

## Charge correlation factor of the random binary chain determined by Monte Carlo simulation

Radu Pitiş\*

*Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129*

(Received 11 January 1993)

We present stationary-state Monte Carlo experiments evaluating the dc conductivity of the one-dimensional lattice gas with binary energetic disorder. The resulting correlation factor is compared to previous analytic calculations.

### I. INTRODUCTION

Hopping transport in one-dimensional (1D) random systems has been a subject of interest for many years. In particular, the single-particle random walk was intensively studied (see Refs. 1 and 2 and references cited therein). In the case of hopping with symmetric jump rates  $W_{ij} = W_{ji}$  between sites  $i$  and  $j$ , Miller and Abrahams<sup>3</sup> demonstrated the equivalence between the random-walk problem (in any space dimension) and that of a resistor network, with the same geometry. The conductances involved,  $G_{ij}$ , are proportional to  $W_{ij}$ . For nearest-neighbor 1D hopping, this mapping leads to the well-known result that the dc conductivity  $\sigma$  is given, up to a constant factor, by the harmonic mean value of the jump rates [or the inverse of their  $(-1)$  moment]<sup>1</sup>

$$\sigma \approx m^{-1} = \left[ \int P(W) \frac{1}{W} dW \right]^{-1}, \quad (1.1)$$

provided that the right-hand side of Eq. (1.1) exists and has a finite value. Here  $P(W)$  is the distribution function of the jump rates.

The case of many-particle hopping is a much more intricate problem, due to the necessity of taking interactions into account (see Ref. 4 and references cited therein). Even in the most simplified case of only hard-core repulsion the problem is not at all trivial. Except for lattices with equivalent sites for which  $\sigma$  is given exactly by the (one-particle) mean-field approximation  $\sigma_{MF}$ , the site-blocking interaction gives rise to correlations which make  $\sigma$  lower than  $\sigma_{MF}$ .<sup>5</sup> The effect is usually described with the aid of the charge correlation factor, defined as<sup>4</sup>

$$f = \frac{\sigma}{\sigma_{MF}}. \quad (1.2)$$

Richards<sup>6</sup> presented a model with inequivalent sites, the only one known for which  $f$  can be calculated exactly. This is the 1D system with two alternating types of sites  $A$  and  $B$ , having different energies  $\epsilon_A$  and  $\epsilon_B$ .

Disorder makes correlated hopping even more difficult to deal with. The problem was considered by Tahir-Kheli<sup>7</sup> in connection with tracer diffusion. Chase and Thouless<sup>8</sup> pointed out the equivalence between the many-particle problem in real space ( $N$  sites) and the random walk in configuration space ( $2^N$  sites) and thus, by analogy with the Miller-Abrahams treatment, they devised a mapping on a resistor network. They discussed the increase of the activation energy due to hard-core in-

teraction, both for ordered and disordered chains.

In an earlier paper<sup>9</sup> (Ref. 9 will be referred to as I in what follows), Pitiş and Gartner reported a stationary-state calculation of  $\sigma$  for random 1D systems, with numerical illustration for the binary chain. In a subsequent paper<sup>5</sup> (Ref. 5 will be further referred to as II), the same authors showed that the former result was the 1D version of a new mapping of the correlated problem onto a resistance network. As a consequence, the approximate correlation factor of I was shown to be an upper bound for the exact value, but up to now no possibility was found to estimate the error analytically.

An obvious way to get a very close approximation to the true value of the correlation factor is to measure it by computer experiments. The Monte Carlo method was used both for the one-particle problem on disordered lattices (see, e.g., Ref. 10), and the site-blocking correlated one in ordered systems (a review is found in Ref. 4). There are few numerical experiments for the combined correlated-disordered problem. Murch<sup>11</sup> examined the random cubic binary lattice with fixed concentration, so that the number of particles equal that of traps (lower-energy sites). The only Monte Carlo investigation of correlation effects in the disordered binary chain was presented by Pechenik, Susman, Whitmore, and Ratner.<sup>12</sup> Their model included hard-core but *also nearest-neighbor* interaction. The coupling constant of the latter,  $\epsilon$ , was equal to  $(\epsilon_B - \epsilon_A)/2$ , i.e., half the site-energy difference. This constraint prevents the recovering of the hard-core-only case from the simulation of Ref. 12; disorder would also disappear when taking the  $\epsilon \rightarrow 0$  limit.

This paper presents results for the charge correlation factor  $f$ , Eq. (1.2), measured by Monte Carlo experiments. The model is the 1D site-disordered binary lattice. Because of the considerably long computer time needed to obtain a reliable value for the mean value of  $f$ , we have restricted our investigation to a single temperature value  $T = T^*$ , for which we made the same choice as in I, namely, so that

$$\exp \frac{\epsilon_B - \epsilon_A}{kT^*} = 10. \quad (1.3)$$

In Sec. II the model is presented and the theoretical background of the simulations is outlined. The simulation method is described in Sec. III. The Monte Carlo time needed to reach the stationary state is investigated. Stationary-state averages of occupation numbers and of nearest-neighbor pairs of occupation numbers are mea-

sured and discussed. Experimental values of  $f$  are presented. Section IV contains a short summary.

## II. THE MODEL

We consider a chain of  $N$  equidistant sites with two possible values for the site energy,  $\epsilon_A$  and  $\epsilon_B$ , randomly distributed, in equal proportion. Thus, the numbers of sites of each type are given by

$$N_A = N_B = \frac{N}{2}. \quad (2.1)$$

There are  $N_p$  particles in the system so that concentration is given by

$$c = \frac{N_p}{N}. \quad (2.2)$$

No interaction is considered except the hard-core repulsion. The occupation number of site  $i$ , denoted by  $n_i$ , takes the values 0 or 1. The equilibrium average of  $n_i$  is given by the Fermi function ( $\beta = 1/kT$ ):

$$f_i = \langle n_i \rangle_0 = \{1 + \exp[\beta(\epsilon_i - \mu)]\}^{-1}, \quad (2.3)$$

where  $\mu$  is the chemical potential. Let  $z$  denote the fugacity,

$$z = \exp(\beta\mu) \quad (2.4)$$

and let

$$E_{A,B} = \exp(\beta\epsilon_{A,B}). \quad (2.5)$$

The fugacity is determined from

$$c = \frac{1}{2}(f_A + f_B) \quad (2.6)$$

as<sup>9</sup>

$$z = \frac{1}{1-c} \left\{ \frac{(2c-1)(E_A + E_B)}{4} + \left[ \left[ \frac{(2c-1)(E_A + E_B)}{4} \right]^2 + c(1-c)E_A E_B \right]^{1/2} \right\}. \quad (2.7)$$

The Fermi functions are now given by

$$f_{A,B} = \frac{z}{z + E_{A,B}}. \quad (2.8)$$

Particles move on the chain by nearest-neighbor (NN) hops. The jump rates satisfy detailed balance

$$W_{i,i\pm 1} f_i (1 - f_{i\pm 1}) = W_{i\pm 1,i} f_{i\pm 1} (1 - f_i), \quad (2.9)$$

which allows for the following definition of symmetrized jump rates:

$$\mathbf{W}_{i,i\pm 1} = W_{i,i\pm 1} f_i (1 - f_{i\pm 1}). \quad (2.10)$$

The end jump rates  $\mathbf{W}_{N,N+1}$  and  $\mathbf{W}_{0,1}$  are also defined if an infinite chain is constructed. This is achieved by periodically repeating the above system and imposing cyclic properties to all site-dependent quantities:

$\epsilon_i, n_i, \mathbf{W}_{i,i\pm 1}$ . Except for Eq. (2.9) no restriction is imposed on the jump rates, which leaves some freedom in choosing their energy dependence. We make the same choice as in I:

$$W_{i,j} = W \exp \frac{\beta(\epsilon_i - \epsilon_j)}{2}, \quad (2.11)$$

which gives

$$\begin{aligned} \mathbf{W}_{AA} &= W f_A (1 - f_A), \\ \mathbf{W}_{BB} &= W f_B (1 - f_B), \\ \mathbf{W}_{AB} &= \sqrt{\mathbf{W}_{AA} \mathbf{W}_{BB}}. \end{aligned} \quad (2.12)$$

A uniform dc electric field  $E$  parallel to the chain modifies the jump rates as follows:

$$W_{i,i\pm 1}^E = W_{i,i\pm 1} \left[ 1 \pm \frac{eEa}{2kT} \right] = W_{i,i\pm 1} (1 \pm \Delta) \quad (2.13)$$

with  $e$  the elementary charge,  $a$  the NN distance, and  $\Delta$  an obvious shorthand notation. Equation (2.13) was written so that detailed balance is satisfied up to first order in  $E$ , since we are interested in the conductivity  $\sigma$ , which is the linear-response coefficient.

In the stationary state,  $\sigma$  is calculated from

$$\sigma = \frac{j}{E}, \quad (2.14)$$

with the current density given by<sup>9</sup>

$$j = \frac{ea}{N\Omega} \sum_{i=1}^N [W_{i,i+1}(1+\Delta)\langle n_i(1-n_{i+1}) \rangle - W_{i+1,i}(1-\Delta)\langle n_{i+1}(1-n_i) \rangle], \quad (2.15)$$

$\Omega$  being the volume per site. In Eq. (2.15), the notation  $\langle \rangle$  indicates a stationary-state average. From Eq. (2.14) the mean-field conductivity is calculated as<sup>9</sup> [compare to Eq. (1.1)]

$$\begin{aligned} \sigma_{\text{MF}} &= \frac{e^2 a^2}{\Omega kT} \left[ \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{i=1}^N \frac{1}{\mathbf{W}_{i,i+1}} \right]^{-1} \\ &= \frac{e^2 a^2}{\Omega kT} \langle \langle \mathbf{W}^{-1} \rangle \rangle^{-1} \\ &= \frac{4e^2 a^2}{\Omega kT} \left[ \frac{1}{\mathbf{W}_{AA}} + \frac{1}{\mathbf{W}_{BB}} + \frac{2}{\mathbf{W}_{AB}} \right]^{-1}, \end{aligned} \quad (2.16)$$

where  $\langle \langle \rangle \rangle$  denotes theoretical configurational averaging.

## III. SIMULATION

### A. The method

We have used a stationary-state Monte Carlo method, inspired from Refs. 6 and 11. A chain of  $N = 10^4$  sites is considered, slightly larger than the 8000 sites chain used by Richards.<sup>6</sup> Equal numbers of  $A$  and  $B$  sites are placed at random on the lattice. At a given value of the concentration,  $f_A$  and  $f_B$  are determined as in Sec. II and then the  $A$  and  $B$  sites are randomly filled with  $f_A N/2$  and

$f_B N/2$  particles, respectively, so that the system is initially at equilibrium. Occupied sites are memorized in a special array. Particles are then allowed to jump, in the presence of the electrical field  $E$ . After some tests of the linearity of the response  $j$  with respect to the field, we have taken  $2\Delta=0.05$ .

Cyclic conditions are imposed, and so the end jumps occur really between sites 1 and  $N$ . The jump probabilities are given by Eq. (2.11), where energies are chosen so that  $E_B/E_A=10$ . This choice is that of I and it was made in order to render comparison possible. For the sake of efficiency, the value of  $W$  was chosen so that the largest of all jump probabilities is equal to 1, i.e.,

$$W_{BA}(1+\Delta)=1. \quad (3.1)$$

Every step of the simulation follows three phases.

- (i) An occupied site  $i$  is chosen at random and Monte Carlo time (number of steps)  $N_t$  is increased by 1.
- (ii) One of the two NN sites  $i+\delta$  (where  $\delta=\pm 1$ ) is chosen with probability

$$p_\delta = \frac{1}{z_c} = 0.5, \quad (3.2)$$

where  $z_c=2$  is the coordination number. If the site  $i+\delta$  is found occupied, the whole operation is taken from the beginning.

- (iii) A jump is attempted to site  $i+\delta$  with probability  $W_{i,i+\delta}^E$ . If the jump is performed, the number of jumps to the right  $N_r$  (or to the left  $N_l$ ) is increased by 1, for  $\delta=1$  (or  $\delta=-1$ , respectively).

The current density is given by Eq. (2.15), which must be written in terms of Monte Carlo quantities. First, it is clear that  $j$  is proportional to

$$N_{\text{jumps}} = N_r - N_l, \quad (3.3)$$

so that we only have to specify the correct factors. Due to the fact that in phase (i) sites are considered at random, rather than in increasing index order, and because phase (i) is repeated  $N_t$  times, the sum in Eq (2.15) is taken over Monte Carlo steps and  $N$  is replaced by  $N_t$ . Moreover, due to the fact that in phase (i), occupied rather than general sites are chosen, the result must be multiplied by a second factor, namely  $c$ . Finally, in phase (ii), only one of the  $z_c=2$  jump directions is considered in every Monte Carlo step [while they are both present in Eq. (2.15)]; this gives a factor of  $1/p_\delta=2$ . In the end we get

$$j = \frac{ea}{N_t \Omega} 2c N_{\text{jumps}}. \quad (3.4)$$

The experimental value of the correlation factor is obtained from Eqs. (1.2), (2.14), (2.16), and (3.4) as

$$f_{\text{exp}} = \frac{c N_{\text{jumps}}}{\Delta N_t \langle \langle \mathbf{W}^{-1} \rangle \rangle^{-1}}. \quad (3.5)$$

The method was successfully tested on two exactly soluble models: the uniform chain ( $\varepsilon_A = \varepsilon_B$ ) and the ordered model of Richards,<sup>6</sup> in which the two types of sites alternate.

## B. Onset of the stationary state

Because we start with equilibrium initial conditions, the stationary state is reached, theoretically, at infinite time. For practical purposes, after a long but finite time  $\tau$  has passed, the system can already be considered in the steady state. The value of  $\tau$  can be estimated from the relaxation curve of the current density, which was determined as follows.

Preliminary simulations were performed at concentration  $c=0.5$ , where the largest statistical errors occur. The current was measured and averaged over time intervals of 4 MCS/particle, for ten different equilibrium conditions on each sample out of a set of 100. In Fig. 1, we have illustrated the resulting time dependence of the configurational-averaged current density normalized by its MF value. It can be seen that the stationary state is established after a time  $N_t/N_p \approx 50$ , which is similar to the result obtained by Richards for the ordered  $AB$  chain.<sup>6</sup>

## C. Stationary-state averages

During the previously described experiment, at  $c=0.5$ , we also recorded the populations of the two types of sites, in the stationary state. First we counted the total number of particles  $N_{pA}$  on  $A$  sites. After temporal and configurational averaging, the value of  $c_A = N_{pA}/N_A$  was found not to be different from its equilibrium value  $f_A$ , at least within statistical errors. A significant change was observed in two particular NN pair-correlation functions, namely the ones relating sites of different type. These are defined as follows:

$$c_{AB} = \frac{4}{N} \sum_{i=1}^N n_{i,A} n_{i+1,B}, \quad (3.6a)$$

$$c_{BA} = \frac{4}{N} \sum_{i=1}^N n_{i,B} n_{i+1,A}, \quad (3.6b)$$

where

$$n_{i,A} = \begin{cases} 1 & \text{if } i \text{ is an occupied } A \text{ site,} \\ 0 & \text{otherwise.} \end{cases} \quad (3.7)$$

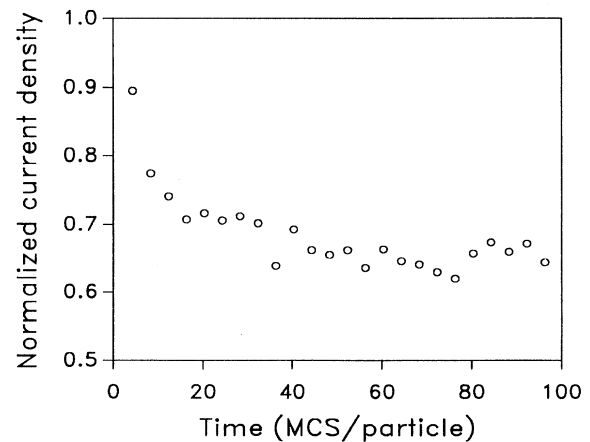


FIG. 1. Time dependence of the normalized current density, for  $c=0.5$ . The units of time are Monte Carlo steps per particle.

The equilibrium values of Eqs. (3.6a) and (3.6b) are equal. For  $c=0.5$  they are given by

$$c_{AB} = c_{BA} = f_A f_B = 0.1825 \quad (3.8)$$

while the simulated stationary-state values are

$$c_{AB} = 0.181 \pm 0.0001, \quad (3.9a)$$

$$c_{BA} = 0.187 \pm 0.0001. \quad (3.9b)$$

The difference is easy to understand by an argument similar to that of Richards.<sup>6</sup> Particles on  $A$  sites have a lower average jump rate and are thus "slower" than those on  $B$  sites. A particle sitting behind a slow one (with respect to the direction of the flow) will have to spend more time there than a particle which is preceded by a fast one. Therefore  $c_{BA} > c_{AB}$ . The 0.006 difference is of the same order of magnitude as the exact value 0.0102 obtained by Richards for the ordered chain, with the same choice of parameters.

#### D. The correlation factor

The main experiment was performed for five values of the concentrations:  $c=0.1, 0.2, 0.3, 0.4,$  and  $0.5$ . We considered 300 realizations of the binary chain for configurational averaging. For each case the current was averaged over 100 MCS/particle, in the stationary state, for 100 different initial conditions. Each of the five experimental points thus obtained took about 40 h of computer time. The result,  $f_{MC}$ , which was continued by symmetry up to  $c=1$ , is presented in Fig. 2, together with the theoretical upper bound of I,  $f_{th}$ , and with Richards' exact result  $f_R$  for the ordered chain, which is a lower bound for all 1D binary models. The experimental error is lower than the size of the circles in Fig. 2.

As can be seen from the picture, the error of  $f_{th}$  is maximal at  $c=0.5$ . At this concentration,  $f_{th}$  corrects the MF result by 0.27 (and not 0.22 as was reported in I due to a numerical error), while  $f_{MC}$  brings a 0.35 correction. As was mentioned in II, further corrections to  $f_{th}$  can also be calculated. We did this<sup>13</sup> for the second term denoted in II by  $f^{(2)}$ , and obtained an additional decrease of 0.015 in  $f_{th}$ . This, together with the present MC result, gives an overall image of the quality of the sequence of upper bounds in II.

#### IV. SUMMARY AND CONCLUSIONS

The hopping conductivity of the one-dimensional lattice gas with two randomly distributed site energies was studied for concentrations  $c \in [0, 0.5]$  by Monte Carlo simulation. Starting from equilibrium initial configur-

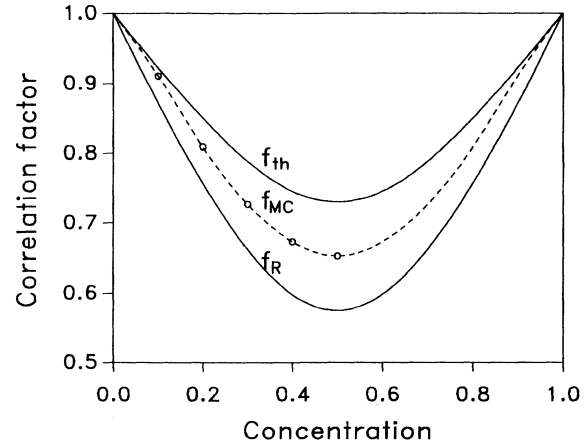


FIG. 2. The correlation factors of the random chain: theory of Ref. 9 ( $f_{th}$ ) and simulations ( $f_{MC}$ ) and of the Richards model ( $f_R$ ), vs concentration, for values of parameters chosen so that  $\exp(\epsilon_B - \epsilon_A/kT^*) = 10$ . Monte Carlo results are represented by circles. The dashed line was drawn as a guide to the eye and then continued by symmetry for  $c > 0.5$ . The experimental error is lower than the size of the circles.

ation, in the presence of an external uniform and constant electric field  $E$ , a stationary state was reached after a time  $\tau \approx 50$  MCS/particle. In the stationary state, correlation functions of nearest-neighboring sites were studied, showing similarities to the exact soluble ordered model of Richards.<sup>6</sup>

The correlation factor of the dc conductivity,  $f$ , was measured and compared to previous theoretical upper bounds.<sup>5</sup> As was expected, the present computer experiments showed no qualitatively new features of the problem, but were aimed merely at getting a good value for  $f$  and, thus, an estimate for the approximation sequence of II.

*Note added in proof.* After submitting the manuscript we learned about a recent simulation study<sup>14</sup> of similar systems in one, two, and three dimensions, using a different algorithm.

#### ACKNOWLEDGMENTS

The author would like to express his gratitude to Professor W. Dieterich of the University of Konstanz, Germany, for hospitality during the first part of the work. He would also like to thank Professor W. Dieterich and Dr. T. Wolf for helpful discussions. Financial support from Deutsche Akademische Austauschdienst (DAAD) during the stay in Konstanz is hereby acknowledged.

\*Permanent address: Institute of Physics and Technology of Materials, P.O. Box MG-7, Bucharest-Magurele, R-76900, Romania.

<sup>1</sup>S. Alexander, J. Bernasconi, W. R. Schneider, and R. Orbach, *Rev. Mod. Phys.* **53**, 175 (1981).

<sup>2</sup>J. W. Haus and K. W. Kehr, *Phys. Rep.* **150**, 263 (1987).

<sup>3</sup>A. Miller and E. Abrahams, *Phys. Rev.* **120**, 745 (1960).

<sup>4</sup>G. E. Murch and J. C. Dyre, *CRC Crit. Rev. Solid State Mater. Sci.* **15**, 345 (1989).

<sup>5</sup>P. Gartner and R. Pitiş, *Phys. Rev. B* **45**, 7739 (1992).

<sup>6</sup>P. M. Richards, *Phys. Rev. B* **16**, 1393 (1977).

<sup>7</sup>R. A. Tahir-Kheli, *Phys. Rev. B* **31**, 644 (1985).

<sup>8</sup>K. S. Chase and D. J. Thouless, *Phys. Rev. B* **39**, 9809 (1989).

<sup>9</sup>R. Pitiş and P. Gartner, *Phys. Rev. B* **43**, 11 294 (1991).

<sup>10</sup>P. M. Richards and R. L. Renken, *Phys. Rev. B* **21**, 3740 (1980).

<sup>11</sup>G. E. Murch, *J. Phys. Chem. Solids* **46**, 53 (1985).

<sup>12</sup>A. Pechenik, S. Susman, D. H. Whitmore, and M. A. Ratner, *Solid State Ion.* **18-19**, 403 (1986).

<sup>13</sup>The details of the calculation are beyond the scope of this report and will be omitted.

<sup>14</sup>K. W. Kehr and O. Paetzold, *Physica A* **190**, 1 (1992).