Exponential Time Differencing Methods for Numerical Self-Consistent Field Theory

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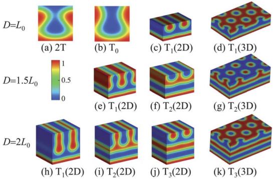
Outline

- Introduction
- Numerical Methods
- Performance of ETDRK4 Methods
- Applications of ETDRK4 Methods
- Summary
- Acknowledgments

Introduction

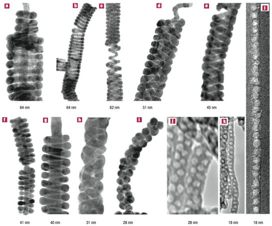
Self-Assembly of Block Copolymers under Confinements

In practice, most of block copolymers are more or less under confinement.



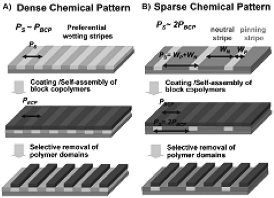
Self-assembly in thin films

D. Meng et al. *Soft Matter* **2010**, *6*, 5891



Self-assembly in nanopores

Y. Wu et al. *Nat. Mater.* **2004**, *3*, 816



Directed self-assembly (DSA)

H. Kim et al. *Chem. Rev.* **2010**, *110*, 146

Surface and interfacial effects play an important role in determining the self-assemble structures.

Approach I:
Using a masking technique and introducing surface interaction terms.

Approach II:
Imposing Robin boundary conditions on the modified diffusion equations for propagators.

$$\frac{\partial q}{\partial n} + \kappa q = 0 \quad \text{at the boundary}$$

Operator splitting with Fourier collocation (OSF, OSS, OSC).

- Fast, $O(M \log M)$.
- Often 2nd order convergence in temporal domain.
- Accuracy degradation for Dirichlet and Neumann boundary conditions (DBC and NBC).
- Not applicable for Robin boundary conditions (RBC).

Operator splitting with Cheyshev collocation (OSCHEB).

- $O(M \log M + \alpha M)$ with large coefficients α.
- Often 2nd order convergence in temporal domain.
- Can handle RBC but requires even larger coefficients.

Other real space methods (finite difference), spectral methods.

Modified diffusion equation in matrix form

$$\frac{\partial q}{\partial s} = \mathbf{L}q + \mathbf{F}(q, s)$$

In exponential form

$$\frac{\partial}{\partial s} e^{-\mathbf{L}s} q = e^{-\mathbf{L}s} \mathbf{F}(q, s)$$

Stepping a single contour step

$$q(s_{n+1}) = e^{\mathbf{L}s} q(s_n) + e^{\mathbf{L}s} \int_0^h d\tau \mathbf{F}\left[q(s_n + \tau), s_n + \tau\right]$$

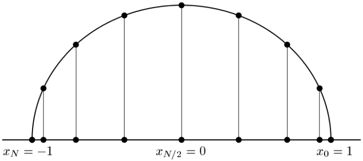
Then a 4th order Runge-Kutta method is employed to approximate the integral.

Numerical Methods

Chebyshev Collocation and Boundary Conditions

To efficiently handle non-periodic boundary conditions, we discretize spatial variables on a Chebyshev-Gauss-Lobatto grid with a set of points

$$x_j = \cos\left(\frac{\pi j}{N}\right), \quad j = 0, 1, \ldots, N$$

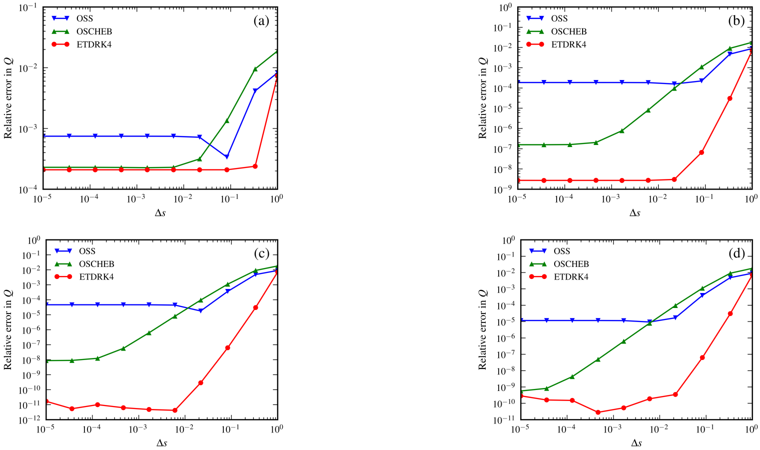


- **L** can be constructed from the Chebyshev differentiation matrix **D**.
- Boundary conditions are imposed by incorporating appropriate terms in **L**.

Performance of ETDRK4

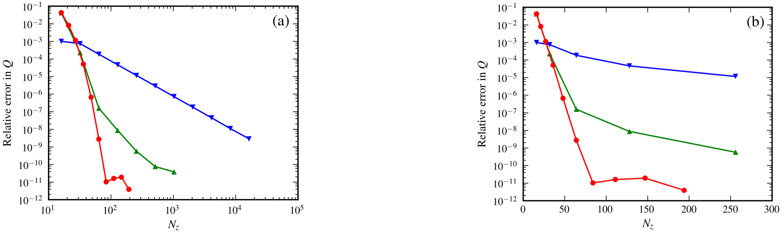
Convergence in Temporal Domain

ETDRK4 exhibits 4th order accuracy in temporal domain.



(a) $N = 32$, (b) $N = 64$, (c) $N = 128$, (d) $N = 256$

ETDRK4 retains spectral convergence in spatial domain.

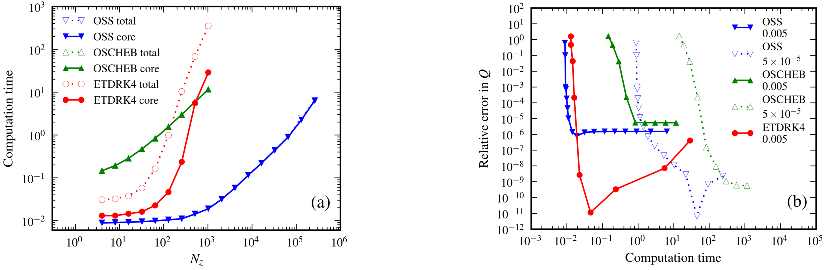


(a) log-log plot, (b) semilog plot. Disk: ETDRK4, up triangle: OSCHEB, down triangle: OSS.

Performance of ETDRK4

Computational Cost

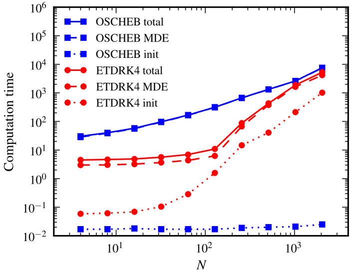
For high accuracy calculations (error$< 10^{-6}$), ETDRK4 is more efficient than OSS and OSCHEB.

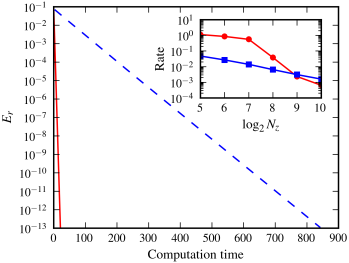


Performance of ETDRK4

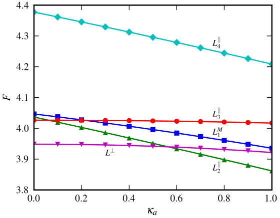
Full SCFT Calculations

With ETDRK4, the SCFT algorithm also converge exponentially.

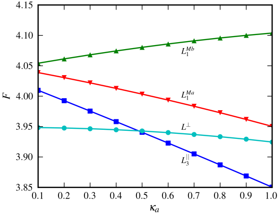




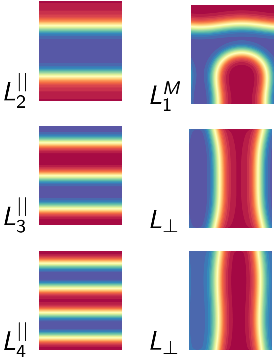
AB diblock copolymer confined by two parallel flat surfaces.



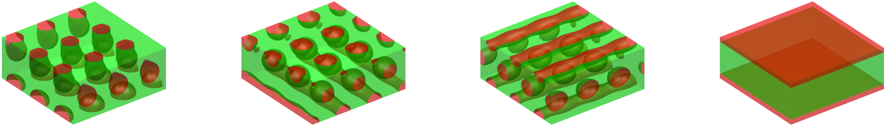
Symmetric surface interactions



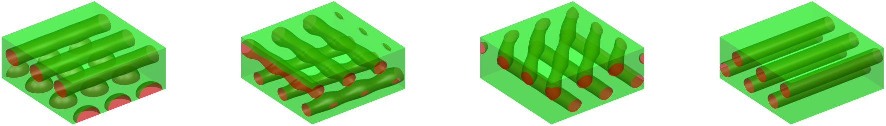
Asymmetric surface interactions



AB diblock copolymers confined by two parallel flat surfaces.



$\kappa_a = 0$ $\kappa_a = 1$ $\kappa_a = 2$ $\kappa_a = 3$



$\kappa_a = -0.1$ $\kappa_a = -0.2$ $\kappa_a = -0.3$ $\kappa_a = -0.5$

Summary

ETDRK4 methods

- Fast for high accuracy calculations.
- 4th order accuracy in temporal domain.
- Spectral accuracy in spatial domain.
- Applicable to RBC without significant increase of computational cost.

Limitations

- Computational cost increases rapidly for non-periodic boundary conditions in two or more dimensions.

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Thanks!