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Fluid diffusion through a porous solid: Nonequilibrium molecular-dynamics simulation

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Fluid mass transport through a porous solid is studied by carrying out nonequilibrium molecular-dynamics simulations for a simple model. It is found that through the porous solid, the steady state density distribution is not linear, even in the case of a quite small current. Hence, Fick's law cannot be applied simply. Nevertheless, the density distribution is piecewise linear. An adequate interpretation can be made by applying Fick's law piecewise with different diffusion coefficients in different regions. Thus a distinct diffusion coefficient can be unambiguously defined for the interfacial region, which can be seven times smaller than the diffusion coefficient in the interior of the porous solid. So the surface crossing is a limiting step in the overall process of mass transport through a porous solid.

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Fluid diffusion in porous media plays an important role in a variety of processes, e.g., heterogeneous catalysis, membrane separation, etc. A considerable amount of works have been devoted to this subject (see Ref. [1], for example). For experimental study, many techniques can be used [1]. They are usually classified into two main categories: one called microscopic methods and the other macroscopic ones. For the microscopic methods, NMR is a typical example. By such methods, the mean square displacement is determined as a function of time, and then the diffusion coefficient can be obtained with the help of the Einstein formula [2]. In a macroscopic measurement, a density gradient is created. Fick's law allows us to determine the diffusion coefficient from the gradient-current relation. The results from both macroscopic and microscopic methods from which an experimental puzzle has emerged are abundant [1,3]. In some cases, the diffusion coefficients measured by the two methods are very different under apparently the same conditions.

In the past years, the molecular-dynamics (MD) simulation method is also applied to study fluid diffusion in porous solids [4–13]. In general, there is good agreement between MD results and those obtained from microscopic experimental methods. Although this confirms the results of microscopic measurements, the puzzle remains unsolved. Hence, some fundamental questions arise naturally. Should one discredit the macroscopic methods? Have the comparisons been made properly between the two methods? These are the questions we would like to examine in this work.

The MD simulations [4–13] carried out until now have been exclusively designed to simulate the situation under which microscopic measurements are made, i.e., aiming at the determination of the mean square displacement in the *interior* of a porous solid. However, the situation in a macroscopic experiment is somewhat different. In this case, a surface crossing process is necessarily involved. In order to enter into the porous solid, fluid molecules have to cross first the interface region between the porous solid and the bulk fluid phase. During this surface crossing, a fluid molecule undergoes a change of physically distinct media. Therefore, one can reasonably conceive that the transport property through the interfacial zone might be different from either the bulk fluid or that inside the porous solid. The results to be presented in the following show that this is indeed the case. We will reveal that there exists a well defined interfacial transport property, and failure to take this fact into account can give a misleading interpretation of the results of macroscopic measurements.

For our purpose, nonequilibrium molecular-dynamics (NEMD) simulations are carried out. To our knowledge, no such simulation to study any transport processes through porous solids has been done. To reduce computational efforts, we will restrict ourselves to a two-dimensional model. It is well known [14] that due to the long time tail of the velocity autocorrelation function, the thermodynamic limit of the diffusion coefficient does not exist for two-dimensional systems. But it will be shown that for our goal here, we need not make any explicit evaluation of the diffusion coefficient. The porous solid is modeled by a regular lattice with hard disks fixed on it (see Fig. 1). The fluid is modeled also by hard disks, but they can move through the space unoccupied by the solid particles. Although this is a highly idealized model, the

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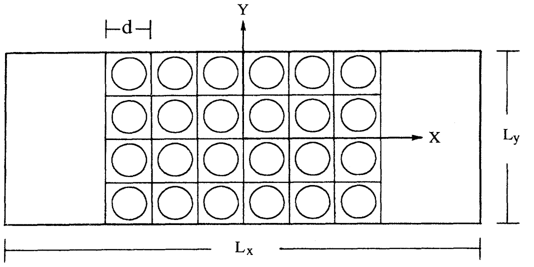


FIG. 1. Schematic presentation of the model.

results in the following will show that it is already capable of giving us some valuable insight into the problem we are interested in here. The fluid distributions at equilibrium of this model have been previously studied by Dong and Bigot [15].

In order to mimic the experimental conditions of some macroscopic measurements, e.g., the zeolite membrane permeability measurement, one needs to establish a nonequilibrium steady state and study the gradient-current relation. The nonequilibrium molecular-dynamics simulation method is a suitable means for such investigations. There exist a variety of NEMD methods for different transport processes [16]. We adopt a method devised by Erpenbeck, and Wood [17] which is designed originally to study self-diffusion in a pure fluid. An elegant scheme is prescribed in this method for introducing a colored species and a gradient of the colored species is set up gradually and maintained when the steady state is reached. The reader is referred to Ref. [17] for a detailed description of the technique.

Our simulations are made under the conditions given in Table I. The parameters are defined as follows: the fluid particle diameter σ is chosen as the length unit, the central simulation box size is given by L_x and L_y, d is the unit cell size (see Fig. 1), σ_s is the solid particle diameter, n_{cx} and n_{cy} specify the number of unit cells in the x and y directions, N is the number of fluid particles, and ρ_T the total fluid density. In Table I, we also give the number of configurations N_{cf}, from which statistical calculations are made.

In the NEMD method of Holian, Erpenbeck, and Wood, the particle's color is changed with a probability p when the crossing of simulation box boundaries normal to the current takes place. This probability determines the magnitude of the colored species current; a larger p leading to a larger current. As pointed out in Ref. [17], p should be given values near 1 to obtain a reasonable accuracy in the determination of the current. In the problem we are considering, the presence of a porous solid membrane produces a quite large resistance to mass transport. So we chose p equal to 1 in all our calculations. Even with this value of p, the current is so small that the computational error in this quantity is quite large. However, the determination of the steady state density distribution of the colored species will be sufficient for our purpose here. So this does not really pose a serious problem.

The steady state density distribution of the colored species is calculated in the following way:

$$\rho_c(x)=\langle N_c(x,x+\Delta x)\rangle/(\Delta x L_y) , \tag{1}$$

where $\langle N_c(x,x+\Delta x)\rangle$ is the average number of colored particles falling in a slice between x and $x+\Delta x$. For the results presented below, the average is taken over several tens of thousands of configurations (see Table I) after the steady state has been established. In Eq. (1), the magnitude Δx determines the length scale over which structural information can be obtained from $\rho_c(x)$. With a finer resolution, the density profile yields greater details of the inhomogeneous fluid distribution in the porous solid. Very detailed structural information at thermodynamic equilibrium can be found in Ref. [15].

In Fig. 2(a) we present the steady state density profile $\rho_c(x)$, determined by $\Delta x=0.5\sigma$ and under the conditions specified in the first line of Table I. At this length scale, the inhomogeneity induced by the porous solid still manifests itself clearly. Hence at this length scale, Fick's macroscopic law is not applicable. To interpret the result by using Fick's law, some coarse graining is needed. Here, we would like to emphasize that the density oscillation in Fig. 2(a) is due to the crystal structure of the solid. Even at this resolution ($\Delta x=0.5\sigma$), the fine oscillatory structure due to the excluded volume effect of the hard disk fluid is already averaged out. Figure 2(b) shows the result of $\rho_c(x)$ determined under the same conditions as in Fig. 2(a) but with $\Delta x=2.0\sigma$. Now, the microscopic structural details induced by solid crystal are also smeared out. The most important thing revealed in Fig. 2(b) is that $\rho_c(x)$ is not linear throughout but is only piecewise linear. The important consequence of this fact is that one cannot simply apply Fick's law with a single diffusion coefficient all over. An adequate treatment is to apply Fick's law in the zones S_1S_2 and S_2S_3 with two different diffusion coefficients, D_1 for S_1S_2 and D_2 for S_2S_3 [see Fig. 2(b)]. More precisely, the coarse grained density distribution can be accounted for in the following phenomenological way:

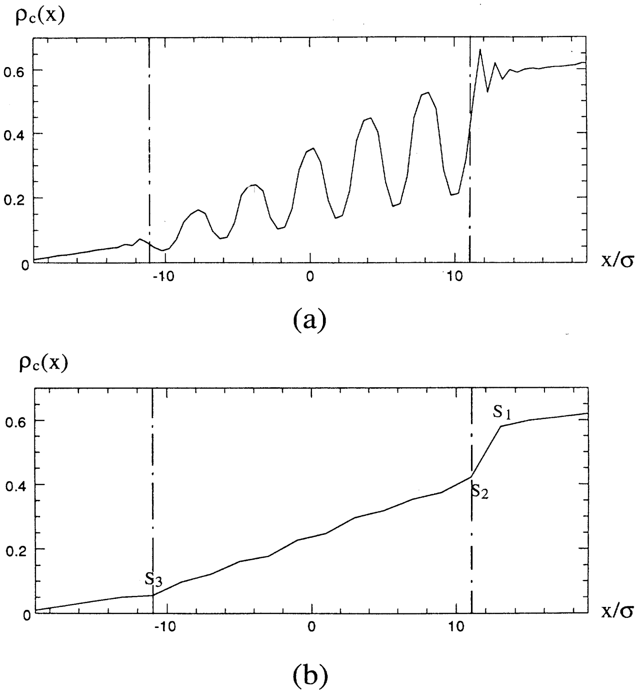
$$J=-D_0\frac{d\rho_c(x)}{dx} , \quad -L_x/2<x<S_3 , \; S_1<x<L_x/2$$

$$J=-D_1\frac{d\rho_c(x)}{dx} , \quad S_2<x<S_1$$

$$J=-D_2\frac{d\rho_c(x)}{dx} , \quad S_3<x<S_2$$

TABLE I. Computational parameters.

No.	L_x/σ	L_y/σ	d/σ	σ_s/σ	n_{cx}	n_{cy}	N	$\rho_T\sigma^2$	10^4N_{cf}
I	40.0	16.0	4.0	2.0	6	4	336	0.5951	2
II	64.0	16.0	4.0	2.5	6	4	550	0.5371	6
III	64.0	16.0	4.0	2.5	6	4	275	0.2685	8
IV	112.0	28.0	7.0	5.5	6	4	350	0.1364	8



(a)

(b)

FIG. 2. (a) Steady state density profile of colored species with $\Delta x=0.5\sigma$ (simulation I). (b) Steady state density profile of colored species with $\Delta x=2.0\sigma$ (simulation I). The two vertical dot-dash lines delimit the surfaces of the porous solid.

where D_1 and D_2 are defined as before, D_0 is the diffusion coefficient of the bulk fluid outside the porous solid, and J is the current, which is constant through the system for a steady state. The solution of these equations with some boundary condition, e.g., $\rho_c(x=L_x/2)$, provides a very simple model for describing the coarse grained density. From Fig. 2(b), it is obvious that $D_1<D_2$ holds. This reveals that there exists a distinct surface resistance to mass transfer that is larger than that inside the porous solid. Here, we define the resistance to mass transfer as a quantity inversely proportional to the diffusion coefficient, i.e., $1/D$. Quantitatively, D_2/D_1 can be determined from the ratio of the slopes of S_1S_2 and S_2S_3 since the current is constant throughout for a steady state. For the results given in Fig. 2(b), D_2/D_1 is equal roughly to 4.

Another simulation is carried out under the conditions given in the second line of Table I. Here, the solid particle diameter is increased to raise the resistance to mass transfer of the porous solid since the channel size decreases. In Fig. 3, $\rho_c(x)$ determined with $\Delta x=2.0\sigma$ is presented. In this case, the distinction between surface resistance and the resistance inside the solid is even more marked. D_2/D_1 is now equal roughly to 7. The results given in both Figs. 2(b) and 3 show that the size of the zone over which D_1 is defined is of the order of one solid layer. It is remarkable that in such a small region there exists a distinct and well defined surface resistance, i.e., $\rho_c(x)$ is linear between S_1 and S_2 and its gradient has discontinuities at S_1 and S_2.

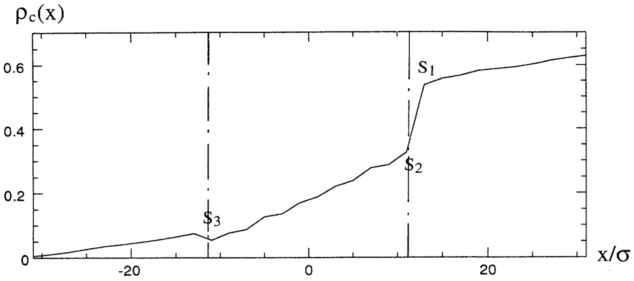


FIG. 3. Steady state density profile of colored species with $\Delta x=2.0\sigma$ (simulation II). The two vertical dot-dash lines delimit the surfaces of the porous solid.

As described in the Introduction, our main goal here is to try to understand the experimental puzzle. Since the experimental measurements are usually made at low densities in the gas phase, it is important to make certain that the abrupt density drop in the interface zone found at high densities will show up also at low densities. Hence, two simulations at low densities are also carried out. Simulation III (see Table I) is made under essentially the same conditions as those of simulation II but with a density that is half that for simulation II. The result of simulation III is presented in Fig. 4. Another simulation at an even lower density, which is reduced again by a factor of 2 compared to simulation III, is also carried out. Moreover , the size ratio of the fluid particle to the solid particle is reduced by more than two times (see simulation IV in Table I). The result of simulation IV is given in Fig. 5. From Figs. 4 and 5, we see that the abrupt density drop in the interface region persists at low densities and for smaller size ratio between fluid and solid particles. Therefore, the decreased permeability across the interface is a general feature of the fluid mass transport through a porous medium.

Now, let us see the implication of the above results on the interpretation of experimental results. In a microscopic measurement, the determined diffusion coefficient is essentially D_2 since the detected trajectories and thus the mean square displacement are essentially those of the

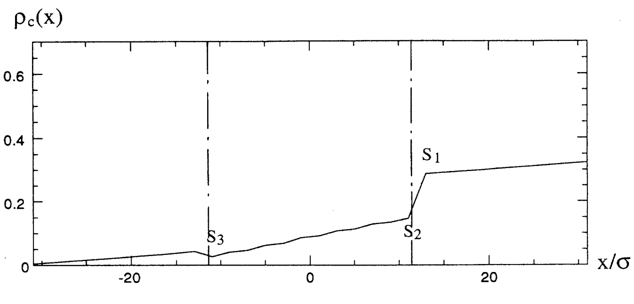


FIG. 4. Steady state density profile of colored species with $\Delta x=2.0\sigma$ (simulation III). The two vertical dot-dash lines delimit the surfaces of the porous solid.

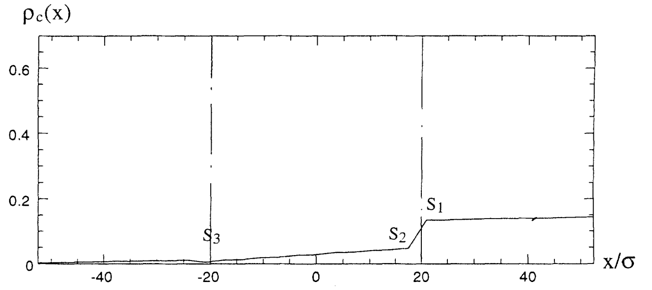


FIG. 5. Steady state density profile of colored species with $\Delta x = 3.5\sigma$ (simulation IV). The two vertical dot-dash lines delimit the surfaces of the porous solid.

fluid particles inside the porous solid. However, in macroscopic measurements, both D_1 and D_2 are involved because the surface crossing takes place commonly in all the macroscopic methods. So the effective diffusion coefficient measured by a macroscopic method must be smaller than that obtained from a microscopic measurement because the surface crossing has a much smaller diffusion coefficient and it is thus the limiting step in this case. This is indeed what is found experimentally [1,3]. More concretely, let us examine the membrane permeability measurement, which is an experiment our simulation mimics closely. Usually, the results of such a measurement are interpreted as follows. It is supposed that Fick's law can be simply applied throughout the porous solid, i.e., the density distribution is supposed to be linear between S_1 and S_3 [see Figs. 2(b), 3, 4, and 5]. In fact, the resistance of the membrane to mass transfer causes an abrupt concentration drop in the interfacial zone even in the case of a quite small current. Therefore, a proper treatment of the overall process must be worked out piecewise. Taking no account of this fact will inevitably give misleading results. For example, if the density distribution is supposed to be linear between S_1 and S_3 in Fig. 4, one will find a diffusion coefficient about two times smaller than D_2. Quantitatively, this is of course still far from accounting for the discrepancy between the results found by microscopic and macroscopic methods [1,3]. It is noted that the model studied here is an extremely idealized one. For this model, the only way to increase the mass transfer resistance is to increase the solid particle size. With more elaborate models that incorporate some specific surface resistances, one can expect to obtain larger difference between D_1 and D_2. Although what we find here does not seem to be the unique cause for the experimental puzzle, it is certainly one among the others. Only when the distinct resistance is properly taken into account can the overall mass transport through porous solids be interpreted correctly by using Fick's law.

Before closing, we would like to draw particular attention to this subject from experimentalists in this field. We believe it would be a very challenging investigation to devise laboratory experiments to confirm our findings [18].

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[18] After our manuscript was submitted, a very recent work of MacElroy appeared in J. Chem. Phys. **101**, 5274 (1994). In MacElroy's work, the diffusion through a random porous solid is studied. Although the model and the NEMD simulation method are different from ours, his results for the density profile are qualitatively similar to those presented in this paper. In MacElroy's work, the case of extremely low density is also examined.