equal to its lower thermodynamic limit. This would appear to have been the origin of chain folding and subsequent crystallization, the source of near zero entropy production. Along similar lines regime theory was born. In later years further interest in this model was sparked by controversies on the molecular trajectories in a crystal, a problem raised by Flory and others.

In this note however, we have shown that HL theory does not apply to any actual linear polymer system. Unfortunate as this appears even the most basic concepts of this theory; (i) rate of crystallization limited by a large free energy barrier, and (ii) regime transitions are all invalid. Our group has offered alternative explanations for chain folding and breaks in growth rate curves giving the thermal dependence of the rate of crystallization of polymers<sup>3,4</sup>.

### Summary

We have endeavoured to establish in a novel manner justification for inequality (8). When discussing the numerous papers that refer to HL and the revised updates of HM theory we propose that enthusiasts of regime theory proceed by following two basic steps. The first asks whether the estimated value of  $L/a$  falls within a sensible range. As shown here, this step involves neither sophisticated mathematics nor complicated physics. Reasoning is achieved by use of simple laws based on primitive models. As shown by HM<sup>1</sup>, this is not the case for the second step (concerning the thermal dependence of  $G$ ). This step also involves assumptions noteworthy of debate, see pp. 3166, 3201, ... of Ref. 1. Somewhat fortuitous if unacceptable are the values of  $L/a$  obtained in step one and avoided altogether in step two. The interested reader may wish to consult Ref. 4 for further details. Trying to understand the underlying physical transformations that give rise to the breaks sometimes observed in the curves giving the thermal dependence of  $G$  is regarded as a way forward to advancing the science in this area. Our group have made definite advances in this area, particularly in the case of polyethylene<sup>5</sup> (the polymer more specifically



**Figure 2** A plot of  $\log G + U^*/2.303R(T_c - T^*) - \log(\Delta T)$  versus  $1/[T(\Delta T)f]$  for an isotactic polypropylene fraction of molecular mass 15,000; data and analysis from Ref. 7. The factor  $f$  equal to  $2T_c/(T_c + T_m^0)$  is used to take into account the thermal dependence of the entropy of fusion. The factor  $1/\Delta T$  is introduced to take into account the length of a stem (and thus its lateral surface) and is assumed to be approximately proportional to the inverse of supercooling. The introduction of the additive term  $U^*/2.303R(T_c - T^*)$  along the ordinate is a compensating factor used to express the effect of a WLF term  $\beta$ . In HL theory this factor express the reduced mobility of molecules when temperature is decreased.  $\beta$  allows as shown by Phillips to modify (even change sign) the slope of the growth rate curve. By prodigious selection of input values for  $U^*$  and  $T^*$  the ratios of the slopes of segments AC, AB and BC can be adjusted to achieve coherence with predictions from HL theory. In the present case when the slopes of the segments are adapted to fit theory the difference between the ordinates of A and B is less than 1. This implies as described in the text that the ratio of the length of the substrate to the width of a stem is less than 10. On such a substrate it would be impossible to accommodate several nuclei. If we ignore this obvious conclusion we would have to ask whether the slopes of segments AC and BD allows one to calculate a nucleation barrier. It is not easy to accept such an idea from the pictorial description given in Figure 2 of Ref. 1 for regime 1 growth. Matters are complicated further in the pictorial representations given for regimes II and III where analytical expressions for the nucleation barrier is the same as in regime I

considered in the work of Hoffman and Miller<sup>1</sup>) and polyethylene oxide<sup>13,14</sup> also discussed in Ref. 1. In a forthcoming paper we will discuss the case of poly (pivalolactone).

#### References

- Hoffman, J. D. and Miller, R. L., *Polymer*, 1997, **28**, 3151.
- See Refs. [89–91,123,158] in Ref. 1; note that in the paper of Hoffman and Miller<sup>1</sup> the papers of our group [89,90,123,158] are cited and said to be erroneous. The *raison d'être* of this communication.
- Refs. [84,87] of Ref. 1
- Point, J.-J., *Macromolecules*, 1979, **12**, 770.
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- Ref. [123] of Ref. 1
- Cheng, S. Z. D., Janimak, J. J., Zhang, A. and Cheng, H. N., *Macromolecules*, 1990, **23**, 298.
- Ref [89,91,158] of Ref 1.
- Ref. [153] of Ref. 1
- Ref. [80] of Ref. 1
- This value differs from  $1 \mu\text{m}$  (Lauritzen) and from “20 to 50 nm” (a previous estimate from HM theory, see Ref.<sup>12</sup>). Note also that the existence of this hypothetical length is not evidenced by any morphological observation. The value of 87.5 nm is not discussed because this estimate relies on the here contested theory and an extrapolation of uncertain and to our knowledge never duplicated results (they are not measured values) of the growth rate of PE crystals at 90 and 100°C (see Fig. 13 of HM<sup>1</sup>)
- According to HM theory the dependence of calculated values of  $\sigma_c$  is related to quantised chain folding in PE fractions: “In a crystal of homodisperse PE molecules the number of folds per molecule is fixed. For lamellae of constant thickness which consequently changes in a discrete manner (from  $\nu$  to  $\nu + 1$ ) with molecular weight. Therefore, the length of cilium or more specifically the nature of the fold surface and its specific free energy depend upon molecular weight in a more or less periodic manner; this would account for the observed variations in the slope of the growth rate curves.” In PE lamellae of definite thickness the number of folds in a molecular fraction depends on its individual length. If no segregation occurs the distribution of molecules according to the number of folds is easily calculated and does not change significantly if the mean molecular weight is modified by, let us say one to two thousand. The observed changes in  $K_g$  are thus in total contradiction with the predictions of HL theory. The issue of this contentious value  $K_g$  is re-addressed in a forthcoming paper
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