

Mechanisms of directed self-assembly in cylindrical hole confinements

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Introduction

As conventional optical lithographic techniques reach their resolution limit, and with many of the proposed replacements growing in cost, the directed self-assembly (DSA) of block copolymers has attracted considerable industrial interest as a means to achieve cost-efficient, high-resolution patterning at the nanoscale [1]. Of particular interest for the fabrication of device-oriented structures is the assembly of cylindrical-phase block copolymers within cylindrical confinements (or “holes”), known as the hole-shrink process. Such a process offers an inexpensive route towards efficient production of vertical interconnect accesses (VIAs) or cut masks [2].

Here, we utilize a theoretically informed coarse grained model for block copolymers to explore the emergence of metastable states within cylindrical confinements with a critical dimension of approximately one domain spacing. Subsequently, we use the string method to analyze the transition between competitive states, uncovering the free energy barriers opposing the transition from metastable defects to through-film cylinders. The influence of the strength of the affinity of the sidewall and bottom substrates on these free energy barriers is also considered. Additionally, the transition from a disordered state to a through-film cylinder is investigated at varying template conditions.

Main Objectives

1. To identify metastable states that exist when assembling block copolymers in cylindrical confinements.
2. To identify the free energy barriers opposing the annihilation of those metastable states, and how the barriers are influenced by substrate wetting conditions.
3. To identify the pathways of assembly of a through-film cylinder from the disordered morphology, and how those pathways are influenced by substrate wetting conditions.

Simulation Methods

We use a theoretically informed coarse-grained model for block copolymers [3] in conjunction with the string method [4] to simulate block copolymer melts under confinement and find minimum free energy pathways between states, respectively. The coarse-grained model simulates a compressible melt of block copolymers as Gaussian chains with repulsive interactions between unlike monomers (parameterized by χN). Substrate interactions are parameterized by Λ , which can be defined uniquely at each substrate; the magnitude of Λ captures the strength of the interaction, while the sign controls whether the substrate is attractive ($\Lambda < 0$) or repulsive ($\Lambda > 0$). Our polymer is parameterized to model poly-styrene-*b*-(methylmethacrylate) (PS-*b*-PMMA) with $f_{PS} = 0.7$ (the bulk periodicity, L_0 , is equal to 37 nm).

The string method iterates over a gradient descent to minimize the local gradient of the free energy and a re-parameterization to enforce that states along the pathway do not all fall into a local free energy minimum; it results in a minimum free energy pathway between states.

Full simulations details are available in [5].

Results

We performed a number of independent Monte Carlo simulations to investigate the impact of the combination of these parameters on a predicted morphology for constant confinement dimensions. A height of 62 nm, $1.67 L_0$ and diameter of 43 nm, $1.16 L_0$, were chosen.

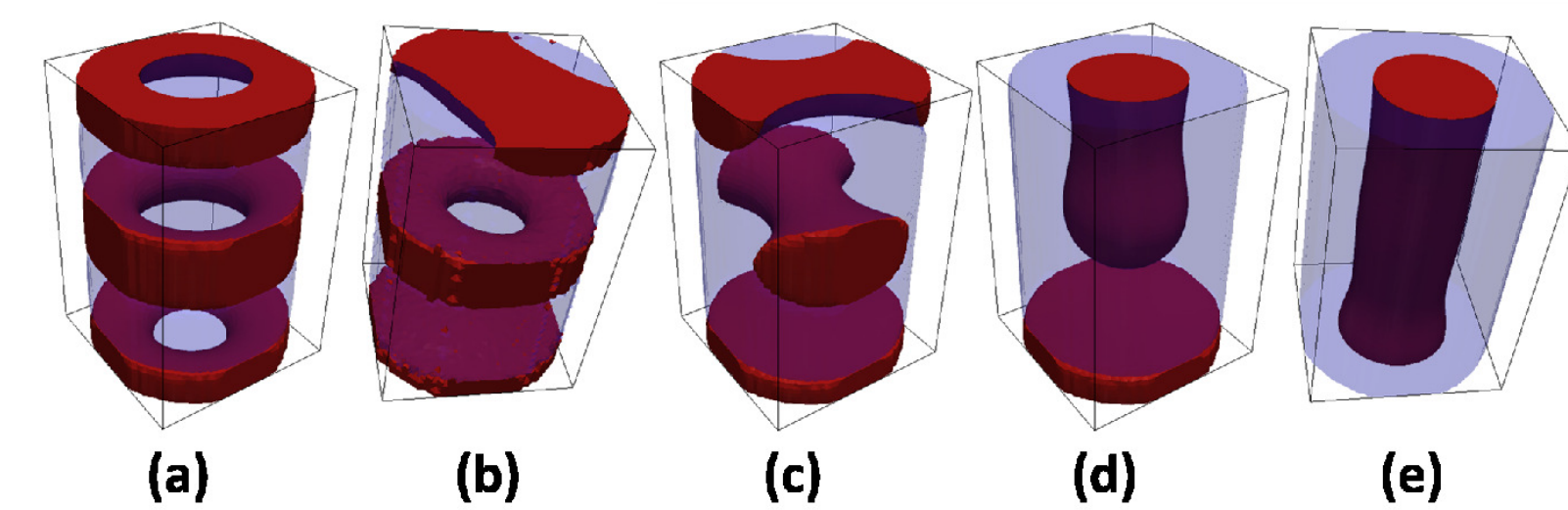


Figure 1: The stable states found to exist under cylindrical confinement.

The results of these simulations revealed that five unique, well-defined morphologies were stable within this range of parametric combinations. A 3D rendering of those morphologies can be seen in Figure 1, which includes the double donut (2D), the donut-bar (DB), the double bar (2B), the disconnected cylinder (DC), and the full cylinder (C). In some confinements, only one of these morphologies was stable across the set of simulations; however, there were many cases where more than one morphology was stable. This implies that either the states have comparable free energies, or that the stabilized morphologies represent kinetically trapped metastable states. Figure 2 shows a diagram that illustrates which morphologies were stable at each parametric combination of substrate energies.

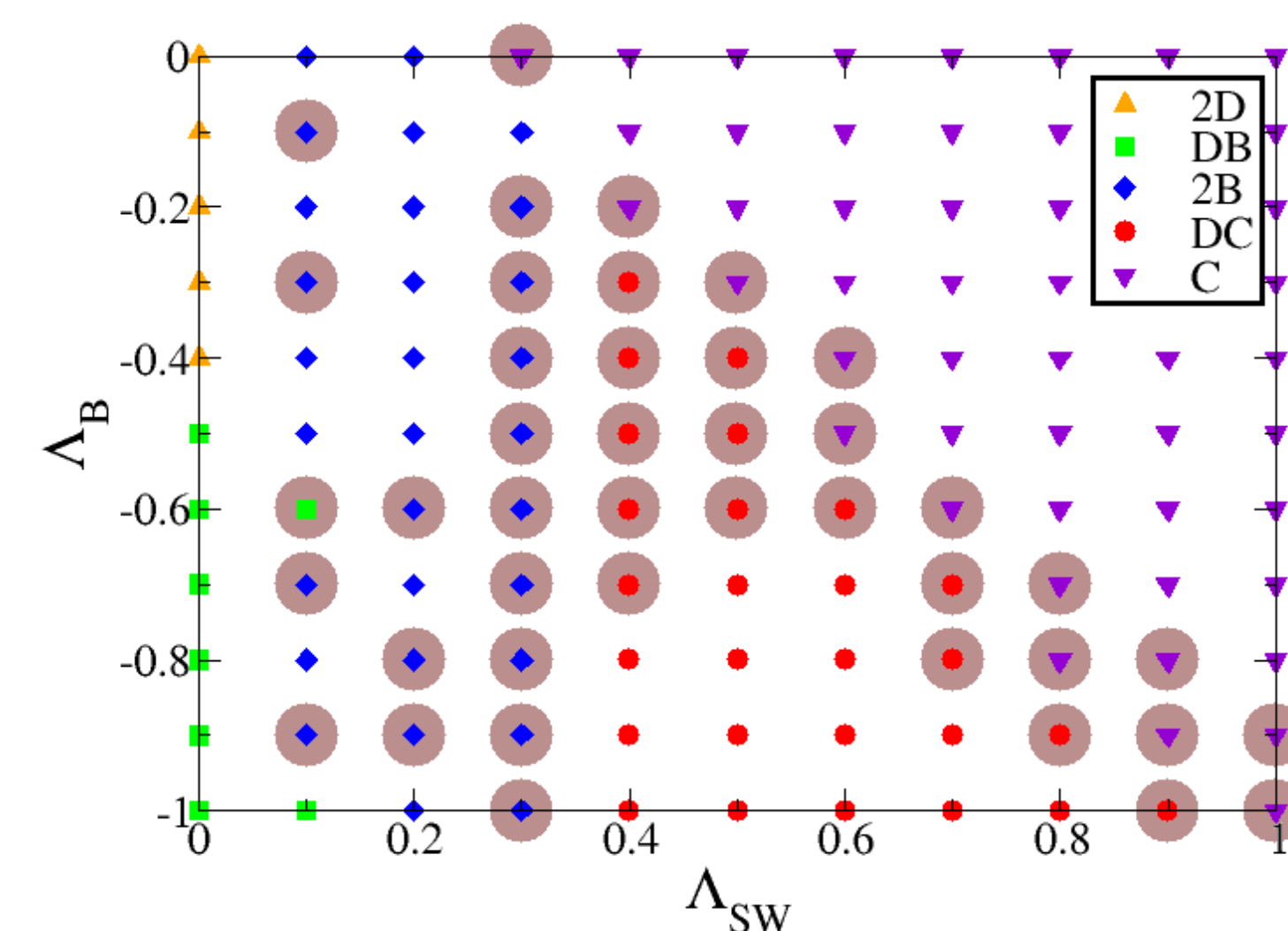


Figure 2: A “phase diagram” of stable states at different combinations of interfacial energies. A beige circle indicates multiple (meta)stable morphologies.

We chose to analyze the transition pathway between a defective morphology and a cylinder at ($\Lambda_{SW} = 0.4$ and $\Lambda_B = -0.2$), then subsequently in its immediate vicinity in parameter space. Figure 3 shows the effect that the sidewall interfacial energy has on the transition barriers by varying the value of $\Lambda_{SW} = \{0.3, 0.4, 0.5\}$ while $\Lambda_B = -0.2$. There is a significant reduction in the free energy barriers associated with both transition states as the sidewall becomes more preferential for the majority block, PS. Mean-

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while, the free energy barriers grow much larger if the interaction parameter on the sidewall becomes more weakly preferential for PS. Figure 3 also shows how the MFEP changes when the interfacial energy corresponding to the interaction between the bottom of the confinement and the polymer changes if we use $\Lambda_B = \{-0.1, -0.2, -0.3\}$ while $\Lambda_{SW} = 0.4$. In contrast to the sidewall interfacial energy, the bottom of the confinement has only a small effect on the barrier heights of the transition states. The first transition is virtually unaffected, and there is a minor influence on the height of the second free energy barrier.

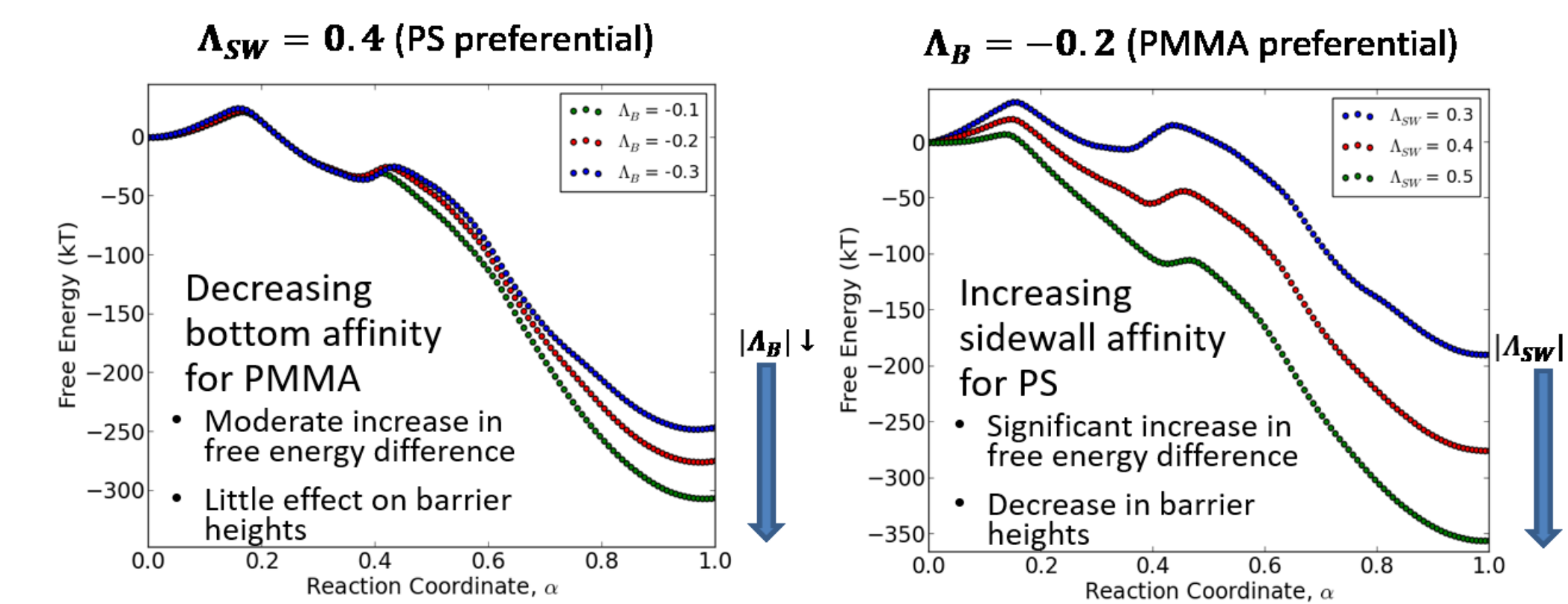


Figure 3: Transition pathways along the reaction coordinate α between a double bar morphology and a cylinder, varying the (top) bottom substrate preference and (bottom) the sidewall preference.

To explore the assembly from a disordered morphology, a series of pathways were calculated that connect a disordered state and a through-film cylinder in confinements having varying sidewall energy strengths; the resulting MFEPs are shown in Figure 4 and Figure 5. Along a pathway with intermediate sidewall preference for the majority block, a defective states first forms; then significant free energy barriers exist to oppose its annihilation.

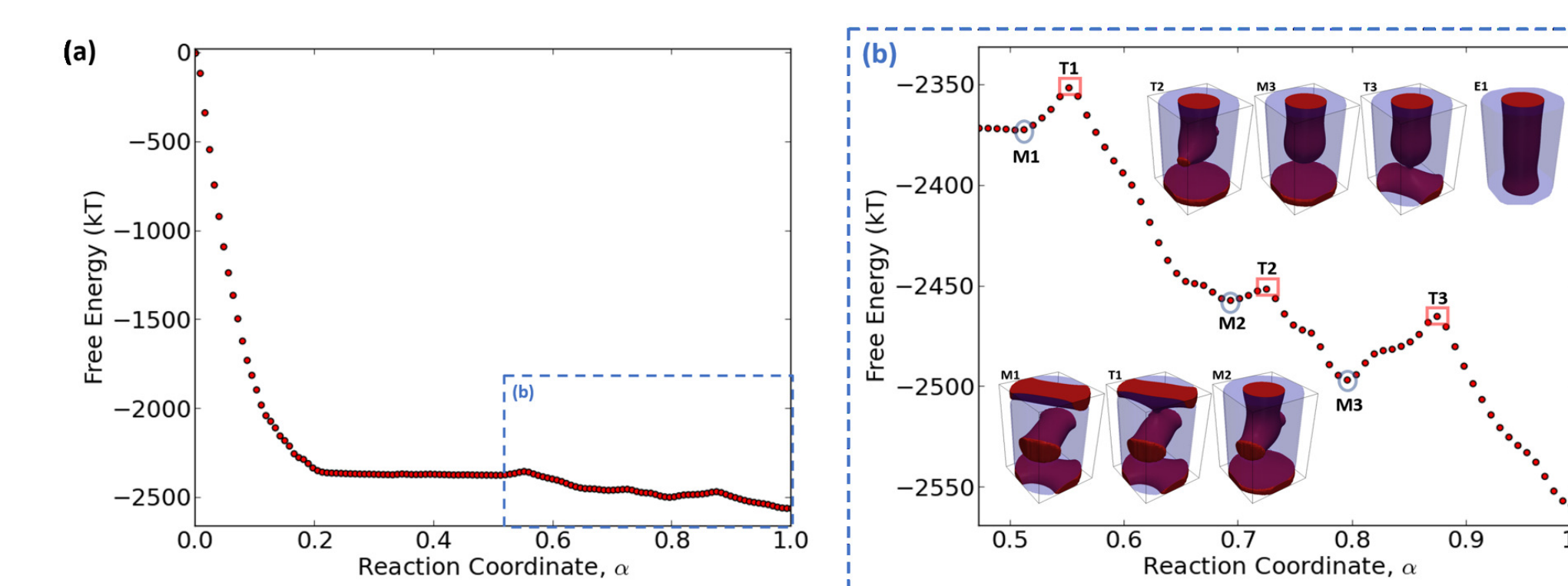


Figure 4: The transition pathway along the reaction coordinate α between a disordered block copolymer and a cylinder with $\Lambda_{SW} = 0.3$, $\Lambda_B = -0.2$.

By contrast, when the sidewall preference for the majority block is quite strong, the MFEP has no defects, and directly forms the through-film cylinder. This suggests that there is a higher probability of avoiding defective states when the sidewall preference for the majority block is large.

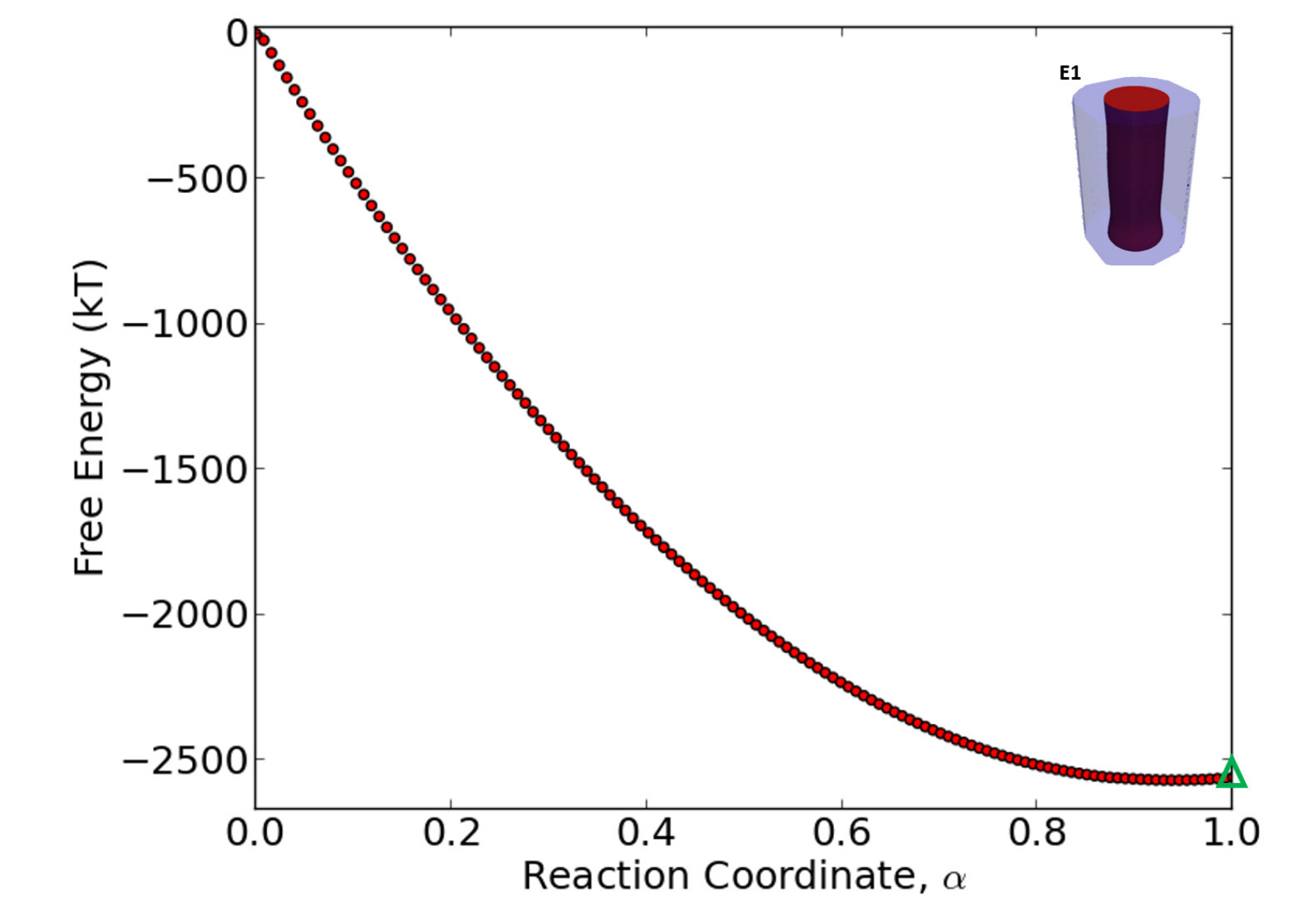


Figure 5: The transition pathway along the reaction coordinate α between a disordered block copolymer and a cylinder with $\Lambda_{SW} = 0.5$, $\Lambda_B = -0.2$.

Conclusions

- Several metastable defective states exist for block copolymer assembly in cylindrical holes.
- Increasing the sidewall preference for the majority block has a strong influence on defect annihilation; the bottom substrate has little influence on free energy barriers of annihilation.
- Defects arise in block copolymer assembly as part of the minimum free energy pathways. By increasing the sidewall preference for the majority block, the probability of forming defects at all is reduced.

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