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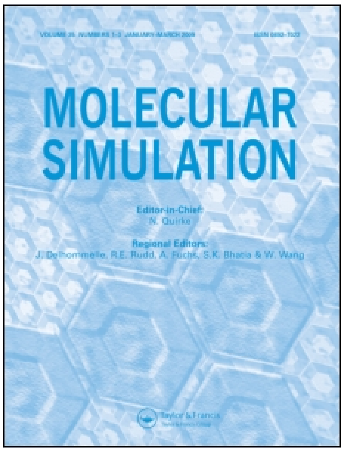

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Diffusion in Random Structures in the Critical Region

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Diffusion in Random Structures in the Critical Region

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We present computer simulation results showing how proximity to the critical point affects transport phenomena in fluids confined in quenched, random porous structures. The simulation approach taken is based upon a relaxation-dynamics method, which we have previously studied in homogeneous systems. The method utilizes an ensemble consisting of two identical isothermal chambers initially separated by an impermeable partition. The fluid configurations in each chamber are initially pre-equilibrated at densities $\bar{\rho} + \varepsilon$ and $\bar{\rho} - \varepsilon$, respectively, where $\bar{\rho}$ reflects an average density of interest and ε a small perturbation about this value. After the pre-equilibration step the partition is removed and the entire ensemble is allowed to relax towards an equilibrium state guided by a heat-bath, kinetic Monte Carlo computer simulation algorithm. Fickian transport coefficients are found from quantities calculated during this relaxation process.

We illustrate the method's application to transport property calculations in purely diffusive lattice-gases confined in quenched random porous structures. We provide, to our best knowledge, the first simulation results of *critical dynamical properties* in this system.

Keywords: Critical phenomena; Transport; Porous systems; Diffusion; Separations

NOMENCLATURE

B	field term in Ising model
D	Fickian (bulk) diffusion constant
E_i	energy in state i
H_{LG}	lattice-gas Hamiltonian
H_{I}	Ising Hamiltonian
J	spin–spin interaction parameter
K	spin–surface interaction parameter
k	period, $2\pi/L$
k_{B}	Boltzmann's constant
L	size of the system
$m(t)$	number of molecules in chamber at time t
n_i	particle number
N	Number of particles is the system
N_{eq}	iteration counter in simulation algorithm
$P_{i\to f}$	acceptance probability for state i to f
s_i	spin at site i
t	time
T	temperature
T^*	reduced temperature
T_{c}	critical temperature
z	lattice co-ordination number

Greek letters

β	$1/k_{\mathrm{B}}T$
ε	density perturbation
$\bar{\rho}$	mean density
μ	chemical potential
Γ	fluid particle–surface interaction parameter
$\Im$	fluid–fluid interaction parameter

INTRODUCTION

The main phenomenological parameter for calculating concentration-driven transport fluxes in fluid systems is the Fickian diffusion constant. This coefficient allows one to calculate molecular fluxes in both homogeneous and heterogeneous systems; since transport rates in such systems often determine the efficacy of chemical processes, a reliable method for computing these quantities has been a problem of longstanding interest in both chemical and materials engineering. For confined media, the use of computer simulation for doing these types of calculations has been the preferred approach, given the difficulty of

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developing analytic theories for transport properties in complex structures. As a result, the two most common simulation approaches for evaluating these transport coefficients are sometimes referred to as direct and indirect methods, respectively. Direct methods use a phenomenological setup to simulate transport phenomena in the system, a good example of which is the dual control volume grand canonical Molecular Dynamics (DCV-GCMD) method [1,2]. Indirect methods, on the other hand, evaluate dynamical quantities derived from linear response [3] and/or Green–Kubo theory [4,5].

Recently, we described a novel, intuitively formulated computer simulation method for studying diffusion phenomena which we believe has advantages over alternative direct methods [6]. In particular, a method like DCV-GCMD relies upon the calculation of fluxes in the presence of a linear composition profile. This requirement may in practice be quite difficult to ensure during the course of a simulation, where molecular configurations are independently "directed" by the equations of molecular dynamics, for example. Furthermore, Fickian diffusion coefficients found with these direct approaches are usually calculated by dividing flux values by the corresponding composition (density) gradient over which diffusion occurs. This strategy is inherently inaccurate especially in the critical region where the control volume density calculations will be subject to large fluctuations that ordinarily characterize this region.

The method described here adopts a different perspective, one that simulates the dynamics of a diffusive system as it relaxes from an initial non-equilibrium state constructed in a two-chamber ensemble as shown schematically in Fig. 1. We term this entity a *Fickian ensemble* given its phenomenological construction, which was chosen to mimic density-driven diffusion processes. The square-wave profile in the ensemble represents pre-equilibrated high and low density regimes separated initially by an impermeable partition. The two profiles meet at a discontinuous density interface; once the partition is removed, inter-diffusion occurs between both chambers, as the system attempts to relax towards its equilibrium state. No linearity in the composition profile between chambers is required, as we show in a subsequent section where we discuss the computational procedures in more detail.

We have studied the application of the relaxation-dynamics method to transport simulations in homogeneous systems, while in this paper, we present some new results with its application to diffusion in quenched, random porous structures. Diffusion in such media is both practically important and an issue that continues to pose outstanding theoretical questions. For example, the dynamics in such systems are notorious for long equilibration times and are thought to belong to a different critical universality class from the homogeneous case [7]. It is of interest then to see how this simulation method performs in heterogeneous structures, particularly when we extend the simulations into the critical region of the confined fluid for which there are few published results.

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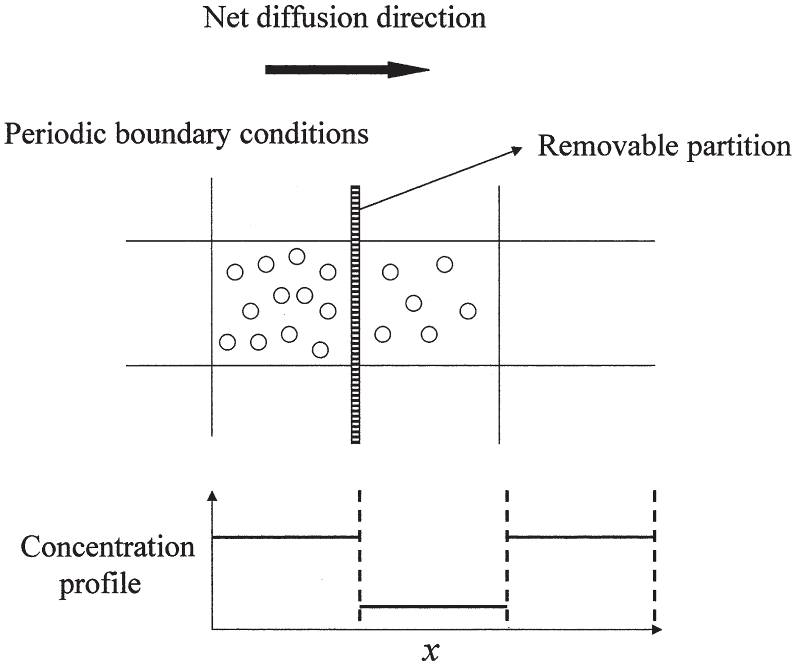

FIGURE 1 Schematic of the Fickian ensemble used for the relaxation-dynamics computer simulation method.

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THE CONFINED FLUID SYSTEM

The Hamiltonian Structure

The confined lattice-gas we consider has a fixed number of matrix pore-blocked sites randomly assigned throughout the structure with density p. The remaining lattice sites are void spaces that may, or may not, be occupied by fluid particles. We consider a simple cubic lattice in d dimensions and for each site define a quenched random variable ε_i, where ε_i can take on either the values 0 or 1. The value of 0, found with probability p, implies the existence of a solid matrix particle at that position in the lattice, while the value 1 designates a void space. In addition, at each void site, we assign an annealed variable n_i which can assume either the value 0, denoting the absence of a fluid particle, or 1 which represents the presence of a fluid particle; the variable n_i is the usual particle density variable associated with the lattice-gas partition function. The variables ε_i are assumed to be uncorrelated, an assumption justified for aerogels, for example. Both nearest-neighbor fluid particle and solid matrix–fluid interactions are accounted for through respective coupling constants.

Given these assumptions, the Hamiltonian H_{LG} for this model system can be formulated as follows:

$$-H_{\mathrm{LG}} = 4\Im\sum_{\langle ij\rangle}\varepsilon_i\varepsilon_j n_i n_j + \Gamma\sum_{\langle ij\rangle}[\varepsilon_i n_i(1-\varepsilon_j) + \varepsilon_j n_j(1-\varepsilon_i)] + \mu\sum_i \varepsilon_i n_i \tag{1}$$

where $4\Im$ is the coupling constant between two adjacent fluid particles, Γ, the coupling constant between a fluid and solid particle and μ, the chemical potential of the fluid. The summation in Eq. (1) (represented by the notation $\langle i,j\rangle$) is over all nearest neighbor i, j pairs but the effect of the ε_i, ε_j variables is to ensure that the first term in the Hamiltonian captures fluid–fluid interactions, the second term represents fluid–solid ones while the third term is the standard field term. By using the relationship connecting lattice–gas variables n_i and Ising spin variable s_i, namely:

$$s_i \equiv 2n_i - 1 \tag{2}$$

we can easily transform Eq. (1) into an equivalent Ising Hamiltonian (up to a constant term) given by the equation:

$$-H_{\mathrm{I}} = J\sum_{\langle ij\rangle}\varepsilon_i\varepsilon_j s_i s_j + K\sum_{\langle ij\rangle}[\varepsilon_i s_i(1-\varepsilon_j) + \varepsilon_j s_j(1-\varepsilon_i)] + B\sum_i \varepsilon_i s_i + F(\varepsilon_i,\ldots\varepsilon_j) \tag{3}$$

where

$$F(\varepsilon_{i,}\ldots\varepsilon_j) = \left[\frac{\mu}{2} + \frac{\Gamma z}{2}\right]\sum_i \varepsilon_i - \Gamma\sum_{\langle ij\rangle}\varepsilon_i\varepsilon_j \tag{4}$$

The variable z in Eq. (4) represents the lattice coordination number while the function $F(\varepsilon_{i},\ldots\varepsilon_j)$ is dependent only upon the quenched variables ε_i and the parameters shown. At a specific value of the chemical potential it is constant for a given realization of the disorder in the system, and hence can be omitted from subsequent consideration.

The relationships between the various parameters in the two Hamiltonians given in Eqs. (1) and (3) are given by the following equations [8]:

$$J = \Im \tag{5}$$

$$K = \left(\frac{1}{2}\Gamma - \Im\right) \tag{6}$$

$$B = \left(\frac{\mu}{2} + \Im z\right) \tag{7}$$

This isomorphism between our model and the equivalent Ising system is extremely useful. When the fluid–surface interaction parameter in our model Γ is set to the value $2\Im$, our model's Hamiltonian corresponds to the randomly site-diluted Ising system with dilution p, as can be inferred from Eq. (6). This condition allows calculations from our system to be directly compared with the equilibrium-based results independently done in the randomly site-diluted Ising model [9].

The Fickian Ensemble Dynamics

We have shown previously that the diffusive dynamics of the Fickian ensemble as described are given rigorously by the equation [6]:

$$\Delta m = \frac{4\varepsilon L^3}{\pi^2}\sum_{\mathrm{odd}\,n}\frac{1}{n^2}\mathrm{e}^{-D_{\mathrm{F}}n^2k^2t} \tag{8}$$

where $k = 2\pi/L$, L is the length of both chambers and the quantity Δm, in each chamber (of length $L/2$), is defined as follows:

$$\Delta m \equiv \langle m(t)\rangle - \langle m(\infty)\rangle \tag{9}$$

In Eq. (9), $m(t)$ represents the number of particles in a given chamber at time t while $m(\infty)$ represents the equilibrium value of $m(t)$. Given Eq. (8) it can be established that the Fickian diffusion coefficient can be found from the equation:

$$D_{\mathrm{F}} = \frac{\ln(\Delta m_1/\Delta m_2)}{k^2(t_2 - t_1)} \tag{10}$$

In order to arrive at Eq. (10) high order Fourier modes to the solution for $m(t)$ are ignored. However, the error in doing so, δD_{F}, has been rigorously established [6] from which it is found that:

$$\frac{\delta D_{\mathrm{F}}}{D_{\mathrm{F}}} = \sum_{\mathrm{odd} \quad n \neq 1} (1 - 1/n^2) \mathrm{e}^{-D_{\mathrm{F}}(n^2-1)k^2 t} \tag{11}$$

We see that $\delta D_{\mathrm{F}}/D_{\mathrm{F}} \to 0$ as $t \to \infty$ and, if we begin accumulating simulation data when $t \geq t_0 = 0.5/Dk^2$, it follows from Eq. (11) that:

$$\frac{\delta D}{D} \sim 1.6\% \tag{12}$$

This value of t_0 corresponds to the situation where $m(t)$ in the high density chamber is about half of its initial value. Thus, these results provide a *controlled approximation* with very accurate tolerances on the results achievable. For completeness we now describe details of the method's computational implementation.

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Algorithm Details

For a given system size (an even integer), density and temperature, the simulation follows two principal stages: (1) a pre-equilibration stage followed by (2) the diffusion-dynamics stage. During the pre-equilibration stage, the system is divided into two equal sized chambers, which meet at a planar interface parallel to two faces of the original cube. Two densities close to each other, one slightly greater than the given density, and one less than it by the same amount, are chosen and ascribed to the two chambers of the system. For each of the chambers a fraction of the sites, determined by the density of interest, is filled with particles, while a fraction of sites p is quenched. From a structural viewpoint each chamber is congruent with the other, i.e. the quenchedness is identical in each one. We define the number of Monte Carlo steps (MCS) by N_{eq} with the number of cycles in the pre-equilibration stage by N_{peq}. Each MCS corresponds to an attempted move, on average, of each fluid particle in the system, i.e. a complete lattice sweep. Time in this work is considered to be proportional to the value of lattice sweeps MCS. The total number of particles in the system is designated N with an index n that runs from 1 to N.

The simulation algorithm proceeds as follows:

```
1. Start loop $n_{eq}$ which runs from 1 to $N_{eq}$
2. Start loop $n$ which runs from 1 to $N$.
3. Randomly choose both the particle labeled by $n$ and one of its six neighboring sites.
   ○ *If the site and the particle are in the two different chambers and $n_{eq} \leq N_{peq}$ abandon this attempted move, increment $n$ by one and return to step 3.
   ○ Otherwise, if that neighboring site is filled with another fluid particle or a solid particle, abandon this attempted move, increment $n$ by one and return to step 3.
   ○ Otherwise, if that site is empty calculate the present value of the energy $E_i$ and the value of the energy $E_f$ that corresponds to the state of the system in the event that the particle moves to the chosen empty neighboring site. Calculate the (heat bath) probability [10]

         $p \equiv P_{i \to f} = \frac{1}{1 + e^{\beta(E_f - E_i)}}$     (13)

   ○ Generate a random number $r$ uniformly distributed between 0 and 1.
   ○ If $r < p$ accept the move so that particle $n$ moves to the chosen empty neighboring site.
   ○ If $r > p$ reject the move.
   If $n_{eq} > N_{peq}$ calculate the number of particles throughout the system, their positions and return to step 3.
   End loop $n$.
   End loop $n_{eq}$.
```

The condition denoted by * ensures that there is no particle exchange between the two chambers during the pre-equilibration stage. At the end of this stage both chambers are independently equilibrated at their respective densities, at the given temperature. During the next ("kinetic") part of the algorithm, MCS are run in the same manner as described above, however, without the restriction in the step denoted by * above; thus, particle exchange between the two chambers now becomes possible. During this stage of the simulation the whole system approaches equilibrium, with the two chambers tending to approach the same final fluid density $\bar{\rho}$.

Numerical Results

For many of the results presented here we used the value $\Gamma = 2\Im$ for the fluid–pore surface interaction parameter. In this case, we can benchmark our results with relaxation-dynamics against those of the randomly site-diluted Ising model done in an equilibrium ensemble.

In Fig. 2, we show comparative results between the relaxation-dynamics simulation data developed in this study and an equilibrium-based indirect method [3]. The system size used was $L = 20$ with the density of matrix sites $p = 0.2$. When parameter values in the confined lattice-gas of $\Gamma = 2\Im$ are used the critical density of the confined lattice-gas $\rho_{\mathrm{c}} = 1/2$, irrespective of the value of p. This result can be inferred from the isomorphism between the randomly site-diluted Ising model and our confined lattice-gas developed through Eqs. (3)–(7), and Eq. (2), in conjunction with the fact that at the critical point of the randomly site-diluted Ising model $\langle s \rangle = 0$.

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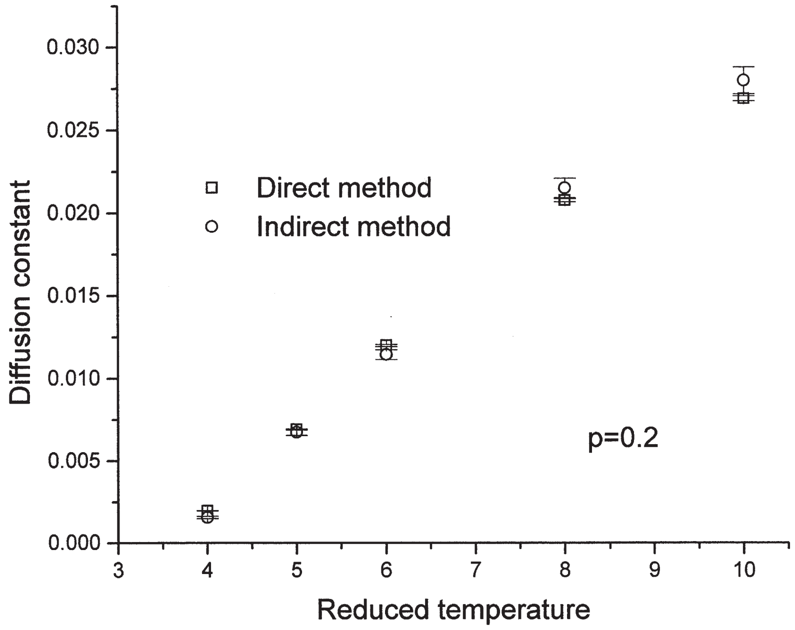

FIGURE 2 Comparison between an indirect method and the relaxation-dynamics method for calculating diffusion coefficients in a quenched random structure with $p = 0.2$.

For $p = 0.2$ the total number of open sites in the entire ensemble is $(1 - p)L^3 = 6400$. Since $\rho_c = 1/2$ then at the critical point this would imply 3200 particles distributed throughout, 1600 on average in each chamber. For the high density chamber we initially took the number of particles to be 1760 (i.e. a density perturbation corresponding to $0.1\rho_c$) from which it follows that there must be 1440 in the lower density chamber. This ratio of initial particle numbers 11/9 was used throughout this work.

Agreement between both sets of simulation results is good. The advent of critical slowing-down as the critical point is approached allows us to estimate T_c in the lattice gas, even in the finite-size system by extrapolating the data shown in Fig. 1 to the zero diffusion limit (as L gets larger the estimate for T_c should become more accurate). We did this for several values of p, see Table I, and compared these results with the critical temperatures (the reduced temperature in the systems is defined as, $T^* \equiv k_B T/\Im$, $L \rightarrow \infty$) found independently for the randomly site-diluted Ising system by *equilibrium simulations* [9]. The agreement between our results and the independent data for T_c is excellent. For parameter values $\Gamma \neq 2\Im$ in the confined lattice-gas, further comparisons like those presented in Table I would require that the critical point of the randomly site-diluted Ising model be available for values of $K \neq 0$ in the site-dilute Ising model. This would be a site-dilute Ising system where spins adjacent to blocked-out (matrix) sites interact with those particular sites through the interaction constant K—see Eq. (3). Such results are, to our best knowledge, currently unavailable.

TABLE I Comparison of critical temperatures in quenched random porous structures at various values of porosity p

P	T_c (this work)	T_c (independently found)
0	4.52	4.53 [12]
0.1	4.04	4.02 [9]
0.2	3.6	3.5 [9]
0.35	2.8	2.7 [9]

These results also afforded us the opportunity of studying the accuracy of a mean-field approximation to the Hamiltonian shown in Eq. (1). The mean-field predictions of the critical properties of the confined fluid at the low p limit are given by [8]:

$$\rho_c = \frac{1}{2} + \frac{1}{2}\tanh\left[\frac{\Gamma' - 2}{2z}\right] \times \left[z^2 - (z-1)^2 \mathrm{sec}\,h^2\left(\frac{\Gamma' - 2}{2z}\right)\right]p \tag{14}$$

$$T_c^* = z[1 - p\{z - (z-1)\mathrm{sec}\,h^2(\Gamma' - 2)/2z)\}] \tag{15}$$

$$\mu_c^* = -2z^2 \tanh\left[\frac{(\Gamma' - 2)}{2z}\right]p - 2z \tag{16}$$

In these equations, $\Gamma' \equiv \Gamma/\Im$ and from the results shown in Fig. 3 we see that when represented in terms of reduced properties the mean-field predictions of the critical temperature in the confined system are extremely accurate in this system. As such, that theory should be useful for estimating critical properties in these systems at a variety of thermodynamic conditions.

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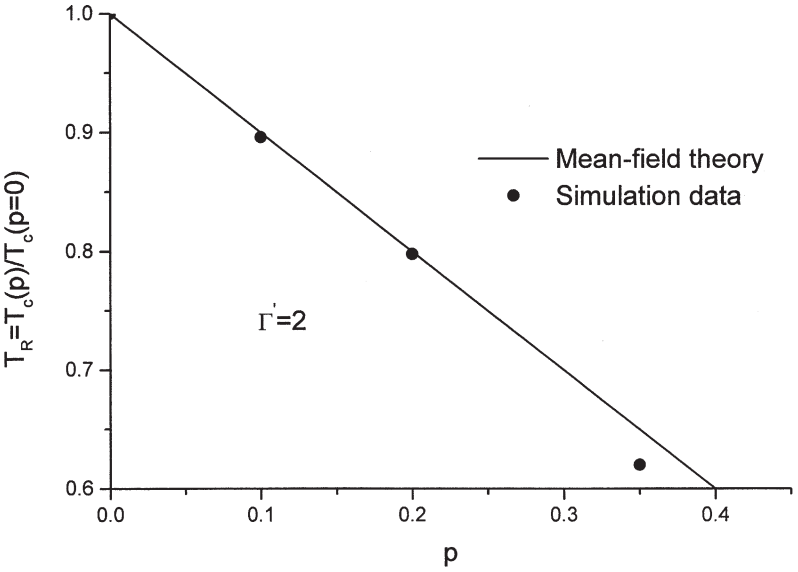

FIGURE 3 Comparison between mean-field predictions and simulation results for reduced critical temperatures in quenched random structures at various values of p.

Given the conjecture that critical dynamics for homogeneous and confined fluids belong to different critical universality classes [7,11] we did an extensive set of calculations for the diffusion constants at various values of p and temperature in these systems including the $p = 0$ limit. It is tempting in this regard to look for a *characteristic relaxation time* τ in terms of the "distance" from the critical point, i.e. $T^* - T_c^*(p)$. If one were available then we should find that an expression of the form:

$$\Delta m_2 = \Delta m_1 \mathrm{e}^{-[k^2(t_2-t_1)/\tau]} \tag{17}$$

should represent all of the dynamic simulation data where we define:

$$\frac{1}{\tau} \equiv \phi(p) f(T^* - T_c^*(p)) \tag{18}$$

In Eq. (18) $\phi(p)$ is an amplitude factor while f is a universal function of $T^* - T_c^*(p)$. From Eqs. (17) and (18) we find that:

$$\phi(p) \equiv \frac{\ln\left(\frac{\Delta m_1}{\Delta m_2}\right)}{k^2 f(T^* - T_c^*(p))(t_2 - t_1)} \tag{19}$$

To complete this definition for $\phi(p)$ we need only specify the temperature used in Eq. (19), a natural one being the high temperature limit, where we require that:

$$\lim_{T^* - T_c^*(p) \to \infty} f \to 1 \tag{20}$$

in which case,

$$\phi(p) = D_\mathrm{h} \equiv \lim_{T^* - T_c^*(p) \to \infty} D_\mathrm{F} \tag{21}$$

In this case, the characteristic relaxation time is given by:

$$\frac{1}{\tau} \equiv D_\mathrm{h} f(T^* - T_c^*(p)) \tag{22}$$

The efficacy of this approach depends upon the applicability of the product $D_\mathrm{h} f(T^* - T_c^*(p))$ in Eq. (22) for describing the relaxation dynamics of many different systems. If this approach holds then a universal relationship of the form:

$$\frac{D_\mathrm{F}}{D_\mathrm{h}} = f(T^* - T_c^*(p)) \tag{23}$$

should fit the data well for disparate systems. This result appears to be borne out, to a very considerable degree, by the results shown in Fig. 4, irrespective of the value of p used. In all of these calculations, the system size used was $L = 20$, $\Gamma = 2\Im$ and the critical density of the confined lattice-gas $\rho_c = 1/2$ for reasons previously discussed.

We have consistently found in this work a weak dependence of the simulation data on the specific realization of disorder used, especially at near-critical conditions. A typical set of data for diffusion coefficients at four realizations of disorder for the previous system studied is shown in Fig. 5. We conjecture that this may follow as a consequence of the confined fluid Hamiltonian used herein. It has only a dilute randomness associated with it, in comparison say, to the usual random field Ising model which can be quite sensitive to the particular realization of disorder used. However, in the standard random field Ising model there are random local ordering fields at each lattice position in the system which makes for a far greater degree of

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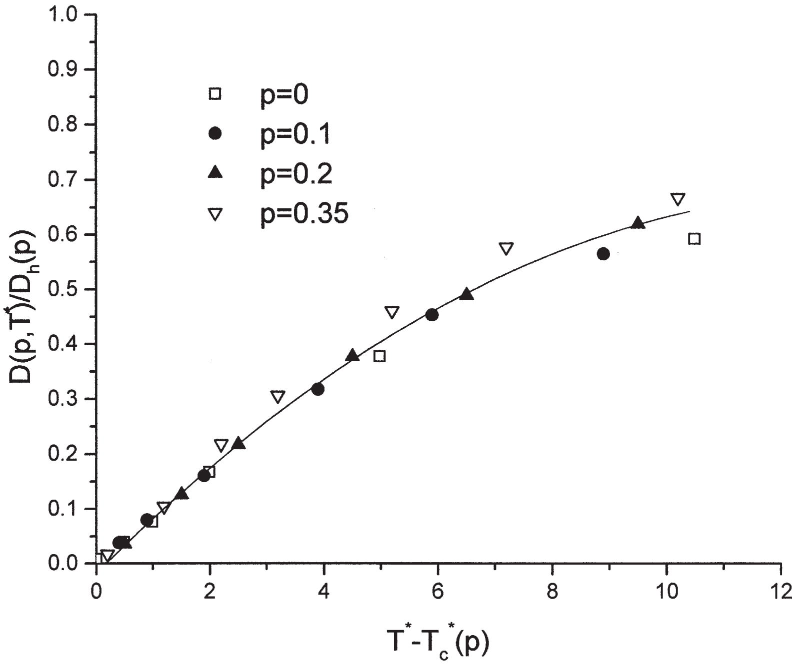

FIGURE 4 Reduced diffusion coefficients calculated by relaxation-dynamics at various values of p in quenched random structures.

"disorder" in this model than in the confined lattice-gas case.

For the final set of simulations in this work, we applied the relaxation-dynamics algorithm to diffusion in an *anisotropic porous system* consisting of nanowire bundles. These are linear strands of matrix material, one lattice unit thick separated by four lattice units in both the x and y directions oriented parallel to the z direction. The results for these simulations are shown in Fig. 6 and illustrate the fact that the anisotropic diffusion coefficients D_z and D_x are different as might be intuitively expected with $D_z > D_x$. Here, the coefficient D_z is meant to denote the diffusion coefficient in the z direction and because of the symmetry in the xy plane $D_x = D_y$. However, as we approach the critical temperature in this system both D_z and D_x should vanish because of the divergence of the susceptibility (isothermal compressibility) at the critical point. This appears to be the case here with the values of both D_z and D_x

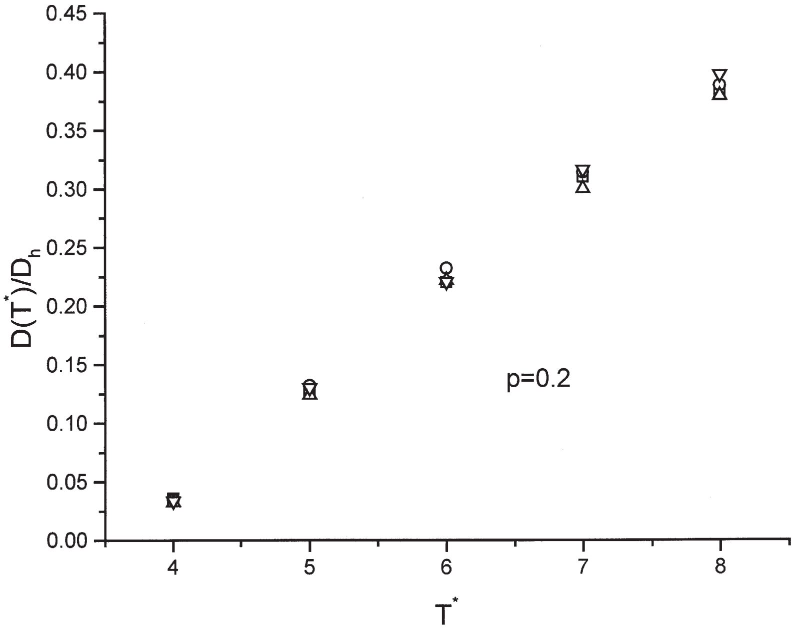

FIGURE 5 Reduced diffusion coefficients calculated by relaxation-dynamics simulations at $p = 0.2$ using four realizations of disorder in a quenched random structure.

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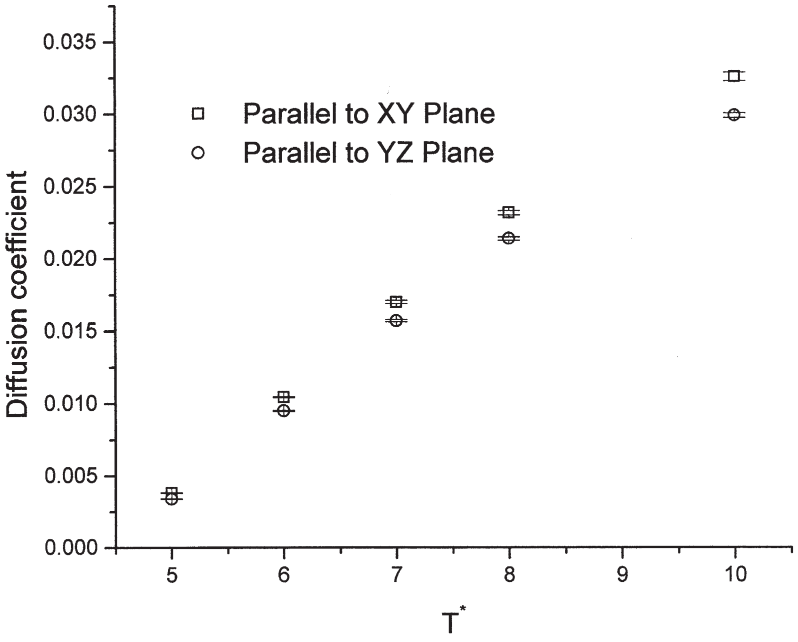

FIGURE 6 Simulation results for diffusion coefficients in an anisotropic medium consisting of nanowire strands with $p = 0.2$.

appearing to approach one another as the critical temperature is approached. Because of the symmetry in the xy plane in this system, the same results would hold true if D_y were to replace D_x in the above discussion.

Conclusions

In this paper, we have described transport calculations in heterogeneous random porous media using a recently proposed relaxation-dynamics simulation algorithm. The Hamiltonian for our model corresponds to that of a lattice-fluid confined in a quenched random pore structure. We specifically chose parameters in this model $\Gamma = 2\Im$ so that our results could be compared with simulation data for the *standard* randomly site-diluted Ising model. The agreement between predicted critical temperatures for both methods over wide ranges of p is excellent; the relaxation-dynamics method furthermore, provides Fickian diffusion coefficients from the simulation data. For parameter values $\Gamma \neq 2\Im$ in the confined lattice-gas, further comparisons like those presented in Table I would require that the critical point of the randomly site-diluted Ising model be available for values of $K \neq 0$ in the site-dilute Ising model. This would be a randomly site-diluted Ising system where spins adjacent to blocked-out (matrix) sites interact with those particular sites through the interaction constant K—see Eq. (3). Such results are, to our best knowledge, currently unavailable.

To our surprise, when reduced according to the concepts described in this work, diffusion coefficients in both homogeneous and random porous systems appear to be tightly distributed around a "universal" function of the variable $T^* - T^*_c(p)$. This variable provides a measure of the "distance" of the system from criticality. We conjecture that this may be so because the confined fluid Hamiltonian used herein has only a dilute randomness associated with it, in comparison say, to the usual random field Ising model. In the standard random field model there are random local ordering fields at each lattice position in the system. Hence, our model's dynamics are faster and closer in character to the homogeneous case than one might expect based upon a cursory association of it with the random field Ising analogue. This may also explain why we have seen little sensitivity of the simulation results presented with the specific realization of disorder used.

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