

# Understanding flow-induced crystallisation in polymers: a perspective on the role of molecular simulations

Richard S. Graham

School of Mathematical Sciences, University of Nottingham, Nottingham NG7 2RD, UK.

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## Abstract

Flow induced crystallisation in polymers is an important problem in both fundamental polymer science and industrial polymer processing. The key process of flow-induced nucleation occurs on a very rapid timescale and on a highly localised lengthscale and so is extremely difficult to observe directly in experiments. However, recent advances in molecular dynamics simulations mean that flow-induced nucleation can be simulated at an achievable computational cost. Such studies offer unrivalled time and lengthscale resolution of the nucleation process. Nevertheless, the computational cost of molecular dynamics places considerable constraints on the range of molecular weights, temperature and polydispersity that can be studied. In this review I will discuss recent progress, describe how future work might resolve or work around the constraints of molecular simulation and examine how multiscale modelling could translate molecular insight into improved polymer processing.

## 1 Introduction

Understanding the dynamics of polymer crystallisation under flow is important to both fundamental polymer science and the polymer processing industry. Semi-crystalline polymers make up a very significant fraction of the world's production of synthetic polymers. Unlike simple molecules, the connectivity of polymer molecules means they crystallise into a composite structure of crystalline and amorphous regions. The proportion of amorphous and crystalline material, along with the arrangement and orientation of the crystals, is collectively known as the morphology. The crystal morphology strongly influences virtually all properties of practical interest, such as strength, permeability, and transparency. Furthermore, polymer crystallisation is radically influenced by the flows that are ubiquitous in polymer processing. Flow drastically enhances the rate at which polymers crystallise and has a profound effect on their morphology. By distorting the configuration of polymer chains, flow breaks down the kinetic barriers to crystallisation and directs the resulting morphology. This flow-induced crystallisation (FIC) in polymers is a fascinating example of an externally driven, non-equilibrium phase transition, controlled by kinetics. Furthermore, FIC is ubiquitous in industrial processing of semi-crystalline polymers. Understanding polymer FIC offers the tantalising possibility of using processing conditions to control the crystallisation kinetics and final morphology. Ultimately, this control of crystallisation could improve a wide range of final product properties. Due to its importance to both fundamental and industrial science, polymer crystallisation has

been widely studied in the polymer physics and chemistry communities. However, many key elements of the field also resonate strongly with the interests of the rheological community. Specifically, the central role of strong flow, the molecular origins of the phenomena and the importance to industrial processing.

Polymer crystallisation occurs via nucleation, whereby small crystallites are unstable due to the free energy cost of their crystal-liquid interface. To become stable crystallites must reach a critical size by diffusing over this nucleation barrier, a process that is very rare on the molecular scale. The nucleation rate depends exponentially on the barrier height and so flow-induced changes in the nucleation barrier drastically alter the nucleation rate. There is somewhat broad agreement on how flow affects polymer nucleation. Namely that polymer chains become unravelled (or stretched) under flow, which causes them to lose some conformational freedom and moves the chains towards the elongated configurations that are necessary for crystallisation. These flow-induced changes in chain configuration make the assembly into stable nuclei more readily achieved. However, the details of this mechanism and what modelling framework should be used to capture this are the subject of ongoing debate.

This review discusses how detailed molecular simulations can assist in understanding polymer FIC. It is intended to complement recent detailed reviews of FIC experiments [1–3] and coarse-grained modelling [4, 5]. I will focus discussion on linear polymers, as these constitute the simplest molecular topology and are widely used in experiments and processing. Section 2 briefly reviews existing experiments, highlighting current limitations that frustrate the development of a definitive model. Section 3 summarises current continuum level approaches to polymer FIC. In section 4 I discuss how molecular dynamics (MD) simulations can provide a complementary probe of polymer FIC, particularly in key areas of experimental difficulty. Section 5 reviews existing MD studies, with a focus on nucleation and flow. Continuing, section 6 discusses future directions for MD simulations, emphasising methods to close the gap with experiments and methods to integrate modelling at different levels of coarse-graining. Section 7 contains summary and conclusions. Figure 1 shows the modelling techniques discussed in this review, in order of increasing level of coarse-graining.

## 2 Overview of experiments

The basic phenomena of polymer FIC have been known for many years [6–9]. Sufficiently strong flows rapidly accelerate the crystallisation kinetics. This acceleration of kinetics stems from a greatly enhanced nucleation density, with these extra nuclei appearing during or soon after the flow. At even higher flow rates the crystal morphology switches from spherulitic crystals to the highly aligned shish kebab structure [6, 10–12]. Both the enhanced nucleation and degree of alignment increase with increased flow rate, applied strain, molecular weight and concentration of long chains [9, 12–14]. More dramatic flow-induced effects can often be achieved by increasing the temperature to just below, or even slightly above, the nominal crystal melting temperature [12, 15–17]. Several decades of experiments have added a rich array of quantitative data to these basic phenomena (see, for example refs [11–15, 17–23]). Recent experimental work has elucidated the role of intermediate phases during flow-induced nucleation, including the orthorhombic, hexagonal and non-crystalline  $\delta$  phases in polyethylene [24] and the helix and all-trans configurations, along with other flow-induced precursors, in polypropylene [3], along with its different crystal polymorphs [25]. Furthermore, studies have shown that flow can produce crystal structures that

are long-lived even above the quiescent melting temperature (see for example [12, 17, 26]). Recently Rhoades *et al.*[16] used fast-scanning chip calorimetry to show the influence of cooling rate on the crystallisation kinetics. Detailed discussions of relevant experimental work can be found in other recent reviews [1–3, 27]. Despite this substantial experimental progress, key elements of polymer FIC are not currently possible to probe directly in experiments, as I will describe below.

There is currently no definitive set of experiments that elucidates the precise nature of nucleation under flow. The effect of flow on nucleation can be measured indirectly by probes of crystallisation kinetics and directly by counting nucleation events when the resulting crystallites become large enough to see with a microscope [18, 22, 28] or detect by fast-scanning chip calorimetry [29]. X-ray and neutron scattering reveal transient structural and orientational changes [11, 26, 30], provided their scattering signal overcomes scattering from other parts of the melt. Techniques such as scanning electron microscopy and atomic force microscopy produce stunningly detailed images of the later stages of morphological development and growth [10, 31]. However, all of these probes give information about the nucleus long after the critical nucleation event has taken place. The critical nucleus is too small and too fast to be resolved with current experimental techniques. Attempts to infer details of the nucleation from the wealth of later stage measurements are plausible but such approaches have not, as yet, definitively identified the nucleation mechanism.

The above experimental challenge affects both quiescent and flow induced nucleation. There is a further difficulty that is specific to FIC. Synthesising monodisperse crystallisable polymer chains in sufficient quantities for flow experiments is very difficult. Even when possible, the resulting molecular weight is usually too low for the chains to be stretched in well-controlled experiments. A common solution when studying the rheology of amorphous polymers is to conduct experiments at temperatures close to the glass transition where the chain dynamics are very slow. However, this is unsuitable for FIC experiments as low temperatures drastically accelerate the nucleation kinetics. Another solution is to create a model bimodal blend, containing a small amount of long chains in a matrix of short material. However, the synthesis in sufficient quantities is still challenging so only a small number of studies have involved narrowly distributed melts and their blends [12, 14, 19, 27, 32] and most FIC experiments are on melts with broad, continuous molecular weight distributions. These polydisperse melts contain a broad distribution of relaxation times, which leads to a broad spread of chain stretch under flow. Typically, this stretch distribution comprises a small fraction of highly stretched long chains, a greater fraction of somewhat stretched moderate length chains and a significant fraction of undeformed short chains. Predicting accurately and reliably this distribution of chain stretch under flow is not straightforward (see section 3.1). Even if the stretching distribution can be computed, it is unclear which part of the stretch distribution determines the nucleation rate. Is it the rare highly stretched chains, the more common moderately stretched chains or a cooperative effect across a range of species? Thus the insufficient spatial resolution and issues of polydispersity in experiments make extracting detailed information about the flow-induced nucleation mechanism problematic and indirect.

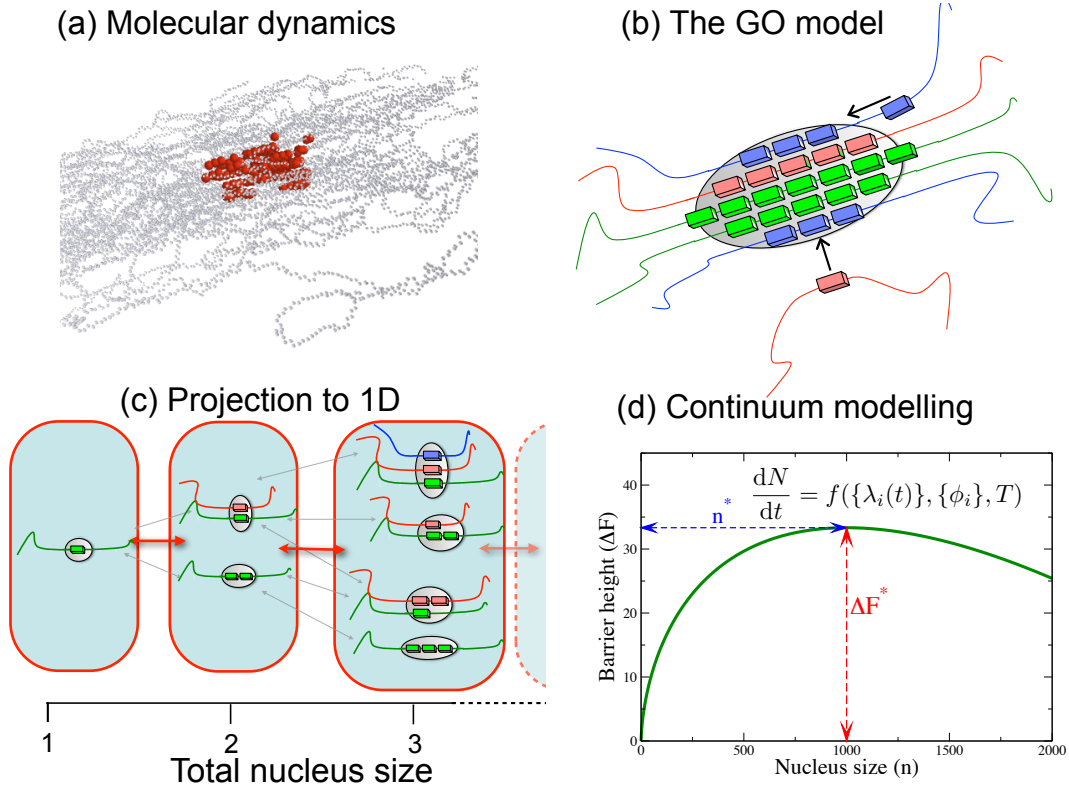


Figure 1: Overview of modelling techniques discussed herein, ordered by increasing level of coarse-graining. (a) An MD snapshot of a crystal nucleus of 100 monomers, approximately the critical nucleus size, from a C1000 melt under shear flow (courtesy of Muhammad Anwar) (b) Schematic diagram of the nucleus structure in the GO model; chain colours represent different degrees of stretch. (c) Projection of the GO model onto a single variable. (d) A 1D nucleation barrier leading to a closed form expression for the nucleation rate,  $\frac{dN}{dt}$ , which depends on the degree of stretch of each chain species,  $\{\lambda_i(t)\}$ , and its concentration,  $\{\phi_i\}$ , along with temperature,  $T$ .

### 3 Overview of continuum-level modelling

Modelling polymer crystallisation is a formidable problem. Strong covalent bonds mean that connected atoms must move co-operatively, whereas unbonded atoms interact via weak van der Waals forces. The resulting huge range of lengthscales spans the monomer size ( $< \text{nm}$ ) up to crystals of near macroscopic dimension ( $\sim \mu\text{m}$ ). The range of timescales is even wider, covering the monomer relaxation time ( $\sim 10^{-9}$  sec) to the quiescent nucleation timescale (hours at low under-cooling). The key physical processes emanate from very rapid local motion on the monomer scale, while the phenomena that influence melt processing and control solid-state properties occur on the meso and macroscales. Modelling of FIC in the complex flow geometries that occur in polymer processing requires macroscale continuum models, where strong coarse-graining assumptions are required to remove the fast degrees of freedom at the monomer and sub-chain level. These models typically use ordinary differential equations to describe the formation and development of crystallites [15, 33–40]. The structure of these models is broadly

1. Compute the **chain deformation** under flow via a rheological model;

2. From the chain deformation compute the current **nucleation rate** (and hence the change in the number density of stable crystallites);
3. Evolve the **growth** of all current stable crystallites.

These models play a key role in establishing the required mathematical framework for FIC modelling, making possible models of FIC during polymer processing and defining and isolating the stages of modelling where more detailed approaches can contribute. However, there are several places where less coarse-grained approaches are required to improve these models. Specifically, predicting chain deformation under flow and how this controls the nucleation rate, particularly for polydisperse systems.

### 3.1 Modelling chain deformation

The chain deformation step in models of polymer FIC is founded upon decades of research on the non-linear rheology of entangled polymers, mostly based around the tube model [41–43]. Models for the stretching dynamics for melts of monodisperse chains have been extensively validated against a wide range of experiments [44–46]. However, as discussed above, polymer FIC experiments and industrial processing are both overwhelmingly performed with polydisperse resins, for which non-linear tube models are less well established. In FIC models the melt flow is usually modelled by a multi-mode version of a simple constitutive equation. Here each Maxwell-mode of the linear spectrum is augmented with a set of non-linear parameters, which are fitted to non-linear stress measurements. This fitting approach has several issues. It is unknown what fraction of the melt is represented by each mode and the flow model neglects non-linear coupling between different elements of the melt. Furthermore, the stress response of a polydisperse melt comprises contributions from each chain species. Thus even if a multimode model agrees with non-linear stress data, this does not guarantee that the stretching dynamics of each individual chain species are accurately captured. It is possible, particularly for broad and bimodal distributions, that the small fraction of chains in the high molecular weight tail make a negligible contribution to the total stress but have a strong influence on the nucleation. Finally, an important tool for optimising processing and crystallisation is to tailor the molecular weight distribution, either by changing reactor conditions or by blending separate resin batches. To predict the effect of such changes multimode models require extensive non-linear measurements on the new resin and a refitting of parameters.

Systematic and predictive non-linear flow models for polydisperse melts have only begun to emerge very recently [47, 48]. These models discretise the true molecular weight distribution into a set of modes and use the tube model to accurately account for the dynamic coupling between these modes, giving more confidence that they predict accurately the dynamics of each chain species, rather than just the total stress. Other significant advantages of these models are that they predict non-linear data without new parameter fitting and can predict the effect of changes in molecular weight distribution. These next-generation models of polymer flow will have a key role in both interpreting FIC measurements and predicting FIC during industrial processing.

### 3.2 Predicting nucleation

We now progress to the step of predicting the nucleation rate from the chain deformation. Existing FIC models [34, 37, 38] generally assume that the nucleation is dominated by the stretch of the longest

Maxwell mode,  $\lambda_N$ , which is only true for very specific molecular weight distributions. They further assume some empirical form for how the nucleation,  $\dot{N}$  rate depends on  $\lambda_N$ , which is fitted to flow-induced nucleation data. For a detailed comparison of different models of this type see ref [49]. These assumptions lead to two prominent difficulties. Firstly, this approach merely describes experiments and cannot infer information about the flow-induced nucleation mechanism from experiments. Secondly, the approach provides no way to predict how  $\dot{N}$  changes with either temperature or the molecular weight distribution, especially the length and concentration of long chains. Changes in these quantities require extensive new experiments and refitting of the model. Thus current FIC models do not meet two key requirements for effective modelling of polymer processing, namely, non-isothermal flows and the capacity to optimise processing by tailoring the molecular weight distribution. Recent work has begun to address these weaknesses [25, 39], but still requires strong *ad hoc* assumptions. Specifically, that the longest relaxation times can be scaled with the average molecular weight, that the relative change in  $\dot{N}$  with chain stretching does not change with temperature, that a single long chain mode is the only contributor to  $\dot{N}$  and that  $\dot{N}$  is proportional to the long chain fraction. Thus, a key question is how to compute  $\dot{N}$  from the combined effect of many differently stretched chain species, at different concentrations (see figure 1(d)).

## 4 Molecular dynamics simulations

As outlined above a full quantitative and predictive understanding of how chain stretch affects nucleation is lacking. In current experiments the nucleation mechanism cannot be observed directly and the key role of chain stretching is obscured by polydispersity. Molecular dynamics (MD) simulations have the potential to address these two issues. In MD classical dynamics are applied to atoms or other molecular subunits. Each atom obeys Newton’s second law and interacts with its neighbours through force fields that represent both chemical bonds and van der Waals interactions. There can be many thousands of atoms and this huge system of coupled differential equations is solved numerically to provide a detailed computer model of molecular motion [50–52]. A review of simulation techniques for polymer crystallisation was recently published by Rutledge [53]. The huge spatial and temporal resolution of MD means it can resolve individual nucleation events (for example see figure 1(a)). Furthermore, MD simulations can be performed on perfectly monodisperse systems and at sufficiently large flow rates to deform even very short chains.

### 4.1 MD as an alternative to experiments?

Since the primary advantages of MD correspond to areas of experimental difficulty in polymer FIC, it is tempting to view MD simulations as a complementary alternative to experiments. While there is some promise to this notion it ought to be exercised with care. Crucially, the accuracy of MD simulations is limited by the accuracy of the force-field. That is, the representation of how nearby atoms interact. In principle, these interactions can be specified from quantum mechanics but, in practice, this is implausible for large macromolecules. Instead, polymer simulations typically use semi-empirical force-fields and neglect non-additive 3 body interactions, that is how the interaction between two atoms is modified by the presence of nearby third atoms. This semi-empirical force field can be designed to correspond to a

particular chemical species (eg polyethylene or polypropylene) and tweaked to capture quantitatively as many measurements as possible, but it will not be a completely faithful representation of the molecular interactions. This is particularly true for united atom descriptions, in which monomer units comprising many atoms are treated as a single effective atom. However, this is not necessarily a serious deficiency because of the high degree of universality in polymer dynamics. Via this concept, which is well-established for polymer dynamics [41], insight gained from one chemical species (or simulation force-field) is also valid for a different species. It is unclear, how far this universality extends to crystallisation as the crystal structure is sensitive to the chemical details of the constituent chains. However, the same core set of polymer FIC phenomena, namely enhanced nucleation, the transition to oriented crystallisation and the role of critical work, that are well established for polyethylene and polypropylene are also emerging for other chemical species, such as isotactic polystyrene [32], poly-1-butene [54], polyamide [55] and polycaprolactone [56]. Thus, we can regard MD as a detailed way to observe how a model polymer, as specified by the force-field, crystallises under flow. Hence simulations will provide useful insight into how to model polymer FIC rather than definitive quantitative predictions for a specific polymer. Universality in polymer dynamics then suggests that a model derived with guidance from detailed observations in MD, could be mapped to a real polymer species by changing a small number of chemistry-specific parameters, obtained from experiments. Of particular note in this context is that the united atom force field for polyethylene, as used in the majority of studies discussed herein, crystallises into the hexagonal phase rather than the more common orthorhombic phase [57]. All-atom simulations of polyethylene crystallisation do show orthorhombic crystals (see for example [58, 59]) but the range of chain lengths that can be simulated is smaller for these more detailed simulations.

## 4.2 Computational limitations

Computational costs significantly constrain what can be achieved with MD [51, 52]. Nucleation in polymers is at the edge of what can currently be achieved and this necessitates compromises in terms of box size, chain length and temperature [53, 60, 61]. The simulation cost per timestep is approximately  $\propto L^3$  where  $L$  is the box length. This assumes the cost is proportional to the number of atoms, which is approximately true when a constant spherical cutoff is used [50]. Typically the box size is chosen to comfortably accommodate the chain size, which gives a large enough box for primary nucleation and lamella growth but does not allow full spherulites or shish kebabs to be simulated. Furthermore, the simulation cost increases very rapidly with chain length. For entangled polymers, the longest relaxation time,  $\tau_{long}$ , scales with molecular weight,  $M_w$ , as  $\tau_{long} \propto M_w^{3.4}$  [41]. An initial simulation comparable in length to  $\tau_{long}$  is needed to properly equilibrate the system before crystallisation can be studied. Finally, nucleation is fundamentally a rare event: it is characterised by very frequent unsuccessful attempts to form a stable nucleus, with very occasional successes [62]. A successful nucleation event is, itself, fast, but requires long simulation times because it occurs so rarely [63]. The success frequency increases strongly with decreasing temperature and so MD simulations that pertain to primary nucleation are typically performed at high-undercooling [57]. The percentage undercooling is given by  $(T_m - T_c)/T_m \times 100\%$ , where  $T_c$  and  $T_m$  are the crystallisation and quiescent melting temperatures respectively, both measured in Kelvin.

## 5 Review of MD studies of polymer nucleation and FIC

This section discusses prior MD simulations for nucleation in polymers, both quiescently and under flow. Early nucleation simulations focused on observing spontaneous nucleation, whereas more recent studies have begun to quantify nucleation in simulations. The most widely studied system is a united atom description of polyethylene, in which CX denotes chains containing X carbon atoms per chain. The entanglement molecular weight for polyethylene is 60-90 carbons [57], meaning most studies are on unentangled or very weakly entangled chains. Yamamoto *et al.* [60] observed primary nucleation of C100 chains at 13% undercooling. Zerze *et al.* [64] simulated C20 chains at  $\sim 19\%$ - $35\%$  undercooling and presented methods for investigating nucleation in this system. There have also been nucleation studies on other coarse-grained force-fields [61, 65]. Gee *et al.* [61] simulated C240 and C768 using a stiffened united atom force-field and saw evidence that a spinodal liquid-liquid phase separation assists nucleation. Luo and Sommer [65] simulated a coarse-grained polyvinyl alcohol system and used primitive path analysis to draw correlations between the entanglement state and the nucleation time.

Simulating non-linear flows for polymers requires non-equilibrium molecular dynamics. The desired flow field is imposed through the SLLOD equations of motion [66] and the boundary conditions must be consistent with the flow field, with the usual choices being Lees-Edwards for shear, Kraynik and Reinelt for planar extension and recent generalisations for uniaxial extension [67]. Temperature is maintained either through the Nose-Hoover [68] or dissipative particle dynamics (DPD) thermostat [69]. More detailed discussions of these algorithms and the care required in their implementation can be found in the following references [50, 66, 70]. Simulations of nucleation in united atom models of polyethylene have been extended to include flow. Ko *et al.* [71] applied a constant load to C400 chains above the melting temperature and then quenched to  $\sim 40\%$ - $9\%$  undercooling to observe rapid nucleation and growth. Lavine *et al.* [72] simulated C25-C400 chains under uniaxial stress, imposed at  $\sim 40\%$ - $14\%$  undercooling, and found that stress promoted nucleation but suppressed growth. Jabbarzadeh and Tanner [73, 74] simulated C20, C60 C162 melts, under steady and preshear and observed nucleation for undercooling in the range 11%-16%. These simulations [73] also considered the effect of cooling rate on flow-induced crystallisation, which is an important parameter for polymer processing.

### 5.1 Quantifying nucleation from simulations

Recent studies from the groups of Rutledge [57, 58, 68, 75, 76] and Schilling [69, 77] aimed to, not just observe nucleation, but to quantify its rate and elucidate its mechanism. Both groups achieved this by applying a collection of analysis tools. The first of these was the use of order parameters to identify crystalline monomers and hence determine the nucleus size. Secondly, they used committor analysis, which involves running short trajectories of pre-prepared nucleus configurations to determine the probability of this configuration melting or crystallising. A final analysis technique was mean first passage time analysis, which quantifies the time required to first observe a nucleus of a given size; and interpretation of MD trajectories with models from classical nucleation theory, that is low-dimensional models of nucleation that are analytically tractable.

Yi, Locker and Rutledge [57, 75] observed and quantified homogeneous nucleation in C20, C150 and C1000 at about 30% undercooling. They analysed their first passage time data using a 2D cylindrical



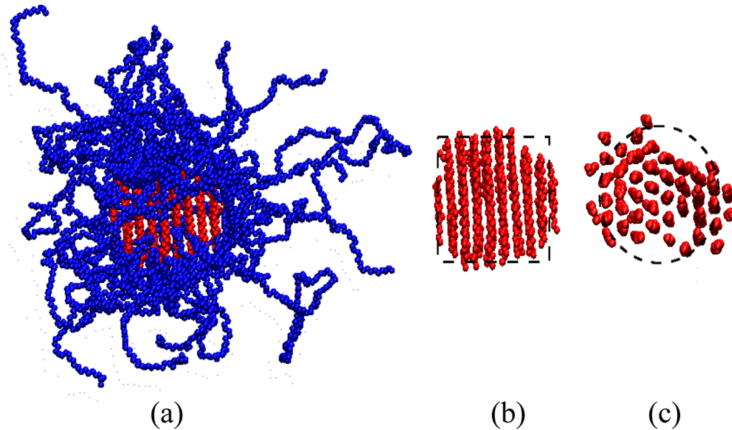


Figure 2: Snapshot of a nucleus of 800 monomers from a simulation of C150 chains by Yi *et al.* [57]. Red monomers are in the nucleus; blue monomers are outside the nucleus but are from chains that participate in the nucleus; and all other chains are not shown. (a) All chains in the nucleus. (b) Nucleus side view. (c) Nucleus top view. Reprinted with permission from ref [57]. Copyright (2013) American Chemical Society.

nucleation model to obtain details of the nucleation barrier and nucleation rate. Significantly, the quiescent nucleation rates for C150 and C1000 were very similar, suggesting that nucleation is controlled by local rearrangement of subchain segments rather than global chain motion. Yi *et al.* [57] extended their results to lower undercooling by using committor analysis to estimate the critical nucleus size for temperatures up to 320K (about 19% undercooling). They then used classical nucleation theory to extract surface energies and, ultimately, to estimate the nucleation rate at these elevated temperatures. The nucleation barrier had a linear dependence on temperature, meaning that the nucleation rate could be further extrapolated to higher temperatures. A nucleus snapshot from Yi *et al.* [57] is shown in figure 2.

The mean first passage time analysis used in the above studies [57, 68] has recently been extended by Nicholson and Rutledge [76] to explore, in greater detail, the distribution of first passage times. Specifically, Nicholson and Rutledge [76] developed a model that can capture non-exponential distributions. Indeed, as shown in figure 3, they demonstrated that their MD data had a strongly non-exponential distribution of first passage times, which they attributed to the lag-time in establishing steady state nucleation following a quench. This illustrates how such analysis can extract further details from the MD data, which will provide more detailed guidance on coarse-graining assumptions. Specifically, the quantitative details of this lag-time are likely to be sensitive to both the nucleation barrier and kinetics.

Anwar *et al.* [77] studied quiescent nucleation of C20 at 19% under-cooling. They used several distinct order parameters to analyse their trajectories, including order parameters sensitive to local density, both global and local chain alignment and crystal ordering. This enabled them to account to some extent for the intermediate stages observed experimentally [3, 24] and provided details of the nucleation mechanism. They used committor analysis to determine the critical nucleus size and observed that nucleation proceeds by chain alignment, chain straightening and then, finally, local crystallisation. They also saw that chains tend to attach in locally correlated clusters. Significantly, they demonstrated all of these conclusions without needing to assume any model of nucleation. Anwar *et al.* [69] subsequently showed that the

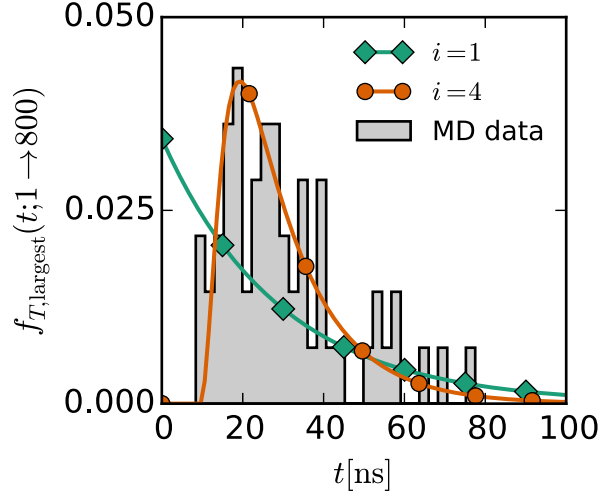


Figure 3: Fitting of the nucleation model of Nicholson and Rutledge [76] to MD data for the distribution of first passage times to form a crystal cluster of 800 monomers ( $f_{T, \text{largest}}$ ). The MD simulations are for C20 at 17% undercooling. Here,  $i$  is number of cumulants used in the model, with  $i = 1$  giving a single exponential distribution. Reprinted from ref [76], with the permission of AIP Publishing.

nucleation mechanism is unchanged for weakly entangled C150 molecules and used mean first passage time analysis to extract the induction time and critical nucleus size, within the classical nucleation framework.

Nicholson and Rutledge [68] studied the nucleation of C20 at 17% undercooling under steady state of both shear and extension. They computed the mean first passage time against crystallite size from simulations and used a 1D nucleation model to extract quantitative information about the nucleation rate, barrier height, critical nucleus size and nucleation kinetics. Their nucleation model assumed that nuclei grow at constant shape, which they verified from their simulations. They also observed that high strain rates influence nucleation through their effect on nematic order rather than the end-to-end vector.

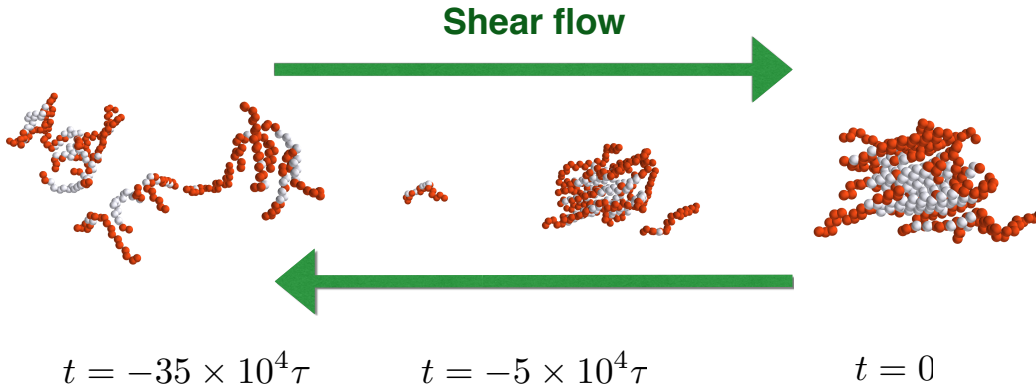


Figure 4: Simulation snapshots showing the formation of a critical nucleus (formed at  $t = 0$ ) for C20 at  $\dot{\gamma}\tau = 0.001$ , where  $\tau$  is the Lennard-Jones time. Only chains that participate in the critical nucleus are shown and monomers that are crystalline in the critical nucleus are coloured grey, while the other monomers are red. Results and figures from [78]

Anwar *et al.* [69] also simulated nucleation in C20 and C150 at 20%-30% undercooling under start-up

shear. They reported the dependence of the nucleation rate on shear rate and identified the critical shear rate for the onset of FIC. For both chain lengths this critical rate was at a Weissenberg number, with respect to the chain Rouse time, of  $\sim 1$ , a flow regime that generally leads to chain stretching. For C20 they also compared the effect of temperature on nucleation rate at a fixed shear rate, deep in the FIC region. They saw only a factor of 5 decrease in nucleation rate despite a decrease in undercooling from 19% to 11%, suggesting that the sensitivity to shear increases with decreased undercooling. The nucleation mechanism at low shear rates was the same as for quiescent conditions. However, at high shear rates the early stages were different. The unentangled C20 chains aligned and straightened simultaneously, whereas the semi-entangled C150 chains first aligned and then straightened. Simulations snapshots of the formation of a critical nucleus under flow are shown in figure 4.

## 5.2 Discussion of MD

The above studies on quantifying nucleation [57, 68, 69, 75, 77] combined several important techniques to exploit the high temporal and spatial resolution of MD. First is the use of order parameters to classify crystalline particles. This allowed transient crystalline clusters to be identified and quantified in terms of their size, shape and likelihood of growing into a stable crystal. Anwar *et al.* [69, 77] took this further by considering other forms or ordering such as alignment and increased density, which elucidated the ordering sequence during nucleation. The further refinements to order parameters are likely to be needed to fully explore the role in nucleation of intermediate phases and crystal polymorphs. The order parameter effectively takes the enormous number of degrees of freedom in a simulation box snapshot and reduces these to a smaller number that locates and counts the monomers in the nucleus. This projection of simulation data to lower-dimensions will be important when comparing with experiments and when using MD simulations to inform more coarse-grained models. To reach continuum level models, several levels of projection may be needed (see figure 1 and section 6.2) and each must be performed with care. Specifically, the chosen order parameter should be a relevant measure of progress of nucleation, which can be a challenging task. A second, and related, technique is using a simple nucleation model to analyse MD results. This continues the process of reducing the number of spatial degrees of freedom to describe the nucleus. The above studies used a low-dimensional version of classical nucleation theory, in which the nucleus was characterised either by just the total number of crystal monomers (1D) or the nucleus length and diameter (2D). The use of mean first passage time data integrates the temporal information from the simulation trajectories into the analysis. Effectively, the authors found the parameters of classical nucleation theory that are most consistent with the mean first passage time data from their MD simulations. This quantified the nucleation barrier, critical nucleus size and nucleation rate, data that can be compared to experiments and used to inform models.

One might anticipate deviations from classical nucleation theory, or at least the need for a higher dimensional nucleus description, especially under strong flow conditions or for wide molecular weight distributions. Thus we can ask how consistent is the chosen form of classical nucleation theory with the MD data? This question was explored somewhat by Yi *et al.* [75] who selected, from a range of possibilities, the order parameter that was most consistent with their nucleation model and by Nicholson and Rutledge [68] who verified one of their model assumptions, namely that nuclei grow with self-similar shapes, was consistent with the crystal clusters extracted from their simulation snapshots. This question

has been explored further by Chen *et al* [79] who used the “plunger” method to measure the crystal-melt interfacial free energies in an atomistic simulation of polyethylene chains, with the ultimate aim of providing an independent test of whether classical nucleation theory can predict nucleation rates in polymers.

Despite the above progress, there remains a gap between experiments and MD simulations. Simulations are on weakly entangled monodisperse chains at high undercooling (10-30% undercooling). In contrast, experiments often involve very highly entangled, polydisperse melts, with FIC occurring at low undercooling or even just above the nominal melting temperature [32]. Similarly, polymer processing typically involves long chains and wide temperature ranges, including regions of low undercooling. Addressing this gap will involve a role for more coarse-grained models and simulations (see section 6.1).

### 5.3 Kinetic Monte Carlo simulations

Kinetic Monte Carlo (kMC) methods offer coarse-graining by discretising some degrees of freedom in the model. Lattice Monte Carlo simulations have been used to model flow induced crystallisation and strain induced nucleation [80, 81]. In these simulations all monomers are resolved but their positions are confined to a lattice. Time is advanced via a kinetic Monte Carlo algorithm. At a further level of coarse-graining are kMC models that do not resolve all monomers and instead resolve only the crystallised monomers. This approach was used to capture quiescent crystal growth [82, 83] and later applied to flow-induced nucleation by Graham and Olmsted [63, 84]. The Graham and Olmsted (GO) model evolves a discretised nucleus (see figure 1(b)), with addition and subtraction of monomers via a free energy condition. The model is iterated stochastically via a kMC algorithm and flow is captured with the GLaMM model [44], a full-chain pre-averaged rheological model. The GO model has a level of coarse-graining between full chain molecular simulations and classical nucleation theory: nucleus degrees of freedom are projected onto a lower-dimensional space but some limited spatial resolution of monomers within the nucleus remains. Its advantages are that it is fast to compute; requires only quiescent nucleation parameters; and can handle chains of arbitrary length, entanglement and polydispersity, provided there is a suitable flow model (see section 3.1). A fast nucleation algorithm [85] has allowed the simulation of high nucleation barriers, which has enabled successful comparison with FIC experiments [86]. All kMC algorithms require a priori choices for which moves are simulated and their rates. This is a key limitation of the KMC approach, but also presents an opportunity to extract the required information from MD simulations. Thus, the GO model’s high level of coarse-graining inevitably leads to some disadvantages. Specifically, it makes strong coarse-graining assumptions about the nucleus structure, which are plausible but, as yet, unverified; it is not known how to vary the model’s parameters with temperature; and, for shish formation, the model predicts only the early stages.

The GO model’s relative simplicity has also allowed some potentially very useful analytic progress. Hamer *et al.* [87] derived an exact analytic expression for the nucleation barrier under flow, although the nested sums in the resulting expression make it sufficiently unwieldy that it has yet to find a useful application. Continuing, the same authors developed a method to project the GO model onto a one-dimensional nucleation model [88] (see figure 1(c)). Jolley and Graham [86] then solved this model analytically, via some empirically validated approximations. The result is a version of classical nucleation theory that captures the GO model’s simulation results. This leads to a simple closed-form expression

that accurately predicts the nucleation rate in the GO model for monodisperse polymers under flow.

## 6 Future simulation work

### 6.1 Closing the gap between MD and experiments

As discussed at the end of section 5.2, there are three factors that separate achievable MD simulations and current experiments. These are temperature, molecular weight and polydispersity. As the temperature increases towards the melting point, nucleation becomes increasingly rare until it no longer occurs within the length and timescales that are accessible in MD. Nucleation is an archetypal rare event, as it comprises very frequent and short-lived attempts to perform a transition that are successful only very rarely. This is a very widely occurring problem across molecular simulation and a number of powerful techniques exist to bias the simulation towards sampling transition events [62, 89–92]. Indeed, such an approach has allowed arbitrarily low undercooling to be simulated in the GO model [85] and Yi *et al.* [57] used rare event techniques to extrapolate their quiescent MD simulations to low undercooling. Extending rare event techniques to MD simulations of polymer nucleation under flow, although technically challenging, will provide a plausible route to simulating experimentally relevant temperatures. A key factor in applying these techniques efficiently is a good choice of order parameter. Existing parameters may be adequate but further refinement may be necessary. Simulations at lower undercooling may also reveal a greater role for entanglements due to the larger critical nucleus size.

Increasing molecular weight in MD causes the computational cost to grow very rapidly, due to the strong increase in molecular relaxation times and the need for larger simulation boxes (see section 4.2). Consequently, current MD simulations of polyethylene are limited to chains of about 1000 carbons ( $\sim 12$  entanglements). Because of the steeply rising cost, accessible chain lengths are not likely to increase significantly, even if there was a dramatic increase in available computing power. In contrast experiments are generally performed on much longer chains, as these are more readily deformed under flow. The Rouse time of a melt of C1000 chains at 430K is  $\sim 10^{-6}$  sec and so is impossible to stretch in a conventional rheometer, where shear rates are typically limited to  $< 100\text{sec}^{-1}$ . An interesting possibility is recent work using an injection moulder as a high shear rheometer [93]. This can achieve deformation rates of  $\sim 10^7\text{sec}^{-1}$ , which is sufficiently fast to deform the moderately entangled polyethylene chains that can be accessed in MD.

Polydispersity is a significant problem for MD simulations. Long chains are prohibitively expensive as they require long equilibration and large simulation boxes. Unfortunately, long chains will inevitably be present in the high molecular weight (HMW) tail of melts with a continuous molecular weight distribution. Furthermore, these HMW chains will influence FIC even if they are at low concentrations because they are the most readily deformed by flow. MD simulation of a broadly distributed melts would require an unfeasibly large simulation box to accommodate the longest chains. Furthermore, many repeat runs would be needed obtain good statistics on the influence of the important but highly dilute HMW chains. Simulations of bimodal blends are possible but must conform to MD's limited range of molecular weights. In contrast, the majority of experiments are on polydisperse melts. Possible routes to monodisperse materials for experiments are fractionated materials (see for example ref [32]) or hydrogenated polybutadienes [12, 19, 27]. However, production of sufficient quantities of these materials for rheometric measurements

is a significant challenge.

In summary, it may be possible in the near future to close some of the gaps between MD and experiments for polymer FIC, particularly by using rare event algorithms in MD [62, 89–92] and ultra-high speed rheometers in experiments [93]. However, the computational cost of simulating HMW chains seems unlikely to be solved in the near future. Hence, there remains a need for coarse-grained simulations to access the very long chains that are present in virtually all realistic melts.

## 6.2 Linking to other levels of modelling

As described above there are several prominent gaps between experiments and MD simulations, with the most problematic being long chains. Long chains are ubiquitous in polymer processing because of the HMW tail in polydisperse melts. Thus, coarse-grained approaches are likely to have a key role in modelling polymer FIC in long chains. A promising potential roadmap is to learn the key physics of FIC from detailed MD simulations of moderately-entangled monodisperse chains, use this insight to inform more coarse-grained approaches, and then validate these models against experiments on long-chain polydisperse melts. This will require a tightly integrated family of progressively coarse-grained simulations and models, covering all relevant lengthscales. A final step is to derive predictive macroscale continuum models suitable to model polymer processing. This section will focus on predicting the nucleation rate under flow as a prerequisite to explaining and predicting more drastic FIC effects such as shish-kebab formation. I will use the GO model as an illustrative example because some integration tools are already in place [85, 88] and some analytic solutions are known for this model [86, 87]. Similar approaches may also enable other coarse-grained simulation methods, such as [80, 81], to bridge from MD to continuum models.

### 6.2.1 Coarse-graining from MD to the GO model

In this section I will outline some ways that MD simulations could verify the assumptions and predictions of the GO model and address its weaknesses. The GO model makes unverified assumptions about the nucleus structure, namely the arrangements of monomers into stems and which spatial details ought to be retained. Basic predictions of the GO model that cannot be verified with current experiments, could be directly checked by MD simulations. For example, the GO model predicts that, for monodisperse chains, the change in nucleation barrier depends only on chain stretch and is independent of temperature and molecular weight [86]. Furthermore, the relationship between the barrier modification and chain stretch is sensitive to the GO model’s assumptions about the nucleus structure. Hence, these assumptions could be refined to match MD results for the nucleation barrier under flow, of the type obtained by [68]. MD also provides detailed information about the size, shape and distribution of monomer indices along the chain in a critical nucleus, which could guide improvements of the coarse-graining assumptions in the GO model. Furthermore, the GO model makes predictions about the early stages of the formation anisotropic nuclei. These are difficult to verify against experiments but could be tested and refined against quantitative data from MD.

The most appropriate form for the nucleus structure is likely to change with both temperature and the fraction of stretched chains. Using MD to explore the effect of temperature on flow-induced nucleation would illustrate how to vary the GO model’s parameters with temperature. This would also expose

changes in the nucleation mechanism upon reduced undercooling, perhaps as larger critical nuclei mean a greater role for entanglements. By exploring the space of model bimodal blends that are achievable in MD, modelling assumptions about how concentration affects monomer attachment rates could be refined. This is particularly important if the GO model is to be used to extrapolate to chain lengths and distributions that are unachievable in MD. This extrapolation builds towards a detailed molecular model of nucleation for arbitrary polydispersity, which is needed to improve continuum models for polymer processing.

### 6.2.2 Coarse-graining from the GO model to continuum models

Modelling polymer processing in complex geometries requires macroscale continuum models [4]. The same is often true of comparison with experimental data [86]. Macroscale continuum models require pre-averaged expressions for both the chain deformation and the resulting nucleation rate. Reliable predictive models for chain deformation in polydisperse melts under flow, such as the Rolie-Double-Poly model [47], are beginning to emerge. Thus, as discussed in section 3.2, the central unsolved problem is how the combination of many differently stretched chain species, at different concentrations, competing to attach to a nucleus affects the nucleation barrier. The GO model, particularly with the improvements outlined in section 6.2.1 above, is well-placed to address this on the mesoscale. However, full solution of the GO model requires stochastic methods and this must be bypassed to coarse-grain to the continuum level. In particular, we need simple closed-form expressions for key quantities such as the nucleation rate.

A useful strategy here is to project the simulation algorithm onto a lower dimensional nucleation model as seen in both section 5.1 [57, 68] and section 5.3 [86, 88]. The resulting low-dimensional model can be solved analytically to give the required closed form expression for the nucleation rate. Central factors to the accuracy of this projection are which variables to project onto and how to efficiently compute the nucleation barrier and kinetics under this projection.

Due to its relative simplicity the GO model strongly suggests that the total number monomers in a nucleus is an appropriate projection choice. Indeed, this projection has been shown to accurately predict the model's nucleation kinetics [85, 86, 88], at least for moderate flow rates and blend compositions. However, for MD there are many more possible order parameters, so the choice is less clear and may need to be verified and refined. In both cases the projection must be extended to higher dimensions to capture anisotropic nucleation, perhaps by including quantities such as the aspect ratio and distribution of chain lengths within the nucleus.

For the nucleation barrier, Hamer *et al.* [87] have derived an exact result for arbitrary distributions of chain stretching. However, the resulting expression is currently too unwieldy for practical use. Jolley and Graham's semi-analytic approach [86] is more practical but is limited to bimodal blends where only one species is stretched. To extend to fully polydisperse system suitable approximations of the exact result need to be found.

The nucleation kinetics are determined by two factors, the effective nucleus surface area and the basic rate for attachment of a monomer. Current approaches compute the surface area by assuming either a spherical, cylindrical or self-similar nucleus shape during nucleation. These assumptions will likely need improvement when nucleus anisotropy becomes important. Indeed 1D projection of results from both MD [68] and the GO model [48, 86, 88] showed dramatic increases in the effective kinetics for high flow rates and extreme blends. It is not yet clear whether these shifts in effective kinetics are due to inadequacies

in the choice of projection or are genuine evidence of an increase in local monomer mobility under strong flow.

## 7 Summary and conclusions

Polymer FIC is an important problem of both academic and industrial relevance. Interpreting FIC experiments and modelling polymer processing requires quantitative, predictive models based on simple, deterministic differential equations on the continuum level. However, current continuum models cannot robustly predict how the flow-induced nucleation rate changes with temperature and molecular weight distribution. Of particular difficulty is predicting how multiple chains species, with varying concentration and degrees of stretch combine to influence the nucleation barrier. This difficulty arises because the nucleation mechanism under flow is not clearly understood. Inferring this mechanism from experiments is difficult because experiments on monodisperse melts are uncommon and because current experimental techniques cannot directly observe nucleation events as they are short-lived, highly localised and rare. MD simulations have huge potential to address these issues and provide a complementary probe of polymer FIC. MD offers unrivalled spatial and temporal resolution and perfectly monodisperse chains can be prepared. Simulating polymer nucleation has recently become possible due to advances in computing power and simulation algorithms. Recent studies have elucidated details of the nucleation mechanism under flow and provided quantitative nucleation data [68, 69]. However, MD simulations are limited to high undercooling and short chains: chains of  $\sim 10$  entanglements have been simulated but most studies of FIC have consider weakly entangled or unentangled chains. Thus current simulations are substantially short of the well entangled polydisperse chains that characterise experiments and polymer processing.

There are options for future work to work around the constraints imposed by the computational cost of MD. Specifically, the limited range of undercooling accessible in MD may be resolved by rare event algorithms, which have specifically addressed this issue in other fields of molecular simulation. However, the limitation of chain length, which is due to slow diffusion rather than rareness, appears insurmountable even with the ongoing progress in computational power. Therefore, there remains a role for coarse-grained simulations such as the GO model [63] to address long chains and wide polydispersity that are essential to model polymer processing. Hence, an immediate task is to resolve coarse-graining questions in kMC simulations by ensuring quantitative agreement with MD simulations. These MD simulations need to fully explore the space accessible to MD, in terms of molecular weight, polydispersity and undercooling. Not only must nucleation from monodisperse chains be simulated and understood, but also the effect of different chain lengths and concentrations via carefully chosen model bimodal blends. The resulting improved kMC models can then extrapolate quantitative insight from MD to industrially relevant polymers and confirm these predictions against experiments. The final coarse-graining step is to produce macroscale continuum models, based on deterministic differential equations. These models should be cheap enough for use in computational fluid dynamics calculations of polymer processing in complex geometries. They need to cover non-isothermal flows of fully polydisperse polymers. An important related development are recent non-linear rheological models of polydisperse polymers [47, 48]. The success of these models in predicting chain deformation under flow for polydisperse melts is an essential pre-requisite for predicting polymer FIC.



An important technique to link models and simulations of different coarse-graining is the projection onto lower dimensional models. At the MD level, Rutledge and co-workers [57, 68, 75] analysed mean-first passage time data from simulations using one or two dimensional versions of classical nucleation theory. This analysis quantified the nucleation rate and barrier. At the kMC level, projection of the GO model onto a 1D nucleation model has led to accurate closed-form expressions for the nucleation rate for this model for monodisperse chains and some bimodal blends [86, 88]. Generalising this approach to full polydispersity is the next step in improving the predictive capacity of continuum models of polymer FIC. Ultimately, this may create a flexible pathway to use molecular insight from MD to inform the modelling of FIC during polymer processing. If the resulting models achieve genuine predictive capacity from molecular principles, this will open up the possibility of designing molecular weight distributions and other processing conditions to optimise process behaviour and final product properties.

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