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Multicomponent percolation: Probabilistic properties and application to nonisothermal reactions in granular materials

Massimiliano Giona[1,2,*] and Alessandra Adrover[1,3]
[1]Centro di Ricerca sui Sistemi Disordinati e Frattali nell'Ingegneria Chimica, Via Eudossiana 18, 00184 Roma, Italy
[2]Dipartimento di Ingegneria Chimica, Università di Cagliari, Piazza d'Armi, 09123 Cagliari, Italy
[3]Dipartimento di Ingegneria Chimica, Università di Roma "La Sapienza," Via Eudossiana 18, 00184 Roma, Italy

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Multicomponent percolation schemes are introduced and discussed. They represent a generalization of usual percolation models to an arbitrary number of species. A detailed analysis of the probabilistic properties of multicomponent percolation is developed and extended to a non-numerable (continuous) distribution of species. Some initial results on transport properties are presented. The connection between multicomponent percolation models and (chemical) reaction schemes in granular materials is analyzed in detail and an application to exothermal self-propagating reactions proposed.

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I. INTRODUCTION

Percolation theory represents a general framework for analyzing disordered structures (e.g., porous media) and geometric phase transitions [1–3]. The application of percolation models is widespread in all fields of science from biology to statistical physics. Many different simulation models have been developed for the analysis of dynamic phenomena in disordered structures (e.g., invasion percolation), for the extension of the purely probabilistic model of percolation in the form of a growth scheme (e.g., spreading percolation and Leath algorithm) [4], and for the analysis of off-lattice percolation in a continuous space (e.g., continuous percolation [5]).

In general, percolation models are two-state spatially distributed systems: the state of each site is equivalent to a Boolean variable which may assume 0 (1) value: spin up (spin down) in random magnetic systems; pore (walls) in porous media, insulator (conductor) in dielectric models.

A useful generalization of percolation theory is to consider an n-state model representing a distribution of species with different physical properties, and with an aggregation kinetics which is specific for each pair of species. This generalization is similar to the q-state Potts model of statistical physics. This percolation model can be called *multicomponent percolation.*

The extension of percolation models to more than two components was first discussed by Zallen [6], who named his model *polychromatic percolation.* The polychromatic percolation problem in the form proposed by Zallen is essentially a geometrical equilibrium problem regarding the possible number of species which can simultaneously percolate (i.e., form infinite clusters of the same species) in a given lattice. The original polychromatic percolation model has been extended by Halley and Holcomb [7] to consider a *reactive percolation model.* More explicitly, Halley and Holcomb considered a three-component polychromatic percolation in which two *atomic* species, say A and B, react to form a *molecular* species AB, $A+B \rightleftharpoons AB$. The chemical reaction between A and B is defined through the equilibrium constant K, which determines the fraction of molecules AB formed in the lattice. A review on polychromatic percolation models can be found in [8].

As will be made clearer in the next section, multicomponent percolation differs radically from polychromatic percolation in the sense that a unique infinite cluster is present through the formation of bonds between the different species, so that the model is not only characterized by species heterogeneity but also by dynamic parameters describing the probability of forming a bond between the species.

To quote Halley [8], polychromatic percolation models have not received a large amount of attention because they belong to the same universality class as ordinary percolation. This is also the case of multicomponent percolation. However, as will be discussed in the article, a multicomponent percolation scheme can be generalized to describe simultaneously heat and mass transfer, and lead to a new class of models which deserve attention in the study of dynamic scaling phenomena (in the sense extensively discussed by Family and Vicsek [9]).

The article is organized as follows. We introduce the multicomponent percolation scheme and develop the probabilistic analysis for an arbitrary finite and non-numerable distribution of species. We briefly analyze the transport properties of the resulting clusters. This analysis is similar to that developed by Bunde, Dieterich, and Roman [10], Rojo and Roman [11], and Roman Youssouff [12] in connection with the random resistor network problem in two-component systems and applied by the authors to the analysis of dispersed ionic conductors. We then analyze the application of multicomponent percolation to nonisothermal reactions in granular ma-

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[*] Author to whom correspondence should be addressed. Electronic address: max@giona2.ing.uniroma1.it

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terials, discuss the simulation techniques, and present some initial results on the stability properties of simple exothermal reactions.

II. MULTICOMPONENT PERCOLATION

The percolation-theory model of uncorrelated spatial disorder can be adapted to describe more complex granular structures in order to model transport phenomena with reactions in granular materials by introducing a level of structuring in the model. The structuring of percolation models can be obtained by considering that (1) the granular matrix is formed by n distinct species; and (2) the aggregation probabilities in forming a cluster are specific and depend on the species.

In accordance with the second assumption we can define a reaction matrix $\mathbf{R}=(r_{ij})$ where r_{ij} represents the probability that the species A_i and A_j react to form the product cluster. In the case of a solid-solid reaction in a powder mixture, the reaction matrix $\mathbf{R}$ characterizes the kinetics in terms of the probabilities of forming a bond between the nearest neighbors of species A_i and A_j.

These positions can be expressed in formal terms by asserting that multicomponent percolation is described by a triplet $(\mathcal{L},\underline{p},\mathbf{R})$, where $\mathcal{L}$ is a d-dimensional lattice with its topology of nearest neighbors; $\underline{p}$ an n-dimensional probability vector $\underline{p}=(p_1,\dots,p_n)$, $\sum_i p_i=1$, representing the fraction of species distributed randomly in the lattice; and $\mathbf{R}$ an $n\times n$ symmetric matrix, $0\le r_{ij}\le 1$, whose elements r_{ij} are the probabilities that the i species react with the j species to form a bond in the reacting cluster.

Two general observations can be made about the definition of multicomponent percolation. Multicomponent percolation models are introduced to describe an intrinsic dynamic phenomenon leading to a growth algorithm for the evolution of the product cluster.

The aggregation process can be simulated on the lattice by means of a modified Leath algorithm in which the growth probabilities are specific for the considered species: if the actual growth site is A_i and one of its first nearest neighbors belonging to the product cluster is A_j, the growth site will aggregate to the product cluster with probability r_{ij} and otherwise will be blocked.

Moreover, the probability structure of the species distribution and of the reactive events induces a double level of probabilistic description which can be used for modulating percolation phenomena with the probability distribution vector $\underline{p}$ and with the reaction matrix $\mathbf{R}$. This redundancy allows us great versatility in simulating kinetic phenomena. However, we can define two limiting situations, in which the percolation process is controlled exclusively by the distribution vector $\underline{p}$ (called for simplicity distribution percolation) or by the reaction matrix $\mathbf{R}$ (reaction percolation). Referring for simplicity to a two-component system, and letting p be the percolation probability, distribution percolation corresponds to the case of a random distribution of the two species, of which only one (say A_1) is fully reactive ($r_{11}=1$) and the other completely inert ($r_{12}=r_{22}=0$). In this situation, the tuning parameter of the percolation phenomenon is p_1, i.e., $p=p_1$. The opposite case, which can be called reaction percolation, is represented by a single species in the lattice, $p_1=1$, in which the tuning parameter of the process is the reaction probability r_{11}, i.e., $p=r_{11}$. Distribution percolation is defined by $r_{11}=1$, $r_{12}=r_{22}=0$, and $p=p_1$, while reaction percolation is defined by $p_1=1$ and $p=r_{11}$.

III. PROBABILISTIC PROPERTIES

An initial problem connected with multicomponent percolation schemes lies in the evaluation of the percolation threshold p_c as a function of the probabilistic parameters $\underline{p}$ and $\mathbf{R}$, and more generally in the evaluation of the equivalent percolation probability p as a function of these parameters.

Let us first consider the case of a two-component system. In this situation we have

$$p=\Phi(p_1,\mathbf{R})\ , \tag{1}$$

since $p_2=1-p_1$.

Letting $p(A_i;\mathcal{C})$ be the probability that a site belonging to the infinite cluster $\mathcal{C}$ is of A_i species ($i=1,2$), we have

$$\begin{aligned} p&=p(A_1;\mathcal{C})[p_1r_{11}+p_2r_{12}]+p(A_2;\mathcal{C})[p_1r_{21}+p_2r_{22}]\\ &=p(A_1;\mathcal{C})\Pi_1+p(A_2;\mathcal{C})\Pi_2\ . \end{aligned} \tag{2}$$

The probabilities $p(A_i;\mathcal{C})$ can be evaluated by considering that if $p_g(A_i)$ ($i=1,2$) are the probabilities that a site A_i will form in the growth process, then

$$\begin{aligned} p_g(A_1)&=p(A_1;\mathcal{C})p_1r_{11}+p(A_2;\mathcal{C})p_1r_{12}\ ,\\ p_g(A_2)&=p(A_1;\mathcal{C})p_2r_{21}+p(A_2;\mathcal{C})p_2r_{22}\ . \end{aligned} \tag{3}$$

From the asymptotic steady-state behavior of the growth process, the probability that an aggregate site is to be of A_i species is equal to $p(A_i;\mathcal{C})$, i.e.,

$$\frac{p_g(A_1)}{p_g(A_1)+p_g(A_2)}=p(A_1;\mathcal{C})\ . \tag{4}$$

Correspondingly, we obtain a single equation in $x=p(A_1;\mathcal{C})$,

$$x=\frac{\alpha x+\beta(1-x)}{\Pi_1x+\Pi_2(1-x)}\ , \tag{5}$$

where $\alpha=p_1r_{11}$ and $\beta=p_1r_{12}$. The solution Eq. (5) reads

$$x=\begin{cases} -\Gamma/2\pm\sqrt{\Gamma^2/4+\beta/(\Pi_1-\Pi_2)} & \text{if } \Pi_1-\Pi_2\neq 0\\ \beta/(\Pi_2+\beta-\alpha) & \text{if } \Pi_1-\Pi_2=0\ , \end{cases} \tag{6}$$

where $\Gamma=(\Pi_2+\beta-\alpha)/(\Pi_1-\Pi_2)$. In the case of $\Pi_1-\Pi_2\neq 0$ only one solution (6) is admissible, lying in the interval [0,1]. Once x is known, the percolation probability can be evaluated through Eq. (2). Figure 1 shows the behavior of the percolation probability p as a function of the probabilistic parameters p_1 and $\mathbf{R}$ together with the estimate of p deriving from Monte Carlo simulations. Satisfactory agreement is reached between the theoretical estimate of p and the simulations.

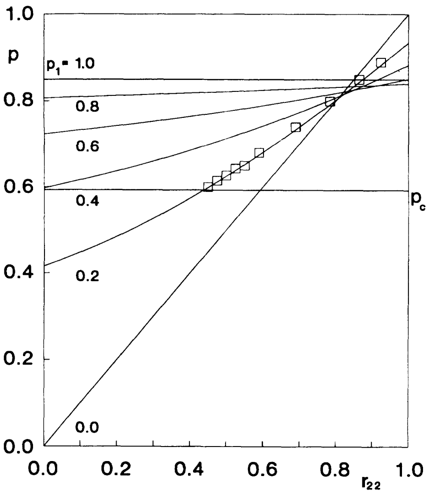

FIG. 1. Behavior of the equivalent percolation probability p vs r_{22} for a two-component system with $r_{11}=0.85$; $r_{12}=0.80$ for several values of p_1. The solid lines are the theoretical predictions, Eqs. (2) and (6); the points are the simulation results obtained from the analysis of the infinite cluster grown by means of the Leath algorithm (modified according to the definition of multicomponent percolation schemes) in two dimensions: 600×400 lattice averaged over 100 realizations.

The theoretical considerations developed for two species can be extended in a straightforward way to n species. By applying the same analysis we have

$$p=\sum_{i=1}^{n} p(A_i;\mathcal{C})\Pi_i,\quad \Pi_i=\sum_{i=1}^{n} p_j r_{ij} . \tag{7}$$

The growing probabilities $p_{gi}=p_g(A_i)$ are given by $p_{gi}=p_i\sum_j p(A_j;\mathcal{C})r_{ij}$, and from the steady-state assumption we have

$$p(A_i;C)=p_i\frac{\sum_{j=1}^{n} p(A_j,\mathcal{C})r_{ij}}{\sum_{h=1}^{1}\sum_{j=1}^{n} p_h p(A_j;\mathcal{C})r_{hj}} , \tag{8}$$

which is a system of n nonlinear equations in the n unknown variables $p(A_i;\mathcal{C})$.

The same analysis can also be extended to a continuous distribution of reacting species. By adopting the same notation, and letting $p(\alpha)$ be the probability distribution function (PDF) associated with the distribution of species parametrized with respect to the continuous parameter $\alpha\in\mathcal{A}$, $r(\alpha,\beta)$ the corresponding reaction kernel (which in the continuous formalism plays the role of the reaction matrix), and $p(\alpha;\mathcal{C})$ the PDF associated to the species distribution in the infinite cluster, we have

$$p=\int_{\mathcal{A}} p(\alpha;\mathcal{C})\Pi(\alpha)d\alpha,\quad \Pi(\alpha)=\int_{\mathcal{A}} p(\beta)r(\alpha,\beta)d\beta , \tag{9}$$

$$p(\alpha;\mathcal{C})=\frac{p(\alpha)\int_{\mathcal{A}} p(\beta;\mathcal{C})r(\alpha,\beta)d\beta}{\int_{\mathcal{A}} p(\gamma)d\gamma\int_{\mathcal{A}} p(\beta;\mathcal{C})r(\gamma,\beta)d\beta} , \tag{10}$$

$$\int p(\alpha;\mathcal{C})d\alpha=1 .$$

A special case which can be solved analytically comes from the assumption of Gaussian distribution in the reacting species, $\mathcal{A}=(-\infty,\infty)$,

$$p(\alpha)=\frac{1}{\sqrt{2\pi\sigma^2}}\exp[-\alpha^2/(2\sigma^2)]$$

by also assuming a Gaussian convolutory reaction kernel

$$r(\alpha,\beta)=\exp[-\rho(\alpha-\beta)^2] .$$

Under this hypothesis, $p(\alpha;\mathcal{C})$ is still Gaussian distributed,

$$p(\alpha;\mathcal{C})=\frac{1}{\sqrt{2\pi\lambda^2}}\exp[-\alpha^2/(2\lambda^2)] ,$$

with λ^2 satisfying the equation

$$\frac{2\rho\lambda^2}{1+2\lambda^2\rho}+\frac{\lambda^2}{\sigma^2}=1 , \tag{11}$$

which admits only one positive solution. After some algebraic manipulation, we obtain from Eqs. (9) and (10) the expression for the probability p,

$$p=\frac{1}{\sqrt{1+2\rho(\sigma^2+\lambda^2)}} . \tag{12}$$

Figure 2 shows the behavior of the percolation probability p as a function of the two parameters ρ and σ^2 entering into the model. The analysis of the continuum limit developed above is purely mathematical. However, it is to be expected that such models may have some practical relevance in dealing with the structural properties of amorphous materials (e.g., glasses) characterized by highly heterogeneous structures of bonds [13].

Attention should be drawn to the fact that multicomponent percolation generalizes the usual percolation models but belongs to the same universality classes induced by the dimensionality of the lattice [2].

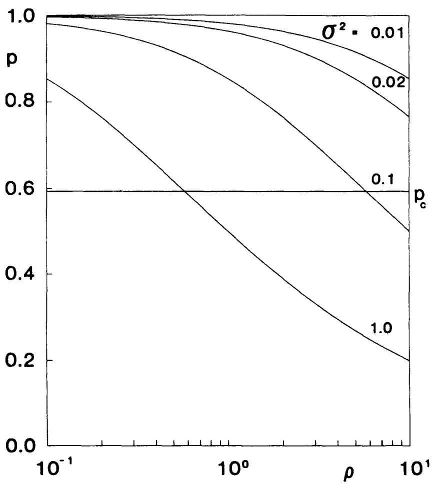

FIG. 2. p vs ρ for the continuous distribution percolation, Eqs. (11) and (12), for different values of σ^2. p_c is the threshold for two-dimensional square lattices.

IV. TRANSPORT PROPERTIES

The transport properties of multicomponent percolation clusters can be studied in exactly the same way as the conduction properties in random resistor networks (RRN) [10–12] by introducing an $n\times n$ symmetric matrix $\mathbf{D}=[D_{ij}]$ of diffusivities. The element D_{ij} represents the diffusivity associated with a jump from a site A_i to one of its neighboring sites which is of A_j species. The diffusivity matrix $\mathbf{D}$ is related to the hopping rate matrix $\mathbf{w}=[w_{ij}]$ through the relation [11]

$$D_{ij}=\frac{Za^2}{2d}w_{ij} \, , \tag{13}$$

where a is the lattice constant (characteristic length between nearest neighboring sites), d the dimensionality of the lattice, and Z the coordination number.

For the development of an effective-medium approximation (EMA) theory of transport properties in multicomponent percolation clusters, it is necessary to determine the quantities $p_{ij}^B(\mathcal{C})$ representing the fractions of A_i—A_j bonds in the infinite percolation cluster $\sum_{i,j\; i<j}p_{ij}^B(\mathcal{C})=1$. For a generic discrete n-component system, $p_{ij}^B(\mathcal{C})$ is given by the product of the probability that a site belonging to the infinite percolation cluster is A_i, $p(A_i;\mathcal{C})$, times the probability that a reactive event will form a bond A_i—A_j, i.e.,

$$\begin{aligned}&p_{ii}^B(\mathcal{C})=p(A_i;\mathcal{C})p_i r_{ii}/\Pi_i \, ,\\&p_{ij}^B(\mathcal{C})=p(A_i;\mathcal{C})p_j r_{ij}/\Pi_i+p(A_j;\mathcal{C})p_i r_{ij}/\Pi_j, \quad i\neq j \, .\end{aligned} \tag{14}$$

It is evident from these equations that multicomponent percolation clusters differ from ordinary percolation structures in that the probabilities $p_{ij}^B(\mathcal{C})$ depend on the reaction matrix elements, i.e., on the kinetic condition associated with the growth.

Figures 3 and 4 show the simulation results for $p(A_1;\mathcal{C})$ and $p_{ij}^B(\mathcal{C})$ for a two-component system with $r_{11}=0.6$, $r_{12}=0.8$, $r_{22}=0.6$, as a function of $p^*=p_1$. The Monte Carlo results were obtained by the analysis of the resulting infinite cluster on a 600×400 square lattice averaged over 50 realizations. The solid lines are the theoretical expressions (6), (14). The agreement between simulations and theory is satisfactory.

Given $p_{ij}^B(\mathcal{C})$, the effective diffusion coefficient D_e can be calculated by means of EMA theory [14,11], and is given by

$$\sum_{i,j\; i<j} p_{ij}^B\frac{D_e-D_{i,j}}{D_e+D_{ij}}+(1-p)=0 \, , \tag{15}$$

where $p_{ij}^B=pp_{ij}^B(\mathcal{C})$ and p is the equivalent percolation probability, Eq. (1). Figure 5 shows EMA calculations in the case $D_{11}=1.0$, $D_{12}=10.0$, $D_{22}=0.1$ arbitrary units, as a function of $p^*=p_1$, together with the simulation results obtained by applying a finite-difference algorithm and by making use of the exponential scaling typical of diffusional relaxation for the numerical evaluation of the diffusion coefficient. The details of the numerical simulation method are fully described in [15,16] and are therefore omitted here. In [15] it is discussed how finite-difference techniques can be applied to transport problems in fractal and disordered lattice structures and can be extended to analyze nonlinear transport phenomena [17] which would be extremely difficult to handle within the framework of Monte Carlo simulations. In [16] a detailed description is presented of the relaxation analysis of a diffusion experiment in a random resistor network leading to the estimate of D_e.

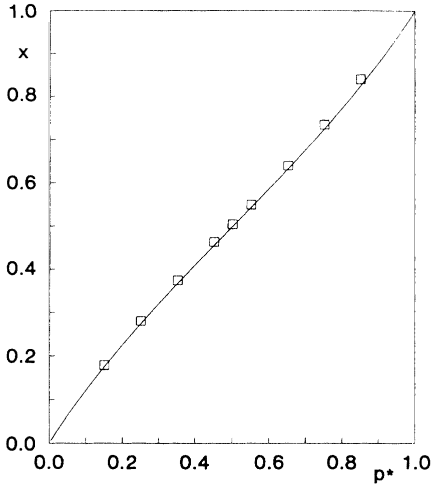

FIG. 3. $x=p(A_1;\mathcal{C})$ vs $p^*=p_1$ for $r_{11}=0.6$, $r_{12}=0.8$, $r_{22}=0.6$. The solid line is the theoretical result, Eq. (6), and the points the simulation results.

Comparison of the simulation results and EMA predictions indictates that EMA theory is able to capture the behavior of D_e qualitatively: the value of $p^*=p_1$ for which D_e attains its maximum predicted by EMA theory coincides practically with the numerical result. However, theory and experiments show a significative quantitative discrepancy. This is fundamentally due to the fact that for p^* ranging between 0.15 and 0.85, the value of

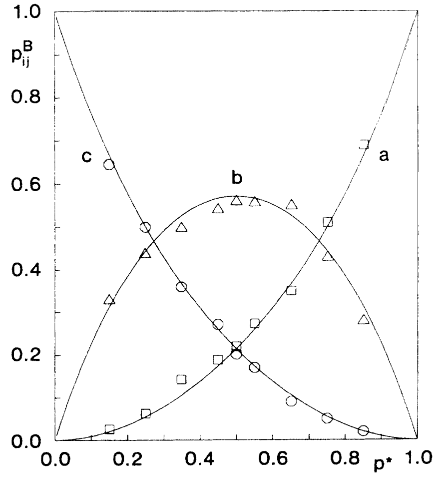

FIG. 4. $p_{ij}^B(\mathcal{C})$ vs $p^*=p_1$ under the same conditions as Fig. 3: (a) $p_{11}^B(\mathcal{C})$; (b) $p_{12}^B(\mathcal{C})$; (c) $p_{22}^B(\mathcal{C})$. The solid lines are the theoretical results, Eq. (14), and the points the simulation results.

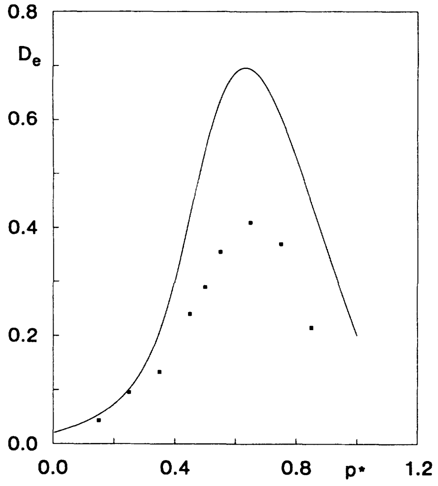

FIG. 5. D_e vs $p^*=p_1$ for the two-dimensional multicomponent percolation clusters of Figs. 3 and 4: $D_{11}=1.0$; $D_{12}=10.0$; $D_{22}=0.1$. The solid line is the value predicted by EMA theory, Eq. (15), the points are the numerical results. The diffusivities are expressed in arbitrary units.

the equivalent percolation probability varies between 0.65 and 0.70, and it is known that for such low values of the percolation probability EMA theory is not able to furnish a correct value of the diffusivity (conductance) [14].

Of course, similar calculations can be performed for different operating conditions, i.e., for different **R** and $\underline{p}$. It is important to point out that the numerical method employed [16] is a powerful tool for the numerical estimate of transport parameters and is more closely related to the phenomenological description of transport than Monte Carlo simulations based on "complex" definitions of the random walk probabilities (as in the case of the RRN problem, which in random walk simulation implies the introduction of a process having different properties in the normal and in the superconductive regions of the material; see [18] for more details).

V. APPLICATION TO NONISOTHERMAL REACTIONS IN GRANULAR MATERIALS

One of the most interesting applications of multicomponent percolation is the analysis of chemical reaction schemes in granular materials. The most relevant case is given by exothermal reactions, in particular in conditions where the enthalpy of reaction is sufficiently high to maintain the reactions with no external energy transfer (self-sustained propagation). These reactions are usually indicated with the acronym SHS, self-sustained high-temperature synthesis, and arise in the production of ceramic materials [19,20]. Following Varma, Cao, and Morbidelli [19], SHS reactions can be modeled by simple kinetic schemes $A+B\rightarrow$product. By assuming a simple axial dispersion model of the heat transfer and by considering that the reaction can be modeled as first order with respect to one of the reactants (e.g., A) and zero order with respect to the other (B) [19], the energy and balance equation reads

$$\begin{aligned} \langle \rho c_p \rangle \frac{\partial T}{\partial t} &= k\frac{\partial^2 T}{\partial z^2} + k_0(-\Delta H)c\exp(-E/RT) \\ &\quad - U'(T-T_0) - \sigma(T^4-T_0^4)\,, \\ \frac{\partial c}{\partial t} &= -k_0 c\exp(-E/RT)\,, \end{aligned} \tag{16}$$

where T is the temperature, c the reactant concentration (in this case A), $\langle \rho c_p \rangle$ the average specific heat per unit volume, k the thermal conductivity, k_0 the prefactor in the reaction rate, T_0 the external temperature, ΔH the enthalpy of reaction (negative for an exothermal reaction), E the activation energy, $U'=4U/D$ the effective heat transfer coefficient in cylindrical geometry (U is the heat transfer coefficient and D the pellet diameter), T_0 the external temperature, and $\sigma(T^4-T_0^4)$ the radiative contribution to heat transfer. Unless explicitly mentioned we shall overlook the radiative term. The standard initial and boundary conditions read $T(z,0)=T_0$, $c(z,0)=c_0$; $T(0,t)=T_h$ (T_h is the forcing temperature on one side of the pellet); $k[\partial T(L,t)/\partial z]=U(T-T_0)$. In dimensionless terms, by setting

$$\begin{aligned} &T_{\text{ref}}=E/R=T_{\text{activation}},\quad t_{\text{ref}}=1/k_0\,, \\ &\tau=t/t_{\text{ref}},\quad x=z/L,\quad \theta=T/T_{\text{ref}},\quad \eta=1-c/c_0\,, \end{aligned} \tag{17}$$

the differential scheme attains the form

$$\begin{aligned} &\frac{\partial\theta}{\partial\tau}=\gamma\frac{\partial^2\theta}{\partial x^2}+\beta(1-\eta)\exp(-1/\theta)-\delta(\theta-\theta_0)\,, \\ &\frac{\partial\eta}{\partial\tau}=(1-\eta)\exp(-1/\theta)\,, \\ &\theta(x,0)=\theta_0,\quad \eta(x,0)=0,\quad \theta(0,\tau)=\theta_h\,, \\ &\left.\frac{\partial\theta(x,\tau)}{\partial x}\right|_{x=1}=\delta_1(\theta-\theta_0)\,, \end{aligned} \tag{18}$$

where $\gamma=k/(k_0\langle\rho c_p\rangle L^2)$, $\beta=(-\Delta H)c_0/(T_{\text{ref}}\langle c_p\rangle)$, $\delta=4\delta_1/D$, and $\delta_1=U/(\langle\rho c_p\rangle k_0)$.

The conversion η is the fraction of the reactant which has reacted up to time t. This system of partial differential equations can be simply solved numerically, as discussed in various articles [19,20], in order to obtain information on reaction evolution and stability. It is important to stress that the local model of the form (16) comes from a local averaging approach which could be a fairly crude approximation in dealing with solid-solid reactions in granular materials. In particular, these models do not furnish any information about the geometric structure of the product cluster, which is an important parameter for testing the quality of the reaction product, and are not suited for the analysis of instability and oscillation effects deriving from a random distribution of reactants.

In order to obtain such information, kinetic models of reaction propagation in disordered lattice structures are the only alternative, and multicomponent percolation schemes seem particularly suited for this task. This can be simply done by considering the simultaneous propagation of a thermal pointwise field $T=T(\underline{x},t)$ diffusing on the structure (lattice) and by assuming that the reaction matrix depends in each site on the local temperature

$$r_{ij}=r_{ij}(T)=r_{ij}^0\exp[-E/RT(\underline{x},t)]\ , \tag{19}$$

with $0\leq r_{ij}^0\leq 1$. The lattice simulation is therefore reduced to the simultaneous propagation of the temperature field and of the reaction front.

In principle, these kinds of simulation can be carried out by means of a modified Leath algorithm [21] which also takes into account the propagation of the thermal field. Since these simulations can be developed in many different ways which admit an interesting physical and kinetic meaning, it is worth considering the simulation details carefully.

VI. SIMULATION CONDITIONS

The dynamic analysis of multicomponent percolation schemes can be developed by considering the Monte Carlo propagation of the reaction front in a similar way to the classical Leath algorithm. To simplify the matters, let us consider the case of a single reactant, analogously to the averaged differential models of the preceding section, forming a product P.

The simulation of the simultaneous heat and mass transfer can be performed in many ways since two different problems can be brought into focus: (1) the "purely" percolation problem of the evolution of a reaction front modulated by the temperature field, which implies the propagation of a spreading percolation in the presence of a variable percolation probability depending on $T(\underline{x},t)$; and (2) the definition of a lattice simulator for exothermic reactions in granular materials in order to study the structural properties of the product cluster.

These two problems are quite similar but show some differences and therefore lead to different simulation strategies. Let us consider first the percolation problem of reaction evolution with a reaction probability depending on the temperature field associated with the heat generation produced by the reaction itself. This phenomenon can be modeled with a classical Leath algorithm, by considering both blocking (as in the case of the classical Leath algorithm) and nonblocking conditions. Nonblocking conditions imply that, given one site on the reaction front, if a nearest-neighbor site will not aggregate to the cluster, it will not be blocked and can eventually aggregate as the reaction proceeds.

In Monte Carlo simulations, the kinetic Arrhenius term (19) must satisfy the closure condition that for a temperature equal to the activation temperature it should be equal to the corresponding percolation threshold, i.e.,

$$r=\exp(-\theta_p/\theta),\quad \theta_p=-\ln(p_c)\ . \tag{20}$$

The evolution equation for the dimensionless temperature $\theta_{(i,j)}^n=\theta(x_i,x_j,t_n)$ may be written on the lattice in terms of an explicit finite-difference scheme. In two dimensions,

$$\theta_{(i,j)}^{n+1}=\theta_{(i,j)}^n+\frac{\Gamma}{4}\sum_{(h,k)\in I(i,j)}[\theta_{(h,k)}^n-\theta_{(i,j)}^n]+\Delta(\theta_{(i,j)}-\theta_0)+Bh_{(i,j)}^{n+1}\ , \tag{21}$$

where $h_{(i,j)}^{n+1}$ is equal to one if the site (i,j) has been aggregated to the growing cluster at time $n+1$ and is zero elsewhere. In Eq. (21), $I(i,j)$ indicates the set of the nearest neighbors of the site (i,j). This kind of modeling implies that the reaction evolves only at the reaction front and therefore only a single connected cluster is formed.

Of course, another simulation alternative arises from the fact that the reactant may react in every point in the lattice depending exclusively on the value of the local temperature field $\theta_{(i,j)}$. Even in this case, blocking and nonblocking conditions can be considered. This situation will not, however, be considered here.

VII. STABILITY AND PROPAGATION

We shall consider here only the percolation problem of the growth of the reaction cluster in blocking conditions. In the adiabatic case $\Delta=0$, the only two parameters entering the model are the dimensionless conductivity Γ and the enthalpic constant B. Of course if an explicit algorithm is adopted for the temperature propagation then $\Gamma\leq 1$.

Figure 6 shows the value of the average conversion $\langle\eta\rangle$ as a function of B for different values of Γ. The average conversion $\langle\eta\rangle$ is defined as the average of $\eta(x,y,t)$ over the y axis, i.e., along the direction orthogonal to the propagation direction of the reaction front. The simulations were performed in the simple case of a single species, $p_1=1$ with $r=r_{11}$ given by Eq. (19). These results were obtained by averaging over 100 realizations on a 200×200 square lattice. The initial conditions of the simulation are uniform temperature $\theta_0=0.1$ over all the lattice and uniform distribution of the reactant $(p_1=1)$. The boundary conditions are a forcing temperature $\theta_h=1.0$ on one side of the pellet $(x=0)$ and adiabatic condition elsewhere. At time $t=0$, $x=0$, a fraction of sites is activated (i.e., belongs to the product cluster) with probability r given by Eq. (20), in which $\theta=\theta_h$: it

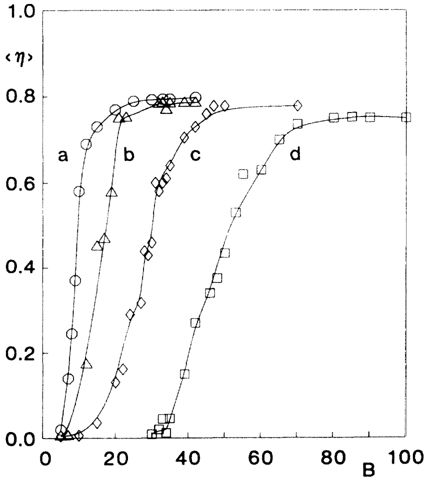

FIG. 6. Average conversion $\langle\eta\rangle$ vs B for different values of Γ: (a) $\Gamma=0.9$; (b) $\Gamma=0.7$; (c) $\Gamma=0.5$; (d) $\Gamma=0.3$. The solid lines are merely a visual aid.

represents the starting condition in the growth of product cluster.

It should be noted that the conversion increases with increasing of the heat conductivity since the heat bursts induced by the reactive events propagate faster in the lattice. The structure of the reaction front averaged over 200 sites is shown in Fig. 7 for two different values of B. Of course, for larger values of B, the velocity of the reaction increases, and the structure of the reaction front is more regular since it is less affected by random fluctuations.

The analysis of the dynamic scaling of the reaction propagation can be studied by means of Monte Carlo simulations. However, it is possible to consider the equivalent stochastic differential model

$$\begin{aligned}
&\frac{\partial\theta}{\partial\tau}=\gamma\frac{\partial^2\theta}{\partial x^2}+\beta(1-\eta)\xi+\delta(\theta-\theta_0)\ ,\\
&\frac{\partial\eta}{\partial\tau}=(1-\eta)\xi\ ,\\
&\theta(x,0)=\theta_0,\quad \eta(x,0)=0,\quad \theta(0,\tau)\theta_h\ ,\\
&\left.\frac{\partial\theta}{\partial x}\right|_{x=1}=\delta_1(\theta-\theta_0)\ ,
\end{aligned}\tag{22}$$

where $\xi=\xi(\underline{x},t)$ is a stochastic perturbation having the following statistical features:

$$\begin{aligned}
&\langle\xi(\underline{x},t)\rangle=\exp[-1/\theta(\underline{x},t)]\ ,\\
&\langle\xi(\underline{x},t)\xi(\underline{y},\tau)\rangle=\sigma_\xi^2\delta(\underline{x}-\underline{y})\delta(t-\tau)\ .
\end{aligned}\tag{23}$$

The analysis of this stochastic scheme can be carried out by means of the same numerical and theoretical techniques typical of the dynamic scaling of surface growth [9]. The dynamic scaling analysis of such models will be considered elsewhere. However, it is important to observe that the conversion η is limited by one (total conversion). Therefore, in order to apply the scaling analysis in similar fashion to that developed for the KPZ equation or for analogous models of unlimited growth, it is convenient to consider the fluctuations in the total conversion along the direction of the reaction front propagation, or other similar global parameters which are unbounded.

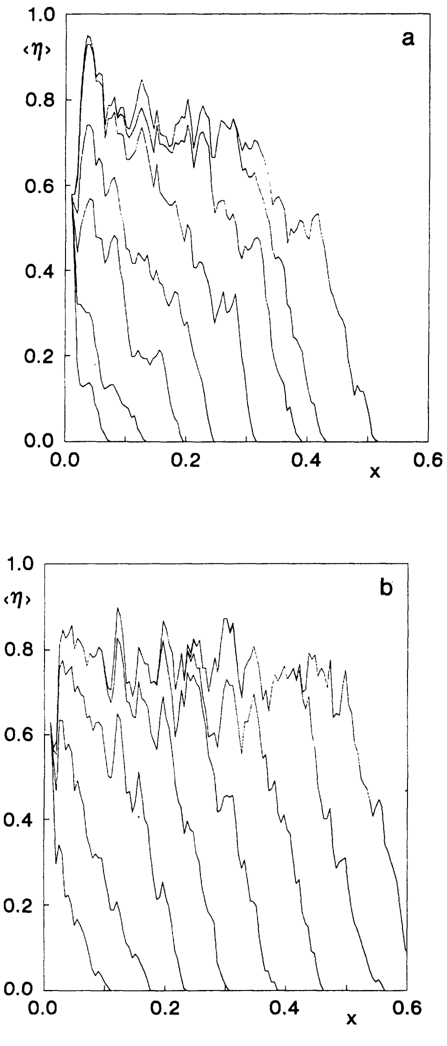

FIG. 7. Average conversion $\langle\eta\rangle$ in different time instants in the direction x of the reaction front propagation, $\Gamma=0.5$. (a) $B=31.0$; (b) $B=35.0$. The conversion profiles of the two figures are evaluated at the same time intervals.

VIII. CONCLUDING REMARKS

We have proposed a method for simulating reactions in a lattice structure involving an arbitrary number of species. The probabilistic analysis developed in this article enables us to obtain the percolation probability as a function of the parameters $(\underline{p},\mathbf{R})$ involved in the model. The estimate of $p(\alpha;\mathcal{C})$ and of $p_{ij}^B(\mathcal{C})$, i.e., of the distribution of the species in the product cluster, can be useful for developing an effective-medium approximation of multicomponent percolation schemes. The initial results show a considerable deviation between EMA theory and simulation results. This point deserves further theoretical analysis.

We have also analyzed the possibility of treating simultaneous heat and mass transfer with reaction in percolation models, presenting some preliminary results on the propagation of the reaction as a function of the diffusive and enthalpic parameters.

The propagation of a reaction front in the presence of a temperature field depending on the reaction itself represents an interesting new model in field theory in the presence of fluctuations [e.g., the Kardar-Parisi-Zhang (KPZ) equation or other models of surface growth [9]]. The presence of the "feed-forward" effect induced by heat generation associated with the reaction evolution should modify the dynamic universality class, in the absence sense that the dynamic exponents of this propagation model are different from those characteristic of the evolution of the reaction front in the absence of thermal effects, extensively analyzed by Sapoval, Rosso, and Gouyet [22]. For this purpose both Monte Carlo simulations on a lattice and stochastic differential formalism can be used.

Apart from these theoretical aspects, the development of multicomponent percolation schemes can be useful for analyzing solid-solid reactions of industrial interest.

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