Supporting information for: A Swarm Intelligence Platform for Multiblock Polymer Inverse Formulation Design

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Surjectivity of SCFT Relaxations

One of the key challenges in inverse design is engineering a robust solution to the forward problem. In the polymer field theory community, it is well known that a high density of low energy metastable states often accompany the lowest free energy solution in bulk calculations of complex polymer blends. In the main text, we argue that while this feature renders inverse design of bulk morphologies untenable at the present time, lateral confinement within thin films imposes sufficiently strong surface fields to reduce the density of states and produce reliable predictions using standard relaxation algorithms. Here, we provide additional evidence in support of this claim.

Well-Defined Inverse In Confined Melts

In Figure S1 we summarize results from a blend of two asymmetric diblock polymers relaxed from 150 random initial conditions either under confinement (top, with strong red block attractiveness on the template walls) or under periodic boundary conditions (bottom). We bin the results by free energy, where care was taken to ensure that each histogram bin indexes a single, unique solution to the SCFT equations. In the unconfined system, at least 8 meta stable states were identified (others were found, but their stability was questionable) in significant numbers. In contrast, the confined system relaxed to the same state regardless of the starting field configuration used.



Figure S1: Density of states estimates, binned by mean field free energy, for an A-b-B + B-b-C diblock polymer blend under confinement (top) and periodic boundaries (bottom) relaxed from random initial conditions. Each system contains a symmetric blend of diblock polymers with $\bar{\phi}_{AB} = 0.5$, $f_A^{AB} = 0.7$, $f_B^{BC} = 0.3$, and $\chi_{AB}N = \chi_{AC}N = \chi_{BC}N = 17$. The confined system has equal side wall lengths of $L = 14.5R_g$ with $\chi_{wA}N = -30$ to simulate attractive walls for the A (red) component. Note that two periods (four cells) of the periodic image are shown in the unconfined system to emphasize the bulk morphology.



Figure S2: Density of states estimate for the final PSO solution reported in the main text. Each calculation was a blend of two A-*b*-B-*b*-C triblock polymers and B homopolymer annealed under confinement. Parameters for each of the 100 random quenches were: $L_x = 11.9R_g$, $L_y = 12.5R_g$, $\mathbf{f}^{t0} = \{.08, .46, .46\}$, $\mathbf{f}^{t1} = \{.36, .64, 0.0\}$, $\alpha_{t0} = 0.93$, $\alpha_{t1} = 1.0$, $\alpha_h = 0.95$, $\phi_{t0} = 0.31$, $\phi_{t1} = 0.49$, $\phi_h = 0.20$ where t0 and t1 index the triblock chains and h indicates the homopolymer.

Ensuring Robust PSO Solutions

We stress, however, that the reduction in the density of solutions under confinement discussed above is not a rigorous feature of the field theory, simply an empirical observation that has held through our investigation. As formulations become more complex, the density of defective states may increase, leading to the possibility of fragile solutions identified by the PSO method. Of course, this issue may be avoided by engineering the fitness metric to bias the algorithm towards more robust solutions. For instance, replacing the current forward problem definition (run an SCFT relaxation from a random seed and compute its pattern error) with a number of parallel SCFT relaxations from different random seeds and reporting the average pattern error. An example from the main text is illustrated in Figure S2 where the final best solutions, and the results of the calculation binned by free energy. While the desired state is both well populated in the histogram and features the lowest free energy, it is still a fragile solution, evidenced by the relative likelihood of relaxing the desired solution from a random seed.

SCFT method

The intensive SCFT Hamiltonian of a weakly compressible melt with Flory-Huggins interactions between each pair of monomer species is

$$\frac{\beta H}{C} = \frac{1}{2} \int d^{3}\mathbf{r}' \sum_{jk}^{n_{species}} \chi_{jk} N \phi_{j}(\mathbf{r}') \phi_{k}(\mathbf{r}') + \frac{\zeta N}{2} \int d^{3}\mathbf{r}' \left(\sum_{j} \phi_{j}(\mathbf{r}') - 1 \right)^{2} - \int d^{3}\mathbf{r}' \sum_{j}^{n_{species}} W_{j}(\mathbf{r}') \phi_{j}(\mathbf{r}') - \sum_{K}^{n_{chains}} \frac{\overline{\phi}_{K} \widetilde{V}}{\alpha_{K}} \log Q_{K}[W^{K}(\mathbf{r}')]$$
(1)

where $\beta = 1/k_BT$, $C = \rho_0 R_g^3/N$, N is a reference chain length, $\alpha_K = N_K/N$ is the relative length of chains of type K, $R_g = \sqrt{N/6b}$ is the radius of gyration for an ideal continuous Gaussian chain, $\mathbf{r}' = \mathbf{r}/R_g$, χ_{jk} are the Flory-Huggins interaction parameters, ζN is a harmonic compressibility penalty, and $\tilde{V} = V/R_g^3$ is the normalized cell volume. All concentration fields are normalized so that $\phi_j(\mathbf{r}') = \rho_j(\mathbf{r}')/\rho_0$ is the local volume (blend) fraction of monomers of type j and $\overline{\phi}_K = n_K N \alpha_K/(V \rho_0)$ is the spatially-averaged volume fraction of chains of type K. The fields $W_j(\mathbf{r}')$ are self-consistently determined auxiliary potentials introduced to decouple the multibody interactions in the original particle-based model, and $Q_K [W^K(\mathbf{r}')]$ is the partition function of a chain of type K. Note that all simulations are performed in two dimensions in laterally confined cells, modelled using the masking method ^{S1,S2} that incorporates a fixed concentration of wall particles $\phi_w(\mathbf{r}')$ into the interaction and compressibility terms of equation (1). The pseudo-spectral methods we employ in solving the SCFT equations are well established and we direct the interested reader to the existing literature^{S3–S5} for details.

Error metric definition

In order to perform global optimization, we require a scalar function of the equilibrium state that measures some distance between predicted and target morphology. Here, we define a metric based on a simple bitmask comparison. As an input to the optimization algorithm, $n_{species}$ binary matrices are provided, corresponding to the desired spatial distribution of the $n_{species}$ distinct monomer types in the system. The pattern error Ω is determined according to:

$$\Omega = \sum_{\mathbf{r}} \sum_{i=1}^{n_{species}} |\rho_i^*(\mathbf{r}) - \widehat{\rho}_i(\mathbf{r}; \mathbf{x})|^2, \qquad (2)$$

where *i* indexes monomer types, $\rho_i^*(\mathbf{r})$ is the thresholded target monomer distribution, and $\hat{\rho}_i(\mathbf{r}; \mathbf{x})$ is the (thresholded) monomer distribution predicted by SCFT under the conditions described by the design vector \mathbf{x} , defined below.

Composition Constraints

In order for the SCFT model to be fully specified, we must supply state parameters \mathbf{x} , including the interaction matrix elements χ_{ij} , the block fractions and architecture of all chains in the system, along with the overall blend composition. The requirements on valid chain specifications (namely the species block fractions $f_i > 0 \quad \forall i$ and $\sum_i f_i = 1.0$) render the raw block fractions impractical variables for unconstrained optimization, so a transformation is applied here. For linear block polymers with n_{blocks} blocks, we may simply define $\beta_{i \in \{1,...,n_{blocks}-1\}}^{K} = f_i^K / f_{i+1}^K$ where f_i^K is the fractional length of the *i*th block of chain K. One may then optimize over the logarithm of these fractional lengths $\gamma_i^K = \log(\beta_i^K)$, so that the chain architecture transitions smoothly between a homopolymer and all possible multiblock polymers, preserving a pre-determined maximum number of blocks, n_{blocks} , and order of block identities, across the range $\gamma \in (-\infty, \infty)$. The same approach is also used for the blend composition by defining $\beta_K^{\bar{\phi}} = \overline{\phi}_K / \overline{\phi}_{K+1}$ (the method for inverting this relationship is provided below). With these transformations in place, a candidate blend formulation may be characterized by the numerical vector $\mathbf{x} = \{\chi_{ij}N \dots, \alpha^K \dots, \beta_i^K \dots, \beta_K^{\bar{\phi}}, \dots, L_x, L_y\}$. We note that the compressibility parameter ζN is not included in this parameter set, as it is a numerical parameter to ensure near incompressibility of the copolymer melt and is held fixed at $\zeta N = 1000$ for all calculations reported here.

Computing Chain Compositions from β Parameters

Computing the associated block fractions f_i from a vector of β values can be achieved by solving the linear system:

$$\begin{bmatrix} -1 & \beta_0 & 0 & \cdots & 0 & 0 \\ 0 & -1 & \beta_1 & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & -1 & \beta_{n-1} \\ 1 & 1 & 1 & \cdots & 1 & 1 \end{bmatrix} \cdot \begin{bmatrix} f_0 \\ f_1 \\ \vdots \\ f_{n-1} \\ f_n \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ 1 \end{bmatrix}$$

The same transformation is applied to the overall blend composition, the distribution of which is subject to identical constraints as the block fractions and leads to the same linear system.

Specific Constraints Used in Example Calculations

Heterogeneous mixed spot and line pattern — Limiting ranges were imposed on the search space corresponding to diblock fraction $f_A \in [0.1, 0.5]$, blend composition $\overline{\phi}_{AB} \in$ [0.7, 1.0], template size $L \in [10, 20]$, and chain lengths $\alpha \in [0.5, 2.0]$. The confining well used in each SCFT simulation was constrained to be square for simplicity, with $L_x = L_y = L$, and with walls that are selective to the matrix component (B), $\chi_{wB}N = -30$. **Embedded squares** — In order to accelerate the search, reasonable constraints were applied to the template size and relative chain length parameters so that $L_x \in [11, 14], L_y \in [12, 16], \alpha_{t0}, \alpha_{t1} \in [0.9, 1.3], \text{ and } \alpha_{Bh} \in [0.5, 2.0].$ Importantly, the parameters associated with the triblock architectures $(\beta_{0,1}^{t0}, \beta_{0,1}^{t1})$ were practically unconstrained, with $\gamma \in [-4, 4]$.

References

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