

Testing the consistency of the Maxwell–Stefan formulation when predicting self-diffusion in zeolites with strong adsorption sites

Marc-Olivier Coppens¹ and Vijay Iyengar

Physical Chemistry and Molecular Thermodynamics, DelftChemTech, Delft University of Technology, Julianalaan 136, 2628BL Delft, The Netherlands

E-mail: M.O.Coppens@tnw.tudelft.nl

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Abstract

The Maxwell–Stefan (MS) formulation, as applied to zeolites that contain both weak and strong adsorption sites, such as ZSM-5, is compared to dynamic Monte Carlo simulations, for the limiting case of single-component self-diffusion. This study is intended as a consistency check, and as a step towards an analytical or semi-analytical theory for self-diffusion in zeolites with multiple types of sites. In its original form, when it is assumed that ζ , the ratio of the self-exchange coefficient to the corrected diffusivity, is equal to 1, the MS formulation performs well for silicalite, the all-Si version of ZSM-5. However, when there are lattice heterogeneities or the topology of the pore network differs from that of silicalite, it is necessary to assume $\zeta \neq 1$. Because ζ is generally occupancy dependent, the theory is unsuited as a fully predictive theory for self-diffusion in heterogeneous microporous solids, unless a theory for ζ is derived. However, since several studies have demonstrated that the MS formulation is able to predict multi-component diffusivities from single-component diffusivities for zeolites with one type of site, an extension to zeolites with multiple types of sites would be very valuable.

Notation

d	dimension of the system
D	self-diffusivity, $\text{m}^2 \text{s}^{-1}$
D_0	self-diffusivity close to $\theta = 0$, $\text{m}^2 \text{s}^{-1}$
\mathcal{D}_i	Maxwell–Stefan (corrected) diffusivity attributed to interaction of species i with the zeolite matrix, $\text{m}^2 \text{s}^{-1}$
\mathcal{D}_{ij}	Maxwell–Stefan cross-term attributed to intermolecular interactions between species i and j , $\text{m}^2 \text{s}^{-1}$
f	fraction of strong sites, $0 \leq f \leq 1$
\vec{r}	position vector, (m, \dots, m)
u	absolute fluid velocity, m s^{-1}
R	gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
T	absolute temperature, K
x_i	mole fraction of component i in adsorbed phase
t	time, s

Greek letters

θ	total molecular occupancy or loading
θ_i	molecular occupancy or loading of species i
θ_s, θ_w	occupancy on strong, resp. weak sites
$\theta_{\beta_s}, \theta_{\beta_w}$	occupancy on strong, resp. weak β sites
θ_α	occupancy on α sites
μ_i	molar chemical potential, J mol^{-1}
ζ	ratio of self-exchange coefficient to corrected diffusivity
τ_s, τ_w	average adsorption time on a strong, resp. weak site, s
Subscripts	
i, j	associated to species numbers
s	associated to strong sites
w	associated to weak sites
Superscripts	
MFT	prediction using mean-field theory

¹ Author to whom any correspondence should be addressed.

1. Introduction

Zeolites are widely used in processes such as separations, ion exchange and catalysis. Studying diffusion in zeolites is important, since it is the rate-limiting step in many of these processes. Due to the limitations of experimental studies [1], computational methods have been widely used to study diffusion in zeolites, including dynamic Monte Carlo simulations [2–5] molecular dynamics [6–8] and transition state theory [9–11]. Diffusion in zeolites is typically activated, with molecules hopping from site to site. Analytical theories have been proposed to estimate self-diffusivities in zeolites, including a mean field theory (MFT) proposed by us [3], and the application of Maxwell and Stefan’s theory for multi-component diffusion of fluids by Krishna and co-workers [12]. We will abbreviate the latter to the Maxwell–Stefan (MS) formulation for zeolites, with the understanding that it is a formal extension of a continuum theory to the highly confined environment of micropores in which molecules cannot pass each other. These theories may be predictive, once the single-component diffusivities at zero loading as well as information on the adsorption isotherm are known. The MS formulation has been used with reasonable success in the case of silicalite, which contains adsorption sites that are all of the same strength [13, 14]. Especially when single-component diffusivities are known, the MS approach predicts multi-component diffusivities remarkably accurately [15–17]. This adds to the interest of investigating whether the approach can be extended even further.

Most of the industrially used zeolites, e.g., ZSM-5, have ‘hetero’ atoms such as Al, in addition to Si and O atoms, so there are at least two different types of adsorption sites: strong and weak. In an earlier study [18], we have shown that in such zeolites the MS approach may be quantitatively or even qualitatively inaccurate in predicting binary self-diffusivities. Neither the MFT nor the MS theory accounts for the topology of the pore network, in particular for the low connectivity of the pores in many zeolites. The significance of such a topological effect has been illustrated before [2, 3].

Although the MS theory was developed to describe multi-component diffusion, one could argue that it should be consistent in its formulation of single-component self-diffusion as a special limiting case. In this work, we therefore test the MS theory for the case of single-component self-diffusion in ZSM-5 and compare it to a mean field approach we proposed earlier [3], as well as to data from dynamic Monte Carlo simulations performed on different lattice models.

Our study is limited to single-component self-diffusion, i.e., gradient-less diffusion, or the motion of tracer molecules surrounded by molecules of identical properties, as described by Einstein’s equation for Brownian motion:

$$D = \lim_{t \rightarrow \infty} \frac{\langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle}{2dt}, \quad (1)$$

where d is the dimension of the system, and $\vec{r}(t)$ the position of a molecule at time t . Since we do not explicitly include interatomic potentials, as in molecular dynamics (MD) studies, the theory is not intended as a predictive, *ab initio* theory. In particular, we restrict ourselves to diffusion on a lattice model of the pore space, and assume that the activation energy for

attempted hops of molecules from site to site is independent of the occupancy of neighbouring sites. This need not be the case, and the diffusion behaviour may be considerably affected by the degree of confinement, and all the various interactions [19, 20]. Nevertheless, we argue that in order for a (semi-)analytical theory to work in more complicated situations, it should at least agree for simple lattice models. Such models can also be extended to calculate the transport diffusivity of a component, which results from an imposed gradient in concentration or in chemical potential. One way to do this is via the adsorption isotherm and the calculation of the ‘corrected’ diffusivities. It is the latter that appear in the Maxwell–Stefan formulation.

2. Dynamic Monte Carlo simulations

Our simple simulation model of the zeolite pore network consists of a lattice in which the nodes are assumed to be sites where the diffusing molecules adsorb. Diffusion is activated and occurs by hops of molecules between neighbouring sites. Every site can be occupied by one molecule only, and every molecule occupies a single site.

Three different lattices are considered: the square lattice, the cubic lattice and the ZSM-5 lattice. ZSM-5 has two different types of pores: straight channels with an elliptical cross section, and a set of channels which intersect the straight pores at right angles and have a circular cross section. The unit cell used in the simulations is shown in figure 1; notice that this is the unit cell for the pore space, which is half as large as the unit cell of ZSM-5 itself [2]. In general, ZSM-5 contains both strong and weak adsorption sites. The sites present in the channels are called α sites, and are all assumed to be weakly adsorbing. The β sites are present at the intersections and may be either strongly or weakly adsorbing. The fraction of strong sites present in the lattice is denoted by f . Since silicalite and ZSM-5 share the same topology, $f = 0$ represents silicalite, while f is non-zero for ZSM-5. In case of the square and cubic lattices only β sites are present. In this study, it is assumed that the adsorption strengths on the weakly adsorbing α sites and the weak β sites are the same. It is also assumed that there is only one site per intersection. Both assumptions can easily be relaxed.

The attempted hopping times of the molecules (events) are chosen from an exponential distribution of residence times. The average residence time on a strong site is denoted as τ_s and that on a weak site τ_w . The self-diffusivity is calculated from Einstein’s equation. Details of the event-oriented, dynamic Monte Carlo method are discussed in [2, 3].

3. Analytical methods

3.1. Mean field theory (MFT)

A mean field theory [3] was introduced as a simple method to analytically estimate self-diffusivities. It assumes that the coverage of the diffusing molecules on sites of the same type is the same, and equal to the average occupancy, θ . The approach is based on calculations of the flows to and from the adsorption sites, and applying the principle of microscopic reversibility to flows between neighbouring sites. The diffusivity is predicted

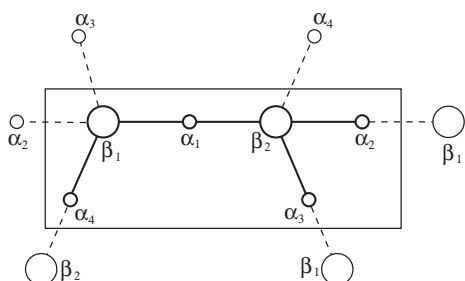


Figure 1. Lattice representation of ZSM-5 unit cell for the pore network. Each unit cell contains four α sites that are weakly adsorbing and two β sites that may be strong or weak.

as a function of the occupancy of the species (θ), the relative adsorption strengths on the sites (τ_s/τ_w) and the fraction of strong sites (f). The two main drawbacks of the MFT as a predictive theory are that the expression does not include any information on the topology of the system and also does not take into account the correlation effects present in the system. In reality, correlations arise due to the fact that a molecule hopping from one site to another has the tendency to return to the original site, since the probability of the previous site being vacant is higher than that of the other sites. Such correlations become more significant for low lattice connectivities. The mean field expression for a cubic lattice is given by [3]

$$\frac{D^{\text{MFT}}}{D_0} = \frac{\{1 + [(\tau_s/\tau_w) - 1]f\}(1 - \theta)^2}{f(1 - \theta_s)[(\tau_s/\tau_w) - 1] + (1 - \theta)}, \quad (2)$$

where θ_s is the occupancy of the molecules on a strong site and θ is the total occupancy on all sites, and

$$D_0 = \lim_{\theta \rightarrow 0} D(\theta). \quad (3)$$

The occupancy θ_s is calculated from the flow equations. The relation $\theta_s f + \theta_w(1 - f) = \theta$ follows from a simple mass balance, with θ_w the occupancy of the molecules on weak sites. Occupancies are real numbers between 0 and 1, with 1 corresponding to full occupancy of all sites of a given type.

In the case of the ZSM-5 lattice, the occupancies for the three types of adsorption sites are denoted by θ_α , θ_{β_w} and θ_{β_s} . The mean field expression in this case is more complex, and is given by

$$\frac{D^{\text{MFT}}}{D_0} = A \left(\frac{B}{C} \right), \quad (4)$$

where

$$A = \frac{f(\tau_s/\tau_w) + 2 - f}{2},$$

$$B = 2(1 - \theta_\alpha)[(1 - f)\theta_{\beta_w} + f\theta_{\beta_s}/(\tau_s/\tau_w)] + 4\theta_\alpha[(1 - f)(1 - \theta_{\beta_w}) + f(1 - \theta_{\beta_s})],$$

$$C = \frac{2(1 - \theta_\alpha)[(1 - f)\theta_{\beta_w} + f\theta_{\beta_s}/(\tau_s/\tau_w)]}{(1 - f)(1 - \theta_{\beta_w}) + f(1 - \theta_{\beta_s})} + \frac{4\theta_\alpha[(1 - f)(1 - \theta_{\beta_w}) + f(\tau_s/\tau_w)(1 - \theta_{\beta_s})]}{(1 - \theta_\alpha)}.$$

The consistency of the MFT was demonstrated in [3] by dynamic Monte Carlo simulations, with multiple sites, q , per intersection, showing that, in the limit of $q \rightarrow \infty$, the MFT is exact.

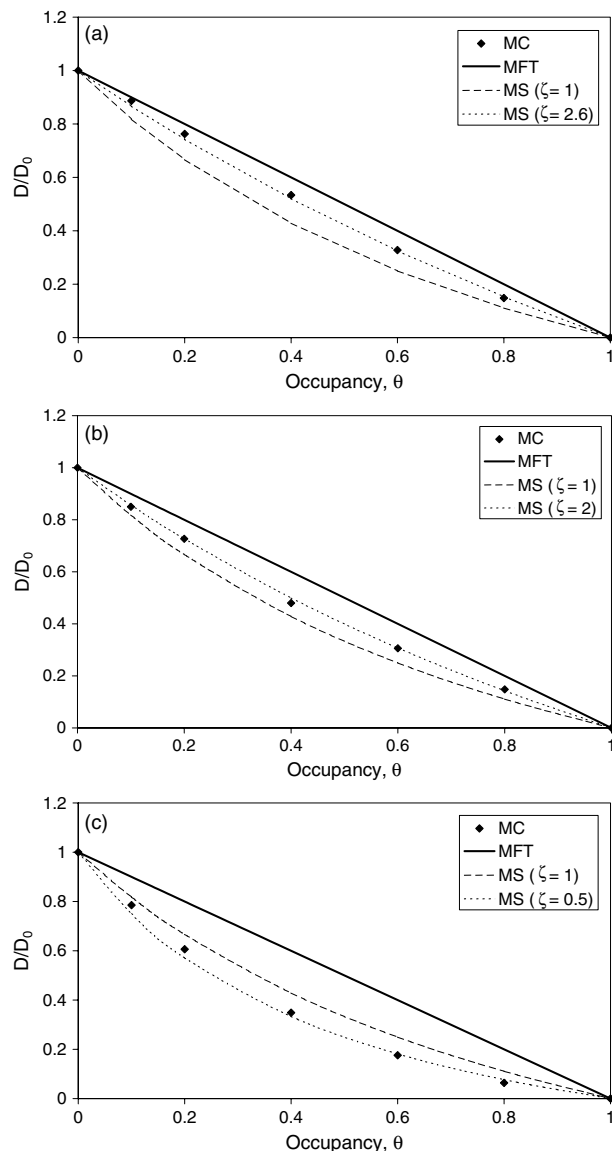


Figure 2. Normalized self-diffusivities for $f = 0$. Mean-field theory (line), MS ($\zeta = 1$) (dashed), dynamic Monte Carlo simulations (symbols): (a) Cubic lattice—MS ($\zeta = 2.6$) (dotted); (b) square lattice—MS ($\zeta = 2$) (dotted); (c) ZSM-5 lattice—MS ($\zeta = 0.5$) (dotted).

3.2. Maxwell–Stefan (MS) formulation

The MS formulation for zeolites was proposed by Krishna [15] as an intuitive extension of the continuum theory for multi-component diffusion of bulk fluid mixtures. The driving force for diffusion is the chemical potential gradient, $\nabla\mu$. This gradient is balanced by the friction between the diffusing species [15]. The force balance is given as

$$-\nabla_{T,p}\mu_i = \sum_j \frac{RT}{\mathcal{D}_{ij}} x_j (\mathbf{u}_i - \mathbf{u}_j). \quad (5)$$

The term (RT/\mathcal{D}_{ij}) is the friction coefficient between components i and j . x_j is the mole fraction of the species j , and \mathbf{u}_j is its velocity. Since the molecules also interact

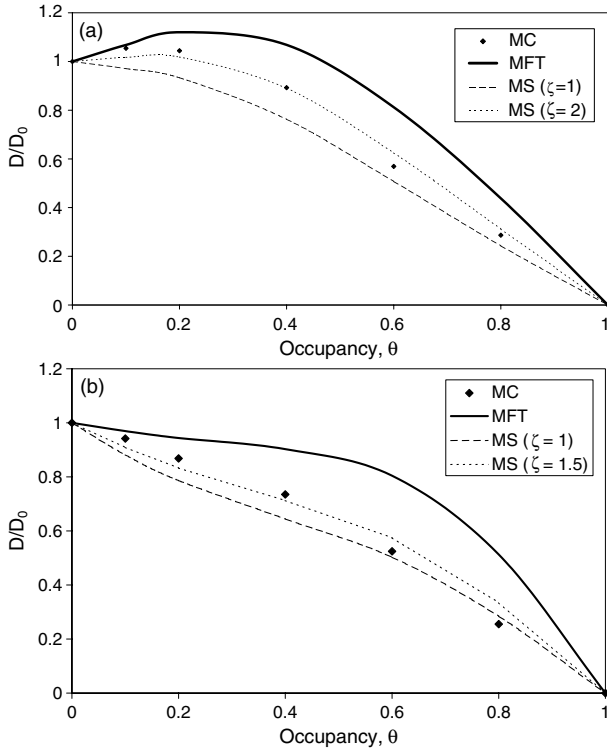


Figure 3. Normalized self-diffusivities on a cubic lattice. Mean-field theory (line), MS ($\zeta = 1$) (dashed), dynamic Monte Carlo simulations (symbols), $(\tau_s/\tau_w) = 10$: (a) $f = 0.2$ – MS ($\zeta = 2$) (dotted), (b) $f = 0.5$ – MS ($\zeta = 1.5$) (dotted).

with the zeolite matrix, the zeolite itself is also considered a ‘species’ in the above expression.

It has been shown [13, 14] that the Maxwell–Stefan theory works reasonably well for predicting multi-component diffusivities in silicalite. However, in the case of ZSM-5 we [18] have already given indications that the theory may break down in the presence of strong lattice heterogeneities and when correlations are present in the system. The MS formulation is based on the dusty gas model [21] for diffusion in porous media, which is adapted to describe activated diffusion in microporous materials. In the case of multi-component diffusion, the MS approach assumes that there are two types of diffusivities in the system:

- \mathcal{D}_i , also known as corrected diffusivity, present due to the interaction of the diffusing species i with the zeolite;
- \mathcal{D}_{ij} , due to intermolecular interactions between species i and j .

The self-diffusivity is then calculated by the expression

$$D_i = \left(\frac{1}{\mathcal{D}_i} + \sum_j \frac{\theta_j}{\mathcal{D}_{ij}} \right)^{-1} \quad (6)$$

where j is summed over all species including species i itself [15]. However, in the case of single component diffusion of a species (1), the expression reduces to

$$D \equiv D_1 = \left(\frac{1}{\mathcal{D}_1} + \frac{\theta_1}{\mathcal{D}_{11}} \right)^{-1}, \quad (7)$$

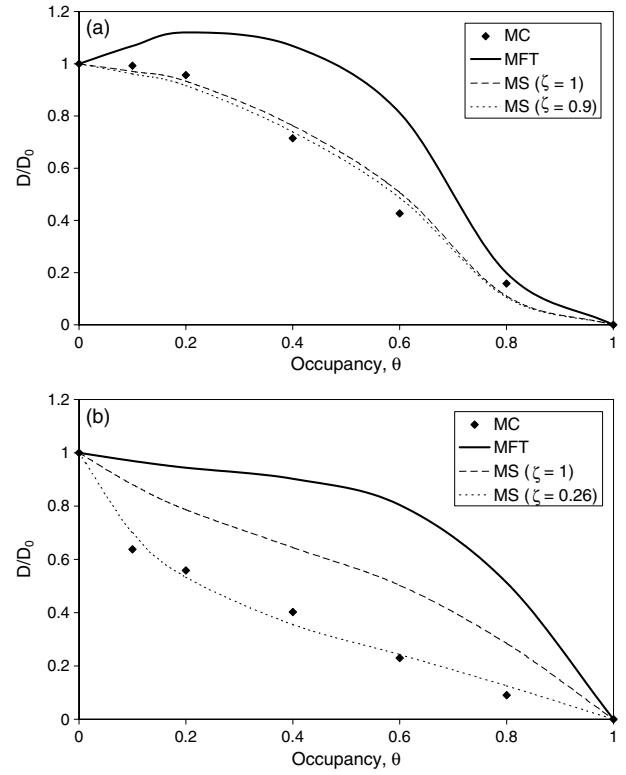


Figure 4. Normalized self-diffusivities on a square lattice. Mean-field theory (line), MS ($\zeta = 1$) (dashed), dynamic Monte Carlo simulations (symbols), $(\tau_s/\tau_w) = 10$: (a) $f = 0.2$ – MS ($\zeta = 0.9$) (dotted), (b) $f = 0.5$ – MS ($\zeta = 0.26$) (dotted).

which may serve as a definition for \mathcal{D}_{11} . The following relationship was proposed in the case of silicalite [15]:

$$\mathcal{D}_i = \mathcal{D}_i(0) \left(1 - \sum_j \theta_j \right) = \mathcal{D}_i(0)(1 - \theta). \quad (8)$$

It is well known [1] that, at very low loadings,

$$\mathcal{D}_i(0) = D_{0,i}. \quad (9)$$

All the zeolite–molecule interactions, as well as the lattice topology, are included in $D_{0,i}$. When molecule–molecule interactions are ignored, the occupancy dependence is given by a mean field approximation. This corresponds to a factor $(1 - \theta)$, representing a simple ‘crowding’ effect of the molecules.

To account for strong sites in zeolites such as ZSM-5 in a consistent way, the corrected diffusivities are modelled by a mean-field expression, just like for the case of one type of sites. The mean-field expression was derived in the previous section. Thus, we propose more generally:

$$\mathcal{D}_i = D_i^{\text{MFT}}. \quad (10)$$

It can be seen that for the case of $f = 0$, i.e. silicalite, the expression reduces to equation (8).

Until very recently, studies using this approach, such as [14], considered that the self-exchange coefficient \mathcal{D}_{11} be equal to \mathcal{D}_1 when calculating the self-diffusivities. However,

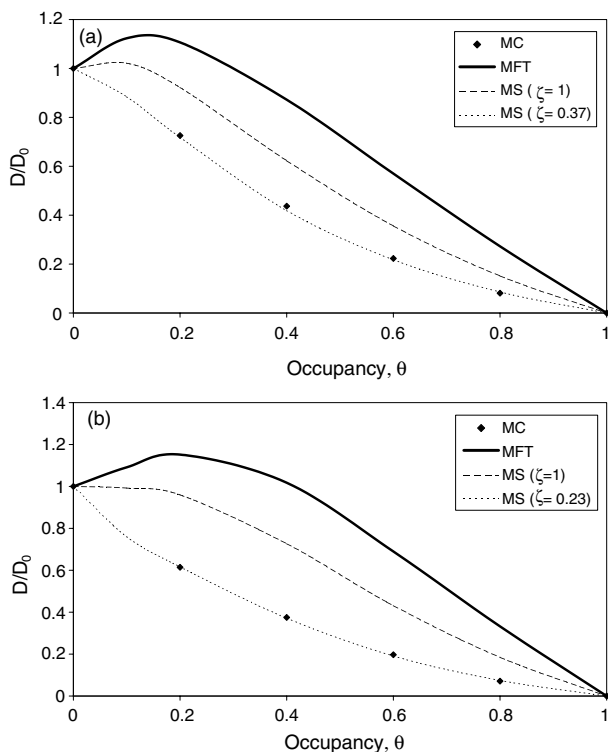


Figure 5. Normalized self-diffusivities on a ZSM-5 lattice. Mean-field theory (line), MS ($\zeta = 1$) (dashed), dynamic Monte Carlo simulations (symbols), $(\tau_s/\tau_w) = 10$: (a) $f = 0.2$ – MS ($\zeta = 0.37$) (dotted), (b) $f = 0.5$ – MS ($\zeta = 0.23$) (dotted).

most recent results [16, 17, 20] have suggested that this is not necessarily the case. For silicalite, the ratio

$$\zeta = \frac{\mathcal{D}_{11}}{\mathcal{D}_1} \quad (11)$$

was shown to be a function that depends on occupancy, θ [16, 20]. When $\zeta \rightarrow \infty$, there is no friction between the diffusing molecules ($RT/\mathcal{D}_{11} \rightarrow 0$), which corresponds to the mean-field theory. Here, we check the validity of the MS approach for the cases $\zeta = 1$ and $\zeta \neq 1$, as well as $\zeta \rightarrow \infty$ (MFT) for the square, cubic and ZSM-5 lattices. Since we consider a single component system, from now on we use the notation $D = D_1$ and $\theta = \theta_1$.

4. Results and discussion

Figure 2 compares single component, dynamic Monte Carlo simulations with MFT and MS predictions in a cubic (a), square (b) and ZSM-5 lattice (c) respectively, in the case of one type of adsorption site ($f = 0$). The results are normalized with respect to the diffusivities D_0 at very low occupancy ($\theta \rightarrow 0$). For $f = 0$, the MS expression for self-diffusivity, equation (7), reduces to

$$D = \frac{\mathcal{D}_1}{1 + (\theta/\zeta)} = D_0 \frac{(1 - \theta)}{(1 + \theta/\zeta)}, \quad (12)$$

where equation (1) was used. A value for ζ can be chosen in such a way that an excellent fit is obtained: $\zeta = 2.6$

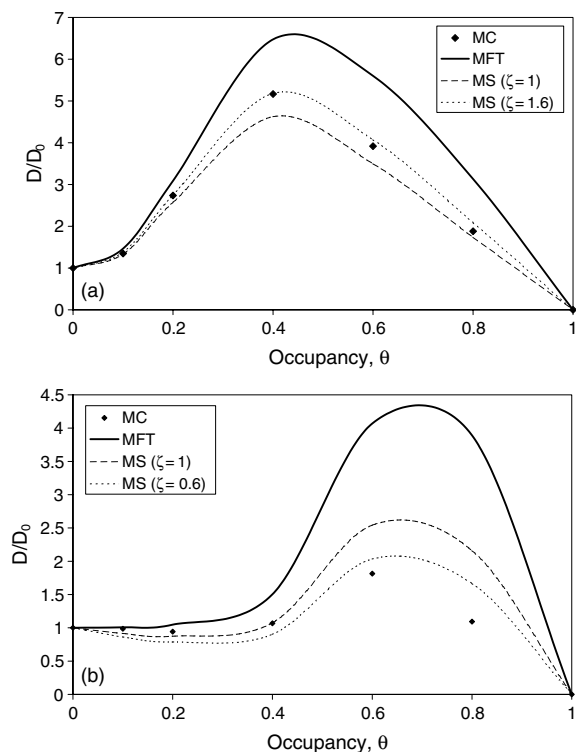


Figure 6. Normalized self-diffusivities on a cubic lattice. Mean-field theory (line), MS ($\zeta = 1$) (dashed), dynamic Monte Carlo simulations (symbols), $(\tau_s/\tau_w) = 100$: (a) $f = 0.2$ – MS ($\zeta = 1.6$) (dotted), (b) $f = 0.5$ – MS ($\zeta = 0.6$) (dotted).

for a cubic lattice, $\zeta = 2$ for a square lattice and $\zeta = 0.5$ for silicalite. Note that, without additional theory for ζ , this fit is merely a lucky coincidence, because topological effects have not been explicitly included in the MS theory. Using the original assumption that $\zeta = 1$, the prediction is qualitatively good, but is the same for all lattices, despite the difference in topology.

Figure 3 shows similar comparisons for $f = 0.2$ (a) and $f = 0.5$ (b) values and for $\tau_s/\tau_w = 10$ in the case of a cubic lattice. Corresponding results for the square and ZSM-5 lattices are shown in figures 4 and 5 respectively. Changing the relative adsorption strength has an effect on the diffusivities, as shown in figures 6 and 7 respectively for the cubic and ZSM-5 lattices for the case where $\tau_s/\tau_w = 100$. As shown previously [3], the deviations from MFT are due to the correlations that are induced in the system because of the lattice heterogeneities. The MS ($\zeta = 1$) and MFT predictions for a cubic and square lattice again coincide since the theories are topology independent. Via a non-trivial ζ , a very good fit is obtained for the cubic lattice and ZSM-5, in particular for $\tau_s/\tau_w = 10$. Also for a square lattice, a non-trivial ζ leads to quite a good fit. The importance of correlations can be clearly seen ($\zeta \ll \infty$). There is a trend in the values of ζ as a function of τ_s/τ_w . Correlations appear stronger in the order: cubic lattice, square lattice, ZSM-5 (decreasing ζ). It is to be noted that the lattice connectivities decrease in the same order: cubic ($Z = 6$), square ($Z = 4$) and ZSM-5 (average $Z = 8/3$). For $\tau_s/\tau_w = 100$, i.e., a significant difference in adsorption strengths between weak and strong sites, the MS theory with a

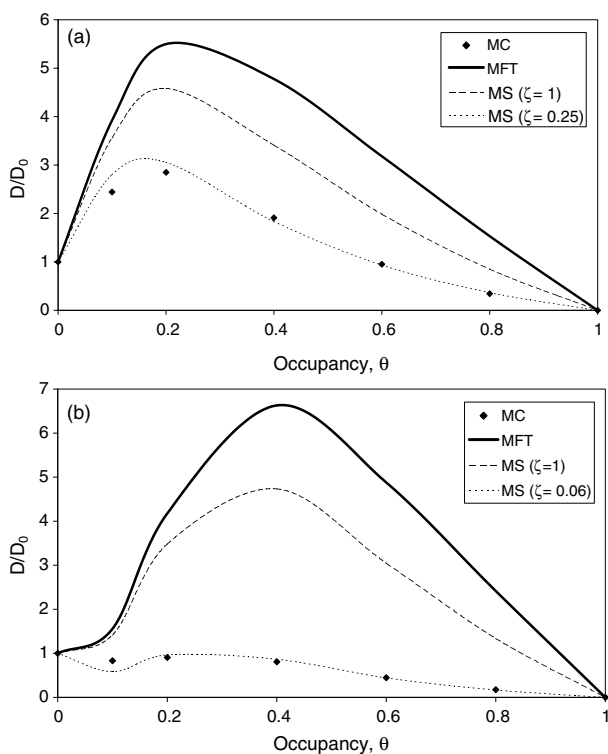


Figure 7. Normalized self-diffusivities on a ZSM-5 lattice. Mean-field theory (line), MS ($\zeta = 1$) (dashed), dynamic Monte Carlo simulations (symbols), $(\tau_s/\tau_w) = 100$: (a) $f = 0.2$ – MS ($\zeta = 0.25$) (dotted), (b) $f = 0.5$ – MS ($\zeta = 0.06$) (dotted).

non-trivial, optimal ζ fits the dynamic MC data very well for $f = 0.2$ and rather well for $f = 0.5$. Note that in these cases even the MFT ($\zeta \rightarrow \infty$) gives a qualitatively good picture of the self-diffusivity for cubic lattices, which have a relatively high connectivity ($Z = 6$). For ZSM-5, with $\tau_s/\tau_w = 100$, the fits are less good. For $f = 0.5$ a rather good fit can be obtained with $\zeta = 0.06$ (implying strong correlations), for high values of θ . This good fit is a result of a quasi-linear dependence of D on θ at high occupancies ($\theta \geq 0.4$), where most strong sites are occupied ($f = 0.5$). At lower f values no good fit for any ζ can be obtained as shown in figure 7. The MS results mostly follow the MFT prediction, which is quantitatively inaccurate at low θ . Figure 8 shows ζ as a function of f for ‘best fits’ for $\tau_s/\tau_w = 10$ and 100 for the ZSM-5 lattice. Optimal ζ -values are lower for $\tau_s/\tau_w = 100$ and for intermediate values of f , as a result of strong correlations. A similar figure emerges for the cubic lattice, although the values of ζ are higher in this case, because of the higher lattice connectivity.

Until now, we have assumed ζ to be independent of θ , so as to not introduce even more parameters. Skoulidas *et al* [16] and Chempath *et al* [17], however, showed that in the case of silicalite or faujasite, ζ is actually a function of occupancy θ . In the case of ZSM-5, ζ can be seen to change widely with τ_s/τ_w and f (figure 8). In general, ζ is dependent on lattice heterogeneity, occupancy, the fraction of strong sites, and the relative adsorption strengths. While it is true that dynamic Monte Carlo simulations do not capture the chemical specifics, any theory should at least be consistent with these lattice simulations, which contain fewer parameters than full

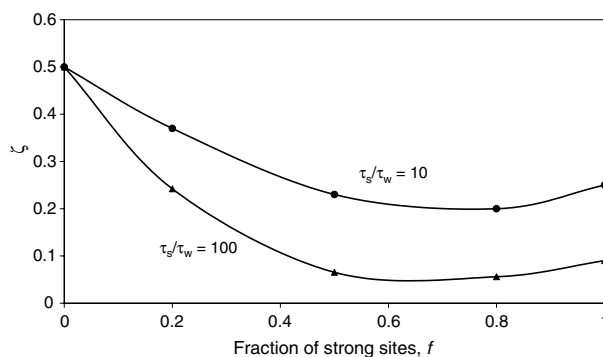


Figure 8. Best fits of ζ as a function of f for the ZSM-5 lattice for $(\tau_s/\tau_w) = 10$, $(\tau_s/\tau_w) = 100$.

MD simulations. This becomes even clearer when we consider heterogeneous lattices with $f > 0$. Here, we have considered only basic parameters such as topology and the presence of strong adsorption sites. It is seen that the MS formulation, as adapted to zeolites, may need additional input to be consistent for single-component diffusion (see, for example, figure 7). If there are deviations for the lattice model, it means that there are more parameters to be considered, in which case all these would have to be accounted for by the single function ζ . Unless ζ is predictably dependent on all parameters and is only weakly dependent on θ , which does not seem to be the case for the ZSM-5 lattice, the MS formulation cannot be trivially extended to zeolites, without explicit knowledge of \mathcal{D}_{ii} . On the other hand, this does not rule out that the theory may be applied to multi-component mixtures, when single-component parameters are determined by simulation. There is still a need to derive a theoretical expression for ζ , as this parameter is now empirically determined. Another possibility is to use different ways to calculate self-diffusivities, for example, based on correlation functions.

5. Conclusion

Several studies demonstrate the success of the Maxwell–Stefan formulation in predicting multi-component diffusivities from single-component values [14–17]. In our study, we addressed the limiting case of single-component self-diffusion, which corresponds to the diffusion of a tracer in the zeolite, amongst molecules of an indistinguishable species. The zeolite pore space was represented by a lattice model. Unlike molecular dynamics studies, dynamic Monte Carlo simulations using a lattice model are not predictive for diffusion in zeolites, but they allow us to investigate some of the most essential ingredients of the diffusion behaviour. Only self-diffusion was considered here, but lattice models are equally useful to simulate corrected and transport diffusion.

Our study was aimed at investigating the self-consistency of the Maxwell–Stefan formulation, as applied to zeolites [12]. Results based on the Maxwell–Stefan formulation were compared to dynamic Monte Carlo simulations of self-diffusion on heterogeneous cubic, square and ZSM-5 lattices, with both strong and weak adsorption sites. This distribution of adsorption sites introduces heterogeneities that are important in many applications but are typically not included in studies

of diffusion in zeolites. Lattice models are particularly useful to investigate such effects. It was seen that the ratio of the self-exchange coefficient to the corrected diffusivity, ζ , plays an important role in the MS expression. Confirming and extending earlier studies [16, 17, 20], the MS formulation should involve a factor $\zeta \neq 1$, to include lattice heterogeneities. Different values of ζ yield better agreement with the dynamic Monte Carlo results, but there is as yet no coherent theory behind the dependence of ζ on occupancy, connectivity and the heterogeneity due to the different adsorption sites.

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