Connecting structure evolution and chain diffusion in dense polymeric systems using dynamical self-consistent field theory

by

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We explore the role of chain diffusion in the structure formation of dense, inhomogeneous polymeric systems, in the first application to polymers of our recently-developed dynamical self-consistent field theory [1, 2]. Our approach enables us to study large length and time scales in these dense systems, while remaining connected, in a self-consistent manner, to the dynamics of our microscopic model for the many-body interacting problem. Our theory is highly flexible, can be modified to describe different polymeric systems, and can even be extended to applications beyond polymers, in the broader field of classical soft matter. We describe the numerical implementation of our technique, and characterize the sources of numerical error and the presence of finite chain-length effects. We apply the theory to the problem of spinodal decomposition in the binary homopolymer blend, and show that the theory captures the physics of spinodal decomposition, through our analysis of the early-time growth of composition fluctuations and the late-time coarsening of domains. The late-time scaling regime, characteristic of spinodal decomposition, sets in and a single growing
length-scale $L(t)$ emerges, describing the domain sizes, which satisfies the Lifshitz-Slyozov-Wagner power law $L(t) \sim t^{1/3}$. We then construct a theoretical framework in which the chain self-diffusion in ordered phases of the unentangled diblock copolymer melt can be explored systematically. The chain dynamics in the lamellar (LAM), cylindrical (HEX), spherical (BCC) and gyroid (GYR) phases exhibit distinct diffusive behaviours corresponding to diffusion parallel to the domain interfaces (free diffusion, independent of segregation strength) and suppressed diffusion perpendicular to the interfaces (hopping diffusion, with a segregation strength dependence), leading to an anisotropy in diffusivity for the lamellar and cylindrical phases that is in agreement with the literature. In the gyroid phase, our diffusion measurements are consistent with a network tortuosity value of 1.72, close to the literature value of 1.5. Finally, we measure the chain centre-of-mass diffusion coefficients during a phase transformation from metastable LAM to stable HEX over long times. This demonstrates the ability of our theory to simultaneously track the dynamics of individual chains (short time-scales) and simulate large-scale structure evolution (long time-scales).
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Chapter 1

Introduction

This thesis introduces a novel computational field-theoretic approach to polymer dynamics. Our technique has a flexibility that, in principle, allows its application to a wide range of problems, both within the field of polymer science and without, in the broader field of soft matter. This flexibility will be a recurring theme throughout this thesis. Although in this work we focus on the application to polymers, we have attempted to present our approach in such a way that its extension to other systems can be easily envisioned. The description of the technique, and particularly the development of practical numerical methods for its solution, thus constitutes a major part of this work.

Another theme that will be common throughout this thesis is the bridging of time- and length-scales. The idea that the slow evolution of a material on mesoscopic, or even macroscopic, length-scales is connected with the much faster dynamics of that material’s constituent molecules is one that pervades all areas of materials science. The viscoelasticity of polymeric materials, for instance, only began to be understood once the theories for the dynamics of single polymer molecules due to Rouse and Zimm, and later Edwards, de Gennes and Doi, had been developed in the mid- to late-20th century [3]. Polymers exhibit other fascinating properties, such as the ability
to self-assemble into ordered nano-structures, many aspects of which are still not fully understood. Understanding the dynamics of self-assembly is crucial for the processing of these materials, and in many situations the dynamics of individual molecules is known to play a key role.

The advent of the computer has allowed the dynamics of large numbers of polymeric molecules to be simulated. With the development of field-theoretic simulation methods combined with present-day computing power, the evolution of large, dense polymeric systems over long time-scales is now achievable in simulations [4]. However, many contemporary dynamical field-theoretic approaches are coarse-grained to the extent that the information about what single molecules are doing is lost. In our technique, we retain this information, without losing the ability to simulate large-scale evolution. Thus, our approach allows us to access information that many other field-theoretic techniques cannot, information that in some cases is difficult to obtain even in experiments. As we progress through this thesis, we will build up a theoretical framework in which the motion of single polymer molecules within larger structures, both in and out of equilibrium, can be explored systematically in dense (highly concentrated) polymeric systems.

1.1 What are polymers?

Polymers are long-chain macromolecules that are composed of chemical repeat units (also called monomers) that are covalently bonded together (see Figure 1.1). Due to rotational degrees of freedom in the covalent bonds, a polymer possesses flexibility, which for a chain with a large number of monomers (or degree of polymerization $N$) leads to a tendency to coil, so as to maximize its entropy. Over the years, the importance of polymers has grown to the extent that, in modern society, they are ubiquitous. In addition to their appearance in the biological world, in the form of
proteins and DNA, the industrial and technological uses for polymers are numerous. In some forms, polymers provide amusement (bubble gum, Silly Putty) and in others they play a more critical role, such as styrofoam insulation, vulcanized rubber used in seals and tires, and so on. At the cutting edge of polymer science, the invention of new synthesis techniques by chemists, expanding the range of possible molecular architectures, has led in recent years to the application of polymers in such areas as nanolithography, high performance energy devices [5] and drug delivery [6].

![Polymer Composition](image)

**Figure 1.1**: A polymer composed of two blocks of styrene (red) and isoprene (blue) monomers. In the molten state, such *diblock copolymers* can self-assemble into ordered structures such as lamellar (LAM), cylindrical (HEX), spherical (BCC) and gyroid (GYR) phases.

The ubiquity of these macromolecules is due to their extreme versatility. Many of the large-scale properties of polymeric materials are *universal*, in that they obey scaling laws with exponents that are independent of the specific monomeric species that comprise the polymer. For instance, the configuration of a polymer coil in a
melt is essentially a random walk, and the coil’s size can be characterized by the \textit{radius of gyration} $R_g$ which scales with $N$ according to $R_g \sim \sqrt{N}$. This relation holds equally well for different species of flexible polymers. Similarly, the \textit{steady-state viscosity} $\eta$ of a polymer melt scales with the molecular weight $M$ according to $\eta \sim M$ for short polymers and $\eta \sim M^{3.4}$ for long polymers, the crossover signaling the onset of \textit{entanglement} effects at the entanglement molecular weight $M_e$ [7]. Remarkably, these relationships hold just as well for polystyrene (PS), for instance, as they do for polyisoprene (PI). This is in spite of the fact that the chemical structures of the styrene and isoprene monomers are very different (see Figure 1.1). These universal properties simplify the theoretical treatment of polymers, and afford the chemical engineer a flexibility to tune the chain architecture (in this case, the molecular weight $M$) in order to achieve a desired bulk property (such as the viscosity).

Another example of the versatility of polymers comes in the form of the block architectures. A so-called \textit{block copolymer} is composed of covalently bonded sections, or blocks, of different monomeric species. Figure 1.1 illustrates the simplest of these block copolymer architectures, the diblock copolymer. In the molten state, diblock copolymers exhibit phase-separation, due to the incompatibility of the two monomeric species, but the two blocks cannot dissociate completely because they are covalently bonded together. The result is \textit{micro-phase separation}, where ordered phases containing nano-scale domains, rich in the individual monomeric species, self-assemble. By varying the temperature and/or the relative sizes of the blocks, a range of different structures can be formed, including lamellar, cylindrical and spherical phases, and the more exotic gyroid phase, shown in Figure 1.1. When one considers the extension to compositions with more than two species, more than two blocks, or chain architectures beyond the linear chains (star polymers, ring polymers, etc.), the block copolymer phase space quickly becomes immense [8]. The exploration of these large-dimensional parameter-spaces, by experiment alone, can be an expensive and
time-consuming process that can be accelerated by the use of theory and simulation to construct theoretical phase diagrams. Such collaborations between theory and experiment become more powerful than either approach on its own, for the efficient design of polymeric materials.

1.2 The theory of polymeric systems

Although one might expect that the large size of macromolecules leads to increasingly complicated theories that describe them, remarkably, the opposite is true. For a dense system of these molecules, the large degree of interpenetration between coils means that a given polymer is interacting with hundreds of its neighbours, or possibly more depending on its length. A random-walk coil spans a volume \( V \approx R_g^3 \sim N^{3/2} \), but its monomeric segments only actually occupy a volume \( v \sim N \). Thus, the number of other chains that a given coil shares the volume \( V \) with goes like \( V/v \sim \sqrt{N} \), and becomes large if \( N \) is very large. Due to the sheer number of interactions for such a long polymer, the effects of the surrounding chains can be well approximated by their average. The behaviour of these systems can thus be described by mean-field theories with a confidence that would not be justified for a simple molecular liquid, for instance, with its 8–10 nearest neighbours and resulting strong fluctuation effects [7].

Indeed, many significant advances in theoretical polymer science have been driven by the notion of the mean-field approximation [9–14]. Notably, equilibrium self-consistent field theory (SCFT) has become the primary theoretical tool for investigating the equilibrium phase behaviour of block copolymer melts. SCFT has been successfully applied to many systems including, but not limited to, diblock copolymers [14, 15], triblock copolymers [16, 17], ternary blends [18, 19], and block copolymers in various states of confinement (thin films [20, 21], cylindrical nanopores [22, 23], etc.). For such dense polymeric systems, mean-field theory is a practical tool with
substantial predictive power. The theoretical mean-field phase diagram for the di-block copolymer melt, calculated using equilibrium SCFT [24], is shown in Figure 1.2 along with the experimental phase diagram for polystyrene-polyisoprene (PS-PI) due to Bates and co-workers [25]. The phase behaviour in mean-field theory depends only on the block fraction $f$, and the Flory-Huggins interaction parameter $\chi$ (which contains a $1/T$ temperature dependence) and the degree of polymerization $N$ through their product $\chi N$. Many of the phases predicted by mean-field theory are observed in the experimental system as well, as can be seen in Figure 1.2.

![Figure 1.2: Theoretical mean-field (left, from Ref. [24]) and experimental (right, from Ref. [25]) phase diagrams for the diblock copolymer melt, showing stable regions for lamellar (L/LAM), hexagonal cylindrical (C/HEX), bicontinuous gyroid (G/Ia\bar{3}d) and body-centred cubic spherical (S/I\bar{m}3m) phases. The mean-field phase diagram also contains a stable close-packed spherical ($S_{cp}$) phase, and the experimental phase diagram shows a region where the hexagonally perforated layer (HPL) phase is observed. The disagreement in phase behaviour near the order-disorder transition (ODT) is due to compositional fluctuation effects, and the asymmetry in the experimental phase diagram is due to compositional asymmetry between polystyrene and polyisoprene.

In equilibrium mean-field theory, a microscopic description of the system of interest is used to construct a free energy functional, which depends on a set of fields including the appropriate order parameters. The transformation from a description in terms of microscopic coordinates to field configurations is achieved through standard techniques such as the Hubbard-Stratonovich transformation. The set of mean-
field equations is generated by extremizing the free energy functional with respect to the fields, and their solution gives the set of saddle-point field configurations which are assumed to be the only configurations that contribute to the partition function. Clearly, the mean-field approximation neglects even those field configurations that are very close to the saddle-point. This is a valid approximation in most cases, an exception being near critical points, where fluctuation effects are known to become significant [26]. These fluctuation effects can be seen in the disagreement near the ODT between the mean-field and experimental phase diagrams shown in Figure 1.2.

Sophisticated methods have been developed that make fluctuation corrections to mean-field theory [27–30], by including the effects of such fluctuating field configurations near the saddle-point. These corrections have brought the equilibrium theory of polymers more closely into alignment with experiment. For instance, mean-field theory predicts that the ODT in the symmetric diblock copolymer melt is 2nd-order [12], but this is not observed in experiments; rather, the critical point is destroyed by composition fluctuations, and the ODT is shifted to lower temperatures and becomes weakly 1st-order [31]. The fluctuation corrections to mean-field theory by Fredrickson and Helfand [27] reproduced this behaviour.

It is thus fair to say that the equilibrium behaviour of dense, inhomogeneous polymeric systems is rather well-understood; however, the theory for their dynamical behaviour is less developed. The dynamics of dense polymeric systems is characterized by a range of processes that are orders-of-magnitude separated in their time scales. On one hand, there are rapid degrees of freedom that operate on microscopic length-scales (the fastest conformational changes of individual polymers, and collisions between monomers, with time-scales on the order of pico- or nano-seconds). On the other hand there are much slower, larger length-scale degrees of freedom (such as the evolution of the density during phase-separation, with time-scales on the order of seconds or longer) [32]. Understanding the interplay between chain dynamics and structural
evolution is crucial to understanding why certain morphologies form during processing scenarios. Also, once a morphology has been formed, many of its structural properties (such as viscoelasticity) are related to the dynamics at the individual chain level. The presence of chain entanglements, glass transitions, shear flow, confinement, etc. complicates things further. A sample’s processing history can lead to the formation of long-lived defects or metastable states [33], but the history can also be exploited as in the case of so-called process-controlled structure formation [34]. Notable examples of the latter include the long-range alignment of lamellar and cylindrical phases by application of oscillating shear flows [35, 36], the fabrication of polymer foams where the pore size is sensitive to the kinetics of phase separation [37], and the kinetic trapping of nonequilibrium morphologies [34].

Many of the existing models for single-chain dynamics are based on coarse-grained bead-spring models [7]. The Zimm model is a bead-spring model with long-range hydrodynamic interactions, and is able to describe single chains in dilute and semi-dilute solutions, for which hydrodynamic effects are important. In more concentrated solutions and melts, the hydrodynamic interaction becomes screened and the Zimm model reduces to the Rouse model, but this is only appropriate for chains that are short enough that they are unentangled. For long enough chains in a melt, topological constraints imposed by the surrounding chains begin to significantly affect the dynamics. These so-called entanglement effects restrict the motion of the chain to be primarily along its own backbone. The resulting snake-like motion, first coined reptation by De Gennes [38], dramatically affects dynamical properties such as the viscosity, as mentioned in Section 1.1. The dynamics of entangled chains can be treated using tube models [11, 38], where a bead-spring chain undergoes diffusion in a tube that represents the average effect of the topological constraints. None of these models, however, are able to describe the dynamics of dense, inhomogeneous polymeric systems; for that, computer simulations are typically employed.
A long-standing challenge in the simulation of polymer dynamics, at large enough length- and time-scales to capture structure formation, has been to include as accurately as possible the effects of the fast degrees of freedom without requiring a prohibitively large computational effort. Particle-based simulation methods, such as molecular dynamics (MD) or Brownian dynamics (BD), struggle to access the regime of large length- and time-scales in dense systems. As a result, computational approaches to these problems often employ more heavily coarse-grained models that effectively average over the fast degrees of freedom, taking advantage of the separation of time scales. The coarse-graining procedure results in parameters that must be calibrated or mapped so that they reproduce certain thermodynamic or structural aspects of the original model [32, 39]. The most efficient, and most heavily coarse-grained, field-theoretic approaches [4, 40–43] are phenomenological dynamical models that typically employ thermodynamic driving forces from equilibrium free-energy models to drive the dynamics. However, the level of phenomenology is such that the information about what individual chains are doing is lost. As a result the connection to a microscopic model (and thus the parameter-mapping procedure) becomes unclear, which introduces difficulty when attempting to interpret simulation results, particularly time-scales, in the context of experiments.

Although great progress has been achieved using these techniques, the exploration of large parameter spaces for dynamical problems still involves significant computational effort. Thus, phase diagrams that relate processing variables to final morphologies are still impractical [44]. In addition, the assumptions inherent to many of the dynamical field theories may limit their applicability; for instance, the simplification of the chain dynamics, and the use of equilibrium concepts such as free energies to relate the density to the driving forces may be invalidated in situations where the relaxation of individual chains proceeds in tandem with the evolution of the density, rather than on a much shorter time-scale. Such situations, where the chains are not
in equilibrium with the instantaneous density, can arise e.g. during the early stages of phase separation or for particularly large driving forces \[39, 45\]. In such cases, or in cases where the chain dynamics themselves are of interest (for their relevance to transport properties, for instance \[46\]), the dynamical field theories that coarse-grain out the single-chain dynamics may not be suitable.

These last points foreshadow our goal in this work: the development of an alternative, purely dynamical field-theoretic tool for studying polymer dynamics, which applies the notion of the mean-field approximation to the statistical dynamics in a manner that is analogous to what is done in equilibrium mean-field theory. The dynamical saddle-point approximation results in a formalism that describes the dynamics of a single chain evolving in a self-consistent dynamical mean force-field, which is related to the density field(s) of the different species via the dynamical mean-field equations. The formalism itself has been described in detail in previous work \[1, 2\], but at the time we did not have a practical solution to the set of mean-field equations for polymeric systems, and resorted to studying simpler problems. Here, we demonstrate that the formalism can be solved practically for polymeric systems, without further approximation; this constitutes a significant portion of this work. The single-chain dynamics is treated exactly via the Langevin simulation of an ensemble of independent replica-chains. Our approach thus resembles certain hybrid particle-in-field methods, such as the Single-Chain-in-Mean-Field (SCMF) theory of Müller and Smith \[45\], and the dynamical mean-field theory of Ganesan and Pryamitsyn \[47\]. Unlike these theories, however, our theory does not resort to equilibrium concepts or ad-hoc phenomenology beyond that of the starting microscopic model that describes the dynamics. We will discuss in more detail the connection between these theories and our own in Chapter 2.

The formalism itself can also be viewed more generally as a recipe for deriving a dynamical mean-field theory starting from a given microscopic model. Thus, we
anticipate that our technique has a broad range of applications in soft matter beyond just polymer dynamics: colloidal dynamics, granular matter, and active matter, to name a few. In this work, we will focus on the application to polymer dynamics, and our intention is to demonstrate that the approach can be used as a practical computational tool to that end, and that it offers some capabilities that other methods lack. In particular, emphasis will be placed on the ability of our theory to study problems where the behaviour of individual molecules, in a larger, dense system of molecules evolving over long time-scales, is of interest.

1.3 Computational techniques in polymer dynamics

The contemporary computational approaches for polymer dynamics can be broken up into two general categories: the particle-based or atomistic approaches, where the system is described in terms of explicit particle coordinates, and the field-theoretic approaches, where the system is described in terms of collective field variables such as the density. As mentioned earlier, due to the struggles of the atomistic approaches in accessing the large time- and length-scale regime in dense systems, the field-theoretic approaches tend to be favoured for studying problems of structure formation in block copolymer melts. Nevertheless, the particle-based approaches remain powerful and versatile, due to their conceptual simplicity and the fact that they make few approximations. Below is a brief discussion of some of the more popular computational techniques; they are presented in the order of increasing level of coarse-graining/approximation.
1.3.1 Particle-based approaches

In the particle-based approaches, the evolution of particle coordinates is achieved by calculating the appropriate pair-wise forces between particles and applying them via classical equations of motion. One of the least coarse-grained options is molecular dynamics, in which a detailed microscopic model that explicitly describes all of the particles in the system, in terms of either particle or generalized coordinates, is evolved using deterministic Newtonian or Hamiltonian equations of motion, respectively [48]. Due to the lack of coarse-graining, one is forced to choose a very short time-scale in order to resolve the fastest degrees of freedom. This makes molecular dynamics the most computationally expensive of the simulation techniques.

A less computationally expensive alternative to MD is Brownian dynamics, in which the fastest degrees of freedom are no longer described explicitly, and instead their effects are included via coarse-graining in the form of dissipative and random forces that must be appropriately calibrated in order to ensure the proper relaxation to thermodynamic equilibrium. The resulting equations of motion are stochastic instead of deterministic, and by eliminating the fast degrees of freedom, allow for larger time-steps than in MD. However, the equations are not Galilean-invariant and the dissipative and random forces do not conserve momentum, which makes BD incapable of incorporating hydrodynamic effects, for instance [44, 49].

A similarly coarse-grained approach called Dissipative Particle Dynamics (DPD) properly accounts for conservation of momentum and is Galilean-invariant. Like BD, DPD includes dissipative and random forces as a result of the coarse-graining but, unlike BD, the forms of these terms are such that Newton’s third law is respected. As a result, DPD is capable of including hydrodynamic effects. In recent years, DPD has become a popular choice for simulations of block copolymers, for which hydrodynamic effects have been shown to play a role in certain situations, for instance by accelerating phase transitions in asymmetric diblock copolymers [50]. Simulations can be sped up
by the use of soft repulsive interactions between particles (allowing for even larger time steps), but this also leads to artificially high compressibilities, a loss of topological constraints, and large fluctuation effects [47].

The Monte Carlo (MC) method can also be modified to study dynamics of polymeric systems [51]. In so-called kinetic Monte Carlo [44] simulations, new configurations are randomly generated using a set of simple rules intended to mimic realistic dynamics (such as local moves and no chain crossings) and those proposed configurations are either accepted or rejected based on a Boltzmann weighting, employing a Monte Carlo algorithm. Since the dynamics is artificial (albeit realistic), a drawback of the approach is that the time-scale is unknown a priori in terms of a microscopic model for real dynamics; thus one has to devise a way to map the Monte Carlo time onto real time.

1.3.2 Hybrid particle-in-field theories

There are several techniques, developed in recent years, that can be considered as hybrids of the particle-based and field-based approaches (ours fits into this category). In such methods, the chains making up the system, described by their particle coordinates, are decoupled such that they interact only with a mean field and not with each other. This greatly simplifies the many-body problem, and also makes such schemes highly amenable to a numerical solution that takes advantage of parallel computing. At a given time, the snapshot of configurations of the ensemble can be used to calculate the instantaneous density field, which itself is then used to calculate the mean field through a prescribed relationship between the two.

Notably, Ganesan and Pryamitsyn proposed a dynamical mean-field theory for inhomogeneous polymeric systems [47], in which each chain of the ensemble evolves under the influence of the mean field, as well as a velocity field, via a Brownian dynamics scheme. The mean field is related to the instantaneous density via an \( ad \)
hoc phenomenological relationship whose form is motivated by a previous mean-field theory of Doi [13]. More recently, Milano and Kawakatsu proposed a similar approach of hybrid particle-field molecular dynamics simulations [52], where each chain evolves via a molecular dynamics scheme, and the mean field is related to the density via the equilibrium SCFT equations.

The Single-Chain-in-Mean-Field (SCMF) theory of Müller and Smith [45] was originally devised as a method for solving the equations of equilibrium SCFT. In their approach, the density is related to the mean-field via the SCFT equations, and the chains in the ensemble evolve under the influence of the mean-field using a Monte Carlo scheme; in this way, one time-step in the SCMF framework can be likened to one loop of the iterative convergence scheme that is more traditionally used to converge to the self-consistent solution of the SCFT equations. In addition to obtaining the final, converged solution to the SCFT equations, in the SCMF theory one also obtains a realistic dynamics as the system of chains approaches equilibrium. As a result of the fact that, during this evolution, the chains are by definition not in equilibrium with the instantaneous density (otherwise the scheme would have converged already), the SCMF approach is suitable for e.g. the early stages of spinodal decomposition, whereas other field-theoretic approaches do not capture the out-of-equilibrium chain dynamics.

Fredrickson and Orland [53] recently derived a dynamical mean-field theory that is essentially equivalent to our own. They emphasized the connection between their approach and the SCMF theory, and pointed out that the long-time limit of their theory (and thus our own) corresponds also to equilibrium SCFT. We will see more evidence for this in Chapter 4.
1.3.3 Field-based approaches

In the field-based approaches, the dynamics is described only in terms of collective fields such as the density or appropriate order parameters, and the dynamics of relaxing modes internal to the chains is not explicitly described. The validity of this treatment, as mentioned earlier, relies on the chain relaxation in the real system proceeding much more quickly than the evolution of the field variables, so that the chains are in equilibrium with the local field at each stage of the evolution. Present dynamical field-based theories involve the calculation of a free energy functional for the system. This is supplemented with a dynamical evolution equation in which the thermodynamic driving force for diffusion is a chemical potential calculated from functional derivatives of the free energy. The evolution equation is typically chosen on a phenomenological basis; for instance, models B or H (in the classification of Hohenberg and Halperin [54]) are appropriate for conserved fields such as the density depending on whether the dynamics is purely diffusive [40] or if hydrodynamic effects are important [55], respectively.

In the dynamic density functional theory (DDFT) [40], a detailed free energy functional is constructed from a starting microscopic model. The DDFT free energy depends only on the density configurations of the various species, and it is asserted that this is sufficient to describe the thermodynamics. The kinetics of the system is then determined by the shape of the free energy landscape and the kinetic coefficients appearing in the dynamical evolution equations. In the similar approach of dynamic self-consistent field theory (DSCFT) [41], the free energy functional from equilibrium SCFT is used, meaning that the SCFT equations must be solved at every time step. This involves some extra computational effort, the advantage being very accurate mean-field free energies that properly take into account the polymeric nature of the molecules. The recent hydrodynamic self-consistent field theory is capable of describing nonequilibrium systems in complex channels with flow fields, where hy-
dynamic effects are important; such theories begin to come close to being able to describe complex fluid flows in industrial processing applications [56]. Modifications to such theories to include the effects of entanglement (reptation dynamics) are also possible [57].

The time-dependent Ginzburg-Landau (TDGL) field theories [44] follow the same basic scheme as the DDFT and DSCFT approaches, but use a Landau free energy functional of either the Ohta-Kawasaki [58] or Landau-Brazovskii [4] form that describes the energy cost for deviations from the uniform disordered phase (where the order parameter \( \phi(r) \) is zero). If one remains close to the mean-field critical point, such that \( \phi(r) \) is small, the free energy density can be assumed to contain terms with increasing powers of \( \phi(r) \), usually truncating at \( \phi^4 \), and gradient terms that account for interfacial free energy and chain connectivity [59, 60]. Such remarkably simple forms for the functional free energy are able to produce many of the observed ordered phases of block copolymers, but are valid only near the weak segregation limit. Due to this simplicity of the free energy, and the fact that there is no need to solve self-consistent equations at each time-step, TDGL simulations are very fast and thus able to examine very large systems over long times, corresponding to slow domain rearrangements.

An issue with all of the field-based approaches has to do with the phenomenological Onsager kinetic coefficient \( \Lambda(r, r') \) which, in the evolution equation, relates the contribution of the chemical potential at position \( r' \) to the order parameter current \( j(r) \) at position \( r \). Many of these theories approximate \( \Lambda(r, r') \) as being local \((\Lambda(r, r') = \Gamma(r)\delta(r - r') [40])\), or in some cases being entirely independent of position \((\Lambda(r, r') = \Gamma [4])\), both of which reduce the computational effort significantly. Due to the extended nature of polymeric molecules, however, a faithful treatment of this kinetic coefficient would require that it remain non-local. In some theories that incorporate this non-locality, \( \Lambda(r, r') \) is proportional to the single-chain pair correla-
The inclusion of such a non-local kinetic coefficient, however, reduces the computational advantage of these field-theoretic approaches over the less coarse-grained theories.

Practitioners of computational polymer dynamics are faced with the dilemma of maximizing accuracy at minimal computational cost. Ultimately, a quantitative description of large, dense polymeric systems evolving over long time-scales will most likely require the use of a hierarchy of approaches that span length- and time-scales with different levels of coarse-graining [44]. The recent development of hybrid particle-in-mean-field approaches may play a crucial role in bridging the gap between the regimes that are covered by the purely particle- and field-based techniques.

1.4 Statistical dynamics via the functional integral approach

The basis for our formalism is an approach to the statistical dynamics of classical systems that was pioneered by Martin, Siggia and Rose (MSR) in 1973 [62]. They had set out to devise a Heisenberg operator theory for classical systems that would be amenable to the same type of renormalized perturbation and diagrammatic techniques as, at that time, had been so successful in quantum field theory but had not yet been applied to classical systems. Soon after, Janssen [63] and De Dominicis [64] developed a functional integral approach that is equivalent to the original operator theory, and analogous to Feynman’s path integral formalism of quantum field theory [65, 66]. In this approach, a functional integral $Z$ is constructed that sums over all possible space-time particle trajectories that satisfy the Newtonian or Hamiltonian equations of motion for the system in question. Applied to classical many-body problems, this functional integral can be used to calculate averages, correlation and response functions, etc., in an analogous way to the partition function from classical equilibrium
physics. A transformation from a description in terms of particle coordinates to fluctuating dynamical field configurations is achieved using standard mathematical techniques, resulting in an exact description that is generally intractable and thus must be subjected to approximations in order to proceed.

The functional integral approach was first applied to polymer dynamics in the context of single chains by Stepanow [67]. Fredrickson and Helfand [68] applied the MSR approach to semi-dilute polymer solution dynamics, where they expressed $Z$ in terms of concentration and elastic stress fields and looked at hydrodynamic effects for a semi-dilute polymer solution. Remaining near the dilute regime (where the concentration field is small) allowed them to make a Gaussian approximation, expanding their effective Lagrangian in powers of the fields and truncating at second-order, then evaluating the resulting Gaussian integral. Vilgis et al. [69] followed a similar approach for a melt of polymeric manifolds, making use of Gaussian and self-consistent Hartree approximations in order to perform their calculations. Beyond these few applications, it would appear that the MSR functional integral approach did not become well established in the polymer dynamics community.

Our work follows a different track. Instead of applying perturbation approximations to $Z$ in situations where the fields are small, we made a saddle-point approximation to $Z$, in analogy with equilibrium self-consistent field theory. Such a mean-field approximation can be justified for dense polymeric systems, at least in equilibrium, as has been emphasized earlier in this chapter. The derivation of our functional integral (which shall henceforth be referred to as the dynamical partition function), and the details of the saddle-point approximation, are very briefly described in Chapter 2, but many details that are crucial to the derivation have been described in our previous publications [1, 2] and are thus omitted here. The focus of Chapters 2 and 3 instead is the development of the framework into a practical computational tool.
1.5 The kinetics of dense polymeric systems in- and out-of-equilibrium

In Chapter 4, we will apply our technique to problems dealing with the dynamics of the binary homopolymer mixture and the diblock copolymer melt. For the binary homopolymer mixture, we will examine the growth kinetics of spinodal decomposition in the early- and late-time regimes. For the diblock copolymer melt, we will examine anisotropic chain diffusion in the ordered phases, both in- and out-of-equilibrium. These problems deal with the kinetics of processes spanning a wide range of time- and length-scales and thus are fitting choices for the development of our theoretical framework. The next sections will describe the physics that is relevant to our treatments of these two problems in Chapter 4.

1.5.1 Spinodal decomposition

The stability of a fluid phase is determined by its free energy as a function of composition (the free energy landscape), and can be placed into one of three categories (see Figure 1.3): i) if, for a particular phase, the composition is at a global minimum of the free energy, it is said to be stable; ii) if the composition is at a local minimum, but not a global one, the phase is said to be metastable; and iii) if the composition is at a maximum or an inflection point of the free energy, the phase is said to be unstable. Naturally, the composition of any system (characterized by a spatially varying order parameter $\phi$) is subject to fluctuations which can be characterized by their magnitude $|\delta \phi|$ and their wavelength $\lambda$. The growth or decay of these fluctuations is determined by a combination of the shift in the local free energy density (which depends on $\phi$), and the free energy cost of forming a spatial non-uniformity in the composition (the interfacial free energy, which depends on gradients of $\phi$ and is almost always penalized by an increase in the free energy).
Figure 1.3: An example free energy density landscape $f(\phi)$, which exhibits compositions that are stable, metastable and unstable with respect to fluctuations of the compositional order parameter $\phi$.

In terms of phase transitions, case i) of a system in a stable phase is somewhat straightforward: no phase transition will occur. Although fluctuations can cause the formation of metastable droplets within the stable phase, such a droplet would inevitably shrink and vanish since neither the bulk free energy difference between the two phases, nor the interfacial free energy, favour its growth. Case ii), a system in a metastable phase, is more interesting and can result in a phase transition by the nucleation and growth mechanism. Here, small-magnitude compositional fluctuations will not result in a phase transition, since the phase is locally stable, but fluctuations with a large enough magnitude will overcome the free energy barrier between the metastable phase and an adjacent (more stable) phase with lower free energy, resulting in the formation of a nucleus, or droplet, of the competing phase. This nucleus will
then either grow or shrink, determined by the competition between the interfacial free energy (which always favours shrinking) and the bulk free energy of the nucleus volume (which favours growing, since it is the more stable phase).

We will primarily concern ourselves here with case iii), of an unstable phase, where a phase transition to an adjacent metastable or stable phase is inevitable, and proceeds via a mechanism called *spinodal decomposition*. In this process, fluctuation modes of *arbitrarily small* magnitude can grow if they have a large enough wavelength, since the only contribution to the free energy that does not favour growth is the interfacial term, but this is guaranteed to be small if the magnitude of the fluctuation is small and its wavelength is large [70]. The growth behaviour of fluctuations in spinodal decomposition is thus distinctly different than in the nucleation and growth mechanism, since whether a fluctuation mode grows or decays becomes primarily a question not of its magnitude but of its wavelength, or alternatively, its wave vector magnitude \( q \). Qualitatively speaking, at the *onset* of spinodal decomposition, small-magnitude fluctuations will form and if their wave vectors are less than some critical wave vector \( q_c \) they will grow; otherwise (for \( q > q_c \)) they will decay due to the high free energy cost of forming large amounts of interface [59]. The critical wave vector \( q_c \) is related to a fundamental length-scale for the system in question, i.e. the molecular size (for polymers, the radius of gyration \( R_g \)).

The stability of a fluctuation mode is determined by the free energy, but this only tells us whether a mode will grow or decay, not how fast it will do so. Fluid phases with a conserved order parameter such as the density can be modeled approximately using the model B dynamics (if the fluid’s only mode of transport is diffusion), and driven by a Landau free energy, in the style of the TDGL approaches. The first theory to describe the kinetics of spinodal decomposition, known as linearized Cahn-Hilliard-Cook (CHC) theory [71–74], was along these lines. This approach is *linearized* in that it includes only thermodynamic driving force terms that are linear in the fluctuation...
δφ, and thus is only valid in the initial stages of phase separation when the magnitudes of the fluctuations δφ are still small. The linearized CHC theory predicts the exponential growth (or decay) of fluctuation modes according to their wave vectors, and has the general form shown in Figure 1.4. For small q, the suppression of the growth rate (R(q) \sim q^2 as q \to 0) is due to the fact that the growth of a large-wavelength fluctuation is limited by the rate at which molecules can move through the fluid, i.e. the rate of diffusion. The CHC growth rate also predicts the decay of fluctuations with wave vectors q > q_c, due to interfacial effects.

![Figure 1.4](image)

**Figure 1.4**: The growth rate R(q) of fluctuations as a function of their wave vector magnitude q, in the linearized Cahn-Hilliard-Cook (CHC) theory. The growth rate has the form $R(q) \approx -\left(\frac{\partial^2 f}{\partial \phi^2} q^2 + \frac{c}{2} q^4\right)$ [59], where c is a phenomenological coefficient that is related to the interfacial tension.

For binary polymer mixtures, descriptions of spinodal decomposition in the early-time regime were based on the CHC theory, through its extension to polymeric sys-
tems by de Gennes, Pincus and Binder [75–77]. In that theory, the binary symmetric homopolymer blend phase-separates for $\chi N > 2$. The resulting growth rate has essentially the same form as in Figure 1.4, and predicts a fastest-growing mode with a time-independent wave vector $q_m \approx R_g^{-1}$. In real binary fluid systems, the growth rate can be obtained by measuring the growth of the structure factor in scattering experiments. Such experiments on small molecule fluids [78] as well as binary mixtures of high molecular weight polymers [79] have shown good agreement with the linearized CHC theory. The CHC theory is thus considered quite successful in describing the early-time phase separation of polymer mixtures. The growth rate can also be measured in our theory, through the analysis of fluctuations that form in the density field at the onset of spinodal decomposition.

Beyond the early-time regime, there is a transient period during which the domains, rich in their respective species, form and approach their equilibrium compositions, and the interfaces approach their equilibrium profiles. During this intermediate stage, non-linear effects become important, and the linearized CHC theory is no longer appropriate. The construction of an analytical theory that is able to leave the early-time regime is difficult due to the challenge of incorporating non-linear effects (i.e. the inclusion of mode-coupling terms that are higher order in $\delta \phi$), although such mode-coupling theories have been devised [80, 81]. Thus, dynamical simulations, such as particle-based simulations of fully interacting systems [51] and dynamic density functional theories [82] are commonly used to access the late-time regime.

As the late-time regime is approached, the domains continuously coarsen (grow) and a single characteristic length scale $L(t)$, describing the domain sizes, emerges and grows monotonically. The system enters a late-time scaling regime where the growth of $L(t)$ is described by a simple power law. If the coarsening process is dominated by diffusion it is referred to as Ostwald ripening [83]; in this case, the power law
prediction

\[ L(t) \sim t^{1/3} \]  

(1.1)

of Lifshitz, Slyozov and Wagner [84, 85] holds. Other power laws for late times are appropriate in cases where hydrodynamic effects are important (for small molecule fluids, for instance), such as \( L(t) \sim t \) in the “viscous hydrodynamic regime” [86] and \( L(t) \sim t^{2/3} \) in the “inertial hydrodynamic regime” [87]. In Chapter 4 we will measure the domain growth in the late-time regime, and make comparisons with the Lifshitz-Slyozov power law.

Spinodal decomposition is a highly non-linear phenomenon which has been studied extensively in the literature. Systems of high molecular weight polymeric fluids are very useful model systems for this problem due to their long molecular relaxation times, which allows access to the early-time regime in experiments (which is difficult to access for small molecule fluids). For a new technique such as ours, aiming to describe phase separation and phase transitions in polymeric systems, spinodal decomposition is an ideal testing bed. Applying our theory to this problem not only allows us to establish that our theory produces phase separation, but also indicates the extent to which our theory is able to capture the effects of diffusion, interfacial tension, non-linear effects, and so on.

1.5.2 Chain diffusion in the diblock copolymer melt

In the second half of Chapter 4, we will be concerned with single-chain diffusion (or self-diffusion) in the diblock copolymer melt. This is in contrast with collective diffusion, which is normally a significantly slower process [88], and is not our focus. In recent decades, efforts to study the relationship between microdomain structure and chain self-diffusion in diblock copolymer melts, both theoretically and experimentally, have revealed that self-diffusion on large length-scales is strongly dependent on the
presence and arrangement of interfaces (i.e. the morphology of the ordered structure) and the shapes of the interfacial profiles (i.e. the degree of segregation). The manner in which self-diffusion is affected by these properties is also fundamentally changed by the presence of entanglements. In this section, we will first describe the physical picture that has emerged, as a result of work by Fredrickson, Bates, Kramer, Yokoyama, Lodge and many others (much of which is summarized in Refs. [88] and [89]), which relates the domain morphology, degree of segregation, and presence (or absence) of chain entanglements to the chain self-diffusion in the diblock copolymer ordered phases. We will then summarize the experimental and theoretical studies of chain self-diffusion in the ordered phases, which have motivated, and provided evidence in support of, this picture.

The self-diffusion can be characterized by the chain centre-of-mass diffusion coefficient. In theory, unentangled chains in a homogeneous melt are well described by the Rouse model, for which the centre-of-mass diffusion coefficient is

$$D_0 = \frac{k_BT}{N\zeta}. \quad (1.2)$$

This is the Stokes-Einstein relation for a particle with a friction coefficient that, in the Rouse model, is given by $N\zeta$ (the sum of the monomeric friction coefficients $\zeta$). This is the expected diffusion coefficient in the disordered phase of an unentangled diblock copolymer melt, far from the ODT. For entangled chains in the disordered phase, the diffusion is much slower, and the diffusion coefficient is proportional to $N^{-2}$ rather than the $N^{-1}$ dependence for unentangled chains [7]. The diffusion coefficient $D$ in an ordered phase will in general be different than in the disordered phase, and can be characterized by the ratio of the diffusion coefficient to that of the disordered phase, $D/D_0$.

An ordered phase that is in the vicinity of the critical point is said to be in the
Figure 1.5: Example cross-sectional composition profiles for a symmetric diblock copolymer in the ordered (lamellar) phase, in the segregation limits of weak segregation (WSL) and strong segregation (SSL). In the WSL, dissimilar blocks overlap significantly at the interface, whereas in the SSL such overlap is strongly discouraged.

*weak segregation limit* (WSL), where the *degree of segregation*, usually characterized by $\chi N - (\chi N)_s$, is small. Here $(\chi N)_s$ is the mean-field spinodal for the disordered phase, which is $(\chi N)_s \approx 10.5$ [12] for the diblock copolymer melt. Note that this is significantly higher than the spinodal for the symmetric binary homopolymer blend $(\chi N)_s = 2)$. For a diblock copolymer, the fact that the two blocks are connected (and thus cannot completely dissociate) means that phase separation has implications for the chain conformations. Compared with phase separation in the binary homopolymer blend, where chains can phase separate and still maintain a Gaussian conformation, the entropic cost for phase separation in a diblock copolymer melt is much higher. Thus, the phase transition in a diblock copolymer melt occurs at a significantly lower temperature (or equivalently, higher interaction strength) than in a binary homopolymer mixture composed of the same monomeric species. In the WSL
regime, which extends up to $\chi N \approx 12$ [89], the composition does not venture too far from that of the disordered phase, and in the case of the lamellar phase, for instance, the composition profile at equilibrium in the WSL is well described by a sinusoid (see Figure 1.5). Here the dissimilar blocks are able to mix considerably at the interface, and their configurations can be considered close to Gaussian; the interfacial width $w$ in this regime is proportional to $R_g$, so $w \sim N^{1/2}$. For lamellar phases at lower temperatures (higher $\chi N$), the composition of the domains becomes saturated (such that each domain is essentially pure in its respective component) and the interfaces sharpen. The composition profile at equilibrium in this so-called strong-segregation limit (SSL) approaches a step function and the dissimilar blocks are strongly discouraged from mixing. The interfacial width $w$ in the SSL is independent of $N$. The real system often lies in between these two limits, in the intermediate-segregation regime (ISR), for which the composition profiles are somewhere in between the two extremes shown in Figure 1.5.

A physical picture has emerged in the literature, that connects the chain diffusion in ordered phases to the degree of segregation and the dimensionality of the ordered domains. According to this picture, diffusion parallel to an interface (so-called interface diffusion) is distinctly different from diffusion perpendicular to an interface (sometimes referred to as hopping diffusion [88], where a chain hops between domains). For unentangled chains, motion along the interface is unimpeded, and the diffusion coefficient in those directions is equal to that in the disordered phase ($D_{||}/D_0 \approx 1$). Diffusion perpendicular to the interface on length-scales that are large compared with the interfacial width requires that one of the blocks be exposed to the domain rich in the other species, and thus is accompanied by an enthalpic cost (which is proportional to $\chi N$). The resulting diffusion is suppressed ($D_\perp/D_0 < 1$), with a dependence on the segregation strength, i.e. $\chi N$. In an ordered phase, the availability of perpendicular and parallel directions for large-scale diffusion depends
on the dimensionality of the domains, as illustrated in Figure 1.6. This can lead to anisotropy \((D_{\parallel}/D_{\perp} > 1)\) in the chain self-diffusion. For instance, in an aligned lamellar phase the domains are extended in two dimensions, which leads to parallel diffusion in two directions and perpendicular diffusion in one. Similarly, in the cylindrical phase the cylindrical domains are extended in one dimension, and in the spherical phase the domains are extended in zero dimensions. In the gyroid phase, due to the interconnectedness of the network of cylindrical struts, the domains are extended in all three dimensions. Thus, in the gyroid phase it is possible to diffuse large distances in any particular direction via interface diffusion alone.

Figure 1.6: An illustration of the availability of directions perpendicular and parallel to the interfaces in a) a domain of the lamellar phase (dimensionality 2), b) a minority domain of the cylindrical phase (dimensionality 1), c) a minority domain of the spherical phase (dimensionality 0), and d) a minority domain in the gyroid phase (dimensionality 3). The dimensionality of these domains leads to distinct diffusive behaviours in the corresponding ordered phases.
For entangled chains, the situation is somewhat different. Whereas unentangled chains experience little (or no) barrier to interface diffusion, entangled chains are topologically constrained, meaning that in order to move parallel to the interface, either i) one of the blocks must first be pulled into the domain rich in the other block via reptation (an “activated reptation” mechanism, which carries an enthalpic penalty), or ii) one of the blocks must retract toward the interface, allowing the block junction to move along the interface (a “block retraction” mechanism, which carries an entropic penalty). In the case of the activated reptation mechanism, the motion parallel and perpendicular to the interface become coupled (as they both depend on $\chi N$) and the anisotropy in the diffusion is weakened, if present at all.

Experimental determinations of $D$ have been done using a variety of techniques. Most of the experiments that we will discuss, relevant to diblock copolymer self-diffusion, employ forward recoil spectrometry (FRES), pulsed field-gradient nuclear magnetic resonance spectroscopy (PFG NMR), or forced Rayleigh scattering (FRS). In FRES, a high-energy ion beam is fired at the surface of a sample and the lighter elements $^1H$ and $^2H$ are recoiled. The kinetic energy of the recoiled particles is indicative of their original depths in the sample, which allows concentration depth profiles for $^1H$ and $^2H$ to be constructed. If a surface layer of the sample initially contains deuterated molecules, the self-diffusion coefficients can be extracted from the evolution of the depth profiles. In pulsed field-gradient NMR, a standard NMR radiofrequency (RF) pulse sequence is modified to include the application of two identical magnetic field gradient pulses. If the molecules diffuse during the pulse sequence, their interaction with the field gradient pulses results in a diminished NMR signal, which can be analyzed to extract diffusion coefficients. This technique is useful for obtaining directional diffusion coefficients, since the direction of the field gradients can be controlled. In the FRS technique a dye, which can be photoisomerized, is attached to the polymer molecules. Two coherent lasers are used to create an interference
pattern, and the dye molecules exposed to that pattern are photoisomerized. This
results in a change in the refractive index of the sample which follows the original
interference pattern, and produces Rayleigh scattering when probed with a third
incident laser. As the molecules in the sample diffuse, the scattering intensity fades
and the diffusion coefficient can be extracted. Again, because the orientation of the
interference pattern is controllable, FRS can be used to extract directional diffusion
coefficients.

Early experiments on chain self-diffusion in the diblock copolymer melt quickly
revealed that even in the disordered phase, the self-diffusion displays non-trivial be-
haviour. As such a system approaches the ODT, mean-field theory would suggest
that chain diffusion is isotropic and that the diffusion coefficient is unchanged from
$D_0$, since the mean composition is simply equal to its average (leading to ideal chain
behaviour). However, experiments have shown that in fact the diffusion is suppressed
even in the disordered phase as the ODT is approached. Shull et al. [90] examined
symmetric, entangled diblock copolymers of poly(ethylene-propylene)-poly(ethyl-
ethylene) (PEP-PEE) using FRES and measured the diffusion coefficients above and below the
ODT. Fleischer et al. [91] measured symmetric, unentangled poly(styrene)-poly(isoprene)
(PS-PI) diblock copolymers using PFG NMR. Dalvi and Lodge [92] measured sym-
metric entangled and unentangled PEP-PEE diblock copolymers using FRS. These
experiments all supported the conclusion that the diffusion in the disordered phase
is suppressed close to the ODT due to the presence of long-lived composition fluctu-
ations. This effect has also been seen in particle-based simulations due to Murat [93]
and in theoretical calculations due to Guenza [94] and Leibig and Fredrickson [95],
that include fluctuation effects. Additionally, all of the experiments noted that the
angle-averaged diffusion coefficient displayed no discontinuity at the ODT. This in-
sensitivity of the diffusion coefficient to the ODT was also seen in PFG NMR exper-
iments due to Rittig et al. [96], on cylinder- and sphere-forming asymmetric diblock
copolymers.

These early experiments also saw evidence for the onset of anisotropy in the diffusivity when crossing the ODT into the lamellar phase. For instance, the FRES measurements of Shull et al. [90] could only be modeled by assuming that two diffusion coefficients were involved (these were attributed to $D_{\parallel}$ and $D_\perp$). This anisotropy in diffusivity in the lamellar phase was first predicted by Barrat and Fredrickson [46], who showed that for unentangled chains, the parallel diffusion should be independent of $\chi N$ ($D_{\parallel}/D_0 \approx 1$), whereas the perpendicular diffusion should be slowed exponentially with $\chi N$ ($D_\perp/D_0 < 1$), characteristic of a thermally activated process. The particle-based simulations of Murat et al. [93] saw these behaviours for $D_{\parallel}$ and $D_\perp$. Experiments by Lodge and coworkers [97, 98] using FRS on entangled PEP-PEE and unentangled PS-PI diblock copolymers in the lamellar phase confirmed that the perpendicular diffusion had the form

$$D_\perp = D_0 e^{-\alpha(\chi N - \beta)},$$

(1.3)

and in the unentangled case anisotropies in the range $D_{\parallel}/D_\perp = 4 - 40$ were seen. In their experiments on the entangled PEP-PEE, they also saw evidence for the activated reptation and block retraction mechanisms for parallel diffusion, which suggested that activated reptation is the dominant mechanism at weak segregation strengths, and block retraction is dominant at strong segregation strengths, since this process does not require the different blocks to mingle.

The various mechanisms discussed above for the lamellar phase are relevant to the other ordered phases as well. Hamersky et al. [99] performed FRS measurements on unentangled asymmetric poly(ethylene oxide)-poly(ethylethylene) (PEO-PEE) in the cylindrical phase and saw anisotropies in diffusivity as high as $D_{\parallel}/D_\perp \approx 80$. Other experiments by Lodge and coworkers [100, 101] using FRS on entangled cylindrical
phases measured weak anisotropies (or no anisotropy at all), and more evidence for the exponential suppression of $D_\perp$, as well as the existence of the activated reptation and block retraction mechanisms for $D_{||}$, were found.

In the body-centred cubic spherical phase, no anisotropy is expected in the diffusivity, since the body-centred cubic phase itself is isotropic. Yokoyama and Kramer [102] performed FRES experiments on entangled asymmetric poly(styrene)-poly(vinylpyridine) (PS-PVP) that formed spherical PVP domains. Cavicchi and Lodge [103] performed FRS measurements on entangled asymmetric poly(ethylene-alt-propylene-b-dimethylsiloxane) (PEP-PDMS) in the spherical phase. Both experiments confirmed that $D \approx D_\perp$ and showed an exponential suppression of the diffusion with segregation strength, which could become as strong as $D_\perp/D_0 \approx 10^{-4}$ (for the PS-PVP sample). Yokoyama, Kramer and Fredrickson [104] performed Langevin simulations of chains obeying both Rouse (unentangled) and reptational (entangled) dynamics in an imposed BCC spherical potential field, and showed exponential suppression of diffusion in both cases, verifying that the perpendicular diffusion is thermally activated whether the chains are entangled or not. PFG NMR measurements by Fleischer et al. [105] on entangled PS-PI in the spherical phase have also suggested the possibility that collective diffusion, i.e. micelle diffusion, as well as the free diffusion of chains in the majority domain, may also play a role in the observed diffusion.

The literature on chain diffusion in the gyroid phase is limited, although combined PFG NMR and FRS measurements by Hamersky et al. [99] on unentangled PEO-PEE in the gyroid and cylindrical phases showed isotropic diffusion in the gyroid phase, which was reduced relative to $D_0$. They were also able to measure the self-diffusion in the cylindrical and gyroid phases at the same temperature by taking advantage of a morphological hysteresis. They argued that the reduced isotropic diffusion in the gyroid phase could be understood as motion mainly along the interfaces of the cylindrical struts that comprise the gyroid network. Their measurements showed that
the diffusion coefficient in the gyroid phase was consistent with the parallel diffusion in
the cylindrical phase being reduced by the so-called network tortuosity, for which they
obtained a value of $D_{||}(\text{HEX})/D_{||}(\text{GYR}) \approx 1.5$. This value also agreed with theoretical
calculations by Anderson and Wennerström [106] of the tortuosity for a bicontinuous
cubic phase that is closely related to gyroid.

Although there is extensive theoretical work on the anisotropy of chain diffusion
in the lamellar phase, the literature for the non-lamellar phases is almost entirely
experimental. In particular, simulations of cylindrical and gyroid phases, testing the
dependence of chain diffusion on the degree of segregation, do not appear to have
been done. In the Langevin simulations of Ref. [104] due to Yokoyama, Kramer and
Fredrickson, the potential field imitating BCC spheres is imposed, not self-consistently
related to the configuration of the system. The tortuosity calculations of Ref. [106] did
not actually include the gyroid phase. Neither of these cases constitutes a complete
framework for systematically investigating self-diffusion in block copolymer ordered
phases. The experimental measurements on these systems are complicated by issues
such as imperfect alignment of phases, the presence of defects (which can obscure the
$D_\perp$ signal, if defects allow interface diffusion in all directions), polydispersity, etc.,
which make the analysis and interpretation more difficult. In a theoretical setting,
many of these factors are either not present or can be easily controlled; thus, simula-
tions of these systems may help to clarify the experimental results, and even expand
upon them by measuring properties that might not be accessible in experiments due
to the limitations of measuring equipment.

1.6 Organization of the thesis

The thesis is organized as follows. In Chapter 2, we describe the microscopic model
which forms the basis for our many-chain interacting system, and briefly outline the
derivation of the mean-field equations. The exact solution to the mean-field equations is then described, including a basic explanation of the numerical procedure (which will be expanded upon in detail in Chapter 3). Finally, the specific mean-field equations for both the binary blend and the diblock copolymer melt, which will be used in Chapter 4, are presented.

A significant emphasis of this work is the presentation of a new technique for computational polymer dynamics. Chapter 3 describes the implementation of our technique, and thus can be considered the beginning of the results for this thesis. This chapter is divided into three parts. In the first part, the technical details of the numerical solution to the mean-field equations are given, and this includes descriptions of the procedures for calculating crucial quantities (such as the density and mean force fields). This section should provide the necessary details to act as a guide for the reader to develop their own algorithm for solving the same (or similar) equations. The second part describes the algorithms that we use for the data analysis of Chapter 4. The third part of Chapter 3 is a characterization of the numerical errors that are inevitably present due to our method, the main sources of which are the time and space discretizations (the time step $\Delta t$ and the grid spacing $\Delta$), and the chain ensemble size, or number of replicas $n_r$. We also investigate effects due to the finite chain length $N$, which has implications for Chapter 4.

Chapter 4 is divided into two parts. In the first part, we present our results for the spinodal decomposition in the symmetric binary blend, which we primarily use as a benchmarking problem as a first test of the capabilities of our technique. We examine the growth of composition fluctuations in the early-time regime and the coarsening of the domains in the late-time regime. In the second part, we present our results for the chain diffusion in the diblock copolymer melt. We first show that our theory, applied to the diblock copolymer melt in the long-time limit, generates a phase diagram which resembles the mean-field phase diagram. We then perform
a detailed examination of chain diffusion in the lamellar, cylindrical, spherical and
gyroid phases of the diblock copolymer. These results are in good agreement with the
physical picture that has emerged in the literature for unentangled chain diffusion in
the ordered phases. Finally, we observe the time-dependent anisotropy of diffusivity
during the lamellar to cylindrical transition. Here we demonstrate the ability of our
theory to simultaneously measure microscopic dynamics on short time-scales (chain
self-diffusion) and structure evolution on long time-scales (phase transformations).

In Chapter 5, we make some concluding remarks, summarizing the main results
of the work and placing them in the context of the field of computational dynamics
of soft matter systems.
Chapter 2

Dynamical self-consistent field theory

This chapter describes the formalism of the dynamical self-consistent field theory, starting from a microscopic description of the dynamics of the many-body interacting problem of a polymer melt and arriving at the set of dynamical mean-field equations. The derivation is discussed in sufficient detail that the nature of the dynamical mean-field approximation is made clear, but for the more technical details the reader should see previous work [1, 2]. The solution methodology for the mean-field equations is then explained, and the final sets of mean-field equations describing the two systems which we will study in Chapter 4, the binary homopolymer blend and the diblock copolymer melt, are described. They are given in their dimensionless forms, which involves the definition of characteristic length-, time-, and force-scales.

2.1 A microscopic model for dynamics

As a starting point, we must construct a microscopic model that describes the dynamics of the many-body system we are interested in. The features of this model must be carefully considered, as they will determine the essential physics that emerges in
the resulting dynamical mean-field theory. The full extent of the range of classical systems that can be described by our method has yet to be explored, as we have thus far limited ourselves to the regime of overdamped particles interacting via short-range forces. There is no obvious reason why, in principle, models for systems outside of this regime could not also be considered.

The large-scale static properties of polymers in concentrated solutions and melts are well-described by the ideal, or Gaussian, chain model. Similarly, dynamic properties of these systems can be described by a number of models, all of which, for long enough chains, recover Gaussian chain properties at equilibrium. These models, such as the Rouse model or freely jointed chain model, typically differ in their behaviours for short time- and length-scales but agree for long time- and length-scales [7]. The Rouse model is a dynamical bead-spring analogue to the Gaussian chain model which is exactly solvable and thus an appealing choice as a starting point.

![Figure 2.1: A pictorial representation of a many-chain interacting bead-spring model for a diblock copolymer melt. The three $F_{int}$ arrows indicate that there are interactions between like species (A-A and B-B) and between unlike species (A-B).](image)

Our model consists of $n_P$ interacting Rouse chains, each with degree of polymerization $N$. Although the standard Rouse model is non-interacting, in our case we include a non-bonded interaction force which acts between all pairs of beads in the system. The dynamics of this system can be described by a set of coupled Langevin
equations, each describing the evolution of the position $R_n^{(l)}(t)$ of one of the beads in the system, labeled by the bead and chain labels $n$ and $l$, respectively:

$$\zeta \frac{dR_n^{(l)}(t)}{dt} = F_{spr,n}^{(l)} + \sum_{l',n'} F_{int}(R_n^{(l)}, R_{n'}^{(l')}) + f_n^{(l)}.$$  \hfill (2.1)

Each bead is subject to a drag force, characterized by the friction coefficient $\zeta$, a spring force due to the adjacent beads $F_{spr,n}^{(l)}$, the non-bonded interaction force $F_{int}(R_n^{(l)}, R_{n'}^{(l')})$ and a random force $f_n^{(l)}$. The drag, spring and random forces are all connected to the coarse-grained nature of the model. The covalent bonds between monomers in a polymer are in fact quite rigid (although they do possess some degrees of freedom, through which a polymer is able to acquire different conformations). The beads and springs of the Rouse model do not represent the monomers and the covalent bonds between them explicitly, but rather are “effective monomers” that model sections of the polymer (called Kuhn segments) whose relative orientations are uncorrelated. These segments behave like springs because entropy favours a coiled configuration over a stretched one. The spring force has the form

$$F_{spr,n}^{(l)} = \frac{3k_B T}{b^2} \left( R_{n+1}^{(l)}(t) - 2R_n^{(l)}(t) + R_{n-1}^{(l)}(t) \right)$$  \hfill (2.2)

for beads not at the ends of the chain, whereas for beads at the ends

$$F_{spr,1}^{(l)} = \frac{3k_B T}{b^2} \left( R_2^{(l)}(t) - R_1^{(l)}(t) \right) \hfill (2.3)$$

$$F_{spr,N}^{(l)} = \frac{3k_B T}{b^2} \left( R_{N-1}^{(l)}(t) - R_N^{(l)}(t) \right). \hfill (2.4)$$

The entropic origins of the spring constant can be seen through its dependence on $k_B T$, and the statistical segment length $b$ characterizes the size of the Kuhn segments and is sometimes referred to as the Kuhn length. The random force $f_n^{(l)}(t)$ is a Gaussian-distributed, zero-mean force that contains the effects of the fast degrees of freedom.
freedom that are not explicitly described due to having been coarse-grained out. This force, along with the drag force, has its origins in the rapid conformational changes and collisions between particles that allow the exchange of energy and momentum. The system is also allowed to exchange energy with a heat reservoir, which maintains it at a constant temperature \( T \) and ensures that the system relaxes to the appropriate thermodynamic equilibrium; for this reason \( f^{(l)}(t) \) is sometimes referred to as a thermostat. The fluctuation-dissipation theorem allows us to calibrate the random force in order to satisfy these requirements, and establishes a connection between the magnitude of fluctuations and the rate of energy dissipation through viscous drag. The random force \( f^{(l)}(t) \) must satisfy

\[
\langle f^{(l)}(t) \rangle = 0 \quad (2.5)
\]

\[
\langle f^{(l)}(t)f^{(l')}_{\alpha',n'}(t') \rangle = 2\zeta k_B T \delta_{\alpha\beta} \delta_{n'n'} \delta(t-t'), \quad (2.6)
\]

where \( \alpha, \beta \) label the components of \( f^{(l)}(t) \) and Eq. (2.6) is a statement of the fluctuation-dissipation theorem.

### 2.2 The non-bonded interaction

The non-bonded interaction force \( F_{\text{int}} \) can be chosen to model whatever interactions are appropriate for the system. This flexibility to choose \( F_{\text{int}} \) is part of the power of our approach. In our case, we will consider two important interactions. Firstly, the excluded volume interaction which is a short-range steric repulsion that discourages overlap of the beads; although for the actual monomers this repulsion is necessarily harsh (and could be modeled by a hard-core potential), for coarse-grained models such as ours a soft repulsion is sufficient as some overlap of beads is allowed [39]. Secondly, for a system of neutral, non-polar molecules the dominant attractive force is between induced dipoles [107]. Often referred to as the London dispersion or van
der Waals force, the force per monomer due to this interaction is very weak, but still sufficient to drive phase separation in concentrated systems (particularly for long chains in a melt).

A common choice of potential when modelling this combination of short-range repulsion and slightly-longer-range weak attraction is the Lennard-Jones potential

\[ V_{LJ}(r) = 4\epsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right) , \]  

(2.7)

where \( \epsilon \) characterizes the depth of the attractive well and the range of the interaction is characterized by \( \sigma \). The potential transitions from being strongly repulsive for \( r < 2^{1/6}\sigma \) to weakly attractive for \( r > 2^{1/6}\sigma \), and for a bead-spring model \( \sigma \) would be chosen to be of the same order as the Kuhn length \( b \). Lennard-Jones bead-spring models have a long history as a popular choice for models of polymeric systems with a relatively low level of coarse-graining [93, 108, 109].

An important feature of the standard Lennard-Jones potential of Eq. (2.7) is that it diverges at the origin. The use of diverging interaction potentials in coarse-grained field theories (such as a contact interaction or, in our case, the Lennard-Jones potential) has the well-known consequence that it can lead to discretization effects [110]. This is a manifestation of *UV divergence*, in which small-wavelength fluctuations behave unphysically, an artifact of the coarse-graining [26]. In our case, the consequence of a diverging interaction potential becomes directly apparent once we derive the mean-field equations: we will see that the equation for the mean force-field \( \psi(r, t) \) involves a weighted integral over space of the interaction force, weighted by the appropriate density \( \rho(r, t) \). Due to the divergence in the Lennard-Jones force \( F_{LJ}(r) = -\nabla V_{LJ}(r) \), the numerical evaluation of this integral gives a result that depends on the space discretization of the system: the integral does not converge as the resolution (with which it is calculated) is increased.
The solution to the UV divergence problem is to remove the divergence in the interaction potential, a procedure known as regularization [26, 110]. The Lennard-Jones potential can be regularized by adding a shift term \( r_0 \) in the denominator:

\[
V_{LJ}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r + r_0} \right)^{12} - \left( \frac{\sigma}{r + r_0} \right)^{6} \right],
\]

(2.8)

where \( r_0 \) should be less than \( 2^{1/6}\sigma \) (otherwise we will cut off the repulsive part of the potential entirely). As \( r_0 \) is increased, the repulsive part of the interaction becomes weaker and its effective range \( \sigma - r_0 \) decreases, so \( \sigma \) should be increased in step with \( r_0 \) to maintain an effective range of \( \sigma - r_0 \approx b \). In this work we will fix the parameters to \( r_0 = 1.1b \) and \( \sigma = 2b \); using these values, the ratio of the depth of the attractive well, \( \epsilon/k_B T \), to the height of the repulsive part of the potential at the origin, \( V_{LJ}(0)/k_B T \), is \( \sim 1 : 5000 \). This ensures that the repulsive part is more than strong enough so that, in a molecular or Brownian dynamics simulation, beads would be very unlikely to overlap (unless \( \epsilon \) is very small). We would expect such simulations using our regularized Lennard-Jones interaction to be qualitatively consistent with those using the standard Lennard-Jones, although quantitative differences would not be surprising.

For a two-species system, there are three interaction potentials \( V_{AA}(r) \), \( V_{BB}(r) \) and \( V_{AB}(r) \), shown in Fig. 2.2. For simplicity, we use just one like-species interaction potential

\[
V_{AA}(r) = V_{BB}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r + r_0} \right)^{12} - \left( \frac{\sigma}{r + r_0} \right)^{6} \right],
\]

(2.9)

and for the unlike-species potential we use a regularized version of the purely repulsive
Weeks-Chandler-Andersen Lennard-Jones potential [111]:

\[
V_{AB}(r) = \begin{cases} 
4\epsilon \left[ \left( \frac{\sigma}{r+r_0} \right)^{12} - \left( \frac{\sigma}{r+r_0} \right)^6 + \frac{1}{4} \right], & r + r_0 \leq 2^{1/6} \sigma \\
0, & r + r_0 > 2^{1/6} \sigma.
\end{cases}
\]  

(2.10)

Using this set of regularized Lennard-Jones potentials, we can drive phase separation by varying just one interaction strength parameter \( \epsilon \). It is possible to choose a set of potentials characterized by three interaction strengths \( \epsilon_{AA}, \epsilon_{BB} \) and \( \epsilon_{AB} \), but for our purposes this serves only to increase the complexity of the phase space. Since at this stage we are merely looking to investigate the ability of our theory to produce physically reasonable behaviour such as phase separation, we have deemed that a single interaction-strength parameter is sufficient.

### 2.3 The dynamical mean-field approximation

The microscopic model described above, along with the set of regularized Lennard-Jones interaction potentials, constitutes a sufficient description to perform, for instance, a Brownian dynamics simulation of the fully interacting system. We will, however, take a different approach: starting with this microscopic model, we will instead derive a dynamical mean-field theory which is analogous in many ways to the equilibrium self-consistent field theory that has had so much success in describing the equilibrium properties of dense inhomogeneous polymeric systems. The derivation of the mean-field equations is described in considerable detail in previous work [1, 2], so many of the technical details will be omitted here. We will concisely outline the main steps of the derivation here, in the context of a single-species system with a single non-bonded interaction force \( \mathbf{F}_{\text{int}} \). This is for the sake of clarity, as the derivation for multiple species is not crucially different, does not provide additional insight into the procedure and is more cumbersome. The mean-field equations for the systems with
two monomeric species (the binary homopolymer blend and diblock copolymer melt) are provided in Section 2.5.

The general idea is to construct a so-called dynamical partition function $Z(t|t_0)$ that contains the statistical information from the dynamics of the fully interacting microscopic model. This dynamical partition function can in principle be used to calculate averages in an analogous way to what is done with the standard partition function from equilibrium physics. Essentially, it consists of a functional integral over the space-time trajectories of all of the chains in the system, where all of these trajectories are constrained to satisfy the original set of coupled Langevin equations from Eq. (2.1), albeit for different realizations of the random force term $f_n(t)$. Through a
series of exact transformations, $Z(t|t_0)$ is re-expressed in terms of a set of collective field variables, chosen based on the properties one is interested in examining. In our case, we introduce the four fields $\rho(r, t), \omega(r, t), \psi(r, t)$ and $\phi(r, t)$; of particular consequence are the density field $\rho(r, t)$ and the force-field $\psi(r, t)$, as we will see. $Z(t|t_0)$ is written as a functional integral over the four dynamical field configurations

$$Z(t|t_0) = \int D[\rho] D[\omega] D[\psi] D[\phi] e^{-L[\rho, \omega, \psi, \phi]}$$

(2.11)

where $L[\rho, \omega, \psi, \phi]$ is referred to as the effective action and has the form

$$L[\rho, \omega, \psi, \phi] = i \int dr \int_{t_0}^t dt' \left[ \phi(r, t') \cdot \int dr' \mathbf{F}_{int}(r, r') \rho(r', t') - \phi(r, t') \cdot \psi(r, t') \right. - \omega(r, t') \rho(r, t') \left] - n_P \ln Q([\omega, \psi], t).$$

(2.12)

In Eq. (2.12), conjugate pairs of fields are coupled; that is, the density field $\rho(r, t)$ is coupled with its conjugate field $\omega(r, t)$ and the force field $\psi(r, t)$ is coupled with $\phi(r, t)$. The quantity $Q([\omega, \psi], t)$ is the dynamical single-chain partition function, and is the exact dynamical partition function for a single chain under the influence of the fluctuating fields $\omega(r, t)$ and $\psi(r, t)$. $Q([\omega, \psi], t)$ can be defined in terms of the single-chain configuration propagator $q(\{r_n\}, t)$, which gives the probability of finding a chain in the configuration $\{r_n\}$ at time $t$. $Q([\omega, \psi], t)$ is given by

$$Q([\omega, \psi], t) = \int \prod_n \{dr_n\} q(\{r_n\}, t) = \int dr q_n(r, t).$$

(2.13)

Note that the argument of the propagators does not make reference to an initial condition. This has been done for the sake of brevity, and the status of the propagator as a conditional probability distribution, subject to some initial condition at time $t_0$, shall from here on be assumed to be understood. For convenience we have also defined the bead propagator $q_n(r, t)$, which gives the probability of finding the $n^{th}$ bead on
a chain at the position \( \mathbf{r} \) at the time \( t \), again subject to the initial conditions. The bead and chain configuration propagators are related by

\[
q_n(\mathbf{r}, t) = \int \prod_m \{d\mathbf{r}_m\} \delta(\mathbf{r}_n - \mathbf{r}) q(\{\mathbf{r}_m\}, t). \tag{2.14}
\]

We have shown that the chain configuration propagator satisfies a modified Smoluchowski equation [1, 2]:

\[
\frac{\partial q(\{\mathbf{r}_n\}, t)}{\partial t} = \frac{k_B T}{\zeta} \sum_n \nabla_{\mathbf{r}_n}^2 q(\{\mathbf{r}_n\}, t) - \frac{1}{\zeta} \sum_n \nabla_{\mathbf{r}_n} \cdot \{[\mathbf{F}_{spr,n}(t) + \psi(\mathbf{r}_n, t)] q(\{\mathbf{r}_n\}, t)\} - i \left[ \sum_n \omega(\mathbf{r}_n, t) \right] q(\{\mathbf{r}_n\}, t). \tag{2.15}
\]

Interestingly, despite the fact that such a description of single-chain dynamics has emerged in the form of Eq. (2.15), this treatment (Eqs. (2.11)-(2.15)) still constitutes an exact description of the original fully-interacting many-chain problem. The appearance of the single-chain dynamics is a consequence of the fact that during the introduction of the collective field variables, the chains were decoupled from one another such that instead of interacting directly, they interact with the set of fluctuating fields \( \omega(\mathbf{r}, t) \) and \( \psi(\mathbf{r}, t) \) which, through their dependence on the configuration of the system, effectively transmit to each chain the status of the others. Constructing \( Z(t|t_0) \) in this fashion is deliberate, as it sets us up to make the saddle-point approximation in which the fields, instead of fluctuating, take on their saddle-point dynamical configurations.

The saddle-point field configurations are those for which the action \( L[\rho, \omega, \psi, \phi] \) is stationary. Taking the functional derivatives of the action with respect to the four fields and setting them to zero, we find that, in the saddle-point approximation, the fields \( \omega(\mathbf{r}, t) \) and \( \phi(\mathbf{r}, t) \) vanish [1, 2]. The remaining fields, and the propagator,
satisfy the set of mean-field equations

\[ \rho(\mathbf{r}, t) = n_P \sum_n q_n(\mathbf{r}, t) \quad (2.16) \]

\[ \psi(\mathbf{r}, t) = \int d\mathbf{r}' \rho(\mathbf{r}', t) \mathbf{F}_{\text{int}}(\mathbf{r}, \mathbf{r}'), \quad (2.17) \]

and the single-chain dynamics, now simplified through the vanishing of the \( \omega(\mathbf{r}, t) \) term, satisfies the functional Smoluchowski equation

\[ \frac{\partial q(\{\mathbf{r}_n\}, t)}{\partial t} = \frac{k_B T}{\zeta} \sum_n \nabla_{\mathbf{r}_n}^2 q(\{\mathbf{r}_n\}, t) - \frac{1}{\zeta} \sum_n \nabla_{\mathbf{r}_n} \cdot \left\{ [\mathbf{F}_{\text{spr}, n}(t) + \psi(\mathbf{r}_n, t)] q(\{\mathbf{r}_n\}, t) \right\} \quad (2.18) \]

which takes the familiar form describing the dynamics of a single Rouse chain evolving in the force-field \( \psi(\mathbf{r}, t) \).

The mean-field nature of the approximation is apparent: each chain in the system now interacts only with the dynamical mean force-field \( \psi(\mathbf{r}, t) \), which contains the average effect of all of the chains in the system, through its functional dependence on the average density \( \rho(\mathbf{r}, t) \), according to Eq. (2.17). The solution to the set of mean-field equations, Eqs. (2.16), (2.17) and (2.18), must be self-consistent, since the density \( \rho(\mathbf{r}, t) \) depends on the propagator \( q_n(\mathbf{r}, t) \) (through Eq. (2.16)), the dynamics of the propagator in turn depends on the mean force-field \( \psi(\mathbf{r}, t) \) (through Eq. (2.18)), and

![Figure 2.3: Depicted on the left, the fully-interacting problem, where each chain interacts with all of the others. Depicted on the right, the dynamical mean-field approximation, where each chain interacts just with the dynamical mean force-field \( \psi(\mathbf{r}, t) \) (orange) that contains the average effect of all of the chains in the system.](image-url)
ψ(r, t) itself depends on the density ρ(r, t) (through Eq. (2.17)). This is not unlike the situation in equilibrium self-consistent field theory, where the mean-field equations for the density, mean field and single-chain propagator are solved self-consistently, usually using an iterative convergence scheme [44]. Although it is possible in principle to employ a similar iterative scheme to converge to the exact self-consistent solutions for the spatio-temporal configurations of \( q(\{r_n\}, t) \), \( ρ(r, t) \) and \( ψ(r, t) \) [1, 2], a simpler approach exists, owing to the fact that our dynamics is a continuous-time Markov process, meaning that the system is memory-less; that is, knowing the state of the system at some time \( t' \), and only at \( t' \), is sufficient to calculate the state of the system at any later time \( t > t' \) [112]. For our purposes, this means that we can calculate the state of the system \( q(\{r_n\}, t + \Delta t) \) as long as we know the state of the system \( q(\{r_n\}, t) \). Indeed, this will be the basis for our approach: if \( q(\{r_n\}, t) \) is known, \( ρ(r, t) \) and \( ψ(r, t) \) can be calculated via Eqs. (2.16) and (2.17) and then the system can be evolved forward one time-step via Eq. (2.18), to obtain \( q(\{r_n\}, t + \Delta t) \). This procedure, illustrated in Fig. 2.4, is then repeated for each time step. Provided that the time step \( \Delta t \) is small compared to the spectrum of relaxation times for the modes of the chain, the dynamics using this scheme should closely resemble the exact solution (see Sec. 3.3.2 for an analysis of the \( \Delta t \)-dependence of the error introduced by our method).

The scheme described above assumes that the Smoluchowski equation (Eq. (2.18)) can be numerically solved to begin with. In specific cases, analytical solutions using basis function techniques may be feasible. Unfortunately, in the general case Eq. (2.18) is too complicated to solve directly for chains of any appreciable length due to the high-dimensional nature of the chain configuration propagator \( q(\{r_n\}, t) \).

For less complicated molecules, such as simple Brownian particles (the \( N = 1 \) case), Eq. (2.18) simplifies considerably and can be practically solved as we have shown in previous work [1, 2], but in order to apply our technique to polymeric systems we
need to calculate $q(\{r_n\}, t)$ through a different approach.

### 2.4 Exact solution to the functional Smoluchowski equation

Although the functional Smoluchowski equation (Eq. (2.18)) cannot be solved directly, the single-chain configuration propagator $q(\{r_n\}, t)$ is indirectly accessible through an alternate approach: the Langevin simulation of an ensemble of $n_r$ independent chain replicas interacting with the mean force-field $\psi(r, t)$. Each chain replica evolves according to the set of Langevin equations for each bead

$$\zeta \frac{dR_n(t)}{dt} = F_{spr,n}(t) + \psi(R_n(t), t) + f_n(t).$$

(2.19)

The dynamics of such an ensemble will obey the same statistics as the propagator $q(\{r_n\}, t)$. This can be shown by constructing the dynamical partition function ac-
cording to Eq. (2.19), in much the same fashion as we had done for the fully-interacting model. This dynamical partition function would turn out to be $Q(t|t_0)$, the same dynamical single-chain partition function as the one that appears in the effective action after the saddle-point approximation, and it would again be solvable in terms of the propagator $q(\{r_n\}, t)$ which would satisfy Eq. (2.18).

For our purposes, the set of chain replica configurations $\{R_n^{(k)}\}$ from the ensemble substitutes for the propagator $q(\{r_n\}, t)$. Here $k$, which ranges from $1 \rightarrow n_r$, labels the chain replicas; it is important to note the distinction here between the chain replicas and the actual chains in the system: the number of actual chains is $n_P$, and it is not physically connected to the number of chain replicas $n_r$, which is simply a numerical parameter that determines how accurately we are able to calculate the single-chain statistics. The larger the number of chain replicas $n_r$, the more accurately we capture the statistics, and technically only in the limit of an infinitely large ensemble do we recover the exact propagator $q(\{r_n\}, t)$. Since the use of a finite chain ensemble introduces an error in the results (characterized in Sec. 3.3.1), the goal in choosing an ensemble size is to find a balance between accuracy (larger $n_r$) and efficiency (smaller $n_r$).

Since our method for calculating the single-chain statistics has changed, our approach for calculating the density $\rho(\mathbf{r}, t)$ is changed slightly as well. Instead of calculating the density using the bead propagator according to Eq. (2.16), we sum over the replica beads from the ensemble and each chain replica’s contribution is weighted appropriately:

$$\rho(\mathbf{r}, t) = \frac{n_p}{n_r} \sum_{k=0}^{n_r-1} \sum_n \delta(\mathbf{r} - R_n^{(k)}(t)),$$

where the sum over $k$ is again for the chain replicas, not actual chains in the system. Practically speaking, then, the set of mean-field equations consists of Eq. (2.20) (for calculating the density), Eq. (2.17) (for calculating the mean force-field), and Eq. (2.19) (for evolving the chain replicas forward to the next time step); the recur-
sive loop is depicted in Fig. 2.5.

\[
\begin{align*}
\{\mathbf{R}_n^{(l)}(t)\} & \quad \{\mathbf{R}_n^{(l)}(t + \Delta t)\} \\
\psi(\mathbf{r}, t) & \quad \psi(\mathbf{r}, t + \Delta t) \\
\rho(\mathbf{r}, t) & \quad \rho(\mathbf{r}, t + \Delta t)
\end{align*}
\]

Figure 2.5: The recursive loop that is actually used to solve the dynamical mean-field equations. The set of chain replica configurations at the current time \(\{\mathbf{R}_n^{(l)}(t)\}\) is used to calculate the mean fields \(\rho(\mathbf{r}, t)\) and \(\psi(\mathbf{r}, t)\), which are then used to evolve the chain replicas forward one time-step via Eq. (2.19) to obtain \(\{\mathbf{R}_n^{(l)}(t + \Delta t)\}\), which is then the starting point for the next loop of the recursion.

It is worth reminding the reader here of the similarities that are now apparent between our approach and some techniques already established in the literature. The single-chain-in-mean-field approach of Marcus Müller and co-workers [45, 113] was originally devised as a method for solving the equations of equilibrium self-consistent field theory. They simulate an ensemble of independent chains which evolve via Monte Carlo dynamics, in a mean field which is related to the instantaneous density via the equilibrium self-consistent field equations. The system thus converges to the solution of equilibrium self-consistent field theory, but the dynamics during this process also has some relevance to the actual dynamics of these systems, although interpreting it requires that the Monte Carlo time be mapped onto real time.

Our approach bears an even more striking resemblance to the dynamical mean-field theory of Ganesan and co-workers [47]. Again, they simulate an ensemble of independent chains in order to generate single-chain statistics, but with the additional similarity that their chain dynamics is of the same Langevin form as ours (although
they also include a velocity field term \( \mathbf{v}(\mathbf{R}_n^{(l)}) \), given by Eq. (2) of Ref. [47]:

\[
\zeta \left( \frac{d\mathbf{R}_n^{(l)}}{dt} - \mathbf{v}(\mathbf{R}_n^{(l)}) \right) = \mathbf{F}_{spr,n}(t) + \mathbf{F}_P(\mathbf{R}_n^{(l)}, t) + f_n^{(l)}(t).
\]

They calculate the mean force-field \( \mathbf{F}_P(\mathbf{r}, t) = -\nabla W(\mathbf{r}, t) \) by proposing a phenomenological relation along the same lines as the mean-field theory of Doi [7], where the mean-field potential is assumed to be proportional to the instantaneous local density:

\[
W(\mathbf{r}, t) = B \rho(\mathbf{r}, t)
\]

where \( B \) is a parameter characterizing the strength of the excluded-volume interaction.

The crucial difference between our technique and those described above lies in the derivation of our dynamical mean-field approximation: the relationship between the mean force-field \( \mathbf{\psi}(\mathbf{r}, t) \) and the density \( \rho(\mathbf{r}, t) \) is rigorously derived from the underlying microscopic model which is purely dynamical, rather than being postulated \textit{ad-hoc} based on phenomenological arguments that rely on equilibrium concepts such as the free energy. In this way, our theory clarifies the mean-field nature of the assumptions made in these other approaches (such as the assumption that the mean-field depends only on the instantaneous density, as pointed out by Fredrickson [53]), and places them in a broader context. For instance, our theory becomes essentially equivalent to the description of Ganesan et al. if we use a contact interaction for \( \mathbf{F}_{int}(\mathbf{r}, \mathbf{r}') \), but our theory also straightforwardly opens up the possibility of using other microscopic models and interactions.

In fact, the flexibility of our approach goes even beyond choices of microscopic models and interaction forces. The prescription that has been outlined in this chapter produces a dynamical mean-field theory that depends on more than just the microscopic model for the dynamics. The mean-field equations are directly connected
to the choice of collective field variables, and it is possible that different choices of collective field variables than the ones used here would result in a distinct set of mean-field equations and a different dynamical mean-field theory. The collective field variables should naturally be chosen based on the properties one is interested in examining, which may not always be the density field $\rho(\mathbf{r}, t)$, for instance. Perhaps one is interested in the pair correlation function $\langle \hat{\rho}(\mathbf{r}, t)\hat{\rho}(\mathbf{r}', t) \rangle$ [7]:

$$\langle \hat{\rho}(\mathbf{r}, t)\hat{\rho}(\mathbf{r}', t) \rangle = \sum_{l,l'} \sum_{n,n'} \langle \delta(\mathbf{r} - \mathbf{R}_{ln}(t))\delta(\mathbf{r}' - \mathbf{R}_{ln'}(t)) \rangle,$$

(2.23)

where $\hat{\rho}(\mathbf{r}, t)$ is the microscopic density. As another example, in order to develop such a theory for liquid crystals or entangled chains, a bond tangent vector field $\langle \hat{\mathbf{u}}(\mathbf{r}, t) \rangle$ may be of interest:

$$\langle \hat{\mathbf{u}}(\mathbf{r}, t) \rangle = \sum_{l} \sum_{n} \langle \mathbf{U}_{ln}(t)\delta(\mathbf{r} - \mathbf{R}_{ln}(t)) \rangle$$

(2.24)

where $\mathbf{U}_{ln}(t) = \mathbf{R}_{n+1}(t) - \mathbf{R}_{n}(t)$ is the bond vector connecting the $n^{th}$ and $(n + 1)^{th}$ beads. If the corresponding dynamical mean-field theories for these collective fields exist, our prescription would describe how they would be derived.

Additionally, it may be possible to go beyond the dynamical mean-field approximation by including fluctuations about the saddle-point in one or more of the fields. Instead of $Z(t|t_0)$ being given simply by the integrand of Eq. (2.11) evaluated at the saddle-point, it would involve functional integrals over the fluctuating fields. If the fluctuations are small, the effective action could be amenable to certain perturbation techniques that might allow the evaluation of the functional integral. In any case, the techniques that have been applied to equilibrium mean-field theory to include fluctuations [27–30] would be a clue as to how one might proceed.
2.5 The dynamical mean-field equations for two monomeric species

The mean-field equations above were described in the context of a single-species system, for the purposes of clarity. In order to apply the theory to such systems as the binary homopolymer blend or the diblock copolymer melt, the mean-field equations must be modified to describe two monomeric species, $A$ and $B$, that interact via the like- and unlike-species interactions $F_{int}^{(AA)}$, $F_{int}^{(BB)}$ and $F_{int}^{(AB)}$. We make the simplifying assumptions that $b_A = b_B = b$ and $\zeta_A = \zeta_B = \zeta$. The modifications to the mean-field equations are straightforward, and although they can be derived starting from the microscopic models describing the diblock copolymer and binary homopolymer systems, respectively, we will not describe the derivations here, only the results, since in the end the differences are mainly in bookkeeping. Indeed, our technique can easily be modified to treat a variety of linear chain architectures.

Our mean-field equations can be made dimensionless, in order to facilitate the numerical solution. The re-scaling of the mean-field equations requires choosing a set of characteristic length-, time-, force- and energy-scales; different choices will result in different numerical coefficients or pre-factors in our dimensionless equations. For convenience and brevity, we will present the equations in their dimensionless form for the remainder of this thesis; this will be assumed to be understood. We choose the length-scale to be given by the Kuhn length $b$, and the time-scale $\tau$ to be given by the ratio of the friction coefficient $\zeta$ to the spring constant $\frac{2k_BT}{b^2}$:

$$\tau = \frac{\zeta b^2}{3k_BT}. \quad (2.25)$$

For some perspective on this time-scale, we can compare it with the molecular relaxation time (also referred to as the Rouse time $\tau_R$), which is the characteristic time for
the relaxation of the chain’s slowest internal mode, and also describes the time-scale for a chain to diffuse a distance approximately equal to its own size. The Rouse time is given by

$$
\tau_R = \frac{\zeta b^2}{6 k_B T \left[ 1 - \cos \left( \frac{\pi}{N} \right) \right]} = \frac{1}{2 \left[ 1 - \cos \left( \frac{\pi}{N} \right) \right]^T},
$$

(2.26)

for the discrete Rouse model. In the limit of long chains,

$$
\tau_R \approx \frac{N^2}{\pi^2} \tau,
$$

(2.27)

in which case the Rouse time is much longer than our time-scale \( \tau \) (this is the case for \( N = 64 \), which is the chain length we use for the majority of this work). Our time-scale is much closer in its magnitude to the relaxation time for the fastest modes in the chain. We show in Section 3.1.5.2 that the fastest Rouse mode has a relaxation time \( \tau_{N-1} = \tau/4 \) in the limit of long chains.

The spring constant multiplied by the Kuhn length gives us a force-scale \( 3k_B T/b \), and multiplied again by the Kuhn length gives the energy-scale \( 3k_B T \). All quantities can now be re-defined according to their dimensionless counterparts, for example:

$$
t \to \tau t, \quad r \to br, \quad \psi(r, t) \to \frac{3k_B T}{b} \psi(r, t), \quad \rho(r, t) \to \frac{1}{b^3} \rho(r, t), \quad \epsilon \to 3k_B T \epsilon.
$$

(2.28)

### 2.5.1 The binary homopolymer blend

In the description of the binary blend, the system consists of \( n_A \) polymers of species \( A \) and \( n_B \) polymers of species \( B \), with degrees of polymerization given by \( N_A \) and \( N_B \), respectively. This leads to a doubling of the set of mean-field equations, with a set for each species corresponding to its density, mean force-field and the evolution of its chain configuration propagator (or equivalently, its set of chain replica configurations).

The number of chain replicas for each species is \( n_{r,A} \) and \( n_{r,B} \), respectively. The
dimensionless densities $\rho_A(r, t)$ and $\rho_B(r, t)$ for each species are given by

$$\rho_A(r, t) = n_A \sum_{n=0}^{N_A-1} q_{n,A}(r, t) = \frac{n_A}{n_{r,A}} \sum_{k=0}^{n_{r,A}-1} \sum_{n=0}^{N_A-1} \delta(r - R_{n,A}^{(k)}(t)), \quad (2.29)$$

$$\rho_B(r, t) = n_B \sum_{n=0}^{N_B-1} q_{n,B}(r, t) = \frac{n_B}{n_{r,B}} \sum_{k=0}^{n_{r,B}-1} \sum_{n=0}^{N_B-1} \delta(r - R_{n,B}^{(k)}(t)). \quad (2.30)$$

The dimensionless mean force-fields $\psi_A(r, t)$ and $\psi_B(r, t)$ experienced by each species are given by

$$\psi_A(r, t) = \int dr' \left( \rho_A(r', t) F^{(AA)}_{int}(r, r') + \rho_B(r', t) F^{(AB)}_{int}(r, r') \right), \quad (2.31)$$

$$\psi_B(r, t) = \int dr' \left( \rho_B(r', t) F^{(BB)}_{int}(r, r') + \rho_A(r', t) F^{(AB)}_{int}(r, r') \right) \quad (2.32)$$

and the dimensionless chain configuration propagators $q_A(\{r_n\}, t)$ and $q_B(\{r_n\}, t)$ for each species evolve according to

$$\frac{\partial q_A(\{r_n\}, t)}{\partial t} = \sum_{n=0}^{N_A-1} \nabla^2 r_n q_A(\{r_n\}, t) - \sum_{n=0}^{N_A-1} \nabla r_n \cdot \left\{ [F_{spr,n}(t) + \psi_A(r_n, t)] q_A(\{r_n\}, t) \right\},$$

$$\frac{\partial q_B(\{r_n\}, t)}{\partial t} = \sum_{n=0}^{N_B-1} \nabla^2 r_n q_B(\{r_n\}, t) - \sum_{n=0}^{N_B-1} \nabla r_n \cdot \left\{ [F_{spr,n}(t) + \psi_B(r_n, t)] q_B(\{r_n\}, t) \right\}. \quad (2.33)$$

Equivalently, the Langevin equations for the evolution of the bead positions $R_{n,A}^{(k)}$ and $R_{n,B}^{(k)}$ of the ensembles of chain- replicas are given by

$$\frac{\partial R_{n,A}^{(k)}}{\partial t} = F_{spr,n}(t) + \psi_A(R_{n,A}^{(k)}, t) + f_n(t), \quad (2.35)$$

$$\frac{\partial R_{n,B}^{(k)}}{\partial t} = F_{spr,n}(t) + \psi_B(R_{n,B}^{(k)}, t) + f_n(t). \quad (2.36)$$
2.5.2 The diblock copolymer melt

In the description of the diblock copolymer melt, the system consists of \( n_P \) polymers with degrees of polymerization given by \( N \). The block lengths for species \( A \) and \( B \) are \( N_A \) and \( N_B \), respectively, and the \( A \)-monomer composition is described by \( f = N_A/N \).

The dimensionless density fields are given by

\[
\rho_A(r, t) = n_P \frac{N_A}{n} \sum_{n=0}^{N-1} q_{n,A}(r, t) = n_P \frac{N_A}{n} \sum_{k=0}^{n-1} \sum_{n=0}^{N-1} \delta(r - R_n^{(k)}(t)),
\]
\[
\rho_B(r, t) = n_P \frac{N_B}{n} \sum_{n=fN}^{N-1} q_{n,B}(r, t) = n_P \frac{N_B}{n} \sum_{k=0}^{n-1} \sum_{n=fN}^{N-1} \delta(r - R_n^{(k)}(t)),
\]

and the dimensionless mean force-fields are given by

\[
\psi_A(r, t) = \int d\mathbf{r}' \left( \rho_A(\mathbf{r}', t) \mathbf{F}_{int}^{(AA)}(\mathbf{r}, \mathbf{r}') + \rho_B(\mathbf{r}', t) \mathbf{F}_{int}^{(AB)}(\mathbf{r}, \mathbf{r}') \right),
\]
\[
\psi_B(r, t) = \int d\mathbf{r}' \left( \rho_B(\mathbf{r}', t) \mathbf{F}_{int}^{(BB)}(\mathbf{r}, \mathbf{r}') + \rho_A(\mathbf{r}', t) \mathbf{F}_{int}^{(AB)}(\mathbf{r}, \mathbf{r}') \right).
\]

However, since all chains in the system have the same composition, there is only one chain configuration propagator \( q(\{r_n\}, t) \) (and thus one chain ensemble), whose evolution is described by the functional Smoluchowski equation

\[
\frac{\partial q(\{r_n\}, t)}{\partial t} = \sum_{n=0}^{N-1} \nabla_{r_n}^2 q(\{r_n\}, t) + \sum_{n=0}^{N-1} \nabla_{r_n} \cdot \left\{ [\mathbf{F}_{spr,n}(t) + \psi_n(\mathbf{r}_n, t)] q(\{r_n\}, t) \right\},
\]

where the mean force-field \( \psi_n(\mathbf{r}_n, t) \) experienced by the \( n^{th} \) bead depends on whether that bead belongs to species \( A \) or species \( B \), and is thus given by

\[
\psi_n(\mathbf{r}_n, t) = \begin{cases} 
\psi_A(\mathbf{r}_n, t) & \text{if } n < fN \\
\psi_B(\mathbf{r}_n, t) & \text{if } n \geq fN.
\end{cases}
\]
The Langevin equation for the evolution of the diblock copolymer chain replicas is

\[
\frac{\partial \mathbf{R}^{(k)}_n}{\partial t} = \mathbf{F}_{spr,n}(t) + \psi_n(\mathbf{R}^{(k)}_n, t) + f_n(t). \tag{2.43}
\]

The full set of mean-field equations for these polymeric problems have now been described. In Chapter 3, the focus shifts to the numerical solution to this set of equations (many aspects of which are non-trivial), and the characterization of the numerical error incurred by our solution, which depends on the space-time discretizations and the size of the ensemble of chain replicas.
Chapter 3

Numerical solution to the mean-field equations

This chapter is divided into three parts. The first part describes the numerical implementation of the dynamical self-consistent field theory (described in Chapter 2). We use a parallelized algorithm, built from the ground up, that solves the mean-field equations and evolves the system forward in time. A general schematic outline of the algorithm is provided, and the crucial subroutines for the system initialization, the calculation of the fields $\rho(r, t)$ and $\psi(r, t)$, the time evolution of the system, and the communication between processors, are described in some detail. Again, for the sake of brevity our description will be in the context of a single-species system, and we note that the extension of the algorithms described here, to systems with two monomeric species, is straightforward. The goal of this section is to outline and sufficiently describe our numerical method so that a reader interested in using our technique would be set up to do just that. The second part describes the algorithms for the data analysis that we will perform in Chapter 4, in order to characterize the growth of fluctuations in the binary homopolymer blend and chain diffusion in the diblock copolymer melt.
The third part deals with the characterization of numerical errors that arise due to our numerical schemes. Understanding the sources of error is crucial if one hopes to minimize their effects. Our algorithm has three main sources of error, being the space discretization $\Delta$, the time discretization $\Delta t$, and the size of the chain ensemble which can be characterized by the number of replicas $n_r$ or the average number of replica-beads per grid point $\langle N_b \rangle$ (this latter quantity turns out to be more directly relevant to the error). Our use of operator splitting and Euler schemes for the evolution via the Langevin equation is investigated, and alternate schemes are explored.

3.1 Description of the numerical method

The main algorithm is designed to be run in parallel on $P$ processors, which communicate using the Message Passing Interface (MPI). Each processor operates on its own sub-set of the full chain ensemble, which contains $n_r/P$ chain replicas. This parallelization splits the workload for not only the evolution of the chain ensemble (which is trivial to parallelize, since the chain replicas only interact with the mean force-field $\psi(r,t)$ and not directly with each other), but also for the calculations of the density and mean force-fields on the $M_x \times M_y \times M_z$ grid. Our optimizations place certain restrictions on the number of processors $P$, the length of the chains $N$ and the number of grid points $M_x M_y M_z$:

- $P$ must be a power of 2. This is due to our optimization of the communication algorithms (described in Section 3.1.4).

- $N$ must be a power of 2. This is due to our use of the fast Rouse transform (briefly described in Section 3.1.5.2). More sophisticated fast cosine transforms are possible that would extend the possible choices of $N$ beyond just powers of 2.
The total number of grid points $M_xM_yM_z$ must be divisible by the number of processors $P$. This is due to the parallelization of the mean force-field calculation (described in Section 3.1.3).

Figure 3.1: A schematic outlining the basic arrangement of subroutines that comprise the main iterative loop for the time evolution. Rectangular boxes indicate subroutines corresponding to the calculation described by the text, and the hourglass-shaped boxes indicate communication, between the processes running in parallel, of the array described by the text. The $\frac{dR_n}{dt}$ subroutines will be referred to as Langevin operators or subroutines.

Figure 3.1 illustrates the main iterative loop for the time evolution of the system. The top half of the loop contains the field calculations, indicated by the rectangular boxes; here a given processor calculates its contribution to the field in question. The hourglass-shaped subroutines are the transmission routines, where the processors combine their density and mean force-field calculations to obtain the complete fields on the full grid. The bottom half of the loop contains the Langevin operators, where the beads of the chain ensemble are evolved forward one time-step. Note the use of operator splitting here. This schematic does not include any analysis or output.
subroutines, but simply the essential routines that run frequently (i.e. every time step). Any analysis or output functions can be inserted in the loop as long as they are not placed between any of the three Langevin operators; these operators should always be applied together, in sequence.

### 3.1.1 Initialization

In the initialization stage, global variables are declared, such as the system dimensions $(M_x, M_y, M_z)$, time-step $\Delta t$, grid spacing $\Delta$, as well as physical properties such as the chain length $N$, number of chains $n_p$, block volume fraction $f$, etc. Memory is also allocated for any arrays, the largest being the chain ensemble, densities and mean force-fields. The storage requirements are largest for the chain ensemble array, which for $\langle N_b \rangle = 60$ requires storing 60 replica-bead positions per grid point. For an idea of the storage requirements for a large system, in the $M_x M_y M_z = 128^3$ system of Section 4.1) which uses $P = 128$ processors, each processor’s chain ensemble position array is approximately 23 MB in size (for a total of 3 GB in chain ensemble position arrays).

Two crucial calculations that are performed in this stage are the calculation of the mean force-field vertex coefficients, and the initialization of chain ensemble bead positions. The former makes the most sense in the context of Sec. 3.1.3, and so will be discussed there. We initialize the bead positions according to equilibrium Gaussian-chain distributions; that is, the chain replica configuration probability distribution should be [7]:

$$P(\{R_n\}) = \left( \frac{3}{2\pi b^2} \right)^{3N/2} \exp \left[ -\sum_n \frac{3(R_n - R_{n-1})^2}{2b^2} \right]. \quad (3.1)$$

The positions of the first bead for each chain replica are randomly generated inside the box and the remaining bead positions are generated via a Gaussian random walk.
which satisfies the distribution given by Eq. (3.1); for the \( m^{th} \) bead on the \( l^{th} \) chain replica:
\[
R_{\alpha,m}^{(l)} = R_{\alpha,m-1}^{(l)} + \frac{1}{\sqrt{3}} N(0,1)
\]  
where \( N(0,1) \) is a Gaussian-distributed random number that satisfies \( \langle N(0,1) \rangle = 0 \) and \( \langle N(0,1)^2 \rangle = 1 \); we generate \( N(0,1) \) using the \( ran1 \) random number generator and the standard Box-Muller method [114]. This produces initial chain configurations with average end-to-end vectors \( \langle R_{ee} \cdot R_{ee} \rangle / b^2 = N - 1 \), giving a uniform density with random fluctuations having a magnitude that depends inversely on the size of the ensemble (these fluctuations are characterized in Sec. 3.3.1).

### 3.1.2 Calculation of the density field

At each time-step, the \( p^{th} \) processor calculates its own density array \( \rho^{(p)}(r,t) \) from its sub-set of the ensemble; these density arrays are ultimately combined to produce the total density array \( \rho(r,t) \). The total density \( \rho(r,t) \) is a sum over the entire chain ensemble:
\[
\rho(r,t) = \frac{n_P}{n_r} \sum_{k=0}^{n_r-1} \sum_n \delta \left( r - R_n^{(k)}(t) \right).
\]  

In practice, the positions \( R_n^{(l)}(t) \) of the chain ensemble beads evolve off-grid, whereas the density field \( \rho(r,t) \) is calculated on the \( M_x \times M_y \times M_z \) grid, with grid spacing \( \Delta \) and periodic boundary conditions. The number of polymers is chosen such that the average total density is \( \rho_0 = 1/V_0 = 1/b^3 \), giving
\[
n_P = \frac{M_x M_y M_z \Delta^3}{NV_0} = \frac{M_x M_y M_z}{N} \left( \frac{\Delta}{b} \right)^3.
\]
It is more useful here to refer to the density array $\rho_{i,j,k}(t)$, rather than the field $\rho(\mathbf{r}, t)$.

For the density array, Eq. (3.3) becomes

$$
\rho_{i,j,k}(t) = \frac{n_P}{n_r} \sum_{k=0}^{n_r-1} \sum_n \delta \left( \mathbf{r}_{i,j,k} - \mathbf{R}_n^{(k)}(t) \right).
$$

(3.5)

For a given replica-bead, we must determine to which grid point its density contribution will be added, but since the beads evolve off-grid, there is no guarantee that they lie within the box (whose volume is $V = L_xL_yL_z = M_xM_yM_z\Delta^3$). For this reason the periodic image of the bead, which lies within the box, is calculated if necessary and this image contributes to the density only at the grid point to which it is closest. Other strategies for assigning bead contributions to the density at nearby grid points are possible, for instance the approach of Milano and Kawakatsu [52] where a bead in a cell of the grid contributes, to the density at all vertices of that cell, an amount that is weighted based on the bead’s relative position inside the cell. Figure 3.2 illustrates

![Figure 3.2: An illustration of the density calculation: if the bead in question (black) lies outside the box, the periodic image (blue) which lies in the box is calculated. The bead then contributes to the density at the grid point (red) that is closest to the bead image.](image)

our strategy for calculating the density. Here, a periodic image is constructed for a bead which lies outside of the $V = L_xL_yL_z$ box, and then the image contributes to
the density at the closest vertex of the cell that contains it. The grid spacing that we choose, \( \Delta = b \), should be small enough to resolve important features in the density (such as domain interfaces, which we expect to be characterized by length scales \( \sim R_g \) as long as we are not approaching the strong segregation limit). We will show in Section 3.3.3 that this value for \( \Delta \) should be sufficient as long as the gradient of the density is not changing significantly within a volume element of the grid.

### 3.1.3 Calculation of the dynamical mean force-field

The mean force-field \( \psi(r, t) \) is also calculated on the \( M_x \times M_y \times M_z \) grid, thus here it is also more useful to refer instead to the mean force array \( \psi_{i,j,k}(t) \). Parallelization for this calculation is achieved by dividing the grid into \( P \) sections, one for each processor, each containing \( \frac{M_x M_y M_z}{P} \) grid points. Again, after each processor has completed its mean force array calculation, the \( \psi^{(p)}_{i,j,k}(t) \) are combined to produce the total mean force array \( \psi_{i,j,k}(t) \). We will describe the details of the calculation generally, noting that the procedure is not changed by the fact that each processor only performs the calculation for a sub-set of the grid. At the grid point labeled by \( (i, j, k) \), \( \psi_{i,j,k}(t) \) is defined by

\[
\psi_{i,j,k}(t) = \int d\mathbf{r}' \rho(\mathbf{r}', t) \mathbf{F}_{\text{int}}(\mathbf{r}_{i,j,k} - \mathbf{r}'),
\]

where the integral is over the volume of a sphere centred on \( \mathbf{r}_{i,j,k} \) with radius 3\( b \). \( \mathbf{F}_{\text{int}}(\mathbf{r} - \mathbf{r}') \) is truncated at \( |\mathbf{r} - \mathbf{r}'| = 3b \), where the modified Lennard-Jones potential is approximately 5% of its value at the bottom of the attractive well (\( V_{\text{LJ}}(3b)/\epsilon \approx 0.05 \)). Each processor receives a full copy of the density array \( \rho_{i,j,k}(t) \) in order to perform its calculation. Since the density is discretized on the grid, it is convenient to break up the volume integral of Eq. (3.6) into a sum, over the cells that are in the vicinity
of the grid point \((i, j, k)\), of the integrals over the volumes of those cells:

\[
\psi_{i,j,k}(t) = \sum_{i',j',k'} \int d(\Delta \mathbf{r}) \rho(\mathbf{r}_{i',j',k'} + \Delta \mathbf{r}, t) F_{\text{int}}(\mathbf{r}_{i,j,k} - \mathbf{r}_{i',j',k'} - \Delta \mathbf{r}).
\] (3.7)

This sum over cells includes only those cells that lie, either entirely or partially, inside the sphere of radius \(3b\) centred on \(\mathbf{r}_{i,j,k}\); there are 184 such cells for our choice of \(\Delta = b\). Thus the indices \((i', j', k')\) could be alternatively written as \((i + \Delta i, j + \Delta j, k + \Delta k)\), in which case the sum over \((i', j', k')\) would instead be a sum over \((\Delta i, \Delta j, \Delta k)\).

This alternate labeling is cumbersome at this stage, but will be invoked later in the discussion; the reader should thus keep it in mind. In Eq. (3.7) we have introduced \(\Delta \mathbf{r}\), which gives the relative position inside the given cell, and is related to \(\mathbf{r}'\) by \(\mathbf{r}' = \mathbf{r}_{i',j',k'} + \Delta \mathbf{r}\). The indices \((i', j', k')\) unambiguously label the cell in question; this is possible because the number of grid points in the system is the same as the number of cells, but since there are 8 possible choices (corresponding to a cell’s 8 vertices) we must be careful to be consistent. Figure 3.3a illustrates our choice of label as well as a pictorial representation of the vector \(\Delta \mathbf{r}\).

![Diagram illustrating the choice of label and relative position inside a cell](image)

**Figure 3.3:** Diagrams illustrating a) the choice of vertex to be used as a label for a given cell, the vector \(\Delta \mathbf{r}\), which describes relative positions within the cell, and b) the parameters \(t, u\) and \(v\) which are used in the trilinear interpolation of \(\rho(\mathbf{r}')\).

We wish to perform the integrals of Eq. (3.7) as accurately as possible. Since the interaction force \(F_{\text{int}}\) contains features on length scales significantly smaller than
the grid spacing \( \Delta \), we will numerically evaluate the cell volume integrals using a smaller discretization \( \delta \), where \( \delta \ll \Delta \). This involves evaluating the integrand inside the cell volumes, which is straightforward for \( F_{\text{int}}(r - r') \), for which we have an exact analytical form, but less straightforward for the density field \( \rho(r', t) \), for which we only have values on the vertices of the cell. Making use of our assumption that the density is changing slowly on length scales of \( \Delta \), we employ a trilinear interpolation scheme. By first calculating the components of the relative position inside the cell, which are illustrated in Figure 3.3b:

\[
\begin{align*}
t &= \frac{\Delta r_x}{\Delta} \quad (3.8) \\
u &= \frac{\Delta r_y}{\Delta} \quad (3.9) \\
v &= \frac{\Delta r_z}{\Delta}, \quad (3.10)
\end{align*}
\]

we can then interpolate the density via

\[
\rho(r'_{i'+j'+k'} + \Delta r, t) = (1 - t)(1 - u)(1 - v)\rho_{i'+j'+k'} + t(1 - u)(1 - v)\rho_{i'+1,j'+k'} + tu(1 - v)\rho_{i'+1,j'+k'+1} + tuv\rho_{i'+1,j'+1,k'+1} \\
\quad + (1 - t)u(1 - v)\rho_{i',j'+1,k'} + (1 - t)uv\rho_{i',j'+1,k'+1} \\
\quad + (1 - t)(1 - u)v\rho_{i',j',k'+1}
\]

\[
= \sum_{\Delta i', \Delta j', \Delta k' = 0} C_{\Delta i', \Delta j', \Delta k'}(\Delta r)\rho_{i'+\Delta i', j'+\Delta j', k'+\Delta k'} \quad (3.11)
\]

where we refer to the \( C_{\Delta i', \Delta j', \Delta k'}(\Delta r) \) as trilinear interpolation coefficients. Eq. (3.7)
becomes

\[
\psi_{i,j,k}(t) = \sum_{i',j',k'} \int d(\Delta r) \left( \sum_{\Delta r'} \left( C_{\Delta r', \Delta j', \Delta k'}(\Delta r) \rho_{i' + \Delta i', j' + \Delta j', k' + \Delta k'}(t) \right) \times F_{int}(r_{i,j,k} - r_{i',j',k'} - \Delta r) \right).
\] (3.12)

We can collect the terms that contain a \( \Delta r \) dependence \( (C_{\Delta r', \Delta j', \Delta k'}(\Delta r) \) and \( F_{int}(r_{i,j,k} - r_{i',j',k'} - \Delta r) \)) and rearrange Eq. (3.12):

\[
\psi_{i,j,k}(t) = \sum_{i',j',k'} \sum_{\Delta r', \Delta j', \Delta k'} \rho_{i' + \Delta i', j' + \Delta j', k' + \Delta k'}(t) \times \int d(\Delta r) C_{\Delta r', \Delta j', \Delta k'}(\Delta r) F_{int}(r_{i,j,k} - r_{i',j',k'} - \Delta r)
\]

\[
= \sum_{i',j',k'} \sum_{\Delta r', \Delta j', \Delta k'} \rho_{i' + \Delta i', j' + \Delta j', k' + \Delta k'}(t) \phi_{i' - i, j' - j, k' - k, \Delta i', \Delta j', \Delta k'}
\] (3.13)

where for convenience we have defined the coefficients \( \phi_{i' - i, j' - j, k' - k, \Delta i', \Delta j', \Delta k'} \) which contain the result of the cell volume integrals and depend on \( (i, j, k) \) only through the difference \( (i' - i, j' - j, k' - k) \), due to the translational invariance of \( F_{int} \). As mentioned, the first sum in Eq. (3.13) contains 184 terms (one for each cell) and the second sum contains 8 terms (one for each vertex of a given cell), for a total of 1472 terms. However, repeating sets of the same \( \rho_{i' + \Delta i', j' + \Delta j', k' + \Delta k'}(t) \) will appear throughout this double sum, due to the fact that many combinations of \( (i', j', k') \) and \( (\Delta i', \Delta j', \Delta k') \) are degenerate (i.e. result in the same \( (i' + \Delta i', j' + \Delta j', k' + \Delta k') \)).

In fact many (although not all) of these combinations are eightfold degenerate, since a given grid point is a common vertex to 8 of the surrounding cells. The common factors of \( \rho_{i' + \Delta i', j' + \Delta j', k' + \Delta k'} \) due to such degenerate terms can be factored out in Eq. (3.13), simplifying the sum to involve only the unique grid points, of which there are only 311, that construct the 184 volume elements involved in the original sum. Here we invoke the alternate labeling mentioned earlier: we replace \( (i', j', k') \) with
\( (i + \Delta i, j + \Delta j, k + \Delta k), \) and the sums over \((i', j', k')\) with sums over the allowed combinations of \((\Delta i, \Delta j, \Delta k)\):

\[
\psi_{i,j,k}(t) = \sum_{\Delta i, \Delta j, \Delta k} \rho_{i+\Delta i, j+\Delta j, k+\Delta k}(t) \Phi_{\Delta i, \Delta j, \Delta k}, \tag{3.14}
\]

where the \( \Delta i, \Delta j, \) and \( \Delta k \) can each range from \(-3 \rightarrow 3\), but the sum contains a total of 311 terms (not \( 7^3 = 343 \) terms) due to certain \((\Delta i, \Delta j, \Delta k)\) lying outside of the sphere with radius \(3b\). The coefficient \( \Phi_{\Delta i, \Delta j, \Delta k} \) is the sum of the \( \phi_{i'-i, j'-j, k'-k, \Delta i', \Delta j', \Delta k'} \) terms for the degenerate sets of \((i', j', k')\) and \((\Delta i', \Delta j', \Delta k')\). Eq. (3.14) is the one that is implemented at each time-step when the mean force-field is calculated. We must be careful here if \((i, j, k)\) is at or close enough to the boundary of the box, such that the sum over \((\Delta i, \Delta j, \Delta k)\) would lead \((i + \Delta i, j + \Delta j, k + \Delta k)\) to venture outside of the box. In these cases we enforce periodic boundary conditions and enter the box at the opposite side; this is mainly a matter of bookkeeping.

This scheme allows for an accurate calculation of \( \psi_{i,j,k}(t) \) at the cost of only \( 3 \times 311 = 933 \) operations per grid point, per time-step (we multiply by 3 since \( \psi_{i,j,k}(t) \) has \( x-, y- \) and \( z-\)components). The calculation of the set of coefficients \( \Phi_{\Delta i, \Delta j, \Delta k} \) can be made very accurate, due to the fine discretization (we use \( \delta = \Delta / 50 \)), but only has to be done once at the beginning of the simulation (in the initialization stage), after which it is stored for use each time the mean force-field needs to be calculated via Eq. (3.14). Thus, the calculation of the \( \Phi_{\Delta i, \Delta j, \Delta k} \) is negligible in terms of its impact on the overall efficiency of the simulation. The calculation of \( \psi_{i,j,k}(t) \) is also accelerated due to the use of parallelization, as mentioned. It is crucial to optimize the communication between processors when these parallelized density and mean force-field calculations are ultimately combined at each time-step. The next section will describe our optimization of the communication algorithms.
3.1.4 Communication routines

If the number of processors $P$ running the simulation in parallel is large, the communication stages (where the processors exchange information) can significantly impact the efficiency, if not optimized. In our case, during the calculation of the density and mean force-fields for instance, each processor calculates a data array and these arrays must be combined and the result sent back out to all of the processors. Such routines, for the density and mean force-fields, are indicated by the hourglass-shaped boxes in the schematic of Figure 3.1.

A given processor can only send or receive data to or from one processor at a time, respectively. In a “sequential” communication algorithm, processors form a queue and, one at a time, send their array to the main (rank 0) processor. This procedure involves $P - 1$ steps, during each of which the $p^{th}$ processor is sending its data to the rank 0 processor and the remaining $P - 2$ processors are idle either from waiting for their turn to send or from waiting for the rest of the processors to finish (since none of the processors can proceed with their other calculations until they have received the total density or mean force-fields). That is, during the $P - 1$ steps, the $p^{th}$ processor (if $p \neq 0$) is active for 1 of those steps and idle for the remaining $P - 2$ steps.

This “sequential” communication algorithm is highly inefficient, particularly when the number of processors $P$ is large. A so-called “tree-structured” approach makes a much more efficient use of the available processors, and is described schematically in Figure 3.4 for the case of $P = 8$. This scheme requires that $P$ is a power of 2, but involves only $\log_2 P$ steps (instead of the $P - 1$ steps of the sequential approach) each time an array is transmitted to or from the set of processors. Such tree-structured algorithms are well-established in the field of high-performance computing [115].
3.1.5 The Langevin equation and operator-splitting

We solve the Langevin equation using a sequential operator-splitting scheme, in which the three right-hand-side operators of Eq. (2.19) are applied in the order

\[ \frac{dR_n}{dt} = \psi(R_n, t) \]  
\[ \frac{dR_n}{dt} = F_{spr,n}(t) \]  
\[ \frac{dR_n}{dt} = f_n(t). \]

The use of operator splitting allows one to take advantage of the ability to diagonalize one or more of the operators. In the case of Eq. (2.19), in the absence of the \( \psi(\mathbf{r}, t) \)
term a Rouse mode analysis would result in a set of decoupled equations that could be solved exactly with high efficiency; however, the $\psi(r, t)$ term prevents this decoupling and forces one to take a different approach. By operator splitting, we can still solve Eqs. (3.16) and (3.17) exactly using Rouse modes, and Eq. (3.15) using an Euler scheme. Operator splitting is not exact, however, and thus incurs some numerical error (we explore the error due to our scheme in Section 3.3.2).

### 3.1.5.1 Application of the dynamical mean force-field

Eq. (3.15) is solved using an Euler scheme according to

$$
\mathbf{R}_n(t + \Delta t) = \Delta t \psi(\mathbf{R}_n(t), t) + \mathbf{R}_n(t),
$$

(3.18)

where the mean force-field $\psi(\mathbf{R}_n, t)$ must be evaluated at the position $\mathbf{R}_n(t)$ of the bead in question. Since we only know values of the mean force-field on the grid, $\psi_{i,j,k}(t)$, we employ a trilinear interpolation in order to obtain $\psi(\mathbf{R}_n, t)$. We must first identify the cell containing the bead in question: since the beads evolve off-grid, a periodic image of the bead is generated which lies inside the box (if necessary, similarly to the density calculation). Then the mean force-field can be evaluated at the bead image position:

$$
\psi(\mathbf{R}_n, t) = (1 - t)(1 - u)(1 - v)\psi_{i,j,k} + t(1 - u)(1 - v)\psi_{i+1,j,k} + t u(1 - v)\psi_{i+1,j+1,k} \\
+ t(1 - u)v\psi_{i+1,j,k+1} + t uv\psi_{i+1,j+1,k+1} + (1 - t)u(1 - v)\psi_{i,j+1,k} \\
+ (1 - t)uv\psi_{i,j+1,k+1} + (1 - t)(1 - u)v\psi_{i,j,k+1}
$$

(3.19)
where $t$, $u$ and $v$ give the relative position of the bead inside the given volume element

\begin{align*}
  t &= \frac{R_{n,x} - x_{i,j,k}}{\Delta} \\
  u &= \frac{R_{n,y} - y_{i,j,k}}{\Delta} \\
  v &= \frac{R_{n,z} - z_{i,j,k}}{\Delta}.
\end{align*}

(3.20)

The Euler scheme is not exact and therefore introduces some numerical error. We will characterize this error and explore alternate schemes for the evolution of Eq. (3.15) in Section 3.3.2.

### 3.1.5.2 Application of the spring force

The solution to Eq. (3.16) is achieved using Rouse modes, which permit an exact solution by diagonalizing the spring force operator. The spring force term $\mathbf{F}_{spr,n}(t)$ acting on the $n^{th}$ bead can be written in terms of the spring force matrix $A_n^{(m)}$, and takes the (dimensionless) form

\[ \mathbf{F}_{spr,n}(t) = \sum_m A_n^{(m)} \mathbf{R}_m(t) \]  

(3.21)

where $A_n^{(m)}$ is an $N \times N$ tridiagonal matrix:

\[
\begin{pmatrix}
-1 & 1 & 0 & 0 & 0 \\
1 & -2 & 1 & 0 & 0 \\
0 & 1 & \ddots & \ddots & 0 \\
0 & 0 & \ddots & -2 & 1 \\
0 & 0 & 0 & 1 & -1 \\
\end{pmatrix}
\]
which can be diagonalized via a transformation to \( N \) Rouse modes \( X_p(t) \) (where \( p \) and \( n \) range from 0 \( \rightarrow \) \( N - 1 \)):

\[
X_p(t) = \sum_n \phi_p^{(n)} R_n(t)
\]  

(3.22)

where the \( \phi_p^{(n)} \) are orthonormal eigenvectors given by

\[
\phi_0^{(n)} = \frac{1}{\sqrt{N}}
\]

(3.23)

\[
\phi_p^{(n)} = \frac{2}{N} \cos \left( \frac{\pi p (n + 1/2)}{N} \right), \text{ for } p \neq 0.
\]

(3.24)

After the transformation to Rouse modes, Eq. (3.16) becomes

\[
\frac{dX_p}{dt} = -\lambda_p X_p,
\]

(3.25)

where \( \lambda_p \) are the Rouse mode eigenvalues

\[
\lambda_p = 2 \left[ 1 - \cos \left( \frac{\pi p}{N} \right) \right].
\]

(3.26)

The exact solution to Eq. (3.25) is

\[
X_p(t + \Delta t) = X_p(t)e^{-\lambda_p \Delta t} = X_p(t)e^{-\Delta t/\tau_p},
\]

(3.27)

where the relaxation times \( \tau_p \) are given by

\[
\tau_p = \frac{1}{2 \left[ 1 - \cos \left( \frac{\pi p}{N} \right) \right]}, \quad \tau = \frac{\zeta b^2}{6k_BT \left[ 1 - \cos \left( \frac{\pi p}{N} \right) \right]},
\]

(3.28)

\( \tau \) being our characteristic time-scale (defined in Section 2.5). For \( p \neq 0 \), Eq. (3.27) describes the relaxation of the modes internal to the chain. The \( p = 0 \) mode corresponds
to the centre of mass of the chain, and does not evolve at this stage

\[ \mathbf{X}_0(t + \Delta t) = \mathbf{X}_0(t), \tag{3.29} \]

because the random noise is not applied until the next operator splitting step. We will show in Section 3.1.5.3 that the application of the random noise correctly produces centre-of-mass diffusion. The \( \tau_p \) correspond to the spectrum of relaxation times for the internal modes of the discrete-chain Rouse model. Although they are different from those of the continuous-chain Rouse model, it is known that if \( N \) is not too small, the discrete- and continuous-chain Rouse models agree for long times [7]. Indeed, for small \( p/N \) (corresponding to the slower modes in the discrete chain), Eq. (3.28) becomes

\[ \tau_p = \frac{\zeta N^2 \hbar^2}{3 k_B T \pi^2 p^2} \tag{3.30} \]

which are exactly the continuous-chain relaxation times. For short times, the two models do not agree and for the discrete-chain the fastest mode has a relaxation time

\[ \tau_{N-1} = \frac{1}{2} \left[ \frac{1}{1 - \cos \left( \frac{\pi (N-1)}{N} \right)} \right] \tau. \tag{3.31} \]

As \( N \to \infty \), \( \tau_{N-1} \to \frac{\tau}{4} \); therefore, if we wish to resolve the relaxation of the fastest modes, we must choose \( \Delta t < \frac{\tau}{4} \) (our choice of \( \Delta t = \frac{\tau}{5} \) is motivated by this). We will explore the consequences of this choice of \( \Delta t \) in Section 3.3.2.

In order to evolve our ensemble of chains, we must do a Rouse transform from \( \{ \mathbf{R}_n \} \to \{ \mathbf{X}_p \} \), then implement Eq. (3.27), then do a reverse Rouse transform from \( \{ \mathbf{X}_p \} \to \{ \mathbf{R}_n \} \). From Eq. (3.22), the complete Rouse transform for each chain involves \( \mathcal{O}(N^2) \) operations. However, since the Rouse mode eigenvectors are shifted cosines, it is possible to employ a fast cosine transform (similar to the fast Fourier transform), which involves only \( \mathcal{O}(N \log N) \) operations. We have adapted a routine
from Numerical Recipes [114] which performs the fast Rouse transform, but only if 
\( N \) is a power of 2. We restrict ourselves to such values of \( N \) in this work.

### 3.1.5.3 Application of the random noise

The solution to Eq. (3.17) is found via

\[
R_n(t + \Delta t) = R_n(t) + \int_t^{t+\Delta t} dt' f_n(t'). \tag{3.32}
\]

Since \( f_n(t) \) is a random, Gaussian-distributed force it follows that \( \Delta R_n(t) = R_n(t + \Delta t) - R_n(t) \) is also Gaussian-distributed and therefore can be characterized by the first and second moments \( \langle \Delta R_{n,\alpha}(t) \rangle \) and \( \langle \Delta R_{n,\alpha}(t) \Delta R_{m,\beta}(t) \rangle \). Here \( \langle \ldots \rangle \) denotes an average over realizations of the noise \( f_n(t) \). The first moment is

\[
\langle \Delta R_{n,\alpha}(t) \rangle = \int_t^{t+\Delta t} dt' \langle f_{n,\alpha}(t') \rangle = \int_t^{t+\Delta t} dt' 0 = 0, \tag{3.33}
\]

and the second moment is

\[
\langle \Delta R_{n,\alpha}(t) \Delta R_{m,\beta}(t) \rangle = \int_t^{t+\Delta t} \int_t^{t+\Delta t} dt' dt'' \langle f_{n,\alpha}(t') f_{m,\beta}(t'') \rangle
= \int_t^{t+\Delta t} \int_t^{t+\Delta t} dt' dt'' \frac{2}{3} \delta_{\alpha\beta} \delta_{nm} \delta(t' - t'')
= \frac{2}{3} \delta_{\alpha\beta} \delta_{nm} \Delta t. \tag{3.34}
\]

In practice, the random Gaussian variable \( \Delta R_{n,\alpha}(t) \) that satisfies Eqs. (3.33) and (3.34) can be generated using a Box-Muller transformation. The bead positions are evolved according to

\[
R_{n,\alpha}(t + \Delta t) = R_{n,\alpha}(t) + \sqrt{\frac{2\Delta t}{3}} \mathcal{N}(0, 1) \tag{3.35}
\]

where \( \mathcal{N}(0, 1) \) is the Box-Muller generated random Gaussian variable that satisfies \( \langle \mathcal{N}(0, 1) \rangle = 0 \) and \( \langle \mathcal{N}(0, 1)^2 \rangle = 1. \)
We can show that evolution according to Eq. (3.35) correctly produces chain centre-of-mass diffusion. The centre-of-mass coordinate $R_{cm}(t)$ is defined by

$$R_{cm}(t) = \frac{1}{N} \sum_n R_n(t) = \frac{1}{\sqrt{N}} X_0(t). \quad (3.36)$$

The mean-squared displacement of $R_{cm}(t)$ over one time-step is

$$\langle (\Delta R_{cm}(t))^2 \rangle = \langle (R_{cm}(t + \Delta t) - R_{cm}(t))^2 \rangle = \sum_\alpha \langle \Delta R_{cm,\alpha}(t)^2 \rangle = \sum_\alpha \frac{1}{N^2} \sum_{n,m} \langle \Delta R_{n,\alpha}(t)^2 \rangle. \quad (3.37)$$

From Eq. (3.34), this becomes

$$\langle (\Delta R_{cm}(t))^2 \rangle = \frac{2\Delta t}{3N^2} \sum_\alpha \sum_{n,m} \delta_{nm} = \frac{2\Delta t}{N} \quad (3.38)$$

in dimensionless units. Re-inserting the characteristic time-scale $\tau$ and the length-scale $b$:

$$\langle (\Delta R_{cm}(t))^2 \rangle = \frac{2\Delta t b^2}{3N \tau} = \frac{6k_B T \Delta t}{N \zeta} = 6D_0 \Delta t \quad (3.39)$$

and we recover the free Rouse diffusion coefficient $D_0 = \frac{k_B T}{N \zeta}$. Thus, our treatment of the random noise produces centre-of-mass diffusion in the correct amount.

This concludes our description of the numerical algorithms that are central to the main iterative loop of Figure 3.1, i.e. those which run every time-step and are used to calculate the time evolution of the system, and for which optimization is crucial.
3.2 Analysis and related algorithms

The next sections deal with the main analysis algorithms that we use to calculate quantities of interest for Chapter 4. Since these algorithms are generally not running frequently, their impact on the runtime is not as significant and thus their optimization is not a focus.

3.2.1 Calculation of the angle-averaged structure factor

In Chapter 4, we will be interested in characterizing the instability that forms in the density of a symmetric binary polymer blend due to the onset of spinodal decomposition. Composition fluctuations are usually characterized by the structure factor \(S(q, t)\), which is experimentally accessible through scattering experiments. We characterize composition fluctuations via the quantity 

\[ |\tilde{\rho}(q, t)|^2 = \tilde{\rho}(q, t)\tilde{\rho}(-q, t), \]

where \(\tilde{\rho}(q, t)\) is the Fourier-transformed density

\[
\tilde{\rho}(q, t) = \int d\mathbf{r} \rho(\mathbf{r}, t) e^{i\mathbf{q}\cdot\mathbf{r}}. \tag{3.40}
\]

These quantities are related to the structure factor \(S(q, t)\)

\[
S(q, t) = \langle \tilde{\rho}(q, t)\tilde{\rho}(-q, t) \rangle \tag{3.41}
\]

where \(\tilde{\rho}(q, t)\) is the Fourier transform of the microscopic density \(\hat{\rho}(\mathbf{r}, t)\):

\[
\tilde{\rho}(q, t) = \int d\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}} \hat{\rho}(\mathbf{r}, t) = \int d\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}} \sum_l \sum_n \delta(\mathbf{r} - \mathbf{R}_n^{(l)}(t)) = \sum_l \sum_n e^{i\mathbf{q}\cdot\mathbf{R}_n^{(l)}(t)}. \tag{3.42}
\]

The microscopic density must be distinguished from the density field \(\rho(\mathbf{r}, t)\). The two are related by

\[
\rho(\mathbf{r}, t) = \langle \hat{\rho}(\mathbf{r}, t) \rangle. \tag{3.43}
\]
where \( \langle \ldots \rangle \) denotes an ensemble average. From Eqs. (3.41) and (3.42), the structure factor is

\[
S(q, t) = \left\langle \sum_{n,m} \sum_{l,l'} e^{i q \cdot (R_n(t) - R_m(t'))} \right\rangle,
\]

(3.44)

where \( n, m \) label beads, and \( l, l' \) label chains in the system. In our theory, the \( n_p \) chains in a single-species system are decoupled through the mean-field approximation, such that the probability of finding the system in a certain configuration is given by

\[
q(\{R_n(t)\}, t) = \prod_l q^l(\{R_n\}, t).
\]

(3.45)

Furthermore, since each \( q^l(\{R_n\}, t) \) is identical (and given by the single-chain propagator \( q(\{R_n\}, t) \)), the structure factor can be written as

\[
S(q, t) = n_p (n_p - 1) \bar{S}(q, t) + n_p S_0(q, t)
\]

\[
= n_p (n_p - 1) \int D[\{R_n\}] D[\{R'_m\}] \sum_{n,m} e^{i q \cdot (R_n(t) - R_m(t'))} q(\{R_n\}, t) q(\{R'_m\}, t)
\]

\[
+ n_p \int D[\{R_n\}] \sum_{n,m} e^{i q \cdot (R_n(t) - R_m(t'))} q(\{R_n\}, t)
\]

(3.46)

where we have broken the sum over \( l \) and \( l' \) into \( n_p (n_p - 1) \) terms having \( l \neq l' \) and \( n_p \) terms having \( l = l' \); these terms are the contributions to the scattering intensity from correlations between different chains and the same chain, respectively. The first term can be re-written

\[
\bar{S}(q, t) = \int D[\{R_n\}] D[\{R'_m\}] \sum_{n,m} \int dr dr' e^{i q \cdot (r - r')} \delta(r - R_n(t)) \delta(r' - R'_m(t))
\]

\[
\times q(\{R_n\}, t) q(\{R'_m\}, t)
\]

\[
= \int D[\{R_n\}] \sum_n \int dr e^{i q \cdot r} \delta(r - R_n(t)) q(\{R_n\}, t)
\]

\[
\times \int D[\{R'_m\}] \sum_m \int dr' e^{-i q \cdot r'} \delta(r' - R'_m(t)) q(\{R'_m\}, t)
\]

(3.47)
which can be expressed in terms of the density $\rho(r, t) = n_p \sum_n q_n(r, t)$:

$$\bar{S}(q, t) = \frac{1}{n_p^2} \int dr e^{iqr} \rho(r, t) \int dr' e^{-iqr'} \rho(r', t)$$

$$= \frac{1}{n_p^2} \tilde{\rho}(q, t) \tilde{\rho}(-q, t).$$

(3.48)

The single-chain structure factor $S_0(q, t)$ can be calculated via an average over the chain ensemble and, in the disordered phase at equilibrium, should reduce appropriately to the Debye function [7]. The structure factor in our theory, then, can be calculated according to

$$S(q, t) = \left(\frac{n_p - 1}{n_p}\right) \tilde{\rho}(q, t) \tilde{\rho}(-q, t) + n_p S_0(q, t).$$

(3.49)

The quantity $\tilde{\rho}(q, t) \tilde{\rho}(-q, t)$ differs from the structure factor $S(q, t)$ simply by the single-chain contribution $n_p S_0(q, t)$. The simplification of the inter-chain correlation term to depend solely on the single-point density $\rho(r, t)$ rather than the pair correlation function $C(r, r', t)$ suggests that pair correlations are not being treated correctly within the mean-field approximation. However, our motivation for calculating $\tilde{\rho}(q, t) \tilde{\rho}(-q, t)$ is not to examine pair correlations but to characterize fluctuations in the density during phase separation. In a binary blend containing species $A$ and $B$, the onset of spinodal decomposition will be accompanied by growing, isotropic fluctuations in the density of the two species. We are therefore interested primarily in the magnitude of the wave vector $q = |q|$ of the growing modes rather than their direction. For this reason, we perform an angle average of $\tilde{\rho}(q, t) \tilde{\rho}(-q, t)$, defined by

$$\langle \tilde{\rho}(q, t) \tilde{\rho}(-q, t) \rangle_\Omega = \frac{1}{4\pi} \int d\Omega \tilde{\rho}(q, t) \tilde{\rho}(-q, t).$$

(3.50)

The discrete Fourier-transform $\tilde{\rho}(q, t)$ is first calculated using the FFTW package [116], on the cubic $M^3$ grid with a grid spacing $\Delta q = \frac{2\pi}{M\Delta}$. It has real and imaginary parts
and the wave vector is given by \( \mathbf{q} = (i \Delta q, j \Delta q, k \Delta q) \) where \( i, j \) and \( k \) range from \(-M/2\) to \(M/2\). We calculate \( \tilde{\rho}(\mathbf{q}, t)\tilde{\rho}(-\mathbf{q}, t) \) by

\[
\tilde{\rho}(\mathbf{q}, t)\tilde{\rho}(-\mathbf{q}, t) = (\text{Re}\{\tilde{\rho}(\mathbf{q}, t)\})^2 + (\text{Im}\{\tilde{\rho}(\mathbf{q}, t)\})^2,
\]

(3.51)

and then perform the angle average over shells of width \( \Delta_q \):

\[
\langle |\tilde{\rho}(\mathbf{q}, t)|^2 \rangle_\Omega = \langle \tilde{\rho}(\mathbf{q}, t)\tilde{\rho}(-\mathbf{q}, t) \rangle_\Omega = \frac{1}{V_q} \sum_{q'<q \leq q+\Delta_q} \Delta_q^3 \tilde{\rho}(\mathbf{q}', t)\tilde{\rho}(-\mathbf{q}', t)
\]

(3.52)

where \( V_q \) is the volume (in \( q \)-space) of the shell associated with wave vector magnitude \( q \). If, for a given \( q \), \( n_q \) grid points are implicated in the sum of Eq. (3.52), then \( V_q = n_q \Delta_q^3 \).

If we quench the system past the spinodal at time \( t = 0 \), the growth of density fluctuation modes will be reflected in the quantity \( \langle \tilde{\rho}(\mathbf{q}, t)\tilde{\rho}(-\mathbf{q}, t) \rangle_\Omega \). At early times, the growth is expected to be exponential, with growth rates \( R(q, t) \):

\[
\langle \tilde{\rho}(\mathbf{q}, t)\tilde{\rho}(-\mathbf{q}, t) \rangle_\Omega = \langle \tilde{\rho}(\mathbf{q}, 0)\tilde{\rho}(-\mathbf{q}, 0) \rangle_\Omega e^{R(q,t)t}.
\]

(3.53)

\( R(q, t) \) thus measures how much these modes have grown relative to their values before the quench (at equilibrium), and can be calculated for those discrete values of \( q \) for which we have \( \langle \tilde{\rho}(\mathbf{q}, t)\tilde{\rho}(-\mathbf{q}, t) \rangle_\Omega \). A feature of the growth rate that we will calculate is the wave vector \( q_m \) which maximizes \( R(q, t) \); since we only have a finite set of \( R(q, t) \) for discrete values of \( q \), calculating \( q_m \) using an interpolation scheme will be more accurate than simply finding the \( q \) associated with the largest \( R(q, t) \) from the discrete set (we shall denote this value \( q_l \)). Using a quadratic interpolation scheme, \( q_m \) can be calculated using the data point \( \{q_l, R_l\} \) and its two adjacent data points \( \{q_{l-1}, R_{l-1}\} \) and \( \{q_{l+1}, R_{l+1}\} \) as shown in Figure 3.5. Once these points have been identified, the coefficients \( A, B \) and \( C \) from the quadratic equation \( R(q, t) = Aq^2 + Bq + C \) which
Figure 3.5: An illustration of the quadratic interpolation of $q_m$, using the discrete set of $\{q, R(q, t)\}$.

satisfies those three points are calculated and $q_m$ is obtained according to $q_m = \frac{-B}{2A}$.

The solutions for $A$ and $B$ are (note the use of the shorthand notation $R_l = R(q_l, t)$):

\[
A = \frac{1}{q_l - q_{l+1}} \left( \frac{R_{l-1} - R_l}{q_{l-1} - q_l} - \frac{R_{l-1} - R_{l+1}}{q_{l-1} - q_{l+1}} \right) \tag{3.54}
\]
\[
B = \frac{R_{l-1} - R_l}{q_{l-1} - q_l} - A (q_{l-1} + q_l). \tag{3.55}
\]

### 3.2.2 Ordering fields and the epitaxial relationship

In Chapter 4, we will perform measurements of chain diffusion in the lamellar, cylindrical, spherical and gyroid phases of the diblock copolymer melt. We apply *ordering fields* to the system in order to ensure that the ordered phases are aligned in the way that we want, and free of defects. These ordering fields are then released, and the system is allowed to equilibrate prior to the measurements. This section will describe the construction of the ordering fields.

The ordering fields for the lamellar, cylindrical, spherical and gyroid phases can
all be constructed if we know the period $L_0$ for the lamellar phase, by assuming that the phases obey epitaxial relationships. Figure 3.6 illustrates how the cylindrical and spherical phases can be related to the lamellar phase via epitaxy. The assumption that these relationships hold is not necessarily perfect and so one should keep in mind that the true preferred period for these phases may differ by as much as 10% from those calculated via epitaxy [117]. For the purposes of this section, we will assume that the lamellar period is $L_0$; we describe the calculation of the actual value of $L_0$ in Section 3.2.3.

Figure 3.6: Schematic showing the epitaxial relationships between a) the lamellar phase and the hexagonal cylindrical phase, and b) the lamellar phase and the body-centred cubic spherical phase.

The ordering field will be applied to the system as a contribution to the mean force-field $\psi({\mathbf r}, t)$. Specifically, species $A$ will be subject to the ordering field $\psi_A^{(ord)}({\mathbf r}, t)$, and likewise for species $B$. These fields are calculated using Eqs. (2.39)-(2.40) for the two-species mean force-fields, but the density fields are replaced with density fields $\rho_A^{(ord)}({\mathbf r}, t)$ and $\rho_B^{(ord)}({\mathbf r}, t)$, which correspond to the phase in question. We can approximate density fields for the lamellar, cylindrical and spherical phases by the superposition of a “single-mode” of reciprocal lattice vectors with the correct symmetry for that phase; the gyroid phase requires the use of a second mode.
The two-species ordering density fields for the lamellar phase in this *single-mode approximation* can be generated according to

\[
\rho^{(\text{lam})}_A(r) = f + b_1 \sum_{i=1}^{2} \cos \left( q_0 G_i^{(\text{lam})} \cdot r \right)
\]

\[
\rho^{(\text{lam})}_B(r) = 1 - \rho^{(\text{lam})}_A(r)
\]  

(3.56)

where \( f \) is the volume fraction of species A (such that \( \rho^{(\text{dis})}_A(r) = f \) and \( \rho^{(\text{dis})}_B = 1 - f \) in the disordered phase), \( b_1 \) is the amplitude of the modulations, and \( G_i^{(\text{lam})} \) are the set of reciprocal lattice vectors for a lamellar phase with layer normals oriented along the \( y \)-axis (we list them in Appendix A). The wave vector magnitude \( q_0 \) characterizes the periodicity of the phase; in this case, since the lamellar period is \( L_0 \), we have \( q_0 = 2\pi/L_0 \) for all of the phases (not just the lamellar phase). A 3D density plot of the lamellar phase with such an orientation is shown in Figure 4.8a for reference.

The ordering density fields for the hexagonal cylindrical phase are similarly generated, but there are six reciprocal lattice vectors:

\[
\rho^{(\text{hex})}_A(r) = f + b_1 \sum_{i=1}^{6} \cos \left( q_0 G_i^{(\text{hex})} \cdot r \right)
\]

\[
\rho^{(\text{hex})}_B(r) = 1 - \rho^{(\text{hex})}_A(r)
\]  

(3.57)

where the cylinders are aligned along the \( z \)-axis, and satisfy the epitaxial relationship with lamellae having layer normals parallel to any of the reciprocal lattice vectors \( G_i^{(\text{hex})} \) (also given in Appendix A). In order to be commensurate, the dimensions of the box must satisfy \( L_x = \frac{2}{\sqrt{3}} n L_0 \) and \( L_y = 2mL_0 \), where \( n \) and \( m \) are some positive integers. A 3D density plot of the hexagonal cylindrical phase is shown in Figure 4.8b for reference.

Ordering density fields for the body-centred cubic spherical phase are generated
with 12 reciprocal lattice vectors \( G_i^{(bcc)} \) (see Appendix A):

\[
\rho_A^{(bcc)}(\mathbf{r}) = f + b_1 \sum_{i=1}^{12} \cos \left( q_0 G_i^{(bcc)} \cdot \mathbf{r} \right)
\]

\[
\rho_B^{(bcc)}(\mathbf{r}) = 1 - \rho_A^{(bcc)}(\mathbf{r}).
\] (3.58)

In order to be commensurate, the box must have sides of length \( L_x = \sqrt{2}nL_0 \), \( L_y = \sqrt{2}mL_0 \) and \( L_z = \sqrt{2}lL_0 \) where \( n, m \) and \( l \) are some positive integers. Figure 3.6b illustrates the epitaxial relationship between the body-centred cubic spherical phase, oriented in this way, and the lamellar phase, which can form in any one of the \( (110), (101), (011), (\bar{1}10), (\bar{1}01) \) and \( (0\bar{1}1) \) planes. A 3D density plot of the body-centred cubic spherical phase is shown in Figure 4.8c for reference.

For the gyroid phase, in addition to the first-mode vectors \( G_i^{(gyr)} \), it is also necessary to include a set of second-mode vectors \( K_i^{(gyr)} \) (see Appendix A). Altogether, an ordering density field for the gyroid phase can be generated by

\[
\rho_A^{(gyr)}(\mathbf{r}) = f + b_1 \sum_{i=1}^{6} \cos \left( q_0 G_i^{(gyr)} \cdot \mathbf{r} \right) - b_1 \sum_{i=7}^{12} \cos \left( q_0 G_i^{(gyr)} \cdot \mathbf{r} \right)
\]

\[
+ b_2 \sum_{i=1}^{6} \cos \left( q_0 K_i^{(gyr)} \cdot \mathbf{r} \right)
\]

\[
\rho_B^{(gyr)}(\mathbf{r}) = 1.0 - \rho_A^{(gyr)}(\mathbf{r}).
\] (3.59)

In order to be commensurate in this case, the box dimensions must satisfy \( L_x = \sqrt{6}nL_0 \), \( L_y = \sqrt{6}mL_0 \) and \( L_z = \sqrt{6}lL_0 \), where \( n, m \) and \( l \) are some positive integers. The orientations of the gyroid and lamellar phases are epitaxially related such that the \([001]\) directions in the lamellar unit cell are parallel to the \([211]\) directions in the gyroid unit cell \([118, 119]\). A 3D density plot of the gyroid phase is shown in Figure 4.8d for reference.

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3.2.3 Calculation of the lamellar period

The construction of the ordering fields, just described, relies on knowing the characteristic wave vector \( q_0 = \frac{2\pi}{L_0} \), which in turn depends on the lamellar period \( L_0 \). Thus, we must determine the preferred period for the lamellar phase. If we are near the weak segregation limit, we expect this period to be close to \( L_0 = 4R_g \approx 13b \) (see Figure 1.5), where \( R_g \) is the radius of gyration for the chains with \( N = 64 \). This provides us with a starting point. If we set up a system with dimensions \((L_x, L_y, L_z)\) in which an \( n \)-layer lamellar ordering field is applied having the lamellar normal aligned with the \( y \)-axis, this forces the system to take on the lamellar period \( L_y/n \). We expect the free energy of such a configuration to have a minimum when \( L_y/n = L_0 \). If \( L_y/n \) is far enough offset from \( L_0 \), the configuration becomes unfavourable enough that the system will transition to either an \((n - 1)\)- or \((n + 1)\)-layer configuration, depending on the direction of the offset. Figure 3.7 illustrates this concept: free energy curves for various \( n \)-layer systems are shown schematically as a function of \( L_y/L_0 \).

The distance between free energy minima should give the lamellar period \( L_0 \), as shown in Figure 3.7. However, we do not have access to these free energy curves; thus, we do not know where the minima lie. The down-triangles in Figure 3.7 correspond to the values of \( L_y \) for which the system first transitions from an \( n \)-layer system to an \((n - 1)\)-layer system as \( L_y \) is decreased (we shall denote these values as \( L_y^{(n \rightarrow n-1)} \)), and the up-triangles correspond to the \( n \)- to \((n + 1)\)-layer transitions as \( L_y \) is increased (we shall denote these as \( L_y^{(n \rightarrow n+1)} \)). These values we can obtain, by decreasing (or increasing) \( L_y \) for fixed \( n \) until the system transitions to an \((n - 1)\)-layer (or an \((n + 1)\)-layer) system. The filled black circles indicate the averages of \( L_y^{(n \rightarrow n+1)} \) and \( L_y^{(n+1 \rightarrow n)} \) (we shall denote these as \( L_y^{(n+1/2)} \)). In Figure 3.7 these lie halfway between consecutive free energy minima, because the schematic free energy curves are symmetric. However, these free energy curves in a real system are not necessarily symmetric. Even in the asymmetric case, though, the difference between the \( L_y^{(n+1/2)} \)
for adjacent values of $n$ should give the lamellar period.

Figure 3.8 shows our data for such simulations, including $L_y^{(n\rightarrow n+1)}$ (up-triangles), $L_y^{(n\rightarrow n-1)}$ (down-triangles) and $L_y^{(n+1/2)}$ (filled black circles). We explore $n = 2 \rightarrow 8$ and for each $n$ perform a series of simulations in which $L_y$ is varied, using $L_y \approx 4nR_g$ as a starting point for each $n$. The slope of the linear fit to the values of $L_y^{(n+1/2)}$ gives us $L_0 = 14b$. These simulations are all run at common values of $f = 0.5$ and $\epsilon N = 0.256$, thus we do not account for a possible dependence of $L_0$ on $\epsilon N$ in this work.

### 3.2.4 Calculation of the centre-of-mass diffusion coefficients

In Chapter 4, we will examine chain self-diffusion in the ordered phases of the diblock copolymer melt. We will focus on the anisotropy in diffusivity, and the suppression of
diffusion perpendicular to the domain interfaces for the lamellar, cylindrical, spherical and gyroid phases. These aspects will be characterized by the diffusion coefficients in the $x$-, $y$- and $z$-directions, $D_x$, $D_y$ and $D_z$. The diffusion coefficients are obtained from the late-time linear behaviour of the centre-of-mass mean-squared displacements (MSD) in the $x$-, $y$- and $z$-directions, which are calculated according to

$$\langle \Delta R_{cm,\alpha}(t)^2 \rangle = \frac{1}{n_r} \sum_{k=1}^{n_r} (R_{cm,\alpha}^{(k)}(t) - R_{cm,\alpha}^{(k)}(0))^2$$  \hspace{1cm} (3.60)$$

where $k$ labels the chain replicas, and $\alpha = x, y, \text{or } z$. If the motion of the chain centres-of-mass is diffusive, the mean-squared displacements will satisfy

$$\langle \Delta R_{cm,\alpha}(t)^2 \rangle = 2D_\alpha t,$$ \hspace{1cm} (3.61)
and $D_\alpha$ can be extracted from the slope of the $\langle \Delta R_{cm,\alpha}(t)^2 \rangle$ versus time graph. If a chain is undergoing free diffusion, the MSD plot will be linear with a slope $2D_0$, where

$$D_0 = \frac{k_B T}{N\zeta}$$

is the Rouse diffusion coefficient. However, as we will see in Chapter 4, the motion perpendicular to the domain interfaces in the ordered phases of the diblock copolymer melt is more complicated. In this case, motion on length-scales larger than the interfacial width is achieved by the hopping of chains across the domain rich in the other species. At late times, this motion is diffusive but suppressed relative to $D_0$. The MSD curves display a crossover from free diffusion at early times where the chains are not moving far enough to leave their own domain, suppressed diffusion at late times where the chains hop between domains, and a crossover region in between.

These regimes can be seen in Figure 3.9, where we plot some example MSD curves for the lamellar, cylindrical, spherical and gyroid phases that demonstrate such suppressed late-time diffusive behaviour. Three curves are provided for each phase, representative of the range of segregation strengths that we explore for those phases, with red curves being the most weakly segregated of the three, green curves being the most strongly segregated of the three, and blue being intermediate. The data are plotted with logarithmic axes, and $\langle \Delta R(t)^2 \rangle \propto t^1$ curves (dashed lines) are provided for reference on each plot. The diffusion coefficients are calculated by a linear regression of late-time $\langle \Delta R_{cm,\alpha}(t)^2 \rangle$ versus $t$ data, in the fit window which is indicated by the vertical dotted lines, and includes data approximately in the range $t = 10\tau_R \to 15\tau_R$ for the HEX, BCC and GYR phases, and $t = 25\tau_R \to 30\tau_R$ for the LAM phase. Due to the large number of data points within the fit window ($5\tau_R \approx 1 \times 10^4 \Delta t$), the error associated with the fit is negligible ($\sim 10^{-2\%}$).

Our main concern for the data of Figure 3.9 is whether or not the MSD curves have set into the late-time linear regime within the fit window. In almost all cases, this requirement is satisfied. The exception is the strongly suppressed data of the lamellar phase (blue and green curves on the LAM plot). The characteristic time-
Figure 3.9: Centre-of-mass mean-squared displacement curves on logarithmic axes, for the lamellar (LAM), cylindrical (HEX), spherical (BCC) and gyroid (GYR) phases. The red, blue and green curves, in that order, correspond to increasing segregation strengths for each phase. The dashed lines are $\langle \Delta R(t)^2 \rangle \propto t^1$, corresponding to diffusive behaviour. The vertical dotted lines are the fit windows used to calculate the diffusion coefficients for each phase.

scale for the hopping process is evidently significantly longer for the lamellar phase than for the others, and since the late-time linear regime only sets in for times longer than this characteristic time, we must move our fit window out to later times for the lamellar phase. Thus, for our chain diffusion calculations on the lamellar phase, we shift the fit window to times $t = 25\tau_R \rightarrow 30\tau_R$. For the other phases we use the original $t = 10\tau_R \rightarrow 15\tau_R$ fit window.

This concludes our description of the relevant calculations for the analysis in Chapter 4, and is the end of the first half of Chapter 3. The remainder of this chapter
will deal with the characterization of numerical errors due to our implementation.

### 3.3 Characterization of the numerical method

Our numerical solution to the mean-field equations involves the introduction of several parameters, which should have no physical relevance as they do not appear in the original theory. There are three such parameters: the time discretization $\Delta t$, the space discretization $\Delta$, and the average number of replica-beads per grid point $\langle N_b \rangle$ (or equivalently, the number of chain replicas $n_r$). If our algorithms are working as intended, the accuracy of our numerical solution should improve as $\Delta t \to 0$, $\Delta \to 0$, and $\langle N_b \rangle \to \infty$. Ideally, one wishes to operate in a regime where the results of our simulations do not depend significantly on the values of these parameters. Thus, the main goal of this section is to characterize how the numerical error incurred by our simulation scheme depends on $\Delta t$, $\Delta$ and $\langle N_b \rangle$.

We will address each of these parameters in turn, examining their effects on the error in such quantities as the local density, bead displacements, and $(\epsilon N)_{ODT}$ for the symmetric diblock copolymer melt. In our discussion of the time step $\Delta t$, we will explore alternate, more sophisticated (but more computationally expensive) schemes to the operator-splitting and Euler schemes described in Section 3.1, to determine whether or not using them would be warranted. We will also briefly explore the effects of chain length $N$ on $(\epsilon N)_{ODT}$, to see if finite chain length effects are significant near $N = 64$.

#### 3.3.1 Chain ensemble size

As mentioned, the ensemble size is characterized by the average number of replica-beads per grid point, $\langle N_b \rangle$. If the volume of the box is $V = M_x M_y M_z \Delta V = M_x M_y M_z \Delta^3$, then for a chain ensemble consisting of $n_r$ replicas of chains of length
The average number of replica-beads per grid point \( \langle N_b \rangle \) is

\[
\langle N_b \rangle = \frac{n_r N}{M_x M_y M_z}.
\] (3.62)

Note the terminology *replica-beads*, which distinguishes the set of beads that comprise the ensemble from the set of *actual* beads that comprise the \( n_P \)-chain system. The total number of replica-beads \( N_b(\mathbf{r}) \) at a given grid position \( \mathbf{r} \) will fluctuate about \( \langle N_b \rangle \), and the size of these fluctuations \( \delta N_b(\mathbf{r}) \) will have some dependence on \( \langle N_b \rangle \). We can approximate \( \delta N_b(\mathbf{r}) \) by assuming that each replica-bead is randomly distributed throughout the system, and thus that each replica-bead is uncorrelated with the others. Although this is *not* the case for beads on the same chain (such beads *are* in general correlated), the assumption nevertheless is good enough for our purposes (as we will see). With this assumption, the probability of finding \( N_b(\mathbf{r}) \) replica-beads is independent of the position \( \mathbf{r} \) and satisfies a Poisson distribution. If the number of replica-beads is large, however, this probability distribution becomes approximately Gaussian, with a dependence on \( \langle N_b \rangle \):

\[
P(N_b) \sim \exp \left[ -\frac{M_x M_y M_z}{2 n_r N} (N_b - \langle N_b \rangle)^2 \right] = \exp \left[ -\frac{1}{2 \langle N_b \rangle} (N_b - \langle N_b \rangle)^2 \right],
\] (3.63)

which leads to fluctuations \( \delta N_b \sim \sqrt{\langle (N_b - \langle N_b \rangle)^2 \rangle} \sim \langle N_b \rangle \). Ultimately, we are interested in the local error in the density \( \delta \rho \) that results from the finite size of the chain ensemble. If, for a system with average density \( \rho_0 \), there are \( N_b(\mathbf{r}) \) replica-beads at a given grid point, then the density \( \rho(\mathbf{r}) \) is given by

\[
\rho(\mathbf{r}) = \frac{N_b(\mathbf{r})}{\langle N_b \rangle} \rho_0.
\] (3.64)
The probability distribution for the density $\rho(r)$ can be derived by combining Eqs. (3.64) and (3.63):

$$P(\rho) \sim \exp \left[ -\frac{1}{2\langle N_b \rangle} \left( \frac{\langle N_b \rangle \rho(r) - \langle N_b \rangle}{\rho_0} \right)^2 \right] = \exp \left[ -\frac{\langle N_b \rangle}{2} \left( \frac{\rho(r)}{\rho_0} - 1 \right)^2 \right]$$ (3.65)

and we find that the local error in the density has an $\langle N_b \rangle$-dependence of the form

$$\delta \rho \sim \langle N_b \rangle^{-1/2} = \left( \frac{n_r N}{M_x M_y M_z} \right)^{-1/2},$$ (3.66)

as expected [53]. To verify this relationship, we may calculate histograms of the density for different ensemble sizes (see Fig. 3.10). The essential characteristic, that the width $\sigma$ of the distributions $P(\rho)$ decreases as the chain ensemble size increases, is clearly visible in Fig. 3.10; also notable is that for $\langle N_b \rangle = 15$ artifacts due to the small ensemble size are already heavily distorting the shape of the distribution. We may measure the width $\sigma$ of the distributions, and thus the local error in the density $\delta \rho$, via Gaussian fits to

$$P(\rho) = A \exp \left[ -\frac{1}{2\sigma^2} \left( \frac{\rho}{\rho_0} - 1 \right)^2 \right].$$ (3.67)

In Figure 3.11 we show $\sigma$ as a function of $\langle N_b \rangle$ on logarithmic axes, from which we see that the $\delta \rho \sim \langle N_b \rangle^{-1/2}$ prediction of Eq. (3.66) is verified.

The fluctuations in the density introduced by the finite chain ensemble stabilize the disordered phase and thus shift the ODT to higher values of $\epsilon N$. To demonstrate this effect, we have performed simulations of a symmetric diblock copolymer with $N = 64$ and located $(\epsilon N)_{ODT}$ for various values of $\langle N_b \rangle$, shown in Fig. 3.12. The ODT is located by performing a series of simulations at different $\epsilon N$, initializing the system in the disordered phase and waiting a long time ($\sim 100$’s of $\tau_R$) to see if phase separation occurs. Indeed, for $\langle N_b \rangle < 45$ the ODT begins to shift to higher $\epsilon N$, but
Figure 3.10: Probability distributions for the density, averaged over the system, as the chain ensemble size is changed such that $\langle N_b \rangle$ varies from $\langle N_b \rangle = 15$ to $\langle N_b \rangle = 500$ (neither the system size nor the grid spacing $\Delta$ were changed here). The system contained symmetric diblock copolymers of length $N = 64$, with $\rho_0 = 1$ and $\epsilon N = 0.2176$ (in the lamellar phase), initialized in the disordered phase. The distributions were calculated after long times (of $\mathcal{O}(100\tau_R)$), allowing time for phase separation to occur. The operating chain ensemble size of $\langle N_b \rangle = 60$ is highlighted (blue).

for our operating value of $\langle N_b \rangle = 60$ (which is circled in Figure 3.12) we are in the region where the ODT is not changing significantly, within the error. The error bars are due to the finite $\Delta \epsilon$ by which we change $\epsilon$ for each subsequent run: $\Delta \epsilon$ cannot be made too small as it becomes difficult to pin down the precise location of the critical point due to the associated critical slowing down behaviour [59]. That is, as we get close to the ODT it becomes difficult to distinguish whether the system appears to be disordered because $\epsilon N < (\epsilon N)_{ODT}$ or because the simulation time is not long
Figure 3.11: A log-log plot of the width $\sigma$ of the density probability distribution $P(\rho)$, as a function of the average number of beads per grid point $\langle N_b \rangle$, which agrees with the predicted $\sigma \sim \langle N_b \rangle^{-1/2}$ dependence (solid line).

enough to see phase separation and ordering, due to the critical slowing down effect; this reduces our confidence for those values of $\epsilon N$ that may be very close to the true $(\epsilon N)_{ODT}$.

Whether or not the fluctuations due to the finite chain ensemble size can be related to physical composition fluctuations is not clear. Beyond characterizing the effect of $\langle N_b \rangle$ on $(\epsilon N)_{ODT}$, we have not investigated this possibility. Thus, in this work we simply treat these fluctuations as being nothing more than a sampling error in the local density.
Figure 3.12: The critical point $(\epsilon N)_{ODT}$ as a function of $\langle N_b \rangle$, for a symmetric diblock copolymer melt with $N = 64$. Our operating chain ensemble size of $\langle N_b \rangle = 60$ (highlighted) is in the region where the ODT is no longer changing within the error, at $(\epsilon N)_{ODT} \approx 0.183 \pm 0.003$.

### 3.3.2 Time step $\Delta t$

There are several approximations in our numerical solution to the mean-field equations which produce an error with a sensitivity to the time step size $\Delta t$, particularly in the evolution of replica-bead positions via the Langevin equation. We use operator splitting on the Langevin equation which allows us to treat each of the three operators of the right-hand side efficiently and conveniently; however, the simple sequential operator splitting that we employ introduces an error that scales linearly with $\Delta t$. 
To illustrate this, consider the Langevin equation

\[
\frac{\partial R_n(t)}{\partial t} = F_{spr}(t) + \psi(R_n(t), t) + f_n(t) = (A + B + C) R_n(t) \tag{3.68}
\]

where \(A\), \(B\) and \(C\) are operators associated with the spring force, mean force-field and random force, respectively. For our purposes, we do not require knowledge of their exact form; it is sufficient merely that these operators exist. An exact formal solution to Eq. (3.68) can be written as

\[ R_n(t + \Delta t) = e^{(A+B+C)\Delta t} R_n(t). \tag{3.69} \]

With the sequential operator splitting scheme, Eq. (3.68) is split into three equations, which at each time step are applied sequentially to evolve the bead position from \(R_n(t)\) to \(R_n(t + \Delta t)\):

\[
\frac{\partial R_n(t)}{\partial t} = F_{spr}(t) \tag{3.70}
\]

\[
\frac{\partial R_n(t)}{\partial t} = \psi(R_n(t), t) \tag{3.71}
\]

\[
\frac{\partial R_n(t)}{\partial t} = f_n(t), \tag{3.72}
\]

which are equivalent to approximating Eq. (3.69) as

\[ R_n(t + \Delta t) = e^{A\Delta t} e^{B\Delta t} e^{C\Delta t} R_n(t). \tag{3.73} \]

This is equivalent to the approach that we describe in Section 3.1.5. We may evaluate the error introduced by the sequential operator splitting scheme by expanding the right-hand sides of Eqs. (3.69) and (3.73) in powers of \(\Delta t\). For Eq. (3.69), which is
exact, we obtain

\[ R_n(t + \Delta t) = \left[ 1 + A\Delta t + B\Delta t + C\Delta t + \frac{1}{2}\Delta t^2 (A^2 + B^2 + C^2) + \frac{1}{2}\Delta t^2 (AB + BA + AC + CA + BC + CB) + O(\Delta t^3) \right] R_n(t), \]  

(3.74)

whereas for Eq. (3.73) we obtain

\[ R_n(t + \Delta t) = \left[ 1 + A\Delta t + B\Delta t + C\Delta t + \frac{1}{2}(A^2 + B^2 + C^2) + AB + BA + AC + CA + BC + CB + [A, B] + [A, C] + [B, C] \right] \Delta t^2 + O(\Delta t^3) R_n(t), \]  

(3.75)

where for example \([A, B] = AB - BA\) is the commutator for the operators \(A\) and \(B\). Comparing the \(O(\Delta t^2)\) terms in Eqs. (3.74) and (3.75), we can see that the dominant error terms introduced in \(R_n(t)\) per time-step by the sequential operator splitting scheme are the commutator terms, which are order \(\Delta t^2\):

\[ \delta \Delta R_n(t) = \delta (R_n(t + \Delta t) - R_n(t)) \approx ([A, B] + [A, C] + [B, C]) \Delta t^2 R_n(t). \]  

(3.76)

which leads to a global error \(\delta R_n(t)\) of \(O(\Delta t)\). This error will be present even if Eqs. (3.70)-(3.72) themselves are solved exactly; however, the Euler scheme used to solve Eq. (3.71) is not exact and thus also contributes some error. To illustrate this,
consider the Taylor series expansion of the bead position $R_n(t + \Delta t)$, near $t$:

$$R_n(t + \Delta t) = R_n(t) + \frac{d R_n(t)}{dt} \Delta t + \frac{1}{2} \frac{d^2 R_n(t)}{dt^2} \Delta t^2 + \ldots$$

$$= R_n(t) + \psi(R_n(t), t) \Delta t + \frac{1}{2} \frac{d \psi(R_n(t), t)}{dt} \Delta t^2 + \ldots$$

$$= R_n(t) + \psi(R_n(t), t) \Delta t$$

$$+ \frac{1}{2} \left( \sum_{\alpha=x,y,z} \frac{\partial \psi(R_n(t), t)}{\partial R_{n,\alpha}(t)} \frac{\partial R_{n,\alpha}(t)}{\partial t} + \frac{\partial \psi(R_n(t), t)}{\partial t} \right) \Delta t^2 + \ldots$$

$$= R_n(t) + \psi(R_n(t), t) \Delta t$$

$$+ \frac{1}{2} \left( \sum_{\alpha=x,y,z} \frac{\partial \psi(R_n(t), t)}{\partial R_{n,\alpha}(t)} \psi_{\alpha}(R_n(t), t) + \frac{\partial \psi(R_n(t), t)}{\partial t} \right) \Delta t^2 + \ldots$$

(3.77)

from which, by comparison with the Euler scheme

$$R_n(t + \Delta t) = R_n(t) + \psi(R_n(t), t) \Delta t,$$  \hspace{1cm} (3.78)

we can see that the Euler scheme introduces an error per time-step of $O(\Delta t^2)$, and thus a global error in $R_n(t)$ of $O(\Delta t)$. The spring force equation is solved exactly using Rouse modes, and thus introduces no error, and the error introduced by the random noise equation is a sampling error due to the finite chain ensemble and thus should have no $\Delta t$ dependence. The sources of error due to the time step size $\Delta t$ are thus limited to the sequential operator splitting scheme and the Euler scheme used to solve the mean force-field equation.

It is possible to improve the error scaling from $O(\Delta t)$ to $O(\Delta t^2)$, by replacing the sequential operator splitting scheme with a symmetric operator splitting scheme and using a 2nd-order Runge-Kutta scheme for the mean force-field equation instead of the Euler scheme. In a symmetric operator splitting scheme, we replace Eq. (3.73)
with
\[ R_n(t + \Delta t) = e^{A\Delta t/2}e^{B\Delta t/2}e^{C\Delta t}e^{B\Delta t/2}e^{A\Delta t/2}R_n(t). \] (3.79)

In this scheme, two of the three operators must be applied twice, which increases the computational cost; however, we are free to choose the operator that is applied only once, and so the operator \( C \) would be chosen to be the most computationally expensive step, which in our case is the 2\(^{nd}\)-order Runge-Kutta mean force-field step since it requires that the mean force-field be re-calculated at the mid-point of the time-step each time it is applied. Again, we evaluate the error introduced by this scheme by expanding Eq. (3.79) in powers of \( \Delta t \):

\[
R_n(t + \Delta t) = \left(1 + \frac{1}{2}A\Delta t + \frac{1}{8}A^2\Delta t^2 + \ldots \right) \left(1 + \frac{1}{2}B\Delta t + \frac{1}{8}B^2\Delta t^2 + \ldots \right) \\
\times \left(1 + C\Delta t + \frac{1}{2}C^2\Delta t^2 + \ldots \right) \left(1 + \frac{1}{2}B\Delta t + \frac{1}{8}B^2\Delta t^2 + \ldots \right) \\
\times \left(1 + \frac{1}{2}A\Delta t + \frac{1}{8}A^2\Delta t^2 + \ldots \right) R_n(t) \\
= \left[ 1 + A\Delta t + B\Delta t + C\Delta t + \frac{1}{2}\Delta t^2 (A^2 + B^2 + C^2) \\
+ \frac{1}{2}\Delta t^2 (AB + BA + CA + AC + BC + CB) + \mathcal{O}(\Delta t^3) \right] R_n(t).
\] (3.80)

By comparison with Eq. (3.74), the terms match up to \( \mathcal{O}(\Delta t^2) \) and therefore the error introduced by the symmetric operator splitting scheme, per time-step, is at most of \( \mathcal{O}(\Delta t^3) \); this scheme therefore introduces a global error of \( \mathcal{O}(\Delta t^2) \) (as opposed to the \( \mathcal{O}(\Delta t) \) error of the sequential operator splitting scheme).

We must also remove the other source of the \( \mathcal{O}(\Delta t) \) error (the Euler scheme used to solve Eq. (3.71)), which can be achieved by implementing a 2\(^{nd}\)-order Runge-Kutta scheme. The evolution of the bead positions in this scheme is essentially an Euler scheme where the mean force-field is evaluated at the midpoint of the interval; that
is, $\psi$ is evaluated at the position $R_n(t) + \frac{\Delta t}{2} \psi(R_n(t), t)$ and the time $t + \frac{\Delta t}{2}$:

$$\mathbf{R}_n(t + \Delta t) = \mathbf{R}_n(t) + \Delta t \psi \left( \mathbf{R}_n(t) + \frac{\Delta t}{2} \psi(R_n(t), t), t + \frac{\Delta t}{2} \right). \quad (3.81)$$

In order to calculate the error due to this method, we can expand the mean force-field, evaluated at the midpoint, near $\mathbf{R}_n(t)$ and $t$:

$$\psi \left( \mathbf{R}_n(t) + \frac{\Delta t}{2} \psi(R_n(t), t), t + \frac{\Delta t}{2} \right) = \psi \left( \mathbf{R}_n(t), t + \frac{\Delta t}{2} \right)$$

$$+ \sum_{\alpha = x,y,z} \frac{\partial \psi}{\partial R_n,\alpha(t)} \frac{\Delta t}{2} \psi_\alpha(R_n(t), t) + O(\Delta t^2)$$

$$= \psi(R_n(t), t) + \frac{\partial \psi(R_n(t), t)}{\partial t} \frac{\Delta t}{2}$$

$$+ \sum_{\alpha = x,y,z} \frac{\partial \psi}{\partial R_n,\alpha(t)} \frac{\Delta t}{2} \psi_\alpha(R_n(t), t) + O(\Delta t^2), \quad (3.82)$$

and insert Eq. (3.82) into Eq. (3.81):

$$\mathbf{R}_n(t + \Delta t) = \mathbf{R}_n(t) + \Delta t \psi(R_n(t), t)$$

$$+ \frac{\Delta t^2}{2} \left( \sum_{\alpha = x,y,z} \frac{\partial \psi(R_n(t), t)}{\partial R_n,\alpha(t)} \psi_\alpha(R_n(t), t) + \frac{\partial \psi(R_n(t), t)}{\partial t} \right) + O(\Delta t^3), \quad (3.83)$$

which up to $O(\Delta t^2)$ matches Eq. (3.77). The 2nd-order Runge-Kutta scheme thus introduces an error per time-step of $O(\Delta t^3)$ and a global error of $O(\Delta t^2)$.

To illustrate the $\Delta t$-dependence of these various schemes, we will examine various properties of the lamellar phase, with lamellar normals aligned with the $y$-axis, in a symmetric diblock copolymer melt with $N = 64$, at $\epsilon N = 0.2176$ (in the ordered phase region, aligned using a lamellar ordering field). We will focus on the diffusion of the chain centres-of-mass perpendicular to the lamellae (see Section 3.2.4 for a
reminder of how this calculation is performed), the displacements of the junction point between $A$ and $B$ blocks, and the degree of segregation which will be measured by the amplitude $a/\rho_0$ of the modulations in the density of species $A$ in the lamellar phase. Figure 3.13 shows $D_\perp/D_0$ as a function of $\Delta t$, for scheme i) the sequential operator-splitting with the Euler scheme, and for scheme ii) the symmetric operator-splitting with the $2^{nd}$-order Runge-Kutta scheme. We can see that for small $\Delta t$, the perpendicular diffusion coefficient $D_\perp/D_0$ appears to decrease linearly with increasing $\Delta t$ when using scheme i). Both schemes produce an error in the diffusion coefficient for $\Delta t = 0.2\tau$ between approximately 5% and 7%. For scheme ii), we would expect...
to see a \((\Delta t)^2\) dependence, but the precise dependence of the error on \(\Delta t\) seems to be obfuscated by fluctuations, which we suspect are due to the sampling error associated with the finite size of the chain ensemble. It may be that these fluctuations can be reduced, or perhaps made negligible by increasing \(\langle N_b \rangle\). Unfortunately, due to the requirement to run for relatively long times (10’s of \(\tau_R\)) in order to calculate \(D_L/D_0\), increasing \(\langle N_b \rangle\) significantly is not practical in this case. Regardless, with our operating value of \(\langle N_b \rangle = 60\), using more sophisticated schemes than our symmetric operator splitting and Euler scheme do not appear to provide an improvement, at least in terms of the effect of \(\Delta t\) on the centre-of-mass diffusion.

We may choose instead to evaluate the error for a quantity which can be calculated on shorter time-scales, such as the root mean-squared displacement of the junction point, \(R_{\text{MSD}}(t) = \sqrt{\langle (R_{N/2}(t) - R_{N/2}(0))^2 \rangle}\). This makes it feasible to increase \(\langle N_b \rangle\) significantly. In general, for some value of \(\Delta t\), we can write \(R_{\text{MSD}}(t, \Delta t)\) as

\[
R_{\text{MSD}}(t, \Delta t) = \tilde{R}_{\text{MSD}}(t) + \alpha(\Delta t)^\beta
\]  

(3.84)

where \(\tilde{R}_{\text{MSD}}(t)\) is the exact (but unknown) result for \(R_{\text{MSD}}(t)\), and the second term on the right-hand side is an error introduced by the finite time step \(\Delta t\), which is characterized by the constants \(\alpha\) and \(\beta\). We may obtain \(\beta\) by varying \(\Delta t\) in powers of 2 and calculating the quantity \(\Delta R_{\text{MSD}}(t, \Delta t)\), which is defined as

\[
\Delta R_{\text{MSD}}(t, \Delta t) = R_{\text{MSD}}(t, 2\Delta t) - R_{\text{MSD}}(t, \Delta t)
= \tilde{R}_{\text{MSD}}(t) + \alpha(2\Delta t)^\beta - \left(\tilde{R}_{\text{MSD}}(t) + \alpha(\Delta t)^\beta\right)
= \alpha\Delta t^\beta (2^\beta - 1).
\]  

(3.85)

The quantity \(\Delta R_{\text{MSD}}(t, \Delta t)\) is plotted on logarithmic axes in Fig. 3.14 for scheme i) the sequential operator-splitting with Euler step, and scheme ii) the symmetric...
operator-splitting with $2^{nd}$-order Runge-Kutta scheme. The chains are evolved only a very short time of $t = 1.6\tau$ (8 time steps), to enable us to increase the chain ensemble size by several orders of magnitude in order to reduce the sampling error as much as possible, without the simulation run-times becoming prohibitively large. As expected, for small $\Delta t$ scheme i) displays a linear $\Delta t$ dependence and scheme ii) displays a $(\Delta t)^2$ dependence, although for very small $\Delta t$ we see a deviation from $(\Delta t)^2$ in scheme ii): this can be attributed to the sampling error which, despite the generous $\langle N_b \rangle = 2 \times 10^5$ ensemble size, is not negligible in comparison with the error due to $\Delta t$ for these small values of $\Delta t$. If indeed this deviation from $(\Delta t)^2$ for scheme

![Graph](image)

Figure 3.14: $\Delta R_{MSD}(t, \Delta t)$ versus $\Delta t$, for scheme i) the sequential operator-splitting with Euler (filled circles) and scheme ii) the symmetric operator-splitting with $2^{nd}$-order Runge-Kutta (filled squares). A large chain ensemble of $\langle N_b \rangle = 2 \times 10^5$ is used to reduce the fluctuations due to sampling error. Our operating value of $\Delta t/\tau = 0.2$ is highlighted (outlined).
ii) is due to the chain ensemble sampling error, we should see the deviation effect increase if we decrease the size of the chain ensemble. Figure 3.15 shows this effect, varying $\langle N_b \rangle$ from $1 \times 10^4$ to $2 \times 10^5$.

![Figure 3.15: $\Delta R_{MSD}(t, \Delta t)$ versus $\Delta t$, using scheme ii), for varying chain ensemble sizes.](image)

The fact that the numerical errors due to schemes i) and ii) scale with $\Delta t$ in the way that we expect is also an indication that our integration code is working correctly. The algorithm employed in this work corresponds to scheme i), despite the fact that we have shown here that scheme ii) produces a more desirable $(\Delta t)^2$ scaling of the error. There are two reasons for choosing scheme i) over scheme ii) in our case. First of all, scheme ii) is more computationally expensive than scheme i). Secondly, at our operating time-step $\Delta t = 0.2\tau$ the error is not reduced significantly in using scheme ii) over scheme i), at least in the case of the diffusion coefficients of Figure 3.13; this
is because the fluctuations due to the sampling error for $\langle N_b \rangle = 60$ dominate the error for $\Delta t = 0.2\tau$ and thus wash out any advantage we would gain by using scheme ii). It is also impractical to increase $\langle N_b \rangle$ by the orders-of-magnitude that would be required to reduce the sampling error enough that the $(\Delta t)^2$ scaling of scheme ii) is revealed.

Ultimately, our choice of the time-step $\Delta t = \tau/5$ is motivated by the fact that the fastest Rouse mode has a relaxation time $\tau_{N-1} \approx \tau/4$. Choosing a larger time-step, such that $\Delta t \geq \tau_{N-1}$ would mean that at each time-step we allow some of the fastest Rouse modes to relax essentially completely during each iteration of the spring force step (Eq. (3.70)). This is made worse by the fact that the spectrum of relaxation times for the discrete-chain Rouse model (see Eq. (3.28)) has the feature that many of the fast discrete modes have relaxation times that are very close together. For instance, for $N = 64$, half of the discrete Rouse modes have relaxation times $\tau_p < \tau/2$. This is shown in Figure 3.16, where various Rouse mode relaxation times are plotted as vertical dashed lines. If we were to just double our time-step to $\Delta t = 0.4\tau$, we would no longer be resolving the relaxation of almost half of the modes in the chain.

We can investigate this effect by varying $\Delta t$ and observing its effects on the degree of segregation. We expect our resolution of the Rouse modes to affect the way that the chains relax in an applied field, and anticipate that this may have an effect on the degree of segregation which could be seen in the amplitude of the modulations in the lamellar phase at fixed $\epsilon N$. The error introduced by the Euler step of our mean force-field calculation could also influence the density profile, and therefore the degree of segregation. Figure 3.16 shows the amplitude of density modulations for species A in the lamellar phase at equilibrium for $\epsilon N = 0.2176$, as a function of $\Delta t$. As $\Delta t$ increases, our treatment of the dynamics of the fastest Rouse modes worsens. Eventually we enter the regime where $\Delta t > \tau$ and we begin to see a significant effect on the modulation amplitude; the modes that we are cutting off likely play a role.
Figure 3.16: The amplitude $a$ of modulations in the density of species $A$ in the lamellar phase at equilibrium, as a function of the time step $\Delta t$. We initialize the system using a lamellar ordering field, at $\epsilon N = 0.2176$, with the period $L_0 = 14b$ and lamellar normals aligned with the $y$-axis. The cross-sectional density profiles in the $y$-direction are fit to $\rho_A(y) = 0.5 + a \cos \left[ \frac{2\pi}{L_0} (y - b) \right]$. Selected Rouse mode relaxation times are also shown for reference (vertical dashed lines).

in the relaxation of the interfaces, and as a result we see an effective reduction in segregation strength. Our operating value of $\Delta t = 0.2\tau$ lies in the region where the amplitude does not appear to be changing significantly.

### 3.3.3 Grid spacing $\Delta$

The density field $\rho(r, t)$ and the mean force-field $\psi(r, t)$ are calculated on an $M_x \times M_y \times M_z$ grid with grid spacing $\Delta$. When choosing the grid spacing $\Delta$, we must consider a balance between accuracy/resolution (improved by decreasing $\Delta$) and computational
efficiency (improved by increasing $\Delta$). Since we estimate $\rho(r, t)$ and $\psi(r, t)$ inside a cell using a trilinear interpolation, we expect that our approximation will be good as long as the gradients of these fields are not changing quickly on length scales of $\Delta$. Consider, in one dimension, the Taylor series expansion of the density $\rho(x, t)$ near $x = x_0$:

$$\rho(x, t) \approx \rho(x_0, t) + \frac{\partial \rho(x, t)}{\partial x}_{x_0} (x - x_0) + \frac{1}{2} \frac{\partial^2 \rho(x, t)}{\partial x^2}_{x_0} (x - x_0)^2,$$  \hspace{1cm} (3.86)

and if $x - x_0 = \Delta$:

$$\rho(x_0 + \Delta, t) \approx \rho(x_0, t) + \frac{\partial \rho(x, t)}{\partial x}_{x_0} \Delta + \frac{1}{2} \frac{\partial^2 \rho(x, t)}{\partial x^2}_{x_0} \Delta^2.$$ \hspace{1cm} (3.87)

Now consider the interpolated density $\bar{\rho}(x, t)$ inside of a cell with vertices at $x_0$ and $x_0 + \Delta$:

$$\bar{\rho}(x, t) = \rho(x_0, t) + \frac{\rho(x_0 + \Delta, t) - \rho(x_0, t)}{\Delta} (x - x_0),$$ \hspace{1cm} (3.88)

which, from Eq. (3.87), can be written as

$$\bar{\rho}(x, t) = \rho(x_0, t) + \left( \frac{\frac{\partial \rho}{\partial x}_{x_0}}{x_0} + \frac{1}{2} \frac{\partial^2 \rho}{\partial x^2}_{x_0} \right) (x - x_0)$$

$$= \rho(x_0, t) + \frac{\partial \rho}{\partial x}_{x_0} (x - x_0) + \frac{1}{2} \frac{\partial^2 \rho}{\partial x^2}_{x_0} \Delta(x - x_0)$$

$$= \rho(x_0, t) + \frac{\partial \rho}{\partial x}_{x_0} (x - x_0) + \frac{1}{2} \frac{\partial^2 \rho}{\partial x^2}_{x_0} (x - x_0)^2$$

$$+ \frac{1}{2} \frac{\partial^2 \rho}{\partial x^2}_{x_0} (x - x_0)(\Delta - x + x_0).$$ \hspace{1cm} (3.89)

By comparison with Eq. (3.86) we can see that, to leading order, the error introduced by the interpolation algorithm in one dimension (given by the last term in Eq. (3.89)) is proportional to $\frac{\partial^2 \rho}{\partial x^2}$, is zero at both vertices and, assuming that $\frac{\partial^2 \rho}{\partial x^2}$ is constant
inside the cell, is largest at the cell midpoint \((x = x_0 + \frac{\Delta}{2})\):

\[
\delta \rho_{\text{max}}(x, t) \approx \frac{1}{2} \frac{\partial^2 \rho}{\partial x^2} \frac{\Delta^2}{4}.
\]  
(3.90)

A similar argument could be applied to the interpolation of the mean force-field \(\psi(\mathbf{r}, t)\). If our grid size \(\Delta\) is a fraction of \(R_g\) \((\frac{\Delta}{R_g} < 1)\), and we remain relatively near to the weak-segregation limit (where the interfacial width \(w\) is proportional to \(R_g\)), the error of Eq. (3.90) should remain small. When crossing an interface, \(\frac{\partial \rho}{\partial x}\) changes approximately from 0 to \(\frac{1}{R_g}\) over the interfacial width \(w\), and thus \(\frac{\partial^2 \rho}{\partial x^2}\) can be estimated as

\[
\frac{\partial^2 \rho}{\partial x^2} \approx \frac{1}{R_g w} \approx \frac{1}{R_g^2}.
\]  
(3.91)

and our maximum error becomes

\[
\delta \rho_{\text{max}}(x, t) \approx \frac{1}{2} \frac{\Delta^2}{R_g^2} \frac{\Delta^2}{4} = \frac{1}{8} \left( \frac{\Delta}{R_g} \right)^2.
\]  
(3.92)

Thus, we expect the error introduced by the trilinear interpolation approximation of the density \(\rho(\mathbf{r}, t)\) to be proportional to \(\left( \frac{\Delta}{R_g} \right)^2\), as long as we stay in the weak-to intermediate-segregation regime. This in principle allows us to scale the grid size \(\Delta\) with the chain length \(N\) without sacrificing accuracy, as long as we preserve the ratio \(\frac{\Delta}{R_g}\); this favours the extension of our technique to longer chains. In the strong-segregation limit, however, the interfacial width is expected to no longer depend on the chain length \(N\) and this argument breaks down; in that case one must be more conservative with increasing \(\Delta\) for longer chains.

Since the interfaces play a crucial role in phase separation, the accuracy with which we resolve those interfaces should have some bearing on the observed ODT. Fig. 3.17 shows that indeed, increasing \(\Delta\) appears to stabilize the disordered phase and shift \((\epsilon N)_{ODT}\) to higher values, and for small values of \(\Delta\), the ODT asymptotes
Figure 3.17: The Δ-dependence of \((\epsilon N)_{ODT}\), for a system of symmetric diblock copolymers with \(N = 64\). Systems were initialized in the disordered phase, quenched to the desired \(\epsilon\) and observed after long times (\(\sim 100\)’s of \(\tau_R\)). Our operating value, \(\Delta = b\), is highlighted.

\(\text{to } (\epsilon N)_{ODT} \approx 0.165\). Our operating value of \(\Delta/b = 1.0\) lies just outside this range at \((\epsilon N)_{ODT} \approx 0.18\).

### 3.3.4 Chain length \(N\) effects

A crucial difference between the discrete Rouse model and the continuous one is that in the discrete case, the chains are comprised of a finite number of segments. Although we use the discrete Rouse model in our theory, the standard equilibrium mean-field theory uses continuous Gaussian chains. Certain predictions of mean-field theory, such as the segregation strength depending on \(\chi\) and \(N\) only through their product...
\( \chi_N \), is a result that is expected to hold for long discrete chains but not necessarily for short discrete chains [120]. Such finite-chain effects are important to characterize, especially if we wish to interpret our results in the context of equilibrium mean-field theory.

Matsen has performed finite-chain SCFT studies [120] using the freely-jointed chain model (which has a finite number of segments), and found finite-chain effects that cause deviation from \((N \to \infty)\) equilibrium mean-field behaviour. For instance, the ODT was observed to shift to higher \( \chi_N \) in a diblock copolymer melt for short chains. The effect was significant only for chains with \( N < 200 \), and was shown to be related to the finite range of the non-bonded interaction. We have performed

\begin{center}
\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.18}
\caption{The ODT \((\epsilon N)_{ODT}\) as a function of \( N \) for the symmetric \((f = 0.5)\) diblock copolymer, demonstrating a shift in the ODT to higher \( \epsilon N \) for short chains.}
\end{figure}
\end{center}
simulations of the diblock copolymer melt and located \((\epsilon N)_{ODT}\) for \(N = 32, 64, 128\) and 256. We observe a similar trend in the ODT: a shift to higher \((\epsilon N)_{ODT}\) as \(N\) decreases which can be seen in Figure 3.18. The effect appears to be small already for \(N = 256\), although we admit that the number of data points is small, since we are limited to \(N\) being powers of 2. Figure 3.18 is consistent with the result of Matsen, in that the finite-chain effect seems to be significant only for, in our case, \(N < 256\). We also use a non-bonded interaction with a finite range, which suggests that our finite-chain effects may have the same origin as in Ref. [120]. This also suggests that if we were to replace our modified Lennard-Jones interaction with a contact interaction, these finite-chain effects may vanish. We do not investigate this possibility here. The fact that, at our operating value of \(N = 64\), we seem to be in the regime where finite-chain effects are important, suggests that we should be careful in interpreting our results in the context of Gaussian, continuous-chain \((N \to \infty)\) mean-field theory. This will be relevant in Chapter 4, and so should be kept in mind.

This concludes Chapter 3. In Section 3.1, we described the details of our numerical algorithm, including the crucial subroutines that run frequently (i.e. every time-step) such as the density and mean force-field calculations, the application of the Langevin equation to evolve the chain ensemble, and the communication routines. We also described certain algorithms that do not run frequently, such as those used for the data analysis that produce our results for Chapter 4. In Section 3.3, we characterized the numerical effects of the parameters \(\Delta t\), \(\Delta\) and \(<N_b>\) that describe the time-discretization, the space-discretization and the size of the chain ensemble, respectively. The goal was to understand how finite values of these parameters lead to numerical errors, and to determine how strongly our results depend on the chosen values of these parameters. We also explored more sophisticated numerical schemes for our time evolution algorithm, and showed that these should in principle provide a better scaling of the numerical error with \(\Delta t\), but that this advantage is washed out.
by the error produced by the finite size of the chain ensemble, except for prohibitively large ensemble sizes. Finally, we showed that for the chain length we use in this work ($N = 64$), finite-chain effects appear to be present.

In the next chapter, we will discuss our application of dynamical self-consistent field theory to problems of structure formation and chain diffusion in the binary homopolymer blend and the diblock copolymer melt.
Chapter 4

Structure formation and chain diffusion in polymeric systems

Having established an efficient numerical procedure that enables us to solve the dynamical mean-field equations for dense polymeric systems, the next steps are to (i) establish that the theory is capable of producing physically sensible results in the context of our problems of interest (the dynamics of phase separation in dense polymeric systems), and (ii) demonstrate the novelty of our technique, and that it has the potential to go beyond what has been done before and make new contributions to the field of polymer dynamics, in the context of chain self-diffusion in the ordered phases of the diblock copolymer melt, both in and out of equilibrium.

We will address point (i) first by applying the theory to spinodal decomposition in a symmetric binary homopolymer blend, which is a well-studied problem with a long history of use as a test bed for theories of polymer dynamics. The initial stages of phase separation, on time-scales less than the molecular relaxation time, will be examined in the context of the predictions of the linearized Cahn-Hilliard-Cook (CHC) theory [75–77] as well as the recently-proposed Single-Chain-in-Mean-Field (SCMF) theory [45]. In the later stages, we will examine the coarsening of the
domains and compare our results with the process of Ostwald ripening, which can be described by the power law of Lifshitz, Slyozov and Wagner, Eq. (1.1).

Then, for point (ii), we turn to the diblock copolymer melt, and explore the effects of segregation strength and the dimensionality of domains on chain diffusion in the ordered phases, both in and out of equilibrium. Our results can be interpreted in the context of the physical picture that has emerged to describe the diffusion of unentangled chains in ordered phases, although for the non-lamellar phases we mainly draw on experimental work for our comparisons, noting the lack of theoretical studies particularly for the cylindrical and gyroid phases. We then demonstrate that our technique also allows us to obtain measurements on chain diffusion that have not been made before, i.e. the measurement of variable anisotropic diffusivity during a phase transition between the lamellar and hexagonal cylindrical phases.

All of the results in this chapter correspond to chains of length \( N = 64 \). The two monomeric species (\( A \) and \( B \)) have the same Kuhn length \( b \) and the same monomeric friction coefficient \( \zeta \). It is possible to explore \( b_A \neq b_B \) and \( \zeta_A \neq \zeta_B \) in our theory, and the modifications would be straightforward, but we do not consider such asymmetry here. The Langevin equation is solved using a time-step \( \Delta t = 0.2 \tau = \frac{\pi^2}{5N^2} \tau_R \) and the fields \( \rho(\mathbf{r}, t) \) and \( \psi(\mathbf{r}, t) \) are calculated on a 3D \( M_x \times M_y \times M_z \) grid (the binary blend results use a cubic \( M \times M \times M \) grid) with spacing \( \Delta = b \). The number of replicas is chosen so that we have \( \langle N_b \rangle = 60 \) replica-beads per grid point, according to Eq. (3.62), and the number of polymers \( n_P \) (in the case of the binary blend, \( n_P = n_A + n_B \)) can be calculated from Eq. (3.4).
4.1 Spinodal decomposition in a symmetric binary homopolymer blend

We will examine a system consisting of a symmetric blend \( n_A = n_B \) of homopolymers in a cubic box of volume \( V = (Mb)^3 = (128b)^3 \approx (40R_g^{(0)})^3 \) (\( R_g^{(0)} \) being the ideal chain radius of gyration) with periodic boundary conditions. By application of Eq. (3.4), the number of polymers is \( n_P = 32768 \), such that \( n_A = n_B = 16384 \). By Eq. (3.62), the chain ensemble consists of \( n_r \approx 2 \times 10^6 \) chain replicas, and the workload is split up amongst 128 processors running in parallel. The numerical methods of Chapter 3 are applied to obtain the solution to the set of mean-field equations for the binary blend which are described in Chapter 2, by Eqs. (2.29)-(2.36).

![Figure 4.1: Snapshots of the local order parameter, \( \rho_A - \rho_B \), of a symmetric binary homopolymer blend at the indicated times following a quench from the disordered phase (\( \epsilon_N = 0.0128 \)) to the two-phase region (\( \epsilon_N = 0.32 \)). Red regions are \( A \)-rich and blue regions are \( B \)-rich. The segment density in the simulation is \( b^{-3} \), the volume is \( (128b)^3 \approx (40R_g^{(0)})^3 \), and the chains are 64 segments long; \( \tau_R \) is the Rouse time.](image)

All systems described in this section were initialized in the disordered phase (via the generation of close-to-Gaussian chain replica configurations at random positions within the box, according to the procedure of Section 3.1.1) at \( \epsilon_N = 0.0128 \) for \( 10\tau_R \), where we observe no phase separation, prior to the quench to the desired \( \epsilon_N \). By varying the quench depth, and observing the morphology via the order parameter
\( \rho_A - \rho_B \), we have found the order-disorder transition (ODT) to be \( (\epsilon N)_{ODT} = 0.030 \pm 0.002 \). To investigate the growth behaviour, we perform a quench to \( \epsilon N = 0.32 \), well past the spinodal. Qualitatively, we can already see the characteristics of the early- and late-time phase separation, prior to any analysis, simply by visual inspection of \( \rho_A - \rho_B \) which is plotted for various times following the quench in Figure 4.1. The phase separation in the initial stages is system-wide and immediate upon changing \( \epsilon N \), indicating that we are indeed observing spinodal decomposition and not the nucleation and growth mechanism. There is also no visible indication of lattice anisotropy, suggesting that our density and mean force-field algorithms are working as intended.

Figure 4.2: A morphological comparison between cross-sectional slices of the spatially varying order parameter \( \rho_A - \rho_B \) in our simulation (left) and a cross-sectional laser scanning confocal microscopy image of a phase separating blend of poly(styrene-ran-butadiene)-poly(butadiene) from Ref. [121] (right).

We can also see qualitatively, in Fig. 4.1, the growth of domains which is characteristic of the intermediate and late stages. This indicates the incorporation of non-linear effects in our approach, since the linearized CHC theory predicts a fastest-growing mode with a time-independent wave vector magnitude \( q_m \sim R_t^{-1} \), whereas in the coarsening process the wave vector for the fastest growing mode has a magnitude that decreases monotonically with time, in accordance with the increasing size of the
domains. Eventually, the characteristic domain size is expected to satisfy a simple power law in time, at which point the observed morphologies at two different times will look similar if scaled appropriately. This property of self-similarity also suggests that in this regime of spinodal decomposition, the dynamics is universal, meaning that two systems in the same universality class, which may be very different on the molecular level, will also look similar if scaled appropriately. This can be seen in Figure 4.2, where we compare our morphology, at \( t \approx 10\tau_R \) following the quench, to that seen in a confocal microscopy cross-sectional image of a phase separating blend of poly(styrene-ran-butadiene)-poly(butadiene) from Ref. [121]: here we can already see that our system qualitatively resembles a real polymeric system undergoing spinodal decomposition.

4.1.1 The early-time growth of the instability

We characterize the composition fluctuations in the system via the angle-averaged square of the Fourier-transformed density for species \( A \), \( \langle |\rho_A(q,t)|^2 \rangle_\Omega \). In the early-time regime, the elapsed time since the quench is less than the molecular relaxation time, i.e. the Rouse time \( \tau_R \); for such times, the fastest-growing composition fluctuations are due to the adjustment of the internal degrees of freedom of the chains rather than large-scale diffusion. Figure 4.3 plots \( \langle |\rho_A(q,t)|^2 \rangle_\Omega \) as a function of \( qR_g \) (\( R_g \) is the measured chain radius of gyration from the simulation) for these initial stages, in the same system as the one from Fig. 4.1 which has been quenched to \( \epsilon N = 0.32 \).

The black curve in Fig. 4.3 corresponds to \( \langle |\rho_A(q,t = 0)|^2 \rangle_\Omega \), i.e. composition fluctuations in the disordered phase. Although this curve resembles the disordered phase structure factor prediction of the random-phase approximation (RPA) [122], the fluctuations that produce this curve are not physical in origin but rather are a result of the local error in the density due to the finite size of the chain ensemble.
Figure 4.3: The angle-averaged square of the Fourier transform of the density of species A in the symmetric binary homopolymer blend at several early times, $t \ll \tau_R$, shows the growth of composition fluctuations following a quench into the two-phase region. The wavevector $q$ is scaled by the average chain radius of gyration, $R_g$, observed in the simulation. The simulation parameters in this figure are the same as those used in Figure 4.1.

(These effects have been characterized in Sec. 3.3.1). In the limit of an infinitely large ensemble, these fluctuations would vanish, the distribution of the density would become a delta function at the average density $\rho_0$, and the black curve of Fig. 4.3 would be zero everywhere except at $q = 0$, where $\langle |\rho_A(0,t)|^2 \rangle_\Omega = n_A^2 N^2$ (we have left this $q = 0$ point off of Figure 4.3 because it is trivial). The noisy behaviour of $\langle |\rho_A(q,t)|^2 \rangle_\Omega$ as $q R_g \rightarrow 0$ is an artifact that results from poor averaging due to our angle-averaging algorithm. For a given $q$, our algorithm averages over a shell of width $\Delta q$, so shells at small $q$ suffer from poor averaging since the number of grid points...
contained in the shell is small.

The growing composition fluctuations for \( t > 0 \), however, do have physical significance. The growth of \( \langle |\rho_A(q, t)|^2 \rangle_\Omega \) is due to the instability in the density (brought on by the quench past the spinodal) that leads to the formation of interfaces on short time-scales. The fact that the growth is significant on such short time-scales confirms that during this early stage the chains are not in equilibrium with the instantaneous density (as a reminder, many of the contemporary field-theoretic approaches involve the inherent assumption that they are). We note that in Müller’s application of SCMF theory to spinodal decomposition in the binary homopolymer blend [45], this was also observed.

According to the linearized CHC theory, the early-time growth of composition fluctuations is described by exponentially growing modes, with a time-independent growth rate \( R(q) \):

\[
\langle |\rho_A(q, t)|^2 \rangle_\Omega = \langle |\rho_A(q, 0)|^2 \rangle_\Omega e^{R(q)t}.
\tag{4.1}
\]

The growth rate in the CHC theory, from Figure 1.4, has the generic form

\[
R(q)\tau_R = -\tau_R \left( \frac{\partial^2 f}{\partial \phi^2} q^2 + \frac{c}{2} q^4 \right) = A(qR_g)^2 - B(qR_g)^4.
\tag{4.2}
\]

This growth rate has a maximum at \( q_m = \sqrt{\frac{A}{2B}} R_g^{-1} \). Our growth rate \( R(q, t) \) can be calculated by a rearrangement of Eq. (4.1):

\[
R(q, t) = \frac{1}{t} \ln \frac{\langle |\rho_A(q, t)|^2 \rangle_\Omega}{\langle |\rho_A(q, 0)|^2 \rangle_\Omega}.
\tag{4.3}
\]

The growth rate \( R(q, t) \) from our simulation is shown in Figure 4.4 for \( t \approx 0.2\tau_R \). We have performed a two-parameter fit of Eq. (4.2) to our small \( q \) growth rate data \( (qR_g < 2.5) \). The general features of our growth rate are qualitatively consistent with the predictions of the linearized theory at small \( q \). The fastest-growing wave
Figure 4.4: The scaled growth rate $R(q,t)\tau_R$, Eq. (4.3), at $t = 0.193\tau_R$, obtained from the data in Figure 4.3. The vertical dotted line indicates the fastest growing wavevector, near $qR_g = 2$. The dashed line is a fit of Eq. (4.2) to our small-$q$ data ($qR_g < 2.5$). The simulation parameters in this figure are the same as those used in Figure 4.1.

Vector has magnitude $q_m \approx 2R_g^{-1}$, which is in line with our expectations from the linearized theory that $q_m \sim R_g^{-1}$. For small $qR_g$ (corresponding to large wavelengths) our growth rate approaches zero, in accordance with the requirement that on large length-scales the growth of fluctuations is achieved through diffusion of large amounts of material. In this regime, the agreement between our growth rate data and the fit to the CHC theory is quite good, and includes the expected $(qR_g)^2$ dependence, which is characteristic of this regime.

In the large $q$ regime ($q > 2R_g^{-1}$), we see that the growth of modes is slowed due to the unfavourability of forming the large amounts of interface that result from
a short-wavelength fluctuation. Eventually these large-\(q\) modes become damped instead of growing; this agrees with the linearized theory in the sense that \(R(q, t) < 0\), although the curves are quite different for large \(q\). The negative growth rate in our theory appears to asymptote to zero \((R(q, t)\tau_R \rightarrow 0)\) for large \(qR_g\) whereas the linearized theory predicts that the growth rate continues to become more negative, as \(-(qR_g)^4\), for large \(qR_g\). Such disagreement between our theory and the CHC theory is not surprising however, particularly on small length-scales (for large \(q\)), since the microscopic models are very different (the linearized theory is based on a phenomenological Landau free energy, whereas ours has its origins in the interacting Rouse model with a modified Lennard-Jones interaction). Growth rates with similar characteristics (asymptoting to zero at large \(q\)) have also been seen in the SCMF simulations and the fully interacting Monte Carlo simulations of spinodal decomposition in Ref. [45], although in those cases the growth rate asymptoted to zero from above \((R(q, t) \rightarrow 0^+)\). This behaviour was attributed to the presence of thermal fluctuations which balance the negative growth rate and lead to \(R(q, t) \rightarrow 0\).

### 4.1.2 The late-time regime

To characterize the coarsening of domains in the late-time regime, we can calculate the fastest-growing mode and plot its wave vector magnitude \(q_m(t)\) with time. If the growth of the domains follows a scaling law at late times, we can expect \(q_m(t)\) to satisfy a power law such that

\[
q_m(t) \sim t^{-\alpha},
\]

thus we plot \(q_m(t)\) versus time on logarithmic axes, which is shown in Figure 4.5. We scale \(q_m(t)\) by the ideal chain radius of gyration \(R_g(0)\), and scale the time by \(\tau_R\). At early times \((t \ll \tau_R)\), \(q_m(t)\) is constant, in agreement with the linearized theory. For \(t \approx \tau_R\), non-linear effects are already seen, as the system enters the
Figure 4.5: Over longer time-scales, we plot the fastest growing wavevector, \( q_m(t) R_g^{(0)} \), in the coarsening symmetric binary homopolymer blend, as a function of scaled time, \( t/\tau_R \), following a quench in the two-phase region. We obtain these data from the growth rate curves, similar to Fig. 4.4. \( q_m(t) \) is scaled in terms of the ideal chain radius of gyration \( R_g^{(0)} \). The dashed line represents the \( q_m \sim t^{-1/3} \) power-law predicted by Lifshitz, Slyozov and Wagner for domain coarsening [84, 85]. The simulation parameters are the same as those used in Fig. 4.1.

intermediate-time regime where the coarsening process has begun. For later times, we see the emergence of the power law for \( q_m(t) \) which continues until the end of the simulation. The agreement in this region with the \( L(t) \sim t^{1/3} \) (or equivalently, \( q_m(t) \sim t^{-1/3} \)) growth law, which is also plotted (dashed line), indicates that we obtain the diffusive growth regime predicted by Lifshitz, Slyozov and Wagner [84, 85]. This is in accordance with our expectations, since our model only incorporates diffusion as a mechanism for large-scale motion. Indeed, we have no reason to expect to observe hydrodynamic or inertial scaling regimes, since we do not include hydrodynamic or inertial effects in the theory. Inevitably, in the long-time limit of our simulation the
system would become completely macro-phase separated, in which case the system would be divided evenly into two domains, each pure in its respective component (species $A$ or $B$). As this limit is approached, the growth should slow and deviate from the $q_m(t) \sim t^{-1/3}$ growth law, due to finite system size effects. In the case of Figure 4.5, the simulation ends before this regime is reached with a wavevector having a magnitude $q_m(t)R_g^{(0)} \approx 0.3$, whereas the smallest resolvable non-zero wavevector in our finite box has a magnitude $qR_g^{(0)} \approx \frac{2\pi}{40} \approx 0.15$.

Our results for the spinodal decomposition of the symmetric binary homopolymer blend are encouraging. The modified Lennard-Jones interaction, in our dynamical mean-field approximation, is able to produce phase separation. We do not see artifacts or lattice anisotropies, indicating that our numerical scheme is working correctly. The system exhibits a well-defined spinodal at $\epsilon N = 0.03$, and at early times after a quench into the two-phase region we see that the instability in the density forms quickly compared with the Rouse time $\tau_R$, meaning that the chains are not in equilibrium with the density during the initial stages. The early-time growth of composition fluctuations is in good qualitative agreement with the linearized Cahn-Hilliard-Cook theory, which is known to describe the early stages of phase separation well. The morphology of the system resembles that of real phase-separating polymer mixtures. In the later stages, non-linear effects set in and we observe coarsening of the domains via diffusion, which is the only mode of transport in our model and thus leads to the $L(t) \sim t^{1/3}$ power law of Lifshitz, Slyozov and Wagner, indicating that diffusion is being properly treated. Our approach is able to access the late-time regime, while maintaining a connection to the individual chain dynamics. We know the time-scale in terms of $\tau_R$, which allows us to identify that the late-time regime sets in at $t/\tau_R \approx 10 - 100$. These results allow us to proceed to the problem of chain diffusion in the ordered phases of the diblock copolymer melt, with confidence that we are describing the relevant physics correctly (chain diffusion and relaxation, interfacial...
tension, etc.), and that we are able to access the long time-scales that are relevant to structure formation.

4.2 Chain diffusion in the diblock copolymer melt

Our first task is to determine whether or not our diblock copolymer melt will micro-phase separate, and if it does, what phases it can form in the long-time limit (at equilibrium). We are not limiting ourselves to the symmetric case, as we did for the binary blend, so we have an additional phase-space parameter to vary (in addition to the interaction strength parameter $\epsilon$), which is the $A$-species block fraction $f = N_A/N$. Note that $f$ is also the $A$-species volume fraction since the two species have the same Kuhn length $b$. The diblock copolymer melt system contains $n_P$ diblock copolymers in a box of volume $V = (M_x M_y M_z) \Delta^3 = (M_x M_y M_z) b^3$, with periodic boundary conditions. The size of the box will vary throughout this section, in order to ensure that the dimensions of the box are close to commensurate with the periodicity of the phase we are examining (our protocol for determining the box sizes was described in Sections 3.2.2 and 3.2.3). The number of polymers $n_P$ again enforces that $\rho_0 = 1/b^3$ and the number of chain replicas $n_r$ enforces that $\langle N_b \rangle = 60$, and both vary with the volume of the box $V$ according to Eqs. (3.4) and (3.62), respectively. The number of processors $P$ also varies with the box size; we use $P$ as small as 16 and as large as 64, for the smallest and largest systems, respectively. The set of mean-field equations for the diblock copolymer melt, given by Eqs. (2.37)-(2.43), are solved using the numerical methods described in Chapter 3.

4.2.1 The diblock copolymer melt phase diagram

We will begin by mapping out the diblock copolymer phase diagram. We are concerned with locating regions of stability for the “classic” ordered phases: the lamellar
(LAM), hexagonal cylindrical (HEX), body-centred cubic spherical (BCC) and gyroid (GYR) phases, so that we can perform chain diffusion measurements on those phases. Our goal is not to construct a rigorous equilibrium phase-diagram. In equilibrium mean-field theory, the symmetric diblock copolymer melt will phase separate for $\chi N \geq 10.5$ [12], whereas a symmetric binary homopolymer blend will phase separate for $\chi N \geq 2$ [45]. We can therefore equilibrate our diblock copolymer melt in the disordered phase (using the same protocol as we did for the binary homopolymer blend) at $\epsilon N = 0.03$, which is the ODT for the symmetric binary homopolymer blend from the previous section. Our protocol for determining what phase may be stable for given values of $\epsilon$ and $f$ is straightforward: we initialize the system in the disordered phase for $10\tau_R$, then quench to the given $\epsilon$ and observe the structure that forms after long times (100’s of $\tau_R$). By visual inspection, the resulting structures can then be associated with the appropriate ordered morphology, although many of the morphologies remain poorly aligned, or with defects, after long times. This procedure is sufficient for our purposes, and we again emphasize that this does not constitute a rigorous calculation of the equilibrium phase diagram. The best way to obtain an accurate phase diagram would involve an equilibrium self-consistent field theory calculation [123], where the free energies of different structures can be compared; this is not within the scope of this work, nor is it our focus.

We find that the system, for $f = 0.5$, remains disordered until $(\epsilon N)_{ODT} = 0.183 \pm 0.003$, above which it forms a lamellar phase (see Figure 4.6). We can compare our critical point, $(\epsilon N)_c$, to the mean-field critical point $(\chi N)_c$, to get an idea of the mapping between $\epsilon$ and $\chi$, by proposing that $\chi \approx \gamma \epsilon$. A comparison of the binary blend critical points yields $\gamma \approx 67$, and a comparison of the diblock copolymer critical points yields $\gamma \approx 57$, which suggests that $\chi$ can be very roughly related to $\epsilon$ by

$$\chi \approx 60 \epsilon,$$

(4.5)
Figure 4.6: Density plots of the order parameter, $\rho_A(r) - \rho_B(r)$, for ordered morphologies in the $N = 64$ diblock copolymer melt at various points in the phase diagram, formed after long-times ($t \approx 100\tau_R$) following quenches from the disordered phase ($\epsilon N = 0.03$) in a cubic box with volume $V = (32b)^3 \approx (10R_g)^3$. $A$-rich domains are shaded red, and $B$-rich domains are transparent. We identify: a) a lamellar morphology for $f = 0.5$ and $\epsilon N = 0.2$, b) a poorly-aligned cylindrical morphology for $f = 0.25$ and $\epsilon N = 0.4$, c) a BCC spherical morphology for $f = 0.25$ and $\epsilon N = 0.3$, and d) a “gyroid” morphology for $f = 0.375$ and $\epsilon N = 0.275$, note the three-fold connections (circled) which suggest that we can associate this structure with the gyroid phase.

at least in this range of segregation strengths. A precise mapping between $\epsilon$ and $\chi$ may involve higher order terms and the inclusion of finite chain length effects [124] (which we know are present, from the results of Section 3.3.4).

For the asymmetric case ($f \neq 0.5$) we see other morphologies, in addition to lamel-
lae, forming after long times. Figure 4.6 shows examples of the kinds of morphologies we observe in different regions of the phase diagram, which we have identified (by visual inspection) as lamellar, cylindrical, spherical and gyroid phases. It is important to note here that at this stage, where we are simply trying to narrow down what phases may be stable in a given region, we do not apply any ordering fields nor do we attempt to adjust the box size. For our chain diffusion measurements in the next sections, ordering fields will be applied so that we can control the orientation of the morphology, and match the period of the morphology with the box size. Here, the system is free to orient itself so as to achieve a morphology that is commensurate with the box size, if possible. This effect can be clearly seen in the aligned lamellar phase of Figure 4.6. The spherical phase of Figure 4.6 is also at least partially aligned in what appears to be a body-centred cubic arrangement.

The phase diagram of Figure 4.7 shows where in the phase-space we observe the different morphologies of Figure 4.6. The lamellar, cylindrical and spherical phases can be assigned relatively unambiguously to the morphologies in Figure 4.6a, b and c, respectively; thus we have high confidence in the regions corresponding to these phases in Figure 4.7. The gyroid phase, however, is more difficult to identify with high confidence by visual inspection alone, especially when it contains numerous defects. In Figure 4.6d, the characteristic three-fold connections between cylindrical struts (which are circled for emphasis) are suggestive of the morphology being that of the gyroid phase (see Figures 1.1 and 1.6 for illustrations of these connections). The regions of Figure 4.7 where we see the morphology of Figure 4.6d also correspond approximately to the region of the equilibrium mean-field phase diagram (see Figure 1.2) where the gyroid phase is known to be stable. As an extra precaution, we have also initialized the system using a gyroid ordering field in this region and confirmed that the gyroid phase is at least metastable at the points indicated in Figure 4.7 (our protocol for applying ordering fields is described in Section 3.2.2).
Figure 4.7: Phase diagram showing the classic phases that we observe in the long-time limit (100's of $\tau_R$) in our simulations of the $N = 64$ diblock copolymer melt. Runs were performed in a box with volume $V = (32b)^3 \approx (10R_g)^3$, and quenched after equilibrating in the disordered phase at $\epsilon N = 0.03$ for $10\tau_R$.

Again, rigorously calculating the equilibrium phase diagram is not our goal; we need only establish that there are regions of the phase-space for which we obtain the phases that we are interested in performing chain diffusion studies on, and that those phases are stable at least for the duration of a simulation. With that said, it is encouraging that the phase diagram of Figure 4.7 qualitatively resembles the equilibrium mean-field phase diagram (shown in Figure 1.2). We have not seen evidence for any other diblock copolymer phases, e.g. Fddd or close-packed spherical phases, but we did not attempt to find such phases either. We have also only investigated the phase behaviour for $N = 64$, but we expect that our phase diagram is sensitive
to changes in $N$ for chains with lengths near $N = 64$, due to the presence of finite chain-length effects that we demonstrated in Section 3.3.4. Overall, we seem to be recovering the predictions of equilibrium mean-field theory in the long-time limit of our simulations. This is also in agreement with Fredrickson and Orland [53], who showed that this should be the case.

At this point, our search for the classic phases has not relied on the use of ordering fields. However, for a chain diffusion anisotropy measurement we ensure that the phase in question is aligned, without defects and that the box size is commensurate with the periodicity of the phase. This is achieved by equilibrating the system in an ordering field, and then turning off the ordering field and allowing the system to relax prior to beginning measurement. The ordering field appears as a contribution to the mean force-field $\psi(r, t)$, and can be calculated using Eq. (2.17) if we know the ordered density fields $\rho_{\text{LAM}}(r)$, $\rho_{\text{HEX}}(r)$, $\rho_{\text{BCC}}(r)$ and $\rho_{\text{GYR}}(r)$ that correspond to the lamellar, hexagonal cylindrical, body-centred cubic spherical, and gyroid phases. These can be calculated using single-mode approximations (see Section 3.2.2), provided that we know the appropriate size of the unit cell for each phase.

We have determined the period $L_0$ for the lamellar phase at $\epsilon N = 0.256$ to be $L_0 = 14b$. Our procedure for determining this is described in detail in Section 3.2.2. This value of $L_0$ is in line with our expectations that near the weak segregation limit the period should be $L_0 \approx 4R_g \approx 13b$ (for $N = 64$). Knowing $L_0$ allows the estimation of the periodicities of all of the other phases through their epitaxial relationships with the lamellar phase, which relate the sizes and orientations of their respective unit cells to that of the lamellar phase. For our purposes, the epitaxial relationships allow us to calculate the appropriate unit cells for the HEX, BCC and GYR phases once we know the lamellar period $L_0$, but they are not necessarily completely accurate and the true equilibrium unit cell sizes for the non-lamellar phases may be as much as 10% off of those calculated via epitaxy [117]. As long as the mismatch is only slight, the stress on
Figure 4.8: Density plots of ordered phases in the diblock copolymer melt, as generated by the ordering fields with $L_0 \approx 14b$: a) lamellar phase in $(L_x, L_y, L_z) = (112b, 112b, 112b)$ box, b) hexagonal cylindrical phase in $(L_x, L_y, L_z) = (112b, 112b, 112b)$ box, c) body-centred cubic spherical phase in $(L_x, L_y, L_z) = (100b, 100b, 100b)$ box, and d) gyroid phase in $(L_x, L_y, L_z) = (68b, 68b, 68b)$ box. The simulations of Section 4.2.2 use the same orientations as these, but do not use the same system sizes.

the system should remain small. Nonetheless, in any cases where the system becomes obviously stressed due to a period mismatch, we adjust the period accordingly. We deal with these situations on a case-by-case basis. Plots of the density for the ordered phases (equilibrated by the ordering fields) are shown in Figure 4.8.
4.2.2 Chain diffusion in the ordered phases at equilibrium

In this section, we will investigate how the morphology of ordered phases affects the chain self-diffusion, for the lamellar (LAM), cylindrical (HEX), spherical (BCC) and gyroid (GYR) phases. The chain self-diffusion can be characterized by tracking the mean-squared displacement (MSD) of the chain replica centres-of-mass:

$$\langle \Delta \mathbf{R}_{cm}(t) \cdot \Delta \mathbf{R}_{cm}(t) \rangle = \frac{1}{n_r} \sum_{k=0}^{n_r-1} \left( \mathbf{R}_{cm}^{(k)}(t) - \mathbf{R}_{cm}^{(k)}(0) \right) \cdot \left( \mathbf{R}_{cm}^{(k)}(t) - \mathbf{R}_{cm}^{(k)}(0) \right).$$  (4.6)

The MSD can be broken up into components along the $x$, $y$ and $z$-directions which, if the ordered phases are properly oriented with the $x$, $y$ and $z$-axes, can tell us about chain motion parallel and perpendicular to the interfaces of the domains. If the motion can be considered diffusive, the MSD in the direction $\alpha$ will satisfy

$$\langle \Delta R_{cm,\alpha}(t)^2 \rangle = 2D_\alpha t$$  (4.7)

where $\alpha = x, y \text{ or } z$. $D_\alpha$ is then given by the slope of the MSD plot, and compared with the ideal (Rouse) chain diffusion coefficient $D_0$:

$$D_0 = \frac{k_B T}{N\zeta}.$$  (4.8)

In our theory, which does not include fluctuation effects or entanglements, $D_0$ is also the diffusion coefficient in the disordered phase. Our protocol for the calculation of diffusion coefficients was described in detail in Sec. 3.2.4.

All systems are initialized from disorder under the application of the appropriate ordering field for $5 - 10\tau_R$ and then the ordering field is turned off and the system allowed to equilibrate for a further $50 - 75\tau_R$. We allow more time for equilibration in this case than we did when equilibrating in the disordered phase, due to the presence of the non-zero mean force-field. In the disordered phase, where the mean force-field
is zero (or very small), the molecular relaxation time is simply the Rouse time $\tau_R$ and the chains undergo diffusion at their normal rate, which leads to fast equilibration. The presence of a non-zero mean force-field, however, could slow the relaxation of the chain’s internal modes and it certainly slows large-scale diffusion, as we will show; thus we give the system more time to equilibrate once it is in an ordered phase. For all of the results in this section, the phases are oriented according to Figure 4.8; that is, for the lamellar phase, the $x$ and $z$-directions are parallel to the lamellae and $y$ is perpendicular, for the cylindrical phase the $z$-direction is parallel to the cylinder axis and $x$ and $y$ are perpendicular, etc.

4.2.2.1 The lamellar phase

The lamellar system (at $f = 0.5$) is equilibrated in a box with $(L_x, L_y, L_z) = (32b, 28b, 32b)$, and contains 2 full lamellar periods ($L_y = 2L_0$). Some representative MSD data for the parallel and perpendicular directions in the lamellar phase are shown in Figure 4.9 for $\epsilon N = 0.192$, $\epsilon N = 0.224$ and $\epsilon N = 0.256$. Already the qualitative aspects of Figure 4.9 agree with the physical picture proposed for unentangled chains in a lamellar phase: that is, the motion parallel to the interface is the same as diffusion in the disordered phase ($D_\parallel / D_0 \approx 1$) and is insensitive to $\epsilon$, whereas the motion perpendicular to the interface is more complicated, but clearly suppressed and dependent on the segregation strength.

At early times ($t \ll \tau_R$), i.e. for motion on length-scales much less than the width of the interface (which is comparable to $R_g$ as long as we remain close to the weak segregation limit), the chains can diffuse freely in the perpendicular direction without paying the enthalpic cost associated with one of the blocks moving into the domain rich in the other species. We can see this in Figure 4.9 where, in the limit as $t \to 0$, $D_\perp \to D_0$. For late times, i.e. for motion on length-scales larger than the interfacial width, a chain diffuses by jumping over the energetic barrier presented by the other
Figure 4.9: The mean-squared centre-of-mass displacements, in directions parallel and perpendicular to the interface, as a function of time, in the lamellar phase of the symmetric ($f = 0.5$) diblock. The system was equilibrated in a lamellar ordering field, in a box with $(L_x, L_y, L_z) = (32b, 28b, 32b)$ at $\epsilon N = 0.192$ (red), $\epsilon N = 0.224$ (blue) and $\epsilon N = 0.256$ (green). The parallel diffusion (dashed) is independent of $\epsilon N$ and corresponds to free diffusion with the Rouse diffusion coefficient $D_0$. The perpendicular diffusion (solid) is suppressed with increasing $\epsilon$. The inset shows the cross-sectional domain profiles for the three values of $\epsilon N$.

domain. This is essentially the Kramers barrier-crossing problem [125], for which the rate of hopping is suppressed exponentially according to the height of the energy barrier. The motion in this regime is also diffusive but with a diffusion coefficient $D_\perp$ that is proportional to the rate of hopping and thus also has an exponential dependence on the energy barrier, as pointed out by Barrat and Fredrickson [46]. This explains both the suppression of perpendicular motion in Figure 4.9, as well as the fact that at late times it is linear (i.e. diffusive). The early non-linear regime
marks the crossover between the early- and late-time behaviour just described.

The inset of Figure 4.9 shows cross-section density profiles for one period of the lamellae. This demonstrates the connection between the interaction strength $\epsilon$ and the degree of segregation. As $\epsilon$ is increased, the interfacial profiles adjust in a self-consistent manner that is not connected to the ordering fields; indeed, the system is given ample time to relax after the ordering field is released, as we have discussed. This self-consistency is a crucial feature that distinguishes our approach from other chain diffusion simulations due to Fredrickson and co-workers on lamellar [46] and spherical [104] phases, which have used imposed potential fields that were not self-consistently related to the configuration of the system. We can also see from the sinusoidal shape of the interfacial profiles that in this range of $\epsilon N$ we are close to the weak segregation limit, although for $\epsilon N = 0.256$ the domains are approaching full saturation ($\rho_A \to 1$ in an $A$-domain, and $\rho_A \to 0$ in a $B$-domain), indicating that for $\epsilon N \geq 0.256$ the system may be entering the intermediate-segregation regime.

To quantitatively examine the suppression of the perpendicular diffusion with increasing segregation strength, we plot $D_x/D_0$, $D_y/D_0$ and $D_z/D_0$ as a function of $\epsilon N$ in Figure 4.10. Data points corresponding to $D_\perp/D_0$ are solid symbols, and those corresponding to $D_\parallel/D_0$ are hollow symbols. Above the ODT ($\epsilon N < (\epsilon N)_s$), the system is in the disordered phase, and the diffusion is isotropic ($D_x = D_y = D_z$) and equal to the disordered phase diffusion coefficient $D_0$. Below the ODT ($\epsilon N > (\epsilon N)_s$), in the parallel directions ($x$ and $z$), the diffusion is independent of $\epsilon$, and equal to that of the disordered phase ($D_\parallel/D_0 \approx 1$), as was indicated in Figure 4.9. The diffusion within the plane of the lamellae is also isotropic ($D_x \approx D_z$).

The perpendicular diffusion below the ODT is suppressed with the segregation strength, as we already observed in Figure 4.9. The dependence of $D_\perp$ on $\epsilon$ is exponential, in agreement with the extensive literature on chain self-diffusion in the lamellar phase. For instance, the chain diffusion experiments using forced Rayleigh
Figure 4.10: Diffusion coefficients, as a function of $\epsilon N$, for diffusion perpendicular to the lamellar interface (filled squares), and for two orthogonal directions in the plane of the interface (circles, diamonds) for the lamellar phase of the symmetric ($f = 0.5$) diblock copolymer. The critical point is $(\epsilon N)_{c} \approx 0.18$. The dashed line is an exponential fit of perpendicular diffusion data for the lamellar phase, described by $D_{\perp}/D_0 = e^{-\alpha(\epsilon N - \beta)} = e^{-32.3(\epsilon N - 0.177)}$. The error in $\alpha$ and $\beta$ are approximately 1%, giving $\alpha = 32.3 \pm 0.3$ and $\beta = 0.177 \pm 0.002$.

scattering (FRS) on entangled and unentangled diblock copolymers in the lamellar phase, due to Lodge and co-workers [97, 98], the theoretical calculations by Barrat and Fredrickson [46] and particle-based simulations by Murat [93] have all shown $D_{\perp}$ to be exponentially suppressed with the segregation strength. We obtain a fit to $D_{\perp}/D_0 = e^{-\alpha(\epsilon N - \beta)}$:

$$\frac{D_{\perp}}{D_0} = e^{-32.3(\epsilon N - 0.177)}. \tag{4.9}$$

Although we express the exponential dependence in terms of $\epsilon N$, in analogy with the
exponential dependence on $\chi N$ from the literature, we do not vary $N$ here and thus cannot explicitly confirm the $N$-dependence. We therefore note the possibility that the coefficient $\alpha$ could contain an $N$-dependence (for instance, due to the finite-$N$ effects which we have seen in Section 3.3.4).

The insensitivity to the ODT of the angle-averaged diffusion coefficient for symmetric diblock copolymers, which has been observed in the computer simulations of Murat [93] and in experiments using FRS [92], pulsed field-gradient nuclear magnetic resonance (PFG NMR) [91] and foward recoil spectrometry (FRES) [90], has been attributed to the influence of composition fluctuations. In a system with fluctuation effects, the diffusion is suppressed above and below the ODT. The composition profiles on small length-scales (relevant to motion of a single chain) above and below the ODT are not significantly different; it is only on larger length-scales that the effects of ordering are seen [89]. In our theory, fluctuation effects are not present, and the suppression of diffusion only sets in once the ODT has been crossed. The perpendicular diffusion coefficient in our theory is continuous at the ODT, which reflects the fact that the transition is 2$^{\text{nd}}$-order in mean-field theory. From Figure 4.10, the anisotropy of diffusivity becomes as large as $D_{\parallel}/D_{\perp} \approx 25$, which is comparable with observed anisotropies of $D_{\parallel}/D_{\perp} \approx 4 - 40$ from the FRS experiments of Hamersky [98] on unentangled diblock copolymer melts.

4.2.2.2  The cylindrical and spherical phases

The hexagonal cylindrical system (at $f = 0.25$) is equilibrated in a box with $(L_x, L_y, L_z) = (42b, 48b, 32b)$ that contains 3 cylinders in the $x$-direction ($L_x = 3L_0 \frac{2\sqrt{3}}{3}$) and 4 stacked layers of cylinders in the $y$-direction ($L_y = 4L_0$). In this case we are using $L_0 \approx 12b$; the system’s preference for a smaller period than $L_0 = 14b$ is apparent in our preliminary simulations of the lamellar to cylindrical transition, where the cylinders transitioning from a lamellar phase were stretched such that they had elliptical cross-
sections (when $L_0 = 14b$) instead of circular ones (when $L_0 = 12b$). The diffusion measurements in the cylindrical phase are shown in Figure 4.11 (blue data). Our data for the cylindrical phase persists only down to $\epsilon N \approx 0.3$, below which the cylindrical phase appears to no longer be stable, and transitions into the spherical phase (if $\epsilon N > (\epsilon N)_{ODT} \approx 0.25$) or the disordered phase (if $\epsilon N < (\epsilon N)_{ODT} \approx 0.25$) once the ordering field is released.

As in the lamellar phase, we see that the diffusion parallel to the cylindrical interface (corresponding to $D_z$) is insensitive to $\epsilon$ and that $D_\parallel/D_0 \approx 1$. The $D_z$ data is noticeably more noisy than the corresponding $D_\parallel$ data from the lamellar phase. This could be due to undulations in the cylindrical interface, that may be more pronounced than in the lamellar phase. The diffusion perpendicular to the interface is isotropic ($D_x \approx D_y$) and again exponentially suppressed with $\epsilon$. We fit the $D_\perp$ data to $D_\perp/D_0 = e^{-\alpha(\epsilon N - \beta)}$:

$$\frac{D_\perp}{D_0} = e^{-5.65(\epsilon N - 0.25)}.\quad(4.10)$$

The anisotropy in the diffusivity for the hexagonal cylindrical phase, in the range of $\epsilon N$ that we examine, becomes only as large as $D_\parallel/D_\perp \approx 3 - 4$, which is significantly weaker than the anisotropy we saw in the lamellar phase. The strongest anisotropies seen in experiments, however, have been in the cylindrical phase, not the lamellar phase. Hamersky et al. [99] performed FRS experiments on unentangled asymmetric cylinder-forming poly(ethylene oxide)-poly(ethylethylene) (PEO-PEE) and saw anisotropies as high as $D_\parallel/D_\perp \approx 80$ at $\chi N \approx 20$ (i.e. not in the weak segregation regime). Extrapolating from our exponential fit, our cylindrical system would approach an anisotropy similar to $D_\parallel/D_\perp \approx 80$ at $\epsilon N \approx 1$, which is not an unreasonably high segregation strength (although certainly not near the weak segregation limit).
Figure 4.11: Diffusion coefficients, as a function of \( \epsilon N \), for diffusion perpendicular to the interface (filled symbols) and diffusion parallel to the interface (hollow symbols) for the hexagonal cylindrical (blue) and body-centred cubic spherical (green) phases of the asymmetric \((f = 0.25)\) diblock copolymer. The ODT is \((\epsilon N)_{ODT} \approx 0.25\). The window for the BCC-HEX order-order transition (OOT) (vertical dotted lines) is estimated from the phase diagram (Figure 4.7). The short-dashed line is an exponential fit of perpendicular diffusion data for the cylindrical phase, described by 
\[
\frac{D^{(HEX)}}{D_0} = e^{-5.65(\epsilon N - 0.25)}.
\]
The long-dashed line is 
\[
\frac{D^{(BCC)}}{D_0} = \frac{1}{3} + \frac{2}{3} \frac{D^{(HEX)}}{D_0}.
\]

The body-centred cubic spherical phase (also at \( f = 0.25 \)) is equilibrated in a box with \((L_x, L_y, L_z) = (68b, 68b, 68b)\) that contains 64 BCC unit cells \((L_x = L_y = L_z = 2\sqrt{2}L_0)\). This corresponds to a period \( L_0 \approx 12b \) (the same as the period used for the cylindrical phase). We are forced to use a significantly larger box in this case than we used for the lamellar or cylindrical phases, due to the requirement that the number of grid points (in this case, for a cubic grid) be divisible by the number of processors (which itself must be a power of 2). The data for the spherical phase is shown also
in Figure 4.11 (green data). Although the data persists only up to \( \epsilon N \approx 0.4 \), this is not because we observe the spherical phase transitioning into the cylindrical phase; rather, the BCC spheres appear to still be metastable in this range.

Above the ODT (\( \epsilon N < (\epsilon N)_{ODT} \approx 0.25 \)), the diffusion coefficient is \( D_0 \), and is isotropic since the system is in the disordered phase. At the ODT, it is difficult to tell if there is a discontinuity in the diffusion coefficient. Since this is a 1st-order phase transition, which is accompanied by a discontinuous change in the order parameter, one would expect a discontinuous \( D^{(BCC)} \). It is therefore likely that the discontinuity is present but small. If there is such a discontinuity, it would have a magnitude \( \Delta D^{(DIS\rightarrow BCC)} = D^{(DIS)} - D^{(BCC)} \approx 0.05 - 0.1 \), estimated from Figure 4.11. We can estimate the relative magnitudes of the discontinuities in the diffusion coefficient due to the ODT (DIS \( \rightarrow \) BCC) and the OOT (BCC \( \rightarrow \) HEX), using the relative magnitudes of the discontinuities in first-mode amplitudes for DIS \( \rightarrow \) BCC and BCC \( \rightarrow \) HEX from equilibrium SCFT. This allows us to determine if such a small discontinuity in \( D^{(BCC)} \) at the ODT is plausible. According to equilibrium SCFT, in the DIS \( \rightarrow \) BCC ODT at \( f = 0.25 \), the BCC first-mode amplitude \( \phi_1^{(BCC)} \) jumps according to \( \phi_1^{(BCC)} = 0 \rightarrow 0.11814 \). In the BCC \( \rightarrow \) HEX OOT at \( f = 0.25 \), three of the six BCC mode amplitudes vanish according to \( \phi_1^{(BCC)} = 0.2192 \rightarrow 0 \), and the other three mode amplitudes change only slightly. For small order parameters, we can assume that the diffusion coefficients will scale as \( D \sim \phi^2 \), following the perturbation treatment of Barrat and Fredrickson [46], and thus the discontinuity in \( D \) will scale as \( \Delta D \sim (\Delta \phi)^2 \). The relative magnitudes of the discontinuities in \( D \) are thus

\[
\frac{\Delta D^{(DIS\rightarrow BCC)}}{\Delta D^{(BCC\rightarrow HEX)}} \approx \left( \frac{\Delta \phi_1^{(DIS\rightarrow BCC)}}{\Delta \phi_1^{(BCC\rightarrow HEX)}} \right)_SCFT^2 \approx \frac{(0.11814)^2}{(0.2192)^2} \approx 0.3. \tag{4.11}
\]

In the OOT window of Figure 4.11, the discontinuity in \( D \) for the BCC \( \rightarrow \) HEX transition is \( \Delta D^{(BCC\rightarrow HEX)} \approx 0.15 - 0.2 \), which places the relative magnitudes of
these discontinuities in the range of

\[
\frac{\Delta D^{(DIS\rightarrow BCC)}}{\Delta D^{(BCC\rightarrow HEX)}} \approx 0.25 - 0.67, \tag{4.12}
\]

which overlaps the value estimated in Eq. (4.11). Thus, such a small discontinuity in \(D^{(BCC)}\) at the ODT is plausible.

Below the ODT, the diffusion in the spherical phase is isotropic. This is expected, since the BCC phase itself is isotropic. Translational motion in all three directions, on length-scales that are large compared with the interfacial width in the spherical phase, must involve the same process of extraction of a minority block from its spherical domain. As a result, \(D^{(BCC)}\) is suppressed with segregation strength although in our case the dependence appears to be linear rather than exponential (however, from our analysis below, we suspect that it is weakly exponential). This is in contrast with FRES [102] and FRS [103] experiments on entangled diblock copolymers in the BCC phase, as well as the Langevin simulations of Fredrickson et al. [104], which showed that the suppression is exponential. The suppression of \(D^{(BCC)}\) has been measured to be as strong as \(D^{(BCC)}/D_0 = 10^{-4}\), as in the FRES measurements of Yokoyama et al. [102] on entangled poly(styrene)-poly(vinylpyridine) (PS-PVP). This is orders of magnitude stronger than the suppression that we see in Figure 4.11. However, this result was from experiments on significantly longer \((N \approx 10^3)\) and significantly more asymmetric \((f \approx 0.12)\) chains. Yokoyama et al. also performed measurements on a much shorter PS-PVP sample \((N \approx 300)\) and found that the diffusion was only weakly suppressed, despite the fact that the sample was well ordered in a spherical domain structure. They suggested that this was plausible provided that the monomeric friction coefficients for the PS and PVP monomers were similar, and the ordered domain structure produced only a weak enthalpic barrier. In our case, we know that the friction coefficients for species \(A\) and \(B\) are the same, and the ordered
domains producing a weak barrier is plausible since we remain relatively close to the ODT.

We can show that our data for the cylindrical and spherical phases suggest that the angle-averaged diffusion coefficients for both phases are the same at a given $\epsilon N$. We define the angle-averaged diffusion coefficient as $D = \frac{1}{3} (D_x + D_y + D_z)$. If the angle-averaged diffusion coefficient in the spherical phase ($D^{(BCC)}$) is the same as that in the cylindrical phase ($D^{(HEX)}$), then

$$D^{(BCC)} = D^{(HEX)}$$

$$\frac{1}{3} (D_x^{(BCC)} + D_y^{(BCC)} + D_z^{(BCC)}) = \frac{1}{3} (D_x^{(HEX)} + D_y^{(HEX)} + D_z^{(HEX)})$$

$$\frac{1}{3} (3D^{(BCC)}) = \frac{1}{3} \left( 2D_\perp^{(HEX)} + D_0 \right). \quad (4.13)$$

Eq. (4.13) corresponds to the long-dashed line in Figure 4.11, where $D_\perp^{(HEX)}$ is the exponential fit to the perpendicular diffusion data from the cylindrical phase. This curve agrees surprisingly well with the data for the spherical phase. This relationship is derived from the dimensionality of the domains (the cylindrical phase has 1-dimensional domains, whereas the spherical phase has 0-dimensional domains), and the presence of anisotropy in the diffusivity of the cylindrical phase. The implication of the agreement between Eq. (4.13) and the data for the spherical phase is thus that the angle-averaged diffusion coefficients in these phases are approximately the same ($D^{(BCC)} = D^{(HEX)}$), as we stated earlier. This is an intriguing (and perhaps unintuitive) result, suggested by our data, for which we do not presently have an explanation. Nevertheless, we will discuss the idea in more detail in Section 4.2.3, where we will see evidence that $D^{(LAM)} = D^{(HEX)}$ also.
4.2.2.3 The gyroid phase

The gyroid phase (at $f = 0.375$) is equilibrated in a $(L_x, L_y, L_z) = (68b, 68b, 68b)$ box that contains 8 gyroid unit cells, each with volume $(\sqrt{6}L_0)^3$ where $L_0 \approx 14b$.

The chain diffusion measurements in the gyroid phase are shown in Figure 4.12. The observed diffusion is isotropic (which is expected since the gyroid phase itself is isotropic), exponentially suppressed with $\epsilon N$, and asymptotes to a finite (non-zero)
value of \( \frac{D^{(GYR)}}{D_0} \). We obtain a three-parameter exponential fit:

\[
\frac{D^{(GYR)}}{D_0} = e^{-16.5(\epsilon N - 0.125)} + 0.58.
\] (4.14)

In the large-\( \epsilon N \) limit, the contribution to \( D^{(GYR)} \) from diffusion perpendicular to the interface of the cylindrical struts (which comprise the gyroid network) is sufficiently suppressed that it is negligible, compared with the diffusion along the interfaces of those struts. This interface diffusion is present even as \( \epsilon N \to \infty \), since there is no enthalpic barrier to motion parallel to the interfaces, as we have also seen in the lamellar and cylindrical phases. \( D^{(GYR)} \) remains suppressed relative to \( D_0 \), however, since in order to diffuse in any particular direction, a chain must diffuse a larger distance (along the cylindrical struts) than it would via unconstrained diffusion. This suppression is a feature of the gyroid network which is referred to as the network tortuosity, given by \( \frac{D_{\parallel}^{(HEX)}}{D^{(GYR)}} \). In our case, the parallel diffusion coefficient in the cylindrical phase \( D_{\parallel}^{(HEX)} \) (see Figure 4.11) is simply that of the disordered phase \( (D_0) \). We obtain a network tortuosity value of

\[
\frac{D_{\parallel}^{(HEX)}}{D^{(GYR)}} = \frac{D_0}{D^{(GYR)}} = \frac{1}{0.58} \approx 1.72.
\] (4.15)

As \( \epsilon N \) decreases, \( D^{(GYR)} \) begins to increase relative to its asymptote value. The exponential dependence of \( D^{(GYR)} \) on \( \epsilon N \) indicates that chains are leaving the minority cylindrical domains, and paying the associated enthalpic cost. Thus, diffusion perpendicular to the interfaces of the cylindrical struts of the gyroid network is playing a role in the chain diffusion for small \( \epsilon N \). For \( \epsilon N < 0.2176 \), gyroid is no longer metastable and dissolves into the disordered phase.

The behaviour that we see in the large-\( \epsilon N \) limit is consistent with the PFG NMR and FRS experiments by Hamersky and co-workers [99], on unentangled poly(ethylene oxide)-poly(ethylethylene) (PEO-PEE) in the cylindrical and gyroid phases. They
showed that the isotropic diffusion coefficients $D^{\text{GYR}}$ measured in the gyroid phase were reduced relative to the parallel diffusion coefficient $D^{\text{HEX}}_\parallel$ measured in the cylindrical phase (which in our theory is $D_0$) at the same temperature, by a network tortuosity factor of 1.5:

$$\frac{D^{\text{HEX}}_\parallel}{D^{\text{GYR}}} \approx 1.5.$$  \hspace{1cm} (4.16)

This tortuosity value of 1.5 has also been suggested based on theoretical calculations by Anderson et al. [106] of the tortuosity of a bicontinuous cubic phase that is closely related to gyroid. Our tortuosity value of 1.72 is reasonably close to the proposed (and measured) value of 1.5.

The exponential dependence of the diffusion coefficient on $\epsilon N$, in our simulations of the gyroid phase at small $\epsilon N$, has not been seen in experiments. However, diffusion measurements on the gyroid phase are scarce. It is not unrealistic a priori that diffusion perpendicular to the cylindrical struts could contribute significantly to the chain diffusion in the gyroid phase at low segregation strengths. In the equilibrium mean-field phase diagram, the gyroid phase terminates at a triple point at $\chi N = 11.14$ [14], and the weak segregation regime ends at $\chi N \approx 12$. The window for the existence of gyroid in the weak segregation regime is thus quite narrow, and the gyroid phase primarily exists within the intermediate segregation regime. It may be that gyroid is simply not seen in real systems at those weak segregation strengths for which the enhancement of $D^{\text{GYR}}$ due to perpendicular diffusion becomes a measurable effect.

### 4.2.3 Diffusion during the lamellar to cylindrical transition

The measurement of diffusion coefficients while a structural phase transition is in progress is feasible provided that the time-scale for the transition is much longer than the $\sim 15\tau_R$ that we require to calculate the chain diffusion coefficient from the
centre-of-mass mean-squared displacement. This is not unrealistic, given the fact that a phase transition requires collective motion and thus we could expect the transition to occur on significantly longer time-scales than those characteristic of chain self-diffusion. When the lamellar phase transitions to the hexagonal cylindrical phase, the cylinders will form within the lamellae [4, 118]. For our diffusion measurements, it is crucial that the cylindrical phase that forms be aligned and free of defects. We initialize our lamellar phase (at \( f = 26/64 = 0.40625 \)) in a box with \((L_x, L_y, L_z) = (111b, 96b, 8b)\) containing 8 lamellar periods \((L_0 = 12b)\) with normal aligned with the \(y\)-axis. This thin slab encourages the cylinders to form along the \(z\)-axis and reduces the likelihood of defects. The width of the box is such that it accommodates 8 cylinders \((L_x \approx 8 \times \frac{2}{\sqrt{3}}L_0)\).

We use the same period as in the cylindrical phase measurements of Sec. 4.2.2.2 \((L_0 = 12b)\) to minimize stresses on the cylinders. Since the ideal period for the lamellar phase is \(L_0 = 14b\), this likely places some stress on the lamellar phase; however, we see no adverse effects. The ordering field is released and the system is allowed to equilibrate at \(\epsilon N = 0.256\), where the lamellar phase is stable, for \(\approx 30\tau_R\). The system is then instantaneously “heated” to \(\epsilon N = 0.1984\) (where we have identified that cylinders are stable), at which point the system transforms to the hexagonal cylindrical phase. Figure 4.13 plots the coefficient of chain centre-of-mass diffusion along the \(x\)-, \(y\)- and \(z\)-directions (circles, squares and diamonds, respectively), versus elapsed time since the temperature jump. Initially, the lamellar normal is along the \(y\)-direction. The cylinder axis forms along the \(z\)-direction, and the cylinders form in the plane of the lamellae. The phase transformation appears to take approximately \(200\tau_R\), starting with a \(50\tau_R\) incubation period where undulations in the lamellae form, after which complete cylinders begin to appear and take over the system; these various stages can be seen in the insets of Figure 4.13. The diffusion initially exhibits the characteristic anisotropy of the lamellar phase, with one suppressed perpendicular
Figure 4.13: Time-resolved centre-of-mass diffusion coefficient, $D$, relative to the free diffusion coefficient, $D_0$, for an $N=64$ chain, as a diblock copolymer melt with $f = 0.41$ transforms from lamellae to hexagonally-packed cylinders. The time $t$ is the elapsed time following a temperature jump from an ordered lamellar state at $\epsilon N = 0.256$ to a point where the cylinder phase is stable, at $\epsilon N = 0.1984$. Circles, squares and diamonds correspond to the component of chain diffusion along the $x$-, $y$- and $z$-directions, respectively. The inset shows density snapshots of the thin slab system, in initial, intermediate and final states of the transition.

diffusion coefficient and two free parallel diffusion coefficients. $D_x$ and $D_y$ change continuously until, once the phase transformation is complete, they exhibit the characteristic anisotropy of the hexagonal cylindrical phase (two suppressed perpendicular diffusion coefficients and one parallel diffusion coefficient).

During the early incubation period ($t \leq 50\tau_R$), the diffusion coefficients in the $x$- and $y$-directions do not change significantly, i.e. they are not particularly sensitive to the formation of undulations in the lamellae. Once these undulations begin to
break the lamellae into cylinders, $D_x$ begins to decrease and $D_y$ begins to increase. These two diffusion components have a sigmoidal behaviour through the transition, and after the transition has completed ($t \approx 200\tau_R$), diffusion in the $x-y$ plane is isotropic ($D_x = D_y$). The decreasing of the $D_x$ component intuitively reflects the fact that once a lamella has broken in the $x$-direction, motion along that direction is slowed due to the barrier formed by the majority domain. The fact that $D_y$ increases during the transition is intriguing, and less intuitive. One might have expected $D_y$ to remain constant, since the degree of segregation ($\epsilon N$) is not changing and there is a barrier to motion in the $y$-direction before and after the transition. In that case, only $D_x$ would change, decreasing until $D_x = D_y$. Instead, $D_y$ is not constant, and in fact $D_y$ increases by the same amount that $D_x$ decreases. This increase of $D_y$ may be a result of the fact that free chains in the majority domain have paths for unimpeded motion in the $y$-direction (between cylinders) available to them, whereas in the lamellar phase they did not. $D_z$ remains unchanged ($D_z \approx D_0$) throughout the transition.

An interesting feature that is apparent from Figure 4.13 is that the anisotropy in the diffusivity in the cylindrical phase ($D_{\parallel}^{(\text{HEX})}/D_{\perp}^{(\text{HEX})}$) is weaker than that in the lamellar phase ($D_{\parallel}^{(\text{LAM})}/D_{\perp}^{(\text{LAM})}$), at least for $\epsilon N = 0.1984$. In this case, the suppression of perpendicular diffusion in the lamellar phase ($D_0 - D_{\perp}^{(\text{LAM})} \approx 0.29D_0$) is approximately twice that of the cylindrical phase ($D_0 - D_{\perp}^{(\text{HEX})} \approx 0.15D_0$). The diffusion data of Sections 4.2.2.1 and 4.2.2.2 had already suggested that there may be a general feature, that the strength of the suppression of perpendicular diffusion decreases as the dimensionality of the domains decreases. That is, the ordering

$$\frac{D_{\perp}^{(\text{LAM})}}{D_0} < \frac{D_{\perp}^{(\text{HEX})}}{D_0} < \frac{D_{\perp}^{(\text{BCC})}}{D_0}$$

(4.17)

is the opposite of the ordering of the dimensionality of the domains in those phases.
(lamellae (2-dimensional) have the strongest suppression, cylinders (1-dimensional) are intermediate and spheres (0-dimensional) are the most weakly suppressed of the three). It is unclear why this would be the case, but it may be connected to the extent to which chains in the cylindrical and spherical phases can diffuse easily through the interstitial (majority domain) regions between the cylinders or spheres once they have been extracted from the minority phase.

We have already discussed in previous sections that the angle-averaged diffusion coefficient is not particularly sensitive to the ODT (although there is a sudden onset of anisotropy upon crossing it), as seen in the FRES, FRS and PFG NMR experiments of Refs. [90–92, 96]. This lack of sensitivity has also been seen for order-order transitions (OOT). Lodge et al. [100] performed FRS experiments on asymmetric entangled poly(ethylene-propylene)-poly(ethylethylene) (PEP-PEE) across the cylinder to sphere OOT. Rittig et al. [126] examined the gyroid to lamellar OOT in entangled poly(ethylene-propylene)-poly(dimethylsiloxane) (PEP-PDMS) using PFG NMR. In neither case were discontinuities in the angle-averaged diffusion coefficients seen. Our results from Figure 4.13 show that the angle-averaged diffusion coefficient for the lamellar phase \(D^{(\text{LAM})}\), at the beginning of the phase transformation) and the cylindrical phase \(D^{(\text{HEX})}\), at the end) are approximately the same. From Figure 4.13, the angle-averaged diffusion coefficient for the lamellar phase (at \(t = 0\)) is given by

\[
D^{(\text{LAM})} \approx \frac{1}{3} \left( 2D_0 + D^{(\text{LAM})}_\perp \right) \approx 0.9D_0,
\]

and the angle-averaged diffusion coefficient for the cylindrical phase (at late times) is given by

\[
D^{(\text{HEX})} \approx \frac{1}{3} \left( D_0 + 2D^{(\text{HEX})}_\perp \right) \approx 0.9D_0 = D^{(\text{LAM})}.
\]

Due to the fact that the lamellar phase has 2-dimensional domains, whereas the cylindrical phase has 1-dimensional domains, if the angle-averaged diffusion coefficients for
both phases are the same, and the chains are unentangled (leading to anisotropy in
diffusivity for these phases), then the suppression of $D_{\perp}^{(\text{HEX})}$, relative to $D_0$, is 1/2
that of the suppression of $D_{\perp}^{(\text{LAM})}$. Our data suggests that this is the case, at least for
this value of $\epsilon N$. As we mentioned in Section 4.2.2.2, the diffusion measurements in
the cylindrical and spherical phases indicate that for a given $\epsilon N$ the angle-averaged
diffusion coefficients are approximately equal ($D^{(\text{HEX})} \approx D^{(\text{BCC})}$) as well. This is
purely an empirical observation based on our data.

As we have discussed, theoretical treatments of chain self-diffusion in the non-
lamellar phases are sparse. In the case of the gyroid phase, even the experimental
literature is limited. To our knowledge, studies measuring the chain self-diffusion
during a phase transition have not been done, either theoretically or experimentally.
Experimentally, such a measurement could be very difficult. It would at the very least
require that the time-scale for measurement of diffusion coefficients be significantly
less than the time-scale for the transition. This could be aided by using longer chains
in experiment, to slow down the dynamics, but if the chains are long enough to be
entangled the anisotropy in diffusivity is reduced. Thus, some clever experimental
techniques could be required. Our approach appears to be the first complete theo-
retical framework for performing these systematic chain-diffusion studies on ordered
phases. In addition, we are able to access time-scales that are relevant to structure
evolution (in this case, 100’s of $\tau_R$), while tracking the chain motion over the entire
time-scale. This could have implications for future studies on nucleation, the kinetics
of order-order transitions, and the effect of defects on chain diffusion. Thus, there is
much opportunity for our technique to make contributions in this field.
Chapter 5

Conclusion

We have developed our dynamical self-consistent field theory for polymeric systems into a practical computational tool for studying dynamics in dense, inhomogeneous polymeric systems. The formalism, which is described in Chapter 2, can be thought of as a dynamical analogue to the celebrated equilibrium self-consistent field theory for inhomogeneous polymeric systems, and has potential applications even beyond polymeric systems, in the broader field of classical soft matter. Within the context of polymeric systems, our approach is highly flexible and is easily modified for different chain lengths $N$, numbers of polymers $n_P$, chain architectures, numbers of species, non-bonded interaction forces $F_{\text{int}}$, etc. In our previous work, where the theory was originally derived, we resorted to studying simpler problems that rendered the functional Smoluchowski equation, which describes the statistical dynamics of a single-chain in a mean force-field, practically solvable. Here, we have shown that the full polymeric problem can also be practically solved, not by tackling the functional Smoluchowski equation directly, but by an equivalent Langevin simulation of an ensemble of independent chain replicas in the mean force-field. We use the ensemble to build up the probability distributions that are solutions to the Smoluchowski equation. Through this solution method, the theory takes on characteristics similar to
certain hybrid particle-in-field theories such as the Single-Chain-in-Mean-Field theory of Müller and coworkers [45], and the dynamical mean-field theory of Ganesan and Pryamitsyn [47].

Computational approaches to polymer dynamics that are capable of accessing the large time- and length-scale regime usually make use of coarse-graining, which can blur the connection between the fast-varying and slow-varying degrees of freedom. This connection is crucial, particularly for processes such as structure formation where there is an interplay between collective motion of the density field and the motion of individual molecules. Our approach maintains a connection to the microscopic dynamical model upon which it is based, since the description of single-chain dynamics remains in the final theory. Thus, the time-scale in our theory is easily relatable to the molecular relaxation time (in this case, the Rouse time), and to the interaction strength parameter that characterizes the microscopic pair-wise interaction force, which is based on the Lennard-Jones potential. In more heavily coarse-grained field theories, where chain conformation statistics are lost, it is more difficult to relate the simulation time to real time. Our theory should be able to facilitate the mapping of coarse-grained parameters, such as the Onsager kinetic coefficient, for such field theories onto specific microscopic models. Our approach is also well suited to studying problems of structure formation for which the individual chain dynamics are of interest.

The development of the numerical tools necessary to solve the mean-field equations opens up the possibility to apply our technique to a wide range of problems in polymer dynamics. In the hopes that there will be interest from the polymer dynamics community to use our technique, we have presented a complete, pedagogical discussion of the crucial details of our numerical implementation in Chapter 3. Also in Chapter 3, we characterize the numerical errors due to our algorithm, produced by the space and time discretizations as well as the finite size of the chain ensemble.
We found that finite chain-length effects are present for $N < 256$, consistent with the equilibrium SCFT finite chain-length studies due to Matsen [120]. The error due to the chain ensemble size can be mitigated by using a large number of replicas. The numerical solution can be made highly efficient through parallelization, which is made easier by the fact that the chain replicas are independent of one another. Thus, increasing the size of the chain ensemble, and simultaneously the number of processors, appears to be the most effective way to improve accuracy without impacting the runtime of the simulations. Our approach can easily take advantage of large numbers of processors, which favours its extension to GPUs.

As a first test of the theory on the dynamics of polymeric systems, we have explored the problem of spinodal decomposition in the symmetric binary blend. The results are given in the first half of Chapter 4. The goal was to ascertain how well our theory is able to capture the kinds of physical properties that are essential for a proper description of the dynamics of structure formation in more complicated systems (i.e. the diblock copolymer melt). We showed that the theory produces phase separation, and that the morphology induced by spinodal decomposition is similar to that observed in real polymeric systems. In the initial stages of spinodal decomposition, the growth rate of composition fluctuations agreed well with the linearized Cahn-Hilliard-Cook theory in the large-wavelength regime and was correctly damped at small wavelengths due to the free energy cost of forming interfaces. The instability in the density at early times grows significantly on time-scales that are short compared with the Rouse time, indicating that the chains are not in equilibrium with the instantaneous density during the initial stages. It is plausible that the quantitative differences between our growth rate and that of the linearized theory, in the small wavelength regime, are due to differences in the microscopic models. We saw a maximum growth rate at $q_m \sim R_g^{-1}$ which is a well-accepted relation. At late times, we saw the coarsening of domains which indicated the incorporation of non-linear
effects in our theory. The system set into a scaling regime at late times, where the growth of the domain length-scale was given by the Lifshitz-Slyozov-Wagner power law \( L(t) \sim t^{1/3} \). This growth law applies to systems for which the only mode of transport on large length-scales is diffusion, which is the case for our model. This indicated that the chains are properly diffusing in our simulations. Our theory captured the relevant physics correctly, and was able to simulate long-time \((100\tau_R)\) evolution, with a time-scale that is known in terms of the molecular relaxation time \(\tau_R\), while maintaining a connection to the individual chain dynamics. This indicated that our approach could be used for the diblock copolymer melt problem.

Our approach is well-suited to studying problems involving chain diffusion, since we retain the single-chain conformation statistics. Many other field-theoretic approaches do not have access to this information (such as dynamic density functional and time-dependent Ginzburg-Landau field theories). We have shown in the second half of Chapter 4 that we can construct a theoretical framework in which chain diffusion in various diblock copolymer ordered phases can be studied systematically. This is not something that existed prior to this work, and in fact theoretical treatments of chain diffusion in the non-lamellar ordered phases are sparse.

We found that our theory appears to recover equilibrium mean-field behaviour in the long-time limit, with a phase diagram containing lamellar, cylindrical, spherical and gyroid phases in the expected places. Our chain diffusion measurements confirmed the physical picture for the diffusion of unentangled chains in ordered phases. In this picture, there is no cost for diffusion parallel to the domain interfaces, and for those directions the diffusion coefficient equals that of the disordered phase (i.e. the free diffusion coefficient). Diffusion perpendicular to the interfaces carries an enthalpic cost for extraction of a block from its domain, leading to perpendicular diffusion coefficients that are suppressed with segregation strength. We observed the anisotropy in diffusivity, and exponential suppression of perpendicular diffusion, in the lamellar
and cylindrical phases which have also been seen in experiments [97–99, 101]. For the spherical phase, we saw isotropic diffusion that was also suppressed with a dependence on the segregation strength, and was shown to satisfy a simple relationship with the perpendicular diffusion in the cylindrical phase. This relationship suggests that the angle-averaged diffusion coefficients in the BCC and HEX phases are equal at the same \( f \) and \( \epsilon N \). In the gyroid phase, diffusion is isotropic and at high segregation strengths \( D^{(GYR)} \) is independent of \( \epsilon N \), which supports the hypothesis that, in this regime, diffusion is dominated by interface diffusion along the cylindrical struts of the gyroid network. At low segregation strengths, there is a contribution to diffusion from motion perpendicular to the strut interfaces, which is exponentially suppressed with segregation strength. We recovered a network tortuosity value of 1.72, which is reasonably close to the proposed value of 1.5 for the gyroid phase [99]. When compared with experiment, our theory obtains qualitatively correct relationships between the ordered domain structures, the chain self-diffusion, and the segregation strength, in unentangled diblock copolymer melts near the weak segregation regime.

The relative degrees of suppression that we saw for the perpendicular diffusion in the lamellar, cylindrical and spherical phases suggest a connection with the dimensionality of their domains. The lamellar phase exhibits the strongest suppression, and has the highest dimensionality \( (d = 2) \). The cylindrical phase exhibits a weaker suppression than the lamellar phase but stronger than the spherical phase, and its dimensionality is also between those of the lamellar and spherical phases \( (d = 1) \). The spherical phase exhibits the weakest suppression and also has the smallest dimensionality \( (d = 0) \). We measured the anisotropy of diffusivity during the kinetics of the lamellar-to-cylindrical transition, which directly showed that the suppression of perpendicular diffusion in the lamellar phase is stronger than in the cylindrical phase, at least for that segregation strength. We showed that our theory is able to simultaneously measure single-chain dynamics (short time-scale processes) and simulate
structure evolution (a long time-scale process, the LAM $\rightarrow$ HEX transition). To our knowledge, such a measurement has not been done before, in theory or experiment. Our diffusion measurements, as well as our suggested connection between the suppression of perpendicular diffusion and domain dimensionality, are all consistent with the angle-averaged diffusion coefficients being equal for the lamellar and cylindrical phases ($D^{(LAM)} = D^{(HEX)}$) and for the cylindrical and spherical phases ($D^{(HEX)} = D^{(BCC)}$). This observation is indirectly supported by experiments that have seen continuous diffusion coefficients at OOT’s in the diblock copolymer melt [100, 126].

Our theory, and numerical solution procedure, can be applied to a wide variety of problems involving structure formation in dense polymeric systems. For examining unentangled chain diffusion in other block copolymer contexts than we have addressed here, the modifications should be straightforward. Our approach is also amenable, in principle, to modifications for the inclusion of different interactions (such as hydrodynamic effects, entanglements, etc.), fluctuations beyond mean-field theory, and even applications of the theory outside of polymer physics. Some of these modifications are admittedly challenging. Nonetheless, it would be very interesting to explore such avenues. For many of these modifications, the general recipe for generating the corresponding dynamical mean-field theory would be more or less the same as in this work, although the details could be very different. The theoretical tools that have been applied to equilibrium self-consistent field theory may also have some relevance for modifications of our theory, due to the analogy between the two. Thus, future work could be taken in many different directions with the potential for exciting physics. We hope that by showing that the method is practical, and that it produces non-trivial, physically reasonable results, this work will encourage further development of the theory and help to guide the way forward.
Bibliography


Appendix A

Reciprocal lattice vectors for the diblock copolymer melt ordered phases

The single-mode approximation, which is sufficient to generate ordering fields for the LAM, HEX and BCC phases, uses the reciprocal lattice vectors which can be derived from the primitive basis vectors of each phase’s unit cell. The reciprocal lattice vectors given here are rotated such that they will generate phases that conveniently satisfy the periodic boundary conditions for a \((L_x, L_y, L_z)\) box. For the lamellar phase we have

\[
\mathbf{G}_{1}^{\text{lam}} = (0, 1, 0) \\
\mathbf{G}_{2}^{\text{lam}} = (0, -1, 0),
\]

(A.1)
for the hexagonal cylindrical phase we have

\[
\begin{align*}
G_{\text{hex}}^1 &= (0, 1, 0) \\
G_{\text{hex}}^2 &= \left(-\frac{\sqrt{3}}{2}, \frac{1}{2}, 0\right) \\
G_{\text{hex}}^3 &= \left(-\frac{\sqrt{3}}{2}, -\frac{1}{2}, 0\right) \\
G_{\text{hex}}^4 &= (0, -1, 0) \\
G_{\text{hex}}^5 &= \left(\frac{\sqrt{3}}{2}, -\frac{1}{2}, 0\right) \\
G_{\text{hex}}^6 &= \left(\frac{\sqrt{3}}{2}, \frac{1}{2}, 0\right),
\end{align*}
\]  

(A.2)
and for the body-centred-cubic spherical phase we have

\[
\begin{align*}
G_{\text{bcc}}^1 &= \left( \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0 \right) \\
G_{\text{bcc}}^2 &= \left( \frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}, 0 \right) \\
G_{\text{bcc}}^3 &= \left( \frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}} \right) \\
G_{\text{bcc}}^4 &= \left( \frac{1}{\sqrt{2}}, 0, -\frac{1}{\sqrt{2}} \right) \\
G_{\text{bcc}}^5 &= \left( 0, \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}} \right) \\
G_{\text{bcc}}^6 &= \left( 0, \frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}} \right) \\
G_{\text{bcc}}^7 &= \left( -\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}, 0 \right) \\
G_{\text{bcc}}^8 &= \left( -\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}, 0 \right) \\
G_{\text{bcc}}^9 &= \left( -\frac{1}{\sqrt{2}}, 0, -\frac{1}{\sqrt{2}} \right) \\
G_{\text{bcc}}^{10} &= \left( -\frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}} \right) \\
G_{\text{bcc}}^{11} &= \left( 0, -\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}} \right) \\
G_{\text{bcc}}^{12} &= \left( 0, -\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}} \right). 
\end{align*}
\]  
(A.3)
A second mode of vectors is necessary to form the gyroid phase. The first mode contains 12 reciprocal lattice vectors:

\[ G_{\text{gyr}}^1 = \left( \frac{2}{\sqrt{6}}, \frac{1}{\sqrt{6}}, \frac{1}{\sqrt{6}} \right) \]
\[ G_{\text{gyr}}^2 = \left( \frac{2}{\sqrt{6}}, -\frac{1}{\sqrt{6}}, \frac{1}{\sqrt{6}} \right) \]
\[ G_{\text{gyr}}^3 = \left( \frac{1}{\sqrt{6}}, \frac{2}{\sqrt{6}}, \frac{1}{\sqrt{6}} \right) \]
\[ G_{\text{gyr}}^4 = \left( \frac{1}{\sqrt{6}}, \frac{2}{\sqrt{6}}, -\frac{1}{\sqrt{6}} \right) \]
\[ G_{\text{gyr}}^5 = \left( \frac{1}{\sqrt{6}}, \frac{1}{\sqrt{6}}, \frac{2}{\sqrt{6}} \right) \]
\[ G_{\text{gyr}}^6 = \left( -\frac{1}{\sqrt{6}}, \frac{1}{\sqrt{6}}, \frac{2}{\sqrt{6}} \right) \]
\[ G_{\text{gyr}}^7 = \left( -\frac{2}{\sqrt{6}}, \frac{1}{\sqrt{6}}, \frac{1}{\sqrt{6}} \right) \]
\[ G_{\text{gyr}}^8 = \left( \frac{2}{\sqrt{6}}, \frac{1}{\sqrt{6}}, -\frac{1}{\sqrt{6}} \right) \]
\[ G_{\text{gyr}}^9 = \left( -\frac{1}{\sqrt{6}}, \frac{2}{\sqrt{6}}, \frac{1}{\sqrt{6}} \right) \]
\[ G_{\text{gyr}}^{10} = \left( \frac{1}{\sqrt{6}}, -\frac{2}{\sqrt{6}}, \frac{1}{\sqrt{6}} \right) \]
\[ G_{\text{gyr}}^{11} = \left( \frac{1}{\sqrt{6}}, -\frac{1}{\sqrt{6}}, \frac{2}{\sqrt{6}} \right) \]
\[ G_{\text{gyr}}^{12} = \left( \frac{1}{\sqrt{6}}, \frac{1}{\sqrt{6}}, -\frac{2}{\sqrt{6}} \right) \]  

(A.4)
and the second mode is given by

\[
\begin{align*}
K_{1}^{gyr} &= \left( \frac{2}{\sqrt{6}}, \frac{2}{\sqrt{6}}, 0 \right) \\
K_{2}^{gyr} &= \left( \frac{2}{\sqrt{6}}, 0, \frac{2}{\sqrt{6}} \right) \\
K_{3}^{gyr} &= \left( 0, \frac{2}{\sqrt{6}}, \frac{2}{\sqrt{6}} \right) \\
K_{4}^{gyr} &= \left( -\frac{2}{\sqrt{6}}, \frac{2}{\sqrt{6}}, 0 \right) \\
K_{5}^{gyr} &= \left( -\frac{2}{\sqrt{6}}, 0, \frac{2}{\sqrt{6}} \right) \\
K_{6}^{gyr} &= \left( 0, -\frac{2}{\sqrt{6}}, \frac{2}{\sqrt{6}} \right).
\end{align*}
\] (A.5)

These unit vectors are used in the context of Section 3.2.2.