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# A finite element approach to self-consistent field theory calculations of multiblock polymers

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ABSTRACT

Self-consistent field theory (SCFT) has proven to be a powerful tool for modeling equilibrium microstructures of soft materials, particularly for multiblock polymers. A very successful approach to numerically solving the SCFT set of equations is based on using a spectral approach. While widely successful, this approach has limitations especially in the context of current technologically relevant applications. These limitations include non-trivial approaches for modeling complex geometries, difficulties in extending to non-periodic domains, as well as non-trivial extensions for spatial adaptivity. As a viable alternative to spectral schemes, we develop a finite element formulation of the SCFT paradigm for calculating equilibrium polymer morphologies. We discuss the formulation and address implementation challenges that ensure accuracy and efficiency. We explore higher order chain contour steppers that are efficiently implemented with Richardson Extrapolation. This approach is highly scalable and suitable for systems with arbitrary shapes. We show spatial and temporal convergence and illustrate scaling on up to 2048 cores. Finally, we illustrate confinement effects for selected complex geometries. This has implications for materials design for nanoscale applications where dimensions are such that equilibrium morphologies dramatically differ from the bulk phases.



## 1. Introduction

The morphology of multiblock polymers has been of interest for many years due to potential applications that depend on tailored microstructure. Numerical simulation can allow study of systems that are outside the limited analytically solvable cases. However, simulation of equilibrium multi-block polymer microstructures requires significant computational resources. A fully atomistic approach treating every atom in the system individually [1–3] is impractical due to the large number of atoms comprising even a single unit cell of a microstructure and prohibitive relaxation times for both bulk materials and non-periodic, complex geometries. The computational cost for even a small system is high enough to render this unsuitable as a general tool. Instead, a coarse-graining approach using an abstracted bead-spring model (see Fig. 1b) as a substitute for the full molecular structure (see Fig. 1a) is an often used [4–6] alternative. In this method, each 'bead' is actually multiple monomer units with individual beads interacting via carefully designed local and non-local potentials. Despite the abstraction, this approach is generally successful at retaining the physics of chain behavior on length scales

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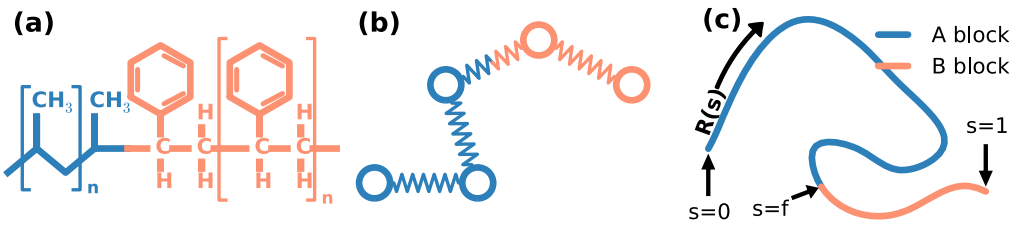


**Fig. 1.** Varying levels of abstraction for polymer chain models. (a) An atomistic schematic of a diblock system. (b) A bead spring model. (c) An abstracted, continuous chain model.

beyond a nanometer. While this is far less demanding than a fully atomistic model, it is still a computationally intensive approach for calculating equilibrium microstructures especially for larger and more complex geometries. A more attractive, continuum approach is the self-consistent field theory (SCFT) method. SCFT is a mean field theory that starts with the coarse grained chain and interaction models used in particle methods, but transforms the partition function into a field-theoretic framework.

We consider the popularly used model of the continuous Gaussian chain [4] which is well suited for flexible polymers. This model is based on a linearly elastic chain where the chain stretching is governed by a harmonic potential. Chain segments interact via pair potentials that are usually assumed to be attractive or repulsive contact interactions (delta functions). The relevant partition function integral is re-expressed using Hubbard–Statonovich transforms into an integral over auxiliary fields, and is taken to be dominated by a single set of fields (the mean-field approximation). The procedure is then to solve for these mean fields, which is done iteratively, to obtain the equilibrium field values and with them, the microstructure of the system. This approach has been used in a wide variety of systems and applications including lithography [7], polymer brushes [8–10], self-assembly [11,12], polymer nano-composites [13], organic electronics [14], and thin films [15]. Several recent advances include the use of SCFT in a hybrid SCFT–liquid state theory using charged polymers [16,17]. The addition of electrostatics leads to previously unseen structures with promising potential for energy storage applications due to favorable mechanical and electrical properties [16]. SCFT has also been used to study the directed self-assembly approach to lithography [18]. In this work, SCFT simulations were used to identify confining template geometries and polymer formulations that can achieve 10 nm scale patterns targeted by the microelectronics industry, along with acceptable defect levels. Although much SCFT work has been done using linear AB diblock chains, the method is not limited to those systems. Multiblock polymers [19–21], star and branched polymers [22,23], and tapered diblock polymers [24] have been studied as well. In the last case, the taper is block of mixed $A$ and $B$ monomers with the ratio changing along the length of the chain. The addition of the tapered block was found to change the phase behavior of the system, leading to a wider range of stability of the bicontinuous phase.

Spectral methods have been the predominant tool for solving SCFT problems. The approach is efficient, and has high spatial accuracy. This makes it an excellent choice for many applications. However, there are applications where the frequency-domain approach (of spectral, and quasi-spectral methods) has limitations; which encourages consideration of alternate real space approaches, like the finite element (FE) method. First is the ease of handing complex geometries. While a purely spectral model requires masking techniques for complex geometries, real space methods require no addition actions. Second, real space methods are not limited to periodic systems and naturally allow the use of heterogeneous and mixed boundary conditions. Finally, real space methods allow local mesh adaptation to selectively increase the resolution in a targeted position without requiring increased computational effort over the entire system. This restriction on spectral methods is partially alleviated by use of Chebyshev or other localized bases. Finite Element approaches, in particular, can incorporate rigorous *a posteriori* error estimates (due to the variational treatment) for mesh adaptivity that enable substantial computational gains. Furthermore, there is a substantial push to design solvers and frameworks (like FASTMath) for real space approaches that are suitable for deployment on next generation exascale computers. Motivated by these factors, we develop a real space formulation of the SCFT problem using the finite element method. The implementation is discussed in detail along with example results and a detailed study of the accuracy of implementation. Our contribution in this paper include: (a) formulating the SCFT problem in real space using a finite element based variational form, (b) exploring and implementing various high order contour stepping methods, (c) incorporating Richardson extrapolation for multiblock systems, (d) software engineering informed efficient implementation, and (e) illustrative examples (complex geometry, non-periodic domains, scalability studies) of the implementation highlighting the strengths of the method. The key factors affecting the accuracy of the results are discussed in detail.

The SCFT approach has been covered in great detail elsewhere [25], but we will review the key points before discussing the finite element implementation. Broadly, the SCFT approach is a mean field theory where the partition function is dominated by the mean field values of $W(\boldsymbol{r})$. The task then becomes finding the value of the mean fields such that:

$$\left.\frac{\delta H[W]}{\delta W}\right|_{W=W^*} = 0 \tag{1}$$