

Diffusion of charged fluids in charged porous matrices

Hector Dominguez^{a)}

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, DF 04510, México

Margarita Rivera

Instituto de Física, Universidad Nacional Autónoma de México, DF 01000, México

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I. INTRODUCTION

Over the last years the study of fluids in confined microporous matrices has been of great interest due to their applications in heterogeneous catalysis, petroleum recovery, membrane separation processes, etc. From the theoretical point of view people have used models which consist of systems of quenched particles usual in an equilibrium configuration.¹⁻³ Moreover, Madden and Glandt¹ and Madden⁴ proposed an extension of the liquid-state theories to study fluids adsorbed in disordered porous materials. On the other hand a new method to prepare disordered pore matrices, inspired by the actual formation process has been used.⁵ The model considers the explicit presence of a template material, i.e., the system is composed of a binary system where one specie is the matrix and the other is the template.⁶ Once the system is equilibrated at a particular thermodynamic state, it is frozen and the template particles are removed, i.e., the remaining particles form the pore matrix. Of particular interest is the study of diffusion in these disordered media. Few works have been done to understand how diffusion depends on the pore configuration or on the pore-fluid interaction.⁷ Other papers have investigated how template and porosity affect diffusion of fluids inside porous matrices.⁸ These investigations have been conducted in systems with short-range interactions. However, diffusion studies of fluids in disordered porous media composed of charge centers are also very important in fields, such as dynamic response of nonmetallic materials, ionic glasses, and polymeric and glassy conductors. In fact, some materials such as zeolites that are used for catalytic and separation processes, exhibit a distribution of charged centers. Diffusion of ions in such materials shows that it changes considerably upon changing the charge on the diffusing particles.⁹ Despite this interest, there are few works to study fluids in disordered matrices with charged centers,¹⁰⁻¹² e.g., Mehrabi and Sahimi studied diffusion of ionic particles in charged matrices observing the creation of deep traps that capture the mobile particles.¹¹ From the present simulations we even observed subtle results which indicate that diffusion increases as the fluid density increases. Therefore, extensive simulations of ionic fluids in a charged porous matrix were conducted which will give us more insights to understand diffusion in disordered matrices.

The first part of the work corresponds to the construction of the porous matrix. For this purpose we prepared a similar model to that used in a previous paper,¹³ i.e., by using a very

simple and crude template models the porous matrix was prepared from a binary mixture. In the model we have a two symmetric $+q:-q$ electrolyte mixture, where the template and the matrix are composed of identical particles. Therefore, the model can be seen as kind of a mixture of two identical molten salts. Moreover, in order to differentiate the different components (molten salts) of the mixture we used labels, i.e., the first electrolyte composed of equal number of $+q_1$ and $-q_1$ charges is the template and the second electrolyte, also with equal number of $+q_2$ and $-q_2$ charges, is the matrix ($|q_1|=|q_2|$).

All charged particles (with the same particle diameter) were placed in a cubic box of lengths $X=Y=Z=54.052\ 01\ \text{\AA}$ embedded in a structureless solvent with a dielectric constant ϵ_m . Therefore, particles were able to interact among each other with short-and long-range forces given by the Lennard-Jones (with argon parameters, $\epsilon/KT=119.8$ and $\sigma=3.405\ \text{\AA}$) and Coulombic potentials, respectively,

$$U_T(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + \frac{1}{4\pi\epsilon_m\epsilon_0} \frac{q_i q_j}{r^2}, \quad (1)$$

where σ is the diameter of the particle, ϵ is the well depth of the Lennard-Jones (LJ) potential (which are the same for all the charged particles), ϵ_0 is the vacuum permittivity, and q_i and q_j are the charge of particles i and j , respectively (equal to one electron charge), and it is assumed that $\epsilon_m=78.0$ (water permittivity).

Simulations were carried out using the molecular-dynamics (MD) method¹⁴ where the electrostatic interactions were handled by using the Ewald summation. Periodic boundary conditions were imposed in the simulation and for the short-range potential we used a cutoff of $r=4.5\sigma$ ($15.3225\ \text{\AA}$).

The initial configuration consisted of random-charged particles of the first electrolyte located in the box. Then the ions of the second electrolyte were randomly added in the same box. A total of 2400 particles were used where 1200 correspond to the matrix and 1200 to the template (i.e., with a reduced density of $\rho_m^*=\rho_t^*=0.3$ each). Then, the bulk mixture was run for $4 \times 10^4 \delta t$ ($\delta t=0.0108$ ps) for equilibration at a temperature of $T=95.84$ K and finally, the last configuration was reached after $1 \times 10^5 \delta t$. Then the whole system was frozen and the disordered porous matrix (with density $\rho_m^*=0.3$) was obtained after the first electrolyte (the template) was removed from the last configuration of the mixture.

This porous model will allow us to study diffusion of mobile ions in the voids created in the matrix. Moreover, if

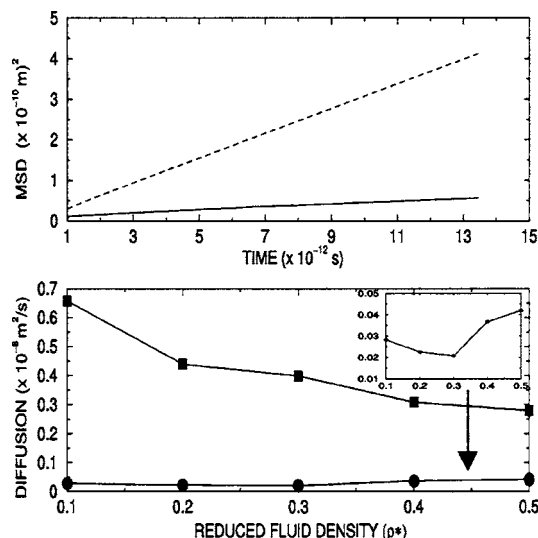


FIG. 1. Mean-square displacements (MSD) of a bulk charged fluid with $\rho_f^* = 0.4$ (dashed line) and the MSD of the same fluid inside the porous matrix (top of the figure). The diffusion coefficient as a function of the fluid density (bottom of the figure). The squares and the circles represent the bulk and the fluid inside the porous matrix, respectively. For clarity the inset shows the diffusion of the fluid in the matrix. The line is given to guide the eyes.

we use a fluid with the same parameters as the template it might be possible to locate its ions inside the voids with a similar distribution as the template ions had. Therefore, we proceeded to study the diffusion of five fluids with densities $\rho_f^* = 0.1, 0.2, 0.3, 0.4$, and 0.5 introduced in the same porous matrix as previously constructed. The fluid particle diameter was the same as the matrix particle. In order to keep the system neutral, the fluid particles were chosen in such a way that half of the particles were positive and the other half were negative (i.e., a $+q:-q$ electrolyte with charges equal to 1 e.u.). It is worth to mention that for the last simulations, the matrix particles were frozen and they did not interact with each other.

II. RESULTS

In Fig. 1 plots of the diffusion as a function of the fluid density for the bulk and the confined fluid are shown. An interesting feature is observed since the diffusion of the adsorbed fluid does not always decrease when the density increases. In fact, at higher densities ($\rho^* = 0.4$ and 0.5) the diffusion increases (inset of bottom figure). The unexpected diffusion behavior was investigated in terms of the possible traps created in the matrix structure. Although the idea of traps has been previously discussed by some authors,¹¹ they did not study in detail diffusion as a function of the fluid density. The increase in the diffusion was recently observed in systems of hard-sphere fluids in disordered matrices.¹⁵ However, the nature of that increase is due to different effects. In the same figure we also plotted the diffusion of the bulk fluids at the same density. We clearly observed that the bulk diffusion is considerably higher and it decays as the fluid density increases. Therefore, we say that the confinement due to the pore matrix reduces the diffusion and in some cases, it causes anomalous behavior.

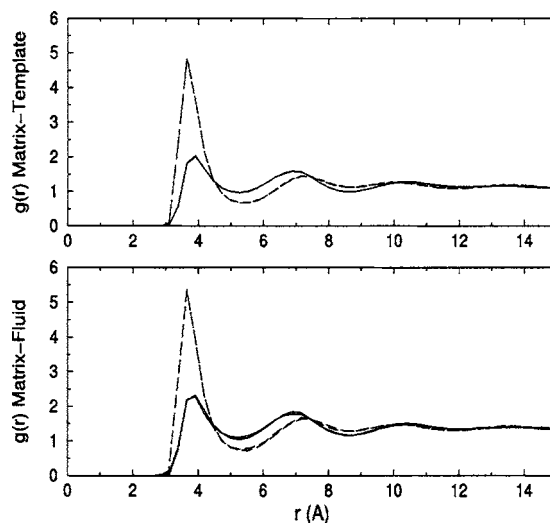


FIG. 2. Pair distribution functions [$g(r)$] of the matrix-template charges with $\rho_m^* = \rho_f^* = 0.3$ (top) and the matrix-fluid charges with $\rho_m^* = 0.3$ and $\rho_f^* = 0.4$ (bottom). The $g(r)$ of equal charges given in solid lines ($+, +$ and $-, -$) and the $g(r)$ of opposite charges given in dashed lines ($+, -$ and $-, +$) are overlapped, respectively.

Molecular-dynamics simulations to calculate the diffusion were carried out at temperature $T = 95.84$ K for $1 \times 10^5 \delta t$. Then, the diffusion coefficient was calculated by the mean-square displacements and the Einstein relation for all the fluid particles. The typical graphs of the mean-square displacements for a fluid with $\rho^* = 0.4$ are shown in Fig. 1.

As a first analysis we studied how fluid ions are distributed in the pore matrix. Then, the pair distribution functions [$g(r)$] between the different particles were investigated. In the bottom of Fig. 2 we show $g(r)$ of positive matrix charges with positive [$g(m+f^+)(r)$] and negative [$g(m+f^-)(r)$] fluid charges and also negative matrix charges with positive [$g(m-f^+)(r)$] and negative [$g(m-f^-)(r)$] fluid charges. We observed that even when it is more favorable to have particles of opposite charge closer to each other, there is also a small probability to have some particles of the same charge to be close. In the figure $g(m+f^-)(r)$ overlapped with $g(m-f^+)(r)$ and $g(m-f^-)(r)$ with $g(m+f^+)(r)$. In the same Fig. 2 (top) we also have included the $g(r)$ of the matrix with the template particles obtained during the preparation method. Similar plots are observed with the same peak positions (as those in the bottom figure) suggesting that the distribution of the fluid particles (charges) somehow are similarly distributed as the template (which created the voids) around the matrix particles. However, (for this particular figure) due to the different fluid density, used compared with the template density, the height of the peaks are different and on the other hand it seems that the fluid ions are not uniformly distributed in the box since the $g(r)$'s do not approach unity.

In order to understand why the diffusion coefficient in some cases increases with the density we studied in more detail the fluid particle's behavior. We investigated the trajectories of the mobile particles inside the porous matrices. Since we are interested on how the matrix affects the movement of these mobile particles, we followed two fluid particles in the matrix which were far from each other. Therefore, we focused only in the interaction produced by the

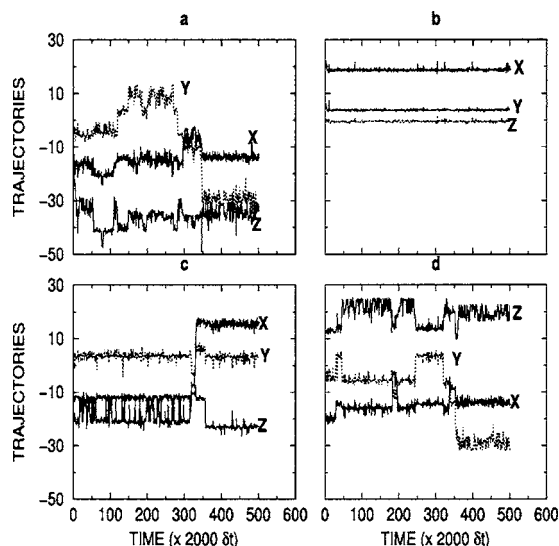


FIG. 3. Trajectories of two different mobile-charged particles placed in different voids inside the porous matrix. The trajectories for the X, Y, and Z axis are shown in each panel. Panels (a) and (c) represent the trajectories of the positive and the negative charged particles in the first cavity, respectively. Panels (b) and (d) represent the trajectories of the negative and the positive charged particles in the second cavity, respectively.

matrix particles over an isolated mobile particle without any other fluid interaction. In order to keep neutrality in the system, a positive charge and a negative charge were selected. Moreover, the initial position of these two charged particles was chosen in the Voronoi centers calculated from the matrix particles.⁸ In this way, we can interchange the position of the positive with the negative particle. Hence, we investigated how the mobility of a positive or negative particle is affected by the same surroundings, i.e., the same matrix particles in the voids which can be positive or negative. The same analysis was performed in several cavities and similar results were found. Only representative results are shown.

The MD simulations of 1×10^6 time steps were performed in the fluid with $\rho^* = 0.4$ at 95.84 K. After each run, positions of the two particles were stored to investigate their trajectories in the matrix. In Fig. 3, the trajectories of the mobile particles in the X, Y, and Z axis are shown. For clarity, the periodic boundary conditions were removed. Initially, a positive charge was placed in the first arbitrary cavity [Fig. 3(a)] where considerable movements in all directions are observed, i.e., it moves without much constriction. When a negative charge is placed instead of a positive one in the same cavity, in general it still has some freedom to move inside the pore [Fig. 3(c)]. If we analyze the trajectories in a second cavity, different plots are observed. When a negative particle is inserted it does not move at all [Fig. 3(b)] suggesting that it is trapped in the cavity the whole time. However, if a positive particle is placed instead, now the particle does not seem to be constrained and it has more movement in the pore [Fig. 3(d)].

Since from Fig. 2 we observed that some fluid charges can be close to few matrix charges of equal sign we investigate the influence of the matrix particle's distribution around the mobile charges. Then the pair-correlation functions $g(r)$'s of the single mobile particles with the positive and the nega-

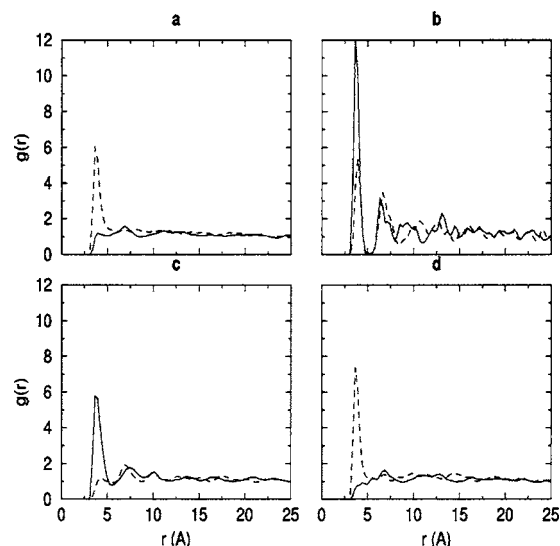


FIG. 4. Pair distribution functions [$g(r)$] of the two mobile-charged particles of Fig. 3. Panels (a) and (c) are the $g(r)$'s of the positive and the negative charged particles in the first cavity, respectively. Panels (b) and (d) are the $g(r)$'s of the negative and the positive charged particles in the second cavity, respectively. The solid line represents the $g(r)$ of the charged fluid particle (positive or negative to each panel) with the positive matrix particles and the dashed line represents the $g(r)$ of the charged fluid particle (positive or negative) with the negative matrix particles.

tive matrix particles were calculated. In Fig. 4, the $g(r)$ of particles of Fig. 3 is shown. In panel 4(a) we observed that the positive charge in the first cavity is mainly surrounded by negative matrix particles (dashed line) and few positive matrix particles (solid line). For a negative mobile particle in the same first cavity the first nearest neighbors are mainly positive matrix particles [Fig. 4(c)]. Since the $g(r)$'s do not show a strong structure (they are smooth graphs oscillating around the unity) they indicate that the mobile particles are not attached to the matrix particles and they can move with some freedom. However, in Fig. 4(b) well structured $g(r)$'s for the negative particles in the second cavity with both positive and negative matrix particles are observed. For instance, the well-defined first peaks (even the second peak) are depicted, indicating that the mobile particle is well constrained by the matrix particles. However, the positive particle in the second cavity is not trapped by the matrix particles since the $g(r)$'s show typical forms of free moving particles [Fig. 4(d)].

III. CONCLUSIONS

It was found that a charged matrix with cavities might capture mobile particles which restrict their motion. The voids created from a template are empty places (surrounded by positive and negative matrix charges) where the fluid ions are distributed with the matrix particles as the template did. In some cases the particles (in a void) can have negligible motion. However, if the charge of the mobile particle is changed it speeds up its motion, increasing the diffusion. The statement of traps is also verified by analyzing the pair-correlation function of single-charge mobile particles with different charged matrix particles. They show that in the cases of slow motions, strong structure of the $g(r)$ with well-

defined peaks are observed indicating that the mobile particles are motionless. From the analysis of trajectories and pair-correlation functions we believe that the new insights of the diffusion of charged fluids inside the charged porous matrices are given. In the fluid, the particles are influenced not only by the matrix particles but also by the other fluid particles which can be captured in traps, slowing their motion and reducing the diffusion. When the trapped particles are freed the fluid diffusion increases. The fact that only some fluid particles can be captured (or can be freed) from these traps can explain the slight increase (or decrease) of the diffusion coefficients.

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- ^{a)}Fax: 52 (55) 56 22 46 02. Electronic mail: hectorde@servidor.unam.mx
- ¹W. G. Madden and E. D. Glandt, *J. Stat. Phys.* **51**, 537 (1998).
- ²J. A. Given and G. Stell, *Condens. Matter Theor.* **8**, 395 (1993).
- ³K. S. Page and P. A. Monson, *Phys. Rev. E* **54**, R29 (1996).
- ⁴W. G. Madden, *J. Chem. Phys.* **96**, 5422 (1992).
- ⁵A. Katz and M. E. Davis, *Nature (London)* **403**, 286 (2000).
- ⁶P. R. van Tassel, *Phys. Rev. E* **60**, R25 (1999).
- ⁷S. Y. Bhide and S. Yashonath, *J. Phys. Chem. B* **104**, 2607 (2000).
- ⁸M. Rivera and H. Dominguez, *Mol. Phys.* **101**, 2953 (2003).
- ⁹J. Krager and D. M. Ruthven, *Diffusion in Zeolites and Other Microporous Solids* (Wiley, New York, 1992).
- ¹⁰A. K. Chakraborty, D. Bratko, and D. Chandler, *J. Chem. Phys.* **100**, 1528 (1994).
- ¹¹A. L. Mehrabi and M. Sahimi, *Phys. Rev. Lett.* **82**, 735 (1999) and references therein.
- ¹²M. Saadatfar and M. Sahimi, *Phys. Rev. E* **65**, 036116 (2002).
- ¹³E. Nuñez, M. Rivera, and H. Domiguez, *Rev. Mex. Fis.* **50**, 331 (2004).
- ¹⁴M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1993).
- ¹⁵R. Chang, K. Jagannathan, and A. Yethiraj, *Phys. Rev. E* **69**, 051101 (2004).