Surface diffusion in mixed overlayers with superlattice ordering: Percolative transport around obstacles and along domain boundaries

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Abstract
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Surface diffusion in mixed overlayers with superlattice ordering: Percolative transport around obstacles and along domain boundaries

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To elucidate surface diffusion in the presence of a coadsorbate with superlattice ordering, we consider particle hopping on a square lattice with some fraction, $\theta_B$, of quenched blocking sites arranged with checkerboard or $c(2\times2)$ ordering. Behavior for low $\theta_B$ corresponds to diffusion around isolated obstacles, and can be described by exact density expansions. Behavior for high $\theta_B$ corresponds to percolative diffusion along (or sometimes away from) domain boundaries. The connectivity of these domain boundaries is closely related to the existence of symmetry breaking [i.e., long-range $c(2\times2)$ order] in the distribution of blocking sites. In some cases, symmetry breaking induces critical behavior for diffusive transport which is fundamentally different from that for the conventional “ant in the labyrinth” problem. Our results apply to recently developed models for CO oxidation, where CO(ads) diffuses rapidly through coadsorbed relatively immobile $c(2\times2)$-O(ads). The characterization of CO diffusion in these systems is key to describing spatial pattern formation. © 2000 American Institute of Physics. [S0021-9606(00)70146-2]

I. INTRODUCTION

Theoretical analysis of transport in disordered systems has constituted a major area of study in statistical mechanics, which has been motivated by diverse applications in condensed matter physics. Typically, in these analyses, the disorder is quenched or frozen. Furthermore, in the simplest such models, disorder is described by a random distribution of “active” sites or bonds through which transport can occur. (Consequently, there is also a random distribution of “inactive” or blocked sites or bonds.) The existence of long-range transport is then directly related to the classic random percolation problem for clusters of active sites or bonds, as first described by Hammersley and Broadbent.\textsuperscript{2} The associated transport problem for hopping of a random walker between adjacent active sites was colorfully termed the “ant in the labyrinth” by de Gennes.\textsuperscript{3} To analyze this problem, one can take advantage of the available detailed characterization of geometric critical phenomena (e.g., the fractal structure of percolation clusters) near the random percolation transition.\textsuperscript{4}

Indeed, there have been extensive studies of the “ant in the labyrinth” focused on determining the dynamic critical exponents characterizing transport near the percolation transition. Of particular note is an interesting conjecture by Alexander and Orbach relating dynamic and geometric critical exponents.\textsuperscript{1} It is, however, now recognized that the conjecture is only a very good approximation (for random percolation). We note that exact density expansions (for low concentrations of blocking sites),\textsuperscript{5–8} and effective medium approximations\textsuperscript{9} have also been developed to describe transport.

In this work, we shall explore a new class of transport problems which derive from atomistic descriptions of spatiotemporal behavior in two-dimensional surface reaction systems.\textsuperscript{10–12} In such systems, spatial pattern formation is controlled by surface diffusion which occurs in a mixed adlayer of two or more distinct reactant species. Surface diffusion terms appear explicitly in the reaction-diffusion equations which describe the spatiotemporal behavior of the system.\textsuperscript{10–12} It is clear that diffusion of each species must be influenced by the mere presence of other coadsorbed species, even in the absence of any adspecies interactions beyond site blocking.\textsuperscript{11} The extent of this interference actually depends on the relative mobilities of the reactant species, and is strongest when the coadsorbed species is effectively immobile.

The latter situation applies for CO oxidation where highly mobile adsorbed CO diffuses through a quasistatic environment of coadsorbed oxygen (i.e., the case of quenched disorder). Long-range CO diffusion occurs up until a critical coverage of O(ads) is reached, where diffusion paths [of sites not blocked by O(ads)] cease to percolate.

Some previous work has analyzed chemical diffusivity in idealized CO oxidation models neglecting all adspecies interactions, and thus incorporating almost randomly distributed immobile oxygen.\textsuperscript{11} In this case, the associated transport problem is only slightly changed from the classic case of random percolation. The main difference was perceived to be a shift in the percolation threshold due to short-range spatial correlations in the immobile coadsorbate.\textsuperscript{11} However, other more subtle differences in behavior for low densities of blocking sites are discussed in the following. The primary
goal of this work is to extend analyses of diffusivity to cover situations arising in more realistic models for CO oxidation which include superlattice ordering of adsorbed oxygen due to strong short-range repulsive interactions. In these cases, adsorbed oxygen is locally ordered in a periodic array with unit cell larger than that of the substrate. Locally ordered domains are degenerate, adjacent domains of different phase being separated by domain or antiphase boundaries. Specifically, we shall consider twofold degenerate "checkerboard" or c (2 × 2) ordering due to strong nearest-neighbor repulsions between adsorbed oxygen on a square lattice of adsorption sites.

It should be noted that there exist other studies of transport with correlated quenched disorder, e.g., described by the equilibrium ferromagnetic Ising model. A particularly interesting situation, arising in both our work and these Ising studies, is that the percolation threshold can correspond to a phase transition where the spatial correlation length diverges. Here, critical transport behavior can be fundamentally different from the "ant in the labyrinth" problem.

In Sec. II, we first give some further background on the specific CO-oxidation model motivating this work, and discuss some issues related to the simplifications made in this idealized model. In Sec. III, we relate the description of chemical diffusion in such systems to a single-particle diffusion problem. The latter problem, which is the focus of this paper, can be described as diffusion of a single particle, A, on a square lattice through a disordered environment created by a quenched coadsorbed species, B, with c (2 × 2) ordering. In most explicit calculations, diffusion of A will involve hopping to nearest-neighbor (NN) empty sites with a fixed rate, h. Rather than focusing on an explicit reaction model, we instead consider this problem for a variety of "canonical" choices of c (2 × 2)-B ordering, as described in Sec. IV. General techniques of analysis for this novel transport problem (borrowed from conventional studies of transport in disordered systems) are described in Sec. V. They are naturally separated into two regimes, low and high coverage of coadsorbate B. In Sec. VI, we present results for low coadsorbate coverage, based on formal density expansions. In Sec. VII, we consider the regime of higher coadsorbate coverage, where a precise analysis of percolative diffusion along (or away from) boundaries between c (2 × 2)-B domains is presented utilizing an efficient node-elimination algorithm. Some discussion and explanation of observed behavior is provided in Sec. VIII. Behavior for a few more complicated models is considered in Sec. IX, and concluding remarks are presented in Sec. X.

II. CO-OXIDATION MODELS

The specific problems studied in this paper are motivated by recently introduced models for CO oxidation. If "gas" denotes gas phase and "ads" denotes adsorbed species on a square lattice of adsorption sites, then these models include the following ingredients: (i) Adsorption of CO(gas) onto single empty sites, very rapid hopping of CO(ads) to nearby empty sites, and possible desorption from the surface. (ii) Dissociative adsorption of O₂(gas) onto second or diagonal NN empty sites, provided that the additional six NN sites are not occupied by O(ads) (the "eight-site rule"). Also O(ads) can hop to NN empty sites provided that no adjacent pairs of O(ads) are thus created. (iii) Reaction of adjacent CO(ads) and O(ads) to form CO₂(gas). Both the "eight-site rule" for O₂(gas) adsorption, and the hopping rule for O(ads), reflect strong NN O(ads)—O(ads) repulsions. These result in c (2 × 2) ordering of the oxygen adlayer. One key simplifying ingredient in these models is the neglect of CO(ads)—CO(ads) and CO(ads)—O(ads) interactions. We shall describe below in Sec. III how the latter simplification reduces many-particle chemical diffusion of CO(ads) to a single-particle percolative diffusion problem.

Before proceeding with a detailed analysis, it is appropriate to clarify the simplifications in our idealized reaction model. We also suggest which features of the behavior of our model, and of the associated CO diffusion problem, should be robust. There are systems, such as CO+O₂/Pd(100), for which our model captures key ingredients: rapid diffusion of CO(ads) and c (2 × 2) ordering of O(ads). However, this system is more complicated in some significant aspects: (i) Adspecies interactions exist, which are neglected in our model. There are significant CO(ads)—CO(ads) interactions, and also significant repulsive interactions between CO(ads) and O(ads). Furthermore, O(ads)—O(ads) interactions extend to a certain degree beyond strong nearest-neighbor repulsions. (ii) CO(ads) occupy on-top adsorption sites, whereas O(ads) occupy fourfold hollow adsorption sites. (Similar complications exist in other CO-oxidation systems.)

The presence of CO(ads)—CO(ads) interactions means that the CO diffusion problem will not reduce to a single-particle problem [except for low coverage, θCO, of CO(ads)] even in the absence of O(ads) (see Sec. III). In general, the diffusion coefficient will depend on θCO, as is well known from studies of diffusion in single species interacting lattice gases. However, these CO—CO interactions should not affect the critical behavior of percolative CO diffusion. The presence of CO(ads)—O(ads) repulsions also means that CO diffusion is not a single-particle problem [even in the absence of CO(ads)—CO(ads) interactions]. CO diffusion now occurs through heterogeneous energetic topography of accessible sites (cf. Ref. 22), and single-particle diffusion can be anomalous on intermediate time scales. In other words, the magnitude of the diffusion coefficient can be strongly influenced by these repulsive interactions, even for relatively low coverages of O(ads). However, again, these CO—O interactions should not affect the critical behavior of percolative CO diffusion. One caveat is that diffusive behavior could be qualitatively different if these interactions change the nature of the ordering transition for O(ads), or its relationship to the percolation transition for diffusion paths. The same applies if one includes finite NN O(ads)—O(ads) repulsions, or longer-range O(ads)—O(ads) interactions. These issues are briefly discussed in Sec. VIII.

Finally, we note that the existence of distinct adsorption sites in real systems for CO(ads) and O(ads) would naturally tend to reduce the influence of coadsorbed O(ads) on CO diffusion. However, the presence of repulsive CO(ads)—O(ads) interactions, neglected in our model, would somewhat counterbalance this effect. Thus, percolative diffusion
III. CHEMICAL VERSUS SINGLE-PARTICLE DIFFUSION

The problem of describing diffusion of CO(ads) in our CO oxidation models (without CO–CO or CO–O interactions) might appear to differ in two respects from single particle diffusion with quenched disorder. First, diffusion in surface reaction systems occurs at finite reactant concentrations (i.e., in a “dense” lattice gas), so it is in fact the chemical or collective diffusivity which enters into the relevant reaction-diffusion equations, and controls spatiotemporal behavior.10–12 Second, based on the ideas of Onsager,24,25 it follows that a mass flux of a diffusing surface reactant species can be induced by a gradient in not just its own coverage, but also in the coverage(s) of any mobile or immobile coadsorbed species.11 (This point is not commonly recognized or incorporated into reaction-diffusion equation modeling.) We elaborate on these issues in the following.

To mimic CO oxidation, consider a reaction model with two adsorbed species, A and B [representing CO(ads) and O(ads), respectively], where the diffusive hopping rate of A is much higher than the rates for all other processes. These include deposition, reaction, and possible diffusion of B on the surface. Even with “slow” hopping of B atoms (at a rate much lower than that for A), only diffusion terms for A appear in the reaction-diffusion equations which describe the behavior of the reaction model in the “hydrodynamic limit” of large A hop rates. However, we emphasize that despite the lack of diffusion terms for B in these equations, hopping of B is significant in that it affects adlayer structure, and thus the diffusion of A (as well as the reaction kinetics).

As it is stressed by Onsager, the driving force for mass transport is a gradient in the chemical potential, \( \mu_A \), of A, i.e., the diffusive mass flux for A satisfies

\[
\mathbf{j}_A = - (\Lambda_A / k_B T) \nabla \mu_A ,
\]

where \( \Lambda_A \) is the linearized Onsager coefficient, and \( \mu_A \) is well-defined since large hop rates for A ensure local equilibration. Consistent with the above-mentioned reaction models, we consider only the case where there are no A–A and A–B interactions aside from site exclusion. Then, it can readily be shown that \( \mu_A = k_B T \log \theta_A / (1 - \theta_A - \theta_B) \). As a result, Eq. (1) can be written in the form

\[
\mathbf{j}_A = - D_{AA} \nabla \theta_A - D_{AB} \nabla \theta_B ,
\]

where \( D_{AB} = \Lambda_A (1 - \theta_A - \theta_B)^{-1} \), and \( D_{AA} = \Lambda_A (1 - \theta_B) (1 - \theta_A - \theta_B)^{-1} \). These relations imply that

\[
D_{AB} = \frac{\theta_A}{1 - \theta_B} D_{AA} ,
\]

demonstrating that \( D_{AB} \) is completely determined by \( D_{AA} \) (which, for convenience, is denoted by \( D_A \) in the following).

The transport coefficient, \( \Lambda_A \) or \( D_A \), depends upon the specific microscopic mechanism for diffusion. Motivated by the above-described reaction models, here we consider the most general choice consistent with the lack of A–A and A–B interactions: A particles can hop to empty first nearest-neighbor (NN) sites with rate \( h_{2NN} \), to empty second NN sites with rate \( h_{3NN} \), and so on. With this dynamics, it is possible to show that the many-particle equations for collective diffusion of a dense lattice gas of A’s reduce to single-particle equations. Consequently, \( D_A \) can be determined by solving the problem of single-particle transport with quenched disorder, and is thus independent of \( \theta_A \). However, we emphasize that \( D_A \) does depend on \( \theta_B \) in a way that is very sensitive to the choice of \( h_{2NN} \). (See the following sections.)

This reduction to a single-particle problem has been demonstrated where only NN hops are operative26,27 (the case of primary interest here) extending Kutner’s elegant analysis for a homogeneous system.28 The proof described in Appendix A, utilizing a formalism compatible with our subsequent discussion, readily extends to the above-mentioned general hopping prescription. As an aside, we note that another derivation of these results for chemical diffusion is possible using a Kutner’s approach to show directly that \( D_{AA} \) (i.e., \( D_A \)) is determined from a single particle problem, that \( D_{AB} \) must be proportional to \( \theta_A \), and noting the requirement that diffusion must vanish for a completely filled surface.11

IV. MODELS FOR c(2×2) ORDERING OF THE COADSORBATE B

Here, we briefly describe several “canonical” models for c(2×2)-B ordering on a square lattice. The following preliminary comments are appropriate. First, we recall that c(2×2)-B domains can reside on one of two sublattices, or have one of two “phases.” Adjacent domains of different phase are separated by domain boundaries. See Fig. 1. In an infinite system, one expects that typically these sublattices will have equal populations of B’s. However, some models display spontaneous symmetry breaking, which results in these populations becoming unequal above some critical coverage. A related issue is the percolation behavior of c(2×2)-B domains, which are most naturally defined by either second NN or third NN connectivity (Fig. 1). In fact, there is a basic connection between percolation and symmetry breaking. Since percolation of a c(2×2)-B domain of one phase would block percolation of the other phase, it follows that
neither phase can percolate below the symmetry-breaking transition (as this would violate the assumed lack of symmetry breaking).29

The connection with diffusion of A via hopping to NN empty sites comes from two observations: (i) For long-range diffusion via this hopping mechanism, percolation of NN vacancy clusters is necessary. (ii) These NN vacancy clusters are dual to second NN $c(2 \times 2)$-B domains, in that either one or the other percolates (so their percolation thresholds must coincide). In other words, the diffusion coefficient must vanish above the B coverage where second NN $c(2 \times 2)$-B domains percolate. One can also modify the diffusion rule for A particles so that the diffusion path is dual to third NN $c(2 \times 2)$-B domains, and long-range diffusion would cease at the associated, possibly lower percolation threshold.30

A. Hard square model

In the equilibrium hard square (HS) model31 for $c(2 \times 2)$-B distributions with $0 \leq \theta = \frac{1}{2}$, all configurations (which have no NN B pairs) are equally likely. This HS model displays a symmetry-breaking order–disorder transition at a critical coverage32 $\theta_0 = 0.367743$, which is believed to be second order and in the Ising universality class.33–35

Numerical studies suggest that the symmetry-breaking transition coincides with percolation for second NN connectivity.36,17 and rigorous analysis demonstrates the coincidence for third NN connectivity.37,38 In the context of the CO oxidation model described in Sec. II, the HS model reflects the regime where the O(ads) distribution becomes equilibrated (subject to infinite NN repulsions) due to significant mobility of O(ads) on the time scale of adsorption and reaction.

B. Dimer adsorption-monomer desorption model

For immobile O(ads), the CO-oxidation model of Sec. II effectively involves just adsorption of O$_2$(gas) dimers (subject to the “eight-site rule”), together with “desorption” of O(ads) monomers mediated via reaction with CO(ads). Thus, one is motivated to consider a model for $c(2 \times 2)$-B ordering where B$_2$(gas) dimers adsorb dissociatively according to the eight-site rule with attempt rate $p$, and immobile B(ads) monomers desorb at rate $d$. This adsorption–desorption model corresponds precisely to the CO oxidation model in the regime of high reaction rate.17 Behavior of the CO-oxidation model in this regime of high reaction rate (which is still far below the rate for CO hopping) has been examined by Zhdanov and Kasemo in Ref. 14, and by us in Ref. 17. [The former study was incorrectly characterized in Ref. 16 as having a reaction rate far greater than the CO(ads) hop rate.]

As $p/d$ increases from zero, the steady-state value of $\theta_B$ increases from zero to a nontrivial value of about 0.4253.16,17

This value being below 1/2 is explained by noting that as $p/d \to \infty$, the “slow” removal of B’s from the interior of $c(2 \times 2)$ domains creates isolated defects which cannot be immediately filled by B$_2$ dimers. In this model, the symmetry-breaking transition occurs at $\theta_B = 0.2964(6)$ and coincides with the percolation transition for third NN $c(2 \times 2)$ domains, but not for second NN $c(2 \times 2)$ domains. The latter occurs at a higher coverage of $\theta_0 = 0.3053(5)$. See Refs. 17 and 39.

C. Random sequential adsorption of monomers with NN exclusion

In this canonical RSA model,29 single empty sites are occupied randomly by B’s, subject to the constraint that no NN pairs of B’s are created. Adsorption occurs until a “jammed” state is reached with $\theta_B$ equal to $\theta_J = 0.36413$. In this state, there are no “isolated defects,” i.e., empty sites with all neighbors empty (cf. Fig. 1). Consequently, the jammed state consists of defect-free $c(2 \times 2)$-B domains separated only by domain boundaries. Since there is no symmetry breaking, percolation of $c(2 \times 2)$-B domains cannot occur even in the jammed state where domains are large and ramified.40

D. RSA of dimers via the “eight-site rule”

This RSA model29 corresponds to the adsorption–desorption model B with $d = 0$. Here, a jammed state is reached with $\theta_B$ equal to $\theta_J = 0.36157$. Now, the jammed state does include isolated defects within the $c(2 \times 2)$-B domains (cf. Fig. 1), but again there is no symmetry breaking or percolation.40 This jammed state is distinct from the steady state for the adsorption–desorption model B in the limit $d/p \to 0$. The latter corresponds to a dynamic equilibrium between dimer adsorption and slow monomer desorption.

E. Biased RSA

One can generalize RSA models to allow preferential adsorption by B’s on one of the two $c(2 \times 2)$ sublattices, thus enforcing symmetry breaking for all coverages.29,40 This produces higher jammed state coverages, and percolation of the $c(2 \times 2)$-B domains for sufficiently strong bias. For RSA of monomers, percolation first occurs (in the jammed state) for a critical ratio of adsorption rates on the two sublattices of 1.38 for second NN connectivity, and 1.14 for third NN connectivity.40 In the extreme case, where one randomly populates just one sublattice (i.e., complete symmetry breaking), percolation of $c(2 \times 2)$-B domains occurs at $\theta_B = 0.2964$ for second NN connectivity, and $\theta_B = 0.2036$ for third NN connectivity.29

V. DETERMINATION OF THE DIFFUSION COEFFICIENT

In this section, and for the explicit results presented in Secs. VI and VII, we consider exclusively the case of A diffusion via hopping only to NN empty sites, so $h = h_{NN} > 0$, and $h_{NN} = 0$ for $i > 1$. However, much of the formalism extends to more general cases.

A. Mean-square displacement and diffusion coefficients

Let $R_A$ denote the displacement (in units of the lattice constant) of the single diffusing A particle after a time $t$. Then, the diffusion coefficient, $D_A$, satisfies
\[ \langle R_\Lambda^2 \rangle \sim 4D_\Lambda t, \quad \text{as } t \to \infty, \]  
(4)
on a square lattice. The \( \langle \rangle \) denotes average over both configurations of \( B \), and starting points of \( A \). We emphasize that since the starting points are chosen at random (from among sites not occupied by \( B \)), a diffusing particle which makes only NN hops can be localized on a finite cluster of non-B sites, even for lower B coverages. Clearly, \( D_\Lambda \) depends on the configuration of \( B \), and decreases from a maximum value of \( D_\Lambda(= h) \) when \( \theta_B = 0 \), to zero at the percolation threshold where NN vacancy clusters cease to span the system (corresponding to the percolation threshold for second NN \((2 \times 2)\)-B clusters). A more detailed characterization of this coverage dependence will be provided in the following sections. Exactly at the percolation threshold, the diffusion path becomes a “labyrinth” exhibiting a fractal structure, and one finds so-called anomalous diffusion behavior with

\[ \langle R_\Lambda^2 \rangle \sim t^{2d_u}, \quad \text{as } t \to \infty, \]  
(5)
where \( d_u > 2 \) is a dynamical critical exponent.

Direct Monte Carlo simulation can of course be used to determine the mean-square displacement, thus extracting estimates of \( D_\Lambda \). However, this approach is not efficient, particularly near the percolation threshold, so other strategies are discussed in the following.

B. Exact master equations for random walks

Consider the transport problem on an \( \Lambda = L \times L \) site square lattice with periodic boundary conditions, and sites labeled by \( n = (n_x, n_y) \). Again, the \( A \) particle can hop to each NN site rate \( h \), provided that it is not occupied by an immobile \( B \) particle. Consequently, the master equation for the probability, \( p_n(t) \), of finding the \( A \) at site \( n \) at time \( t \) can be written as

\[ \frac{d}{dt} p_n(t) = h \rho \left[ \psi_n p_{n + \rho}(t) - \psi_{n + \rho} p_n(t) \right] = - \sum_m L_{nm} p_m, \]  
(6)

where \( \rho \) denotes one of the four NN lattice vectors \([ (\pm 1,0) \) and \((0, \pm 1) \)]. The quenched “impurity field” is described by \( \psi_n \), which equals 0 if there is a \( B \) particle at site \( n \) and equals 1 if there is not. This equation is written succinctly in terms of a linear evolution operator, \( \hat{L} \), with components \( L_{nm} \).

The solution of Eq. (6) with the initial condition \( p_n(0) = \delta_{nm} \) is written as \( p(n,t|m,0) = \exp(-tL)_{nm} \). For later development, it is useful to define an averaged displacement distribution

\[ P_{n-m}(t) = \langle p(n,t|m,0) p_m^0 \rangle, \]  
(7)
where the probability for the particle to be at site \( m \) initially, \( p_m^0 \), is chosen as \( p_m^0 = N^{-1} \psi_m (1 - \theta_B)^{m-1} \) (the spatially uniform stationary state). The mean square displacement can be obtained from

\[ \langle R_\Lambda^2(t) \rangle = \langle n_x^2 + n_y^2 \rangle(t) = \sum_n \langle n_x^2 + n_y^2 \rangle P_n(t) = \sum_{n,m} p(n,t|m,0) |n-m|^2 p_m^0. \]  
(8)

Extracting the behavior of \( \langle R_\Lambda^2(t) \rangle \) from numerical integration, one can then estimate the diffusivity using the defining relation Eq. (4) (after letting \( L \to \infty \)). A common alternative is to analyze numerically the discrete-time version of the master equations, which corresponds exact enumeration of random walk with a fixed number of attempted hops.

C. Formal density expansions

In a series of papers, Ernst et al. developed a systematic density expansion for transport properties in lattice systems with random disorder. This theory is most conveniently formulated in terms of a “response function,” \( F(q,z) \), corresponding to the Fourier–Laplace transformation of \( P_n(t) \), i.e.,

\[ F(q,z) = \sum_{n,m} e^{iq(n-m)} \langle (z + \hat{L})^{-1} \rangle_{nm}, \]  
(9)
where \( p_{nm} = p_n \delta_{nm} \) is a diagonal matrix. Then, one can obtain the diffusion coefficient from

\[ 4D_\Lambda = \lim_{z \to 0} z^2 \langle n_x^2 + n_y^2 \rangle(z) = - \lim_{z \to 0} z^2 (\partial_{n_x}^2 + \partial_{n_y}^2) F(q,z), \]  
(10)
noting that \( \hat{L}(f) = \int_0^\infty f(t) e^{-zt} dt \sim c/z^2 \), as \( z \to 0 \), if \( f(t) \sim c t \), as \( t \to \infty \).

For the case of randomly distributed impurities or blocked sites, B, Ernst et al. implemented a Lifshitz-Stepanov-type density expansion for \( F(q,z) \), to obtain a corresponding density expansion for the diffusion coefficient of the form (expressed in our notation)

\[ D_\Lambda(\theta_B) = D_0[1 - \alpha_1 \theta_B - \alpha_2 \theta_B^2 - \cdots]. \]  
(11)

The coefficients \( \alpha_1 = \pi - 1, \alpha_2 = 0.85571, \ldots \), were obtained by evaluating individual terms in the expansion with the aid of a T-matrix resummation, and correspond to calculating the “response” for systems with a single impurity, a randomly distributed pair of impurities, etc., respectively (in the limit \( L \to \infty \)).

Of key importance here is that this approach generalizes beyond randomly distributed impurities. The linear coefficient \( \alpha_1 \) always involves calculating the response for a single impurity. Thus, for any system where impurities are isolated B’s in the low density limit, \( \theta_B \to 0 \), one obtains \( \alpha_1 = \pi - 1 \). The “canonical” models A and C, listed in Sec. IV belong to this class. However, for models B and D, the impurities do not become isolated B’s in the low density limit. To obtain the linear coefficient of the coverage dependence, it is then necessary to also evaluate the response for a system with a single “dimer impurity.” This analysis, and the associated density expansions, are reported in Sec. VI, with more details in Appendix B. We should also emphasize that for all models, higher-order coefficients must incorporate a suitable
weighted average over the spatial distribution of pairs of impurities, etc., and thus depend on model details.

Finally, we recall that traditional models for CO oxidation involve adsorption of B dimers onto adjacent empty sites. In this case, again the diffusion coefficient for the adsorbed species, A, will deviate from the predictions of Ernst et al. for low densities, \( \theta_B \), a feature not recognized in previous studies. An analysis of this problem is presented in Appendix C.

D. Node-elimination methods

Consider a network of resistors (each with the same resistance) constructed by connecting NN sites not occupied by B’s on a square lattice. The conductivity, \( \sigma \), of this network is related to the diffusion coefficient for the random walker by the Einstein relation

\[
\sigma \propto (1 - \theta_B) D_A,
\]

where the factor \((1 - \theta_B)\) reflects the “carrier density.” Thus, our transport problem can be studied as a resistor network problem, i.e., by solving a Kirchhoff problem.

In the last two decades, many techniques have been developed for solving the random resistor problem. Traditional techniques, such as the relaxation algorithm, suffer from “critical slowing down” near the percolation threshold, and are not appropriate at high density. In this work, we use a node elimination method first proposed by Fogelholm. This method allows exact calculation of the conductivity of any resistor network, and is versatile being adapted easily to all lattice structures and dimensions. It is also very efficient near the percolation threshold, the regime which is most computationally demanding.

A brief description of the Fogelholm algorithm is now provided. To solve the conductivity of the network, we eliminate sequentially internal nodes by adding new resistors between the remaining nodes. We repeat this process until a single resistor remains. Specifically, if the node (lattice site) \( X_0 \) is directly connected to the nodes \( X_1, X_2, \ldots, X_n \) through conductances \( \sigma_1, \sigma_2, \ldots, \sigma_n \), it may be eliminated by (i) deleting \( X_0 \) and \( \sigma_1, \sigma_2, \ldots, \sigma_n \); and (ii) inserting the conductance \( \sigma_{ij} = \sigma_i/\Sigma_k \sigma_k \) between each pair \( X_i X_j \) of nodes.

Another more specialized node-elimination type algorithm is the so-called \( Y - \nabla \) or star–triangle transformation. It has the virtue of uniform efficiency for low and high coverages, but the drawback of not being easy to generalize to more complicated lattices and connectivity rules.

VI. DIFFUSION FOR LOW COADSORBATE COVERAGE

Based on the discussion in Sec. V C, it is natural to first consider two extreme situations for low density behavior. The first is realized for models A and C, where impurities are all isolated monomers (single B’s) of concentration, \( C^{(1)} \), at low \( \theta_B \approx C^{(1)} \). The second is realized by model D, where, in contrast, impurities are all isolated dimers (pairs of B’s on second NN sites) of concentration, \( C^{(2)} \), at low densities \( \theta_B \approx 2C^{(2)} \). For these two cases, we write

\[
D_A(\theta_B)/D_0 \approx \begin{cases} 1 - a^{(1)}(1)C^{(1)} & \text{for models A and C} \\ 1 - a^{(2)}(2)C^{(2)} & \text{for model D}, \end{cases}
\]

where \( a^{(1)} = \pi - 1 \) from Sec. V C, and

\[
a^{(2)} = \frac{32 - 28 \pi + 9 \pi^2}{10 \pi - 16 - \pi^2} \approx 5.92498
\]

from our new calculation (see Appendix B) for hopping of A’s to NN empty sites.

For any model which has a mixture of monomers and dimers at low densities, \( \theta_B \), one can simply superimpose their effects to the linear order to obtain

\[
D_A(\theta_B)/D_0 \approx 1 - a^{(1)}(1)C^{(1)} - a^{(2)}(2)C^{(2)},
\]

where \( a^{(1)} = C^{(1)} + 2C^{(2)} \). Thus, by simply determining the ratio of monomers to dimers, \( C^{(1)}/C^{(2)} \), one can then derive the low density expansion to linear order.

We will now show that the adsorption–desorption model B has a mixture of monomers and dimers at low density. Specifically, we determine the relative concentrations of monomers and dimers using a straightforward rate equation formalism. Given the mechanism of model B, one has

\[
\frac{d}{dt} C^{(1)} = d(2C^{(2)} - C^{(1)}),
\]

at low densities. The first term describes the creation of a monomer via desorption of one atom in a dimer (with a factor of 2 since this can occur in two ways for each dimer). The second term describes the destruction of monomers due to desorption. (At low densities, we can neglect the decrease in \( C^{(1)} \) due to deposition of a dimer next to a monomer creating a trimer, etc.) Therefore, in steady state of this model, one has \( C^{(1)} \approx 2C^{(2)} \). Consequently, from Eq. (15), the linear coefficient in the density expansion Eq. (11) becomes \( a_1 = a^{(1)}/2 + a^{(2)}/4 \) for model B. The values of \( a_1 \) for this and other models are summarized in Table I.

We estimate higher order coefficients in the density expansion as follows. First, kinetic Monte Carlo simulations are used to generate configurations of B’s for the various models in Sec. IV. Then, each such configuration is mapped onto an equivalent resistor network, and the conductivity calculated using the node-elimination (Fogelholm) algorithm. Figure 2 shows the dependence of \( D_A \) on \( \theta_B \) for models A, B, C, and D. Finally, we fit the data for \( 0 < \theta_B \leq 0.2 \) using third-order polynomials and list the resulting coefficients in Table I. In this fit, the linear coefficients \( (a_1) \) are treated as free parameters, so that the results are independent tests of our above-mentioned analytical calculations. Due to finite system sizes in the numerical calculations, and due to truncation effects, it is not possible to accurately determine the coefficients \( a_2 \) and \( a_3 \).
cation errors, the numerical results for $a_1’s$ are slightly larger than the theoretical values, however, the agreement is evidently quite good.

VII. DIFFUSION FOR HIGH COADSORBATE COVERAGES

As indicated in Sec. IV, transport behavior associated with $A$’s hopping to NN empty sites is controlled by the percolation properties of NN vacancy clusters, which is in turn directly related to the percolation of second NN $c(2 \times 2)$-B domains. We also noted that the percolation of second NN $c(2 \times 2)$-B domains (which blocks transport) cannot occur without symmetry breaking. If symmetry breaking occurs, it can coincide with percolation of second NN $c(2 \times 2)$-B domains, as in the hard square model $A$, or occur at a lower coverage, as in the adsorption–desorption model $B$\(^{2,39}\) (or for strongly biased RSA). In the following, we denote the coverage of B species at this percolation transition by $\theta_p$.

Just below the percolation transition, the diffusion coefficient for $A$ behaves as\(^1\)

$$D_A(\theta_p) \sim (\theta_p - \theta_R)^{\mu}.$$  

As indicated in Eq. (5), exactly at the percolation point, diffusion is anomalous, and from general percolation theoretical considerations, one has the scaling relation\(^1\)

$$d_w = d_f + \mu / \nu.$$  

Here, $d_f$ is the fractal dimension of the percolating diffusion path, and $\nu$ the critical exponent for the connectivity length; $d_f$ and $\nu$ are sometimes referred as geometric exponents, and $d_w$ and $\mu$ as dynamical exponents. It is also common to introduce the reduced exponent $\tilde{\mu} = \mu / \nu$, so $d_w = d_f + \tilde{\mu}$.

Note that it is also possible to develop a finite size scaling theory for systems of size $L \times L$, if one imposes periodic boundary conditions, and regards diffusion as occurring on the surface of a torus with unlimited displacement. Thus, $D_L$ as defined in Eq. (4) can have nonzero values for $L < \infty$, satisfying

$$D_L(\theta_p) = L^{-\tilde{\mu}r_0}f((\theta_p - \theta_R)L^{1/r_0}),$$

where $f(x) \sim x^\mu$, as $x \rightarrow \infty$. Thus, one has $D_L(\theta_p) \sim L^{-\tilde{\mu}}$, as $L \rightarrow \infty$. The physical meaning of the diffusion constant for a finite system is more obvious when it is mapped [cf. Eq. (12)] to the equivalent electrical network problem, which is in fact how we calculate the diffusion rate numerically.

In the following, we discuss transport behavior for the models A–D naturally divided into three classes according to their percolation behavior.

A. No percolation transition

For RSA of monomers with NN exclusion (model $C$) and of dimers via the “eight-site rule” (model $D$), there is no symmetry breaking, and thus no percolation of $c(2 \times 2)$-B domains. Consequently, diffusion of $A$ persists in the jammed states of these models, although at much reduced rates. Specifically, we find that $D_A(\theta_p)/D_0 = 0.037$ (model $C$), 0.030 (model $D$).

To further elucidate behavior in these models, one might consider the analytic extension of $D_A(\theta_p)$ for $\theta_R > \theta_p$, to determine whether it vanishes at some “virtual percolation threshold.” This issue is addressed in Appendix D.

B. Percolation with finite correlation length

For the adsorption–desorption model $B$, the gap between symmetry breaking at $\theta_R = 0.296$, and NN vacancy percolation at $\theta_R = 0.305$ (where $D_A$ vanishes), implies the spatial correlation length is finite at percolation. Thus, the critical properties must correspond to random percolation universality. This includes the critical behavior of transport.

In two dimensions, the geometric exponents, $d_f = 91/48$ and $\nu = 4/3$ for random percolation, can be obtained exactly via mapping onto the $q$-state Potts model with $q \rightarrow 1$. Theoretical attempts to calculate the dynamical exponents have been less successful. Notable among them is the Alexander–Orbach conjecture\(^{44}\) that $d_w = 3d_f/2$, which, from Eq. (18), implies that $\tilde{\mu} = \mu / \nu = 0.9479$. A widely cited numerical study\(^{45}\) gives $\tilde{\mu} = 0.9745 \pm 0.0015$, however, a recent study\(^{46}\) using the $Y - \nabla$ algorithm\(^{43}\) gives $\tilde{\mu} = 0.9826 \pm 0.0008$. Our limited simulations for random percolation using the Fogelholm algorithm also favors the latter higher value.

In a previous study,\(^{39}\) we determined that the geometric exponents for the percolation transition for both $c(2 \times 2)$ clusters and vacancy clusters were consistent with the random percolation universality class. Here, we also calculate the transport coefficients using the Fogelholm algorithm. Figure 3 plots $D_L$ at the percolation coverage $\theta_R = 0.305$ for various system sizes $L$. By fitting the data for $L = 32\ldots128$ to the form $D_L \sim L^{-\tilde{\mu}}$ we obtain $\tilde{\mu} = 0.978(3)$. This result is in good agreement with the value for random percolation, consistent with our claim that the percolation problem belongs to the random percolation universality class. However, the error estimate should not be taken seriously without an analysis of corrections to finite size scaling.

C. Percolation with infinite correlation length

Monte Carlo simulation studies for the hard square model $A$\(^{36,17}\) suggest that percolation of particle clusters with
second NN connectivity (and, by duality, of NN vacancy clusters) coincides with the symmetry-breaking transition point. Because of the divergent spatial correlation length at the symmetry breaking (and thus at the percolation) transition, percolation properties can deviate from the random percolation universality class.

In a previous study,\(^3\) we used a cluster algorithm to efficiently generate equilibrium configurations in the hard square (HS) model in order to perform a comprehensive percolation analysis.\(^17\) For NN vacancy clusters, we found a fractal dimension \(d_f = 1.388(6)\), much smaller than the random percolation value. In the following, rather than using \(\theta_0\) as the control parameter, we more conventionally use the activity, \(z\), of this equilibrium model.

To determine the critical behavior for transport in the HS model, we determine \(D_A\) at the critical activity\(^47\) \(z = z_c = 3.796\) on \(L \times L\) lattices (with periodic boundary conditions), for various \(L\). However, we find that corrections to finite size scaling [cf. Eq. (19)] are quite large, so some care is required to reliably extract exponents. As a result, in Fig. 4, we plot the quantity \(\log(D_L/D_\infty)/\log 2\) (diamonds), which represents an effective exponent, \(\mu_{\text{eff}}\), versus \(1/L\). We find that \(\mu_{\text{eff}}\) first increases with increasing \(L\), with a maximum at around \(L = 50\), before decreasing strongly for larger \(L\).

This behavior can perhaps be explained by the following observations. Exactly at the percolation point, the decrease of \(D_L\) with \(L\) is due to three factors. One is the decrease of the diffusivity of a particle on increasingly large percolating clusters, the second is the decrease of the probability that the particle is on the percolating cluster, and the last is the decrease of the spanning probability that there exists a percolating cluster. While for random percolation, the spanning probability (with free boundary conditions) quickly reaches a universal value of 1/2 as \(L\) increases,\(^48\) the spanning probability for vacancy clusters in the HS model decreases significantly over a broad range of \(L\). See Table II. This feature makes \(\mu_{\text{eff}}\) somewhat larger than its true asymptotic value. To support this claim, we plot another set of effective transport exponents (circles) in Fig. 4, but this time obtaining a diffusion constant by averaging only over configurations with percolating vacancy clusters.

Assuming that there is a nonzero spanning probability at the percolation point, the two sets of data in Fig. 4 should merge in the large \(L\) limit. However, this trend is not clear for the "small" range of system sizes simulated (up to \(L = 738\)). The complicated corrections to finite size scaling make a reliable extrapolation to \(L \to \infty\) quite difficult. It seems that the second set of data (circles) in Fig. 4 is most suitable for this purpose, yielding a best estimate of \(\mu = 1.40(3)\) for the dynamical critical exponent.

**VIII. DISCUSSION**

One might have expected that diffusion at high densities in our models with \(c(2 \times 2)\)-B ordering occurs along quasi-one-dimensional domain boundaries, and is thus quite different from diffusion on "nearly" two-dimensional random percolation clusters in the anti-in-the-labyrinth problem. However, the results of Sec. VII show that this view is not necessarily accurate. The key factor controlling behavior is the universality class, and for our models, two situations arise: the standard random percolation universality class (model B), and a new hard square universality class (model A). For the former, long time behavior is "equivalent" to the anti-in-the-labyrinth problem, and only for the latter are the above-mentioned expectations met. In the following, we provide a pictorial view to clarify the distinct diffusive behavior in these models.

In Figs. 5(a) and 5(b), we present real space snapshots of diffusion behavior near the percolation point for the hard square model A, and the adsorption–desorption model B, respectively. Open and closed circles denote B’s on the two sublattices. The gray-scale represents the probability distribution \(p(\text{pair})\) at \(t = 8192\) obtained by numerically solving

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**TABLE II. Probability that there exists a percolating cluster spanning the system for systems of different sizes at the critical point.**

<table>
<thead>
<tr>
<th>(L)</th>
<th>32</th>
<th>64</th>
<th>128</th>
<th>256</th>
<th>512</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_L(z_c))</td>
<td>0.0721</td>
<td>0.0474</td>
<td>0.0337</td>
<td>0.0265</td>
<td>0.0224</td>
</tr>
</tbody>
</table>
mainly of excursions from the domain boundary.

However, for model B, the diffusion paths consist of the NN vacancy clusters. The walker mainly follows the domain boundary, with occasional excursions into one of the domains. To this end, it is instructive to review some additional general concepts and results pertaining to transport in disordered media with fractal geometries. First, we consider the “minimum paths” having the shortest length, \( l_{\text{min}} \), connecting two points separated by \( L \) on a fractal cluster. We write \( l_{\text{min}} \sim L^{d_{\text{fr}}} \), where \( d_{\text{fr}} \) is the fractal dimension of these minimum paths. Neglecting the role of loops in transport, then \( 1/l_{\text{min}} \) gives a lower bound on \( D_L \sim L^{-d_{\text{fr}}} \), so \( d_{\text{fr}} < d_{\text{fr}} \). If the cluster has no loops, then \( d_{\text{fr}} = d_{\text{fr}} \) and \( d_{\text{fr}} = d_{\text{fr}} \). In general, the cluster on which transport occurs is made up of blobs (containing loops) connected by links (which are often described as “hot” or “red”). If the fractal dimension of the links is \( d_{\text{red}} \), then the upper bound on \( D_L \) obtained by neglecting the resistance of the blobs leads to the inequality, \( d_{\text{red}} \geq d_{\text{fr}} \). In summary, one has

\[
d_{\text{red}} \leq d_{\text{fr}} \leq d_{\text{fr}}. \tag{20}
\]

with the equality \( d_{\text{red}} = d_{\text{fr}} = d_{\text{fr}} \) for loopless clusters.

Based on the numerical results presented for the HS model A in Sec. VII C, and based on Fig. 5(a), we surmise that loops in the NN vacancy clusters do not play a significant role in diffusion, so the equality in Eq. (20) is satisfied. In the following, we shall see that behavior is rather similar to that for transport on the hulls of clusters in the ferromagnetic Ising model. On the other hand, for model B which is in the random percolation universality class, loops are important, and \( d_{\text{fr}} \) is satisfied between \( d_{\text{red}} = 3/4 \) and \( d_{\text{fr}} = 1.375 \).

Further insight comes from comparing behavior in the above-mentioned models with that in a broader class of examples. This is done in Table III, where examples are assigned to one of two categories. Those with higher \( d_{\text{fr}} \) involve transport on clusters with a complex geometry including loops. These are chosen from random percolation, the ferromagnetic Ising model, 2NN \( \varepsilon(2 \times 2) \) particle clus-

---

**TABLE III. Geometrical exponents (fractal dimensions) and dynamic exponents (for transport) in various models described in the text. HS (vacancy) is model A, and Random (cluster) corresponds to model B. For random percolation and the HS model, one approaches the critical point by varying the coverage \( \theta \), so exponents might be labeled by a subscript \( \theta \). For the Ising model, one more typically varies temperature, \( T \), but either approach yields the same \( \tilde{\mu} = \mu_T / \nu_T = \mu_{\nu} / \nu_{\nu} \).**

<table>
<thead>
<tr>
<th>Model</th>
<th>( d_{\text{fr}} )</th>
<th>( d_{\text{red}} )</th>
<th>( \tilde{\mu} )</th>
<th>( d_{\text{fr}} )</th>
<th>( d_{\text{fr}} = d_{\text{fr}} = d_{\text{fr}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ising (hull)( ^a )</td>
<td>11/8 = 1.375</td>
<td>1.375</td>
<td>1.375</td>
<td>11/4 = 2.75</td>
<td></td>
</tr>
<tr>
<td>HS (vacancy)( ^b )</td>
<td>1.388(6)</td>
<td>( \approx d_{\text{fr}} )</td>
<td>1.40(3)</td>
<td>( \approx d_{\text{fr}} )</td>
<td>2.80(3)</td>
</tr>
<tr>
<td>Random (hull)( ^c )</td>
<td>7/4 = 1.75</td>
<td>1.75</td>
<td>1.75</td>
<td>7/2 = 3.5</td>
<td></td>
</tr>
<tr>
<td>Random (cluster)( ^d )</td>
<td>91/48 ( \approx 1.896 )</td>
<td>3/4 ( \approx 1.230 )</td>
<td>2.878</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HS (particle)( ^e )</td>
<td>1.946(1)</td>
<td>( \cdots ) ( \approx 2.00 )</td>
<td>( \geq 1 )</td>
<td>2.15</td>
<td></td>
</tr>
<tr>
<td>Ising (cluster)( ^f )</td>
<td>187/96 ( \approx 1.948 )</td>
<td>( \approx 2.00 )</td>
<td>( \geq 1 )</td>
<td>2.15</td>
<td></td>
</tr>
<tr>
<td>Filled lattice (( \theta = 1 ))</td>
<td>2</td>
<td>( \cdots )</td>
<td>2.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

\( ^a \)See Ref. 49.
\( ^b \)This work and Refs. 17 and 39.
\( ^c \)See Ref. 1.
\( ^d \)See Ref. 39.
\( ^e \)See Appendix F.
\( ^f \)See Ref. 50.
\( ^g \)See Ref. 51.

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FIG. 5. Illustration of diffusion near the percolation transition point. Open and closed circles denote particles on the two sublattices. The gray-scale represents the probability distribution at time \( t = 8192 \) of a random walker initially at the center of the lattice: (a) model A; (b) model B.
ters in the HS model (see Appendix F), or a completely occupied lattice (i.e., transport without disorder). Those with lower $d_f$ correspond to transport on clusters where loops are absent (e.g., hulls of clusters in the first class of high-$d_f$ models$^{52}$) or where loops have little effect (HS model A). The low-$d_f$ loopless regime has $\bar{\mu} = d_f$ increasing with increasing $d_f$; the high-$d_f$ regime has $\mu$ strongly decreasing with increasing $d_f$.

IX. OTHER MODELS

In this section, we comment on diffusion behavior in more general models for mixed adlayers with superlattice ordering. There are many possible extensions of the simple model presented in the first paragraph of Sec. II, so here we discuss only a few obvious choices.

First, it is natural to bridge the gap between the equilibrium hard square model (model A) and the nonequilibrium adsorption–desorption model (model B). This is readily achieved by incorporating into the adsorption–desorption model B, the hopping of B’s such that no NN pairs of B’s are created.$^{39}$ It is clear that such mobility will reduce the population of second NN dimers, relative to monomers, at low densities $\theta_B$, and thus will modify the linear coefficient, $a_1$, in the density expansion of $D_\lambda$. In fact, the situation is rather complicated. Hopping creates a distribution of “separated dimer” impurities, which we label by $\alpha$. Their concentrations, $C^{2}_\alpha$, all scale like $\theta_B$, so for each such species one must first determine the linear coefficient, $a^{2}_\alpha$, and then take a suitable weighted linear combination of these and $a^{1}$ to determine $a_1$. Another observation based on previous work is that a small amount of B-mobility suffices to close the gap between symmetry-breaking and percolation transitions which appears in the adsorption–desorption model with immobile B. Once the gap is closed, critical behavior for both geometric and transport properties will not be controlled by the random percolation universality class (as we have seen for the hard square model).

Another possible variation of the models in Sec. II is to retain the “eight-site rule” for adsorption of B’s, but to relax the constraint that no NN B’s are created by B hopping. Specifically, one could allow hopping with rates consistent with (strong) NN repulsions. Then, for rapid B hopping, the B distribution is described by the (lattice-gas representation of the) antiferromagnetic Ising model. Some finite population of pairs of B’s on adjacent sites is created, and thus symmetry breaking is no longer required for percolation of $c(2 \times 2)$-B domains. For this model, the percolation line for NN vacancy clusters extends from the random percolation threshold, $\theta_B = 0.4073$, at $T = \infty$, to the HS model threshold, $\theta_B = 0.3677$, at $T = 0$. Using Midgal–Kadanoff renormalization group approach, Coniglio et al.$^{53}$ argue that this line exhibits random percolation universality, and deviates below the line of thermal phase transitions (of Ising universality class) except for $T = 0$. If true, this implies that the transport problem exhibits random percolation universality for all $T > 0$. However, if the percolation and ordering transitions in fact coincided for a range of $T > 0$, then one might expect HS model universality to apply in this range.

Finally, we comment on the more complicated (and realistic) models mentioned at the end of Sec. II, where interactions between CO(ads) and other adspecies are included. Specifically, we consider the effect of incorporating strong NN CO(ads)–O(ads) repulsions. Our analysis for equilibrium systems reveals the following behavior. The presence of increasing amounts of CO(ads) first reduces the critical coverage for the continuous $c(2 \times 2)$–O(ads) order–disorder transition, and eventually produces a discontinuous transition in the O(ads) adlayer after a tricritical point. These changes would clearly impact diffusion of CO(ads). It is less clear whether these conditions are met under reaction conditions, an issue we shall pursue in future studies.

X. CONCLUSIONS

We have provided a detailed characterization of surface diffusion of noninteracting species, A, through disordered environment provided by a coadsorbate, B, with $c(2 \times 2)$ ordering. This was achieved using a combination of formal density expansions for $D_\lambda$ at lower coadsorbate coverages, and a scaling analysis of critical behavior of $D_\lambda$ for higher coadsorbate coverages near percolation.

These results can be applied to the analysis of spatiotemporal behavior in CO oxidation, where CO→A and O→B. Spatial pattern formation is controlled by the diffusion coefficients $D_{\Lambda} = D_A$ and $D_{AB} = \theta_A (1 - \theta_B)^{-1} D_A$ described in Sec. III. The strong dependence of these quantities on $\theta_B$ will affect not just the propagation velocity of chemical waves, but perhaps more dramatically the reaction front structure.$^{11}$ The latter can be observed experimentally using high resolution electron microscopy techniques.$^{34}$

ACKNOWLEDGMENTS

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APPENDIX A: CHEMICAL DIFFUSION WITH AN IMMOBILE COADSORBATE

We consider diffusion by NN hops to empty sites in a dense noninteracting lattice gas of A’s through a distribution of immobile B’s (recasting the analysis in Refs. 26 and 27). Adopting the notation of Sec. V B, the probability for site $n$ to be occupied by an A satisfies

$$\frac{d}{dt} p_n(t) = h \sum_p \left[ \psi_n p_n(n + \rho, \bar{n}, t) - \psi_n p_n(n, n + \rho, t) \right]. \tag{A1}$$

Here, $p(n, \bar{n})$ is the joint probability for an A at $n$, and no A at $n'$. Using the relations

$$p(n, \bar{n}, t) = p(n', t) \cdot p(n', n, t)$$

(A2)

where $p(n, n', t) = p(n', n, t)$ is the probability that there are A(ads) at both $n$ and $n'$, Eq. (A1) reduces to Eq. (6). This result relies on “complete blocking” by B’s, i.e.,
p(n,n',t) > 0 requires ψn = ψn' = 1. This analysis also readily generalizes for the more general hopping described in Sec. II.

APPENDIX B: LINEAR COEFFICIENT OF $D_A$ FOR SECOND NN DIMER IMPURITIES

Implementing a Lifshitz–Stepanova-type expansion for $F(q,z)$, Ernst et al. showed that the linear coefficient in the density expansion for $D_A$ can be obtained from the behavior as $q \to 0$ and $z \to 0$ of the function

$$f_1(q,z) = N(\psi)[F_1(q,z) - F_0(q,z)]$$

(B1)

(after one also takes the large $N$ limit). Here, $F_1(q,z)$ denotes the response function with exactly one impurity on the lattice [in our case, a second NN dimer with its two atoms located at (0,0) and (1,1)], and $F_0$ the response function for a perfect (impurity free) lattice. If $L_i$, for $i = 0$ and 1, are the corresponding evolution operators [cf. Eq. (6)], then we write $L_1 = L_0 - \delta L$. The associated Fourier transforms can be expressed as

$$L_{q'q}^0 = \omega(q) \delta_{qq'}$$

(B2)

and

$$\delta L_{q'q} = [\omega(q) - \omega(q - q')](1 + e^{i(q-q')\rho_d})$$

(B3)

with

$$\omega(q) = 1 - \frac{1}{2} \cos q_x - \frac{1}{2} \cos q_y,$$

(B4)

and $\rho_d = (1,1)$.

To analyze $f_1(q,z)$, one can implement a $T$-matrix resummation based on the above-mentioned decomposition of the evolution operators. To perform the resummation, it is necessary to expand the $q$ and $q'$ dependence of $\delta L_{q'q}$.

This can be done using the 10×10 matrix and ten-vector formalism in the following. First set

$$e(q) = \left( \begin{array}{c} \cos \frac{q_d}{2} e_5 \\ \sin \frac{q_d}{2} e_5 \end{array} \right)$$

(B5)

with

$$e_5^T = [1, \omega(q), 1/2 \cos q_x - 1/2 \cos q_y, \sin q_x, \sin q_y],$$

(B6)

and $q_d = q_x + q_y$. Then, analogous to Ref. 7, one can show that

$$\delta L_{q'q} = e(q) V e(q') e^{i(q-q')\rho_d^2},$$

(B7)

where

$$V = \left( \begin{array}{cc} V_5 & 0 \\ 0 & V_5 \end{array} \right).$$

(B8)

Here $V_5$ is the 5×5 matrix defined in Eq. (3.14) of Ref. 7. The rest of the derivation then follows Ref. 7 to obtain

$$f_1(q,z) = (z + \omega(q))^{-2} e(q) V e(q),$$

(B9)

where

$$T = (1 - VG(z))^{-1} V,$$

(B10)

The definition of $V$ can be similarly obtained by extending the 5×5 matrix in Ref. 7 as in Eq. (B8). The lattice Green function $G(z)$ in the above-mentioned formula is a 10×10 matrix with elements

$$G_{ij}(z) = \frac{1}{(2 \pi)^{-1}} \int \frac{\rho_z}{2 \pi} \int \frac{\rho_z}{2 \pi} e^{i(z + \omega(q))} dq_x dq_y$$

(B11)

for an infinite system. Finally, one must evaluate those $G_{ij}(0)$ which are finite, e.g.,

$$G_{33}(0) = 1 - \frac{8}{3 \pi},$$

(B12)

in order to determine $b_x = z^2 \sigma_q^2 [f_1(q,z)]_{q=0,z=0}$ or the corresponding $b_y (= b_7)$. Then, substitution into

$$D_A = D_0(1 - \theta B) - [1 - (b_x + b_y) C^{(2)}],$$

(B13)

with $C^{(2)} = \theta_0/2$ leads to the result in Eq. (14).

APPENDIX C: LINEAR COEFFICIENT OF $D_A$ FOR NN DIMER IMPURITIES

If the two atoms of the NN dimer impurity are located at (0,0) and (1,0), we can calculate the linear coefficient of $D_A$ in the same way as in Appendix B, after replacing $\rho_d$ by (1,0) and $q_d$ by $q_x$. The rest of the analysis is similar to Appendix B, except that there is no symmetry between $q_x$ and $q_y$, in $f_1(q)$. The final results are

$$b_x = z^2 \sigma_q^2 [f_1(q,z)]_{q=0,z=0} = \frac{\pi^2}{16 \pi - 16 - 3 \pi^2} \approx 2.11946,$$

(C1)

and

$$b_y = z^2 \sigma_q^2 [f_1(q,z)]_{q=0,z=0} = 4.$$

(C2)

Then, substitution into the last equation of Appendix B yields

FIG. 6. Coverage dependence of $s_w^{-1/2}$ (for second NN particle clusters, and NN vacancy clusters), and $D_A^{zz}$ for the RSA model C. The dotted line shows continuation beyond the jamming coverage with (1,1) Padé fit.
\[ a_1 = \frac{\pi - 1 - 5/\pi^2}{\pi - 1 - 6/\pi^2} \approx 2.05973 \]  

\[ a_2 = \frac{\pi - 1 - 5/\pi^2}{\pi - 1 - 6/\pi^2} \approx 2.05973 \]  

C3

versus \( a_1 = \pi - 1 \) for random impurities. For traditional models for CO oxidation with dimer adsorption onto NN sites (see Sec. V C and Ref. 11), there are twice as many B monomers as NN B dimers at low \( \theta_B \). Thus one has \( a_1 = 2.1007 \) (the average of the above two values).

**APPENDIX D: ANALYTIC EXTENSION FOR RSA MODELS**

It has been suggested that various measures of second NN \( c(2 \times 2) \) domain size in RSA models, when analytically extended beyond jamming, diverge at a common “virtual percolation threshold.” If true, then one expects behavior near the threshold to be described by the random percolation universality class. To test this idea, and its analog for transport phenomena, in Fig. 6, we plot the mean second NN \( c(2 \times 2) \) domain size, the mean size of finite NN vacancy domains (raised to a power \( -1/\gamma \)), and \( D_A/D_0 \) (raised to the power \( 1/\mu \)) versus \( \theta_B \) near jamming. We choose random percolation values for \( \gamma = 43/18 \) and \( \mu = 1.31 \), so that the plotted quantity would vanish linearly if the above-mentioned hypotheses hold. We also include a low order \((1,1)\) Padé fit, extrapolated beyond jamming, which shows the diffusivity vanishing at a different point from that where the domain sizes diverge. However, results are very sensitive to the extrapolation procedure, so it is difficult to assess the possibility of a common virtual percolation threshold.

**APPENDIX E: CRITICALLY BIASED RSA**

Here, we present a model where diffusion is localized to domain boundaries at percolation, and where behavior is described by random percolation universality class. Such a model is provided by RSA of monomers with NN exclusion, but with a critical bias (model E), where percolation coincides with the jammed state. As mentioned in Sec. IV E, the critical ratio of adsorption rates on the two sublattices is 1.38 for second NN clusters, and therefore, for NN vacancy clusters. Again, since this transition does not coincide with any symmetry-breaking transition, it must belong to the random percolation universality class. Diffusion in this state is shown in Fig. 7. Indeed, our numerical calculations indicate that \( \mu = 0.97(2) \) using data from \( L = 8 \) to 256, with a logarithmic correction.

**APPENDIX F: DIFFUSION INCLUDING HOPPING BEYOND NN SITES**

If one allows direct hopping beyond NN empty sites, then it is immediately clear that there is no percolation transition for \( c(2 \times 2) \)-B ordering which will block diffusion. Indeed, at the maximum \( \theta_B = 1/2 \), diffusion occurs on a single “perfect” sublattice, and \( D_A \) can be calculated trivially from the prescribed hop rates. Writing \( D_A/D_0 \approx 1 - a_1 \theta_B \cdots \), for low \( \theta_B \), one expects that \( a_1 \) should approach unity (the mean-field result), allowing a broad range of long range hops. Numerical calculations show that for the hard square model \( a_1 = 1.55 \) allowing just NN and second NN hops with equal rate. Figure 8 shows \( D_A \) vs \( \theta_B \) for several choices of hopping rates.

It should be emphasized that for only second NN hopping on vacancy clusters in the HS model, for an infinite lattice, \( D_A \) is expected to vanish at the order-disorder transition. This follows since the second NN vacancy clusters are dual to second NN + third NN \( c(2 \times 2) \) particle clusters, which are known to percolate at the order-disorder transition.

The feature that the \((0,1)\) curve in Fig. 8 does not vanish at \( \theta_B = 0.367743 \) simply reflects finite size effects. As an aside, we have examined critical behavior of transport for this second NN hopping on vacancy clusters, and find behavior consistent with the Ising universality class (cf. Sec. VIII and Table III). We also find that the Ising universality class applies for second NN hopping on \( c(2 \times 2) \) particle clusters. Details will be reported elsewhere.

This scenario can be achieved if one were to also completely block A from sites with four, three, or a linear pair of two neighboring B’s, mimicking the effect of a many-body A–B repulsive interaction. The analysis in Sec. II of the reduction to a single-particle diffusion problem can be easily extended to this case.