

# Monte Carlo simulation of Fickian diffusion in the critical region

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In this article we describe a novel, phenomenologically based computer simulation approach for studying relaxation dynamics in fluid systems. The method utilizes an ensemble consisting of two 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  $\varepsilon$  a small perturbation about this value. After the pre-equilibration step the partition is removed and the entire ensemble allowed to relax towards an equilibrium state guided by a kinetic Monte Carlo computer simulation algorithm. Fickian transport coefficients are found from quantities calculated during this relaxation process. We present an analysis of the approach and illustrate its application to transport property calculations in purely diffusive lattice-gas systems. Our results focus upon the critical region for which there are few published results and where simulation results face the most challenges because of finite-size effects and the phenomenon known as critical slowing-down. © 2002 American Institute of Physics.  
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## I. INTRODUCTION AND BACKGROUND

The main phenomenological parameter for calculating concentration-driven transport fluxes in fluids is the Fickian (transport) diffusion constant. The two most common techniques for evaluating this transport coefficient 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 this approach is the dual control volume grand canonical Monte Carlo (DCV-GCMC) method.<sup>1,2</sup> The DCV-GCMC algorithm consists of performing cyclic calculations, each cycle comprising a molecular dynamics (MD) simulation followed by a series of grand canonical Monte Carlo (GCMC) steps. The GCMC calculations maintain the required densities in each of the control volumes at either end of the diffusion region, while the MD calculations develop the fluid trajectories within the diffusion region on which to base flux calculations. These molecular fluxes are found by direct enumeration of particle fluxes across a plane perpendicular to the concentration gradient direction as has recently been described in slit pore systems.<sup>2</sup> However, this approach has not been tested near the critical point where the gradient of the chemical potential shows singular behavior.<sup>3</sup> In this case the concentration (density) fluctuations across the system will be large, introducing significant statistical uncertainty into the GCMC equilibrium simulations at each step of the process.

So-called indirect methods evaluate quantities derived from linear response<sup>4</sup> and/or Green–Kubo theory,<sup>5,6</sup> that are related to the Fickian diffusion constant. For example, the diffusive flux  $J_F$  for a lattice-gas species  $i$  with respect to its density can be written in both Fickian and Onsager terms as follows.<sup>7</sup>

$$J_F = -D \nabla \rho \quad (1)$$

$$J_F = -L_o \nabla \mu, \quad (2)$$

where  $D$  is the Fickian diffusion constant,  $L_o$  the Onsager regression constant,  $\rho$  density and  $\mu$  the chemical potential. If we combine these two equations and consider a gradient in chemical potential over a spatial co-ordinate  $x$  we find that:

$$J_F = -L_o \left( \frac{\partial \mu}{\partial x} \right)_T = -L_o \left( \frac{\partial \mu}{\partial \rho} \right)_T \left( \frac{\partial \rho}{\partial x} \right)_T \quad (3)$$

from which it follows that,

$$D = L_o \left( \frac{\partial \mu}{\partial \rho} \right)_T. \quad (4)$$

The Onsager coefficient can be found from simulations using the Einstein equation:<sup>7</sup>

$$L_o = \left( \frac{\beta}{6V} \right) \lim_{t \rightarrow \infty} \frac{1}{t} \left\langle \left[ \sum_{k=1}^{N_i} (\mathbf{r}_k(t) - \mathbf{r}_k(0)) \right]^2 \right\rangle_t, \quad (5)$$

where the subscript  $t$  refers to a time average quantity,  $\mathbf{r}_k(t)$  is the position of the  $k$ th particle at time  $t$ ,  $\beta \equiv 1/k_B T$  and  $V$  the system volume.

The term  $(\partial \mu / \partial \rho)_T$  can be found from GCMC simulations and use of the fluctuation formula:

$$\left( \frac{\partial \mu}{\partial \rho} \right)_{T,V} = \frac{V}{\beta \langle (\delta N)^2 \rangle}. \quad (6)$$

Equations (4)–(6) are the basis for the indirect calculation of Fickian diffusion constants.

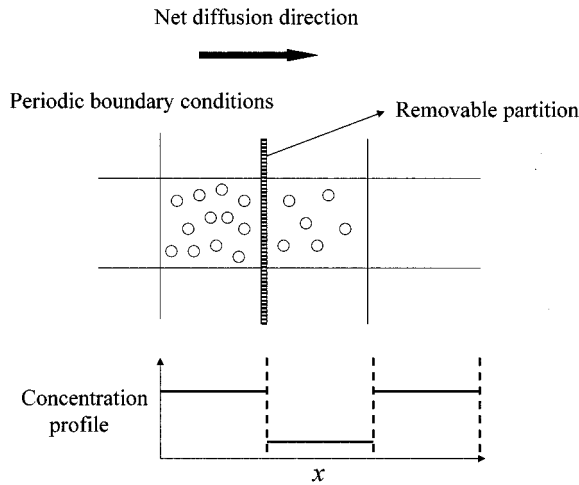


FIG. 1. Schematic of the Fickian two-chamber ensemble.

## II. RELAXATION DYNAMICS: THE BASIS FOR THE PROPOSED METHOD

Another intuitively appealing approach for studying diffusion dynamics has involved the simulation of systems relaxing from a nonequilibrium state. In these relaxation methods a key issue is the preparation of the initial nonequilibrium (perturbed) state. Kutner *et al.*<sup>8</sup> used GCMC in a lattice spin system in the presence of an external sinusoidal field to set up the initial perturbed state. From the ensuing relaxation dynamics process they calculated the Fourier transform of the lattice magnetization profile, which was used to find the lattice diffusion constant. A similar approach was recently used to study collective diffusion on hexagonal lattices.<sup>9</sup> However, Fickian diffusion is only meaningful for small displacements from equilibrium where linear response theory, according to Onsager's regression hypothesis, is obeyed. The method in Ref. 9 does not incorporate pre-equilibration into the simulations at the given thermodynamic conditions, which means that the initial results do not represent sampling in the linear response regime. Furthermore, none of these methods has, to our best knowledge, been studied in the context of critical dynamics in fluids. Kutner's method may be problematic in this region, since at the critical point the divergence of thermodynamic properties like the susceptibility is likely to give rise to large amplitudes in the initial density profile, for even small perturbations of the applied sinusoidal field—i.e., initial conditions well-displaced from equilibrium. Also large fluctuations in this region should lead to widely varying initial density profiles from run to run with concomitant statistical uncertainty in the results.

We propose a new relaxation method for calculating Fickian diffusion coefficients by following the dynamics of a purely diffusive system as it relaxes from an initial nonequilibrium state constructed in a two-chamber ensemble schematically shown in Fig. 1. We call this entity a *Fickian ensemble*, given its phenomenological construction which has been 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, and once the partition is removed, diffusion between both chambers will occur as the system relaxes towards the equilibrium state. The dynamics in such an ensemble can be analyzed by studying the time-dependent Fickian diffusion equation. For illustrative purposes this equation for one-dimensional diffusion in a pure fluid can be written as follows:

$$\frac{\partial \rho(x,t)}{\partial t} = D \frac{\partial^2 \rho(x,t)}{\partial x^2}, \quad (7)$$

where  $D$  is the Fickian diffusion constant,  $\rho(x,t)$  the fluid density and  $x$  the coordinate in the diffusion direction. This equation can be solved for a variety of initial conditions; for a single sinusoidal Fourier component, the dynamic density profile in such a system evolves  $\sim \sin(kx)e^{-Dk^2t}$ . For a periodic initial density profile with period  $L$ , the temporal and spatial dependence of the density profile in the system can be expressed by the general equation:

$$\rho(x,t) = a_0 + \sum_{n=1}^{\infty} a_n \cos(nkx) e^{-Dn^2k^2t} + \sum_{n=1}^{\infty} b_n \sin(nkx) e^{-Dn^2k^2t}, \quad (8)$$

where  $k \equiv 2\pi/L$  is the wave number, and  $a_0$ ,  $a_n$  and  $b_n$  are Fourier coefficients. For the square-wave initial density profile shown in Fig. 1 we find that,

$$\rho(x,0) = \frac{4\varepsilon}{\pi} \sum_{\text{odd } n} \frac{1}{n} \sin(nkx) + \bar{\rho}, \quad (9)$$

in which case the solution to Eq. (7) with this initial condition takes the particular form,

$$\rho(x,t) = \frac{4\varepsilon}{\pi} \sum_{\text{odd } n} \frac{1}{n} \sin(nkx) e^{-Dn^2k^2t} + \bar{\rho}. \quad (10)$$

We now define the ensemble average quantity  $\Delta m$  in each chamber of length  $L/2$  as follows:

$$\Delta m \equiv \langle m(t) \rangle - \langle m(\infty) \rangle, \quad (11)$$

where  $m(t)$  represents the number of particles in a given chamber at time  $t$ . During the relaxation-diffusion process, it is straightforward to show that  $\Delta m$  is given by the result:

$$\Delta m = \frac{4\varepsilon L^3}{\pi^2} \sum_{\text{odd } n} \frac{1}{n^2} e^{-Dn^2k^2t}. \quad (12)$$

For  $t=0$ , the value of this series is 1.233, while for  $t=0.5/Dk^2$  its value is 0.608 with the value of the first term, namely  $e^{-Dk^2t}$ , equal to 0.607. In other words, when  $\Delta m$  equals about half of its initial value, all the Fourier components, except for the first one, have already decayed considerably. Therefore, at a time  $t \geq t_0$ , with  $t_0$  chosen in advance, we have to a good approximation that,

$$\Delta m = \frac{4\varepsilon L^3}{\pi^2} e^{-Dk^2t}. \quad (13)$$

So, for two values of  $t > t_0$ , namely,  $t_1$  and  $t_2$  we get that,

$$\frac{\Delta m_2}{\Delta m_1} = e^{-Dk^2(t_2-t_1)} \quad (14)$$

from which it follows that,

$$D = \frac{\ln\left(\frac{\Delta m_1}{\Delta m_2}\right)}{k^2(t_2-t_1)}. \quad (15)$$

This simple equation is the basis for the proposed simulation method. We now use it to provide error estimates for the simulation results.

We approximate Eq. (15) for small differences in time by the differential form,

$$D = -\frac{1}{k^2 \Delta m} \frac{d(\Delta m)}{dt}. \quad (16)$$

Now if Eq. (12) is true, then using this equation in Eq. (16) gives,

$$D' = D \left\{ \frac{\sum_{\text{odd } n} n e^{-Dn^2 k^2 t}}{\sum_{\text{odd } n} \frac{1}{n^2} e^{-Dn^2 k^2 t}} \right\}. \quad (17)$$

If the higher-order terms are small compared to the leading term, then we may write

$$D' = D + \delta D, \quad (18)$$

where

$$\frac{\delta D}{D} = \sum_{\text{odd } n \neq 1} \left( 1 - \frac{1}{n^2} \right) e^{-D(n^2-1)k^2 t}. \quad (19)$$

Clearly we see that  $\delta D/D \rightarrow 0$  as  $t \rightarrow \infty$ . If we begin data acquisition in the simulations when  $t \geq t_0 = 0.5/Dk^2$ , we have that  $e^{-Dk^2 t_0} \sim 0.607$ . Here  $\Delta m$  equals about half of its initial value and Eq. (19) provides that,

$$\frac{\delta D}{D} \sim 1.6\%. \quad (20)$$

Thus, we have a *controlled approximation* using these results, which are generally applicable for calculating Fickian diffusion coefficients in fluid systems. We now describe the simulation approach for implementing these ideas followed by illustrations of its numerical use.

### A. Simulation approach

We consider a simple lattice gas on a 3D cubic lattice of size  $L$  with periodic boundary conditions applied in the standard manner. For a given particle density in the system, a fraction of the sites, proportional to the density, are occupied by particles, while the rest of the sites are empty. For example, the critical density in such a system corresponds to half the sites being filled. For any configuration of particles in the system the corresponding energy is given by:

$$E = -4J \sum_{\langle ij \rangle} n_i n_j, \quad (21)$$

where  $n_i$  can take the value 1 (presence of a particle) or 0 (absence of a particle) at site  $i$ . The symbol  $\langle ij \rangle$  denotes the summation over all nearest-neighbor pairs of the system. If

the interaction term  $4J$  is written in this way, then the critical temperature in this model is known to be approximately  $T_c^* = 4.52$  with  $T^* \equiv k_B T/J$  for  $L \rightarrow \infty$ . In such a system, at equilibrium spontaneous fluctuations constantly take place and our task is to calculate the Fickian diffusion constant for the fluid at the given density and temperature.

Before providing further details of the simulation algorithm, we define the heat-bath algorithm which provides the basis for the particle ‘‘dynamics’’ used in our Monte Carlo simulations. The heat-bath algorithm gives rise to an acceptance probability for a given Monte Carlo ‘‘move’’ by the following formula:

$$P_{i \rightarrow f} = \frac{1}{1 + e^{\beta(E_f - E_i)}}, \quad (22)$$

which obeys the principle of detailed balance, namely that,

$$\frac{P_{1 \rightarrow 2}}{P_{2 \rightarrow 1}} = e^{\beta(E_1 - E_2)}. \quad (23)$$

In this way particles are free to move throughout the system and dynamic analysis using simulation procedures of this sort are often referred to as kinetic Monte Carlo algorithms. Time intervals with such a method are measured in units of Monte Carlo steps (MCS), each of which is defined to be a complete sweep of the lattice, i.e., an attempted move, on average, of each of the particles in the system.

For a given system size (an even integer), density and temperature, the simulation is comprised of two principal stages: (1) the pre-equilibration stage, and (2) the diffusion-dynamics stage. During the pre-equilibration stage, the system is divided into two equal sized chambers, meeting at a planar interface parallel to two of the 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 corresponding density is randomly filled with particles. The simulations then proceed according to the following algorithm:

### B. Algorithm details

We define the number of Monte Carlo cycles by  $N_{\text{eq}}$  with the number of cycles in the pre-equilibration stage by  $N_{\text{peq}}$ . The total number of particles in the system is designated  $N$  with an index  $n$  that runs from 1 to  $N$ . The simulation algorithm is as follows:

1. **Start loop**  $n_{\text{eq}}$  which runs from 1 to  $N_{\text{eq}}$ .
2. **Start loop**  $n$  which runs from 1 to  $N$ .
3. Randomly choose both a particle labeled by  $n$  and one of its six **neighboring sites**.
  - \* **If** the site and the particle are in the **two different chambers** and  $n_{\text{eq}} \leq N_{\text{peq}}$  abandon this attempted move, increment  $n$  by one and return to step 3.
  - **Otherwise**, if that neighboring site is **filled** with another 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.

#### 4. Calculate the probability

$$p \equiv P_{i \rightarrow f} = \frac{1}{1 + e^{\beta(E_f - E_i)}} \quad (24)$$

- 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.
5. If  $n_{\text{eq}} > N_{\text{peq}}$  calculate the number of particles throughout the system, their positions and return to step 3.
  6. **End loop**  $n$ .
  7. **End loop**  $n_{\text{eq}}$ .

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, Monte Carlo cycles are run in the same manner as described above, however, without the restriction in the step denoted by \* in the above-mentioned; 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 density  $\bar{\rho}$ .

During the diffusion-dynamics stage, the number of particles in each chamber is recorded at regular “time” intervals with time measured in units of Monte Carlo cycles for use in evaluating properties of interest. For example, after a pre-specified time  $t_0$  [see Eq. (11)], the result shown in Eq. (15) can be used to calculate  $D$ . The entire process, including the pre-equilibration procedure, is repeated for several different initial configurations of the system. These different configurations provide a series of results for  $\Delta m$  that are then averaged to get the final values of  $D$  reported here. Without loss of generality we set numerical values for both  $J$  and  $k$  to be unity throughout our calculations; in this case numerically we have that  $T = T^*$ . Calculations done at the critical density of 1/2 yielded acceptance rates of 0.247 at  $T = 100.$ , 0.205 at  $T = 10$  and 0.117 for  $T = T_c = 4.52$ .

### III. NUMERICAL RESULTS

In Figs. 2 and 3 we show some simulation results achieved with this method. In Fig. 2 we present the values for  $\Delta m$  in the denser chamber at  $T = 9.5$  with system size  $L = 20$  (we point out that this temperature is far from the critical one). In total 8000 lattice sites were used, evenly distributed between both chambers, with the overall fluid density maintained at the critical value  $\rho_c = 0.5$ , corresponding to 4000 fluid particles overall. The high-density chamber was initially pre-equilibrated with 2100 particles, while 1900

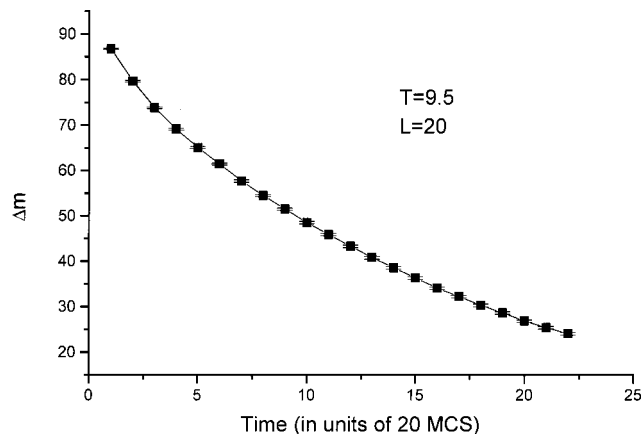


FIG. 2. Density relaxation in the denser chamber at  $L = 20$ ,  $T^* = 9.5$ .

were used in the low density one. In Fig. 3 the density profile in the entire ensemble is shown for these simulation conditions at two different times,  $t = 0$  MCS and  $t = 240$  MCS, respectively. These data correspond to an average over a set of 64 data blocks, each one containing 200 relaxation simulations.

#### A. The critical region

In further evaluating the proposed simulation method, we evaluate it in the critical region where we have well-defined theoretical results and/or simulation data to compare with our results. In the first set of simulations we compared the proposed method’s results with those found using an **indirect method** for calculating diffusion coefficients as recently described by De *et al.*<sup>4</sup> This comparison is shown in Fig. 4 and is typical of other comparisons we have made; there is excellent agreement between both simulation approaches. The density fluctuation calculations for the indirect method were done using GCMC, while the Onsager coefficient was found from simulations in the canonical ensemble at the same thermodynamic conditions.<sup>4</sup> We can also use this approach to estimate the critical temperature  $T_c$  of the fluid. This should follow from the theoretical result that stipulates

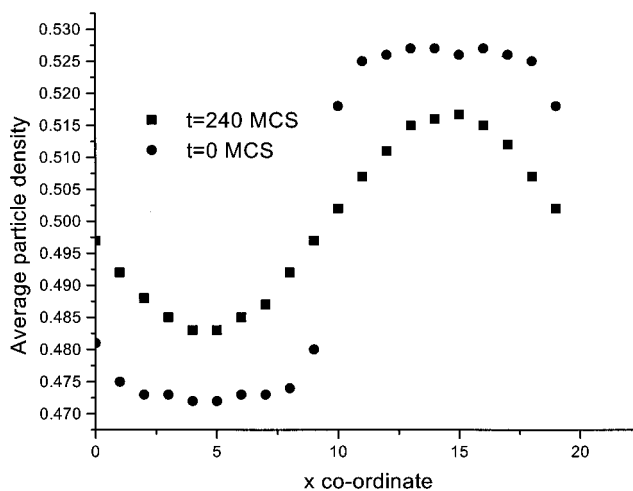


FIG. 3. Density profile in the ensemble at  $t = 0$  MCS and  $t = 240$  MCS.



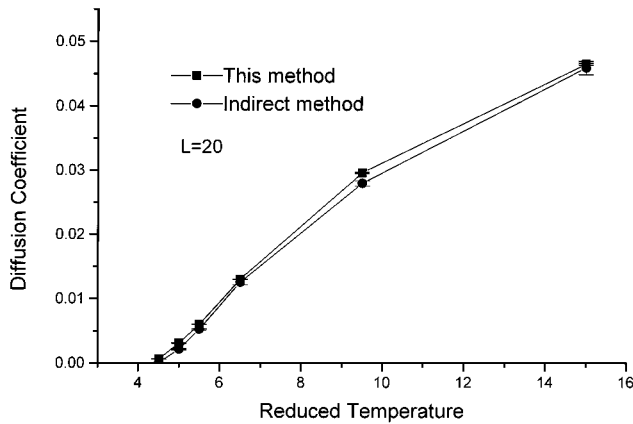


FIG. 4. Comparison of the proposed method and an indirect technique for calculating diffusion coefficients for  $L=20$ .

that fluxes and the Fickian diffusion coefficient approach zero at the critical point, a phenomenon sometimes referred to as critical slowing-down. This particular calculation is a useful benchmark for our method since  $T_c$  is known from prior results with equilibrium Monte Carlo histogram methods.<sup>10</sup> The results of such calculations, found from flux data extrapolated to the zero diffusion limit, yielded a value of the dimensionless critical temperature  $\approx 4.53$  as shown in Fig. 5. This compares very favorably with the value of 4.52 found in the high-resolution Monte Carlo finite-size scaling study of the related Ising system using histogram techniques.<sup>10</sup>

### B. Dynamic scaling exponent from relaxation dynamics

A particularly stringent test for the method involves the calculation of the critical exponent for the Fickian diffusion coefficient. This can be represented near the critical point in terms of finite-size scaling ideas.<sup>11</sup> For small  $\tilde{t} \equiv ((T$

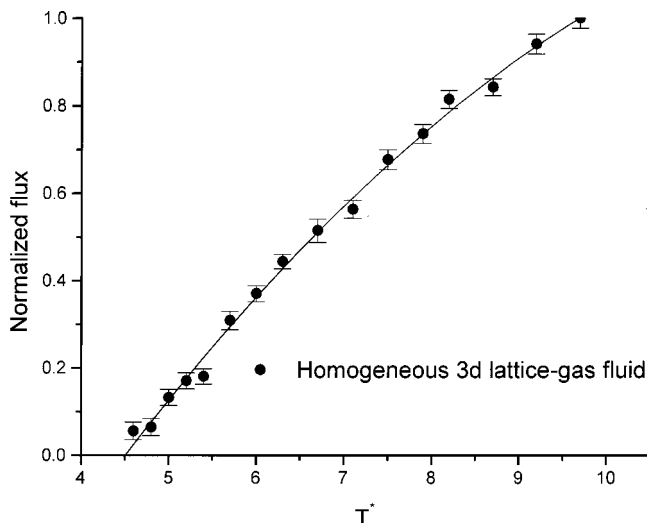


FIG. 5. Particle flux from relaxation dynamic calculations—the critical temperature found by extrapolation to the zero flux limit is  $T^* \sim 4.53$ .

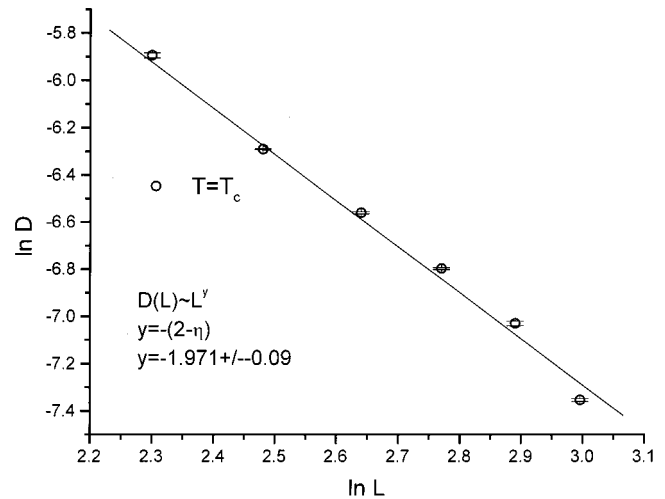


FIG. 6. Diffusion coefficient critical exponent from finite-size scaling calculations at the system's critical temperature and density.

$-T_c)/T_c$ ),  $k$  and large system size  $L$ , finite-size scaling theory postulates the following scaling law for the Fickian diffusion coefficient:

$$D(\tilde{t}, k, L) \sim b^{-(2-\eta)} \Delta\left(\tilde{t} b^{1/\nu}, \frac{L}{b}, kb\right), \quad (25)$$

where  $b$  is a rescaling factor and  $\Delta$  a universal scaling function. At the critical temperature the correct scaling is found by replacing  $b$  by  $L$  in Eq. (25), which thus becomes,

$$D(\tilde{t}=0, k, L) \sim L^{-(2-\eta)} \Delta(0, 1, kL). \quad (26)$$

Now, for each  $L$ ,  $k = 2\pi/L$  so that the scaling of the diffusion coefficient becomes:

$$D(\tilde{t}=0, k, L) \sim L^{-(2-\eta)} \Delta(0, 1, 2\pi), \quad (27)$$

where  $\Delta(0, 1, 2\pi)$  is a constant so that:

$$D\left(\tilde{t}=0, k = \frac{2\pi}{L}, L\right) \sim L^{-(2-\eta)}. \quad (28)$$

Equation (28) is the result we used here to analyze relaxation dynamic simulations at various system sizes  $L$  at the system's critical temperature. These results are presented in Fig. 6, where we show a graph of the simulation data in the form of  $\ln D$  versus  $\ln L$  at the critical temperature of the system. The slope of the line yielded a value for the quantity  $y \equiv -(2-\eta)$  equal to  $-1.971 \pm 0.09$ , where  $\eta$  is the correlation function critical exponent. This result is in excellent agreement with the value for  $y = -1.972$  found using Monte Carlo simulations in an equilibrium ensemble.<sup>10</sup> The result presented here though is the first, to our best knowledge, to find this critical exponent directly from relaxation dynamics simulations.

### IV. CONCLUSIONS

We have described a new computer simulation method for calculating Fickian transport coefficients in lattice fluid

systems using relaxation dynamics. The method uses an isothermal two-chamber “Fickian” ensemble for the simulations. The initial nonequilibrium state in the system is prepared in a particularly simple manner and corresponds mathematically to a pre-equilibrated square-wave density profile. This configuration provides an analytic solution describing interchamber density relaxation rates in the Fickian regime. These results are used to directly calculate Fickian diffusion coefficients from kinetic Monte Carlo simulation data of particle exchange between the two chambers.

We compared the method’s accuracy for calculating transport properties with an indirect method studied by our group based upon linear response theory. We found the new proposed method to be accurate in these comparisons, and are presently unaware of any other simulation data and/or experimental data with which to make these comparisons. In addition, we also used relaxation dynamics to calculate various critical properties of a lattice gas, including the dynamic scaling exponent for the Fickian diffusion coefficient. The results we found were in excellent agreement with those reported independently from detailed Monte Carlo simulations in an equilibrium ensemble.<sup>10</sup> The approach described here is fast, accurate and phenomenologically appealing, and as such, should prove to be of value in simulating diffusive dynamic processes in a wide class of physical systems.

#### ACKNOWLEDGMENT

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#### NOMENCLATURE

$a_0, a_n$	Fourier coefficients
$b_n$	Fourier coefficients
$b$	re-scaling factor
$D$	Fickian (bulk) diffusion constant
$E$	energy
$J_F$	species flux
$J$	particle interaction parameter

$k$	period, $2\pi/L$
$k_B$	Boltzmann’s constant
$L_o$	Onsager coefficient
$L$	length of chamber
$m(t)$	number of molecules in chamber at time $t$
$N_i$	number of molecules species $I$
$P_{i \rightarrow f}$	acceptance probability for state $i$ to $f$
$\mathbf{r}_k(t)$	position of $k^{\text{th}}$ particle at time $t$
$t$	time
$\tilde{t}$	reduced temperature, $((T - T_c)/T_c)$
$T$	temperature
$T_c$	critical temperature
$V$	volume
$x$	axial co-ordinate in direction of diffusion

#### Greek letters

$\beta$	$1/k_B T$
$\varepsilon$	density perturbation
$\rho$	density
$\mu$	chemical potential
$\nabla$	gradient operator
$\gamma$	susceptibility scaling exponent
$\nu$	correlation length scaling exponent
$\eta$	correlation function scaling exponent

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