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A computer simulation study for the permeability of an interacting lattice gas through a percolating system

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Abstract. A Monte Carlo study is presented for the transport of particles interacting with a nearest-neighbour interaction in a two-dimensional percolating system which is connected by a source at the one end and by a sink at the opposite end. Using mobile particles as carriers, permeation of quantity such as charge (or mass) from source to sink is studied in a density gradient. The RMS displacement of carriers shows a nondiffusive power law behaviour. The permeability coefficient for the charge transport depends non-monotonically on the carriers concentration far above the percolation threshold and becomes constant near the percolation threshold; at a constant carriers concentration, it increases continuously on increasing the site concentration.

Because of several new developments [1–10], such as anomalous diffusion, superuniversality, non-diffusive transport, critical slowing down, fractality and multifractality, etc, during the past decade, studying the transport properties of percolating systems has become one of the most active areas in recent years. Considerable progress has been made in understanding single particle transport and lattice gas diffusion in percolating systems [2, 6–10]. However, many questions remain unanswered particularly on the non-diffusive motion [7, 11] in the presence of a biased field and long relaxation [12] time in an interacting lattice gas. Numerous random systems have also been studied experimentally [13–17] where transport of charged (i.e. ions and ionomers) and neutral particles through a random medium is involved. For example, the dielectric measurements [15] on the charge transport in a nafion membrane in various aqueous solutions, and the penetrant motion of plasticizers in a polymeric matrix (PVC) [16] seem to indicate various transport phenomena which are not explained by the traditional theories [6] based on either the lattice gas (with only hard core interactions) calculations or on the approximations that ignore strong correlations. Some of these random systems are successfully modelled [1, 2] by one percolation mechanism or the other.

The problem of transport in Coulomb gas has been noted for its difficulty due to long range interaction. Very little is known, beyond the preliminary computer simulation study [12], of the transport of charge particles in percolating systems. Gefen and Woods-Halley [12] considered the motion of charged particles each with unit charge density on a percolating cluster in which each empty site of the cluster was assigned a charge density of opposite sign such that the total charge of the whole system (the background negative charge plus the positive charge of the particles) is zero. Although, long range (Coulomb) interaction was incorporated in their study, the samples were relatively small. Furthermore, their investigations were concentrated mostly on the

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non-equilibrium aspect, the growth of polarization in the presence of the field and its decay as the field is switched off. Because of extremely long relaxation time, it is rather difficult to predict whether such slow motion of particles in percolating system leads to an asymptotic power law behaviour or to a metastability as in the case of a single particle biased diffusion [11]. One of the commonly studied quantities, the variation of the RMS displacement with time, has not been analysed in detail.

We intend to carry out a similar study on the transport quantities such as variation of the RMS displacement of the tracers and that of the centre of mass (a measure of polarization) with time and permeability but we restrict ourselves here to a nearest-neighbour (NN) interaction for simplicity. Further, we attempt to model the transport in a field induced by a density gradient that may be closer to some of the experiments pointed out above. The background charges of the percolating clusters may capture some of the characteristics of the interacting gas (at least beyond the hardcore interaction) in which their inhomogeneous distribution (of empty sites on the clusters) leads to random but attractive interactions with neighbouring charged particles. In our previous studies [18] of interacting gas in simpler systems (in a homogeneous lattice), we have observed a dramatic decrease in conductivity on increasing the range of interaction from hardcore (zeroth order) to the nearest neighbour. Therefore, for the first time, the investigation of the transport properties such as RMS displacement and permeability of interacting gas in a quenched disorder medium of the percolating system even with an NN interaction with a gradient induced field (see below) might help understand the complex transport phenomena. We hope that we continue our systematic investigation to incorporate the effects of the long range interactions as the computing resources become available.

The random system is modelled by a quenched site percolation [2] in which the geometric inhomogeneity is caused by the random distribution of conducting clusters of various sizes. Such random systems begin to conduct at the percolation threshold where the infinite network of conducting paths appears at the onset of percolation [2]. Therefore, we restrict ourselves to the conducting regime above the percolation threshold to ensure that the source and the sink at the opposite ends are connected by the ramified path of the percolating cluster. The transport of charge (or mass) through such a random system is governed by stochastic motion of the charge carriers, not only through the inhomogeneous geometry but also in a potential gradient caused by a charge source at the one end and a sink at the other (see below). The competition between the potential gradient and the ramified geometry makes the motion of the carriers very complex to understand. We examine RMS displacements of the carriers and an effective permeability coefficient as a function of the volume fraction of the medium, concentration of the carrier and temperature. It is worth pointing out here that, in the dielectric measurements and PVC experiments [13-16] mentioned above, not only a variety of particulates with their charge and mass distributions are involved in their transport properties but also different kinds of interactions such as Coulomb, Lennard-Jones, hydrophobic, hydrodynamic, etc among them may influence their motion. To begin with, two type of particles (charged and neutral) are considered and we assume that the competing effects of the various interactions and their screening lead to an NN dominant interaction.

We consider a two-dimensional lattice of size $L_x \times L_y$ as in our previous study [18] but with an additional disorder of quenched percolating medium here. A charge source is connected with one end of the lattice with a sink at the opposite (the L_xth column) along the x-axis. We randomly select a fraction p_c of these lattice sites and assign them

a conducting (i.e. 'allowed') status. The remaining lattice sites of fraction $(1-p_s)$ are forbidden to particle hopping. Clusters formed by connecting the NN conducting sites thus constitute our inhomogeneous host medium. A fraction p of these conducting sites is then occupied by mobile particles. A particle can have a charge density one or zero. Initially, we distribute the charge among the particles to set up a linear charge density gradient of one at the source and zero at the sink. The empty sites on the clusters are assigned a charge density of opposite sign to keep the whole system neutral. For example, if there are N_c charged particles in the system, then the charge density of each empty site is

$$\rho_e = -N_c/N_e \tag{1}$$

where $N_e = (1-p) \times p_s \times N$ with $N = L_x \times L_y$. Particles are not allowed to hop on the forbidden sites.

The forbidden sites restrict the motion of mobile particles to the conducting clusters and the empty sites, with their negative charge density on the ramified clusters, attract charge particles which repel their neighbouring charged particles. Note that the background charges are not only neutralizing the whole system as in previous studies [12], but also they provide inhomogeneous effective field (due to inhomogeneous distribution of empty sites) for accelerating the hopping of the carriers. Movement of the particles is governed by their energies in which a particle at site i and one of its neighbouring sites j, are selected randomly. If site j is not a forbidden site and it is empty, then we calculate its interaction energy

$$E_0 = \rho_i \sum_k \rho_k \tag{2}$$

where index k runs over neighbouring sites. We evaluate the interaction energy E_1 for the configuration in which the particle and the hole positions as well as their charges are exchanged. Now, as in the Metropolis algorithm [19], if the change in energy ΔE $(= E_1 - E_0) < 0$, then the particle is moved from site i to site j. However, if $\Delta E \geqslant 0$, then the new configuration for the particle's hop is selected with a Boltzmann distribution, $\exp(-\Delta E/k_B T)$, where k_B is the Boltzmann constant and T is the temperature. Charge is also transferred along with the particle's movement. If the site j is at the column connected by the source then a charge transfer $(1-\rho_j)$ is the amount of charge releases from the source as we set the charge density ρ_j of this particle at site j to unity. If the site j is at the column connected by the sink then the charge transfer ρ_j is added to the amount of charge absorbed by the sink and the charge density ρ_j is set to zero. On the other hand, if the site j is occupied or it is forbidden, then the particle remains at site j. This process of selecting a particle, attempting to move and updating its charge density and charge transfer is repeated again and again for all the particles for preset Monte Carlo steps (MCS); an attempt to move each particle once is defined [19] as unit MCS time. A periodic boundary condition is used along the y-axis and an open boundary condition along the x-axis at the source and the sink.

The computer simulation is performed at our mainframe DPS-90 machine. Most of the data are produced with the lattice size 60×60 with up to half a million time steps; the smaller lattices are used to test the reliability of our data. During the simulation we monitor the following transport quantities periodically: RMS displacement of the particles (i.e. the tracers) and of their centre of mass, and the charge transferred at the source and at the sink as a function of both the site concentration p_s as well as the carrier concentration p. From these data, we evaluate the exponent

for the rms displacement and the permeability coefficient [17, 20] for the charge transport across the percolating clusters. Figure 1 shows a typical variation of the RMS displacement of the centre of mass, R_{cm}, with time t at $p_s = 0.70$ (above percolation threshold $p_s^* = 0.592$) and temperature $\tau\ (= k_B T) = 2.0$. Fluctuation in the data gives us an idea about the stochastic motion of the particles in the stochastic geometry of the charged clusters.

A typical variation of the RMS displacement of the carriers with time on a log-log plot is shown in figure 2. The slope of the linear fit gives us an estimate of the power law exponent k for the RMS displacement R_{tr}

$$R_{tr} \simeq t^k. \tag{3}$$

We have estimated the exponent k at various site concentration for several values of particle concentration p and the result is presented in figure 3 at a fixed temperature $\tau = 2.0$. Despite the fluctuations, we see that these data points show a clear trend in the variation of the exponent in which it increases from a minimum value of about 0.30 around $p_s \simeq 0.60$ to a maximum saturation as high as 0.46 at $p_s = 0.80$.

We know [2, 9] that, for a single particle random walk motion in a non-interacting percolating host medium, $k \simeq \frac{1}{3}$ at the percolation threshold $p_s^* \simeq 0.592$ in two dimensions; the random walk diffusion is Fickian above the percolation threshold. In the presence of a bias field, the single particle diffusion in a percolating system, even above the percolation threshold, seems to be non-diffusive; a heuristic argument [11] suggests that the exponent k depends on the bias field and the percolation correlation length. At very low carrier concentrations p, the transport in our model may be viewed as a single particle diffusion. In addition to the field induced by the charge density gradient here, we have background charges distributed homogeneously on the empty sites of the percolating clusters which act as an effective inhomogeneous field on the neighbouring carriers. However, the magnitude of the exponent k near the percolation threshold is close to its anomalous diffusion [2] value $\frac{1}{3}$ (see figure 3). A systematic increase in its magnitude on increasing the site concentration ($p_s \simeq 0.60$–0.70) suggests

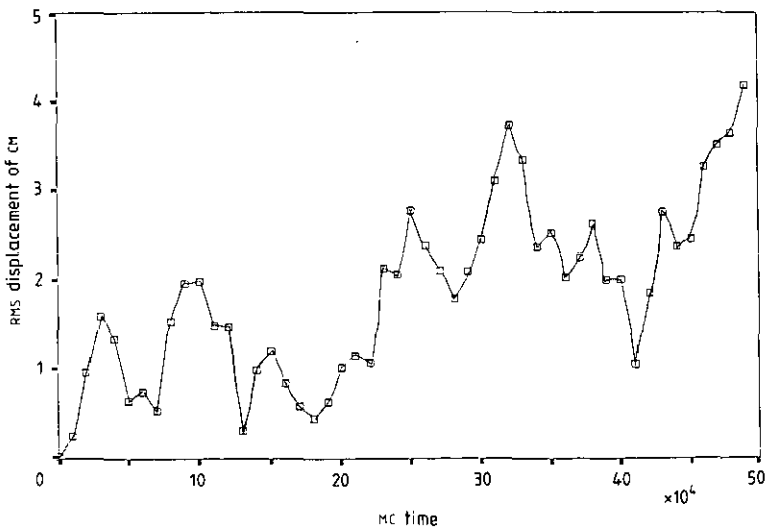

Figure 1. RMS displacement of the centre of mass against time at temperature $\tau = 2.0$, site concentration $p_s = 0.70$, and particle concentration $p = 0.50$ with the sample size 60×60.

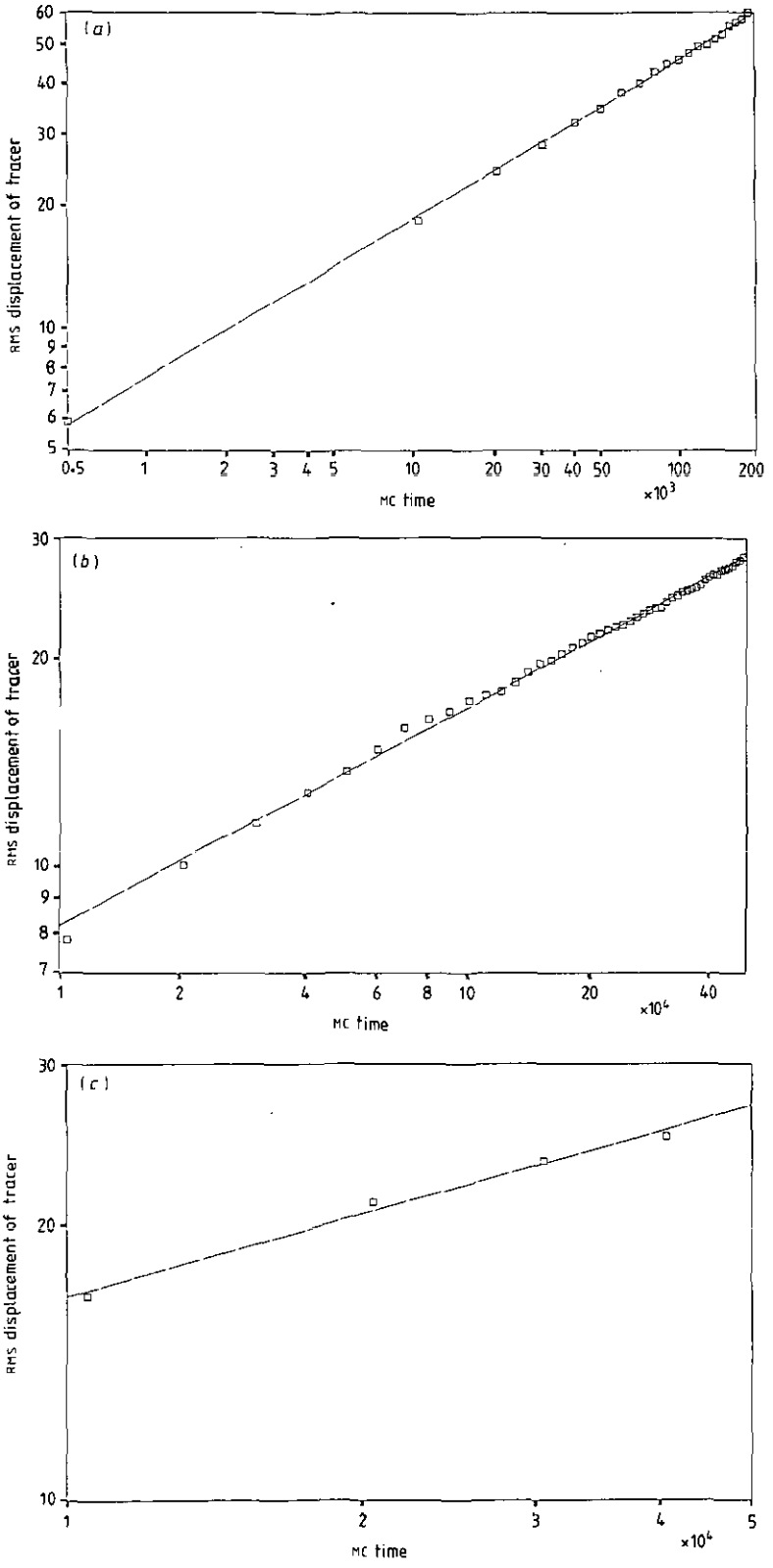

Figure 2. RMS displacement of the tracer against time on a log-log plot with $p_s = 0.62$ and $p = 0.40$ at $\tau = 2.0$ with sample (*a*) 60×60 and (*b*) 30×30 and at $\tau = 0.1$ with sample 60×60 (*c*).

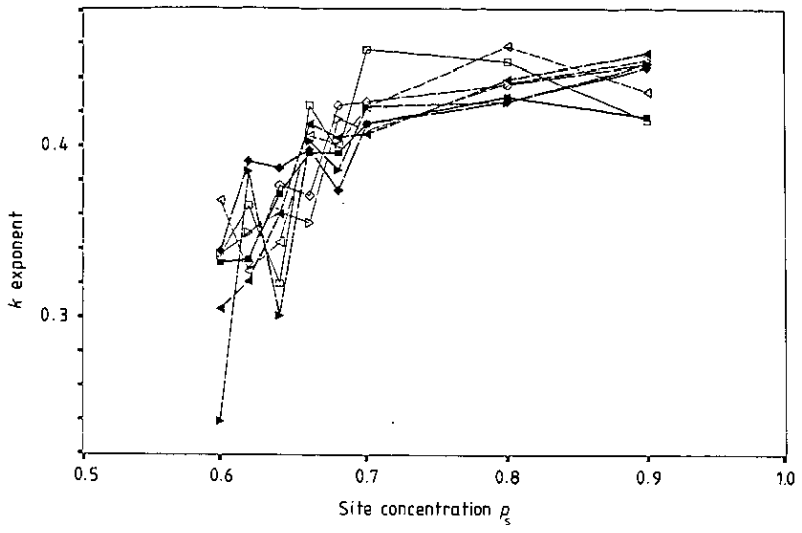

Figure 3. Variation of the exponent k with the site concentration p_s at carrier concentration $p = 0.10$ (□), 0.20 (■), 0.30 (◇), 0.40 (◇), 0.50 (▷), 0.60 (▷), 0.70 (◁), 0.80 (◁). Sample size 60×60 and temperature $\tau = 2.0$.

a non-diffusive behaviour as in the case of global bias [7, 10]; the random distribution of particles and empty sites gives rise to local inhomogeneous fields in addition to the global gradient field. At this stage it is rather difficult to provide more precise estimates of this exponent k as a function of site concentration, other than the prediction of a non-diffusive transport near percolation threshold.

Charge is transferred from the source to the sink, as the particles execute their stochastic motion. In order to satisfy the continuity equation, the charge must be conserved in steady state equilibrium, i.e.

$$Q_i(t) = Q_0(t) + Q_b \tag{4}$$

where $Q_i(t)$ is the amount of charge released by the source, $Q_0(t)$ is the amount absorbed at the sink at time step t and Q_b is the amount of charge remaining uncounted in ramified clusters. We have noticed that, in the steady state, Q_b is constant, leaving the flux of charge entering the system at the source the same as the outgoing flux at the sink. For the charge permeation through the percolating system, we define a permeability coefficient [17]

$$P_e = (\mathrm{d}Q/\mathrm{d}t) \times (L_x/L_y) \tag{5}$$

where $\mathrm{d}Q/\mathrm{d}t$ is the charge permeation rate which is the flux (in or out) and is a measure of current. In fact, the permeability coefficient has also been used as a measure of an effective conductivity [18] in a similar system, and therefore we use these terms interchangeably.

Thus, by measuring the slope of the charge transfer $Q(t)$ (at the source or at the sink) against time one may evaluate the permeability coefficient P_e in the steady state. We have studied the variation of P_e as a function of carrier concentration p at several site concentration above the percolation threshold and the result is presented in figure 4. We observe that, the permeability coefficient shows a non-monotonic behaviour as a function of p at high site concentrations (i.e. $p_s = 0.80$ and 0.90, see figure 4) in which its growth is followed by a decay at a characteristic value of p. On reducing the site

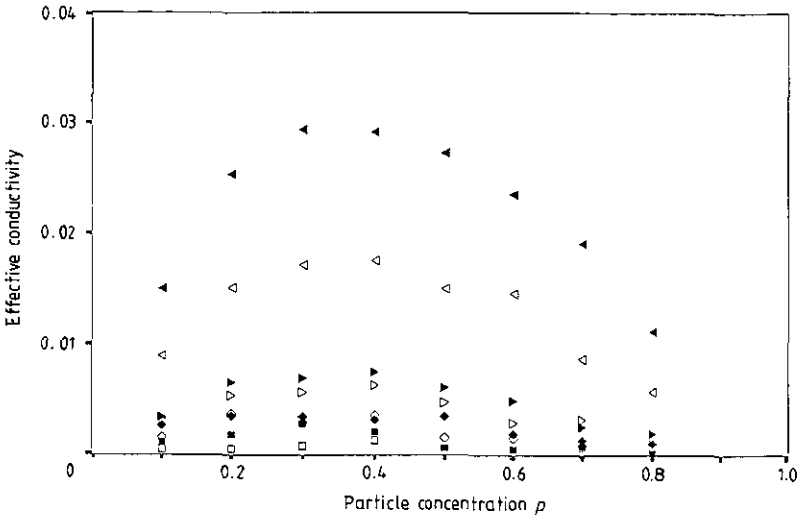

Figure 4. The permeability coefficient against carrier concentration at site concentration $p_s = 0.60$ (□), 0.62 (■), 0.64 (◇), 0.66 (◇), 0.68 (▷), 0.70 (▷), 0.80 (◁), 0.90 (◁). Statistics are the same as in figure 3.

concentration, the permeability coefficient decreases and it approaches a constant value near percolation threshold on varying the particle concentration (see figure 4). At the low site concentration, it appears that the geometrical ramification of the clusters, the field induced by the charge density gradient and the inhomogeneity caused by the random distribution of particles and holes compete/cooperate in such a way that the carrier concentration becomes ineffective as far as the charge transport is concerned.

In summary, we have presented a computer simulation model to study the transport of charge and its carriers through a random percolating medium. The percolating clusters carry background charges and a charge density gradient field produced by a source and a sink at the opposite ends of the sample. We find that the power law exponent for the asymptotic behaviour of the RMS displacement exhibits a non-diffusive value which seems to depend on the site concentration. It is difficult to compare these results of our simplified model with that of experiments on dielectric measurements; however, such a change in the power-law behaviour seems to capture some of the details on the variation of the loss component of the dielectric constant in experiments [15]. At high site concentration, the permeability coefficient for the charge transport depends nonmonotonically on the carrier concentration with a maximum at a characteristic value. Near the percolation threshold, the permeability coefficient remains constant on varying the carrier concentration. It decays continuously on reducing the site concentration and vanishes at the percolation threshold.

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