

Diffusion on a Silicalite Lattice Model*

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A lattice model is proposed for describing the diffusion of small molecules in silicalite, as a special example of zeolite. The lattice structure matches the interlacing of the silicalite channels and the molecules hop randomly from site to site according to simple rules. The diffusion of a single molecule is treated exactly. The ability of the model to meet more complicated situations is briefly discussed.

Key words: diffusion, silicalite, zeolite, lattice model

The diffusion of molecules through periodic media like zeolites has become a standard separation technique, but our understanding of the microscopic processes involved is still incomplete [1] and in order to improve it, studies of the molecular motions have been realized during the last few years by means of computer simulations, particularly in the case of silicalite [2,3,4].

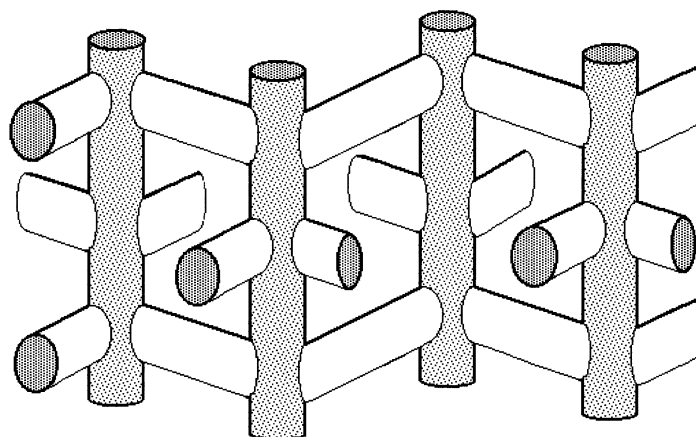


Figure 1. Scheme of the channel network of silicalite.

* Dedicated to Prof. Jan Stecki on the occasion of his 70th birthday.

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Silicalite is a synthetic zeolite with global formula $\text{Si}_{96}\text{O}_{192}$. Its channel network, shown in Fig. 1, is an interlacing of rectilinear and zigzag channels. The free diameter of these channels is close to 0.6 nm, allowing small alkane molecules, such as n-butane and iso-butane, to crawl through them and the diffusion coefficients of these molecules have been evaluated by means of simulations based on the method of Molecular Dynamics.

Such simulations, however, involve extremely long calculations and therefore we think it worthwhile to consider simplified descriptions retaining only the basic features of the problem. It is the aim of the present paper to present a model, where the crawling of the actual molecules inside the channels is replaced by stochastic jumps of point-molecules on a lattice matching the basic structure of silicalite.

RESULTS AND DISCUSSION

The lattice model: Each site corresponds to the intersection of a rectilinear channel and a zigzag channel. The rectilinear channels are parallel to the z axis and made of segments of length a , linking adjacent sites. The zigzag channels are similarly made of segments of length b parallel to the (xy) plane, with an angle u between consecutive segments, and the average orientation of the zigzags is parallel to the x axis. See Fig. 2.

Four bonds are adjacent to each site: two of them correspond to a rectilinear channel (a-bonds), the two others correspond to a zigzag channel (b-bonds). The sites are of two kinds, A and B, with one of each kind in the primitive cell shown in Fig. 2; an

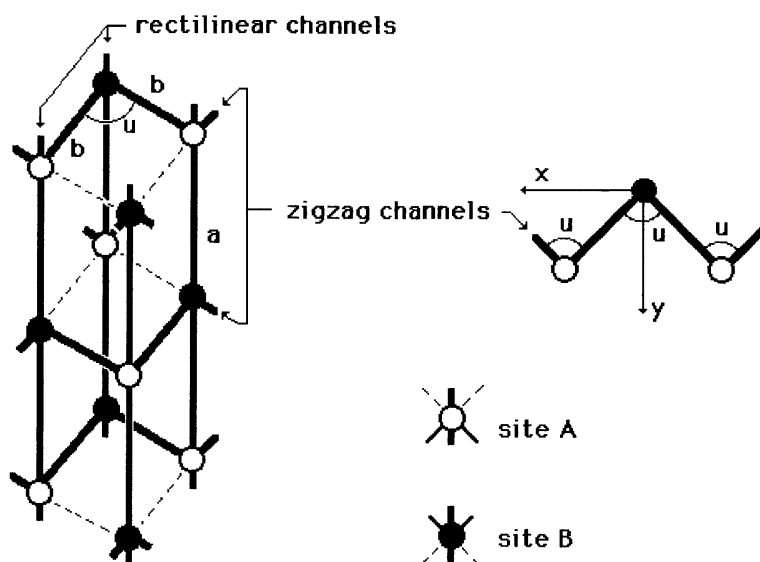


Figure 2. The silicalite lattice model.

A-site is surrounded by four B-sites and conversely, so that each bond links a pair of sites A and B. (This lattice is a frustrated monoclinic lattice, with one out of three bonds missing, and is topologically equivalent to a diamond lattice). In order to match the actual structure of silicalite, the adopted values for the lengths of a- and b-bonds and for the angle u are $a = 0.996$ nm, $b \sin(u/2) = 1.004$ nm, $b \cos(u/2) = 0.670$ nm, *i.e.* $b = 1.207$ nm and $u/2 = 56.28^\circ$.

Diffusion of a single molecule on the lattice: We assume that the molecule occupies one site and that it can jump randomly to one of its four nearest neighbours with frequency $1/\tau$ (τ being the average time between consecutive jumps). These jumps are of two kinds: “a-jumps” along rectilinear channels and “b-jumps” along zigzag channels. Successive jumps are, strictly speaking, uncorrelated, but on account of the structure of the lattice, they are alternatively of type $A \rightarrow B$ and type $B \rightarrow A$ and we shall see that this brings some correlation between the y components of two consecutive b-jumps.

All jumps are subject to the following rules, expressed in terms of the unit vectors ($\underline{1}_x, \underline{1}_y, \underline{1}_z$):

“a-jumps” occur with probability p and generate two equiprobable displacements

$$\pm a \underline{1}_z;$$

“b-jumps” occur with probability $q = (1 - p)$ and generate two equiprobable displacements

$$\begin{aligned} & b [\pm \sin(u/2) \underline{1}_x + \cos(u/2) \underline{1}_y] \text{ when starting from a site A,} \\ & b [\pm \sin(u/2) \underline{1}_x - \cos(u/2) \underline{1}_y] \text{ when starting from a site B.} \end{aligned}$$

Any single jump is described by the vector

$$\underline{r} = \xi \underline{1}_x + \eta \underline{1}_y + \zeta \underline{1}_z$$

with the following averages values:

$$\begin{aligned} \langle \xi \rangle &= 0, \quad \langle \eta \rangle = \pm q b \cos(u/2), \quad \langle \zeta \rangle = 0, \\ \langle \xi^2 \rangle &= q b^2 \sin^2(u/2), \quad \langle \eta^2 \rangle = q b^2 \cos^2(u/2), \quad \langle \zeta^2 \rangle = p a^2, \end{aligned}$$

where the + and – signs respectively apply to $A \rightarrow B$ and $B \rightarrow A$ jumps.

Consider two consecutive jumps \underline{r}_1 and \underline{r}_2 . Their x and z components are totally uncorrelated, meaning that

$$\langle \xi_1 \xi_2 \rangle = 0, \quad \langle \zeta_1 \zeta_2 \rangle = 0$$

and

$$\langle (\xi_1 + \xi_2)^2 \rangle = 2 \langle \xi^2 \rangle, \quad \langle (\zeta_1 + \zeta_2)^2 \rangle = 2 \langle \zeta^2 \rangle.$$

This is not so far their y components, due to the fact that a B \rightarrow A jump always follows an A \rightarrow B jump, and conversely. Hence

$$\langle \eta_1 + \eta_2 \rangle = 0, \quad \langle \eta_1 \eta_2 \rangle = -q^2 b^2 \cos^2(u/2),$$

$$\text{and } \langle (\eta_1 + \eta_2)^2 \rangle = 2 \langle \eta^2 \rangle + 2 \langle \eta_1 \eta_2 \rangle = 2q(1-q)b^2 \cos^2(u/2) = 2pqb^2 \cos^2(u/2).$$

Consider now the general case of n consecutive jumps, leading to the displacement

$$\underline{R}_n = X_n \underline{1}_x + Y_n \underline{1}_y + Z_n \underline{1}_z,$$

$$\text{with } X_n = \sum \xi_i, \quad Y_n = \sum \eta_i, \quad Z_n = \sum \zeta_i \quad (i = 1, \dots, n).$$

On account of the preceding results, one has

$$\langle X_n \rangle = 0, \quad \langle Z_n \rangle = 0 \text{ and } \langle Y_n \rangle = 0 \text{ for } n \text{ even, } = \pm qbc \cos(u/2) \text{ for } n \text{ odd}$$

(depending on the A or B nature of the starting site). One has further

$$\langle X_n^2 \rangle = n \langle \xi^2 \rangle = nqb^2 \sin^2(u/2), \quad \langle Z_n^2 \rangle = n \langle \zeta^2 \rangle = npa^2.$$

The computation of $\langle Y_n^2 \rangle$ is somewhat less obvious. We have

$$\langle Y_n^2 \rangle = \langle Y_{n-2}^2 \rangle + 2 \langle Y_{n-2} (\eta_{n-1} + \eta_n) \rangle + \langle (\eta_{n-1} + \eta_n)^2 \rangle = \langle Y_{n-2}^2 \rangle + 0 + 2pqb^2 \cos^2(u/2)$$

(the second term of the r.h.s. averages to zero, because the (n-1)-th and n-th jumps are necessarily of opposite types A \rightarrow B and B \rightarrow A). Hence, by recurrence:

$$\langle Y_n^2 \rangle = npqb^2 \cos^2(u/2) \text{ for } n \text{ even, } = (np + q)qb^2 \cos^2(u/2) \text{ for } n \text{ odd.}$$

The diffusion coefficients D_x , D_y , D_z , along the directions x, y and z are obtained by dividing the mean square displacements $\langle X_n^2 \rangle$, $\langle Y_n^2 \rangle$ and $\langle Z_n^2 \rangle$ by the elapsed time $t \equiv n\tau$ and by letting n tend to infinity in order to reach the long time limit. One finds

$$D_x = \langle X_n^2 \rangle / 2t = \langle X_n^2 \rangle / 2n\tau \rightarrow q(b^2/2\tau) \sin^2(u/2),$$

$$D_y = \langle Y_n^2 \rangle / 2t = \langle Y_n^2 \rangle / 2n\tau \rightarrow pq(b^2/2\tau) \cos^2(u/2),$$

$$D_z = \langle Z_n^2 \rangle / 2t = \langle Z_n^2 \rangle / 2n\tau \rightarrow p(a^2/2\tau).$$

While the diffusion along the x and z directions proceeds by means of b-jumps and a-jumps, respectively, and are therefore controlled by the probabilities q and p, the diffusion along the y direction requires a combination of a-jumps and b-jumps and depends upon the product p q. The ratio D_y/D_x is equal to $p \operatorname{ctn}^2(u/2)$ and for u close to 90° is of the order of p/2, *i.e.* smaller than 0.5.

Diffusion of short alkanes in silicalite: From recent computer simulations performed on n-butane and iso-butane in silicalite [4], we can obtain reasonable estimates of the probability $p \equiv 1 - q$ involved in the present model. The most realistic simulations, which take into account the vibrations of the silicium and the oxygen atoms forming the actual silicalite lattice, lead to the following values, in the limit of low concentrations:

n-butane:	$D_x = 2.98 \pm 0.20$	$10^{-9} \text{ m}^2/\text{s};$
	$D_y = 0.81 \pm 0.28$	$10^{-9} \text{ m}^2/\text{s};$
	$D_z = 11.25 \pm 3.25$	$10^{-9} \text{ m}^2/\text{s};$
iso-butane:	$D_x = 0.17 \pm 0.09$	$10^{-9} \text{ m}^2/\text{s};$
	$D_y = 0.04 \pm 0.02$	$10^{-9} \text{ m}^2/\text{s};$
	$D_z = 0.41 \pm 0.09$	$10^{-9} \text{ m}^2/\text{s}$

(note that the axis denoted here as y and z are referred to as z and y in [4]). Within the range of their uncertainties, these coefficients can be reasonably fitted by assuming $p \equiv 1 - q \approx 0.7$ for both n-butane and iso-butane, with: $1/\tau \approx 2.5 \cdot 10^9 \text{ s}^{-1}$ for n-butane; $1/\tau \approx 0.11 \cdot 10^9 \text{ s}^{-1}$ for iso-butane.

(using the values of a, b and u quoted at the end of Section “The lattice model”).

Further considerations: Almost all kinds of situations can be met by the silicalite lattice model introduced here. The diffusion of a single molecule on the lattice is easily extended to diffusion at finite concentrations: the hopping rules must be amended in order to exclude the presence of two molecules at the same site (or at least impose some restriction to their number) and to forbid two molecules to crawl through the same channel segment simultaneously. This problem can be studied numerically by the Monte Carlo method or analytically by using the kind of technique introduced by Harrison and Zwanzig [5].

Competitive diffusion of two molecular species is a straightforward extension of the previous case: both kinds of molecules hop on the lattice with specific probabilities and exclude one another from the same site or channel segment according to definite rules. It is also possible to treat molecules capable of two different conformations which, on account of their shapes, diffuse differently through the channels (this is precisely the case of n-butane with its trans and gauche forms, which was handled previously by means of the method of Molecular Dynamics [4]).

More complicated situations can be met by introducing sites capable of adsorbing certain molecules specifically (the diffusion of benzene in the NaY zeolite was previously treated in such a manner [6]) and even capable of catalyzing chemical reactions.

We are looking forward tackling such problems in the near future.

Acknowledgment

This paper is a tribute of one of us (A. Be) to his good friend Jan Stecki to whom he got acquainted in the late fifties and who, as many of us, has now become another victim of the "discrimination by age".

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