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Computer-simulation study of conductivity in a two-dimensional binary fluid mixture

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A computer-simulation model is introduced to study the transport properties of a binary fluid mixture in which the constituents of one fluid (the tracer particles) carry charges in a linear charge-density gradient in the background charge of the second fluid. In the steady-state equilibrium, an effective conductivity $\sigma_c(p,r)$ is estimated as a function of the carrier concentration p and the range of interactions r. The conductivity is observed to vary nonmonotonically with the concentration p, and it exhibits a maximum at a characteristic value p_c. The conductivity decreases when the range of interaction is increased until a characteristic value r_c, beyond which $(r > r_c)$ it begins to saturate as the onset of screening spans with $r - r_c$.

Understanding transport properties such as conductivity, diffusion, polarization, and dielectric response in fluid and fluid mixtures has been a subject of continuous interest. Because of the numerous applications, efforts have been intensified in recent years via a number of experimental methods,[1-3] such as NMR, light scattering, neutrons scattering, and dielectric measurements, in studying the transport properties of a variety of complex polymeric solutions, such as polyelectrolyte and biopolymers, in solvents with diverse reactivities. Transport of charge, mass, or heat, in such complex fluids takes place via numerous carriers (neutral as well as charged particles, such as ions, ionic clusters, ionomers, etc.), which are in constant stochastic motion in matrices of each other. To address the issue of global transport arising from highly correlated stochastic motion of different constituents, it is important to understand transport properties of one component (say, ions) first. While numerous experimental studies exist on the transport properties of such complex fluids, relatively few attempts have been made via theoretical means.[2-5] Most of the analytical treatments are limited due to intractabilities in incorporating the long-range interactions, where one resorts to several approximations involving screenings (Coulomb, excluded volume, etc.) and details of inhomogeneity. Nevertheless, these theoretical studies help in understanding some of the transport processes in extreme limits. Here, we use computer simulations[6-8] to study the transport properties, such as root-mean-square (rms) displacement, and conductivity of an interacting model system, which may provide physical insight into some of the stochastic processes in highly correlated complex fluids. We focus mainly on the transport of one type of charge carrier with a varying range of interactions to address the question, how does transport depend on the range of interactions and concentration of charge carriers and when does the screening come into play? This study may help in understanding the fluid flow and fingering instabilities in interacting systems, which is also one of the current issues,[5] by means of computer simulations and experimental methods.

For simplicity, a two-dimensional discrete lattice[6] of size $L_x \times L_y$ is considered. One end of the lattice (say, the first column) is connected with a charge source, while the opposite end (the L_xth column) is connected by a sink. A fraction p of the lattice sites is randomly occupied by particles, the charge carriers that constitute the components of one fluid. A lattice site cannot be occupied by more than one particle. Each particle, in contact with the source, is assigned a unit charge density, while those in contact with the sink are assigned a zero charge density. The rest of the particles are assigned charge densities (zero or one) to achieve a linear charge-density gradient (of one at the source and zero at the sink, i.e., $\nabla \rho_x \sim 1/L_x$). Each vacant site (a constituent of the second fluid of concentration $1-p$) is assigned a charge density of an opposite sign to maintain the charge neutrality of the whole system. Thus, if there are N_c charged particles in the system, then the charge density of each empty site is

$$\rho_v = -N_c / N_v \ , \qquad (1)$$

where $N_v = (1-p)L_x L_y$, the number of vacant sites. The charges spread over vacant sites thus act as background charges of the second fluid. The sample is now initialized and is ready for studying the transport properties.

Particles interact with each other with a repulsive interaction and with holes (the empty sites) with an attractive interaction. Before initiating the stochastic motion of the particles, we first set the range of interaction r_n, a distance up to nth neighbor ($n=1$ represents the nearest-neighbor interaction, $n=2$ the next nearest neighbor, and so on). All the particles and holes interact with each other only within this range; exclusion of multiple occupancy of a lattice site by particles takes care of hard-core interactions. The technical details of the hopping mechanism of a particle are as follows. A particle at site i and one of its neighbors at site j are selected randomly. If site j is empty, then we calculate the following. (i) The interaction energy E_0 is calculated with particle at site i,

$$E_0=\rho_i \sum_k \rho_k / r_{ik} \tag{2}$$

where the summation index k runs over all the particles and holes starting from first neighbor to the nth neighbor, ρ_k is the charge density of the particle or hole at site k, and r_{ik} is the distance between sites i and k. Note that, for a particle at site k, ρ_k may be either 1 or 0, while for a hole, it may be a noninteger number, depending upon the concentration $1-p$ of the holes and the number of charged particles. (ii) The interaction energy E_1 is evaluated for a configuration in which particle and hole positions as well as their charges are exchanged. (iii) Then we evaluate the change in energy $\Delta E = E_1 - E_0$. If the change $\Delta E \leq 0$, then the new configuration is accepted, and the particle is moved from site i to site j. If site j is at the column connected by the source, then the charge density ρ_j of this particle at site j is set to unity and the charge transfer $(1-\rho_j)$ is counted as the amount of charge released from the source. Similarly, if the jth site belongs to the column connected by the sink, then the charge density ρ_j is set to zero, and the charge transfer ρ_j is added to the total charge absorbed by the sink. Thus the charges can be transferred from source to sink, as the carriers execute their stochastic motion. On the other hand, if site j is occupied, then the particle stays at site i and steps (i) through (iii) are not executed. This process of selecting a particle and its neighboring site randomly, attempting to move it and updating its charge density, is repeated again and again for all the particles. Each attempt, irrespective of its success to move a particle, is counted in the Monte Carlo (MC) time step,[9] and an attempt to move each particle once on average is defined as one MC step. The simulation is performed for a preset (large) number of Monte Carlo steps (MCS), which is the total length of the time scale in our computer experiment. A periodic boundary condition is imposed for motion along the y direction, while a reflecting boundary condition is used along the x direction (where source and sink act as reflectors).

During the simulation, we keep track of the following quantities: (i) charges released from the source $Q_1(t)$, (ii) charges absorbed at the sink $Q_2(t)$, (iii) rms displacement of the particles (i.e., tracers), and (iv) the rms displacement of the center of mass of the particle system at each time step. A limited number of these quantities are, however, printed periodically at equal intervals of time. Samples of various sizes are used to test the reliability of our data, but we limit ourselves here to sample sizes 40×20 and 60×60. The time scales range from 10^4 to 5×10^5 MCS, although most of the data we run at the maximum time of half a million steps. In steady-state equilibrium, the amount of charge released from the source must be nearly the same as that absorbed at the sink. A plot of charge versus time is shown in Fig. 1. The relaxation time to approach the steady state in which the charge released from the source equals the charge absorbed at the sink depends on the concentration of the carriers; the higher the concentration, the larger the relaxation time in which the system approaches its equilibrium state. We also observe that the relaxation time increases sharply on increasing the range of interactions. Most of the data presented here are in the regime where the system has reached the steady state.

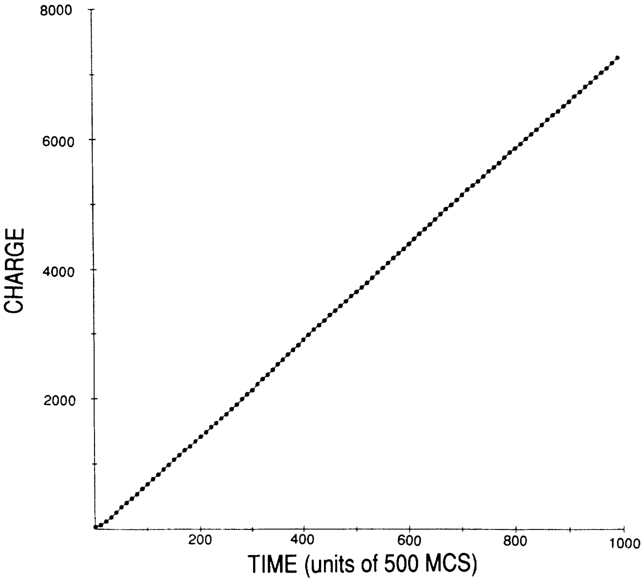

FIG. 1. Charge transfer $([Q_1(t)+Q_2(t)]/2)$ vs time t. Lattice size 60×60 is used at the concentration of the particles $p=0.5$, with nearest-neighbor interaction.

A typical variation of the rms displacement R of the center of mass with time is shown in Fig. 2(a). The carriers execute their random motion in such a way that the rms displacement of the center of mass increases with time until most of the charge carriers hit the other end. Since the random motion of each particle determines the movement of its center of mass, a large fluctuation in R is expected, as seen in Fig. 2(a). A continuous shift in the rms displacement is, however, observed, although with fluctuations, on an average time scale ($\simeq 4\times10^5$ MCS), in which each particle hits the reflecting boundaries (source or sink). The rms displacement of the particles (i.e., tracers), on the other hand, shows a very smooth increase with time [see Fig. 2(b)]. In the asymptotic regime, we define the power-law behavior of the rms displacement R_{tr} of the tracer with time t by

$$R_{\mathrm{tr}} \sim t^k , \tag{3}$$

where k is the asymptotic exponent. We observe a small deviation in the estimate of the exponent k from its drift value as we increase the concentration of the particles. For example, with the nearest-neighbor interaction, $k=0.94\pm0.02$ at $p=0.4$, $k=0.91\pm0.02$ at $p=0.6$, $k=0.84\pm0.02$ at $p=0.8$. The asymptotic value of the exponent k seems to remain unchanged with the range of interaction.

It is worth pointing out that the deviation from its drift value of the rms displacement of the charge carriers in the gradient field here may be attributed to the reflecting boundary conditions at the ends (source and sink), the concentration of particles and holes, their charge distribution, their interactions, etc. If we consider the stochastic motion of a single charged particle in a homogeneous medium in an electric field, its rms displacement will be driftlike in the asymptotic time regime. However, the presence of many charge carriers and holes makes the effective medium complex; the higher the concentration of particles the more inhomogeneous the medium in the long-time regime. As we observe, the deviation from its driftlike behavior becomes more pronounced on increasing the concentration of the particles and therefore we attribute it to the effect of inhomogeneity[10] produced by the random distribution of particles and holes.

We know that in the steady state,[6] the charges released from the source $Q(t)$ in time t is equal to charge absorbed at the sink, which satisfies the continuity equation (i.e., the conservation of charges). Therefore, in the steady state, the charge-density gradient is $\nabla\rho_x \sim 1/L_x$. From the variation of $Q(t)$ with time, one may estimate an effective conductivity σ_e from

$$j=(\nabla\rho_x)\sigma_e , \tag{4}$$

where j is the current density

$$j=\frac{1}{L_y}\frac{dQ(t)}{dt} . \tag{5}$$

Combining Eqs. (4) and (5), we find

$$\sigma_e=\frac{L_x}{L_y}\frac{dQ(t)}{dt} . \tag{6}$$

Thus, by calculating the slope of the $Q(t)$ versus t, we may evaluate the effective conductivity. (Note that this method, in combination with a finite-size scaling, provides a very accurate estimate of conductivity exponent near percolation threshold.[6]) We have performed extensive simulations to study the variation of conductivity

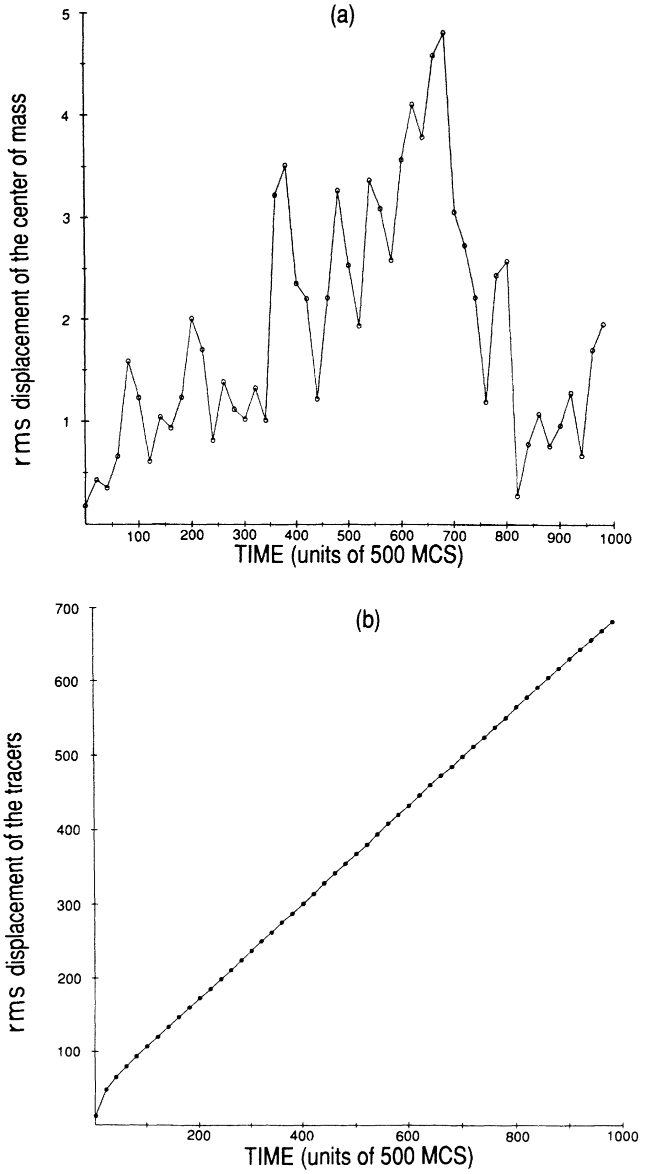

FIG. 2. (a) rms displacement of the center of mass of the particles and (b) rms displacement of the particles (tracers) vs time for the same statistics as in Fig. 1.

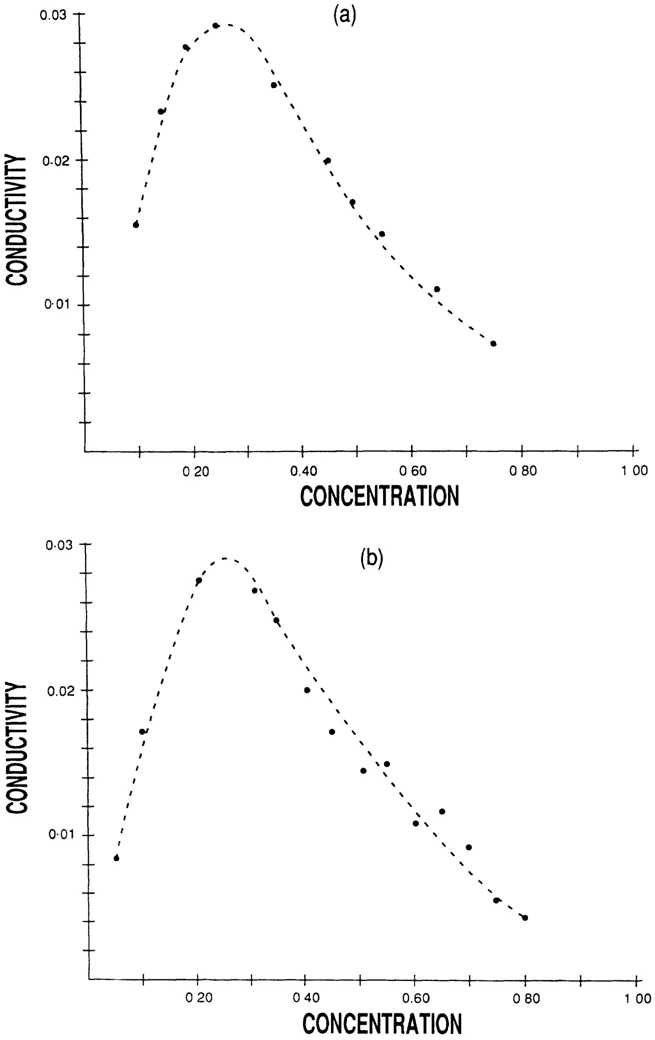

FIG. 3. Conductivity vs concentration p, with nearest-neighbor interaction, (a) sample size 40×20 and (b) sample size 60×60. Time steps from 2×10^5 to 5×10^5 MCS are used.

TABLE I. Effective conductivity data. A sample of size 60×60 is used. The statistical error bars are in the range 0.000 05–0.0002.

Interaction order	$p=0.4$	$p=0.5$	$p=0.6$	$p=0.7$	$p=0.8$
0	0.0436	0.0399	0.0346	0.0331	0.0192
1	0.0201	0.0146	0.0110	0.0095	0.0046
2	0.0130	0.0170	0.0169	0.0149	0.0138
4	0.0011	0.0036	0.0074	0.0114	0.0098
6	0.0022	0.0093	0.0153	0.0179	0.0123

with concentration p of the carriers and with the range of interactions. A typical variation of the conductivity with the concentration p is shown in Fig. 3; data for the conductivity as a function of concentration and order of interaction are presented in Table I. With a fixed range of interaction, we observe that the conductivity depends nonmonotonically on the concentration p and exhibits a maximum around a characteristic value p_c. Both the conductivity as well as the characteristic concentration p_c depend on the range of interaction. At a fixed carrier concentration, the conductivity is maximum at zeroth-order (i.e., with hard core) interaction. It decreases on increasing the range of interaction until the fourth-order interaction, and then it exhibits a saturation when screening comes into play (we have observed a little higher value at the sixth-order interaction, see Fig. 4 and Table I). Thus the conductivity decreases on increasing the range of interaction up to fourth neighbor, beyond which the onset of screening begins to reduce the effects of interactions; as a result, the conductivity tends to remain constant on further increasing the range of interaction. The characteristic concentration p_c, on the other hand, increases to a saturation value ($\simeq 0.7$) on increasing the range of interaction, except in a small region (from zeroth to first order). The onset of a plateau (Fig. 5) and that of the screening seem to lie in the same region.

We therefore infer that in our interacting stirred percolating system a characteristic range of interactions, say, r_c exists at which the conductivity exhibits a minimum. For interaction ranges smaller than this characteristic value, screening is not effective, and, therefore, all the interactions up to this order are important in studying the conductivity. For an interacting system with range of interaction r larger than r_c, screening becomes important. If we define the screening length over which the interactions are important in a long-range interacting system, then screening length decreases as $r-r_c$ increases for our system. A precise relation between the screening length and the range of interaction is hard to establish at this stage, as it requires computational capabilities beyond our access at present. In real fluid mixtures, transport and screening is governed by several parameters, such as quality of solvent, temperature, and nature of solute; and to take into account all these complex details in our exploratory simulation here is rather difficult. However, our crude model does capture some of the basic features through the effect of concentration and range of interaction on the transport properties of the system as a whole.

In summary, we have proposed a computer simulation model to study the transport properties in an immiscible interacting binary fluid mixture, in which the constituents of one component are the charge (in units of discrete charge, mass, or heat) carriers, while the others act as a background (charges for drag resistance which may be

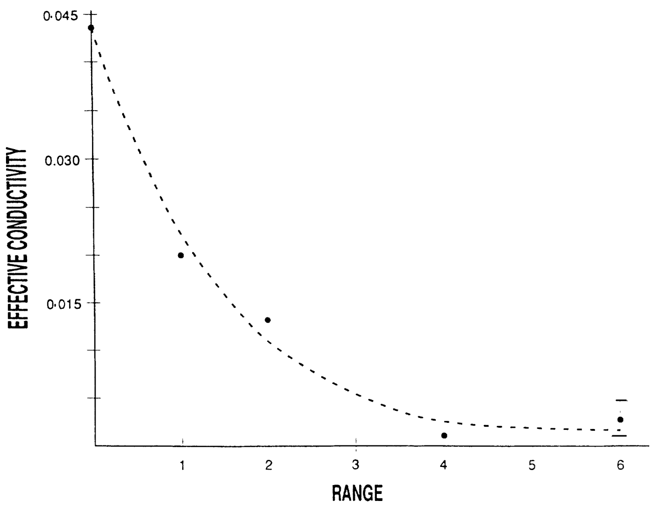

FIG. 4. Effective conductivity vs range of interaction at the concentration $p=0.4$ with the sample of size 60×60.

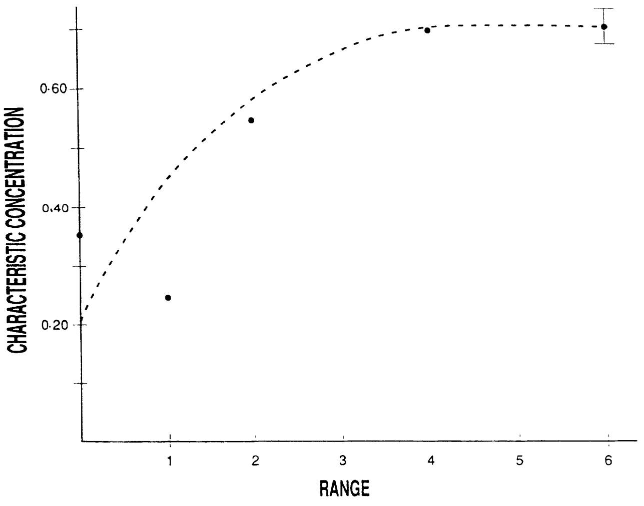

FIG. 5. Characteristic concentration vs range of interactions with the sample of size 60×60.

viscous or capillary) medium. Using a steady-state linear-gradient method, an effective conductivity is studies as a function of both the concentration of carriers as well as the range of interaction. The conductivity exhibits a nonmonotonic dependence on the carrier concentration p with a maximum at about p_c. The conductivity decreases as the range of interaction r increases until a characteristic value, say, r_c is reached. For the range r above r_c, the conductivity seems to saturate due to screening. Thus, the conductivity is minimum at a certain range of interaction, in a specified regime of carrier concentration which depends upon the quality of solvent in fluid mixtures. We hope this study will help in understanding the transport properties in complex fluids where a variety of chemical and physical parameters[1-3] govern the transport process; it may also guide analytical (theoretical) studies to incorporate appropriate interactions in such systems.

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