

Modeling molecular diffusion in channel networks via displacements between the channel segments†

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Molecular diffusion in channel networks (zeolite silicalite-1) is studied by molecular trajectories as a sequence of displacements between the individual channel segments. Alternatively to the method introduced by Kärger (J. Kärger, *J. Phys. Chem.*, 1991, **95**, 5558) for predicting correlated diffusion anisotropy in channel networks, in this concept the diffusants are assumed “to lose their memory” on moving through a channel segment rather than a channel intersection. The pros and cons of this novel approach are illustrated by analysing own simulations with 1-butene as a diffusant.

1. Introduction

Almost all applications of the nanoporous zeolites^{1,2} depend on the diffusion of molecules and ions in the pores and channels of the zeolite crystals.³ The diffusion mechanism can often be described as a random walk of the molecules between the adsorption sites in the pore network. In a three-dimensional network the simplest case is a cubic arrangement of the sites with equal probabilities for all jumping directions. Then,

$$D = L^2 k / 6 \quad (1)$$

holds for the self-diffusion coefficient D , where L is the site-to-site distance and k the site-to-site jump rate which is related to the average residence time $\tau = 1/k$ at the site.³ The validity of eqn. (1) is not restricted to jump-like propagation. It holds quite generally for all types of movement which may be characterized by sequences of displacements with mean square values of L^2 and mean residence times $\tau = 1/k$ between the individual displacements, provided that they occur independently from each other. Hence, also in the following the expression “jump” is generally used as a short-hand expression for the individual steps in such a series of displacements. In zeolites the topology of the sites is usually complicated and depends on the specific zeolite and the type and number of the guest molecules.⁴ Additionally, barriers of different height can be given between the sites so that several site-to-site jump rates k_i influence D and lead to complicated temperature dependences of D .^{5,6} Beside the treatment with kinetic Monte Carlo simulations, analytical jump diffusion models have been developed for the zeolite-guest systems.⁴ The resulting direct connections between the site-to-site jump rates k_i and the self-diffusion coefficient D give insight into the diffusion mechanisms.

The first model for diffusion in zeolite MFI was developed by Kärger.⁷ A schematic of the channel structure of MFI zeolites is shown in Fig. 1. The distances $a/2$ and $b/2$ between the channel intersections in the x - and y -directions are of the order of 1 nm. Diffusion is also possible in z -direction because the

zig-zag channels in x -direction allow alternating displacements in the positive and negative z -directions. The model in ref. 7 assumes uncorrelated displacements between the channel intersections, *i.e.* a molecule arriving at one intersection is assumed to have “forgotten” from which intersection it has come from. Under this condition, the components of the diffusion tensor are correlated by the simple equation

$$\frac{c^2}{D_z} = \frac{a^2}{D_x} + \frac{b^2}{D_y}, \quad (2)$$

where, beside the principal elements D_i of the diffusion tensor, only the structure-related quantities, the unit cell constants $a = 2.007$ nm, $b = 1.992$ nm, and $c = 1.342$ nm in x -, y -, and z -direction, respectively, occur. Having in mind that the real structure of MFI-type crystals is far from being a quasi infinitely-extended homogeneous network with elementary cells as given by Fig. 1,^{8–12} so far experimental studies have not gone any further than to demonstrate qualitative agreement with eqn. (2).^{8,13,14} By contrast, however, for a given model MD simulations may provide arbitrarily accurate values. In order to take account of possible deviations from the rather simple, first order approach, as given by eqn. (2),

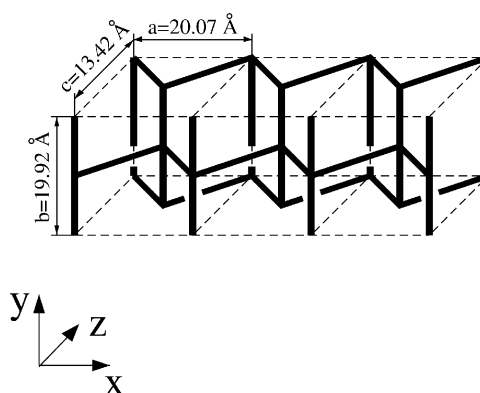


Fig. 1 The channel system of MFI zeolites.

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in¹⁵ a memory parameter β has been introduced by the relation

$$\beta = \frac{c^2/D_z}{a^2/D_x + b^2/D_y}. \quad (3)$$

If $\beta = 1$ eqn. (2) holds, if $\beta > 1$ the diffusion in z -direction is suppressed against the other directions. This indicates that the molecules do not randomly choose the direction of a step but prefer to follow the direction of the previous step. Then, diffusion in x - and y -direction can be significantly faster than in z -direction where diffusion depends on the interchange between x - and y -channels. In the extreme case of hardly any interchange the molecules essentially remain in one channel, so that D_z approaches zero and $\beta \gg 1$. Several papers^{16–21} deal with the possibilities to account for correlations between subsequent displacements and to derive the corresponding relations for the memory parameter β and, thus, for the interrelation of the principal elements D_i of the diffusion tensor.

In this paper (section 2) we develop a model for diffusion in MFI-type zeolites where the channel segments, *i.e.* the positions *between* the intersections, are considered as the distinguished sites between subsequent displacements. The consequences of the model shall be discussed and a comparison with the original model in ref. 7 will be given. Section 3 presents the results of molecular dynamics simulations with 1-butene which nicely confirm the validity of the model. Final conclusions are given in section 4.

2. Step model of molecular displacement

With this new diffusion model for MFI-type zeolites we seek for an alternative description of the diffusion process providing the possibility to get rid of occurring memory effects. The model of⁷ implies that molecules continue their diffusion path from one intersection to the subsequent one without any memory about the intersection from which they have got there. This shall be the case, *e.g.*, if the molecules reside long enough in the channel intersections as a consequence of barriers which prevent them from entering the channel segments.

In contrast to ref. 7, in this paper the molecular trajectories shall be considered as a sequence of displacements between subsequent channel *segments* rather than channel *intersections*. In fact, molecular dynamics simulations²² have shown that *e.g.* short chain length hydrocarbons like *n*-butane and *n*-hexane pass the intersections comparably quickly and have much longer residence times in the channel segments. A schematic of the adsorption sites located in the channel segments between the intersections is shown in Fig. 2. If a molecule reaches an intersection it has four possibilities to proceed:

1. the molecule returns to the channel segment where it has come from so that there is no net effect of displacement,
2. the molecule makes a step forward and stays in the same type of channel,
3. the molecule turns right into a channel of different type, and
4. the molecule turns left into a channel of different type.

The model considers the possibilities 2 to 4.

As a deficiency of the model in ref. 7, oscillations of molecules residing in the channel segments would be counted as steps as soon as too large volumes of the intersection states are assumed. An evaluation of steps of methane molecules between the channel intersections with different definitions of the volume of the channel intersections is given in ref. 21. It clearly shows that the number of registered step events and, in parallel with it, the probability of backward steps increases with the radius of the sphere defining the channel intersection. In this case particle memory has necessarily to be taken into account. By doing so, *e.g.* using the formalism derived in refs. 20 and 21 completely consistent results are obtained. As a great advantage of the present approach, in such cases referring the individual displacements to the channel segments rather

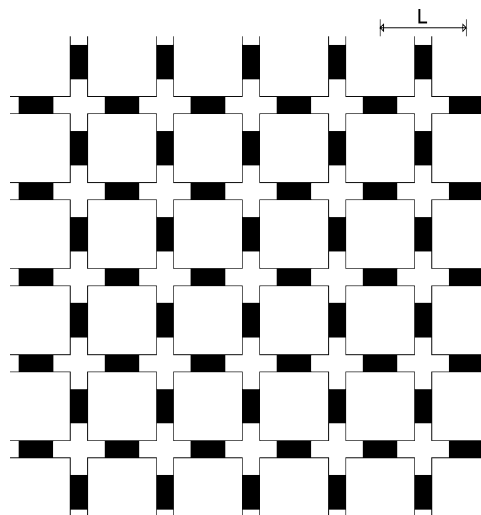


Fig. 2 Schematic of the adsorption sites in the channel segments.

than to the channel intersections renders memory corrections unnecessary.

Under the influence of the intracrystalline energetic profile of 1-butene, as considered here, the molecules are expected to relax in the channel segments rather than in the channel intersections. Whatever happens in the intersection will largely depend on the potential energy surface for the respective molecule. Furthermore, memory effects due to persistence of velocity or orientation occur during the passage of the intersection. For this reason a prediction of the actual probabilities of the four possibilities to proceed is very difficult. By contrast, we expect that molecules which do relax in the intersections, *i.e.* those which have to pass an energetic or entropic barrier to enter the channels, such as isobutane,²³ will very closely follow the model of⁷ without the necessity of any memory corrections.

In first order we assume that the possibilities 3 and 4 have equal probability. Due to the asymmetry between the two ends of the x -channel segments it is possible that differences occur. We checked this for the molecule presently under study, 1-butene, but found no significant differences in this case. This might be different, however, for other molecules. In the subsequent analytical treatment, the three coordinates of the random walker are considered separately.

First, diffusion in the x direction will be considered. It can be seen from Fig. 2 that in this random walk two step lengths $L = L_x = a/2$ and $L_x/2$ may occur. A random walk with equal step lengths is easier to handle as the self-diffusion coefficient D is simply

$$\langle x^2 \rangle = N_x L_x^2 = 2D_x t \quad (4)$$

where $\langle x^2 \rangle$ is the mean square displacement of the molecules after N_x steps of equal length L_x within a time t . For this reason it is preferable to unite sequences of displacements with lengths of $L_x/2$ which result in a step of $\pm L_x$. The number N_x of steps of length L_x is the sum of the number N_{xx} of direct steps between x -channel segments and sequences of steps from an x - to a y -channel and back from a y - to an x -channel (xy -steps) which are counted with the numbers N_{xy} and N_{yx} . Since within one trajectory the number of steps from x - to y -channel segments and, *vice versa*, from y - to x -channel segments can differ by 1 per molecule maximum, we have

$$N_{xy} \approx N_{yx}. \quad (5)$$

If a molecule makes a step from an x - to a y -channel segment (see Fig. 2), the probability to step back in x -direction (either into the original channel segment or a neighbouring one) is 1/2. This means a number of $(N_{xy} + N_{yx})/4$ steps contribute

to N_x so that in total

$$N_x = N_{xx} + \frac{1}{4}(N_{xy} + N_{yx}). \quad (6)$$

For the self-diffusion coefficient, with the eqns. (4) and (6), one finds

$$D_x = \frac{1}{2t} \left(\frac{a}{2} \right)^2 \left(N_{xx} + \frac{1}{4}(N_{xy} + N_{yx}) \right). \quad (7)$$

In an analogous way it follows for the y -direction

$$N_y = N_{yy} + \frac{1}{4}(N_{xy} + N_{yx}), \quad (8)$$

and

$$D_y = \frac{1}{2t} \left(\frac{b}{2} \right)^2 \left(N_{yy} + \frac{1}{4}(N_{xy} + N_{yx}) \right), \quad (9)$$

where N_{yy} is the number of steps between neighbouring segments of the y -channels.

Diffusion in z -direction only proceeds by xy -steps between x - and y -channels and *vice versa*. For a step of the length $L_z = c/2$ two xy -steps are needed. Let the starting point be the x -channel so that the first step ends in the y -channel. The y -channel segment is connected to two x -channel with components in $+z$ - and $-z$ -direction. Only one of these two possibilities is capable of completing the step sequence in z -direction so that $\Delta z = \pm c/2$. On the average, four xy -steps are needed to obtain $\Delta z = \pm c/2$ so that the number N_z of steps of length $c/2$ is

$$N_z = \frac{1}{4}(N_{xy} + N_{yx}), \quad (10)$$

and the self-diffusion coefficient in the z -direction is

$$D_z = \frac{1}{2t} \left(\frac{c}{2} \right)^2 \frac{1}{4}(N_{xy} + N_{yx}). \quad (11)$$

The memory parameter β may now be expressed by the numbers N_{xx} , N_{yy} , N_{xy} , and N_{yx} of displacements between channel segments. By inserting eqns. (7), (9), and (11) into eqn. (3) we obtain with eqn. (5)

$$\beta = \left(\frac{N_{xy}}{2N_{xx} + N_{xy}} + \frac{N_{yx}}{2N_{yy} + N_{yx}} \right)^{-1}. \quad (12)$$

This predicts that β has a minimum value of 0.5 for the case that the diffusion process is dominated by changes between the two types of channels so that N_{xx} and N_{yy} are negligible with respect to N_{xy} and N_{yx} .

3. Simulations and test of the model

We have tested the capabilities of our model by molecular dynamics simulations with 1-butene as a guest molecule in silicalite-1, the SiO_2 form of zeolite MFI without aluminium.

The zeolite was simulated by a flexible lattice according to the harmonic model of Demontis *et al.*^{24,25} Therein, harmonic potentials,

$$U(r_{ij}) = \frac{1}{2}k(r_{ij} - r_{0,ij})^2, \quad (13)$$

are assumed between two neighbouring atoms i and j . The model considers the T–O bonds with a force constant $k = 2.09 \times 10^5 \text{ kJ mol}^{-1} \text{ nm}^{-2}$, and the pairs of O-atoms bound to the same T-atom using a value of $k = 4.31 \times 10^4 \text{ kJ mol}^{-1} \text{ nm}^{-2}$. In order to preserve the equilibrium coordinates of the zeolite atoms in coincidence with the MFI crystal structure data, the equilibrium distances $r_{0,ij}$ were evaluated from the structure data. The zeolite coordinates and the equilibrium distances used in our calculations are accessible as supplementary information to this paper. The simulation box had the dimensions $4.014 \text{ nm} \times 3.984 \text{ nm} \times 5.368 \text{ nm}$ containing

$2 \times 2 \times 4$ unit-cells of silicalite-1. The simulations were performed with 16 molecules in the simulation box, this corresponds to an average loading of one molecule per unit-cell.

1-butene was represented in the united atom approximation with four interaction sites. The molecules are flexible with a potential for the dihedral angle ϕ ,

$$V_D(\phi) = V_0 + V_1 \cos \phi + V_2 \cos^2 \phi + V_3 \cos^3 \phi, \quad (14)$$

with $V_0 = 2.265 \text{ kJ mol}^{-1}$, $V_1 = 7.755 \text{ kJ mol}^{-1}$, $V_2 = 1.83 \text{ kJ mol}^{-1}$ and $V_3 = 9.38 \text{ kJ mol}^{-1}$ according to.²⁶ Furthermore, bending potentials of the form

$$V_B(\Theta) = \frac{k_\Theta}{2}(\Theta - \Theta_0)^2 \quad (15)$$

have been assumed where we chose the force constant to be $k_\Theta = 520 \text{ kJ mol}^{-1}$ as has been used for propane in ref. 27. The equilibrium angles are $\Theta_0 = 123.7^\circ$ for the angle between $\text{CH}_2=\text{CH}-\text{CH}_2$ and $\Theta_0 = 112.8^\circ$ for the angle between $\text{CH}-\text{CH}_2-\text{CH}_3$, respectively. A Morse potential

$$V_{C-C}(r) = D[1 - e^{-\beta(r-r_0)}]^2 \quad (16)$$

was used for the C–C bonds. According to the geometry of 1-butene we set $r_0 = 0.138 \text{ nm}$ for the C=C double bond, $r_0 = 0.152 \text{ nm}$ for the middle C–C bond and $r_0 = 0.154 \text{ nm}$ for the outer single C–C bond. The other parameters are $D = 83.9 \text{ kJ mol}^{-1}$ and $\beta = 18.4 \text{ nm}^{-1}$ as used for ethane in ref. 28. The guest–host interaction has been represented by the potential parameters listed in Table 1.

Fig. 3 shows the positions of the center of mass of the 1-butene molecules registered during the simulation after equal time intervals. This representation nicely visualises that the molecules are situated with a much larger probability in the channel segments than in the channel intersections. At a temperature of 300 K, a quantitative analysis yields values of $P_x \approx 0.5$ and $P_y \approx 0.4$ for the occupation probabilities of the x - and the y -channel, respectively. It is much more appropriate, therefore, to subdivide the trajectories into displacements between adjacent channel segments rather than between adjacent channel intersections, *i.e.* to follow the procedure suggested in this paper.

Table 2 compares the self-diffusion coefficients obtained by application of eqns. (7), (9), and (11), *i.e.* by multiplying the total number of relevant displacements between channel segments with the square of their separation ($D_{x(y,z)}^{(N)}$) with the data obtained from the time dependence of the mean square displacement as directly obtained from the molecular trajectories ($D_{x(y,z)}$). The good agreement between these data demonstrates that the chosen counting of displacements (*i.e.* considering displacements between the channel segments) in fact allows to consider subsequent displacements as to occur independently from each other. Thus, it turned out that the particle “memory” is negligibly small. By contrast, the memory parameter β (eqn. (3)) introduced with respect to a random walk between channel intersections and given also in Table 2, indicates substantial deviations from the “no-memory” case $\beta = 1$.

4. Conclusions

Following the scheme of ref. 7, in the present article molecular trajectories in crystalline nanoporous materials, in particular

Table 1 Lennard-Jones potential parameters for the guest–guest and guest–host interaction, bfc stands for “butene force center”.

Interaction	σ/nm	$\epsilon/\text{kJ mol}^{-1}$
bfc–bfc	0.378	0.866
bfc–O	0.317	1.180
bfc–Si	0.212	0.683

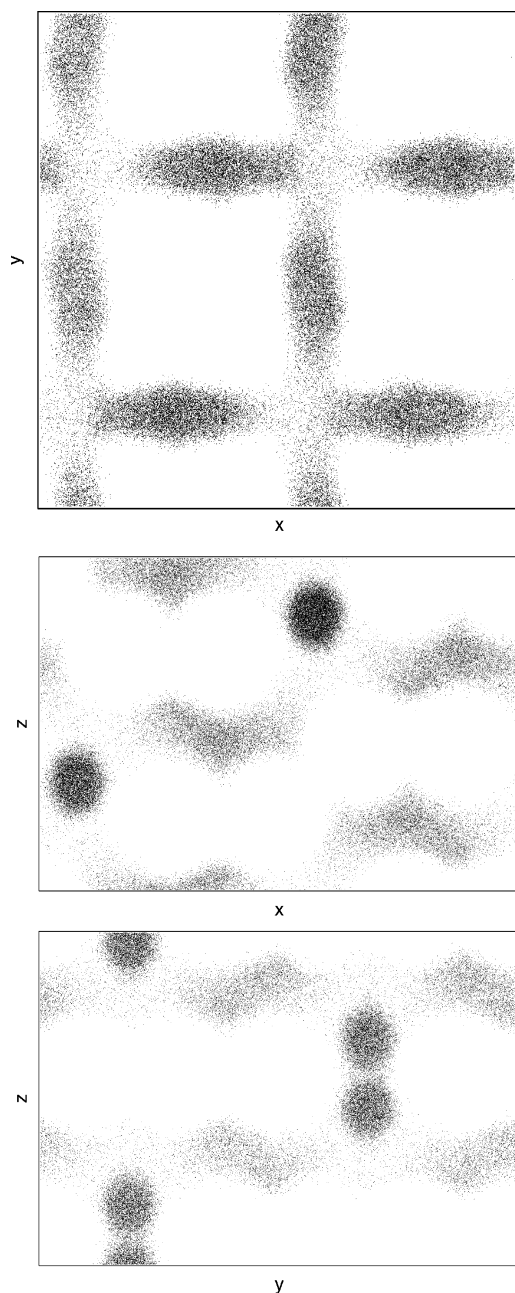


Fig. 3 Positions registered for the center of mass of the 1-butene molecules in the unit cell of silicalite-1 at $T = 300$ K in different projections.

MFI-type zeolites, have been considered to proceed as a sequence of displacements. In contrast to ref. 7, however, the subsequent displacements have been referred to adjacent channel segments rather than adjacent channel intersections. In many cases, including 1-butene as a guest molecule considered in the present study, by this choice molecular propagation may

Table 2 Self-diffusion coefficients (in $10^{-9} \text{ m}^2 \text{ s}^{-1}$) evaluated from the number of “steps” between channel segments, $D^{(N)}$, and from the mean square displacement, D , and the corresponding memory parameters β (eqn. (3)) and $\beta^{(N)}$ (eqn. (12)).

T/K	D_x	$D_x^{(N)}$	D_y	$D_y^{(N)}$	D_z	$D_z^{(N)}$	β	$\beta^{(N)}$
300	0.8	1.0	2.2	2.3	0.20	0.23	1.36	1.34
400	2.7	2.9	6.0	5.8	0.65	0.68	1.29	1.28
500	5.4	5.5	10.1	10.4	1.3	1.3	1.21	1.23
600	8.0	7.9	16.0	14.6	2.0	1.9	1.20	1.19

be much better represented as a sequence of mutually independent “steps” than by considering the individual displacements between adjacent channel intersections. There is no need anymore for including the correlation of subsequent displacements by introducing memory parameters.^{16–21} This simplification, however, doesn’t allow anymore the prediction of structure-related diffusion anisotropy, as the prevailing feature of the original model presented in ref. 7. It is still an open question up to which extent a combination of the two approaches will be able to maintain information about correlated diffusion anisotropy.

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References

- 1 C. Baerlocher, W. M. Meier and D. H. Olson, *Atlas of Zeolite Framework Types*, Elsevier, Amsterdam, fifth revised ed., 2001.
- 2 Eds. A. Galarneau, F. D. Renzo, F. Fajula and J. Védrine, *Proceedings of the 13th International Zeolite Conference, Montpellier*, Elsevier, 2001.
- 3 J. Kärger and D. M. Ruthven, *Diffusion in Zeolites and Other Microporous Solids*, Wiley, New York, 1992.
- 4 S. M. Auerbach, *Int. Rev. Phys. Chem.*, 2000, **19**, 155–198.
- 5 A. Schüring, S. M. Auerbach, S. Fritzsche and R. Haberlandt, *J. Chem. Phys.*, 2002, **116**, 10 890–10 894.
- 6 A. Schüring, PhD thesis, Universität Leipzig, 2003.
- 7 J. Kärger, *J. Phys. Chem.*, 1991, **95**, 5558–5560.
- 8 J. Caro, M. Noack, J. Richter-Mendau, F. Marlow, D. Peterson, M. Griepentrog and J. Kornatowski, *J. Phys. Chem.*, 1993, **97**, 13 685–13 690.
- 9 C. Weidenthaler, R. X. Fischer, R. D. Shannon and O. Medenbach, *J. Phys. Chem.*, 1994, **98**, 12 687–12 694.
- 10 E. R. Geus, J. C. Jansen and H. van Bekkum, *Zeolites*, 1994, **14**, 82–88.
- 11 S. Vasenkov, W. Böhlmann, P. Galvosas, O. Geier, H. Liu and J. Kärger, *J. Phys. Chem. B*, 2001, **105**, 5922–5927.
- 12 O. Geier, S. Vasenkov, E. Lehmann, J. Kärger, U. Schemmert, R. A. Rakoczy and J. Weitkamp, *J. Phys. Chem. B*, 2001, **105**, 10 217–10 222.
- 13 U. Hong, J. Kärger, R. Kramer, H. Pfeifer, G. Seiffert, U. Müller, K. K. Unger, H. B. Lück and T. Ito, *Zeolites*, 1991, **11**, 816–821.
- 14 U. Hong, J. Kärger, H. Pfeifer, U. Müller and K. K. Unger, *Z. Phys. Chem.*, 1991, **173**, 225–234.
- 15 E. J. Maginn, A. T. Bell and D. N. Theodorou, *J. Phys. Chem.*, 1996, **100**, 7155–7173.
- 16 J. Kärger, P. Demontis, G. B. Suffritti and A. Tilocca, *J. Chem. Phys.*, 1999, **110**, 1163–1172.
- 17 F. Jousse, S. M. Auerbach and D. P. Vercauteren, *J. Chem. Phys.*, 2000, **112**, 1531–1540.
- 18 P. Demontis, J. Kärger, G. B. Suffritti and A. Tilocca, *Phys. Chem. Chem. Phys.*, 2000, **2**, 1455–1463.
- 19 P. Demontis, G. B. Suffritti and A. Tilocca, *J. Chem. Phys.*, 2000, **113**, 7588–7592.
- 20 S. Fritzsche and J. Kärger, *J. Phys. Chem. B*, 2003, **107**, 3515–3521.
- 21 S. Fritzsche and J. Kärger, *Europhys. Lett.*, 2003, **63**, 465–471.
- 22 R. L. June, A. T. Bell and D. N. Theodorou, *J. Phys. Chem.*, 1992, **96**, 1051–1060.
- 23 T. J. H. Vlugt, C. Dellago and B. Smit, *J. Chem. Phys.*, 2000, **113**, 8791–8799.
- 24 P. Demontis, G. B. Suffritti, S. Quartieri, E. S. Foïs and A. Gamba, *Zeolites*, 1987, **7**, 522–527.
- 25 P. Demontis, G. B. Suffritti, S. Quartieri, E. S. Foïs and A. Gamba, *J. Phys. Chem.*, 1988, **92**, 867–871.
- 26 W. L. Jorgensen, J. D. Madura and C. J. Swenson, *J. Am. Chem. Soc.*, 1984, **106**, 6638–6646.
- 27 B. Smit, *J. Chem. Phys.*, 1995, **99**, 5597–5603.
- 28 P. Demontis, G. B. Suffritti and A. Tilocca, *J. Chem. Phys.*, 1996, **105**, 5586–5594.