Diffusion of Ionic Particles in Charged Disordered Media

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The results of the first realistic computer simulation of diffusion of charged species in heterogeneous media with a quenched distribution of charge centers are reported. They indicate that the charge centers create deep traps that capture the mobile particles and slow down their motion for a long time. However, the mobile particles eventually escape the traps. Their motion between the traps is diffusive. These results explain several sets of hitherto unexplained experimental data and resolve a long-standing controversy regarding the nature of transport of charged particles in a heterogeneous charged medium. [S0031-9007(98)08280-5]

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Transport in heterogeneous systems, such as flow in porous media [1], conduction in composite solids [2] and in amorphous semiconductors [3], and diffusion through biological tissues [4] constitute an important set of phenomena. Most of the previous studies have considered transport of neutral particles in a disordered but neutral medium. However, transport of charged particles in a disordered medium, especially one with a quenched distribution of charge centers, is also very important, since it is relevant to many important phenomena, such as dynamic response of nonmetallic materials, e.g., ionic glasses and polymeric and glassy conductors, highly defected crystals, and porous materials that are used for catalytic and separation processes. Although this problem has also been studied extensively, no consensus regarding the nature of the transport process has emerged. For example, Zhang [5] studied diffusion of a particle in a random potential (generated by, e.g., quenched charge centers) and argued that for sufficiently strong disorder localized states will exist which, however, do not live forever; rather, the localization center hops discontinuously with its displacement R at time t given by $R \sim t/\ln t$. Engel and Ebeling [6] argued that if in Zhang's model the potential energy fluctuations contain short-range correlations, then the average time spent in a localized state grows as $\exp(\beta^2 E^2)$, where $\beta = (kT)^{-1}$, with k and T being the Boltzmann's constant and the temperature, respectively, and E is the typical depth of potential energy well. De Masi *et al.* [7] predicted that the diffusivity of mobile charged particles in a charged medium should have a finite bound *which can be zero,* thus allowing complete localization. Bouchaud and Georges [8] studied diffusion in disordered media in which the disorder exhibits long-range correlations, such as that induced by Coulombic interactions, and the force-force correlation function decays as $C(r) \sim r^{-\alpha}$. They argued that for a d-dimensional system with $\alpha < d$ and $\alpha < 2$ transport is anomalous, i.e., the mean square displacement (MSD) $\langle R^2(t)\rangle \sim t^z$ with $z < 1$. Chakraborty, Bratko, and Chandler [9] use a variational method to treat diffusion of charged particles in a disordered medium with random distribution of charge centers and argue that for sufficiently strong disorder there should be a crossover from a weakly diffusive behavior to complete localized states, whereas Deem and Chandler [10] use renormalization group techniques to argue that, even for sufficiently strong disorder, one still has diffusive motion between localized states. Therefore, over the years there have been several contradictory results with no consensus emerging. This has also prevented the interpretation of the experimental data for diffusion of ions in random media with a distribution of charge centers. For example, in diffusion of ions through zeolites, which are porous catalytic materials with a distribution of charge center (ions and cations), it has been observed [11] that, upon changing the charge on the diffusing particles (i.e., making the disorder stronger), the diffusivity *decreases by orders of magnitude*. Such puzzling data have remained unexplained.

Despite its great importance, there has been no computer simulation of this problem. This is due to the fact that simulation of diffusion of charged particles in a heterogeneous medium with *quenched distribution of charge centers* is extremely difficult, because (i) the Coulombic interactions between the particles are long ranged and (ii) as we show, the charge centers give rise to deep potential wells that may capture the mobile particles and slow down their motion for long times. In this Letter we report the results of the first Monte Carlo simulation of this problem which we believe resolve the controversy and explain the hitherto unexplained experimental data.

We used both lattice and continuum representation of the disordered medium with periodic boundary conditions. Our simulations indicated that with large enough systems periodic and free boundaries yield the same results. The continuum representation was used when the fixed charge centers were distributed randomly in the medium. The lattice, which was simple cubic, was utilized when we used a potential-potential correlation function, defined below, for generating the potentials due to the fixed charge centers. At time $t = 0$ the charged mobile particles are distributed randomly in the system, but as they move correlations develop between them. In addition to the Coulombic interaction, we also include a short-range,

Lennard-Jones-type repulsive interaction (i.e., $\sim 1/r^{12}$, where r is the distance) between the particles. At each time step a random but finite displacement in a random direction is selected for each particle. If the displacements are too large, the probabilities of their acceptance will be small and the simulation does not generate much new statistics, whereas although very small displacements are accepted more often, they do not contribute significantly to the statistics of the particles' motion. Thus, a displacement vector $\boldsymbol{\delta} = (\delta_x, \delta_y, \delta_z)$ was selected [12] such that $\delta_\alpha = (2R_\alpha - 1)\delta_m$, where $\alpha = x, y, z$; R_α is a random number distributed uniformly in (0,1]; and δ_m is the maximum allowed displacement, which we took it to be of the order of a lattice constant, hence ensuring that the displacements are smaller than the correlation length κ^{-1} of the potential distribution (see below) due to the fixed charge centers (otherwise the simulations are not meaningful). A displacement is accepted with probability 1 if $\Delta\phi_i < 0$, or with probability $\exp(-\beta\Delta\phi_i)$ if $\Delta\phi_i \geq 0$, where $\Delta\phi_i$ is the difference between the potential energy of the system in its present state and that of the new state obtained by moving the ith particle to its new position. The mean square displacements $\langle R^2(t)\rangle$ of the mobile particles are then calculated and averaged over all the particles and many realizations of the medium.

The charge centers are either distributed explicitly throughout the medium or are represented by their potential distribution, generated by the potential-potential correlation function. To make the system neutral, equal numbers of the centers with opposite charges are inserted in the system, and the same is done with the mobile particles. The Coulomb potential ϕ_i acting on the ith mobile particle is written as $\phi_i = \phi_i^{(fm)} + \phi_i^{(mm)}$, where $\phi_i^{(fm)}$ is due to the interaction between the mobile particle and the fixed centers, while $\phi_i^{(mm)}$ is contributed by the interaction between the mobile particles themselves. $\phi_i^{(fm)}$ is calculated by two different methods (yielding identical results). In one method, $\phi_i^{(fm)}$ (and also $\phi_i^{(mm)}$) is computed by the multipole expansion method discussed below. In the second method, we use the fact that diffusion of charged particles in disordered media can be viewed as their motion in an external potential field generated by the quenched disorder that represents the fixed charge centers. Thus, instead of directly distributing the charge centers with a given density $\rho(\mathbf{r})$, $\phi_i^{(fm)}$ is formally represented by the solution of the Poisson's equation which, e.g., in three dimensions (3D), is given by

$$\phi_i^{(fm)}(\mathbf{r}) = -\frac{q_f q_m}{4\pi\varepsilon}\int d\mathbf{r}'\,\frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \qquad (1)$$

where q_f and q_m are the charges for the fixed and mobile particles, respectively, and ε is the permittivity. The charge density $\rho(\mathbf{r})$ is represented by its correlation function $\chi_{\rho\rho}(\mathbf{r})$ which, in the case of Debye-Hückel statistics, is given by

$$\chi_{\rho\rho}(\mathbf{r}) = \rho_0\delta(\mathbf{r}) - \frac{\rho_0\kappa^2 e^{-\kappa|\mathbf{r}|}}{4\pi|\mathbf{r}|}, \qquad (2)$$

where $\rho_0 = \langle\rho(\mathbf{r})\rangle$, and κ^{-1} is the spatial correlation length. The power spectrum $\hat{\chi}_{\phi\phi}(\omega)$ for the potential is calculated from that of the charge density $\hat{\chi}_{\rho\rho}(\omega)$, since Eq. (1) is a convolution integral of the charge density and the Green function for the potential generated by a single charge particle, and therefore in 3D

$$\hat{\chi}_{\phi\phi}(\omega) = \left(\frac{q_f q_m}{\varepsilon}\right)^2 \frac{\rho_0}{\omega^2(\omega^2 + \kappa^2)}. \qquad (3)$$

Hence, a realization of the potential field is generated as follows. Random numbers, distributed uniformly in $[-\sqrt{3}, \sqrt{3})$ (this ensures that their power spectrum is 1, as it should be), are assigned to the sites of the system. The resulting array is then Fourier transformed and multiplied by $\sqrt{\hat{\chi}_{\phi\phi}(\omega)}$ and then inverse Fourier transformed.

$\phi_i^{(fm)}$ and $\phi_i^{(mm)}$ were also calculated by a multipole expansion method [13]. In this method particle i interacts with the nearby particles through the usual Coulomb potential, and with the far away particles through their precalculated multipole expansions of the potential. The total potential $\phi^{(g)}(\mathbf{r}) = \sum_j^N \phi_j(\mathbf{r})$ produced by a group of N charges is

$$\phi^{(g)}(\mathbf{r}) = \frac{q}{r} - \mathbf{P}\cdot\boldsymbol{\nabla}\left(\frac{1}{r}\right) + \frac{1}{2}\mathbf{Q}\!:\!\boldsymbol{\nabla}\boldsymbol{\nabla}\left(\frac{1}{r}\right) - \frac{1}{6}\mathbf{O}\!\vdots\!\boldsymbol{\nabla}\boldsymbol{\nabla}\boldsymbol{\nabla}\left(\frac{1}{r}\right) + \ldots, \qquad (4)$$

where q, $\mathbf{P}$, $\mathbf{Q}$, and $\mathbf{O}$ are, respectively, the monopole, dipole, quadrupole, and octapole moments of the group of charges around the origin. In practice we write $\phi^{(g)}(r) = q/r + (1/r^3)\sum_\alpha P_\alpha r_\alpha + 1/(2r^5)(\sum_\alpha Q_{\alpha\alpha} r_\alpha r_\alpha + \sum_\alpha\sum_\beta Q_{\alpha\beta} r_\alpha r_\beta - r^2 Q) + 1/(6r^7)[15(\sum_\alpha O_{\alpha\alpha\alpha} r_\alpha \times r_\alpha r_\alpha + \sum_\alpha\sum_\beta O_{\alpha\alpha\beta} r_\alpha r_\alpha r_\beta + \sum_\alpha\sum_\beta\sum_\gamma O_{\alpha\beta\gamma} r_\alpha \times r_\beta r_\gamma) - 9r^2(\sum_\alpha O_\alpha)] + \ldots$, with $q = \sum_i q_i$, $P_\alpha = \sum_i q_i R_{i\alpha}$, $Q_{\alpha\alpha} = \sum_i q_i R_{i\alpha}^2$, $Q_{\alpha\beta} = \sum_i q_i R_{i\alpha} R_{i\beta}$, $Q = \sum_i q_i R_i^2$, $O_{\alpha\alpha\alpha} = \sum_i q_i R_{i\alpha}^3$, $O_{\alpha\alpha\beta} = \sum_i q_i R_{i\alpha}^2 R_{i\beta}$, $O_{\alpha\beta\gamma} = \sum_i q_i R_{i\alpha} R_{i\beta} R_{i\gamma}$, and $O_\alpha = \sum_i q_i R_i^2 R_{i\alpha}$, where $r = |\mathbf{r}|$, $\mathbf{R}_i$ is the position vector of the ith charge, α, β, and γ stand for the coordinates x, y, and z, and q_i is the charge of the ith (fixed or mobile) particle.

A highly efficient simulation technique is fundamental to this study. Hence, in addition to taking advantage of the multipole expansion, the 3D simulation box is divided into eight smaller equal boxes, called *children* of the original box [14]. Each child box is a *parent* to eight smaller boxes, with the division continuing up to a certain level which is called the maximum level of division (maxlevel). The data needed for each particle, i.e., its position and type (mobile or fixed), are stored in a *particle object*. A *cell object* contains a list of its *current* particles. Each particle is also "connected" to the next and previous particle in the list. After setting up the entire

data structure, the multipoles of each cell around its center at the maxlevel are calculated using the above expressions. Then, the multipoles of the parent cells are computed by translating and adding the multipoles of their children by a displacement vector $\boldsymbol{\ell} = (\ell_x, \ell_y, \ell_z)$. In terms of the old quantities, the new translated (primed) quantities are given by $P'_\alpha = P_\alpha - q\ell_\alpha$, $Q'_{\alpha\alpha} = Q_{\alpha\alpha} - 2\ell_\alpha P_\alpha + q\ell_\alpha^2$, $Q'_{\alpha\beta} = Q_{\alpha\beta} - \ell_\beta P_\alpha - \ell_\alpha P_\beta + q\ell_\alpha\ell_\beta$, $Q' = Q'_{\alpha\alpha} + Q'_{\beta\beta} + Q'_{\gamma\gamma}$, $O'_{\alpha\alpha\alpha} = O_{\alpha\alpha\alpha} - 3\ell_\alpha + 2\ell_\alpha^2 - q\ell_\alpha^3$, $O'_{\alpha\alpha\beta} = O_{\alpha\alpha\beta} - \ell_\beta O_{\alpha\alpha} + \ell_\alpha[-2Q_{\alpha\beta} + 2\ell_\beta P_\alpha + \ell_\alpha \times (P_\beta - q\ell_\beta)]$, and $O'_{\alpha\beta\gamma} = O_{\alpha\beta\gamma} + \ell_\gamma(\ell_\beta P_\alpha - Q_{\alpha\beta}) + \ell_\beta(\ell_\alpha P_\gamma - Q_{\alpha\gamma}) + \ell_\alpha(\ell_\gamma P_\beta - Q_{\beta\gamma}) - q \times \ell_\alpha\ell_\beta\ell_\gamma$.

Each particle's potential energy is divided into ϕ_i^{near} and ϕ_i^{far}. A particle in a cell at the maxlevel interacts with all other particles in the same cell and in the neighboring cells by the usual Coulomb potential, thus yielding ϕ_j^{near}. It also interacts with its parent's neighbors' children through the corresponding multipole expansions. Computations continue up to the whole simulation box, hence yielding ϕ_i^{far}. In this way the number of the cells that interact with each particle is drastically reduced as one gets away from the particle. For example, in 3D with four levels of division the number of the interacting cells is only 415, rather than the original 4069 cells.

To demonstrate the effect of the quenched disorder, we present and compare the results for a single realization of the system with those averaged over many realizations. Figure 1 presents the time dependence of the MSD of the mobile particles in a single realization of a 1D medium. The fixed charge centers are represented by their potential distribution, i.e., the 1D version of Eq. (3), $\rho_0(q_f q_m/\varepsilon)^2(\omega^2 + \kappa^2)^{-1}$. The mobile particles can travel only in the space *between* themselves, since they cannot "jump" over each other. There are many relatively fast diffusive jumps in the MSD after certain periods of time. In between the jumps one has a slow motion that causes the overall transport to be anomalous, not only in 1D but also in 2D and 3D (see below). For fixed ρ_0 and κ^{-1} the slopes of the straight lines that represent the faster part of the motion are essentially the same, indicating the *same* diffusion coefficient for all of them. The jumps represent the mobile particles' escape from the potential wells (traps) that the quenched distribution of the charge centers creates. The traps have a finite sphere of influence, such that for any particle i within a sphere the potential difference $\Delta\phi_i$ for a displacement that can take i out of the sphere is very large, and thus the probability of an appreciable jump is small. This is represented by the almost horizontal parts of the curves shown in Fig. 1, indicating very small, if not zero, diffusivity. The jumps occur when after some time the particles are close to the boundary of the traps and escape with a displacement that takes them out of the traps. They then resume their diffusive (fast) motion until they are captured by another trap, and so on.

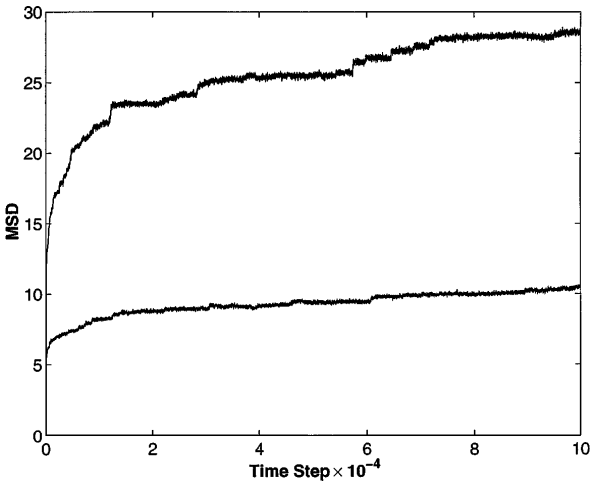

FIG. 1. Mean square displacement versus time t of the mobile charged particles in a single realization of a 1D medium for $\kappa = 0.07$ (top) and $\kappa = 0.05$ (bottom), and $\rho_0 = 0.1$ and $T = 273$ K.

In Fig. 2 we present the time dependence of the MSD in both 1D and 3D for various κ. The results are the average over 50 realizations of the system. The depth of the potential wells, and thus the radius of influence of the traps, is controlled by κ^{-1}. The larger κ^{-1}, the deeper is the potential well, and thus the larger the time spent in such traps. This is indicated by the very small slopes of the curves as κ decreases. In the limit $\kappa^{-1} \to \infty$, the trapping times become infinitely large, and therefore the effective diffusivity is *zero* [15].

Deem and Chandler (DC) [10] proposed that the effective diffusivity $\mathcal{D}$ of the particles in d dimensions obeys the inequality

$$\frac{\mathcal{D}}{\mathcal{D}_0} \geq \exp[-\beta^2 \chi_{vv}(0)/d], \tag{5}$$

where $\chi_{vv}(0) = (4\pi\epsilon)^2\chi_{\phi\phi}(0)$, and $\mathcal{D}_0$ is the bulk diffusivity (in the absence of the charge centers). Furthermore, DC proposed that the equality in (5) holds *exactly* in 1D, and possibly for *all* values of d. Because the overall transport is nondiffusive, $\mathcal{D}$ varies with the time. Therefore, it is not clear what DC mean by the effective diffusivity. Since between the traps the motion is relatively fast and diffusive, we present in Fig. 3 the

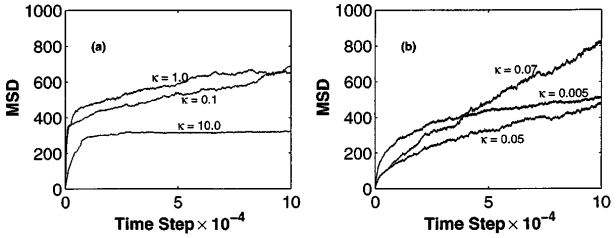

FIG. 2. MSD for (a) a 3D medium with $\rho_0 = 0.005$ and $T = 273$ K and (b) for a 1D medium for the same conditions as in Fig. 1. The results represent averages over 50 realizations.

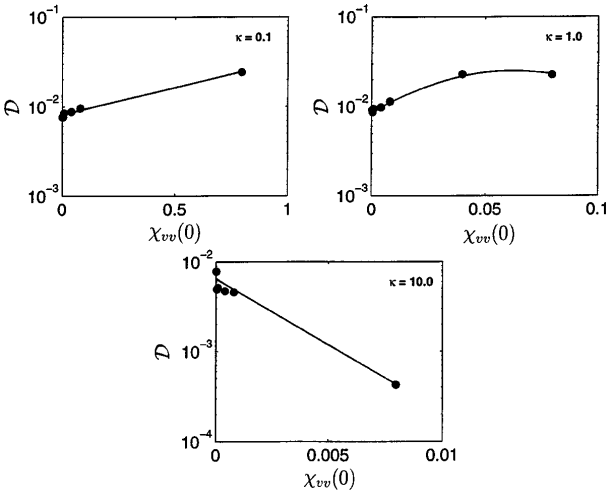

FIG. 3. The dependence of the diffusivity $\mathcal{D}$ (for the faster part of the motion) on the potential-potential correlation function $\chi_{vv}(0)$ in 3D for various values of κ. $\chi_{vv}(0)$ is changed by varying ρ_0 from 10^{-4} to 10^{-1}, and $T = 273$ K.

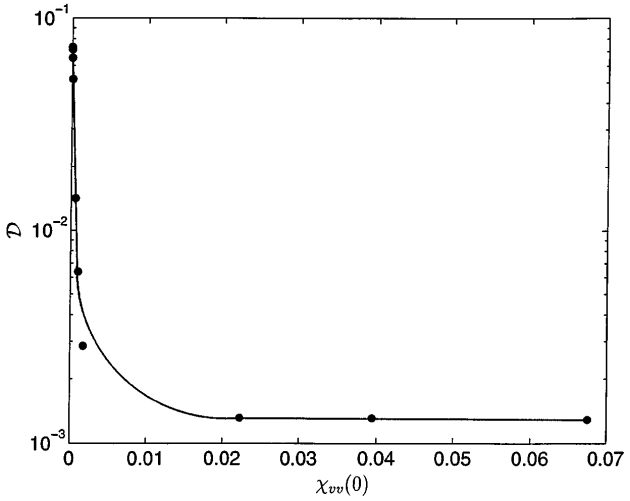

FIG. 4. Same as in Fig. 3, but in 1D.

dependence of $\mathcal{D}$ on $\chi_{vv}(0)$ for 3D systems, where $\mathcal{D}$ now represents the diffusivity between the traps, while Fig. 4 shows the same for 1D systems. As can be seen, even for this diffusivity the inequality in (5) does not hold. In 3D for small values of κ, the slope of the straight line is *positive* [whereas according to (5) it should be negative]. As κ increases, the curves bend over, and finally for large enough κ the slopes become negative. As a further test, we simulated diffusion of charged particles in a 3D medium in which the charge centers were randomly distributed, rather than being represented by the potential distribution (3). The results [15] indicated that (5) does not hold.

In summary, a quenched distribution of charge centers gives rise to deep potential wells that capture mobile charged particles and slow down their motion for some time. The time scale for staying in the well depends on the correlation length κ^{-1}. For any finite κ^{-1} the particles eventually escape from the wells. In between the wells the motion is diffusive with the same diffusivity. The overall motion is subdiffusive with a diffusivity that decreases with the time. Only when the correlation length $\kappa^{-1} \to \infty$ does the diffusivity vanish.

Our results also provide physical interpretation for the experimental data for diffusion of ions in zeolites and similar porous media mentioned above. As the ions diffuse into the charged porous medium, they get trapped in the potential wells and stay there over time scales that are much larger than the measurement times, and thus their measured flux out of the medium and their measured $\mathcal{D}$ are drastically reduced. Moreover, $\mathcal{D}$ would decrease with the time. In such experiments, it is very difficult to measure $\mathcal{D}$ *between* the wells. All one measures is an *effective* $\mathcal{D}$ which would be very small if the time scale for leaving the potential wells is large.

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