# Self-Assembly at a Nonequilibrium Critical Point

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We use analytic theory and computer simulation to study patterns formed during the growth of two-component assemblies in two and three dimensions. We show that these patterns undergo a nonequilibrium phase transition, at a particular growth rate, between mixed and demixed arrangements of component types. This finding suggests that principles of nonequilibrium statistical mechanics can be used to predict the outcome of multicomponent self-assembly, and suggests an experimental route to the self-assembly of multicomponent structures of a qualitatively defined nature.

Nature builds its materials using multiple component types. The properties of these materials depend on the properties of their components, and on how components are distributed spatially: the exciton transfer properties of a light-harvesting complex, for instance, depend on the way that its constituent proteins cluster [1]. Achieving similar mesoscale spatial control with many synthetic self-assembled materials [2] is made difficult by the fact that the self-assembly of multicomponent systems generally happens "far" from equilibrium, where we possess few predictive theoretical tools. Although self-assembly is a nonequilibrium process, much of our understanding of it is based upon a physical picture that assumes dynamics to play no role *except* to convey a system along the "easiest" pathways on its free-energy landscape [3]. This "near-equilibrium" or "quasiequilibrium" assumption tends to hold, for instance, for simple one-component systems under mild nonequilibrium conditions [4–8]. It fails when there exist time scales within a given self-assembly process that exceed the time of the experiment or computer simulation. For one-component systems, long time scales can emerge if bonds between particles are strong, and so break infrequently, which can happen when subjected to "harsh" nonequilibrium conditions (e.g., conditions of deep supercooling). Binding errors made as components associate can then fail to anneal as structures grow, and the result is a kinetically trapped structure rather than an object corresponding to a favored position on the free-energy landscape [9–12].

The self-assembly of multicomponent solid structures, however, is *also* affected by kinetic traps that emerge even under *mild* nonequilibrium conditions. The long time scale responsible for such trapping is the slow interchange of component types within solid structures [13–23]. Consider Fig. 1(a), which shows in cartoon form a fluid of two types of mutually attractive particles (call them "red" and "blue"), present in equal number, self-assembling into a solid structure. The equilibrium pattern of red and blue within

this structure—shown in the figure as demixed red and blue domains—is determined only by the particles' mutual interactions. But achieving this equilibrium pattern via self-assembly requires that particle types interchange their positions within the assembly readily enough to "unmix" themselves. Because the mobility of particles within solid structures is usually very low (red arrows on figure), such interchange can fail to happen on experimental time scales. The result is a structure whose component types are distributed in a nonequilibrium manner [18–23]. Returning to the picture of evolution on a free-energy landscape, one must think of the direction of motion across this landscape as being biased strongly by the underlying microscopic dynamics [22].

Predicting the outcome of such "far-from-equilibrium" self-assembly is not generally possible. For the reasons just described, we cannot do so within the framework of equilibrium statistical mechanics, i.e., by calculating and inspecting the appropriate free-energy landscape. Instead, we need explicit information about the dynamics undergone by components, together with a predictive theory that works "far" from equilibrium. Despite much progress in this direction [13–22], such a theory does not exist. Here we present evidence suggesting that concepts of nonequilibrium statistical physics may provide a route to a predictive theory of far-from-equilibrium self-assembly. We study two-component lattice-based assemblies made of red and blue particles, essentially growing versions of the Ising lattice gas. We find—using dynamic mean-field theory and simulation—that these assemblies undergo, as a function of growth rate, a nonequilibrium phase transition between mixed and demixed arrangements of component types. If component interactions are chosen to mimic the equilibrium ferromagnetic Ising model *below* its critical temperature, then the equilibrium structure of an assembly is a demixed one of phase-separated domains of red and blue. Assemblies grown at a finite rate possess patterns that are more mixed than the equilibrium one, and at a certain
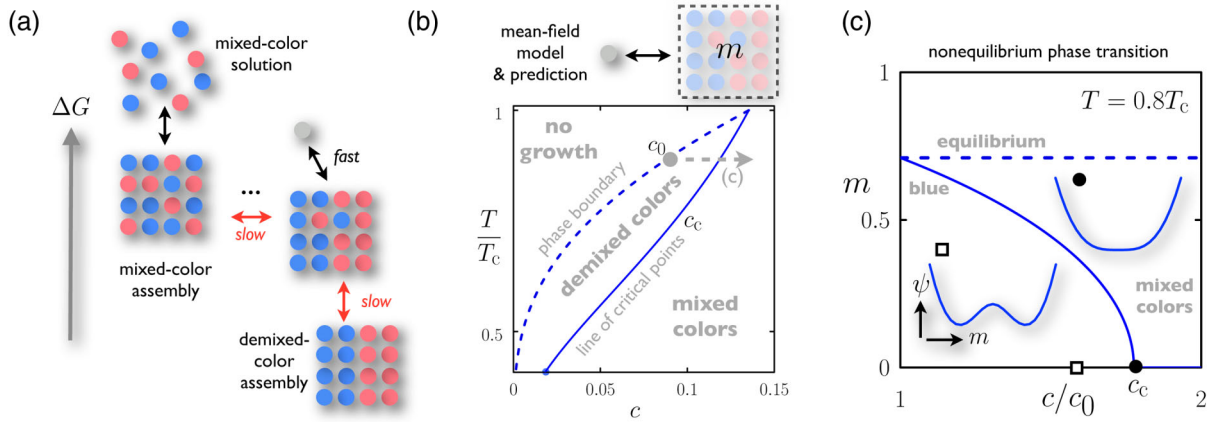
FIG. 1 (color online).   Mean-field theory predicts a nonequilibrium phase transition within a growing two-component structure. (a) The conceptual growth process modeled in this paper: particles possess a free-energetic impetus ($\Delta G$) to assemble in a phase-separated fashion, but the sluggish dynamics of component-type rearrangement (red arrows) can thwart such equilibration. See text for a description of this process. (b) A mean-field model of this process (sketch) predicts the displayed dynamic phase diagram in the temperature-concentration plane (parameters: $\epsilon_d = \epsilon_s/3$). Below the equilibrium critical temperature $T_c$, the structure in equilibrium (along the dashed line $c = c_0$) is demixed. Increasing the concentration at fixed temperature [dashed arrow in panel (b)] 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 and 3). Square and circle symbols on panel (c) link the potential $\psi$ (shown in the inset) to the concentrations at which it was calculated.

growth rate one encounters a dynamic critical point, beyond which component types mix within the assembly in a manner similar to that of the (anisotropic) equilibrium Ising model *above* its critical temperature. Our results suggest a way to generate qualitatively defined two-component structures using, for instance, DNA-linked colloids [18,19]. Such experiments would serve as a test of the predictions of this paper.

We shall model the conceptual two-component growth process (ignoring nucleation) sketched in Fig. 1(a). We assume (1) that red and blue particles are present in solution in equal number, and are randomly mixed, (2) that red and blue particles possess energetic interactions that allow them to associate but encourage them to phase separate, (3) that red and blue particles may bind to a growing structure (called an "assembly") and unbind from it, (4) thereby modifying the composition (red and blue patterns) of that assembly, and (5) that the mobility of red and blue particles *within* the assembly is low, because it is solid. We first describe this process within mean-field theory, accounting for each assumption in a rough manner. We then introduce a lattice-based simulation model of this growth process, which resolves fluctuations and microscopic detail omitted by the mean-field theory.

In Fig. 1(b) we sketch a mean-field model of this growth process. Only two types of microscopic processes are permitted: a particle may bind to an assembly, or unbind from it (Assumption 3). We shall resolve only the rates for these processes, not the individual microscopic events. The assembly itself is described only by a parameter $m \in [-1, 1]$, similar to an Ising magnetization: when

$m = -1$ the assembly is all red; when $m = 1$ the assembly is all blue; and when $m = 0$ the assembly is of mixed color. We further assume that red and blue particles add to the assembly with equal rates $c/2$ (Assumption 1), $c$ being proportional to the solution concentration of particles. We assume that particles leave the assembly with a rate proportional to the abundance of the relevant color within the assembly, multiplied by the Boltzmann weight of the energy of particle removal from the assembly. The latter is computed as follows. To allow us to account for Assumption 2, we set the red-red and blue-blue interactions to $-\epsilon_s$ ("same"), and the red-blue interaction to $-\epsilon_d$ ("different"). We assume that each particle within the assembly makes $z$ energetic bonds, where $z$ is constant (i.e., we do not distinguish between the bulk and surface of the assembly). We consider bonds to connect to a red particle with probability $p_R = (1 - m)/2$, and to a blue particle with probability $p_B = 1 - p_R$. The energy of interaction per bond between a particle of color $\alpha$ ($\alpha = B$ or $R$) and the assembly is then $\epsilon_\alpha = -\epsilon_s p_\alpha - \epsilon_d(1 - p_\alpha)$. Putting these pieces together, we have that the net rates of particle attachments are

$$\Gamma_\alpha = c/2 - p_\alpha \exp\left(\beta z \epsilon_\alpha\right), \qquad (1)$$

where $\alpha = B$ or $R$, and $\beta \equiv 1/(k_B T)$. Finally, we solve for the composition $m$ of the assembly by setting $\Gamma_R/\Gamma_B = p_R/p_B$, which is the self-consistent requirement that the ratio of growth rates of red and blue particles be equal to the relative abundance of red and blue particles in the assembly. This requirement accounts for Assumption 4.

Furthermore, because *only* binding-unbinding processes determine the composition of the assembly, we also account for Assumption 5; specifically, the processes labeled by the red arrows in Fig. 1(a) are assumed to happen with a rate of zero in this mean-field theory.

It is straightforward to verify that Eq. (1), in the equilibrium (zero-growth-rate) limit, describes the usual Ising-like equilibrium red-blue demixing phase transition when $\epsilon_s - \epsilon_d$ is large enough [24] (see Fig. S1 of Supplemental Material [25]). This phase transition happens along the line labeled $c_0$ in Fig. 1(b), on which the assembly neither grows nor shrinks. If we start on this line and increase concentration $c$ in order to make the assembly grow, then one can show (see Supplemental Material [25]) that the composition $m$ of the assembly is described by a particular Landau theory [26],

$$\psi(m) = \frac{1}{2}\left(1 - \frac{\Delta}{\nu}\right)m^2 + \frac{\Delta}{24}\left(\frac{6 - \nu^2}{\nu^3}\right)m^4 + \cdots, \quad (2)$$

in which $\nu \equiv ce^{\Sigma}$ is a rescaled concentration, $\Delta \equiv \beta z(\epsilon_s - \epsilon_d)/2$, and $\Sigma \equiv \beta z(\epsilon_s + \epsilon_d)/2$. This description makes explicit the connection between this growth problem and the field of nonequilibrium critical phenomena [26]. The minima of the potential $\psi(m)$ describe qualitatively the nonequilibrium color patterns generated during the growth of the assembly. Inspection of the coefficients of Eq. (2) reveals the behavior shown in Fig. 1(b). When assembly color patterns are demixed in equilibrium, there exists a line of *nonequilibrium* continuous phase transitions at a critical concentration given by $\nu = \Delta$, i.e., $c_c = \Delta e^{-\Sigma}$ (provided that $\nu < \sqrt{6}$). Figure 1(c) shows that $\psi$ changes from having one well to having two wells at this dynamic critical point.

The prediction of mean-field theory is therefore as follows: if we are below the equilibrium critical temperature, then the two-component structure *in equilibrium* is a demixed one of red or blue. If we supersaturate the assembly in order to make it grow, then it becomes more mixed, and at a critical growth rate it undergoes a dynamic phase transition to a mixed-color structure. If we are not too far below the equilibrium critical temperature then this dynamic phase transition is a continuous one, with an associated dynamic critical point.

Although mean-field theory is not quantitatively accurate, this qualitative prediction is confirmed by our simulations of two-component self-assembly. We again modeled the conceptual growth process sketched in Fig. 1(a), this time in microscopic detail. We considered square and cubic lattices in two and three dimensions, respectively, within rectangular or cuboidal simulation boxes (periodic boundaries were imposed across the short axes only). Lattice sites could be white (unoccupied), or occupied by a red or blue particle. We imposed pairwise nearest-neighbor interactions between particles: $-\epsilon_s$ for like-color interactions

and $-\epsilon_d$ for unlike-color interactions. Each particle is disfavored energetically by a chemical potential term $\mu' > 0$. We chose $\mu'$ small enough that equilibrium configurations corresponded to almost fully occupied lattices, whose equilibrium red-blue patterns are those of the two- or three-dimensional Ising model with ferromagnetic coupling $J = (\epsilon_s - \epsilon_d)/2$. We chose $\beta J = 0.75$ (two dimensions) and $\beta J = 0.275$ (three dimensions) so that equilibrium color patterns were demixed (Assumption 2).

To model a growth dynamics, we used a simulation protocol that satisfies detailed balance but makes no assumptions about relative rates of growth and structural relaxation [27]. We chose at random a lattice site. If it was white, we attempted to make it red or blue, with equal likelihood (Assumption 1), and accepted this proposition with probability $\min(1, e^{-\beta\Delta E - \beta\mu})$. Here $\Delta E$ is the interaction energy felt by the newly placed particle, and $\mu = -k_B T \ln 2 + \mu'$ (see Supplemental Material [25]). If the randomly chosen lattice site was instead blue or red, we made it white with probability $\min(1, e^{-\beta\Delta E + \beta\mu})$, where $\Delta E$ is the energy change upon removing the particle from the simulation box. Assumptions 3 and 4 are naturally accounted for by these microscopic processes. Finally, to account for Assumption 5, we imposed a kinetic constraint that prevents any change of state of a lattice site having exactly $2d$ occupied neighbors. This constraint prevents the relaxation of color patterns within the bulk of an assembly, except in the neighborhood of a vacancy (the processes described by the red arrows in Fig. 1 are then slow, but do happen; see Supplemental Material [25]). The constraint respects detailed balance, and so has no effect on the thermodynamics of the model.

The parameter $c \equiv \exp(-\beta\mu)$ controls the basic rate of growth of an assembly (see Fig. S2 of Supplemental Material [25]). We began each growth simulation from a white box. By making one wall of the simulation box's short axis sticky, and by choosing $c$ not too large, we could cause the growth of an assembly in the direction of the long axis of the box without having clusters nucleate elsewhere. Moreover, by making the wall sticky for only blue particles, we could induce a color symmetry breaking that made the establishment of the steady-state color structure of the assembly relatively rapid.

In Figs. 2 and 3 we show that simulations confirm the prediction of mean-field theory. At low rates of growth, assemblies are almost blue, because of the way we intentionally break symmetry, with only a few red cluster defects: see Fig. 2(a). Given the large length scales involved in equilibrium phase separation, and our relatively small system sizes, we lack the precision to determine if structures grown in this region truly match the equilibrium one. In terms of the parameter $m$, they appear to be close to it; see left panels of Fig. 3 and Fig. S2 of the Supplemental Material [25]. Note, however, that equilibrium structures are effectively one-component ones (because we are below
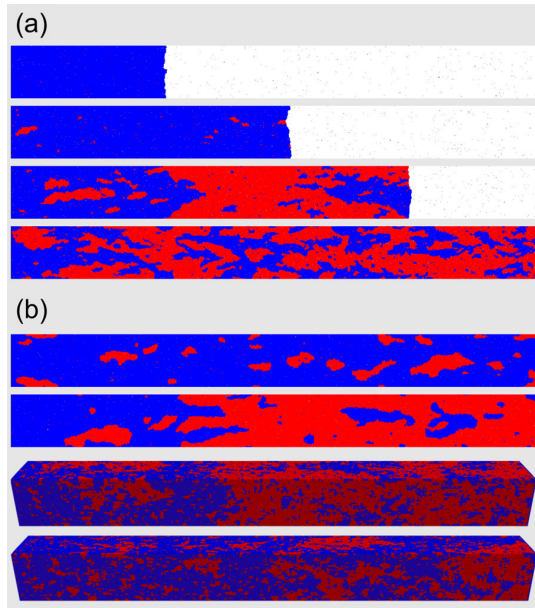
FIG. 2 (color online).  Snapshots illustrating a nonequilibrium phase transition in two- and three-dimensional simulations of self-assembly. (a) Two-component growth in two dimensions. Assemblies generated at increasing rates of growth (top to bottom) reveal the existence of a dynamical phase transition between near-equilibrium demixed structures (top), and mixed-color structures (bottom). At a particular growth rate (second bottom), color structures appear critical. Snapshots are taken at a time corresponding to the completion of growth in the bottom panel. (b) Representative snapshots of growth patterns at dynamic criticality in two and three dimensions, illustrating the large run-to-run variations in color structure.
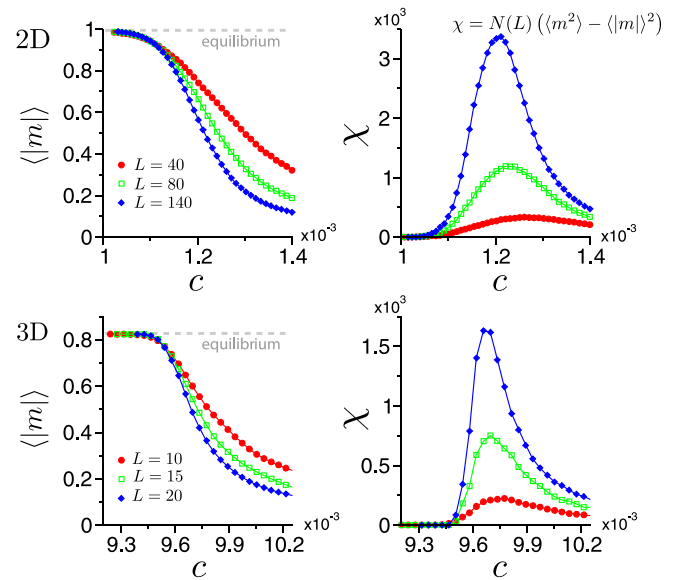


FIG. 3 (color online).  Simulations confirm the existence of a nonequilibrium critical point at a particular growth rate. We plot the color order parameter $m$ (the density of blue particles minus the density of red particles within the assembly) and color fluctuations $\chi$ as a function of the basic rate $c = \exp(-\beta\mu)$. Here $N(L)$ is the number of particles in the sampling volume (see SI for details). The peak in $\chi$ indicates large fluctuations characteristic of criticality.

the critical temperature and we work in the grand canonical ensemble), and so slow growth in this regime is not a viable way of making interesting two-component patterns. At larger growth rates the assemblies harbor larger red clusters, and at a particular growth rate assemblies appear critical, in the sense that from run to run their patterns exhibit large color fluctuations: see Fig. 2(b) and right panels of Fig. 3. At all rates of growth the thermodynamically stable assembly is mostly blue, and so the observed mixing reflects the existence of a nonequilibrium phase transition [28].

In previous work we demonstrated that simple nonequilibrium arguments allow one to predict the patterns made within a growing two-component one-dimensional fiber [23]. Here we considered self-assembly in two and three dimensions, which is more directly relevant to experiment. In all cases we find that simple nonequilibrium arguments can make progress where equilibrium ideas have little to say. The case $d > 1$ is intrinsically richer, however, displaying nonequilibrium phase transitions not seen in $d = 1$ (similar to well-known equilibrium behaviors in different dimensions [26]). Additionally, in $d = 1$ there exists an exact mapping between structures in and out of

equilibrium, allowing one to describe patterns generated at a finite rate of growth in terms of an equilibrium system with "renormalized" coupling constants, but the same cannot be true here: structures seen in snapshots (Fig. 2) are visibly anisotropic [27], reflecting a memory of the assembly's growth direction. Therefore, if there exists an equivalent equilibrium system [23,29], it has an anisotropic energy function. Exploring this equivalence is a subject for future work.

We have shown that patterns formed within growing two-component assemblies undergo, as a function of growth rate, a nonequilibrium phase transition in their component-type arrangements. Qualitatively similar transitions are seen in certain irreversible cellular automata upon variation of interaction parameters [30,31], pointing to a possible connection, away from equilibrium, between irreversible automata and the microscopically reversible simulation protocols used to model self-assembly. Experimentally, the predictions of our paper might be tested using two-component DNA-linked colloids [18,19]. Our results suggest that one can assemble (see Fig. S3 of Supplemental Material [25]) complex mesostructures [1] by exploiting the intrinsically far-from-equilibrium nature of multicomponent self-assembly, even under conditions that give rise to mundane *equilibrium* patterns.

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