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AT MINERAL SURFACES AND IN POKE NETWORKS**

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AUTHOR(S) *J. T. Wells, D. R. Janecky, B. T. Travis*

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**A LATTICE GAS AUTOMATA MODEL FOR HETEROGENEOUS
CHEMICAL REACTIONS AT MINERAL SURFACES AND IN PORE
NETWORKS**

J.T. Wells

Dept. of Geol. Sci., University of Washington,
Seattle, WA 98195

D.R. Janecky

Los Alamos National Laboratory, Isotope Geochemistry Group,
Los Alamos, NM 87545

B.J. Travis

Los Alamos National Laboratory, Geoanalysis Group,
Los Alamos, NM 87545

ABSTRACT

A lattice gas automata (LGA) model is described, which couples solute transport with chemical reactions at mineral surfaces and in pore networks. Chemical reactions and transport are integrated into a FHP-I LGA code as a module so that the approach is readily transportable to other codes. Diffusion in a box calculations are compared to finite element Fickian diffusion results and provide an approach to quantifying space-time ratios of the models. Chemical reactions at solid surfaces, including precipitation/dissolution, sorption, and catalytic reaction, can be examined with the model because solute diffusion and mineral surface processes are all treated explicitly. The simplicity and flexibility of the LGA approach provides the ability to study the interrelationship between fluid flow and chemical reactions in porous materials, at a level of complexity that has not previously been computationally possible.

1. Introduction

Chemical reaction processes are often spatially distributed in both natural and engineered systems. Many of these systems also involve intrinsically coupled hydrologic and chemical processes. In natural systems, a detailed description of mineral-fluid interaction is critical to our understanding of a wide variety of geochemical processes, including weathering, diagenesis, and hydrothermal alteration. There are a variety of practical geochemical problems which demand sophisticated modeling capabilities. In petroleum reservoirs, issues of interest include oil migration, secondary recovery processes, and the evolution and/or manipulation of porosity. Similarly, reactions during groundwater flow and contaminant migration are important in environmental systems.

As chemical reaction models have become increasingly comprehensive, it has been recognized that chemical reactions between rocks and aqueous solutions are heterogeneous on both spatial and temporal scales, and that new modeling approaches are required to better understand many pressing issues. Interrelated factors such as rock texture, mineral distribution, and pore or fracture network geometry all effect processes of mineral dissolution, deposition, and mass transport. For bulk reactions or large scales of tens to thousands of meters, models of geochemical processes have provided significant insights using averaged or phenomenological descriptions of the permeability, fluid flow fields, mineral distributions, and fluid composition.¹ There are also models for reactions on the molecular scale.² Between these two scales, however, there is a paucity of general and flexible models of fluid-rock interaction. This intermediate scale is particularly important to a quantitative understanding of both geochemical and flow processes in natural porous media because it is precisely the scale at which most detailed analytical, experimental, and descriptive methods provide information. In addition, describing coupled fluid flow and chemical reactions has proven to be especially difficult using conventional modeling techniques.³⁻⁶ This is particularly true for transient problems in which fluid flow and/or mineral reaction rates vary as a function of time.

Rothman⁷ and Travis and others⁸ examined potential applications of lattice gas automata (LGA) methods to geological problems by formulating models to simulate flow through complex porous media. We are investigating LGA models for simulating coupled solute transport and chemical reactions at mineral surfaces. Primary advantages of this approach are

that coupled fluid flow-chemical reaction processes are implicitly included, and that processes can be simulated which are heterogeneous in both space and time. Thus, LGA calculations appear to be ideally suited to the analysis of systems in the critical intermediate spatial scale range. The addition of chemical reactions and solute transport to LGA models of porous flow, as described here, constitutes a powerful new tool for the computational analysis of complex geochemical processes. Of particular interest are the pore-scale description of porous media and information about spatial and temporal heterogeneities in flow and reaction.

II. Lattice gas automata hydrodynamic model

The core of our approach is a LGA hydrodynamic model. Such models are being developed and applied to the investigation of 2 and 3-D hydrodynamic processes.⁹⁻¹¹ The chemical reaction algorithm is designed to be integrated into the hydrodynamic codes as a relatively self-contained module. All calculations presented in this paper use the minimal collision 2-D FHP-I model of Frisch, Hasslacher, and Pomeau.¹² In the FHP-I model, fluid particles travel on a hexagonal symmetric lattice. Up to six particles can occupy any node, but exclusion rules allow only one particle travelling in any one direction to occupy a node. This model has been shown to provide a numerical solution to the two-dimensional Navier-Stokes equations, and thus is capable of modeling real systems.^{12,13}

LGA collision rules satisfy conservation of momentum and particle number at every node on a lattice. In an FHP-I model, two types of collisions are recognized, head-on two particle collisions and symmetric three-particle collisions. Particles involved in a collision are simply rotated 60 degrees. For two-particle collisions, particles rotate clockwise half of the time and counterclockwise the other half of the time. Particle-wall collisions result in the 180 degree rotation of the particle, maintaining a no-slip boundary condition.

III. Chemical reaction sub-models

The simplest models for chemical processes in a porous media involve diffusion in the solvent occupying pores, and reactions at solid surfaces. Our predominant interest is in systems involving solutes in an aqueous

solvent, however, chemical processes in oil or gas saturated systems or even two-phase systems¹⁴ can also be examined using the LGA method. Surface reactions may involve significant mass transfer via dissolution and/or precipitation, which modifies the pore network structure and thus the hydrodynamic environment. When the components of interest are at minor or trace concentrations, sorption and desorption reactions become important and the pore network may be either fixed or variable. Catalytic reactions of solutes at solid surfaces could also be modeled using this approach. To provide the flexibility to model such processes, the chemical state of the system is described in parallel to the hydrodynamic state. Thus, the concentration of each chemical species or component is stored for every fluid and solid node. Calculation of chemical processes is integrated with the flow calculations at each time step after movement of the particles on the lattice and before the analysis of collision results. Such an approach is not limited to one solute species or immiscible species. In addition, as noted above, the approach is directly portable between LGA models.

A. Diffusion

Solutes are transported down a concentration gradient by diffusion. To simulate diffusion in an LGA model, a concentration of an hypothetical solute is assigned to each open space node. If the mass of solute or changes in the mass of solute are small relative to the total mass of solution, only minor perturbations of unit momentum for the lattice particles are involved which can be ignored. This approach to solution composition tracking is similar to the energy tracking approach of Sero-Guillaume and Bernardin.¹⁵ Each particle is assigned a concentration equal to that of the node at which it is residing. During each time step, particles travel to new nodes and the concentration of those nodes is assigned the concentration of the arriving particle. If more than one particle arrives at a node during a time step, the resulting concentration at that node becomes the mean concentration of all particles (Figure 1). During the next time step, all particles carry the mean concentration to their next destination. This method of simulating diffusion contrasts with models for inter-diffusion of different types or species of particles,^{16,17} in several ways. Primarily, extension of the approach to multicomponent diffusion is fairly straight forward. In addition, the rate of diffusion can potentially be varied for all solutes or between solutes by merely transferring increments of concentration between

nodes by the flow of LGA particles.

This approach has been examined by performing a set of calculations of diffusion in a closed box (Figure 2). The initial concentration field consists of a step function in which the concentration equals 32 arbitrary units in the left half of the box, and 8 units in the right half. Mean concentration profiles at different time steps for the LGA calculation are in good agreement with profiles calculated using a finite difference technique (Figure 3). Each point on the observed profiles constitute the average value of each column in the box. This calculation was performed with an average density of 1.2 particles per node, or a reduced density (particles per direction per node) of 0.2.

The overall rate of diffusion is a function of the particle density and frequency of interactions (Figure 4). By keeping track of concentration on the level of nodes rather than particles, concentration exchange between particles occurs even without collision when multiple particles reside on a single node. The resulting diffusion coefficients are relatively independent of mean free path for particle collisions. However, diffusion coefficients are strongly dependent on component mass on the lattice, which increases linearly with particle density. In addition, diffusion profiles tend to be smoother and less noisy as particle densities and number of nodes in the box increase.

The LGA model has no intrinsic temporal or spatial scale; however the rate of diffusion may be used to delineate the space-time relationships of models that are being applied to real physical problems. For instance, if we are interested in diffusion of ions in an aqueous solution, we can choose a diffusion coefficient of $10^{-9} \text{ m}^2\text{sec}^{-1}$, which is an appropriate value for several ions of geological importance such as Ca^{++} , Cl^- , and Fe^{+++} .¹⁸ By choosing either the nodal dimension or the length of the time step, the other quantity can be determined by comparing LGA results to Fickian diffusion calculations. For example, at a reduced density of 0.2 if we assume the LGA model time step is 1 second and the diffusion coefficient above, the nodal spacing is 0.002 m.

B. Surface reactions

Surface reactions involving dissolution and precipitation are simulated by allowing wall nodes to serve as sources or sinks for mass of a dissolved component. Whenever a particle collides with a wall, a unit of mass may

be exchanged, thus increasing or decreasing the local concentration in solution depending upon the saturation state of the fluid (Figure 5). A probability of mass transfer is defined for each collision which is a function of the saturation state of the mineral (Figure 6). The maximum probability can be adjusted to match the reaction rate of the mineral of interest. The shape of the probability function in Figure 6 was designed to be consistent with transition state theory in which the rate of reaction is a function of the degree of disequilibrium between fluid and mineral.¹⁹ The probability function is also consistent with thermodynamic theory in that the probability of mass transfer is zero at equilibrium.

After some large number of mass transfer events in an undersaturated fluid, a wall node becomes an open space node, simulating dissolution (Figure 5). Similarly, after some number of supersaturated mass transfer events, an open space node becomes a wall node, simulating mineral precipitation. The number of events required to create or destroy a wall node depends on the relative concentrations per unit volume in the solvent and solid phases.

Many mineral dissolution reactions are spatially heterogeneous. For example, crystallographic defects are sites of excess strain energy which constitute regions especially favorable to dissolution.²⁰ Such heterogeneous surface reactions can be simulated with the LGA model by increasing the probability of mass transfer in linear zones of a mineral. Figure 7a shows the early stages of a dissolution calculation with a central zone of enhanced probability of mass transfer. Over the course of this simulation the entire wall recedes slightly, but the central region dissolves more readily, resulting in an etch pit (Figure 7b). The local solution concentration within the etch pit is about the same as the concentration of the bulk fluid. This is the expected configuration for surface-controlled dissolution in which the rate-limiting step is the actual detachment of molecules from the mineral surface.

The LGA model can also be used to model transport-controlled dissolution in which the rate-limiting step is the diffusion of the dissolved component away from a mineral surface. This is an important capability which is possible because the LGA model explicitly treats both the fluid and the mineral surface. Other modeling approaches are limited to treating only the mineral surface²⁰ which precludes examination of diffusion control on etch pit formation and surface dissolution. Figure 7c illustrates an etch pit dissolution calculation that is partially diffusion-controlled. In this example

the local solution concentration within the etch pit is much higher than the concentration in the bulk fluid. In the etch pit, concentration is close to the saturation point (40 concentration units in this example), thus the local probability of mass transfer is low (Figure 6b) and continued dissolution relies on the ability of the solute to diffuse out of the etch pit. Thus, for similar extents of reaction, the calculation illustrated in Figure 7c was run longer than that for Figure 7b.

Extension of these models to multiple solid phases for a single component or sorption of a trace component on surfaces is straight forward. Reactions among multiple species in solution and reactions involving multicomponent solid phases will involve expansion to multiple component tracking arrays and formulation of an efficient approach to reactions between components.

IV. Coupled Fluid Flow and Chemical Reactions

Numerical models that describe coupled fluid flow and multi-component chemical reactions in geological environments have proven very difficult to implement. The transient form of the flow-reaction equations are particularly computationally unwieldy. The LGA approach is a viable alternative to the more conventional finite difference and finite element methods because it can be applied to systems, such as porous solids, with complex boundary conditions between explicit solid and solution phases. It does not rely on averaged values for porosity and permeability, and it is well-suited for the analysis of spatial and temporal heterogeneities in solute transport and reactions, as discussed above.

Rothman⁷ demonstrated the potential of LGA methods for modeling flow through porous geologic media. Our representations of chemical reactions and diffusion can be added to the LGA model of flow through porous media to give a fully coupled model of water-rock reactions and fluid flow. An example of a simple porous flow model is shown in Figure 8a. In this figure, the vectors represent the local fluid velocity without surface reactions, averaged over seven adjacent nodes and over 1000 time steps. The concentration field that results from the reaction of a wall mineral with an initially undersaturated fluid is clearly inhomogeneous (Figure 8b). The concentration within the principle flow channel is relatively low, whereas the concentration in dead-end pores and around obstructions is relatively high. Dissolution within the pore network is illustrated in figure

8c. This type of simulation has important implications for increasing our understanding of the relationship between porosity and permeability in dynamic systems in which mineral dissolution and growth alter the porous structure of a rock.

The effect of reaction and transport heterogeneities on the overall evolution of fluid composition and rock porosity and permeability is not well understood at this time, but is certainly a function of fluid velocity, rock composition, and the geometry of the porous network. The LGA approach has the great potential to aid in investigations of these phenomena.

V. Summary

We have presented a lattice gas automata model which couples solute transport with chemical reactions at mineral surfaces and in pore networks. The model can treat both surface-controlled and transport controlled mineral reactions because solute diffusion, fluid flow, and mineral surface detachment processes are all treated explicitly. It is particularly useful for the analysis of porous media problems in which fluid flow and mineral reactions are heterogeneous in space and time. The simplicity and flexibility of this lattice gas automata approach provides the ability to study the interrelationship between fluid flow and chemical reactions in porous materials at a level of complexity that has not been computationally possible in the past.

VI. Acknowledgements

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Figure Captions

Figure 1. Diffusion process for a hypothetical solute in the LGA solvent. Concentrations are associated with nodes, and carried by particles which mix when multiple particles reside on a node.

Figure 2. Diffusion profiles at 1600 steps for 128^2 box with initial concentration step of 32 to 8 units. A concentration surface is illustrated in **a**, while **b** shows average profile (solid line), one standard deviation from average for each row (dotted lines), and extrema for each row (dashed lines).

Figure 3. Comparison of diffusion profiles for 0, 1000 and 10000 steps (solid lines) with results from finite element calculation of Fickian diffusion (solid squares).

Figure 4. Reduced diffusion coefficient in nodes per time step relative to average density of lattice particles per direction per node for 128^2 (solid boxes), 32^2 (pluses), and 256^2 (X) boxes.

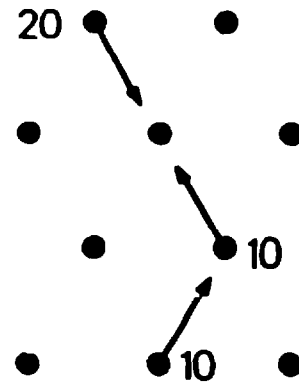
Figure 5. Surface reaction processes for undersaturated lattice particles colliding with solid surface (**a**), rebounding in the next time step (**b**) with one particle having incremented its concentration, and after many concentration transfers to solution, the transformation of a solid node into a solution node (**c**).

Figure 6. Representative probability function for dissolution, equilibrium, and precipitation as a function of concentration which corresponds to a transition state theory rate law.

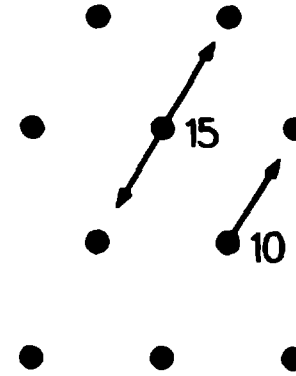
Figure 7. Static dissolution experiment for a hypothetical single component solid into a solution with initial concentration of 10. A line defect in the center of the solid phase dissolves more rapidly to create an etch pit. The system configuration at 1000 time steps is shown in **a**. When surface detachment reactions control the rate of reaction, the concentration in the etch pit is only slightly elevated over bulk solution (**b** at 18000 time steps). In contrast, when the dissolution process is partially controlled by diffusion in solution, the concentration in the etch pit is significantly elevated and equivalent etch pit depth is reached at 24000 time steps (**c**).

Figure 8. An example reaction in a pore network with flowing solution results in modification of the structure from **a** at 0 time steps to **b** at 200 time steps. The initial and input solution has zero concentration and interaction with soluble walls results in a heterogeneous concentration field and dissolution pattern (**c**).

Fig 4

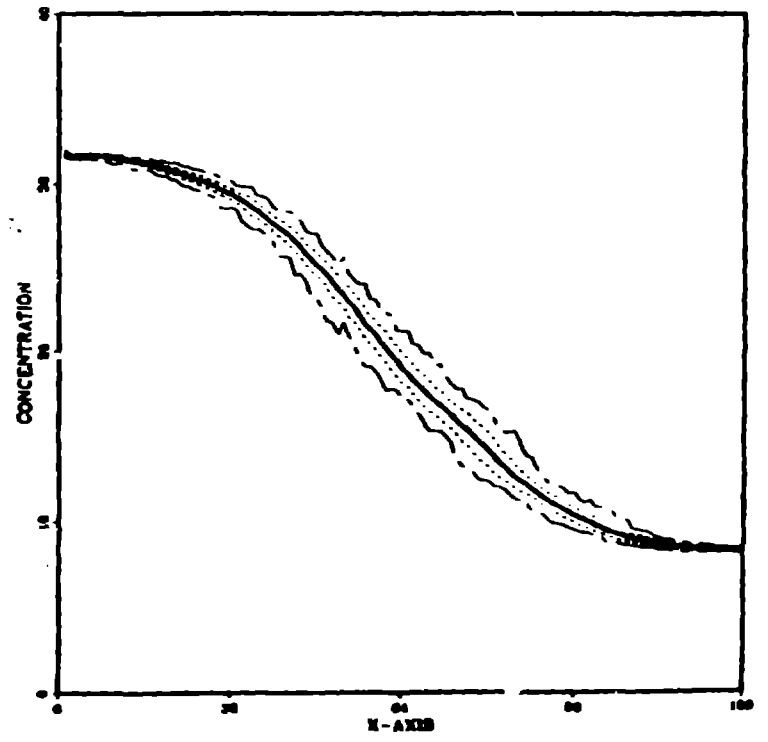
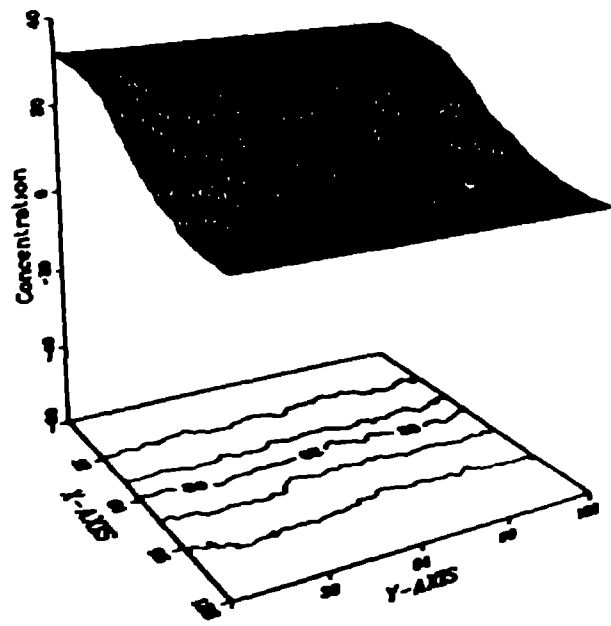


Time = t



Time = t+1

51



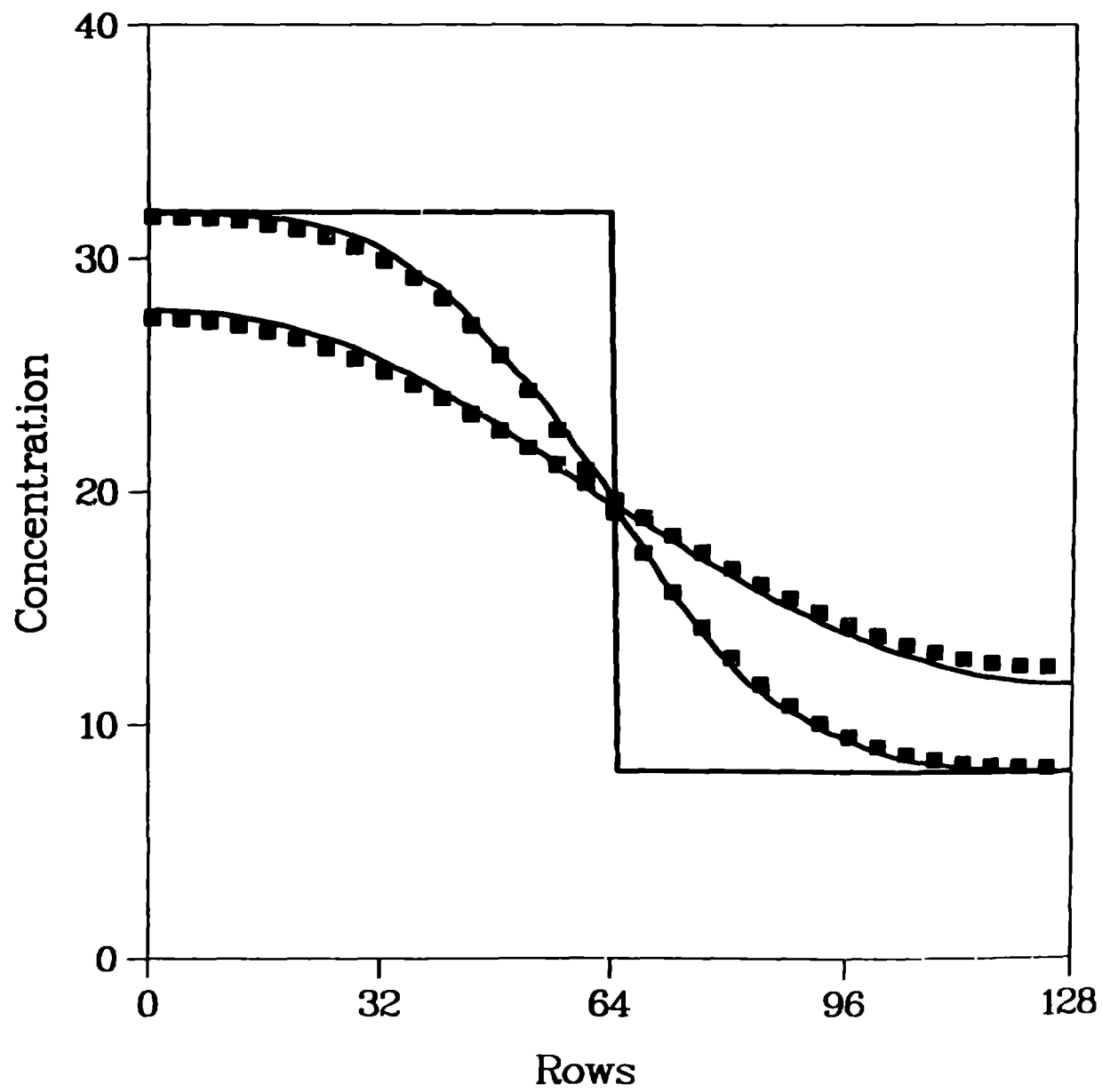


Fig 4

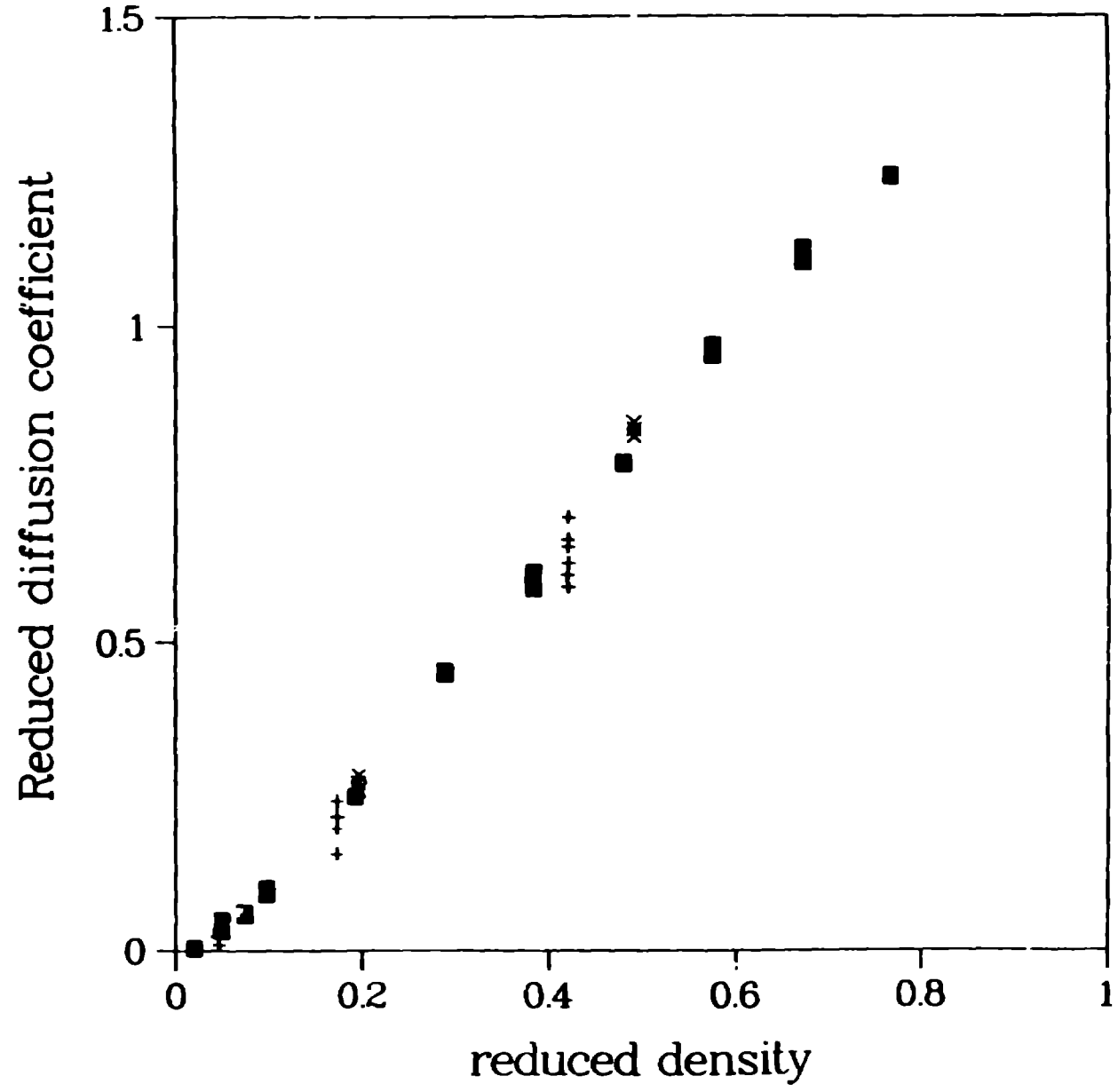
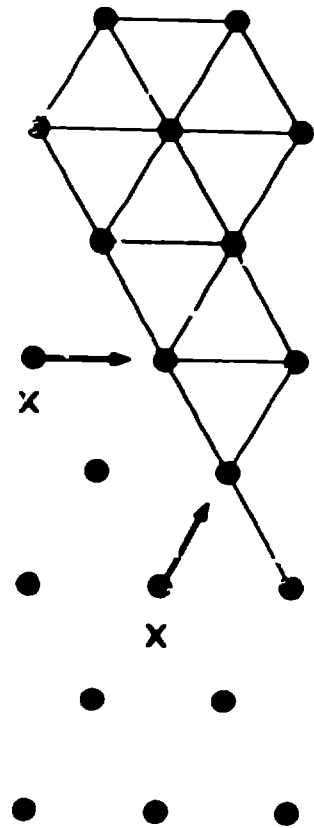
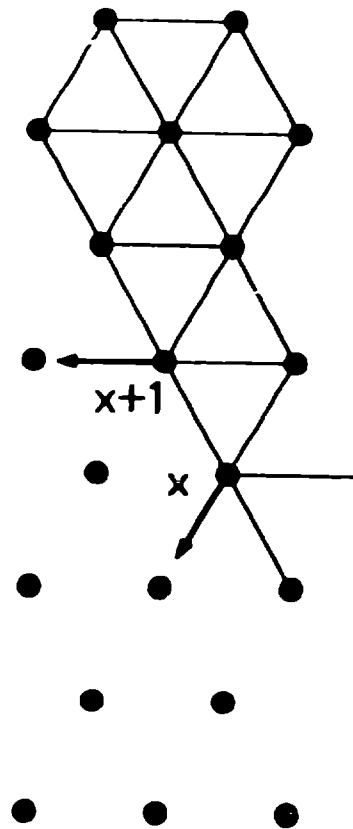


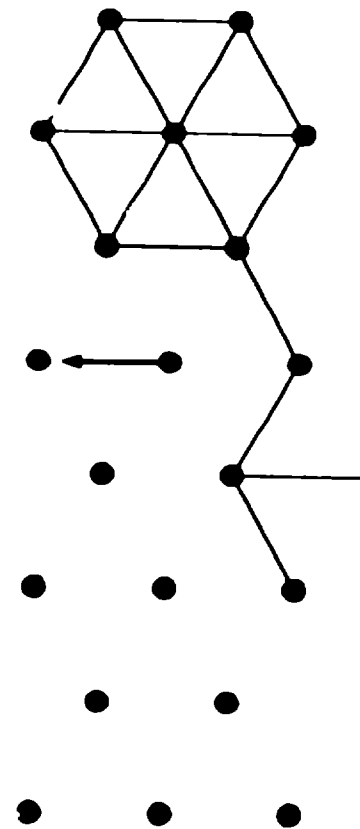
Fig 5



Time = t



Time = t+1



Time = t+n

Fig 6.

100

Probability of Mass Transfer

