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Analytic Structure of the SCFT Energy Functional of Multicomponent Block Copolymers

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Abstract. This paper concerns the analytic structure of the self-consistent field theory (SCFT) energy functional of multicomponent block copolymer systems which contain more than two chemically distinct blocks. The SCFT has enjoyed considered success and wide usage in investigation of the complex phase behavior of block copolymers. It is well-known that the physical solutions of the SCFT equations are saddle points, however, the analytic structure of the SCFT energy functional has received little attention over the years. A recent work by Fredrickson and collaborators [see the monograph by Fredrickson, *The Equilibrium Theory of Inhomogeneous Polymers*, (2006), pp. 203–209] has analysed the mathematical structure of the field energy functional for polymeric systems, and clarified the index-1 saddle point nature of the problem caused by the incompressible constraint. In this paper, our goals are to draw further attention to multicomponent block copolymers utilizing the Hubbard-Stratonovich transformation used by Fredrickson and co-workers. We firstly show that the saddle point character of the SCFT energy functional of multicomponent block copolymer systems may be high index, not only produced by the incompressible constraint, but also by the Flory-Huggins interaction parameters. Our analysis will be beneficial to many theoretical studies, such as the nucleation theory of ordered phases, the mesoscopic dynamics. As an application, we utilize the discovery to develop the gradient-based iterative schemes to solve the SCFT equations, and illustrate its performance through several numerical experiments taking ABC star triblock copolymers as an example.

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Key words: Multicomponent block copolymers, saddle point approximation, SCFT energy functional, gradient-based iterative methods, ABC star triblock copolymers.

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1 Introduction

Due to the efforts of a large number of researchers, it has been well-established that the self-consistent field theory (SCFT) of polymers provides a powerful theoretical framework for the study of inhomogeneous polymeric systems in general and the self-assembly behavior of block copolymers in particular [1–3]. For a given block copolymer system, the SCFT can efficiently describe its architecture, molecular composition, polydispersity, and block types as a series of parameters in the energy functional which is a nonlinear and nonlocal functional of the monomer densities and their conjugate fields. The equilibrium solutions of the SCFT energy functional correspond to the possible stable and metastable phases of the block copolymer system. They are determined by a set of the SCFT equations obtained by assigning the first variations of energy functional with respect to the density profiles and fields to zero. Finding all solutions of the SCFT equations analytically is beyond today's technology, even for the simplest AB diblock copolymer system. A successful alternative is to solve the SCFT equations numerically.

Numerically solving the SCFT equations requires the analysis of the feature of SCFT solutions, and even the mathematical structure of the SCFT energy functional. There have been a number of numerical techniques developed to solve SCFT equations, including from the perspective of three facets – the strategy of screening reasonable initial values [4–6], the numerical solver for the modified diffusion equation of chain propagators [7–13], and the iterative schemes for the convergence of the equations system [9, 14–16]. However, little work has been devoted to further analysing the mathematical structure of the SCFT even through it is well-known that the equilibrium solutions of the SCFT equations are saddle points [3]. Among these researches, Fredrickson and co-workers [3,17,18] have directly analysed the analytic structure of the field-based energy functional which does not use the mean-field approximation for incompressible polymeric systems. They utilized the Hubbard-Stratonovich transformation [19] to decouple the particle-particle interaction, and pointed out that, for binary component system, the physical solutions represent saddle points in which the energy functional is minimized with respect to the exchange chemical potential, and maximized with respect to the pressure potential. It is the latter field that imposes the incompressible constraint and produces the index-1 saddle point character of the problem. The analysis of the mathematical structure of the SCFT energy functional, or more generally, of the field functional, is very useful for the theoretical studies of polymer systems. For this reason, a series of theoretical tools have been developed including the efficient gradient-based iterative methods to solve the SCFT equations [15, 16], the useful technique of partial saddle-point approximation which translates the saddle point problem into an extremum problem [20, 21], and the directly solving strategy for the field theoretic simulation which involves numerically solving the exact partition function of polymer fluid models [17, 18]. Due to the known information of the saddle point character, the SCFT model can be applied to the mean-field mesoscopic dynamics [22,23], and the nucleation theory of ordered phases in which the saddle point problem should be turned into a minimum problem firstly, followed by