Schloegl’s second model for autocatalysis with particle diffusion: Lattice-gas realization exhibiting generic two-phase coexistence

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Abstract
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Keywords
Diffusion in solids, stochastic models, annihilation rates, autocatalytic, contact process, critical values, diffusivities, discontinuous equilibriums, finite populations, lattice gas, metastability, non-equilibrium phase transitions, particle diffusions, phase coexistences, square lattices, thermodynamic systems

Disciplines
Astrophysics and Astronomy | Biological and Chemical Physics | Mathematics | Physics

Comments
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We analyze a discontinuous nonequilibrium phase transition between an active (or reactive) state and a poisoned (or extinguished) state occurring in a stochastic lattice-gas realization of Schlögl’s second model for autocatalysis. This realization, also known as the quadratic contact process, involves spontaneous annihilation, autocatalytic creation, and diffusion of particles on a square lattice, where creation at empty sites requires a suitable nearby pair of particles. The poisoned state exists for all annihilation rates \( p > 0 \) and is an absorbing particle-free “vacuum” state. The populated active steady state exists only for \( p \) below a critical value, \( p_c \). If \( p_f \) denotes the critical value below which a finite population can survive, then we show that \( p_f < p_c \). This strict inequality contrasts a postulate of Durrett, and is a direct consequence of the occurrence of coexisting stable active and poisoned states for a finite range \( p_f \leq p \leq p_c \) (which shrinks with increasing diffusivity). This so-called generic two-phase coexistence markedly contrasts behavior in thermodynamic systems. However, one still finds metastability and nucleation phenomena similar to those in discontinuous equilibrium transitions. © 2009 American Institute of Physics. [DOI: 10.1063/1.3074308]

I. INTRODUCTION

Deterministic nonlinear chemical kinetics and the corresponding bifurcations or phase transitions of nonequilibrium steady states for macroscopic reaction systems have traditionally been analyzed by mean-field rate equations.1,2 The associated deterministic reaction front propagation and pattern formation have also been described by reaction-diffusion equations at the mean-field level.1,3,4 In addition, there are numerous studies examining stochastic effects on chemical kinetics via mean-field master equations1,5,6 and on associated pattern formation via multivariate mean-field master equations.1 The latter can be recast utilizing time-dependent Ginzburg–Landau-type formulations to produce Langevin reaction-diffusion equations.5–8

The deterministic mean-field analyses have been successfully applied to three-dimensional solution-phase, gas-phase, electrochemical, and biochemical systems, with perhaps the best known study of pattern formation being for the Belousov–Zhabotinskii reaction.1,2 Fluctuation effects have been considered particularly in the context of biochemical reactions.9 Heterogeneous catalysis on extended single-crystal surfaces under low-pressure conditions has provided a remarkably rich variety of two-dimensional examples of deterministic nonlinear dynamics10 and pattern formation,11 even for mechanistically simple surface reactions. Again, mean-field analysis is traditionally applied. Fluctuation effects have also been considered in surface reactions under conditions where they become more significant, e.g., for nanoscale systems12,13 and under higher-pressure conditions.13,14

However, it is natural to attempt to advance beyond mean-field-level descriptions of chemical reaction phenomena to statistical mechanical analyses of appropriate atomistic models for interacting particle systems. This is particularly relevant for situations where the reactants are not “well stirred” or spatially randomized, as applies for surface reactions. Two of several possible modeling strategies are as follows. The first applies reactive lattice-gas automata models where particles on a lattice are assigned velocities (generally subject to randomization) and move around colliding and reacting.15,16 One can thereby describe reactive hydrodynamics and reaction-diffusion phenomena which might be analyzed via lattice Boltzmann equations. The second applies traditional stochastic lattice-gas models where the state of sites changes at specified rates associated with reaction, diffusion, etc. (akin to the Glauber model, except that the rates generally do not satisfying detailed balance).17 These models are described by an exact hierarchy of master equations for multisite probabilities which is amenable to approximate analysis. The current study and the following discussion focus on this second class of models.

Indeed, for stochastic lattice-gas “reaction” models, there has been considerable interest in nonequilibrium phase transitions. Most attention has been paid to universality in continuous transitions,17–19 with relatively little investigation of discontinuous transitions. One exception is studies of the Ziff–Gulari–Barshad (ZGB) model20 for monomer-dimer surface reactions which exhibits a discontinuous transition to a monomer-poisoned absorbing state. Various related phenomena have been analyzed in some detail: propagation and fluctuation behavior of interfaces between active and poisoned states;20–22 epidemic properties of an active droplet...
embedded in the poisoned state,\textsuperscript{23,24} and nucleation of droplets within the metastable active state.\textsuperscript{21,25} While a realistic and predictive atomistic-level description of surface reactions generally requires far more complex models,\textsuperscript{26} simple ZGB-type models are invaluable for elucidating basic issues associated with nonequilibrium phase transitions in reaction systems. In fact, it is natural to search for even simpler single-component reaction models to explore remaining fundamental issues for discontinuous phase transitions.

This last observation motivates our consideration in this paper of a stochastic lattice-gas realization of a Schloegl's second model\textsuperscript{1,27,28} for autocatalysis. This model for autocatalysis in a reactive system of particles, $X$, includes the following mechanistic steps:\textsuperscript{3,27,28}

\[ X \rightarrow \emptyset \text{ (spontaneous annihilation)} , \]
\[ 2X \rightarrow 3X \text{ (autocatalytic creation)} , \]

and possibly particle diffusion. Spontaneous annihilation occurs at rate $p$, and autocatalytic creation occurs at a suitably prescribed rate subject to the requirement of at least one pre-existing nearby pair of particles. A more general formulation also includes spontaneous creation $\emptyset \rightarrow X$, but this process is excluded in our study. Traditional off-lattice formulations also include the autocatalytic annihilation process $3X \rightarrow 2X$ in order to avoid population explosion.\textsuperscript{3,27,28} However, in our stochastic lattice-gas formulation, autocatalytic particle creation requires an empty site $\emptyset$, and is thus more accurately represented as\textsuperscript{29–31} $2X + \emptyset \rightarrow 3X$. This empty site requirement automatically limits population growth. It should also be noted that there exist lattice-gas automata treatments of this model.\textsuperscript{15,16} Of course, there is no Hamiltonian or detailed-balance constraint on the rates for lattice-gas formulations this nonequilibrium model.

Both off-lattice and lattice formulations display cubic mean-field kinetics, i.e., the rate of change in particle concentration, $C$, is a cubic function of $C$. Upon increasing the annihilation rate $p$, there is a bifurcation in the steady states from bistability (where a stable active steady state with finite population $C > 0$ coexists with the stable $C = 0$ vacuum state) to monostability (where the $C = 0$ vacuum state is the unique stable steady state).\textsuperscript{27–31} Consequently, this mean-field formulation of Schloegl’s second model provided a nonequilibrium analog of the van der Waals description of discontinuous liquid-gas equilibrium phase transitions in fluids below the critical temperature.

The above characterization of mean-field steady-state behavior suggests that lattice-gas realizations of Schloegl’s second model might provide a prototype for a nonequilibrium discontinuous phase transition. If so, it is perhaps the most simple and natural model which could provide a fundamental understanding of such behavior. However, it turns out that behavior of this nonequilibrium model depends on the specific realization and on the lattice dimension. For two-dimensional lattices, one can find either continuous or discontinuous transitions.\textsuperscript{28,30} Thus, in this contribution, we will restrict our attention to a specific stochastic lattice-gas model realization Schloegl’s second model on a square lattice. This realization is also known as the quadratic contact process\textsuperscript{29–31} (QCP) and it does display a discontinuous transition.

In Sec. II, we describe in detail our QCP realization of Schloegl’s second model with particle hopping on a square lattice, as well as outlining related fundamental concepts. We also review previous results for this model in the limiting cases of zero and infinite particle mobility. Next, in Sec. III, we analyze the steady states and their relative stability which leads to a characterization the discontinuous phase transition in this model and demonstrates so-called generic two-phase coexistence. We also analyze key aspects of the kinetics elucidating metastability associated with this transition. Generic two-phase coexistence in this model is tied to an orientation dependence of the equistability of planar interfaces separating the active and poisoned states. Thus, in Sec. IV, we are motivated characterize both interface structure and propagation. Exploiting these insights, in Sec. V, we present a droplet analysis in order to characterize both phase stability in generic two-phase coexistence regime and the size and structure of critical droplets in the metastable regime. Concluding remarks are offered in Sec. VI.

II. MODEL SPECIFICATION AND FUNDAMENTAL CONCEPTS

A. Model specification, steady states, and critical annihilation rates

Our realization Schloegl’s second model, or equivalently of the QCP, on a square lattice as a stochastic Markov process involves the following components:\textsuperscript{29–31} (i) spontaneous particle annihilation occurring randomly at rate $p$; (ii) autocatalytic particle creation at an empty site requiring one or more diagonally adjacent pairs of occupied sites; specifically, the creation rate is given by $k/4$, where $k$ is the number of such diagonally adjacent occupied pairs and thus can take the values $k = 0, 1, 2, 4$; (iii) hopping of particles to any adjacent empty sites at rate $h$ (per target site). See Fig. 1 for a schematic of these processes. A key variable is the particle density or concentration, $C$, i.e., the fraction of filled sites which satisfies $0 \leq C \leq 1$. In this paper, we shall focus exclusively on the properties of this model for an infinite square lattice. Of course, all kinetic Monte Carlo simulations are
performed on a finite lattice (with periodic boundary conditions) and care must be taken to eliminate finite-size effects.

It is immediately clear that for any \( p > 0 \), the “vacuum state” with no particles (\( C = 0 \)) corresponds to an absorbing steady state for this model (to use the terminology of Markov processes) from which the system can never escape. This state could also be described as a poisoned or extinguished state. However, one also expects that at least for small \( p \), there exists an active or reactive steady state with a nonzero particle density for the model on an infinite lattice. (On a finite lattice, the system will always eventually evolve to the absorbing state.) Indeed, for \( p \ll 1 \), the lattice should be almost completely populated, so most empty sites are completely surrounded by particles and the associated particle creation rate is unity. Thus, in this regime, effectively one is completely surrounded by particles and the associated particle creation rate is unity. In this regime, effectively one has random annihilation of particles at rate \( p \) and random creation of particles at rate \( 1 \), so that the “equilibrium” steady-state concentration will trivially satisfy \( C_{eq}(p) = 1 - p + O(p^2) \).

It is appropriate to now introduce some basic quantities to be investigated for this model. First, we let \( p_c(h) \) denote the critical value of the annihilation rate \( p \) such that an active steady state exists for \( 0 \leq p \leq p_c(h) \) on an infinite lattice.\(^{29}\) Implicitly, the active steady state in this regime is stable against perturbations by vacuum state droplets, i.e., such vacuum droplets must perish. One expects that \( C_{eq}(p) \) will decrease continuously with increasing \( p \) from a maximum value of \( C_{eq}(0) = 1 \) to some minimum value \( C_{eq}(p_c) \). The latter would be strictly positive if the model exhibits a discontinuous transition from the active to the vacuum state, and zero for a continuous transition. Second, we define another quantity, \( p_f(h) \), of the annihilation rate \( p \) such that for \( p_f(h) \leq p \) the vacuum state is stable against perturbations by active state droplets. Said differently,\(^{29}\) there is a nonzero probability of survival of particles starting from a finite set of populated sites for \( p \leq p_f(h) \).

For a broad class of stochastic models, including the QCP with \( h \geq 0 \), general arguments demonstrate that \( p_f(h) \leq p_c(h) \), i.e., survivability of a finite set of populated sites implies existence of an active steady state, but not necessarily the reverse.\(^{29,32}\) The above discussion shows that the strict inequality \( p_f < p_c \) is equivalent to generic two-phase coexistence\(^{30,31,33-36}\) for \( p_f(h) \leq p \leq p_c(h) \) where both the active and vacuum steady states are simultaneously stable.

### B. Interface propagation and equistability

For \( p \leq p_f(h) \), one can consider the propagation of planar interfaces separating the active and vacuum states with various orientations relative to the underlying square lattice.\(^{30,31}\) We will label the slope of the interface by \( S \), measured relative to the principal lattice direction, so the corresponding angle giving the interface orientation is \( \theta = \arctan S \). By rotational symmetry, behavior for orientations \( \theta \) and \( \theta + \pi / 2 \) are equivalent (e.g., \( S = 0 \) and \( S = \infty \) are equivalent). Let \( V(p, h, S) \) denote the propagation velocity of this interface, where \( V > 0 \) corresponds to the active state displacing the vacuum state, and \( V < 0 \) the opposite case. Propagation occurs indefinitely for \( p \approx 0 \), since spontaneous nucleation of the active state within the absorbing vacuum state is not possible for any \( p \geq 0 \), and the active state is by definition stable. As a result, it follows that \( V(p, h, S) \) is well defined for all \( p \approx p_f(h) \). This contrasts behavior in thermodynamic systems where interface propagation away from a single equistability point is transient.

In the absence of particle annihilation for \( p = 0 \), \( V(p=0, h, S) \) is strictly positive (except for \( h = S = 0 \) as discussed below). Propagation for \( p = 0 \) corresponds to expansion of a completely filled region of the lattice into a vacuum region by irreversible autocatalytic creation of particles at the interface. Furthermore, one expects such \( V(p, h, S) \) to decrease with increasing \( p \) as the stability of the active state decreases relative to that of the vacuum state. We anticipate that active and vacuum states separated by a planar interface with slope \( S \) will be equistable, corresponding to a stationary interface, at a unique value the annihilation rate \( p = p_{eq}(h, S) \) (one exception is for \( h = S = 0 \)). For generality, we have allowed for the possibility that \( p_{eq}(h, S) \) depends explicitly on \( S \) and that \( p_{eq}(h, S) < p_f(h) \). In contrast, \( p_{eq} \) and \( p_f \) must be equal and independent of \( S \) in thermodynamic systems. In our general scenario, we have that \( V(p, h, S) > 0 \) for \( p < p_{eq}(h, S) \), and \( V(p, h, S) < 0 \) for \( p_{eq}(h, S) < p < p_f(h) \). For the QCP with \( h \geq 0 \), it is also reasonable to expect that typically \( V \) varies linearly with \( p \) close to equistability, so that in this regime one has

\[
V(p, h, S) = -B(h, S) \frac{\partial p_{eq}(h, S)}{\partial h},
\]

for small \( \partial p_{eq}(h, S) = p - p_{eq}(h, S) \), with \( B > 0 \) (except for \( h = S = 0 \)).

In this general scenario, one also expects that the critical annihilation rates, \( p_c(h) \) and \( p_f(h) \), are related to the annihilation rates, \( p_{eq}(h, S) \), for equistability via

\[
p_c(h) = \max_{0 \leq S \leq 1} p_{eq}(h, S) = p_{eq}(h, \text{max})
\]

and

\[
p_f(h) = \min_{0 \leq S \leq 1} p_{eq}(h, S) = p_{eq}(h, \text{min}).
\]

The first identity should hold since for any \( p \) smaller than \( p_{eq}(h, \text{max}) \), there exists a range of orientations such that an interface expands into the vacuum state creating a stable active state in its wake. For \( p \) above \( p_{eq}(h, \text{max}) \), an active droplet should be destroyed by the surrounding vacuum state encroaching on all sides, so the active state is not stable. For the second identity, a similar rationalization applies except that for \( h = 0 \) there is some ambiguity in defining \( p_{eq}(h = 0, S = 0) \). We will exploit relationships (3) in our simulation analysis in Sec. III. Below, for convenience, we shall often leave implicit the \( h \)-dependence.

### C. Dimensional analysis

It will sometimes be instructive to utilize a simple dimensional analysis to elucidate the behavior of key quantities in terms of a suitably defined characteristic length, \( L_c \), and characteristic time, \( \tau_c \). Since both particle annihilation and creation rates are of order unity in our model, the same applies for \( \tau_c = O(1) \). One might expect that \( (L_c)^2 = (L_o)^2 + (L_d)^2 \), where \( L_o = O(1) \) is a “reaction range” which reflects spatial coupling in the particle creation
process, and \( L_{\text{p}} = (\tau_{\text{p}})^{1/2} \) is the diffusion length. Then, one has that \( L_{\text{p}} \sim (\alpha+x)^{1/2} \), where \( \alpha=O(1) \). Equivalently, one can write \( L_{\text{p}} = (D_{\text{eff}} \tau_{\text{p}})^{1/2} \) in terms of an effective diffusion coefficient \( D_{\text{eff}} \times \alpha+x \). Some motivation for this form of \( D_{\text{eff}} \) comes from the so-called diffusion approximation in classical spatial contact models, and from the approximate analysis of the master equations for spatially nonuniform states in the QCP. In terms of these characteristic quantities, one expects that

\[
V \sim L_{\text{p}} \tau_{\text{p}} \sim (D_{\text{eff}} \tau_{\text{p}})^{1/2},
\]

so that \( V \sim (\alpha+x)^{1/2} \sim h^{1/2} \), for large \( h \). (4)

A more complete representation of behavior near equistability (except for \( h=0 \) only) should be given by \( V(p,h,S) \sim (\alpha+x)^{1/2} \delta_{\text{eq}}(h,S) \) where again \( \delta_{\text{eq}}(h,S) = p_{\text{eq}}(h,S) \) (cf. Sec. II B). For large \( h \), these predictions for the behavior of \( V(p,h,S) \) are confirmed by a mean-field reaction-diffusion equation analysis. See Ref. 3 and Sec. II D.

**D. Model behavior in limiting cases: \( h=0, h \to \infty \)**

We briefly review previous analyses of the QCP with \( h=0 \) (i.e., no particle hopping) on an infinite square lattice. Simulation studies indicate the existence of a discontinuous phase transition. Specifically, starting from a completely populated lattice, the system evolves to an active state for \( 0 \leq p \leq p_{\text{c}}(h=0) = 0.09443 \) \((\pm 0.00003)\), but instead of the “poisoned” \( C_{\text{eq}} = 0 \) vacuum state for \( p > p_{\text{c}}(h=0) \). The active steady-state value, \( C_{\text{eq}}(p) \), of \( C \) decreases from \( C_{\text{eq}} = 1 \) for \( p = 0 \) to \( C_{\text{eq}} = 0.83 \) as \( p \to p_{\text{c}}(h=0) \). As might be anticipated based on mean-field modeling, the discontinuous transition behavior will be preserved for \( h \to 0 \). See Sec. III. A remarkable feature of the QCP with \( h=0 \) emerged from consideration of equistability of the active and vacuum states separated by planar interfaces with various slopes \( S \). The annihilation rate, \( p_{\text{eq}}(S) = p_{\text{eq}}(h=0,S) \), corresponding to equistability does actually depend on interface orientation or slope, \( S \), in marked contrast to a thermodynamic system! Also, \( p_{\text{eq}}(S) \) achieves a maximum value of \( p_{\text{eq}}(\text{max}) \) for \( S=1 \) for a diagonally oriented interface with slope \( S=1 \). For other orientations or slopes \( S \), equistability occurs at lower \( p = p_{\text{eq}}(S) \) with a minimum of \( p_{\text{eq}}(S=0) = 0.0869 \) \((\pm 0.0004)\) being achieved approaching horizontal or vertical interfaces with \( S=0 \) or \( \infty \).

One special quirk for this QCP with \( h=0 \) is that the vacuum state bordered by a vertical interface can never be populated for any \( p > 0 \), i.e., this vacuum region can never shrink. This follows from the rule for autocatalytic creation of particles noting that empty sites in a vertical vacuum strip never have diagonally adjacent occupied neighboring pairs. In an infinite system, one has that the interface is stationary \( V(p,S=0) = 0 \) for all \( 0 \leq p \leq p_{\text{eq}}(S=0) = 0.0869 \). Expansion of the vacuum state into the active state with \( V(p,S=0) = 0 < h \) only occurs for \( p > p_{\text{eq}}(S=0) = 0.0869 \). As a result, there is some ambiguity in defining \( p_{\text{eq}}(\text{min}) \). The second identity in Eq. (2) only applies for \( h=0 \) if one sets \( p_{\text{eq}}(\text{min}) = 0 \), as now discussed.

Another ramification of this quirk of \( h=0 \) is that the critical value for survival of finite populations satisfies \( p_{\text{c}}(h=0) = 0 \). Given the special rule for autocatalytic creation of particles, for the QCP with \( h=0 \), a finite populated region can never expand outside of a rectangle inscribing the initial populated sites. As a result, all particles must eventually be annihilated based on the properties of finite-state Markov processes with absorbing states.

The QCP with \( h > 0 \) avoids the above quirk. The vacuum state separated by a vertical interface from the active state can either expand or shrink depending on the value of \( p \). Also, a finite set of populated sites can, in principle, expand and survive indefinitely. Durrett postulated that \( p_{\text{c}}(h) = p_{\text{c}}(h) \) for the QCP with any \( h > 0 \), which is no doubt a common expectation. However, the current work will, in fact, show that this Durrett postulate does not hold for \( h > 0 \), and that this failure is a direct consequence of called generic two-phase coexistence.

Finally, we mention that for the QCP in the limit \( h \to \infty \) of a well stirred or randomized system, behavior is described exactly by a mean-field treatment. Exact analysis based on the mean-field rate equation for the kinetics demonstrates bistability, i.e., coexistence of stable active and vacuum states, with the concentration in the active steady state satisfying

\[
C_{\text{eq}}(p) = \frac{1}{2} + \frac{1}{2} (1 - 4p)^{1/2},
\]

for \( p_{\text{c}}(h=\infty) = 0 \leq p \leq \frac{1}{2} \). Here, \( p_{\text{c}}(h=\infty) \) denote upper and lower spinodal points. Analysis of interface propagation based on a mean-field reaction-diffusion equation demonstrates that for large \( h \)

\[
V(p,h,S) \sim h^{1/2}[1 - 3(1 - 4p)^{1/2}],
\]

for \( p_{\text{c}}(h=\infty) = 0 \leq p \leq \frac{1}{4} \). Thus, the Durrett postulate is satisfied in the \( h=\infty \) mean-field limit.

**III. STEADY STATES, EQUISTABILITY, AND KINETICS SIMULATION RESULTS**

Conventional kinetic Monte Carlo (KMC) simulation (for some selected constant \( p \)) of the general QCP for \( h > 0 \) can be used to follow evolution starting from a completely populated lattice to the final steady state. This allows determination of the active steady-state concentration, \( C_{\text{eq}}(p) \), versus \( p \), and thus estimation of \( p_{\text{c}}(h) \). See Fig. 2 which displays this “equation of state” for \( h=0.001 \) revealing a discontinuous transition just as for \( h=0 \). However, one shortcoming of such a conventional KMC simulation analysis is that for \( p \) just slightly above \( p_{\text{c}}(h) \), the system tends to get trapped for long times in a metastable active state before reaching the vacuum state. This leads to the potential for overestimation of \( p_{\text{c}}(h) \). These general features of the non-equilibrium discontinuous transition, and the challenges for accurate determination of \( p_{\text{c}} \), are analogous to those seen in
the ZGB model.20,23,40 This prompted development of an alternative approach20,30,31 to determine \( p_c \) and related quantities which we adopt in Sec. III A.

### A. Equistability of active and vacuum steady states

A comprehensive picture of the relative stability of active and vacuum states follows from consideration of the equistability of interfaces between these states with various orientations \( S \). This analysis also leads to a reliable determination of the critical annihilation rate, \( p_c \), for existence of an active state from the relation \( p_c = \max_{0 \leq S \leq \pi} S \equiv p_c(S) = p_c(\text{max}), \) where we leave implicit the \( h \) dependence. Our analysis for \( h > 0 \) presented below indicates that \( p_c(S) \) does depend on \( S \), where the maximum is achieved for \( S = 1 \) so that \( p_c = p_c(S = 1) \) for all \( h > 0 \) (just as for \( h = 0 \)). We also find that \( p_f = p_c(\text{min}) = \min_{0 \leq S \leq \pi} p_c(S) = p_c(\text{S} = 0) = p_c(S = \infty) \) is strictly below \( p_c = \max(p_c(S = 1)) \) for \( h > 0 \), contrasting the Durrett postulate.29

All of our results for \( p_c(S) \) were obtained from so-called constant-population ensemble simulations30,41 involving the following steps: (i) a target population is selected (usually \( C_i = \frac{1}{2} \)); (ii) at each step, a site is picked at random; (iii) with probability \( 4h^2/(1 + 4h^2) \), one attempts to hop in one of four randomly chosen directions (which requires the selected site to be occupied and the chosen adjacent site to be empty); (iv) with probability \( 1/(1 + 4h^2) \), one attempts to either annihilate or create particles; if \( C > C_i \) applies for the current value of \( C \), then annihilation is attempted (occurring if the site is populated), and if \( C < C_i \), then autocatalytic particle creation is attempted (occurring if the site is empty and with a probability \( k/4 \equiv 1 \)); (v) we track the fraction, \( f_s \), of attempts to annihilate particles in (iv). Then, the fraction of attempts to create particles is \( 1 - f_s \) and \( p_f = f_s / (1 - f_s) \). To match the correct relative rates for particle hopping and particle annihilation and creation in conventional simulation, one sets \( 4h^2/(1 + 4h^2) \), starting with a planar interface between completely filled and vacuum states with the selected \( S \), the constant-population ensemble simulation preserves this planar interface geometry for \( C_i = \frac{1}{2} \) and the output pressure automatically corresponds to the desired \( p_c(S) \).

The \( S \)-dependence of \( p_c(S) \) described above is shown in the inset of Fig. 2 for the case \( h = 0.001 \). In our determination of \( p_c(S) \), we have also performed a finite-size scaling analysis30 (not shown) revealing a weak dependence of our estimates on system size. For \( h = 0.001 \), we find that \( p_c = p_c(S = 1) = 0.0958 \) and that \( p_f = p_c(S = \infty) = 0.0941 \) (obtained from interpolating constant coverage simulation results for \( h^2 \) close to 0.001). Based on the general arguments in Sec. II A, one has stability of both the active and vacuum steady states for \( p_f < p < p_c \). Thus, in the “equation of state” plot Fig. 2, we include two vertical lines at \( p = p_c \) and \( p = p_f \) to indicate the extent of regime of generic two-phase coexistence.

A more comprehensive set of results for the \( h \)-dependence of \( p_f = p_c(\text{max}) = p_c(S = 1) \) and \( p_f = p_c(\text{min}) = p_c(S = 0 \) or \( \infty) = p_c(S = \infty) \) are reported in Table I (obtained from interpolation of constant coverage simulation results for various \( h^2 \)). Note that \( p_c \) varies roughly linearly with small \( h \), but \( p_f \) varies nonlinearly quickly approaching \( p_c \). Thus, the width \( \Delta p = p_c - p_f \) of the regime of generic two-phase coexistence decreases quickly with increasing \( h \), and is below 0.0001 for \( h > 0.01 \). From our simulations alone, we cannot rule out the possibility that \( \Delta p \) becomes zero above some critical value \( h_c \) of \( h \). See Sec. VI for further discussion of this point. The limiting behavior, \( p_f(S = \infty) = p_c(\text{S} = 0 \) or \( \infty) = 2/9 \) for \( h = \infty \), follows from Eq. (7). It should be noted that a similar shrinkage to the width of the generic two-phase coexistence region

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occurs upon introducing a spontaneous particle creation. In this case, two-phase coexistence (and the discontinuous transition) terminates at a critical point.30,42

**B. Metastable states, spinodal points, and poisoning kinetics**

For the QCP with $h \geq 0$ on an infinite lattice, one finds evidence for a metastable extension of the active steady state into a regime $p_{c} \leq p \leq p_{+}$. Here, $p_{+}$ denotes an effective upper spinodal point. However, just as for thermodynamic systems, the precise nature and even the existence of the metastable state and spinodal point in an infinite system is a subtle issue. In fact, based on behavior for equilibrium Ising-type systems,43-45 there should not exist a unique analytic metastable extension of the active state steady state, but rather a family of $C^{\infty}$ metastable extensions.31 Consequently, there is no natural unique definition of $p_{+}$. However, from a more practical perspective, concepts of metastability and spinodal points are particularly valuable in characterizing the kinetics of nonequilibrium models in the vicinity of discontinuous transitions.21,25,31 Indeed, analysis of the kinetics is likely the most effective way to define these quantities, a strategy which has been used for equilibrium systems.44 Finally, we note that some studies of equilibrium systems have defined different types of spinodal points specific to finite systems.46 These are distinct from $p_{+}$ specific to an infinite system considered here.

Here, we first consider determination of the location of the effective upper spinodal point through analysis of the “rapid” poisoning kinetics, i.e., evolution to the vacuum state, for $p > p_{+}$. In later sections, we will present two distinct but complementary and consistent strategies to locate $p_{+}$. We emphasize that there is some ambiguity in each of these strategies, so that one never achieves a precise and unambiguous determination of the spinodal point. In the regime $p > p_{+}$, evolution is not nucleation limited (cf. Sec. III C). The system should poison exponentially quickly as $t \rightarrow \infty$ with any $p > p_{+}$. A detailed analysis of these kinetics for $h = 0.001$ where optimum collapse is achieved with $p_{+} = 0.102$ is given in Sec. 3.

Results for $p_{+}$ versus $h \geq 0$ are summarized in Table I. We should caution that results depend to some extent on the choice of the $p$-regime. Even for $h \rightarrow \infty$ where $p_{+} = 1/2$ is well defined,26 the estimate from the above procedure deviates from $1/2$ when using a $p$-regime which is a significant finite distance from $p_{+}$. Note that the width of the metastable regime, $\Delta p_{+} = p_{+} - p_{c}$, appears to shrink slightly as $h$ becomes no zero, and is actually roughly constant for a significant range of $h$ before increasing to its significantly larger $h \rightarrow \infty$ limiting value of 1/36.

Finally, we discuss the lower spinodal, $p_{\text{eq}} < p_{\text{eq}}(\text{min}) \approx p_{+}$. This analysis of kinetics at low $p$ for the QCP indicated that $p_{\text{eq}} = 0.104$. Our simulations of the kinetics of the QCP for $h \geq 0$ (not shown) provide no evidence for existence of a nontrivial lower spinodal with $p_{\text{eq}}$ greater than 0. The mean-field treatment described in Sec. I and higher-order dynamic cluster approximations of exact master equations predict that $p_{\text{eq}} = 0$ for any $h \geq 0$. Thus, we anticipate that $p_{\text{eq}} = 0$ for our lattice-gas realization for the QCP with any $h \geq 0$.

**C. Avrami analysis of nucleation-mediated poisoning kinetics**

Next, we analyze the nucleation-mediated poisoning kinetics, i.e., evolution to the vacuum state, for $p_{c} < p < p_{+}$, which is much slower than and different in nature from the poisoning described above for $p > p_{+}$. A detailed analysis of these kinetics for $h = 0$ can be found in Ref. 31. Behavior for $h > 0$ is qualitatively similar, and is analyzed here in the same way.

Just as for thermodynamic systems, the idea here is that there exists a critical size for droplets of the poisoned or vacuum state above which they will grow and below which they shrink. Poisoning is then controlled by the fluctuation-mediated formation and subsequent growth of such critical droplets. Key parameters are the nucleation rate of critical droplets, $k_{\text{nuc}}$, and the propagation velocity, $V_{\text{grow}}$, of selected interface orientations of the supercritical droplets. Following the postulate in Refs. 25 and 31 for $k_{\text{nuc}}$ and adopting ideas from Sec. II C for $V_{\text{grow}}$, we propose that

$$k_{\text{nuc}} \propto \exp(-c_{\text{nuc}}/\delta p_{\text{eq}})$$

and

$$V_{\text{grow}} \sim (a + h)^{1/2} \delta p_{\text{eq}},$$

where $\delta p_{\text{eq}} = p - p_{c}$.

Also, based on a dimensional analysis or mean-field analysis, we expect that $c_{\text{nuc}}(h) \sim a + h$ for large $h$ (cf. Sec. V D). Then,
an Avrami formulation\textsuperscript{47} demonstrates that the nucleation kinetics is controlled by the characteristic time $\tau_{\text{nuc}} \propto (V_{\text{grow}})^{-2/3}(\delta p_{\text{eq}})^{-1/3}$. Specifically, after a “short” transient period during which the system reaches the metastable active state with particle concentration $C_m$, the time evolution of the particle concentration should be given by\textsuperscript{25,31}

$$C(t)/C_m = \exp[-A(t/\tau_{\text{nuc}})^{3}],$$

choosing $\tau_{\text{nuc}} = (c_{\text{nuc}})^{-1/3}(\delta p_{\text{eq}})^{2/3}\exp[c_{\text{nuc}}/(3\delta p_{\text{eq}})]$.\textsuperscript{(9)}

Plotting $C(t)/C_m$ versus $t/\tau_{\text{nuc}}$ for various $\delta p_{\text{eq}}$ and fixed $h$ and adjusting $c_{\text{nuc}}$ to optimize collapse of this family of curves provides an estimate of $c_{\text{nuc}} = c_{\text{nuc}}(h)$. This analysis has already been successfully applied\textsuperscript{31} to the QCP with $h=0$, but it extends to quantify the variation of $c_{\text{nuc}}(h)$ with $h$. Specifically, for each $h$, we choose the same set of values of $\delta p_{\text{eq}} = 0.0031 + 0.0005 m$, with $m=0$, 1, 2, and 3. Then, in Fig. 4, we show both the “raw” kinetics $C(t)/C_m$ versus $t$, as well as the optimum collapsed curves for four choices of $h=0.001, 0.1, 0.2,$ and 0.4. Behavior for $h=0.001$ is essentially indistinguishable from that reported previously\textsuperscript{31} for $h=0$. Interestingly, nucleation-mediated poisoning is significantly faster for $h=0.1$ than for $h=0.001$ (or $h=0$). It is also somewhat faster for $h=0.2$, but slower for $h=0.4$ and becomes progressively slower for larger $h$. This trend is reflected in the estimated values of $c_{\text{nuc}} = 0.024, 0.023, 0.012, 0.021,$ and 0.048 for $h=0, 0.001, 0.1, 0.2,$ and 0.4, respectively. The nonmonotonic variation of the lifetime of the metastable state with increasing $h$ might be anticipated from the results in Sec. III B for the variation of the width of the metastable region.

Some theoretical underpinning for the above formulation of poisoning kinetics will follow from our analysis of the nature of critical droplets of the vacuum state embedded in the active state, and of the associated nucleation barrier, presented in Sec. V.

IV. INTERFACE STRUCTURE AND PROPAGATION

As discussed in Secs. II and III, generic two-phase coexistence in our QCP realization of Schloegl’s model is directly tied to an orientation dependence of the equistability of planar interfaces separating the active and poisoned states. This motivates a more detailed analysis of interface structure and propagation in this section. The resulting insight will be invaluable for our analysis of critical droplets in Sec. V.

A. Coarse-grained Kardar–Parisi–Zhang description of interface structure

To elucidate the propagation and structure of the interface between active and vacuum states, it is natural to adopt a coarse-grained mesoscale picture. Here, the interface location at time $t$ is described by a continuous “height” function, $y(x,t)$, measured in a direction orthogonal to the global interface orientation for varying location, $x$, along the interface. Then, evolution of $y$ is described by a suitable stochastic partial differential equation. For the $S = 1$ “high symmetry” orientation, this evolution equation should have\textsuperscript{21,22} the Kardar–Parisi–Zhang (KPZ) form\textsuperscript{48,49}

$$\frac{\partial y}{\partial t} = V_0 + \frac{1}{2} \lambda \left(\frac{\partial y}{\partial x}\right)^2 + \nu \frac{\partial^2 y}{\partial x^2} + \cdots + \eta(x,t)$$

(10)

in the regime of small slopes where $V_0 = V(p,h,S=1)$ and $\eta(x,t)$ represents a nonconserved noise term satisfying $\langle \eta(x,t) \rangle \equiv 0$ and $\langle \eta(x,t) \eta(x',t') \rangle = \gamma \delta(x-x') \delta(t-t')$. On the right-hand side of Eq. (10), the kinetic coefficient $\lambda > 0$ in the nonlinear term can be estimated from simple geometric arguments.\textsuperscript{50} The linear term provides stability by damping meandering of the interface, and the kinetic coefficient $\nu$ is discussed further below. The description of interface propagation and structure is more complex for other orientations, but the corresponding evolution equation should have a linear stabilizing term with a possibly orientation-dependent $\nu$.

Analysis of Eq. (10) reveals that for long times the interface achieves a stationary local structure independent of $\lambda$. The slopes $\partial y/\partial x$ adopt a Gaussian distribution with variance $\gamma/(2\nu)$, and a spatial correlation function satisfies\textsuperscript{48}

$$G(x) = \langle [y(x + x',t) - y(x',t)]^2 \rangle = \langle [y(x,t) - y(0,t)]^2 \rangle \approx \gamma/(2\nu) |x|^{2\alpha}$$

(11)

with $\alpha = \frac{1}{2}$ provided that $|x|$ is not too large. Equivalently, the long-time stationary interface roughness, $W_{\text{sat}}(L)$, measured in a “small” finite window of width $L$ satisfies\textsuperscript{48,49}

$$W_{\text{sat}}(L)^2 = L^{-1} \int_{0<x<L} dx [y(x,t) - \langle y(t) \rangle_L]^2 \approx (\gamma/\nu) L^{2\alpha}$$

(12)

where $\langle y(t) \rangle_L$ denotes the average over the window. Thus, the
ratio $\gamma/\nu$ measures the amplitude of interface wandering. Often $\alpha$ is referred to as the wandering or roughness exponent, and $\alpha = \frac{1}{2}$ corresponds to simple random walk behavior of the interface.

In general KPZ-type formulations of interface propagation, the kinetic coefficient $\nu$ is often referred to as an “effective line tension.”49 However, this can be misleading. A more appropriate perspective comes from a coarse-grained formulation of equilibrium interface fluctuations via evaporation-condensation51 which is described by Eq. (10) with $V_0 = 0$ and $\lambda = 0$. In this case, the kinetic coefficient $\nu \propto \Gamma \bar{\sigma} > 0$ is proportional to the product of a suitable mobility $\Gamma$ and the interface stiffness or interface rigidity $\bar{\sigma}$. Also, as a result of the fluctuation-dissipation relation, $\gamma/(2\nu) = kT/\bar{\sigma}$ is independent of $\Gamma$ in the equilibrium case.

For our nonequilibrium application, $\nu$ might most appropriately be regarded as a product of an effective mobility $\Gamma_{eff}$ and an effective stiffness $\bar{\sigma}_{eff}$. In fact, $\nu$ should not just be interpreted as an effective line tension since (i) the interface stiffness and line tension coincide only when the interface properties are isotropic51 and (ii) the presence of the mobility factor means that $\nu$ scales differently with $h$ than either the stiffness or line tension (see Sec. V). On the latter issue, a dimensional analysis (see Sec. II C) indicates that the kinetic coefficient $\nu$ satisfies

$$\nu \sim (L_x)^2/\tau_c \quad \text{so that } \nu \sim a + h \sim h \text{ for large } h. \quad (13)$$

This prediction is confirmed by a mean-field reaction-diffusion equation analysis. See Ref. 3 and Sec. V.

**B. Interface stiffness**

Motivated by the above discussion, we examine the structure of interfaces separating active and vacuum steady states at equistability for different interface orientations, $\theta = \arctan(S)$, and for various $h$. Direct inspection of simulation images provides insight into the dependence on $\theta$ and $h$ of

$$G(x) \propto (|x|/\gamma)/(\Gamma_{eff} \bar{\sigma}_{eff}) \quad \text{or } \quad W_{sat} \propto (L/\gamma)/(\Gamma_{eff} \bar{\sigma}_{eff}).$$

(14)

Figure 5 compares behavior for interfaces with $S=0$ and $S=1$ when $h^* = h = 0$ and also for $h^* = 0.001$ and $h^* = 0.1$. A strong anisotropy in interface structure is evident for $h^* = h = 0$ with significantly greater roughness for $S=1$ than $S=0$. If we assume that there is no strong $\theta$ dependence of $\Gamma_{eff}/\gamma$, then one concludes that a maximum (minimum) in the effective interface stiffness $\bar{\sigma}_{eff}$ is achieved for $S=0$ ($S=1$) when $h = 0$. Upon increasing $h^*$ or $h$ to as little as 0.001, this anisotropy appears to be significantly reduced. For $h^* = 0.1$, interface behavior appears close to isotropic.

The other dramatic feature apparent in Fig. 5 is that the interfaces roughness for $S=0$ increases dramatically as $h$ is increased from $h^* = 0.001$ to $h^* = 0.1$ and further to $h^* = 0.1$. A similar but less dramatic increase is apparent for $S=1$. However, from the dimensional analysis above, eventually $\nu$ must grow with increasing $h$ and thus eventually the interface roughness will decrease. If we assume that the ratio $\Gamma_{eff}/\gamma$ is a nondecreasing function of $h$, then we are forced to conclude that the effective stiffness, $\bar{\sigma}_{eff}$, at least initially decreases with increasing $h > 0$. The decrease in is $\bar{\sigma}_{eff}$ more dramatic for $S=0$ than for $S=1$. However, since $\Gamma_{eff} \bar{\sigma}_{eff} \sim a + h \sim h$, for large $h$, it might be anticipated that $\bar{\sigma}_{eff}$ will increase for large $h$, behavior confirmed in Sec. V. Thus, we conclude that $\bar{\sigma}_{eff}$ varies nonmonotonically with $h$. This proposal seems consistent with the observed nonmonotonic variation with $h$ of the lifetime of the metastable state described in Sec. III C. See Sec. V for further discussion.

To elucidate this proposed nonmonotonic variation of $\bar{\sigma}_{eff}$ with $h$, we recall that interface properties quickly become more isotropic as $h$ increases above zero. Enhanced isotropy generally reduces stiffness in thermodynamic systems. Suppressing the dependence of various quantities on $p$, one can represent the dependence of stiffness on the angle, $\theta = \arctan(S)$, defining the local orientation of the interface in this fourfold symmetric system via

$$\bar{\sigma}_{eff}(\theta) = \bar{\sigma}_1(h) + g(h)[\cos(2\theta)]^2,$$

(15)

where $g(h) > 0$ measures the strength of the anisotropy. Here, we just keep the lowest-order terms in the Fourier expansion, and we have recast55 the conventional expansion in a form so that $\bar{\sigma}_1(h)$ corresponds to the stiffness for an interface with $S=1$. The requirement that $g(h) > 0$ ensures that the stiffness is maximum (minimum) for $S=0$ and $S=1$. We also anticipate that $g(h)$ decreases quickly toward zero as $h$ increases above zero resulting in the above-mentioned initial rapid decease in $\bar{\sigma}_{eff}$ for $S=0$. The less dramatic initial decrease in $\bar{\sigma}_{eff}$ for $S=1$ requires that $\bar{\sigma}_1(h)$ also decreases initially as $h$ increases above zero, although probably much less strongly than $g(h)$. The strong variation of $g(h)$ versus the weaker variation of $\bar{\sigma}_1(h)$ is what motivated our choice of
form (15). The proposed nonmonotonic behavior of \( \tilde{\sigma}_\text{eff}(h) \) requires that \( \tilde{\sigma}_\text{eff}(h) \) also vary nonmonotonically, eventually increasing for large \( h \).

**C. Dependence of interface propagation velocity on annihilation rate**

Here, we consider the propagation velocity of planar interfaces separating the vacuum and both stable and metastable active states with slopes \( S=1 \) and \( S=0 \) (or \( S=\infty \)) as a function of \( p \). As noted in Sec. II, interface propagation for any \( S \) is well defined (i.e., it occurs indefinitely) for \( p < p_\text{c}(h) \). For such well-defined propagation, \( V(p,h,S) \) can be readily determined by monitoring the linear variation with time of empty sites in a finite system with periodic boundary conditions by selecting an initial strip geometry for the vacuum state, say. The increase or decrease in population corresponds to expansion or shrinkage of the vacuum state strip. To convert these variation rates into a velocity, one must also know the particle concentration in the active state. Comparative results are shown for \( V(p,h,S=1) \) and \( V(p,h,S=0 \text{ or } \infty) \) versus \( p \) for \( h=0 \) in Fig. 6(a) and \( h=0.001 \) in Fig. 6(b). Note that these curves provide upper and lower bounds on the \( V(p,h,S) \) for all other \( S \). Behavior is consistent with the general comments in Sec. II B.

In contrast, for \( p > p_\text{c}(h) \), it is not possible to sustain indefinite interface propagation with the vacuum state displacing the metastable active state since spontaneous nucleation of the vacuum state occurs within the metastable active state. More technically, there will not exist an analytic extension of the well-defined \( V(p,h,S) \) from \( p < p_\text{c}(h) \) to \( p > p_\text{c}(h) \). For example, one does not have a well-defined extension of \( V(p,S=1) > 0 \) for \( p < p_\text{eq}(S=1) = p_e \) to \( V(p,S=1) < 0 \) for \( p > p_e \). Interestingly, for \( S=0 \) (or \( \infty \)), interface propagation is well defined for not just \( p < p_\text{eq}(S=0 \text{ or } \infty) \) but also for the regime \( p_\text{eq}(S=0) < p < p_e \) above the relevant equistability pressure where \( V(p,S=0) < 0 \). Thus, one expects \( V(p,S=0) \) to be an analytic function at \( p = p_\text{eq}(S=0) \), where \( V(p,S=0) = 0 \), and also up to \( p_e \) (but not for \( p > p_e \)).

Despite these complications, it is instructive to explore the behavior of \( V(p,h,S) < 0 \) for \( p < p_\text{c}(h) \) estimated from transient propagation. In fact, we will see that such an analysis provides an unconventional second strategy to estimate the upper spinodal, \( p_\text{c}(h) \). However, there are practical issues in the determination of \( V(p,h,S) \) which should be addressed before discussing simulation results. The major challenge is that we wish to determine \( V(p,h,S) \) approaching the upper spinodal where interface motion becomes more transient and less robust since spontaneous nucleation of the vacuum state within the active state regions becomes more facile. The latter leads an additional decrease in the particle population not associated with expansion of the vacuum strip, potentially leading to overestimation of the magnitude of \( V<0 \). We partly ameliorate this problem by determining the size of the vacuum strip counting only those empty sites which are connected to the strip, and excluding those which are part of disconnected isolated vacuum clusters or droplets within the active state. See Fig. 7.

Results for transient interface propagation for \( p > p_\text{c}(h) \) are also presented in Fig. 6. A tendency for the \( V(p,h,S) \) curves for different \( S \) to merge, and for their slopes, \( dV/dp \), to diverge, as \( p \rightarrow p_\text{c}(h) \) might be anticipated noting results from any of (i) a mean-field reaction-diffusion equation analysis (7) for large \( h \); (ii) a more complex analysis of interface propagation based on nonuniform master equations, or (iii) previous simulations for the QCP with \( h=0 \). Indeed, when viewed over a broad range of \( p \), these \( V(p,h,S) \) curves in Fig. 6 do appear to merge and their slopes increase strongly as \( p \rightarrow p_\text{c}(h) \) (based on the estimates of \( p_\text{c}(h) \). However, an expanded view near this upper spinodal, where there is considerable ambiguity in determining \( V(p,h,S) \), does not show complete merging and the slopes do not diverge.
D. Dependence of interface propagation velocity on hop rate

The independence of $p_{eq}$ on $S$ in the limit as $h \to \infty$ is a consequence of the more general feature that $V(p,h,S)$ becomes “independent” of orientation, $S$, for this mean-field reaction-diffusion regime (noting that particle diffusion is isotropic). By independent, we mean that differences in $V$ for different $S$ become insignificant relative to the magnitude of $V$. In fact, a stronger condition applies, as described below. To illustrate this behavior of $V(p,h,S)$, we determine the dependence on $h$ of both $V(p=0, h, S=1)$ and $V(p=1, h, S=0 = \infty)$. The “large” difference between these velocities for $h=0$, where $V(p=0, h, S=1) = 1/8(\beta) = 0.0884$ (in units of lattice constants per unit time) and $V(p=0, h=0, S=0 = \infty) = 0$ quickly shrinks upon increasing $h$. Similar behavior is observed for $p>0$. See Fig. 8 for behavior when $p=0$ and $p=0.05$. Anticipating that $V \sim (a+h)^{1/2}$ (cf. Sec. II C), we plot the square of $V$ versus $h$ in Fig. 8 producing a near-linear variation, $V(p,h,S)^2 = e(p,S)^2 + d(p)^2 h + O(h^{-1})$ with $h \to \infty$. Thus, one has that

$$V(p,h,S) = \left[ d(p)h^{1/2} + \frac{1}{2}(p,S)^2 d(p)^{-1} h^{-1/2} \right] + O(h^{-n-1/2})$$

for large $h$, (16)

so that differences in $V$ for different $S$ decrease like $h^{-1/2}$ if $e(p,S)$ depends explicitly on $S$, or faster otherwise. Close to equistability, one has that $e(p,S) = e(S) \delta p_{eq}(h,S)$ and $d(p) = d_0 \delta p_{eq}(h,S)$, so that $V(p,h,S) = d_0 [d^{-2} e(S)^2 + h]^{1/2} \delta p_{eq}(h,S)$, where $\delta p_{eq}(h,S) = p_0 - p_{eq}(h,S)$.}

V. DROPLET STRUCTURE AND EVOLUTION

In this section, we consider droplets of a stable phase embedded in a distinct stable or metastable phase. These studies elucidate both the feature of generic two-phase coexistence, as well as nucleation-mediated poisoning kinetics.

FIG. 8. KMC simulation results for the square of the propagation velocities $V(p,h,S=1)$ (upper curve) and $V(p,h,S=0)$ (lower curve) vs $h$ for planar interfaces separating active and vacuum states. Insets show $V(p,h,S)$ vs $h$. Left frame (a): $p=0$. Right frame (b): $p=0.05$.

FIG. 9. KMC simulations of droplet evolution for the QCP with $h=0.001$. Evolution of an initially diamond-shaped filled droplet (embedded in the vacuum state) quickly converting to an active droplet and (a) shrinking for $p=0.0950$ within the two-phase coexistence (2PC) region and (b) growing for $p=0.0920$ below the 2PC region. Evolution of an initially square-shaped vacuum droplet (embedded in the completely occupied state which quickly converts to the active state) and (c) shrinking for $p=0.0950$ within the 2PC region and (d) growing for $p=0.0970$ above the 2PC region. Initial occupied droplet sizes are $128 \times 2 \times 128$, 2 sites in (a) and (b). Initial vacuum droplet sizes are $256 \times 256$ sites in (c) and (d). Images are shown at 0, ~8000, ~24 000, and ~40 000 Monte Carlo steps. In all cases, occupied sites are black and empty sites are white.

A. Droplet analysis of phase stability

In Fig. 9, we summarize a droplet analysis of phase stability demonstrating generic two-phase coexistence for the QCP with $h=0.001$ in the regime $p_f = 0.0941 \leq p < p_c = 0.0958$.

First, we discuss stability of the vacuum state for $h=0.001$. In Fig. 9(a), we show the fate of a large diagonal droplet of occupied sites embedded in the vacuum state for $p=0.0950$. This droplet quickly converts to a diagonal droplet of the active state. Initially, the sides expand since $p < p_{eq}(S=1)$. Indeed, the initial diagonal shape was chosen to maximize this initial growth rate. However, these faster growing diagonal facets quickly “grow out” converting the droplet to a square shape with horizontal and vertical facets which then shrink since $p > p_{eq}(S=\infty)$. Thus, the active droplet ultimately disappears no matter how large the initial size, showing that the vacuum state is stable for $p=0.0950$. In contrast, for $p = 0.0920 < p_f$, such a diagonal active droplet converts to a square shape and thereafter expands since $p < p_{eq}(S=0) = p_{eq}(S=\infty)$, i.e., the vacuum state is not stable. See Fig. 9(b).

Next, we explore stability of the active state for $h=0.001$. In Fig. 9(c), we show the fate of a large square droplet of the vacuum state embedded in a sea of an initially completely populated lattice for $p=0.0950$. This surrounding sea quickly converts to the active state. Initially, the droplet sides expand since $p > p_{eq}(S=0) = p_{eq}(S=\infty)$, the initial square shape being chosen to maximize this initial growth rate. However, these faster growing horizontal and vertical facets quickly grow out converting the droplet to a diamond shape with diagonal facets which shrink since $p < p_{eq}(S=1)$. Thus, the vacuum droplet ultimately disappears no matter how large the initial size, showing that the active state is stable for $p=0.0950$. In contrast for $p = 0.0970 < p_f$, such a
square vacuum droplet converts to a diagonal shape and thereafter expands since \( p > p_{\text{eq}}(S = 1) \), i.e., the active state is not stable. See Fig. 9(d).

The qualitative picture described in detail above for \( h = 0.001 \) applies for all \( h > 0 \). Our analysis of droplet evolution also extends to the more general case and corresponds to a kinematic Wulff construction of “growth shapes.”

The above type of droplet analysis also clarifies the feature that critical value for survival of finite populated regions, \( p_{f} = p_{\text{eq}}(\text{min}) \), is strictly below the critical value for existence for an active state, \( p_{e} = p_{\text{eq}}(\text{max}) \), for \( h > 0 \), in contrast to the Durrett postulate.

**B. Critical droplets: Basic formulation**

The concept of a critical droplet of a stable state embedded within a metastable state is quite general. The idea is that stable droplets which are smaller than some critical size will shrink due their high edge curvature. However, those above the critical size will grow. In the regime \( p_{e} < p < p_{f} \), nucleation-limited poisoning is controlled by the spontaneous fluctuation-mediated creation of droplets of the vacuum state with the critical size or larger embedded in the metastable active state. Growth of these supercritical droplets will spread the vacuum state across the system.

Since the vacuum state is an absorbing state, fluctuation-mediated evolution to the active state is not possible for any \( p \). However, consider evolution starting from a state with a low density of randomly distributed particles. Then, a type of nucleation-limited evolution to the stable active state should occur for \( p_{e} < p < p_{f} \) (provided that \( h > 0 \)). This follows since the initial state includes a low concentration of critical and supercritical active droplets whose growth will spread the active state across the system. As noted in Sec. III B, we expect that \( p_{e} = 0 \).

The above observations prompt a detailed analysis of both vacuum and active critical droplets. More precisely, we will define a critical droplet as the smallest droplet of the stable state embedded in the metastable state which is just as likely to grow as to shrink. Thus, a slightly larger droplet is more likely to grow. Three additional comments are appropriate. (i) One must sample over all possible droplet shapes for anisotropic systems where critical droplets are not circular. (ii) The probabilistic aspect of our definition reflects the feature that the evolution of small droplets is stochastic. Indeed, even droplet survival or disappearance is generally ambiguous (see below). (iii) For droplet sizes which are large enough, evolution is, however, effectively deterministic and the critical size and shape are unambiguous.

To provide insight into critical size behavior, it is instructive to consider first the simpler scenario of reaction model with isotropic interface properties where \( p_{e} = p_{f} = p_{\text{eq}}(S) \) for all \( S \). Here, critical droplets are circular with a critical radius, \( R_{c} \), determined by the condition that the curved interface must be stationary. We have proposed that the normal velocity of the planar interface, \( V_{0} \), satisfies \( V_{0} \sim (a + h)^{1/2} \delta p_{\text{eq}} \) for small \( \delta p_{\text{eq}} = p_{e} - p_{f} \) and the kinetic coefficient, \( \nu \), satisfies \( \nu \sim a + h \) (see Secs. II C and IV A),

Then, based on a KPZ formulation (10), the velocity of an interface with nonzero curvature \( \kappa \), or radius of curvature \( R = 1/\kappa \), has the form

\[
V(R) = |V_{0}|/\nu \propto |V_{0}|/\nu R = \kappa, \quad \text{so that}
\]

\[
\kappa_{c} = |V_{0}|/\nu \quad \text{and} \quad R_{c} = \nu/|V_{0}| \propto (a + h)^{1/2} / |\delta p_{\text{eq}}|.
\]

One caveat in the application of this analysis for critical droplets of the vacuum state where \( p > p_{c} \) is that \( V_{0} \) is strictly not well defined and must be extracted from studies of transient interface propagation (cf. Sec. IV B). This form (18) of \( R_{c} \) can be confirmed in the isotropic regime of large \( h \) based on a mean-field reaction-diffusion equation analysis. However, this variation of \( R_{c} \) with \( \delta p_{\text{eq}} \) could be obscured for systems where \( \nu \) and \( \delta \kappa \) decrease strongly to small values with decreasing \( \delta p_{\text{eq}} \).

Analysis of critical droplets for anisotropic systems, such as the QCP with finite \( h = 0 \), is more complicated. The shape of the critical droplet will not be circular due to anisotropy in both the interface propagation velocity and the interface stiffness. The relationship \( \kappa_{c} \propto |V_{0}|/\nu \) can still be used to determine the direction dependent \( \kappa_{c} \) and thus the shape of the critical cluster: (i) For active droplets when \( p < p_{f} \), the smaller \( |V_{0}|/\nu \) for \( S = 0 \) or \( \infty \) should produce critical clusters which tend to be faceted with smaller \( \kappa_{c} \) in the horizontal and vertical directions, i.e., square-shaped critical active droplets. This effect should be amplified by the larger \( \delta \kappa \) and \( \nu \) for \( S = 0 \) or \( \infty \) (relative to \( S = 1 \)). (ii) For vacuum droplets when \( p > p_{c} \), the effect of the smaller \( |V_{0}|/\nu \) for \( S = 1 \) (relative to other \( S \)) should be to produce critical clusters which tend to be faceted with smaller \( \kappa_{c} \) in the diagonal direction. However, this effect should be offset to some degree by the smaller interface stiffness, \( \delta \kappa \), and smaller \( \nu \) for \( S = 1 \) (relative to \( S = 0 \)).

Finally, we consider the \( p \)-dependence of the critical size. For critical vacuum droplets as \( p \rightarrow p_{\text{eq}}(S = 1) = p_{f} \) from above, the curvature of diagonal edges vanishes which one anticipates will force divergence of the critical droplet size. For critical active droplets as \( p \rightarrow p_{\text{eq}}(S = 0) = p_{f} \) from below, the curvature of horizontal and vertical edges vanishes which one anticipates will force divergence of the critical droplet size.

**C. Critical droplets: Simulation results**

One can perform conventional constant \( p \) simulations for different initial droplet sizes to assess the survival probability as a function of size, and thereby determine the critical size (for various \( p \)). However, simulations using the constant-population ensemble provide a way to more directly or “automatically” assess the critical size.

Here, one chooses an initial droplet-type configuration and appropriate target concentration, \( C_{t} \). Constant-population ensemble simulation stabilizes this droplet configuration while allowing conversion to the appropriate critical droplet structure. The simulation outputs the annihilation rate, \( p_{a} \), corresponding to the selected critical size. Inverting these data gives critical size versus \( p_{a} \). All results shown below are obtained from this approach. One caution is while constant-population ensemble simula-
tions must recover results for constant $p$ simulations for large systems, our results for small critical sizes use somewhat small systems in order to help stabilize the droplet. As an aside, our critical size analysis provides a third strategy for estimating spinodal point locations from the condition that the critical size should be of order unity at the spinodal. Below $R_c$ will denote a measure of the critical linear size of the generally nonspherical clusters.

First, we present simulation results for the behavior of the critical size of vacuum droplets embedded in the metastable active state in the regime $p_a \leq p \leq p_v$, for the QCP with $h \geq 0$. As for thermodynamic systems, there is some ambiguity in assessing droplet survival since new droplets of the vacuum state can always be spontaneously nucleated in the surrounding metastable active state. Results for the variation of the critical linear dimension, $R_c$, of vacuum droplets with $p > p_c$ are shown in Fig. 10 for $h^* = 0.001$ (so that $h = 0.0011$). Here, the relevant variable is $\delta p_{eq} = \delta p_{eq+} = p - p_c > 0$. Results in the inset to Fig. 10 are consistent with the dependence $R_c \propto 1/\delta p_{eq}$. Estimating an effective spinodal point, $p_{ss}$, from the condition that $R_c = O(1)$ at $p=p_{ss}$, indicates that $p_{ss} \approx 0.103 - 0.104$ for $h^* = 0.001$. In addition, a similar analysis (not shown) indicates that $p_{ss} \approx 0.102 - 0.103$ for $h^* = h = 0$, and for $h = 0.1$ indicates that $p_{ss} \approx 0.152 - 0.155$. In the former case, $R_c$ measured as a function of $\delta p_{eq}$ is essentially identical to results for $h^* = 0.001$. These estimates for $p_{ss}$ are consistent with those reported in Table I from an analysis of the kinetics in Sec. III B.

Second, we analyze the critical size of active state droplets embedded in the vacuum state when $p \leq p_f$ for the QCP with $h > 0$ (but not with $h = 0$). For $h = 0$, the previously mentioned quirk of the QCP means that droplets never survive.29,30 For $h > 0$, one can precisely define the critical size of active droplets based on a survival probability of 0.5 since survival of such droplets in a background of an absorbing state is unambiguous.7,23 This contrasts the case of vacuum droplets described above, and also the traditional case of droplets in thermodynamic systems. Results for the variation of the critical linear dimension, $R_c$, of active droplets with $p < p_f$ are shown in Fig. 10 for $h^* = 0.001$. Now, the relevant variable is now $\delta p_{eq} = \delta p_{eq-} = p - p_f < 0$ (appropriately modifying the above definition), and again it seems that behavior of $R_c$ is reasonably described by the form $R_c \propto 1/|\delta p_{eq-}|$. However, the average or effective value of $\nu$ for active droplets may be different from that for vacuum droplets for the same $h$. Our results appear consistent with the identification $p_{eq} = 0$, as estimated from the condition that $R_c = O(1)$ when $p = p_{eq}$.

Finally, we describe results for the shape and structure of critical droplets derived from the above simulations. Fig. 11(a) shows critical active droplets of $\sim 10^4$ populated sites for $h^* = 0.001$ and $h^* = 0.1$. For small $h^*$ or $h$, the perimeter of the droplet tends to be faceted along horizontal and vertical directions and the effective stiffness of the interface between active and vacuum states is high. This behavior is consistent with our analysis in Sec. V B. For larger $h^*$ or $h$, the cluster is less faceted, and the interface less stiff. Fig. 11(b) shows critical vacuum droplets of $\sim 10^4$ empty sites for $h^* = 0$, $h^* = 0.01$, and $h^* = 0.1$. Again the interface at the perimeter of the droplets clearly becomes less stiff with increasing $h$. Note that the shape of the critical vacuum droplets is much less faceted than that of the active droplets for the same small $h^* = 0.001$, again consistent with our analysis in Sec. V B. As noted in Sec. V A, interface stiffness will eventually increase with increasing $h$, and critical droplets will become circular due to reduced anisotropy.

**D. Critical droplets: Thermodynamic analogy**

The predicted variation of $R_c$ with $\delta p_{eq}$ from a “kinetic” analysis described in Secs. V B and V C can also be extracted from a heuristic quasithermodynamic analysis.44,54 For simplicity, we first present this analysis for isotropic systems. One introduces an effective free energy advantage per unit area, $\delta U$, for the stable state (relative to the metastable state) which is assumed to satisfy $\delta U = A|\delta p_{eq}|$ with $A > 0$ at most weakly dependent on $h$. In addition, one introduces an effective line tension, $\sigma_{eff}$, for the interface between active
and vacuum states. Then, the effective free energy of a droplet of radius $R$ of the stable state embedded in the metastable state satisfies

$$ F(R) = -\pi R^2 \delta U + 2\pi R \sigma_{\text{eff}}, \quad (19) $$

and critical droplets correspond to maximizing $F$. Thus, the critical radius, $R_c$, and the effective barrier for nucleation of critical droplets, $E_{\text{nuc}} = F(R_c)$, satisfy\textsuperscript{44,54}

$$ R_c = \sigma_{\text{eff}} \Delta U = \Delta^{-1} \sigma_{\text{eff}} |\delta \rho_{\text{eq}}| $$

and

$$ E_{\text{nuc}} = \pi (\sigma_{\text{eff}})^2 / \Delta U = \pi \Delta^{-1} (\sigma_{\text{eff}})^2 |\delta \rho_{\text{eq}}|. \quad (20) $$

The result for $R_c$ is consistent with analysis (18) above in Sec. V B provided that $\sigma_{\text{eff}} \sim (a+h)^{1/2}$ for large $h$. The feature that $\sigma_{\text{eff}} \sim (a+h)^{1/2}$ is confirmed below, and also highlights an issue raised in Sec. IV B: the effective interface stiffness or line tension, $\sigma_{\text{eff}} = \sigma_{\text{eff}}$ for an isotropic system (see below), can have different scaling with $h$ than the kinetic coefficient $\nu \sim \sigma_{\text{eff}}$. The discrepancy is due to the behavior of the effective mobility $\Gamma_{\text{eff}} \sim (a+h)^{1/2}$.

The expression for $E_{\text{nuc}}$ allows assessment of the rate, $k_{\text{nuc}}$, for spontaneous nucleation of critical clusters of the vacuum state embedded in the metastable active state assuming the form\textsuperscript{25,31} $k_{\text{nuc}} \propto \exp(-bE_{\text{nuc}})$ for some constant $b > 0$. Comparing this expression for $k_{\text{nuc}}$ with the form $k_{\text{nuc}} \propto \exp(-c_{\text{nuc}} |\delta \rho_{\text{eq}}|)$ adopted in Sec. III C for our Avrami analysis of nucleation-mediated poisoning, we conclude that

$$ c_{\text{nuc}}(h) = \pi b \Delta^{-1} (\sigma_{\text{eff}})^2 \sim a + h, \quad \text{for large } h. \quad (21) $$

The numerical results that $c_{\text{nuc}}(h) \approx 0.024, 0.023, 0.012, 0.021$, and 0.048 for $h=0, 0.001, 0.1, 0.2$, and 0.4, respectively, indicates that $\sigma_{\text{eff}}$ varies nonmonotonically with $h$.

This thermodynamic analysis of $R_c$ involves the effective line tension, $\sigma_{\text{eff}}$, of the interface between active and vacuum states, whereas the kinetic analysis in the preceding sections involved the stiffness, $\sigma_{\text{eff}}$, through the relation $\nu = \sigma_{\text{eff}}$. For general anisotropic thermodynamic systems, these quantities are related by\textsuperscript{51} $\sigma_{\text{eff}} = \sigma_{\text{eff}} + d^2 \sigma_{\text{eff}} / d \theta^2$. Thus, $\sigma_{\text{eff}}$ and $\sigma_{\text{eff}}$ are equivalent only for isotropic systems, as noted above. If we assume that the same relation applies for anisotropic nonequilibrium systems, then adopting expression (15) for $\sigma_{\text{eff}}(\theta)$, it follows that\textsuperscript{52}

$$ \sigma_{\text{eff}}(\theta) = \sigma_1(h) - g(h) |\cos(2\theta)|^2 / 15, $$

where $\sigma_1(h) = \tilde{\sigma}_1(h) + 8g(h)/15. \quad (22) $

Given the reduced amplitude of terms involving the presumed rapidly decreasing function $g(h)$ compared with Eq. (12) (cf. Sec. IV B), the nonmonotonic variation of $\sigma_{\text{eff}}$ with increasing $h$ should be weaker than the presumed strong nonmonotonicity of $\tilde{\sigma}_{\text{eff}}$. This is consistent with the numerical results for $c_{\text{nuc}}(h)$ presented above.

### E. Ginzburg–Landau-type formulation

Finally, we note that it is possible to provide a solid basis for the above quasithermodynamic analysis if one restricts attention to the regime of large $h$ where mean-field description of kinetics and spatiotemporal behavior applies. In this regime, the reaction kinetics can be formulated in terms of a local effective free energy density,\textsuperscript{3}

$$ U(C) = \frac{1}{2} p C^2 - \frac{1}{3} C^3 + \frac{1}{4} C^4, $$

satisfying $R(C) = -d/dC U(C), \quad (23) $

where $R(C)$ is given in Eq. (5). $U(C)$ has a double-well form for $0 < p_{eq} < p_{cr} = 1/4$, and the difference in well depths is $\delta U \sim 2/9 \delta p_{eq}$ for small $\delta p_{eq} = p_{eq} - p_{cr} = -2/9$.

Spatiotemporal behavior can be described in terms of an associated Ginzburg–Landau-type effective free energy (or Lyapunov) functional,\textsuperscript{3}

$$ F = \int d \chi \left[ U(C(\chi)) + \frac{1}{2} h |\nabla C(\chi)|^2 \right]. \quad (24) $$

The mean-field reaction-diffusion equations for the QCP with large $h$ then take the form of a deterministic Cahn–Allen equation.\textsuperscript{3,55} Thus, it is also possible to explicitly evaluate $\sigma_{\text{eff}} = \sigma_{\text{eff}}(h)^{1/2}$ (independent of $\theta$) from the value (per unit length) of $F$ integrated across an interface between active and vacuum states.\textsuperscript{55} In fact, this result follows from a simple scaling analysis noting that the width of the interface scales like $h^{1/2}$, and thus the magnitude of $\nabla C$ like $h^{-1/2}$. Consequently, one finds that $R_c = \sigma_{\text{eff}} / \Delta U \sim h^{1/2} / |\delta \rho_{\text{eq}}|$. A result reported above which can also be obtained from a more direct analysis of the mean-field reaction-diffusion equations.

Finally, it should also be noted that stochastic aspects of nucleation-mediated poisoning for large $h$ in this regime can be treated within the framework of the appropriate Langevin version of the above reaction-diffusion or Cahn–Allen equation,\textsuperscript{8,54–56}

$$ \partial C / \partial t = -dF[C] / dC + \xi = R(C) + h \nabla^2 C + \xi, \quad (25) $$. but with nontrivial multiplicative noise.\textsuperscript{8,55,56} $\xi$. Here, $\xi = \xi_{\text{eq}} + \xi_{\text{diff}}$ has contributions from nonconserved particle annihilation-creation noise and conserved particle diffusion noise.\textsuperscript{55,56} A detailed analysis will be reported in a separate paper.\textsuperscript{35}

### VI. CONCLUSIONS

Our realization of Schloegl’s second model for autocatalysis including particle diffusion with hop rate $h \equiv 0$ on a square lattice has revealed a nonequilibrium discontinuous phase transition between an active state and an absorbing vacuum state. The critical annihilation rate for existence of an active state, $p_{eq}(h)$, strictly exceeds that for survival of a finite population, $p_{cr}(h)$, for $h > 0$ contrasting the postulate of Durrett.\textsuperscript{29} This feature is a direct consequence of a dependence on orientation, $S$, of the annihilation rate $p_{eq}(h,S)$ for equistability of a planar interface separating the active and vacuum states, as previously identified\textsuperscript{30,31} for the case $h=0$. This orientation dependence, in turn, leads to generic
two-phase coexistence which is quite distinct from behavior in thermodynamic systems. Nonetheless, one does still find existence of a metastable state just above the discontinuous transition and associated nucleation phenomena exhibiting features quite analogous to discontinuous phase transitions in equilibrium systems.

As noted in Sec. III A, from simulation data alone, we cannot rule out the existence of a critical value, $h_c$, of $h$ such that $p_\epsilon = p_f$ for $h \geq h_c$, i.e., generic two-phase coexistence disappears but the discontinuous transition persists in this regime. However, in our realization of the QCP on a square lattice modified to include spontaneous particle creation, and in Toom’s noisy North-East-Center voting model, generic two-phase coexistence does persist until disappearance of the discontinuous transition at a critical point. Also, analysis based on approximate truncation of the exact master equations for the QCP with $h = 1$ indicates that $p_\epsilon > p_f$ for all $h < \infty$.

It is natural to ask whether the features displayed by this model apply more broadly for nonequilibrium models displaying discontinuous phase transitions? We do expect that interface orientation-dependent propagation and equistability, as well as generic two-phase coexistence, do occur more generally. However, the orientation dependence may often be very weak and the regime of two-phase coexistence may be narrow and as a consequence difficult to detect.

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44. P. A. Rikvold, H. Tomita, S. Miyashita, and S. W. Sidis, *Phys. Rev. E* 49, 5080 (1994). This study described the spinodal associated with an infinite Ising system as the “mean-field spinodal point” (MFSP) although it cannot be assessed with a simple mean-field theory.
48. For a planar interface with small slope $\delta y/\delta x$ measured relative to $S = 1$, the normal velocity is denoted $V(S = 1 + \delta y/\delta x)$. By a Pythagorean construction, the velocity in the $y$-direction is $\delta y/\delta x = \sqrt{V(S = 1 + \delta y/\delta x)[1 + (\delta x/\delta y)^2]} \approx V + \delta V + 1/2 V^2 (\delta y/\delta x)^2$, where $V(1) = 1$, and $\delta V = V(S = 1 + \delta y/\delta x) - V(S = 1) = C(\delta y/\delta x)^2$. Thus, one has $\lambda = 2C + V^2$.
50. Writing $\sigma_\theta(0) = \sigma_{\theta}(\cos \theta) = f(\cos \theta)$, it follows that $\sigma_\theta(0) = \sigma_{\theta}(\cos \theta) = f(\cos(\theta))$. These identities are equivalent to Eqs. (15) and (22), noting that $\delta_r(\theta) = \sigma_{\theta}(\cos \theta)$ and $g(\theta)$ are $2\pi$. A number of increasing vacuum clusters which nucleate just ahead of the interface can be incorporated into the advancing interface as time progresses contemplating estimation of $V$.
grained stochastic reaction-diffusion equations for Schloegl’s second model on a square lattice. Here, $\xi_{ac} \sim C^{1/2}(p-C^2)^{1/2}\xi_{ac}$ is the nonconserved particle annihilation-creation noise, and $\xi_{\text{diff}} \sim \nabla[h^{1/2}C^{1/2}(1-C)^{1/2}\xi_{\text{diff}}]$ is the conserved particle diffusion noise. $\xi_{ac}$ and $\xi_{\text{diff}}$ are independent white noises.”