I. MOTIVATION OF ANALYTIC THEORY

The analytic theory developed in the main text is a dynamical mean-field one, which focuses on the likelihood \( \phi \equiv [(\eta_i + 1)/2] \) that a given fiber bond is a bulk one. Here \( \eta_i \equiv S_i S_{i+1} \), is a ‘defect variable’: \( \eta_i = 1 \) describes a bulk (same-color) bond, and \( \eta_i = -1 \) is a defect (unlike-color) one. We expect a mean-field theory of this nature to be most accurate when red and blue blocks are added to the fiber with equal likelihood, because, in this limit, the Ising model representation of fiber energetics can be written in the noninteracting (space-independent) form \( H = -J \sum_i \eta_i \).

To derive Eqns. (1) and (2) of the main text, we argue as follows. At any instant, the end of the fiber is either red or blue. Regardless, the next block added is of matching color with probability \( 1/2 \), and so we expect bulk domains to grow with rate \( c/2 \). We expect bulk domains to shrink with rate \( \phi e^{-\beta \epsilon_s} \): the factor \( \phi \) ensures that the terminal bond is a bulk one, and the factor \( e^{-\beta \epsilon_s} \) contains the energy scale for the bulk interaction. Similarly, we expect the fiber as a whole to grow with rate \( c \), and to shrink with rate \( e^{-\beta \epsilon_s} \) (resp. \( e^{-\beta \epsilon_d} \)) if its rightmost bond is a bulk (resp. defect) one. These arguments imply the drift velocities for bulk domains and for the fiber given in Eqns. (1) and (2) of the main text.

II. DYNAMIC CORRELATION LENGTH

The dynamic correlation length \( \xi \) derived from Eq. (3) of the main text is

\[
\xi(c, \epsilon_s, \epsilon_d) = \frac{2(e^{\beta \epsilon_s} - e^{\beta \epsilon_d})}{e^{\beta \epsilon_s} + e^{\beta \epsilon_d}(c e^{\beta \epsilon_s} - 1) - c^2 e^{2\beta(\epsilon_s + \epsilon_d)}}
\]

when \( \epsilon_s \neq \epsilon_d \), and \( \xi = 2 \) otherwise.

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Dynamical mean-field theory suggests that the far-from-equilibrium assembly strategy motivated by our fiber work is transferrable to higher dimensions. One possible higher-dimensional generalization of the fiber model is a collection of mutually attractive red and blue blocks diffusing in \((d > 1)\)-dimensional solution (see e.g. Ref. [25] of the main text). Post-nucleation, we study the growth of a structure composed of red and blue blocks by following the motion of the interface or front between the structure and solution (see Fig. S6(a)). We can consider such a growth process within mean-field theory. We assume that blue and red blocks are added with equal rates \(c/2\) to the front, whereupon each block makes \(z\) energetic bonds with the front (as an approximation we fix \(z\) to be constant, unaffected by binding events). In units of \(k_B T\) the red-red and blue-blue interactions are both \(-\epsilon_s\), while the red-blue interaction is \(-\epsilon_d\). We allow the composition of the surface to be described by a parameter \(m\) ∈ \([-1, 1]\), similar to an Ising magnetization: when \(m = -1\) the front is all red; when \(m = 1\) the front is blue; and when \(m = 0\) the front is randomly mixed. Each of the \(z\) available surface bonds is then red with probability \(p_R = (1 - m)/2\), and blue with probability \(p_B = 1 - p_R\).

The energies per bond felt by red and blue blocks in a front of composition \(m\) are

\[
\epsilon_{\text{red}}(m) = -\epsilon_s p_R - \epsilon_d p_B = -\frac{1}{2}(\epsilon_s + \epsilon_d) + \frac{m}{2}(\epsilon_s - \epsilon_d),
\]

and

\[
\epsilon_{\text{blue}}(m) = -\epsilon_s p_B - \epsilon_d p_R = -\frac{1}{2}(\epsilon_s + \epsilon_d) - \frac{m}{2}(\epsilon_s - \epsilon_d).
\]

Consideration of possible binding and unbinding events implies that the net rates of attachment of red and blue blocks are respectively

\[
\Gamma_R = c/2 - p_R \exp(\beta z \epsilon_{\text{red}}(m)) = c/2 - \frac{1}{2}(1 - m) \exp(-\Sigma + m\Delta),
\]

and

\[
\Gamma_B = c/2 - p_B \exp(\beta z \epsilon_{\text{blue}}(m)) = c/2 - \frac{1}{2}(1 + m) \exp(-\Sigma - m\Delta),
\]

where \(\Sigma \equiv \beta z(\epsilon_s + \epsilon_d)/2\) and \(\Delta \equiv \beta z(\epsilon_s - \epsilon_d)/2\). The key difference from the one-dimensional case is that the energies felt by red and blue blocks depend in a continuous way on the state \(m\) (redness or blueness) of the growing front.

This dependence introduces a cooperatively not present in one dimension. In equilibrium, i.e. when \(\Gamma_R = \Gamma_B = 0\), Equations (S4) and (S5) give a self-consistent equation for the equilibrium composition \(m_0\):

\[
m_0 = \tanh\left(\frac{\beta z}{2}(\epsilon_s - \epsilon_d) m_0\right).
\]

This equation resembles the familiar Ising model equation of state in zero field, and describes a phase transition between a high-temperature mixed red/blue phase \((m_0 = 0)\), and a low-temperature phase of coexisting red \((m_0 < 0)\) and blue \((m_0 > 0)\) domains (see Fig. S6(b)). The color symmetry of the front is therefore spontaneously broken. The presence of a thermodynamic phase transition at finite temperature, a fundamental property of 2- and 3-dimensional systems generally, constitutes a key difference from the 1d fiber model. A similar color-demixing transition is seen in our simulations of two-color square-well-attractive particles arranged on an fcc lattice (see Fig. S6(c)). Although the critical exponents associated with color demixing in 3d are not the values predicted by mean-field theory, the qualitative behavior is similar.

Significantly, this higher-dimensional model possesses scaling properties similar to those that allow the far-from-equilibrium ‘nonperturbative’ assembly strategy described in the main text (for \(d = 1\)). To solve the present model’s
dynamics, we impose the self-consistent condition $\Gamma_R/\Gamma_B = p_R/p_B$, i.e. the requirement that the relative net attachment rate of red and blue blocks is equal to the relative fraction of red and blue blocks in the growing front. Equations (S4) and (S5) inserted into this condition give the self-consistent equation

$$m = -c + \sqrt{c^2 + 4e^{-2\Sigma} \sinh^2(m\Delta)} \over 2e^{-\Sigma} \sinh(m\Delta).$$

(S7)

Eq. (S7), a dynamical generalization of Eq. (S6), describes a dynamic phase transition between mixed and de-mixed phases, with a critical temperature that depends on the growth speed of the front. In Fig. S6(b) we show dynamic phase behavior for concentrations $c$ twice- and six times the value at the phase boundary, $c_0(T)$ (found by inserting $m_0$, obtained from Eq. (S6), into Eq. (S4), with $\Gamma_R = 0$). Note that the concentration at the phase boundary is temperature-dependent. As in one dimension, structures produced at finite rate of growth are invariably not the equilibrium one, and are more mixed than their equilibrium counterpart.

Importantly, though, Eq. (S7) suggests that the strategy motivated by our fiber work is transferable to higher dimensions. In Fig. S6(d) we show contours of constant front composition $m$, as a function of concentration $c$ and the energetic parameter $\epsilon_s$. This plot is similar to Fig. 2 of the main text in the sense that structures of given composition can be generated at and away from equilibrium. We expect the $d > 1$ mean-field model developed here to describe qualitatively the color patterns within growing structures comprised of simple two-color building blocks in 3d. The two-color square-well particles used to generate Fig. S6(c) fit this description, for example. Concretely, Fig. S6(d) predicts that increasing the value of the like-color building block interaction alone will result in a growing front that is more mixed than the equilibrium structure, because increasing binding energy increases growth front velocity $v(c, m) = \Gamma_R + \Gamma_B$ (which can be straightforwardly calculated from Eqs. (S4) and Eq. (S5)), and so increases the degree of mixing of the front. But by increasing the like-color interaction and decreasing particle concentration according to the prescription described by a given contour, structure can be maintained. Simulations or experiments are now required to test whether such pattern control can be exerted in a regime in which structures remain morphologically ordered.
IV. SUPPLEMENTAL FIGURES

Figs. S1–S4 supplement Fig. 1 of the main text; Fig. S5 supplements Fig. 2 of the main text. Fig. S6 illustrates the behavior of the $d > 1$ dynamical mean-field model described in this supplement.
FIG. S1: Dynamic fiber domain length distributions are exponential. We show $\rho(\ell)$ obtained from simulations (grey lines), for selected concentrations at and past the phase boundary $c = c_0$, for a set of conditions considered in Fig. 1 of the main text. Overlaid are analytic estimates of the domain length distribution, $\rho(\ell) = (\xi - 1)^{-1} \exp\left[\ell \ln(1 - \xi^{-1})\right]$, where the mean domain length $\xi$ is obtained from self-consistent mean field theory (Eq. (S1)) (blue). When $c = c_0$ this reduces to the equilibrium value $\xi_0 = 1 + \exp(\beta(\epsilon_s - \epsilon_d))$ (green); when $c \to \infty$ we obtain the random adsorption limit $\xi_{\infty} = 2$. In all cases the analytic expressions match the simulation results. Because observed domain length distributions are exponential, we consider only the mean domain length $\xi$ in Fig. 1 of the main text.
FIG. S2: Excess free energy $\delta f \equiv f(\phi) - f(\phi_0)$ per fiber block as a function of concentration $c$ and like-color energy scale $\epsilon_s$ (note that $\epsilon_d = 1$). Here $\phi_0$ is the equilibrium bulk fiber fraction, and $\phi$ is its dynamic counterpart, here computed using Eq. (3) of the main text. The free energy is $f(\phi) = \epsilon_s(1 - \phi) + k_B T (\phi \ln \phi + (1 - \phi) \ln(1 - \phi))$; at all points past the phase boundary, dynamically-generated structures lie higher in free energy than equilibrium ones. An exception occurs when $\epsilon_s = \epsilon_d$, because there the compositional correlations of the equilibrium structure are equal to those of random mixing.
FIG. S3: As Fig. 1 of main text, but for the case $\epsilon_d > \epsilon_s$ (here $\epsilon_s = 1$), giving an effective Ising antiferromagnetic coupling $J = (\epsilon_s - \epsilon_d)/2 < 0$. In this case the equilibrium structure mimics that of a binary crystal, consisting (in the limit of large $\epsilon_d$) of alternating blue and red blocks. We observe the same breakdown of the quasiequilibrium assumption as for the case $J > 0$ (phase boundaries and equilibrium correlation lengths are labeled in the same manner). However, because the numerical difference between the domain length associated with random mixing ($\xi_{\infty} = 2$) and equilibrium ($\xi \to 1$ for large $\epsilon_d$) is small, structures grown close to the phase boundary are numerically similar to their equilibrium counterparts.
FIG. S4: For fixed absolute supersaturation $\delta c \equiv c - c_0$, the ‘distance’ $(\xi_0 - \xi)/\xi_0$ from equilibrium of dynamically generated fiber structures grows sharply with increasing energy scale $\epsilon_s$. Here $\epsilon_d = 1$. 

\[ \frac{\xi_0 - \xi}{\xi_0} \]
FIG. S5: Simulations performed at the locations specified by the circles in Fig. 2, main text, bear out the analytic prediction that identical structures are generated along contours (top panel), by growth protocols displaying markedly different degrees of microscopic reversibility (bottom panel). \( \Sigma \equiv N_+ + N_- \) is the total number of binding \((N_+)\) and unbinding \((N_-)\) events taking place during the assembly of fibers of length \(L = 2.5 \times 10^4\) blocks \((\Delta \equiv N_+ - N_- = L\) is the net number of binding events). At the phase boundary, fibers grow only diffusively. As a result, \(\sim L^2\) microscopic events are required to generate a structure of length \(L\). Far from the phase boundary, assembly is much less reversible.
FIG. S6: Extension to higher dimensions of the self-assembly strategy developed in the paper. (a) Schematic of mean-field analog of fiber model for $d > 1$ (see text). (b) Equilibrium and nonequilibrium composition diagrams, from Eqs. (56) and (57). These diagrams describe a phase transition between a mixed-color structure at high temperature, and phase-separated red and blue domains at low temperature. In the dynamical case, the critical temperature is a function of distance past the concentration phase boundary. Parameters: $\epsilon_a = 2, \epsilon_d = 1, \beta z = 1/T$. (c) Qualitatively similar equilibrium demixing is seen in simulations: we show composition diagram (binodal) derived from Monte Carlo simulations of two-color square-well particles in 3d, which are arranged on a perfect fcc crystal lattice. Particle interaction energies, in units of $k_B T$, are $-\epsilon_a$ (like colors) and $-\epsilon_d$ (unlike colors). The demixing transition is qualitatively similar to the mean-field equilibrium behavior of panel (c). (d) Mean-field higher-dimensional analog of Fig. 2 (main text). We show contours of composition $m$, as a function of concentration $c$ and the energetic parameter $\epsilon_a$ (here $\epsilon_d = 1$ and $\beta z = 1$). This plot is similar to Fig. 2 of the main text in the sense that structures of given composition can be generated at and away from equilibrium (the phase boundary), suggesting that the strategy motivated by our fiber work is transferrable to higher dimensions.