



# Analytic calculation of nucleation rates from a kinetic Monte Carlo simulation of flow induced crystallization in polymers

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## ABSTRACT

We present an analytically derived model for flow induced crystallization (FIC), based upon the recent Graham–Olmsted simulation. We use combinatorial techniques to calculate nucleation energy landscapes, which correctly predict simulation data. Applying both the analytic calculation and the simulation, we put forward a simple expression relating nucleation rate to polymer chain stretch. We also investigate bimodal blends, an important step to understanding polydisperse systems and eventually modeling industrial polymer melts.

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## 1. Introduction

The long chain nature of polymer molecules strongly affects their flow properties and crystallization. Semi-crystalline polymers comprise the largest group of commercially useful polymers, and when crystallized they are composed of amorphous or uncrystallized regions combined with crystallites. Crystallites are ordered sections of the semi-crystalline polymer where chains are closely packed and aligned. The amount and arrangement of crystalline material is a key part of the morphology of a semi-crystalline polymer. The morphology has a strong effect on the toughness, strength, permeability and other physical properties of the resulting plastic.

It is widely established that flow significantly increases the polymer crystallization rate, by increasing the density of nuclei [1–5]. This effect is known as flow induced crystallization (FIC), and is of both scientific and industrial importance. The formation of elongated nuclei-shaped like shish-kebabs is one of the more curious effects, the shish-kebab-shaped nuclei have a strong effect on the strength of a material [1,3,6–8]. Quantitative models for FIC are beginning to emerge [9,10]. These offer the possibility of controlling the properties of polymer products by altering the processing conditions. In recent experiments the most dramatic effects of FIC happen at low undercooling [3–8], that is, temperatures around the melting point. Nucleation is rare at low undercooling; this makes molecular dynamics prohibitively expensive and means that even

kinetic Monte Carlo simulations are costly. Thus analytic theory has an important role to play in this temperature regime.

### 1.1. Nucleation

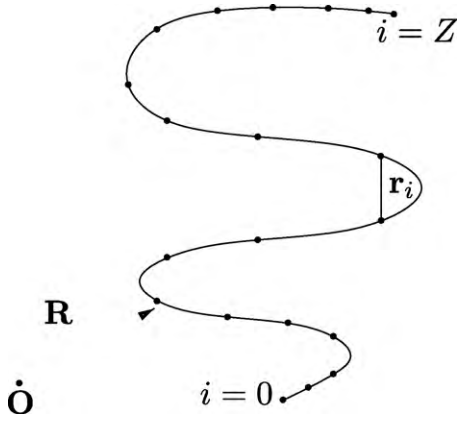
Polymer crystallization proceeds by nucleation and growth. Nucleation in polymers often is very slow because of the large free energy barrier to nucleation. The free energy of a crystal nucleus is a balance between the energy gained by the bulk volume and the surface energy cost. Hence small nuclei are unfavourable due to their relatively high surface energy costs. However, large nuclei are favourable because the bulk volume eventually dominates. The process of nucleation begins when a few monomers bond together. Such bonds are unfavourable due to the high cost of the solid–liquid interface and so they are subsequently very likely to break. However, if enough unfavourable events occur in sequence, a stable crystal is eventually formed. Once this nucleus is large enough, adding to it becomes favourable and spontaneous growth occurs. In this paper we focus on the process of reaching such a critical size.

Applying a flow to polymer chains has a significant effect on nucleation. Flow stretches the chains, lowering the chain entropy. This lowers the entropic cost of monomer attachment, increasing the thermodynamic driving force for crystallization and leading to faster nucleation.

### 1.2. GLaMM model

The Graham, Likhtman and Milner, McLeish (GLaMM) model is based upon the tube model, in which polymer chains are confined by neighbouring chains to a tube-like region and models fast

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**Fig. 1.** Diagram of space curve  $\mathbf{R}(s; t)$  which describes the movement of a polymer chain; an entanglement segment is shown by  $\mathbf{r}_i$ .

flows of entangled polymers [11]. It models the chain configuration under flow, down to the length scale of the tube diameter and has been extensively tested against experimental data for flow of amorphous polymers. It accurately predicts both stresses [11–13] and neutron scattering [14–16] from polymers under strong flow. All chains are considered to have the same molecular weight, i.e. a monodisperse distribution. A chain is divided into  $Z$  entanglement segments, each containing  $N_e$  Kuhn steps or monomers (here we use  $N_e = 100$  throughout). Chain configurations are described by a continuous time-dependent space curve  $\mathbf{R}(s; t)$ , where  $\mathbf{R}$  denotes the monomer spatial position and  $s \in (0, Z)$  is the monomer label, normalised by  $N_e$ , at time  $t$ , as shown in Fig. 1. Note that  $\partial \mathbf{R}(s; t) / \partial s$  is a tangent to the polymer chain at position,  $s$ . Hence  $\mathbf{R}(s; t)$  leads to the following continuous tube tangent correlation function:

$$\mathbf{f}(s, s'; t) = \left\langle \frac{\partial \mathbf{R}(s; t)}{\partial s} \frac{\partial \mathbf{R}(s'; t)}{\partial s'} \right\rangle. \quad (1)$$

A partial differential equation (PDE) is derived for  $\mathbf{f}(s, s'; t)$  from the relaxation mechanisms in the tube model, see [11]. In solving this PDE,  $\mathbf{f}$  is described discretely in  $s$  with the indices  $i$  and  $j$ , the chain is subdivided into  $Z$  entanglement segments each containing  $N_e$  monomers, with  $\mathbf{f}$  given by  $\mathbf{f}_{ij}(t) = \mathbf{f}(i, j; t)$ . For FIC, we are concerned with only the local tangent vector correlation function, i.e.  $i = j$ :

$$\mathbf{f}_{ii}(t) = \left\langle \frac{\partial \mathbf{R}(s; t)}{\partial s} \bigg|_{s=i} \frac{\partial \mathbf{R}(s'; t)}{\partial s'} \bigg|_{s'=i} \right\rangle \approx \left\langle \frac{\Delta \mathbf{R}(i; t)}{\Delta i} \frac{\Delta \mathbf{R}(i; t)}{\Delta i} \right\rangle.$$

For a single entanglement segment we have  $\Delta i = 1$  and  $\Delta \mathbf{R} = \mathbf{r}$  is the end-to-end vector of an entanglement segment. We refer to  $\mathbf{f}_{ii}(t)$  as  $\mathbf{f}_i(t) = \langle \mathbf{r}\mathbf{r} \rangle(i; t)$  from here on.

The GLaMM model computes  $\mathbf{f}_i(t)$  in a transient flow, providing the time-dependent stretch and orientation for each entanglement segment under flow. Deformation induced by flow modifies the free energy of a segment which affects the nucleation kinetics. At a time  $t$ , we have  $\mathbf{f}_i(t) = \langle \mathbf{r}\mathbf{r} \rangle(i; t)$  where each integer  $i$  from zero to  $Z$  labels the entanglement segment number. A free energy is used to derive the dynamics of the model, based on the statistics of random walks. Gradients in this free energy drive chain retraction and influence constraint release. Based on the same statistics, the elastic free energy change on stretching,  $\Delta F_i^{\text{el}}$  is derived for each entanglement segment subject to a constraint on its average end-to-end vector. This derivation is detailed in the appendix of Ref. [9].

$$\Delta F_i^{\text{el}} = \frac{1}{2} \text{Tr} \mathbf{f}_i - \frac{1}{2} \text{Tr} \ln \mathbf{f}_i - N_e \ln \left( 1 - \frac{\text{Tr} \mathbf{f}_i}{N_e} \right) \quad \text{for } i = 0, \dots, Z. \quad (2)$$

The length of a particular segment,  $i$ , is  $\sqrt{\langle \mathbf{r}_i^2 \rangle} = \sqrt{\text{Tr} \mathbf{f}_i}$ . This provides the dominant contribution to  $\Delta F_i^{\text{el}}$  through the first and third

terms in Eq. (2), but the orientation also contributes. If entanglement segments have different elastic free energy values  $\Delta F_i^{\text{el}}$ , then they are considered to be different species. Later, the total stretch ratio for the whole chain will be useful; which is given by the root mean square chain length normalised by its equilibrium value:

$$\lambda = \frac{1}{Z} \sum_{i=1}^Z \sqrt{\langle \mathbf{r}_i^2 \rangle}. \quad (3)$$

The tube model predicts that a large increase in relaxation times occurs around the length scale of the tube diameter. Thus smallest length scale required in the GLaMM model is the tube diameter or primitive path segment. All length scales below this are in equilibrium (with respect to the constraint imposed by deformation on longer length scales). However, nucleation occurs on the Kuhn step or “monomer” level. Nevertheless the monomer statistics can be calculated from the GLaMM model by assuming that monomers are in equilibrium with respect to the slow entangled dynamics. This crossover in timescales occurs at Rouse time of an entanglement segment,  $\tau_e$ , and from here on all deformation rates will be expressed in terms of  $\tau_e$ .

### 1.3. Kinetic Monte Carlo simulation of polymer nucleation

Stochastic simulation of nucleation is difficult because it is intrinsically a rare event. To ease this, the kinetic Monte Carlo Simulations of Graham and Olmsted use a variable step method [9,10]. This method suits nucleation, particularly with high barriers, since large timesteps are taken when nuclei are small, but for the rare occasions when we have larger nuclei, a more refined time resolution is employed. Nevertheless these simulations are still expensive for low undercooling when the free energy barrier to nucleation is especially high. In this work we derive an analytic framework to predict and extend the results given by these simulations.

Here we present a brief outline of the simulation algorithm of Graham and Olmsted, see [9,10] for full details. The simulation describes each nucleus as a list of  $N_S$  stems each containing a number of monomers, with the total number of monomers being  $N_T$ . Nuclei are composed of monomers represented by Kuhn segments of dimension  $b_l \times b_w \times b_w$ . It is assumed that  $N_T, N_S$  define a spheroid independent of the arrangement of monomers on the stems. Therefore  $N_T$  and  $N_S$  fix the volume and surface area and hence define the free energy. To compute the free energy landscape of nucleation for a single species we need the free energy of each individual crystal  $\mathcal{F}^*(N_T, N_S)$  with  $N_T$  total monomers on  $N_S$  stems.  $\mathcal{F}^*(N_T, N_S)$  is a balance between the bulk energy reduction and the surface area cost, defined by

$$\mathcal{F}^*(N_T, N_S) = -E_0^* N_T + \mu_S^* S(N_T, N_S), \quad (4)$$

where  $E_0^*$  is the dimensional bulk energy reduction of adding one monomer,  $\mu_S^*$  is the dimensional surface energy cost per unit area, and where  $S$  is the surface area of the spheroid. We nondimensionalise parameters as  $\mathcal{F} = \mathcal{F}^*/k_B T$ ,  $E_0 = b_l b_w^2 E_0^*/k_B T$ ,  $\mu_S = b_w^2 \mu_S^*/k_B T$  and  $S = b_w^2 \tilde{S}$ . For a prolate spheroid we have

$$\tilde{S}(N_T, N_S) = 2N_S + 2a_r \frac{N_T}{\epsilon_p \sqrt{N_S}} \arcsin \epsilon_p, \quad \epsilon_p = \sqrt{1 - \frac{N_S^3}{a_r^2 N_T^2}}. \quad (5a)$$

For an oblate spheroid we have:

$$\tilde{S}(N_T, N_S) = 2N_S + a_r^2 \frac{N_T^2}{\epsilon_o N_S^2} \ln \left( \frac{1 + \epsilon_o}{1 - \epsilon_o} \right), \quad \epsilon_o = \sqrt{1 - \frac{a_r^2 N_T^2}{N_S^3}}, \quad (5b)$$

where  $a_r = 3\sqrt{\pi} b_l / 4b_w$  is a dimensionless prefactor. From here on all free energies will be expressed in units of  $k_B T$  and we take  $b_l = b_w$  throughout.

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