Supporting information for "Self-assembly at a nonequilibrium critical point"

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I.   ANALYTIC THEORY: EXPLANATION OF NONEQUILIBRIUM POTENTIAL ψ

The equilibrium composition of the mean-field assembly of particles can be calculated by requiring that the growth rate of an assembly is zero, i.e. we set $\Gamma_R = \Gamma_B = 0$ in Eq. (1) of the main text. The concentration c_0 satisfying this condition is $c_0 = (1 - m_0) \exp\left(-\Sigma + m_0\Delta\right)$, where $\Delta \equiv \beta z \left(\epsilon_s - \epsilon_d\right)/2$ and $\Sigma \equiv \beta z \left(\epsilon_s + \epsilon_d\right)/2$. When $c = c_0$ (see Fig. S1(a)) the equilibrium composition m_0 of the assembly is given by the equation

$$m_0 = \tanh\left(m_0\Delta\right). \tag{S1}$$

This equation looks like the Ising model mean-field equation of state in zero field, and describes a phase transition between a mixed-color phase ($m_0 = 0$) and demixed, coexisting red ($m_0 < 0$) and blue ($m_0 > 0$) phases (see Fig. S2(b)). The corresponding equilibrium critical point lies at $\Delta = 1$, implying an equilibrium critical temperature $k_B T_c = z(\epsilon_s - \epsilon_d)/2$.

Although this equation of state comes from the zero-growth limit of a set of rate equations, we are free to imagine instead that it comes from minimizing an hypothetical potential ϕ. This potential can thus be obtained by integrating Eq. (S1). To do so, we let $f(m_0, \epsilon)$ stand for the right-hand side of Eq. (S1) (where $\epsilon = \{\epsilon_s, \epsilon_d\}$). We then write $\phi(m, \epsilon) = \int_0 dm \; (m - f(m, \epsilon))$, i.e.

$$\phi(m, \epsilon) = \frac{1}{2}m^2 + \frac{1}{\Delta}\ln\cosh\left(m\Delta\right). \tag{S2}$$

This potential resembles the familiar mean-field Ising model Landau free energy: it has a double-well form in the two-phase region, and a single-well form in the one-phase region (Fig. S1(b)). Its Maclaurin expansion is $\phi(m, \epsilon) \approx (1 - \Delta)\, m^2/2 + \Delta^3 m^4/12$, allowing one to read off $\Delta = 1$ as the condition for equilibrium criticality. Equilibrium is achieved when $c = c_0 = (1 - m_0) \exp\left(-\Sigma + m_0\Delta\right)$; note that the equilibrium concentrations $c_0^{\pm}$, corresponding to the two solutions $m_0^{\pm}$ in the two-phase region, are equal.

The nonequilibrium potential ψ described in the main text was obtained in a similar way. If we insert Eq. (1) of the main text into $\Gamma_R/\Gamma_B = p_R/p_B$, the requirement that the relative growth rate of red and blue blocks is equal to the ratio of red to blue blocks in the assembly, then we get the nonequilibrium analog of (S1), namely

$$m = \frac{-\nu + \sqrt{\nu^2 + (2\sinh(m\Delta))^2}}{2\sinh(m\Delta)}. \tag{S3}$$

Here $\nu \equiv c\,e^{\Sigma}$ is a rescaled concentration. Analysis of the roots of this equation gives the behavior described in the main text. However, to make clear the connection of this growth problem to the field of critical phenomena, it is convenient to construct the nonequilibrium analog ψ of the equilibrium potential Eq. (S2). To construct ψ we let $g(m, \epsilon, c)$ stand for the right-hand side of Eq. (S3), and write $\psi(m, \epsilon, c) = \int_0 dm \; (m - g(m, \epsilon, c))$. The resulting expression is unwieldy; its Maclaurin expansion, which is more illuminating, is Eq. (2) of the main text. It shows that upon approaching the nonequilibrium critical point, i.e. $\nu = \Delta$, m decays according to $m^2 \sim (\Delta - \nu)/\left(\sqrt{6} - \nu\right)$.

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II. ADDITIONAL SIMULATION DETAILS

Simulation box aspect ratios were $1:10$ (2D) and $1:1:10$ (3D). Interaction strengths were $\epsilon_s = 3.5$, $\epsilon_d = 2$ in 2D and $\epsilon_s = 1.5$, $\epsilon_d = 1$ in 3D. A fully occupied simulation box therefore corresponds to a 2D or 3D Ising model at 59% and 80% of T_c, respectively, the regime in which our mean-field theory suggests that the dynamic transition should be continuous. For convenience we choose to set $k_B T = 1$ throughout. L reported in Fig. 3 is the length in lattice units of the short axis of the box. Simulations were stopped when the interface grew to 95% of the box long axis length.

Because simulations satisfy detailed balance, the color patterns generated within each assembly will age and in principle eventually evolve to equilibrium (this dynamics corresponds to the 'red arrow' processes sketched in Fig. 1(a) of the main text). However, such ageing is mediated only by vacancy diffusion, giving a basic timescale $\sim L^2$ for *single-site* relaxation within the bulk of the assembly. The prefactor of this timescale is roughly $\exp((2d-1)\epsilon_d)$, which is larger than unity. By contrast, assemblies grow to length of order L on a timescale of order L, with a prefactor of order unity.

The magnetization m, the number of blue blocks minus the number of red blocks, divided by the total number of colored blocks, was computed in the region of the box between 50% and 80% of its length, to avoid initial transients and effects associated with the end wall. The number of lattice sites in this volume is $N(L) = 3L^d$. Each growth simulation furnished one value of m; a minimum of 1008 growth simulations were done at any given value of μ. Up to 10,000 simulations were done at μ near the dynamic critical point. While this simulation output was sufficient to confirm the existence of a nonequilibrium 'color' phase transition, it was not enough to measure accurately the exponents associated with the critical point. Because each sample requires an entire growth simulation, rather than a single configuration, further sampling was prohibitively expensive.

The difference of $k_B T \ln 2$ between the parameters μ' and μ discussed in the main text is required to preserve detailed balance with respect to the stated energy function. It arises because of an asymmetry in proposing moves between white and colored sites: if a chosen site is red, then we propose a move to white with probability 1. But the reverse move (starting from a white site) is proposed instead with probability $1/2$ (because a move from white to blue is proposed with equal likelihood). The detailed balance condition for changing one of N lattice sites from white to red, and back again, reads

$$\mathrm{e}^{-\beta E_{\mathrm{white}}} \frac{1}{2N} p_{\mathrm{acc}}(\mathrm{white} \to \mathrm{red}) = \mathrm{e}^{-\beta E_{\mathrm{red}} - \beta \mu'} \frac{1}{N} p_{\mathrm{acc}}(\mathrm{red} \to \mathrm{white}), \tag{S4}$$

where E_{white} is the interaction of a vacancy with its environment (this is zero), E_{red} is the sum of pairwise energies between a red block and its environment, and p_{acc} are the acceptance rates for the two moves. Rearranging gives $p_{\mathrm{acc}}(\mathrm{white} \to \mathrm{red})/p_{\mathrm{acc}}(\mathrm{red} \to \mathrm{white}) = \mathrm{e}^{-\beta E_{\mathrm{red}} - \beta \mu}$, where $\mathrm{e}^{-\beta\mu} \equiv 2\mathrm{e}^{-\beta\mu'}$. This ratio is satisfied by the acceptance rates given in the main text. The same rates hold for moves white $\leftrightarrow$ blue.

To compute equilibrium structures (dashed lines in Fig. 3, left panels) we added to our simulation protocol standard red-blue swap moves that did not feel the effect of the kinetic constraint.
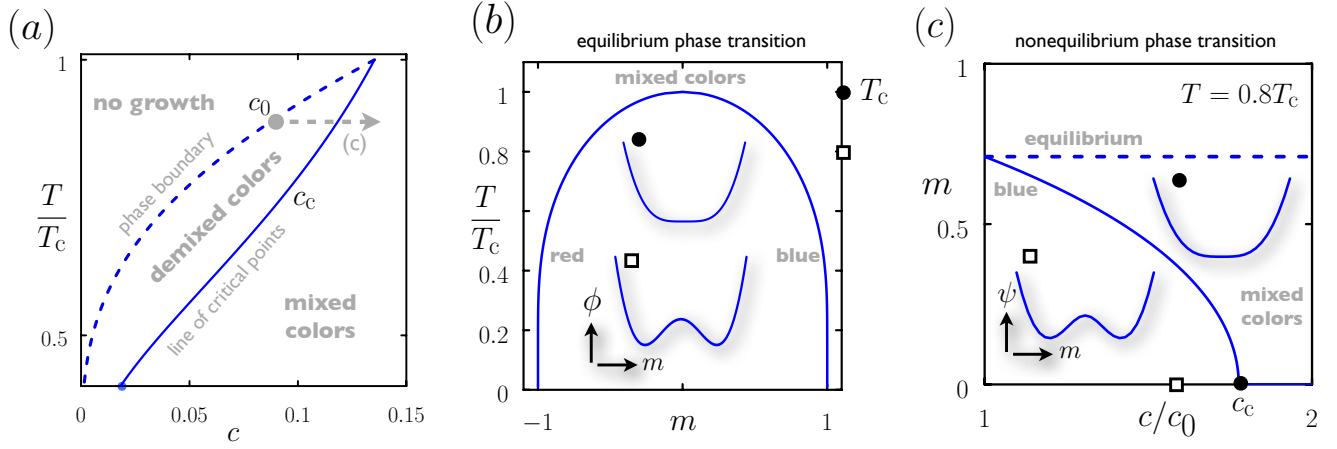
III. SUPPLEMENTAL FIGURES

FIG. S1: Fig. 1 of the main text, modified to show both equilibrium (b) and nonequilibrium (c) phase transitions. (a) Dynamic phase diagram in the temperature-concentration plane (parameters: $\epsilon_d = \epsilon_s/3$). Below the equilibrium critical temperature T_c, the assembly in equilibrium (along the dashed line $c = c_0$) is demixed; panel (b) shows the associated phase transition. Increasing concentration at fixed temperature (dashed arrow in panel (a)) causes the assembly to grow and become more mixed, and eventually to undergo a dynamic phase transition to a mixed-color structure (panel (c)). This prediction is borne out by simulations (Figs. 2 & 3). Square and circle symbols on panels (b) and (c) connect the potentials ϕ and ψ (shown inset) to the temperatures or concentrations at which they were calculated. In panel (a), line of dynamic critical points ends in a dynamic tricritical point at $\nu = \Delta = \sqrt{6}$, shown as a pale blue dot. Beyond this point, a line of of nonequilibrium first-order phase transitions is encountered.
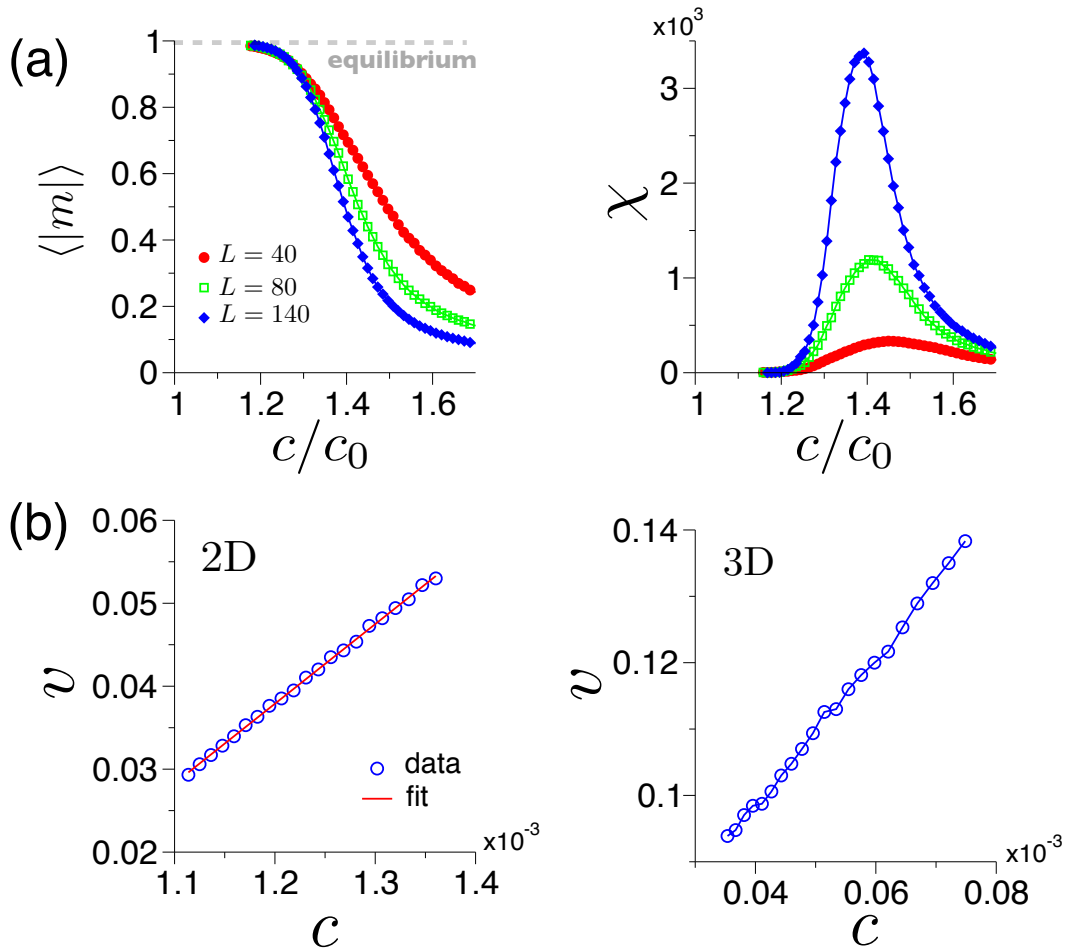
FIG. S2: (a) Top panel of Fig. 3 of main text, plotted in terms of c/c_0. c_0 is the value of $\exp(-\beta\mu)$ at which the growth front of the assembly has zero drift velocity, computed by extrapolation (see panel (b) left-hand side), and so represents equilibrium between the assembly and its environment. In terms of the parameter m, it appears therefore that assemblies grown near to equilibrium have equilibrium-like patterns. Note, though, that given the large lengthscales involved in equilibrium phase separation, and the small systems sizes used in our simulations, we cannot tell if the spatial correlations of defects in near-equilibrium assemblies are equal to those of their equilibrium counterparts. The slower growth of the necessarily larger systems in 3D meant that statistics in 3D were poorer, and so calculation of c_0 was hard to do (panel (b), right-hand side). Given this difficulty, we report quantities in Fig. 3 in terms of c only.
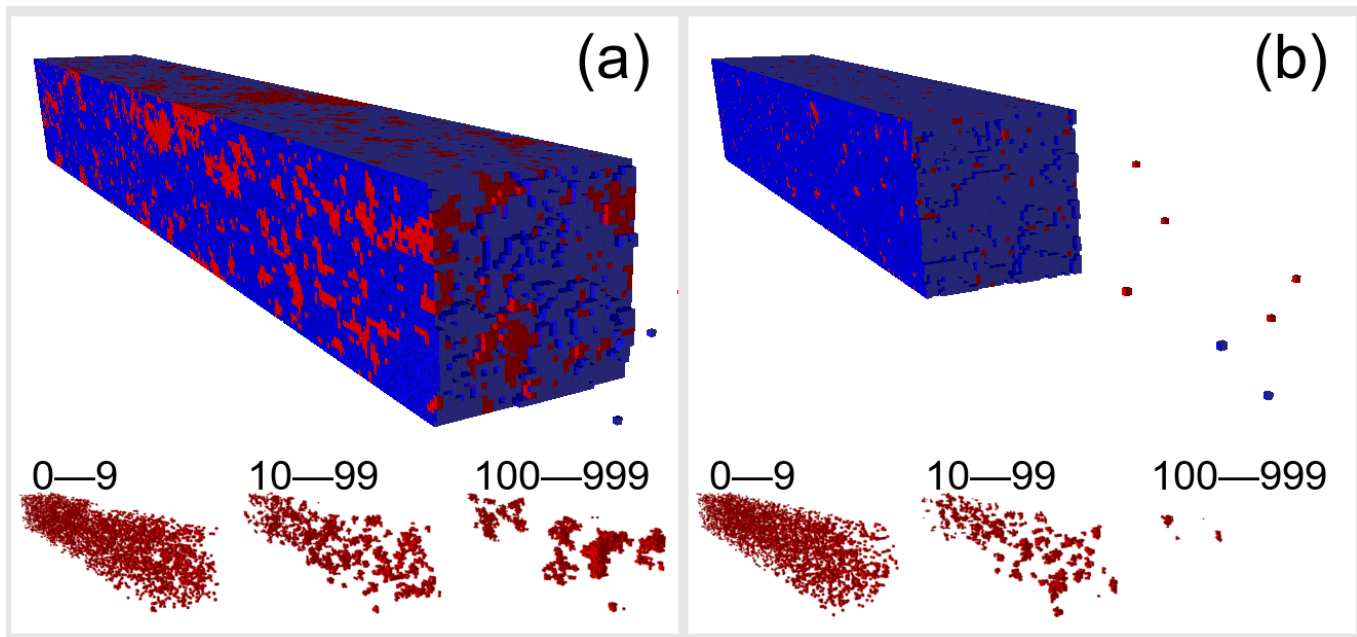
FIG. S3: *The intrinsically nonequilibrium nature of multicomponent self-assembly can be exploited to produce qualitatively defined domain structures.* [If viewing in Adobe Reader, click figure to animate]. Two-component growth in three dimensions. By tuning growth rate it is possible to generate assemblies with different size distributions of red domains. (a) Growth close to color criticality results in red domains of a wide distribution of sizes. (b) Smaller red droplets embedded in a background of blue can be generated at lesser growth rates. Snapshots along the bottom of each panel show the spatial arrangement of red domains within different domain size windows.