Journal of Computational Physics 327 (2016) 168–185

Contents lists available at ScienceDirect

Journal of Computational Physics

www.elsevier.com/locate/jcp

Self-consistent field theory simulations of polymers on arbitrary domains

Gaddiel Ouaknin [a,*], Nabil Laachi [c], Kris Delaney [c], Glenn H. Fredrickson [c,d,e], Frederic Gibou [a,b]

[a] Department of Mechanical Engineering, University of California, Santa Barbara, CA 93106-5070, United States
[b] Department of Computer Science, University of California, Santa Barbara, CA 93106-5110, United States
[c] Materials Research Laboratory, University of California, Santa Barbara, CA 93106-5080, United States
[d] Department of Chemical Engineering, University of California, Santa Barbara, CA 93106-5080, United States
[e] Department of Materials, University of California, Santa Barbara, CA 93106-5050, United States

ARTICLE INFO

Article history:
Received 4 April 2016
Received in revised form 7 September 2016
Accepted 8 September 2016
Available online 19 September 2016

Keywords:
SCFT
Neumann boundary conditions
Sharp boundary conditions
Quad-/Oc-tree
Parallel computing
Fokker–Planck
Level set

ABSTRACT

We introduce a framework for simulating the mesoscale self-assembly of block copolymers in arbitrary confined geometries subject to Neumann boundary conditions. We employ a hybrid finite difference/volume approach to discretize the mean-field equations on an irregular domain represented implicitly by a level-set function. The numerical treatment of the Neumann boundary conditions is *sharp*, i.e. it avoids an artificial smearing in the irregular domain boundary. This strategy enables the study of self-assembly in confined domains and enables the computation of physically meaningful quantities at the domain interface. In addition, we employ adaptive grids encoded with Quad-/Oc-trees in parallel to automatically refine the grid where the statistical fields vary rapidly as well as at the boundary of the confined domain. This approach results in a significant reduction in the number of degrees of freedom and makes the simulations in arbitrary domains using effective boundary conditions computationally efficient in terms of both speed and memory requirement. Finally, in the case of regular periodic domains, where pseudo-spectral approaches are superior to finite differences in terms of CPU time and accuracy, we use the adaptive strategy to store chain propagators, reducing the memory footprint without loss of accuracy in computed physical observables.

1. Introduction

Block copolymers are macromolecules comprised of two or more chemically distinct sequences (or "blocks") of repeated and chemically bound monomers. Ensembles of these molecules exhibit fascinating characteristics: in the melt state, they self-assemble into periodic ordered structures in a wide range of morphologies, thus offering the possibility of designing materials with a broad property spectrum [1]. As such, polymeric materials offer many advantages such as scalability, tunability, ease of functionalization, mechanical flexibility, compatibility with various processing methods and a relatively low cost. We focus here on the important class of *diblock copolymers*, in which each polymer chain is made of two components (see Fig. 1): a minority block component A made of monomers a and a majority block component B made of monomers b.

* Corresponding author.
E-mail address: gaddielouaknin@umail.ucsb.edu (G. Ouaknin).

http://dx.doi.org/10.1016/j.jcp.2016.09.021
0021-9991/

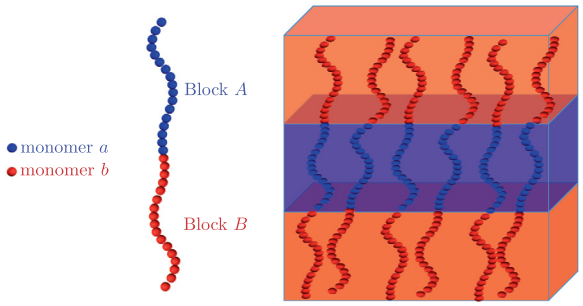

Fig. 1. Schematic of a diblock copolymer in the lamellar phase.

Diblock copolymers are of particular interest because they produce regular structures with a length scale (5 to 100 nm) that is difficult to access with other patterning techniques. As such, they are used in a myriad of applications in the electronics, energy and health industries [2–6].

At the mean-field level, the thermodynamic behavior of diblock copolymer melts is dictated by just two dimensionless parameters: the fraction, f_A, of block A along with $\chi_{AB}N$. χ_{AB} is the Flory–Huggins interaction parameter which quantifies the chemical repulsion between the blocks A and B and N is the number of segments (monomers) in the copolymer chain. One of the most important aspects in the study of diblock copolymers is to predict which ordered structures of polymeric materials can form at equilibrium as a function of f_A and $\chi_{AB}N$ [7,1,8]. The self-consistent field theory (SCFT) [7–9] is a successful mean-field theory and a mature computational tool for describing inhomogeneous phases in the parameter space $(f_A, \chi_{AB}N)$. It has enabled researchers to predict self-assembly in a wide range of situations [7,10–12]. Within this framework, the physical observables such as the densities of the A and B components are expressed in terms of chain propagators, which represent the statistical weight of a polymer chain at a given location and contour length and satisfy a Fokker–Planck equation. In the case of unbounded block copolymer melts, it is justified and convenient to impose periodic boundary conditions and to employ fast pseudo-spectral solvers [13].

In the case of confined domains, other boundary conditions must be imposed. At the atomistic level, the density displays an oscillatory profile in a "boundary layer" with size below ~ 1 nm but at the mesoscopic scale, we are not interested in the details of the solution in this boundary layer. In principle, a Dirichlet boundary condition should be imposed; however the use of a Dirichlet boundary condition is incompatible with the incompressibility assumption [7]. De Gennes derived that the boundary layer and wall effects he introduced earlier with his students Joanny and Leibler [14] must be treated at the mesoscopic scale with an effective Neumann boundary condition [15,7].

Currently, the technique that is used to predict self-assembly of block copolymers in confined domains, while still using a fast pseudo-spectral approach, is to impose a wall density to emulate the presence of a physical wall [16–21]. Effectively, the wall defines a mask that varies smoothly from 0 to 1 over a length scale defined by a parameter describing the width of the "soft" wall. However, while this technique produces accurate solutions inside the irregular domain, it produces fast varying solutions near the boundary that are arbitrarily specified by the mask. In turn, estimating numerically the solution and its derivatives near the boundary, which are needed in the context of free boundary optimization problems [22,23], produces far less robust results. We also note the recent work of Xu [24] where a Lennard-Jones (LJ) potential has been used to model the wall and the results of a 1D serial implementation are presented. In this case the boundary layer is self-consistently resolved but still obviously depends on the assumption of a LJ potential and its parameters as well as the compressibility tolerance. In the present work, and for both the mask model and our novel approach, we compute the mesoscopic solution for which a Neumann boundary condition is justified.

Here we introduce a hybrid finite-difference/finite-volume discretizations of the SCFT equations on irregular domains where effective boundary conditions are imposed in a numerically *sharp* fashion. In addition, we present an adaptive mesh refinement technique that focuses the computational resources in regions where the densities vary rapidly. The adaptivity is based on a forest (or collection) of Quad-/Oc-tree data structures in a parallel environment [25,26]. The paper is organized as follows: in section 2, we present the mathematical model describing the theory of copolymer thermodynamics and the SCFT algorithm. Section 3 details the numerical approach, while section 4 presents the extension to (potentially massively) parallel environments. Section 5 presents a set of numerical results for confined domains and section 5.5 presents the numerical results demonstrating that the use of adaptive grids can be beneficial in term of memory requirement, even in the case where one uses a pseudo-spectral approach.

2. Self-consistent field theory

In this section we describe the equations of the self-consistent field theory (SCFT) [8,9] used in the current computational study. A detailed development of these models can be found in [7] and the references therein, and a more physically-oriented derivation can be found in [27].