A Model for Flow-enhanced Nucleation Based on Fibrillar Dormant Precursors

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A model for flow-enhanced nucleation is presented based on the concept of a polymer melt containing a fixed number of nucleation precursors with a fixed size distribution. Depending on the size, precursors can either be active (i.e. susceptible to nucleation, the characteristic time scale of which is governed by the deformation rate) and grow into a spherulite or remain dormant. The size distribution of precursors is derived by combining nucleation theory and experimentally determined quiescent spherulite number densities. Longitudinal precursor growth, causing activation of dormant precursors, is a function of molecular deformation: the stretch of high molecular weight chains. Both the eXtended Pom-Pom and the Rolie-Poly model are tested to calculate the molecular deformation. A quantitative agreement is found between simulations and experimental results.

Introduction

The mechanical properties of polymer products strongly depend on processing conditions since these determine, to a great extent, the structure. For semi-crystalline polymers, flow-induced crystallization (FIC) plays a major role in this. Crystallization of polymers can be divided into three regimes;

(i) Quiescent crystallization, if no flow is applied or the flow is too weak to have a significant influence on the crystallization process. Spherulitic crystalline structures (spherulites) are formed.
(ii) Flow-enhanced nucleation (FEN) occurs if the flow is sufficiently strong (sufficiently high deformation rate and time) to influence the nucleation kinetics. The number density of spherulites is increased.
(iii) Oriented precursor structures are formed if a flow that is sufficiently strong is applied for a longer period of time. As a result, oriented crystalline structures, such as shish-kebabs, are formed.

Different approaches are used to model FIC. Some researchers start with the classical result for homogeneous nucleation known as the Hoffman/Lauritzen expression.\(^1,2\) It contains the free energy as a driving force of which the entropic part is adapted by including the decrease due to the molecular orientation caused by the flow. A model using this approach was derived by Ziabicki and Alfonso, but the entropy change due to orientation alone could not reproduce effects as dramatic as observed in experiments.\(^3\) A second approach starts from the statistical description of the evolution of the precursor size distribution in the melt\(^4\) and, again, incorporates the effect of flow by adapting the free energy. For a model that
incorporates anisotropic precursors with multiple fluctuating dimensions this leads to a rather cumbersome set of equations, containing a number of undetermined parameters (see Appendix D). On the level of the precursors, a Monte-Carlo approach was used by Graham et al. leading to insight on the relation between segmental orientation and the nucleation process and providing support for modeling on a continuum level. However, this approach is not useful on the level of process modeling, which is the final goal of this work. Based on experimental observations Eder and Janeschitz-Kriegl proposed a set of differential equations,\(^\text{[7]}\) analogous to the Schneider rate equations\(^\text{[8]}\) for (heterogeneous) point nucleation and subsequent spherulitical growth, that captured the observed correlations between crystalline structure measures (number and size of shish) and the applied flow. Shear rate was used as the driving force for flow enhanced nucleation and subsequent shish growth. This set of equations was the starting point for Zuidema et al. who replaced the shear rate with a measure that combines the molecular orientation and stretch of the high molecular weight (HMW) tail\(^\text{[9,10]}\) in line with experimental evidence from, among others, Vleeshouwers and Meijer.\(^\text{[11]}\) With this approach they were successful in capturing the vast amount of experimental observations from the group of Janeschitz-Kriegl. This approach was extended and studied further by Custódio et al.\(^\text{[12,13]}\) and Steenbakkers and Peters.\(^\text{[14,15]}\) Finally, specific work is an often used measure to quantify the effect of flow on nucleation.\(^\text{[16–19]}\) However, we do not see this as a useful starting point for modeling since it does not contain any specific material parameters and, therefore, cannot serve as a tool for understanding the influence of, for example, variations in the molecular weight distribution. Rather, the outcome of our modeling should compare with the experimental results presented in terms of specific work.

The concept of dormant precursors, introduced by Janeschitz-Kriegl and coworkers, assumes that the melt contains a fixed number of precursors\(^\text{[17,19]}\). The free energy won by crystallization of a precursor (a volume term) competes with some kind of surface tension (a surface term). The precursors thus need to be greater than a certain critical size (denoted by \(n^\star\) in this paper) for growth of a precursor to be favorable and for the precursor to become a nucleus. Precursors smaller than the critical size are defined dormant, precursors larger than the critical size are active. Active precursors may nucleate, becoming a nucleus. The terms precursors and nuclei are further clarified in Figure 1. The figure shows a size distribution of precursors where a number of active precursors have turned into nuclei. \(N_p(n)\) is the number of precursors with size \(n\) or greater, \(n^\star\) is the critical size precursors need to overcome to become active. At time zero only precursors are present, as time progresses active precursors will turn into nuclei. At a sufficiently long time scale all active precursors will become nuclei.

**Figure 1.** Size distribution of precursors where a number of active precursors have turned into nuclei. \(N_p(n)\) is the number of precursors with size \(n\) or greater, \(n^\star\) is the critical size precursors need to overcome to become active. At time zero only precursors are present, as time progresses active precursors will turn into nuclei. At a sufficiently long time scale all active precursors will become nuclei.

The goal of this work is not only to model and test the idea of Janeschitz-Kriegl et al. that dormant precursors can be activated by flow, by changing (one of) the dimensions, but also to make it accessible for experimental results. For this reason we will combine classical nucleation theory, extended to two precursor dimensions, with the approach used by Zuidema et al.\(^\text{[9]}\), Custódio et al.\(^\text{[13]}\) and Steenbakkers and Peters\(^\text{[14]}\) to derive a model for flow-enhanced nucleation based on dormant precursors.

In the “Experimental Part” section we briefly summarize experiments from literature that will be used to validate our model. The derivation of the model is presented in “Theory”. Simulation results and validation of the model are shown in the “Results” section. Resulting conclusions are presented in “Conclusion”.

**Experimental Part**

**Quiescent**

Predictions of the model will be compared with experiments on two grades of isotactic polypropylene (IPP). For both materials, HD601CF (previously known as HD120MO, provided by Borealis) and 13E10 (provided by DSM), the quiescent nucleus number density as a function of temperature is described by Equation (1). We should note that this expression is merely an experimental fit that will give good results only in the temperature range investigated in the experiments. However, as the maximum nucleus number density that we encounter in our simulations is not vastly outside the range of the experiments described by Equation (1), we expect this expression to be sufficiently accurate for current purposes. Parameters for the expression and some
physical properties of the materials are shown in Table 1. Numbering of the materials is adopted from Housmans et al.\(^{[16]}\)

\[
N_n = N_{\text{ref}} \exp(-c_0(T - T_{\text{ref}})) 
\]

(1)

The above expression yields a cumulative number density namely that of the nuclei obtained at constant temperature \(T\) in a quiescent melt. Under these conditions, in temperature ranges of practical interest, active precursors nucleate instantaneously, \(^{[17]}\) as evidenced by the narrow size distribution of spherulites even in systems containing very low amounts of heterogeneous substances. Thus \(N_n\) is equal to the cumulative number of active precursors per unit volume of the amorphous phase (their actual number in general depends on the space filling at hand, which depends on the thermal history). The differential number density \(N_n'^{[19]}\), which is obtained by calculating the increase in spherulite number density \(\Delta N_n\) for a certain decrease of the temperature \(\Delta T\), or

\[
N_n' = \frac{\partial N_n}{\partial T} = c_0 N_{\text{ref}} \exp(-c_0(T - T_{\text{ref}})) 
\]

(2)

From this expression the number of nuclei that will appear at a certain temperature can be obtained by integration from the experimental temperature to the nominal melting temperature. Figure 2(a) and 3(a) show both the cumulative number density \(N_n\)

<table>
<thead>
<tr>
<th>Material</th>
<th>Grade</th>
<th>(M_w)</th>
<th>(M_w/M_m)</th>
<th>Isotacticity</th>
<th>(N_{\text{ref}}) (\text{m}^{-3})</th>
<th>(T_{\text{ref}}) (\text{C})</th>
<th>(T_N) (\text{C})</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>iPP2</td>
<td>HD601CF</td>
<td>365</td>
<td>5.4</td>
<td>70</td>
<td>97.5</td>
<td>(1.14 \times 10^{13})</td>
<td>110</td>
<td>0.115</td>
</tr>
<tr>
<td>iPP3</td>
<td>13E10</td>
<td>636</td>
<td>6.9</td>
<td>122</td>
<td>94.7</td>
<td>(4.05 \times 10^{12})</td>
<td>140</td>
<td>0.109</td>
</tr>
</tbody>
</table>

Figure 2. Quiescent nucleus number density of iPP2 versus temperature (a) and flow-enhanced nucleus number density at \(T = 138\) °C for iPP2, as a function of shear time for different shear rates (b). Lines are to guide the eye.

Figure 3. Quiescent nucleus number density of iPP3 versus temperature (a) and flow-enhanced nucleus number density at \(T = 138\) °C for iPP3, as a function of shear time for different shear rates (b). Lines are to guide the eye.
and differential number density $N_r'$ for materials iPP2 and iPP3, respectively. The solid line shows (1), the dashed line shows (2). The circles show measurements of the spherulite number density obtained from optical microscopy.$^{[20,21]}$

**Flow/iPP2**

The first set of experiments are short-term shear experiments on iPP2, from Housmans et al.$^{[16]}$ Short term shear was applied in a rheometer with plate–plate configuration and the evolution of rheological properties was monitored afterwards. Table 2 shows the reptation and Rouse times of the slowest mode of both grades, obtained from a fit of the XPP model to extensional viscosity measurements. See also Appendix B. The spherulite number density was obtained by estimating space filling by modeling the crystallizing melt as a suspension with soft particles$^{[22]}$ and fitting the Avrami equation for 3D growth$^{[23,24]}$ to this. More information on this procedure can be found in recent papers from Housmans et al. and Ma et al.$^{[16,25]}$ Figure 2(b) shows the nucleus number density resulting from crystallization after flow as a function of applied shear time for different shear rates. Note that the quiescent number density is a factor three smaller than Equation (1) predicts with the value for $N_{ref}$ from Housmans et al. Therefore we have used an adjusted value $N_{ref} = 1.14 \times 10^{13}$ m$^{-3}$ for $N_{ref}$ in the remainder of this study. This is justified because the spread on number densities is large, as Housmans already noticed (cf. pg 51 in ref.$^{[26]}$). The circles in Figure 2(a) are averages, but the spread in these kind of measurements is illustrated well in Figure 3(a).

**Flow/iPP3**

The second set of experiments is also taken from Housmans et al.$^{[16]}$ Figure 3(b) shows results from short-term shear experiments. The measured quiescent number density is a factor three larger than the prediction of Equation (1) with $N_{ref}$ from Housmans et al. and therefore we have used an adjusted value of $N_{ref} = 4.05 \times 10^{12}$ m$^{-3}$ in the remainder of this study.

**Theory**

**Quiescent Nucleation**

We consider cylindrical precursors with length $2l$ and radius $r$, consisting of $n$ stems with length equal to that of the precursor and radius $r_s$ so that $r^2 = nr_s^2$. The precursors have a certain distribution in size. In this study we do not take into account a distribution of precursor and stem lengths; only one, uniform, length is considered. For a given $r_s$ and $l$, the precursors are now characterized by the single variable $n$. The size distribution $\rho(n)$ gives the number of precursors present per unit volume in the amorphous phase with a certain size $n$.

Ziabicki and Alfonso derived a model for a similar system.$^{[4]}$ Their approach, based on a Fokker–Planck equation with the volume of the precursor as a stochastic variable, turns out to be unpractical for our purposes. A model with two variables, number of stems and precursor length, is even more complex. See Appendix D.

The free energy change due to growth by crystallization of a precursor with size $n$ becomes

$$
\Delta F(n) = -2n\pi r_s^2/\Delta h(1-T/T_m) + 2n\pi r_s^2\sigma_e + 4\sqrt{n}\pi r_s\sigma_s
$$

(3)

where the first term accounts for free energy decrease due to crystallization. The second and third terms are penalty terms due to surface tension on the ends and side of the precursor, respectively. $T_m$ is the thermodynamic melting point, $\Delta h$ the heat of fusion per unit volume and $\sigma_e$ and $\sigma_s$ are the surface energies on the ends, with surface area $a_e$ and side of the precursor, with surface area $a_s$, respectively. A precursor is schematically depicted in Figure 4. Values for these constants for polypropylene were obtained from Monasse and Haudin$^{[27]}$ and are shown in Table 3. $r_s$ is taken to be the characteristic size of a unit cell of the crystalline phase of polypropylene, $r_s = 0.5$ nm. For other choices, results qualitatively similar to those presented in this study are obtained.

The free energy of nucleation as a function of the number of stems $n$ for a constant precursor length $l$ and temperature $T$ is

**Table 2.** Reptation and Rouse time from XPP fit for slowest modes of iPP2 and iPP3 at $T = 138$ °C.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\lambda_{rep, HMW}$</th>
<th>$\lambda_{OR, HMW}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$s$</td>
<td>$s$</td>
</tr>
<tr>
<td>iPP2</td>
<td>19.3</td>
<td>16.3</td>
</tr>
<tr>
<td>iPP3</td>
<td>750</td>
<td>92.5</td>
</tr>
</tbody>
</table>

**Table 3.** Nucleation parameters for polypropylene.$^{[27]}$

<table>
<thead>
<tr>
<th></th>
<th>$\Delta h$</th>
<th>$\sigma_e$</th>
<th>$\sigma_s$</th>
<th>$T_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$1.4 \times 10^8$ J/m$^3$</td>
<td>0.144 J·m$^{-2}$</td>
<td>$9.2 \cdot 10^{-3}$ J/m$^2$</td>
<td>481 K</td>
</tr>
</tbody>
</table>
shown in Figure 5. It shows a maximum at $n = n^*$, below which the free energy has a positive slope and crystallization is unfavorable; precursors with size $n < n^*$ are dormant. Above this critical size crystallization is favorable and precursors with $n > n^*$ are active. The critical size follows from

$$n = n^* : \quad \Delta \bar{F}(n^*) = \max \Delta \bar{F}(n)$$

(4)

Note that there is no barrier for nucleation in longitudinal direction because $\frac{\partial \Delta \bar{F}}{\partial l}$ is not a function of $l$. Thus, if we talk about the critical size we always mean the critical number of stems. The total number of active precursors can be obtained by integration of the size distribution over the precursors with number of stems greater than the critical number $n^*(T,l)$,

$$N_{p,a}(T) = \int_{n^*(T,l)}^{\infty} \rho(n) dn$$

(5)

Figure 6(a) shows the critical number of stems $n^*$ versus precursor length for fixed temperature. Precursors with length $l < l^* = \frac{\sigma d}{\Delta h}$ form an interesting category. In the current model these precursors are allowed to become active, whereas one might argue that these precursors are unstable and cannot become active, because the free energy won by crystallization is not sufficient to overcome the surface tension, with an extra contribution due to dangling amorphous ends of the chains getting into a squeeze. Also, internal defects which we have not considered, might have a relatively large negative contribution to $\Delta h$ at small lengths. In short: the length to diameter ratio of these precursors is too small to overcome the surface tension at the ends of the precursor. The model might be too simplified below this critical length. The issue is avoided by fixing the precursor length in a quiescent melt at $l_0 = 10$ nm (such that $l_0 > l^*$) in the remainder of this study, then the critical size shows a monotonic decrease as the length of the precursors increases. The exact choice for $l_0$ is somewhat arbitrary. The results that we present in this study (validation with experiments and comparison to another model) hold for other choices for $l_0$ as long as $l_0 > l^*$. For this choice of precursor length, the critical size versus temperature is shown in Figure 6(b).

**Precursor Size Distribution**

We now derive the size distribution of precursors. With the critical precursor size as a function of temperature known from theory and

where we have introduced the size distribution function $\rho(n) = \frac{dn}{dn}$. From Equation (4) it follows

$$\frac{\partial \Delta \bar{F}(n)}{\partial n} = 0$$

(6)

And substituting (3) gives

$$n^* = \left( \frac{1}{T_0} \frac{l a_s}{\Delta h(1-T/T_m)l-T} \right)^2$$

(7)

Figure 6 shows the critical number of stems $n^*$ versus precursor length for fixed temperature. Precursors with length $l < l^* = \frac{\sigma d}{\Delta h}$ form an interesting category. In the current model these precursors are allowed to become active, whereas one might argue that these precursors are unstable and cannot become active, because the free energy won by crystallization is not sufficient to overcome the surface tension, with an extra contribution due to dangling amorphous ends of the chains getting into a squeeze. Also, internal defects which we have not considered, might have a relatively large negative contribution to $\Delta h$ at small lengths. In short: the length to diameter ratio of these precursors is too small to overcome the surface tension at the ends of the precursor. The model might be too simplified below this critical length. The issue is avoided by fixing the precursor length in a quiescent melt at $l_0 = 10$ nm (such that $l_0 > l^*$) in the remainder of this study, then the critical size shows a monotonic decrease as the length of the precursors increases. The exact choice for $l_0$ is somewhat arbitrary. The results that we present in this study (validation with experiments and comparison to another model) hold for other choices for $l_0$ as long as $l_0 > l^*$. For this choice of precursor length, the critical size versus temperature is shown in Figure 6.
the differential nucleus number density at a range of temperatures obtained from experiments, theory, and experiment can be combined to obtain the number of precursors that become active at a certain value for the critical size. Assuming, in accordance with the idea of dormant precursors proposed by Janschitz-Kriegel[17,19] that the size distribution is fixed, this gives us the precursor size distribution. Using the expression for the differential number density as a function of temperature Equation (2), and Equation (7) for the critical size as a function of temperature, we obtain the following expression for the size distribution as a function of critical size \( \rho(n) \):

\[
\int_{n}^{\infty} \rho(n) \, dn = N_{n}(T)
\]

\[
\frac{d}{dn} \int_{n}^{\infty} \rho(n) \, dn = -\rho(n^*) = \frac{dN_{pa}}{dT} \frac{dT}{dn} + \frac{d\rho}{dn}.
\]

\[
\rho(n^*) = c_0 N_{ref} e^{-c_0(T_{m(1-n/n_{i}/\sqrt{\ln(D_n/\Delta_l)})-T_{ref}})} \frac{\sigma_{T_{m}}}{2\Delta h_{T_{ref}} n^2}.
\]

In our model the size distribution of precursors does not change with temperature and thus the above equation is valid as a size distribution function:

\[
\rho(n) = c_0 N_{ref} e^{-c_0(T_{m(1-n/n_{i}/\sqrt{\ln(D_n/\Delta_l)})-T_{ref}})} \frac{\sigma_{T_{m}}}{2\Delta h_{T_{ref}} n^2}.
\]

The size distribution of precursors in the melt calculated using the above procedure for both iPP2 and iPP3 is shown in Figure 7.

**Flow-enhanced Nucleation**

The effect of flow is modeled by increasing the length of the precursors by an amount of \( \Delta l \). Precursors with length \( l \) that are dormant in a quiescent melt (i.e. \( n < n^{*}(l) \)) may become active because, as shown in Figure 6(a), \( n^{*} \) for a precursor with length \( l + \Delta l \) is smaller than the critical size for a precursor with length \( l \); i.e.

\[
\text{activation by flow occurs if } n > n^{*}(l + \Delta l), \text{ where } n^{*}(l + \Delta l) \text{ is the critical number of stems for a precursor with length } l + \Delta l.
\]

The time evolution of the number of active precursors, i.e. the number of precursors pushed over the activation barrier per unit time, can be expressed in the following way

\[
N_{pa} = \frac{dN_{pa}}{dn} = \frac{dN_{pa}}{dt} \frac{dt}{dn} = -\rho(n^*) \left( \frac{\partial n^*}{\partial l} + \frac{\partial n^*}{\partial T} \right) \frac{N_{pa}}{\tau_{pn}}.
\]

where \( l \) is the longitudinal precursor growth rate, the total length increase follows from integration over time of the growth rate, \( \Delta l = \int \Delta l dt \). The first term accounts for the number of precursors activated by the flow per unit time. All simulations in this paper are in isothermal conditions and thus \( T = 0 \), but the model can also be used to simulate non isothermal cases. The second term comes from active precursors nucleating, which happens with a characteristic timescale \( \tau_{pn} \):

\[
N_{p,n} = \frac{N_{pa}}{\tau_{pn}}.
\]

It is well known that microscopic pictures of iPP during flow- enhanced nucleation experiments show that all spherulites become visible at approximately the same moment in time, and that their diameters are nearly equal.[15,28] This means that the large majority of nuclei is created at approximately the same moment in time. Furthermore, we have not observed significant numbers of spherulites during flow in our current and previous experimental work, even when the duration of flow was long enough to observe them with optical microscopy.[14,15] This assumption is supported by X-ray measurements of Mahendra- singam et al. during film drawing of PET.[20] They observed that, for high strain rates, crystallinity only started developing after the end of the draw. Based on these observations, we assume that the characteristic time of nucleation is much longer than the duration of flow in our short-term shear experiments and that nucleation is instantaneous in the absence of flow. Hence we set \( \tau_{pn} = \infty \) during flow and \( \tau_{pn} = 0 \) after flow.

We notice that the precursor activation rate (Eq. 10) can be written as a factor times the longitudinal growth rate \( l \) for isothermal flow-enhanced nucleation. This factor, \( -\rho(n^*) \frac{\partial n^*}{\partial l} \), is shown for a range of lengths in Figure 8. Because this quantity does not vary largely (just a factor 4) over the range of precursors lengths encountered in experiments (the maximum length reached is \( \approx 35 \text{ nm} \), see Figure 12(b)), the creation rate of active precursors (in the absence of nucleation) is approximately proportional to the growth rate of the precursors.

\[
N_{pa} \sim l
\]

It is well known that the high molecular weight (HMW) fraction of a polydisperse melt has a dominant influence on the flow-enhanced nucleation process.[13,30–32] Steenbakkers and Peters found the fourth power of the average stretch of the primitive paths of chains in the HMW mode of the material (\( \Lambda \)) to be a good measure of the increase in nucleation rate.[14,15] Graham and
Olmsted found that a model based on the exponent of the average molecular stretch squared gives quantitative agreement with their Monte Carlo simulations. Both approaches give very similar results for the nucleation rate. Following these studies, we take the growth rate of the precursors to be a function of the molecular stretch of the HMW tail of the material,

\[ \dot{L} = c(\Lambda^4 - 1) \]  

which, because \( N \sim \dot{L} \), is similar to Steenbakkers's nucleation rate (see also the section “Comparison to Steenbakkers’s model”). \( c \) is a scaling parameter containing material properties, e.g. isotacticity and polydispersity. \( \Lambda \) is calculated using the XPP constitutive model. The performance of the Rolie-Poly model in our nucleation model is evaluated in Appendix C. Equations for both constitutive models are given in Appendix A. Similar results could be obtained by replacing \( \Lambda^4 \) with the recoverable strain, quantified by the second invariant of the deviatoric part of the elastic Finger tensor, \( J_2(B^d) \), as in Zuidema et al. because

\[ J_2(B^d) = 9\Lambda^4 J_2(S^d) \]  

and \( J_2(S^d) \), the second invariant of the deviatoric part of the orientation tensor, hardly changes as a function of shear time. In the “alternative precursor growth model” section a different growth model, based on the work of Graham and Olmsted is evaluated.

### Results

#### Model Validation

In this section the present model is validated with results from short-term shear experiments presented in the “Experimental Part” section. Final nuclei number densities from simulations and experiments are compared in Figure 9. We observe a quantitative agreement between simulations and experiments. The scaling parameter \( c \) differs by a factor of 10 between the materials, but the model gives good results with the same scaling parameter for different shear rates. The difference in \( c \) might well be caused by the difference in isotacticity between the two materials; iPP2 has a higher isotacticity than iPP3 (97.5 versus 94.7%, see Table 1) and might thus be more susceptible to flow-enhanced nucleation.

Figure 10 and 11 show the time evolution of the number of active precursors and nuclei of the simulations from Figure 9. The number of nuclei shows an increase after flow because the stretch of the molecules takes some time to relax after the flow is ceased, which seems to contradict Steenbakkers’s remark that all nuclei must have started growing at the same instant in time. However, the maximum time span over which nuclei are created after flow is \( 50 \) s [the measurement with shortest shear time in Figure 11(a)]. Multiplied by the lamellar growth rate of iPP at \( 138 \) °C, \( 1.5 \times 10^{-8} \) m/s, this gives a maximum difference in radius of 0.75 \( \mu \)m between the spherulites, which is below the resolution of optical microscopy. Therefore these simulations are not in disagreement with

**Figure 8.** \(-\rho(n^*) \partial n^* / \partial l\) versus \( l \) for iPP2.
the experimental observation that all spherulites are of approximately the same size.

**Saturation**

A very interesting and surprising feature of the model is that the nucleus number density seems to reach a constant value for increasing shear time, a feature observed experimentally by for example Housmans et al. and Baert et al.\[16,33\] The reason we observe saturation in simulations is explained below.

First, and most importantly, the molecular stretch (and with it the precursor growth rate $\dot{l}$) as a function of shear time first increases rapidly, reaches a maximum and then

![Figure 10.](image1)

*Figure 10. Number densities of active precursors (dashed lines) and nuclei (solid lines) versus time for iPP2 during experiments with different shear times at 138 °C. Model parameter: $c = 2 \times 10^{-19}$ m/s. Three shear rates are shown; (a) $\dot{\gamma} = 5$ s$^{-1}$, (b) $\dot{\gamma} = 15$ s$^{-1}$, (c) $\dot{\gamma} = 30$ s$^{-1}$.**

![Figure 11.](image2)

*Figure 11. Number densities of active precursors (dashed lines) and nuclei (solid lines) versus time for iPP3 during experiments with different shear times at 138 °C. Model parameter: $c = 1.5 \times 10^{-14}$ m/s. Two shear rates are shown; (a) $\dot{\gamma} = 0.7$ s$^{-1}$, (b) $\dot{\gamma} = 5$ s$^{-1}$.**
relaxes toward a steady state, as shown in Figure 12(a). Consequently, the precursor length $l$ resulting from a shear experiment grows fast for increasing shear times when looking at short-term shear experiments, and as the shear times get larger, the length increase for the same increase in shear time gets smaller. This is depicted in Figure 12(b). Precursor length versus time is shown for five experiments, with shear times of 4, 6, 8, 10, and 12 s. The difference in resulting precursor length between the experiments with $t_s = 4$ s and $t_s = 6$ s is $\approx 3$ nm, where the difference between the experiments with $t_s = 10$ s and $t_s = 12$ s is only $\approx 1$ nm. In short, the average precursor growth rate over the full length of the experiment decreases with increasing shear time. Saturation is mostly caused by this effect. It is important to note that saturation already starts during the “softening” in $\Lambda(t)$ before it reaches steady state. According to Housmans et al. the first normal stress difference and the shear viscosity reach their steady state much sooner than saturation. Hence neither the rheology of the HMW tail nor that of the whole melt shows a correlation between steady-state behavior and saturation, as suggested by Martins et al.\textsuperscript{[34]}

A second effect also has a contribution to the saturation effect, albeit smaller than the first one. The factor $-\rho(n^0)$ in Equation (10) decreases after reaching a maximum at $l = 30$ nm (see Figure 8, this precursor length corresponds to $N_{p,a} = 2 \times 10^{13}$ m$^{-3}$ as can be seen from Figure 12(b) and (c)). Consequently, after that number of active precursors is reached the activation rate of precursors decreases. Note that the number of nuclei versus shear time does not actually reach a plateau in our model. With increasing shear time, the activation rate of precursors becomes small, but not zero. At very long shear times the number of nuclei will reach a final value because the critical number of stems reaches 1, which means that every single stem will nucleate. From this point on $n^0$ does not decrease anymore and thus the number of nuclei becomes constant. However, the length at which this happens lies far out of the range accessed in the simulations presented in this study. In experiments, regime 3 with oriented structures (see introduction) would be entered long before this happens.

Figure 12. (a) Molecular stretch, (b) precursor length, and (c) number density of active precursors (dashed line) and nuclei (solid lines) versus time for short-term shear experiments with different shear times (4, 6, 8, 10, and 12 s) on iPP2, $\dot{\gamma} = 15$ s$^{-1}$ at 138 °C.
Comparison with Steenbakkers’s Model

We compare simulation results from our model with the model presented by Steenbakkers and Peters.[14,15] The flow-induced creation rate of active precursors in this model can be simplified to

\[ N_{pf} = g_p (A^4 - 1) - \frac{N_{pf}}{t_{pn}} \]  

(15)

where in the right hand side the first term represents the creation of precursors and the second term originates from precursors nucleating. \( g_p \) is a scaling parameter, \( N_{pf} \) is the number of flow-induced precursors. No dormant precursors exist in Steenbakkers’s model, all precursors formed by the flow are active according to current definitions. Note that the flow-induced nucleation rate from Steenbakkers’s model thus has approximately the same structure as in our model, as follows from Equation (12) with the growth rate as in Equation (13). A part of Steenbakkers’s model that is not present in the current model is that precursors form physical crosslinks, causing the relaxation time of the HMW modes in the material to increase.[9,14,15] This increase is controlled by the parameter \( a \),

\[ \frac{\lambda_{rep}}{\lambda_{0,rep}} = 1 + a(N_{pf} + N_{nf}) \]

\[ \frac{\lambda_{R}}{\lambda_{R,0}} = 1 + a(N_{pf} + N_{nf}) \]  

(16)

where \( \lambda_{rep} \) and \( \lambda_{R} \) are the reptation and Rouse times of the HMW tail as a result of the precursors forming crosslinks, respectively, and \( \lambda_{0,rep} \) and \( \lambda_{R,0} \) are the reptation and Rouse times of the HMW tail in a quiescent melt, \( N_{nf} \) is the number of nuclei created by the flow, i.e. the number of flow-induced precursors that have turned into nuclei. We should also note that Steenbakkers et al. needed the following empirical term to have their model predict saturation

\[ g_p = g_{0,p} \left( 1 - \frac{N_{pf}}{N_{f,\text{max}}} \right) \]  

(17)

where \( N_{f,\text{max}} \) is the maximum number of flow-induced precursors and nuclei, obtained from the saturation level in experiments. In the simulations that we did with this model, we do not require this term to obtain nucleus number densities that are in accordance with experiments (see Figure 14(b)). This is caused by the fact that we have used the XPP constitutive model whereas Steenbakkers et al. used the Rolie-Poly model to calculate the behavior of the polymer on molecular scale. Appendix C shows we experienced that the Rolie-Poly model does not perform as well as the XPP model in our nucleation model.

Alternative Precursor Growth Model

In this section we evaluate another growth model, i.e. another expression for the longitudinal precursor growth rate \( l \). Graham and Olmsted performed Monte Carlo simulations of flow-induced nucleation and observed that the nucleation rate was well described by the relation[5]

\[ \dot{N} = N_0 \eta (\Lambda^4 - 1) \]  

(18)

where \( N_0 \) is the nucleation rate in absence of flow and \( \eta \) is a fitting parameter. In “Theory” we showed that the

Figure 13. Creation rate of active precursors in a shear experiment on iPP2 with \( \dot{\gamma} = 15 \text{ s}^{-1}, \; t_i = 12 \text{s} \). Dashed and dash-dotted line: Steenbakkers’s model. Model parameters are the following. Dashed line: \( g_p = 10^8 \text{ m}^{-3} \text{s}^{-1}, \; a = 0 \text{ m}^3 \). Dash-dotted line: \( g_p = 10^8 \text{ m}^{-3} \text{s}^{-1}, \; a = 10^{-10} \text{ m}^3 \). Solid line: our model with \( c = 2 \times 10^{-11} \text{ m/s} \).

The creation rates of active precursors (in absence of nucleation) from both models are compared in Figure 13. The dashed line show predictions of Steenbakkers’s model with no relaxation time increase, which means \( N_{pf,a} = g_p (A^4 - 1) \). The dash-dotted line shows simulation results from Steenbakkers’s model with nonzero \( a \) parameter, the solid line shows the model presented in this study. For all three cases the total final number densities are shown in Figure 14. We observe that a model where the creation rate of active precursors is simply proportional to \( (A^4 - 1) \) qualitatively agrees with experiments but under predicts the final spherulite number density at the two higher shear rates. Both Steenbakkers’s model and the present model increase the prediction for the higher shear rates, the first by relaxation time increase because of the formation of physical crosslinks and the latter because the factor \( -\rho (n^2) \frac{d \dot{N}}{dt} \) increases for increasing length (up to \( l = 30 \text{ nm} \), see Figure 8).
nucleation rate is approximately proportional to the precursor growth rate. We can thus use the relation found by Graham et al. as a growth model,

$$l = ce^{h(L^2/C_0)}$$

(19)

where $c$ and $h$ are fitting parameters. The physical picture behind this growth model is that $(L^2/\theta C_0)$ represents the elastic energy stored in a chain. Simulation results for this growth model can be seen in Figure 15. We observe a good agreement with simulations and experiments. However,
we prefer the power law of molecular stretch (Eq. 13) because it requires just one scaling parameter to give equally good results.

**Conclusion**

A model was derived for flow-enhanced nucleation based on the concept of a melt containing a fixed number of fibrillar flow-activatable nucleation precursors. Longitudinal precursor growth, causing activation of dormant precursors, is a function of molecular deformation: the average stretch of the primitive path of chains in the HMW tail of the material, calculated from a rheological constitutive model. Both the Rolie-Poly and the eXtended Pom-Pom model were evaluated. The nucleation model was found to perform best in combination with the XPP model. Simulations of the model give quantitative agreement with experiments on two grades of iPP. Per material, a single scaling parameter suffices for the whole range of shear rates applied. The difference in scaling parameter between the two grades can be explained by the different isotacticities of the materials. Surprisingly, the model predicts saturation of the number density of nuclei with increasing shear time without any phenomenological terms. The model can also be applied to non-isothermal cases.

**Appendix A: The XPP and Rolie-Poly models**

This appendix is a slightly adapted form of section 3.3 from Steenbakkers.\[15\]

The Cauchy stress tensor for a polymer melt is written in the form

$$\sigma = -pI + \sum_{i=1}^{M} G_i(B_{e,i} - I)$$

(20)

where \(i = M\) indicates the mode with the longest relaxation time. The elastic Finger tensor \(B_{e,i}\) of mode \(i\) follows from

$$B_{e,i} = -A_i B_{e,i} - B_{e,i} A_i^T$$

(21)

The triangle denotes the upper convected derivative and \(A_i\) is the slip tensor of mode \(i\), which describes the non-affine deformation of the corresponding molecules. Several constitutive models can be written in this form with different expressions for \(A_i\).\[15\] The constitutive models utilized in this paper are listed in Table 4. The Giesekus model is shown for comparison.

The elastic Finger tensor is taken equivalent to the conformation tensor, following Leonov.\[36-38\] The orientation tensor

$$S_i = (\bar{n}_i, \bar{n}_i) = \frac{B_{e,i}}{\text{tr}(B_{e,i})}$$

(22)

gives the average molecular orientation; \(\bar{n}_i\) is a unit vector, tangent to the primitive path of a chain, and the angle brackets indicate an average over the orientation distribution. If the stretch of the primitive path is assumed homogeneous, it is described by the scalar stretch parameter

$$\lambda_{R,i} = \sqrt{1 + \lambda_{0R,i} e^{-\nu_i(\Lambda - 1)}}$$

(23)

which follows from \(B_{e,i} = 3\lambda_{R,i}^2 S_i\).\[19\]

In the XPP model, the Rouse time is dependent on the molecular stretch,

$$\lambda_{R,i} = \lambda_{0R,i} e^{-\nu_i(\Lambda - 1)}$$

(24)

where \(\nu_i = \frac{3}{8}\).

The parameter \(k_i\) was introduced into the Rolie-Poly model by Kabanemi and Hétu to make the chains finitely extensible.

| Table 4. Slip tensors for the Giesekus, XPP, Rolie-Poly, and finitely-extensible (FE) Rolie-Poly models. |
|-----------------|--------|--------|--------|
| \(A_i\)        | \(C_{1,i}\) | \(C_{2,i}\) | \(C_{3,i}\) |
| Giesekus       | \(\omega_0\) | \(-\frac{1-\omega_0}{2\omega_0}\) | \(-\frac{1-2\omega_0}{2\omega_0}\) |
| XPP            | \(\omega_0\) | \(-\frac{1-\omega_0}{2\omega_0}\) | \(-\frac{1-2\omega_0}{2\omega_0}\) |
| Rolie-Poly     | 0       | \(-\frac{1}{2\omega_0} + \frac{\beta_0}{2\omega_0} (1 - \frac{1}{\lambda})\) | \(-\frac{1}{2\omega_0} + \frac{\beta_0}{2\omega_0} (1 - \frac{1}{\lambda})\) |
| FE Rolie-Poly  | 0       | \(-\frac{1}{2\omega_0} + \frac{\beta_0}{2\omega_0} (1 - \frac{1}{\lambda})\) | \(-\frac{1}{2\omega_0} + \frac{\beta_0}{2\omega_0} (1 - \frac{1}{\lambda})\) |
extensible.\(^{[40]}\) \(k_s\) is a nonlinear spring coefficient, given by

\[
k_s(\Lambda) = \frac{(1-1/\Lambda_{\text{max}}^2)(3-\Lambda^2/\Lambda_{\text{max}}^2)}{(1-\Lambda^2/\Lambda_{\text{max}}^2)(3-1/\Lambda_{\text{max}}^2)}
\]

(25)

where \(\Lambda_{\text{max}}\) is the maximum molecular stretch possible.

Appendix B: Parameters for the Constitutive Models

For both materials, the XPP and Rolie Poly model were fitted to extensional viscosity data, see Figure 16 and 17. The resulting relaxation times are shown in Table 5 and 6.

For the Rolie Poly model, we used \(b = 0\), representing no convective constraint release, as this gives the best results.\(^{[14,15]}\) Consequently, the parameter \(\delta\) plays no role. For the modified XPP model, we used \(\alpha_i = 0.1/q_i\).

B.1 iPP2

Best fits are obtained for an XPP model with four non-stretching modes and two stretching modes, and a Rolie-Poly model with three non-stretching and three stretching modes. Reptation times are from Housmans et al.\(^{[26]}\) Rouse times for the Rolie-Poly model are equal to the ones used by Steenbakkers.\(^{[14,15]}\)

B.2 iPP3

Best fits are obtained for an XPP model and a Rolie-Poly model both with five non-stretching and three stretching modes. Reptation times are taken from Swartjes.\(^{[21]}\) The maximum stretch parameter in the finitely extensible Rolie-Poly model \(\Lambda_{\text{max}} = 5\).

Appendix C: Constitutive Behavior from Rolie-Poly Model

One would expect the Rolie-Poly model (developed for linear polymers) to be more suitable than the XPP model (developed for branched polymers) to describe iPP, since iPP is a linear polymer. In this section we evaluate our nucleation model with the constitutive behavior simulated with the Rolie-Poly model (equations shown in Appendix A). Relaxation times and model parameters are given in Appendix B. Simulation results are presented in Figure 18. We observe that the simulations and experimental results are not in as close agreement as when using the XPP model. The predictions can be slightly improved by turning on convective constraint release (i.e., setting \(b \neq 0\)), but this leads to extensional viscosity predictions that are not physical (i.e., lower than the linear viscoelastic response for some strain rates). A possible cause for the poor performance is the high molecular stretch the Rolie-Poly model yields, compare Figure 19 and Figure 12(a). A possible

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**Figure 16.** Extensional viscosity for iPP2 at 180 °C, symbols show measurements, dashed lines show a linear viscoelastic response, solid lines show (a) XPP, (b) Rolie-Poly, and (c) Rolie-Poly with finite extensibility.
solution to this problem might be using a finitely extensible Rolie-Poly model (equations can be found in Appendix A). Simulation results are shown in Figure 20. From this figure we conclude that neither the infinitely extensible, nor the finitely extensible Rolie-Poly model performs nearly as well as the XPP model. For this reason, we have used the XPP model throughout this study.

Appendix D: Precursors with a Distribution of Lengths

In this appendix the expansion of our theory to two dimensions is investigated. This expansion means that, instead of taking just one value for the precursor length \( l \) and varying the number of stems, the precursors have a distribution both in length a fluctuating number of stems. To this purpose, a new dimensionless variable \( s \) is introduced and the length of a stem/precursor is expressed as \( l = sl_0 \) with \( l_0 \) a yet to be determined reference length. We simplify by assuming that stems only interact with precursors of the same length. The only growth mechanism for precursors in a quiescent melt is stem addition, in contrast to the work by Graham and Olmsted who considered a similar system (albeit on a smaller scale).

| Table 5. Parameters for XPP and Rolie Poly models for iPP2 at 138 °C. |
|------------------|-----------------|------------------|------------------|------------------|
| \( \lambda_{\text{rep},i} \) | \( \lambda_{\text{OR},i} \) (XPP) | \( q_i \) (XPP) | \( \lambda_{R,i} \) (Rolie-Poly) |
| \( s \) | \( s \) | \( s \) | \( s \) |
| 0.01 | 0 | 1 | 0 |
| 0.06 | 0 | 1 | 0 |
| 2.16 | 0 | 1 | 0.14 |
| 12.9 | 0 | 1 | 1.1 |
| 77.8 | 16.3 | 11.9 | 7.1 |

| Table 6. Parameters for XPP and Rolie Poly models for iPP3 at 138 °C. |
|------------------|-----------------|------------------|------------------|------------------|
| \( \lambda_{\text{rep},i} \) | \( \lambda_{\text{OR},i} \) (XPP) | \( q_i \) (XPP) | \( \lambda_{R,i} \) (Rolie-Poly) |
| \( s \) | \( s \) | \( s \) | \( s \) |
| 0.0052 | 0 | 1 | 0 |
| 0.0345 | 0 | 1 | 0 |
| 0.174 | 0 | 1 | 0 |
| 0.840 | 0 | 1 | 0 |
| 4.01 | 0 | 1 | 0 |
| 19.3 | 23.1 | 2.4 | 3.86 |
| 104 | 61.6 | 6.2 | 38.6 |
| 750 | 92.5 | 14.9 | 231 |

Figure 17. Extensional viscosity for iPP3 at 220 °C, symbols show measurements, dashed lines show a linear viscoelastic response, solid lines show (a) XPP, (b) Rolie-Poly, and (c) Rolie-Poly with finite extensibility.
where precursors were allowed to grow by both stem addition and stem lengthening.\cite{5, 6}

Because the size distribution $\rho$ now is a function of both $n$ and $s$, the procedure we used in the "Theory" section where $\rho$ was obtained by combining theory and experiment is no longer applicable. Therefore, we investigate a different method to obtain a precursor size distribution. A method to obtain a size distribution from a Fokker–Planck equation for clusters (equivalent to precursors in our case) that are described by one characteristic measure, the number of kinetic units in a cluster (equivalent to the number of stems) was presented by Ziabicki and Alfonso.\cite{4}

As a result of our assumption that stems only interact with precursors of the same length, each species $i$ of stems and precursors with length $l_i = s_i l_0$ has a size distribution density $r(n, s_i)$ determined by a Fokker–Planck equation that is decoupled from the size distributions of other species. If stems and precursors of different lengths were allowed to interact, the size distributions of all species would be determined by a

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure18}
\caption{Number densities for (a) iPP2 and (b) iPP3 after experiments at 138 °C. Open symbols show measurements, filled symbols show simulations. Rheological behavior simulated with the Rolie-Poly model. Model parameters: $c = 1 \times 10^{-14}$ m/s for iPP2, $c = 5 \times 10^{-17}$ m/s for iPP3.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure19}
\caption{Molecular stretch versus time for shear experiments on iPP2, $\gamma = 15$ s$^{-1}$ at 138 °C. Rheological behavior simulated with the Rolie-Poly model. Behavior for different shear times (4, 6, 8, 10, and 12 s) is shown.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure20}
\caption{Number densities for (a) iPP2 and (b) iPP3 after experiments at 138 °C. Open symbols show measurements, filled symbols show simulations. Rheological behavior simulated with the finitely extensible Rolie-Poly model. Model parameters: $c = 2 \times 10^{-14}$ m/s for iPP2, $c = 5 \times 10^{-17}$ m/s for iPP3.}
\end{figure}
system of coupled Fokker–Planck equations with a large number of unknown diffusion parameters, making the model useless for current purposes.

The Fokker–Planck equation for species \( i \) is

\[
\frac{\partial \rho_i(n, s, t)}{\partial t} = \frac{\partial}{\partial n} \left[ D_{gr}(n, s_i) \left( \frac{\partial \rho_i(n, s, t)}{\partial n} \right) + \rho_i(n, s, t) \frac{\partial \Delta F(n, s)}{\partial n} \right] = 0
\]  

(26)

where \( D_{gr} \) is the coefficient of growth diffusion and \( \Delta F \) is the driving force of crystallization of a precursor with sizes \( n, s \). A steady state distribution density can be derived following the same procedure as Ziabicki and Alfonso\(^4\),

\[
\frac{\partial \rho_{st}(n, s)}{\partial t} = \frac{\partial}{\partial n} \left[ D_{gr}(n, s) \left( \frac{\partial \rho_{st}(n, s)}{\partial n} \right) + \rho_{st}(n, s) \frac{\partial \Delta F(n, s)}{\partial n} \right] = 0
\]  

(27)

\[
\frac{\partial \rho_{st}(n, s)}{\partial n} + \frac{\rho_{st}(n, s)}{kT} \frac{\partial \Delta F(n, s)}{\partial n} = \frac{C}{D_{gr}(n, s)}
\]  

(28)

where \( C \) is a constant. We define \( A(n, s_i) = \frac{1}{kT} \frac{\partial \Delta F(n, s)}{\partial n} \). As an ansatz for the steady state distribution density we take

\[
\rho_{st} = \Phi(n, s_i) \exp \left( \int_{n}^{n_{\text{max}}} A(n', s_i) \, dn' \right)
\]  

(29)

where \( n_{\text{max}} \gg n^* \) is a maximum for the precursor size considered. Substituting into Equation (28) gives

\[
\frac{\partial \Phi(n, s_i)}{\partial n} = \frac{C}{D_{gr}(n, s)} \exp \left( - \int_{n}^{n_{\text{max}}} A(n', s_i) \, dn' \right)
\]

\[
\Phi(n, s_i) = \Phi(n_{\text{max}}, s_i) - C \int_{n}^{n_{\text{max}}} \frac{1}{D_{gr}(n', s_i)} \exp \left( - \int_{n}^{n_{\text{max}}} A(n', s_i) \, dn' \right) \, dn'
\]  

(30)

After applying the boundary conditions,\(^4\)

\[
\rho_{st}(n = 1, s_i) = \rho_1(s_i)
\]  

(31)

\[
\rho_{st}(n = n_{\text{max}} \gg n^*, s_i) = \Phi(n_{\text{max}}, s_i) = 0
\]  

(32)

the steady state distribution for species \( i \) becomes

\[
\rho_{st}(n, s_i) = \rho_1(s_i) \exp \left( \frac{\Delta F(n, s_i)}{kT} \right) \int_{n}^{n_{\text{max}}} \exp \left( \frac{\Delta F(n, s_i)}{kT} \right) / D_{gr}(n', s_i) \, dn' \exp \left( \frac{\Delta F(n, s_i)}{kT} \right) / D_{gr}(n', s_i) \, dn'
\]  

(33)

where we have introduced \( \rho_1(s) \), the steady state distribution of single stems as a function of stem length. \( \rho_1 \) can be expressed as \( \rho_1 = \phi(s) \rho_0 \), where the weighting function \( \phi(s) \) gives the fraction of stems that have length \( s \) \( (\int_1^s \phi(s) \, ds = 1) \) and \( \rho_0 \) is the total amount of single stems. The free energy of nucleation \( \Delta F \) is given by Equation (3) and schematically depicted in Figure 5. The coefficient of growth diffusion \( D_{gr} \) can be presented in the form\(^4\)

\[
D_{gr} = D_0(T/T_m) \sqrt{n/r_{gr}}
\]  

(34)

where \( D_0 \) is a constant and \( r_{gr} \) is the relaxation time related with self-diffusion of kinetic units subject to aggregation. The factor \( \sqrt{n} \) accounts for the number of sites available for attachment/detachment of a stem on the surface of an \( n \)-sized precursor. All terms of \( D_{gr} \) will divide out in the expression for the steady state size distribution, except for \( \sqrt{n} \). The total number of active precursors can now be calculated by integration of the steady state size distribution over all precursor lengths and the range of \( n \) for which precursors are active, i.e. \( n > n^* \) up to a certain maximum value \( n_{\text{max}} \).

\[
N_{p,a} = \int_{1}^{\infty} \int_{n^*}^{n_{\text{max}}} \rho(n, s) \, dn \, ds
\]  

(35)

Figure 21 shows the steady state size distribution \( \rho_{st} \) for one species; \( \phi = 1 \) thus \( \rho_0 = \rho_1 \). \( n_{\text{max}} \) is chosen such that increasing \( n_{\text{max}} \) does not visibly change the solution. The deterministic size distribution, calculated using the method explained in the “Theory” section, is shown for comparison. \( \rho_0 = \rho_1 \) was chosen such that both the statistical end...
deterministic size distributions have an equal amount of precursors with size \( n = 1 \).

Unfortunately, at this moment this steady state distribution is of no use for the flow-enhanced nucleation model presented in this study, for the following reasons. First, the statistical model actually describes sporadic nucleation, whereas the nucleation is mainly athermal in flow-induced crystallization. Second, the main motivation for deriving the statistical size distribution was to be able to extend the present model to two dimensions. Because we have no way to directly determine the weighting function \( \phi(s) \), we cannot derive a unique function for the two-dimensional precursor size distribution and therefore the statistical approach, as the deterministic approach, is only applicable to the one-dimensional case.

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