Activated diffusion in relaxed porous clusters

Simcha Srebnik*, Irena Yungerman, Gil Kohav, Moshe Sheintuch

Department of Chemical Engineering, Technion – Israel Institute of Technology, Haifa 32000, Israel

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Abstract

We study diffusion through disordered porous structures, where the size of the diffusing particle is of the order of the pore diameter, and focus on the effect of particle–wall interactions. Such ‘configurational diffusion’ is important in catalysis, separation, and membrane technology, yet it is still poorly understood. We consider three types of cluster cluster aggregation (CCA) structures using simulations carried out on a cubic lattice. Namely, (1) next-neighbor (classic) CCA, where each site may have up to six nearest neighbors; (2) CCA where each site may have up to 26 nearest neighbor in its first coordination shell; and (3) a relaxed CCA solid formed by a process of energy minimization. We find that at low interaction strengths, diffusivity through the various types of CCA structure of similar porosity is independent of the mode of preparation and can be well predicted. However, at high interaction strengths which inhibit the diffusivity considerably, clusters characterized by lower surface-to-volume ratio display lower diffusivities. We suggest a simple model that accounts for the dependence of the diffusivity on the interaction parameter.

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1. Introduction

Predicting the diffusivities of various species through a porous material is academically challenging as well as of commercial importance in various technologies like catalysis, adsorption and membrane separation. Predicting the diffusivity requires information about the pore structure as well as the diffusion regime. While molecular and Knudsen-diffusion through non-interacting smooth pores is well understood, diffusion regimes that account for molecule–solid interaction, like surface or configurational diffusion, are still poorly understood (Keil, 1999). The main goal of this work is to characterize such diffusion through porous structures prepared by gelation. These are not ordered structures, such as zeolites (Arya et al., 2001) or carbon nanotubes (Iijima, 1991; Käger and Ruthven, 1992); activated diffusion through such ‘unordered’ solids have been scarcely addressed in the literature. The effective diffusivity may be calculated from the flux under an imposed concentration gradient (Fick’s law), from the self-diffusion of molecules (Einstein’s law), or from the exit times of molecules that diffuse from one end to the opposite one. We employ these different approaches in our simulation studies, assuming the lack of interaction between the molecules, in which case they should yield similar results (Sholl, 2006).

The parameters characterizing the pore structure, such as porosity, tortuosity and connectivity, do not define the problem uniquely. Simulated structures should be classified according to the various procedures for the manufacture of porous materials. Elias-Kohav et al. (1991) attempted to conduct such a classification and used a family of aggregation procedures like diffusion-limited (DLA), reaction-limited (RLA) and cluster–cluster aggregation (CCA); due to computer limitations at the time all simulated structures were two-dimensional. The latter, which resembles gelation and similar processes in which individual building blocks polymerize randomly to form the solid (gel), applies to the first stage (gelation) in a wide class of material preparation procedures, including the sol–gel synthesis of glasses and ceramics. Hydrolysis and polycondensation polymerize the monomer into oligomers. The repetition of such a process leads to the formation of the sol, and the gelation is performed either by aggregation or by cross-linking. Yet evidently, subsequent stages such as sintering affect the structure,
making it harder and stronger (i.e., higher average site coordination number). Such relaxation processes will tend to minimize the overall energy of the cluster.

Aside from the random percolation clusters, which do not correspond to any specific procedure, and the agglomeration, which imitates gelation, several approaches have been used to model amorphous materials. Sahimi and Tsotsis (2003) and Ghassemzadeh et al. (2000) modeled amorphous carbon by melting of a crystalline structure at high temperature using extensive MD simulations. The accessible pore volume of the material was generated by including breaking and removal of material during the melting process, or by inserting a number of Poisson points in the quenched graphite simulation cell and forming Voronoi polyhedra about these points; the pore space then corresponds to a number of these polyhedra selected to achieve a desired porosity. The obtained pore size distribution is skewed towards lower pore diameters when compared with a Gaussian distribution, better mimicking real membranes. Another computationally less demanding approach for generating porous media is through reconstruction of the original material based on structural correlation functions, as recently reviewed by Torquato (2002). Molecular reconstruction has been recently shown to lead to unstable structures such as three and four-member rings (Jepps et al., 2003). To circumvent this problem, a hybrid reverse Monte Carlo (MC) algorithm has been developed where the total energy of the system as well as the correlation function is optimized. Clearly, reconstruction methods can only reveal information regarding the final structure and not the mechanism of its formation.

The first purpose of this article is to characterize the activated (configurational) diffusion through CCA-like solids under conditions when the pore and molecule sizes are comparable. To that end we use the Lennard-Jones (LJ) potential to characterize the interaction of the solid with the diffusing molecules. Recently, the effect of solid–particle interactions on transport coefficient has been solved exactly for diffusion through a slit and a cylindrical nanopore (Jepps et al., 2003). The theory reveals that the assumption of a non-interacting system largely over predicts the diffusion coefficient within nanopores, whereby most of the deviations arise from excluded volume effects, however, MC methods have been extensively applied to diffusion problems (e.g. Coppens et al., 1999; Isliker and Vlahos, 2003; Karayiannis et al., 2001; Lam et al., 2001; Zalc et al., 2003). We use a simple, relatively fast, dynamic MC algorithm that allows us to pose a problem that is not material-specific and interpret the results with simple, physically reasonable, correlation. A second purpose of this article is to characterize the relaxation process of CCA. While the original CCA structure is defined by contact of adjacent cubes with no energetic considerations, we define CCA by contact of edges or corners and allow the system to relax in a way that reduces the total energy of the cluster as it forms. Further, we study the transport properties of the original and relaxed structures. To understand the diffusivity we characterize the structure of the relaxed CCA by its average coordination number (or specific surface area) and its fractal dimension (which is known to characterize highly porous CCA).

2. Cluster formation and structure

2.1. CCA and NNCCA

In CCA formation, a fraction \((1-\varepsilon)\) of the lattice sites are initially occupied randomly, while avoiding multiple occupancy, where \(\varepsilon\) is the void fraction. Then, successively larger clusters are formed by diffusion and aggregation of smaller units, and once an aggregate is formed, it cannot be broken. The process continues until only one cluster is left. We used the original algorithm developed by Meakin (1983) on a cubic lattice with periodic boundary conditions with two modifications: (1) In each iteration, all clusters move together instead of moving one by one, and (2) if only one large cluster is left, with few single unattached particles (a common case at the end of a simulation, which may take a long time to converge), each particle is moved separately until it aggregates with the main cluster. In this stage, the particles are not allowed to aggregate among themselves but only with the main cluster. The second modification has a negligible effect on the final result, as the aggregation process is nearly completed before this step, but it significantly shortens this final stage of the simulation.

We consider two types of clusters. In the first type, which we refer to as next-neighbor CCA (NNCCA), two particles are considered attached if they share a face (but not a corner); i.e., in aggregation in the plane particles in positions (3,3) and (3,4) are attached, but particles in position (3,3) and (4,4) are not. The NNCCA algorithm was simulated for planar domains of \(128 \times 128\), (and \(\varepsilon = 0.5\) to 0.9375), and three-dimensional domain of sizes that vary between 16 and 128 \((\varepsilon > 0.6)\). In the second type of cluster (CCA) we allow for bonds between particles in any direction, including particles sharing a corner, such as particles in position (3,3) and (4,4) in the example above. That is, a single particle may have a maximum of 26 bonded neighbors. We also consider relaxation of the CCA structure, as described below.

The mass–fractal dimension of the CCA objects can be computed by the box-counting method, which allows calculation of volume (i.e., mass) as well as surface dimension (Feder, 1988; Mandelbrot, 1983). The domain is divided into boxes of edge \(L\). A box is considered occupied if at least one pixel in it is occupied. The number of occupied boxes \(N\) correlates with \(L\) like \(N = L^{-D_v}\), where \(D_v\) is the volumetric fractal dimension. Using the same method, the surface fractal dimension \(D_s\) can be calculated by counting the exposed faces of the boxes. The fractality depends on the dimension and void fraction, with small influence of the domain size. Highly porous NNCCA solids were shown to be mass and surface fractals (Pfeifer et al., 1989). The scaling domain was found to decline with declining \(\varepsilon\). The pore space of these clusters is not fractal.

2.2. CCA with relaxation

We simulate relaxation as restructuring of the cluster by minimization of the total energy of the system. The relaxation simulation was carried out using the following modifications to the
CCA algorithm: (1) particles and clusters are allowed to move in any arbitrary direction, including diagonals, with a step length randomly chosen from a uniform distribution on the interval $[1, L_{\text{max}}]$ where $L_{\text{max}}$ is inversely proportional to the square root of the number of particles in the moving cluster. The new position is rounded to the nearest cell on the lattice. (2) Bonds between particles can be established between the 26 neighboring cells. However, the bond energy $E_c$ is taken to be inversely proportional to the sixth power of the bond length. (3) The clusters are allowed to restructure (relax) after each clustering iteration in the following manner. Each unit particle is allowed to move with a probability of $\exp(-\beta E_c)$, where $\beta$ is a coefficient proportional to the inverse temperature. A new neighboring location is chosen randomly and the move is accepted according to the Metropolis criterion: The new bond energy $E_{cn}$ is calculated; if $E_{cn}$ is lower than $E_c$, then the move is accepted, otherwise the particle moves with a probability $\exp(-\beta (E_{cn} - E_c))$. The simulation continues until only one cluster remains and the rate of the change of the energy of the system approaches zero (the accelerated method is used as described above when one cluster remains with a few single particles).

Values of $\beta$ were taken in the range 1.5–3.0. Lower values of $\beta$ allow for a relatively high probability for bond breaking moves, making the system hard to converge. High values of $\beta$ (lower temperature) reduce the relaxation process and result in clusters similar to the non-relaxed CCA system. Simulation with relaxation requires significantly more computer resources, hence three-dimensional simulations were carried out only for $32^3$ and $64^3$ clusters. Relaxation leads to rearrangement of the particles in a more compact fashion. We show that in general, relaxation forms pores with larger diameters, reduces the surface area and affects the diffusivity at high porosities and strong molecule–solid interactions. In addition, relaxed structures show mass fractal dimensionality at lower void fraction that both NNCCA and CCA media.

3. Diffusion in a cluster

Effective diffusivities are determined by several approaches. Non-activated diffusivities were determined from diffusion experiments in larger solid aggregates using either Fick’s law or Einstein’s law, as explained below. Activated diffusion experiments were carried out in a $20^3$ box cut out from the central section of the original cluster (simulated on a $32^3$ box). The diffusing particles are placed randomly at the top layer and allowed to diffuse through the cluster, applying Einstein’s equation. The diffusivity is determined from the exit times of a large sample of particles that diffuse through the cluster.

3.1. Packing the system

Since the simulated gelation process does not maintain the original box-shaped domain we first place the object in a box whose length in the $z$ direction is that of the cluster, while its $x$ and $y$ dimensions are obtained from the projection of the cluster on the $xy$ plane. All the unoccupied cells that can be accessed (using periodic boundaries and excluding diagonal moves) from unoccupied cells at $z = 0$ are considered to form the real void. The porosity of the formed cluster was determined from the number of accessible unoccupied cells divided by box volume. At void fractions of 0.6–0.9, the diffusion area and the real void fraction were almost identical to their original values.

3.2. Determining diffusivity from exit times

We use dynamic MC simulations to investigate diffusion through the generated porous substrate. We consider diffusion in the low concentration limit of non-interacting ghost particles whose movement inside the medium is governed by interactions with the substrate walls. A two-body LJ potential is used to model the interactions between the medium and a particle at a distance $r$ from the wall,

$$U_{LJ}(r) = K_{LJ} \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right], \quad r \leq r_{\text{cut}},$$

where $K_{LJ}$ characterizes the strength of interactions, $\sigma$ is the effective radius of interactions between the diffusing particle and wall ($\sigma$ also equals the effective size of solid lattice site, and thus corresponds to diffusing particle diameter). The cutoff radius of interactions $r_{\text{cut}}$ was taken to be $5\sigma$.

Diffusion of particles through the cluster is simulated off-lattice through a $20 \times 20 \times 20$ centre cut of the original cluster. The cluster is represented as a potential map, by projecting it onto a fine grid and calculating the potential at each point of the grid at the start of the simulation. In all simulations the resolution used for the potential grid is 0.025$\sigma$. Ghost particles are allowed to simultaneously diffuse through the potential. In each iteration, or time step, each particle is assigned a random kinetic energy calculated from Boltzmann energy distribution according to

$$f(E) = A \exp \left( -\frac{E}{k_B T} \right),$$

where $f(E)$ is the probability of having energy $E$, $A$ is a normalization constant, $k_B$ is the Boltzmann constant, and $T$ is the temperature. The velocity $v$ is related to the molecular mass $m$ and kinetic energy of the particle through

$$E = \frac{1}{2} mv^2.$$ 

Since the average energy is $E_{\text{avr}} = \frac{3}{2} k_B T$, the velocity distribution can be calculated from the root mean square velocity $v_{\text{avr}}$ from

$$v(p) = v_{\text{avr}} \sqrt{-\frac{3}{2} \ln(p)},$$

where $p$ is a random number on the interval (0,1). The displacement $r$ is calculated from $r(p) = -\mu \ln(p)$, where $\mu$ is the mean-free path (MFP). If the first cell along that path is occupied, new displacement and velocity vectors are tried. The particle is allowed to move in the selected direction as long as the initial sum of its potential and kinetic energies is higher than the potential energy of the cell which it enters along its path. Hence, the actual MFP of the particles is usually smaller.
than \( \mu \), and can be up to 60% lower in interacting clusters of low void fraction.

As opposed to molecular dynamics approach, the MC simulation allows us to determine average transport properties while the simulated diffusive path of each particle is not necessarily a real one. Interaction with the solid walls is the acceptance criterion for the move, while the velocity determines the direction and energy of the next move. Each iteration, or time interval, is uncorrelated to the previous one since the velocities of the particles are randomly assigned, and, as such, each iteration gives a possible configuration of the system in accordance with the Boltzmann distribution. A similar MC model was offered for activated diffusion through ZSM-5 (Keil et al., 1999), where a coarse-grained lattice representation included an interacting zeolite framework, channels, and active sites. As opposed to our simulation strategy, passage through the zeolite was simulated on-lattice.

The time interval for particle \( i \) at every accepted trial move is calculated from

\[
d_t^i = \frac{|\Delta r|^i}{v_i},
\]

where \( |\Delta r|^i \) is the displacement and \( v_i \) is the magnitude of the velocity of the particle. The total time it takes each particle to cross the substrate, \( t_i = \sum d_t^i \), is stored. The simulation ends when all the particles have reached the opposite end, or a set simulation time limit has been reached.

The diffusion simulation results are used to estimate the diffusion coefficients of the particles through the CCA substrate by fitting to an analytical curve calculated from the probability of a particle to displace a distance \( L \) in the \( z \) direction at a given time, \( t \),

\[
P(L; t) = \frac{1}{8\sqrt{\piDt}} \int_{-L_x}^{+L_x} dx \int_{-L_y}^{+L_y} dy \exp \left( -\frac{x^2 + y^2 + L^2}{4Dt} \right)
\]

\[= \frac{C}{\sqrt{Dt}} \exp \left( \frac{-L^2}{4Dt} \right) \text{erf} \left( \frac{L_x}{2\sqrt{Dt}} \right) \text{erf} \left( \frac{L_y}{2\sqrt{Dt}} \right),
\]

where \( D \) is the diffusion coefficient, \( L_x \) and \( L_y \) are the maximal observed displacement of the particle in the \( x \) and \( y \) axes, respectively. The function \( P(L; t) \) has a maximum defined by \( D \) for a given \( L \). \( D \) is determined by adjusting the maximum of the analytical distribution to that of the simulated results and minimizing the mean square error (see Fig. 1 for some examples). The diffusion coefficient is normalized relative to the numerically-determined diffusion coefficient in free space.

3.3. Diffusion from Fick’s law

In the diffusion simulation, the diffusion equation based on Fick’s law is solved,

\[\nabla (D \nabla C) = 0,
\]

where \( D \) is the diffusion coefficient and \( C \) is the concentration. The boundary conditions are unit concentration at \( z = 0 \), zero concentration at the upper face, and zero flux at all other faces. The equation was solved using finite difference method. Simple Gauss–Seidel algorithm is used to solve the linear equation system. The results are the fluxes in the upper and lower edges, which are checked for consistency. This mode is appropriate for systems in which the MFP is very small compared with object size.

4. Results and discussion

4.1. Structure

The effect of relaxation on the surface-to-volume ratio, \( S/V \) (i.e., the ratio of total exposed internal surface area to solid volume), and the change in total cluster energy as the simulation progresses is shown in Fig. 2. In general, relaxation leads to a...
porous structure that is characterized by smaller surface area (i.e., thicker walls separated by larger pores, further discussed below), and is energetically more stable. Initially, $S/V$ decreases quickly as clusters form. This stage of the simulation is also characterized by a fast change in energy as particles aggregate into clusters. Subsequently, clustering and relaxation proceeds at a slower (logarithmic) rate which appears to be independent of $\varepsilon$.

Since the connectivity of pores is crucial for understanding the diffusivity through the solid, we characterize the distribution of empty cells by their planar solid coordination number (number of occupied neighboring cells that lie on a plane). Fig. 3 presents the probability distribution $p_{mn}$ (ordinate) of finding a site of solid-coordination number $m$ (abscissa) next to a site with solid-coordination number $n$ (number in legend) in CCA and relaxed CCA solids. $p_{mn}$ is normalized such that $\sum m p_{mn} = 1$. Fig. 3a ($\varepsilon = 0.8$) and b ($\varepsilon = 0.5$) show that the distribution of pores in the CCA solid is essentially random. This is evident from the lack of correlation of finding such an $m$-site next to an $n$-site, i.e., all curves overlap, and from the comparison of the measured distribution with the theoretical probability, $p_q = 4!/q!(4 - q)! \varepsilon^{4-q}(1 - \varepsilon)^q$, at each porosity calculated from simple combinatorics. The slight deviations seen for $n = 4$ arise from the small number of pores with four solid nearest neighbors on a plane present in the solid; averaging over a number of sample solids captures the random distribution. For $\varepsilon = 0.8$, it can be inferred from Fig. 3a that these CCA solids are made up mostly of large pores, since the pore cross-section is characterized by cells with no or only one nearest neighbors occupied by solid, while very few cells have three or more solid neighbors. For $\varepsilon = 0.5$, the probability of pores with very large and very small cross-sections is small, while sites with 1–3 solid neighbors are most common.

After relaxation, the site–site distribution becomes correlated and somewhat more homogeneous (Fig. 3c). Most interestingly, the probability of finding a large pore (i.e., one with a solid-coordination number of 0) increases sharply, and appears to be highly self-correlated. Indeed, Fig. 3 inset, which shows the actual number of neighboring sites of each type for the relaxed solid, reveals that the vast majority of the $p_0$ sites neighbor empty cells. For $n > 0$, however, the distribution remains nearly random, suggesting random solid structure separated by large pores. A cross-sectional view of CCA, NNCCA and relaxed CCA solids are compared in Fig. 4. Visually, the CCA solid appears to be composed of randomly located solid sites. On the other hand, the relaxed solid appears to be composed of large clusters arranged randomly in the solid, separated by wide pore openings. NNCCA appears to have an intermediate structure between the highly non-random relaxed CCA and the random CCA solids.

The random nature of the non-relaxed CCA is also evident from the solid surface-to-volume ratio ($S/V$) and from the mass fractal dimension ($D_v$), shown in Fig. 5. For a random object, $S/V$ can be computed from the solid coordination number of a given site times the probability of encountering such a site, summed over all types of sites, i.e., $S/V = 6 - \Sigma q p_q$, where $p_q = (6!/q!(6 - q)! \varepsilon^{6-q}(1 - \varepsilon)^q)$. It is easily shown that this equation leads to $S/V = 6\varepsilon$ for a random object. Fig. 5a shows that the surface area of CCA follows $6\varepsilon$, as is expected for random objects. It is apparent that relaxation leads to a significant decrease in the $S/V$ ratio to a value that is nearly independent of $\varepsilon$ at moderate porosities, decreasing only at very high porosities ($\varepsilon > 0.95$); $S/V$ decreases with decreasing $\beta$ (Fig. 5b). Note again that relaxation of solids to identical islands of size $i$ will lead to $S/V \sim 6\varepsilon/i$ (assuming cubical non-overlapping islands). This allows some estimates of the pore size from $S/V$ in Figs. 5a and 2 (i.e., island size $i$ is about 2–3). However, the weak independence of $S/V$ on $\varepsilon$ in both figures, along with the fractal nature, suggests that the pore space cannot be characterized by a single pore size. Note also that relaxation in $5(a)$ was conducted for $t = 1000$, as opposed to $t = 10000$ in Fig. 3, which shows much smaller $S/V$ values. NNCCA solid again displays intermediate properties between CCA and relaxed CCA.

The fractal nature of NNCCA has been a subject of extensive investigation (see Introduction) showing the existence of a mass–fractal asymptotic structure for highly porous solids. For realistic porosities, there exists a narrow scaling domain over which fractality exists, while over large distances the object is random. The fractal domain of NNCCA objects occurs in the range $\sigma \ll l \ll \xi$, where $\xi \sim (1 - \varepsilon)^{-1/(d_d - D_v)}$ is the characteristic length of the cluster, $d_d$ is the space dimensionality, and $D_v$ is the fractal dimension of the cluster (Meakin, 1999). For a three-dimensional fractal, $D_v \sim 1.8$. The volume (mass) fractal dimension, $D_v$, was calculated for NNCCA solids for various domain sizes (Fig. 5c). $D_v$ is around 3 for realistic porosities and declines to an asymptotic value as $\varepsilon$ approaches unity. In Fig. 5d we show the fractal dimension in the progress of a relaxation simulation. Relaxation leads to a significant decrease in the volume fractal dimension over time. The results presented...
in Figs. 3–5 suggest that relaxation leads to the formation of more fractal structure (lower $D_v$) that is made up of stretches of thick walls (Fig. 4 and lower $S/V$ ratio) and opening up of large voids (large number of $p_0$ sites).

4.2. Diffusivity determined from exit times

In this section we report the computed diffusivity, scaled with respect to the diffusivity of an empty cell of similar dimension and MFP, for the non-activated and activated structures. We predict the non-activated diffusion with known expressions and develop a one-adjustable-parameter correlation for the activated-diffusion case.

First, we examine the asymptote of non-activated diffusivity ($K_{LJ} = 0$) as a function of porosity for NNCCA, CCA (random structure) and relaxed CCA (Fig. 6). Non-activated diffusivity was found to be independent of the mode of preparation, as is evident by the overlapping data in Fig. 6. Flux calculation in porous media is based on identifying the controlling diffusion regime (molecular, Knudsen, configurational or surface) and correcting the diffusivity for the reduced area available for transport and for the tortuosity of the pore network. The diffusivity here (relative to that of a void) can be approximately described by the common approximation $D^* = \frac{\varepsilon}{\tau}$ (Keil, 1999; Froment and Bischoff, 1990), as expected for a random object where the tortuosity, following Elias-Kohav et al. (1991) has been estimated as $1/\tau = (\varepsilon - \varepsilon_p)/(1 - \varepsilon_p)$ from percolation theory with the percolation threshold $\varepsilon_p \sim 0.31$ (Stauffer, 1985). The prediction from percolation theory yields the same result as the theory by Wakao and Smith (1962) when $\varepsilon_p = 0$. The tortuosity factor is ill-defined and its estimation is usually based either on simplified models (Wakao and Smith, 1962) that usually yield poor predictions, on direct measurements of...
effective diffusivity, or on mathematical modeling of mercury porosimetry or NMR data (Rigby and Gladden, 1996). The prediction of the diffusivity based on the percolation threshold attests to the random nature of the simulated solids. Percolation theory has been found useful in characterizing several disordered systems including the modeling of porous structures used as catalyst supports (Mo and Wei, 1986).

The diffusivity in the activated-diffusion case is plotted as a function of $K_{LJ}$ and for various $\varepsilon$ in Fig. 7. The following asymptotes can be distinguished: (1) at large $K_{LJ}$ the diffusivity seems to approach an asymptote of $D \sim \exp(-E_4 K_{LJ})$ for moderate porosities (where $E_4$ is the determining energy barrier for diffusion). The activation barrier of the aggregate corresponds to the lowest potential energy path through a pore with a given cross-section. This was confirmed by simulating diffusion through well-defined straight pores on a lattice. Similar scaling of $D \sim \exp(K_{LJ} E_i)$ (Fig. 8) was found for a pore with cross-section composed of two vacant sites, each of size $q$.

Such scaling is typically applied to describe activated diffusion in solids (Deen, 1998). (2) The effective value for non-activated diffusivity ($K_{LJ} = 0$, Fig. 7) can be approximately described by the common approximation $D = \varepsilon/\tau$ as discussed earlier. The dependence of the diffusivity on the interaction parameter for the CCA structure is much stronger than that predicted for smooth cylindrical pores (Bhatia, 2006) at large interaction energies (especially for $K_{LJ} > 15$). Trace of particle paths during the simulation at such high energies reveal the presence of several potential ‘traps’ where the particle oscillates between two low energy sites for very long periods, as further discussed below. Such traps cannot be present in a smooth pore with a periodic potential energy map.

We interpret the results in terms of diffusion under a concentration gradient. The engineering approach to diffusion relates the flux to a concentration gradient according to Fick’s law where the flux–gradient ratio is the diffusivity. The observed behavior can be elucidated by modeling the solid as composed of pores with different cross-sections—those that consist of single sites and inhibit diffusion when $K_{LJ}$ is large, and those that have larger cross-sections. We wish to characterize the average distribution of sites within a typical path of a diffusing particle. The probability that a vacant site on a pore skeleton has a solid coordination number (SCN) of $q$ solid neighbors in the planar cross-section perpendicular to flow direction, is

$$p_q = m_q \frac{q^{q-4}}{[(q-4)!]} (1-\varepsilon)^q,$$  \hspace{1cm} (8)

where $m_q = 4!/[q!(4-q)!]$ is the degeneracy of the type of site. Specifically, $p_4 = (1-\varepsilon)^4$ (a 1 × 1 or single-site pore for which $q = 4$), $p_3 = (1-\varepsilon)^3$, $p_2 = (1-\varepsilon)^2$, $p_1 = (1-\varepsilon)$ and $p_0 = \varepsilon$. The diffusivity through a pore of a single site ($q = 4$) is

$$D_4 \sim \exp(-E_4 K_{LJ}).$$  \hspace{1cm} (9)

We can write similar expressions for larger pores. For example, for $2 \times 1$ pores (i.e., two attached sites of $q = 3$),

$$D_3 \sim \exp(-E_3 K_{LJ}).$$  \hspace{1cm} (10)

For clusters of 3 or 4 vacant sites we write

$$D_2 \sim \exp(-E_2 K_{LJ})$$  \hspace{1cm} (11)

and for larger pores $D_1 \sim \text{constant} \sim 1$ since $E_1$ is small and $D_0 = 1$. 

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**Fig. 4.** Image of $x$–$y$ cross-section of cluster for CCA, NNCCA, and relaxed structures for $\varepsilon = 0.8$, from left to right, respectively: (a) single layer cross-section, and (b) 5-layer cross-section.
Pores are produced by a network of sites. We view the solid as a net of pore chains. We discriminated between two kinds of pore chains—those that incorporate \( q = 4 \) sites and those that incorporate only \( q = 3 \) and smaller SCN sites, as is depicted in Fig. 9. Obviously, at large \( K_{LJ} \) the barrier through pores of the former size will be prohibitive and molecules will diffuse predominantly through the latter type. The effective diffusivity \( (D_{1-3}) \) of pore chains consisting only of sites with \( q = 0, 1, 2, \) and 3, will depend on the fraction of sites of each kind, normalized to exclude \( q = 4 \) pores, i.e.,

\[
(1 - p_4)/D_{1-3} = p_3/D_3 + p_2/D_2 + (p_1 + p_0)/D_1.
\]

Similarly, the effective diffusivity in pores that incorporates all types of barriers is

\[
1/D_{1-4} = p_4/D_4 + p_3/D_3 + p_2/D_2 + (p_1 + p_0)/D_1 = p_4/D_4 + (1 - p_4)/D_{1-3}.
\]

Thus, the overall prediction for the activated diffusivity through a random aggregate, assuming parallel non-intersecting pore chains, is

\[
\langle D \rangle = \langle \varepsilon/\tau \rangle [(1 - P_{1-3})D_{1-4} + P_{1-3}D_{1-3}],
\]

where \( P_{1-3} \) is the fraction of pores with \( q < 4 \), which is presumable small. We will treat this parameter as an adjustable one, and later will try to interpret its value. Note that this expression satisfies the two asymptotes above:

1. For large \( K_{LJ} \) the effective diffusivity is due to the second term on the right-hand side of Eq. (14), or

\[
\langle D \rangle = \varepsilon/\tau \langle 1 - P_{1-3} \rangle D_{1-3} \rightarrow p_3/D_3.
\]

2. For non-activated diffusion \( \langle D \rangle = \varepsilon/\tau \).

The second term in Eq. (14) becomes important only for very high \( K_{LJ} \). At such conditions, it is found that a very small

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**Fig. 5.** (a) Surface-to-volume ratio as a function of void fraction, (b) average \( S/V \) at moderate porosities \((0.7 \leq \varepsilon \leq 0.9)\) as a function of relaxation parameter, \( \beta \), after 1000 MC steps, (c) mass fractal dimension of NNCCA as a function of void fraction for various domain sizes, and (d) change in mass fractal dimension during relaxation simulation.
fraction of paths made up of $1 \times 2$ and larger pore cross-section govern the diffusion.

Thus, with one adjustable parameter that depends on the porosity, $\varepsilon$, we are able to predict the activated diffusivity in CCA, treating them as random objects, over a realistic domain of porosities and over a wide domain of interaction ($K_{LJ}$) parameters (solid curves in Fig. 7). This expression applies to other objects, like NNCCA or relaxed CCA, that display similar diffusivity for porosities smaller than 0.75, or for even higher values when the solid-molecule interaction is sufficiently small (Fig. 10).
4.3. Diffusivity determined from Fick’s law

Calculation of the effective diffusivity from Fick’s law, by solving the network of algebraic equations for an imposed concentration gradient, was conducted for the interaction-free case \( K_{LJ} = 0 \). The tortuosity of the diffusion path, calculated from \( D = \varepsilon / \tau \), is shown in Fig. 11. Except for very high porosities, the tortuosity is independent of the object size \((32^3–128^3)\) and of the mode of preparation (initial random solid, NNCCA solid, and relaxed CCA solid). The observed tortuosity can be correlated well by \( 1 / \tau = (\varepsilon - \varepsilon_p) / (1 - \varepsilon_p) \) for \( \varepsilon < 0.95 \) (Fig. 11, solid line denoted as ‘theory’). Although at high porosities the solid was shown to be fractal (Fig. 5), the tortuosity shows slight deviations from the theoretical curve, especially for small sample sizes, due to the breakdown of the mean-field model for the fractal solids.

4.4. Diffusion in relaxed solids

Relaxation of porous solids in general opens up large pores and reduces the surface-to-volume ratio. Simulations reveal that for \( \varepsilon < 0.8 \), diffusivity in CCA and relaxed clusters is similar over the entire range of \( K_{LJ} \) studied. Counterintuitively, diffu-
sion through the relaxed cluster is slower than diffusion through the CCA cluster at high values of $K_{LJ}$, as seen in Fig. 10. This behavior can be elucidated by tracing the particle paths during the diffusion simulation. In Fig. 12a, it is seen that the molecule path in relaxed and non-relaxed solids samples the same distribution of sites, though the site distribution in the solids differ substantially (compare Figs. 3a and c). Fig. 12b indicates that particles get trapped in small pores for longer periods of time in the relaxed cluster. From the cross-sectional views of the particles get trapped in small pores for longer periods of time in the relaxed solid, the attractive particle–wall interactions in activated diffusion draw the particles to the surface; sites with three or more solid neighbors serve as low energy ‘traps’ that retard diffusion of the particle to a significant extent.

5. Conclusions

We have investigated the structure and diffusion behavior of three types of clusters: CCA, NNCCA, and relaxed CCA. Diffusion was studied under ‘non-activated’ and activated conditions. In the former case, when the diffusing particles do not interact with the impenetrable walls of the cluster, diffusion was found to be highly insensitive to the solid structure (at least for $ε < 0.8$) and can be well predicted from $D = ε/τ(ε_p)$, where $ε_p$ is the percolation-threshold, suggesting random structure. In the latter case, we studied the effect of LJ interactions on the diffusion behavior of the particles. The activated-diffusivity was found to strongly depend on the type of structure at high values of the LJ interaction parameter. For the random CCA structure, reasonable fitting was obtained using a model with one adjustable parameter for the range of porosities studied.

Contrary to intuition, activated diffusivity in relaxed solids is observed to be lower than in CCA or NNCCA solids. Relaxation leads to formation of higher SCN clusters separated by large pores, evident also from site-site probability distributions. However, activated diffusion proceeds near the solid walls. Our analysis also indicates that activated diffusion through relaxed structures may possibly be modeled as diffusion through random structure with an effective lower porosity.

The dependence of the diffusivity on molecule-surface interactions, when these interactions are strong, suggests that this approach can be used for separation purposes. The effect of the unique structure of the pore space should also be studied in problems of diffusion and reaction; similar studies of fractal surfaces (Gutfraind et al., 1990) led to behavior that is qualitatively different than that in random objects (i.e., percolation clusters).

### Notation

- $A$: normalization constant
- $C$: concentration
- $d$: space dimensionality
- $d_{r_i}$: displacement of particle $i$
- $d_{t}$: time interval for displacement $d_{r_i}$ of particle $i$
- $D$: diffusivity
- $D^\ast$: diffusivity for a non-interacting solid ($K_{LJ} = 0$)
- $D_i$: effective diffusivity through pore with void cross-sectional area equal to $i$
- $D_s$: surface fractal dimension
- $D_v$: volume (mass) fractal dimension
- $E$: kinetic energy of particle
- $E_{av}$: average particle energy
- $E_c$: current bond energy
- $E_{cn}$: new bond energy
- $E_i$: energy barrier for diffusion through site $i$
- $k_B$: Boltzmann constant
- $K_{LJ}$: Lennard-Jones interaction parameter
- $L$: number of lattice cells per box edge
- $L_{max}$: maximum step size of diffusing particle
- $L_x$: maximum displacement of particle in $x$-axis
- $L_y$: maximum displacement of particle in $y$-axis
- $m$: particle mass
- $m_q$: degeneracy of sites of $q$ solid coordination number
- $N$: number of occupied lattice cells
- $p$: random number on the interval [0,1)
- $p_{mn}$: probability of finding a site of solid coordination number $m$ next to a site with solid coordination number $n$
- $P_{q}$: probability of finding a site of $q$ solid coordination number; $q$ ranges from 0 to 6
- $P_{1-3}$: fraction of pores with $q < 4$
- $r_{cut}$: cut-off radius of interactions
- $S/V$: surface-to-volume ratio
- $(S/V)_{inf}$: surface-to-volume ratio at infinite time
- $t$: time
- $T$: temperature
- $v$: particle velocity
- $v_{avr}$: root mean square particle velocity

### Greek letters

- $β$: $1/kT$
- $ε$: void fraction
- $ε_p$: percolation threshold
- $μ$: particle mean free path
- $ξ$: characteristic length of cluster
- $σ$: radius of interaction between diffusing particle and wall
- $τ$: tortuosity

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### References