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Monte Carlo Simulations of Diffusion in Zeolites and Comparison with the Generalized Maxwell–Stefan Theory

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Diffusion in zeolites is studied by means of Monte Carlo methods and the generalized Maxwell–Stefan theory of irreversible thermodynamics. The influence of the surface occupancy, the surface structure, and the surface chemical potential on one- and multicomponent surface diffusion has been investigated. Mass transfer has been simulated in one- and two-dimensional zeolitic channel structures. For the description of the sorption process two different models have been applied, a Langmuir model and a model with repulsive interactions between sorbed molecules. The one-component Fick diffusion coefficient, in the case of the Langmuir adsorption model, is found to be independent of the surface occupancy and depends weakly on the dimension of the lattice. Tracer diffusion on a one-dimensional lattice shows a linear dependence between the mean square displacement of labelled molecules and the square root of time. The mean square displacement in the case of tracer diffusion on the two-dimensional lattice follows the Einstein relation. The uptake behaviour of binary mixtures, co- and counter-diffusion, on the two-dimensional lattice as obtained from the Monte Carlo simulations is in agreement with a single-file diffusion model. The single-file diffusion matrix can be considered as a limiting case of the generalized Maxwell–Stefan formulation. The results of the Monte Carlo simulations and the single-file diffusion model show that the zeolitic structure has an influence on mass transfer rates in tracer flow and counterdiffusion. The coupling between surface fluxes present in the case of the transient uptake of a multicomponent mixture is demonstrated. © 1992 Academic Press, Inc.

INTRODUCTION

Diffusion in molecular sieves can be modelled as a sequence of elementary events. Molecules are localized on adsorption sites and mass transfer takes place by molecules jumping between nearest-neighbour sites [see Riekert (*1*) and Ruthven (*2*)]. Several previous workers have used a discrete surface diffusion model for the description of mass transfer in (micro-) porous media, both theoretical and computational. Reed and Ehrlich (*3, 4*) studied one-component surface diffusion for different chemical potentials by means of a lattice-gas model and Monte Carlo methods. Using the quasi-chemical approximation the influence of interactions between adsorbed nearest neighbour molecules on the jump rate is investigated. Sundaresan and co-workers (*5, 6*) and Theodorou and Wei (*7*) have used a lattice-gas model to study diffusion and reaction in zeolite crystals. Zhdanov (*8–10*) derived general relations for the description of surface diffusion in the framework of the lattice-gas model, for one- and two-component sorption. Lee and O'Connell (*11, 12*) developed a nonequilibrium statistical mechanical description for adsorption and surface diffusion on homogeneous surfaces. A stochastic model based on the Markov process formulation has also been proposed [see Patwardhan (*13*) and Tsikoyiannis and Wei (*14*)]. In the Markov process formulation every state is associated with a distribution function which gives the probability of occurrence of the next event. Tsikoyiannis and Wei (*14*) also used Monte Carlo simula-

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tions to study tracer and binary diffusion in channel-type structures with different lattice dimensions.

Using Monte Carlo methods one- and two-component mass transfer in zeolites has been studied by a random-walk approach for different surface structures. Palekar and Rajadhyaksha (*15, 16*) applied this method to study one-component uptake and binary diffusion in two different zeolitic pore structures, a pore open at one end and a pore open at both ends. Pitale and Rajadhyaksha (*17*) simulated tracer diffusion in a one-dimensional channel structure as well as in a cage-type structure. Emig and co-workers (*18, 19*) determined, from Monte Carlo simulations of mass transfer in a two-dimensional zeolite grid, one-component, tracer, and binary diffusion coefficients as a function of the occupancy for cage-type structures.

The Monte Carlo simulations can provide new insights into multicomponent surface diffusion phenomena, especially the dependence of the mass transfer rates on the surface occupancy and the dimension of the lattice. A number of workers have found, using Monte Carlo simulations based on the single-file diffusion approach, a non-Fickian behaviour in the case of tracer diffusion in a one-dimensional pore structure (*7, 17*).

A possible method to study multicomponent surface diffusion is by means of a single-file diffusion model. The single-file diffusion model uses the zero-coverage diffusion coefficients and is applicable to channel-type structures where molecules are not able to pass one another. Quereshi and Wei (*20, 21*) performed counter- and co-diffusion experiments of benzene and toluene in ZSM-5 to examine the effects of the amount adsorbed of the two components on the diffusion coefficients. The results are in good agreement with a theoretical single-file model.

In the present work, one- and multicomponent surface diffusion are studied by Monte Carlo methods and the generalized Maxwell–Stefan (GMS) theory of irreversible thermodynamics, cf. Krishna (*22*). Our main objective is to verify the applicability of a surface diffusion model, in terms of the Maxwell–Stefan equations, for the description of diffusion in micropores.

An important contribution to mass transfer in molecular sieve materials, e.g., zeolites, is governed by surface or micropore diffusion. Diffusion in micropores is an activated process and can be modelled as adsorbed molecules performing random jumps between potential energy minima, represented by fixed sites. Modelling of multicomponent mass transfer in zeolites is important for catalysis and for separation applications. Diffusion affects conversion and selectivity and the successful operation of molecular sieves in separation processes is based on a difference in diffusion coefficients.

A number of sorption and diffusion processes in zeolitic channel structures have been simulated to gain more insight into multicomponent mass transfer in the configurational regime. In practice, a random walk method has been used to simulate one- and multicomponent diffusion. The simulations have been performed in one- and two-dimensional surface structures, with respectively two and four nearest-neighbour sites. In the following, the two surface structures are referred to as pore and square lattice. The influence of the thermodynamics of the adsorbed phase has been studied by using two different adsorption models, namely the Langmuir model, characterized by the absence of interactions between the adsorbed molecules, and a model of localized adsorption with a repulsive interaction between adsorbed nearest-neighbour molecules.

The Monte Carlo simulations can be divided into three parts:

First, to investigate the influence of the amount adsorbed on surface diffusion, one-component uptake experiments and tracer flow have been simulated for both the pore and the square lattice structure and with the two different adsorption models.

Second, the effect of the direction of mass transfer on the rates of adsorption and desorption has been investigated for counterdiffusion of a binary mixture on the square lattice.

Third, the coupling effects between different mixture components have been studied in the case of transient uptake of a binary and a ternary mixture on the square lattice.

Furthermore, the results obtained from these simulations are compared with the GMS theory for multicomponent surface diffusion. Elements of the discrete surface diffusion model can be incorporated into the continuum GMS theory through the GMS or intrinsic diffusion coefficients. The multicomponent uptake profiles produced by the Monte Carlo simulations can be explained by a single-file diffusion model and the linearized theory of multicomponent mass transfer (*23*), using discrete GMS diffusion coefficients. As will be shown, the single-file diffusion model can be regarded as a limiting case of the GMS theory.

METHOD

Generalized Maxwell–Stefan (GMS) Theory for Multicomponent Surface Diffusion

In a multicomponent adsorbed phase the transport properties of one component are affected by the presence of the other components. The driving force, the gradient in the chemical potential, is a function of the total amount adsorbed. The relations for the description of mass transfer are coupled through the multicomponent equilibrium isotherm [see Ruthven (*2*) and Marutovsky and Bülow (*24*)].

Using the idea of adsorbed molecules moving between vacant sites, a description of multicomponent surface diffusion based on the generalized Maxwell–Stefan theory of irreversible thermodynamics has been given by Krishna (*22*). In this theory the vacant sites (V) on the surface are viewed as the (n + 1)th component in the mixture. The GMS formulation uses a friction model for the description of multicomponent mass transfer, based on the information of the transfer rates of individual components.

The GMS theory provides the following relation for the Fick diffusion coefficient matrix, which in general is nondiagonal indicating the coupling between the different mixture components

$$[D] = [B]^{-1}[\Gamma] \tag{1}$$

with the matrix of GMS diffusion coefficients

$$\begin{aligned} B_{ii} &= \frac{\theta_i}{\text{Đ}_{iV}} + \sum_{j=1}^{n+1} \frac{\theta_j}{\text{Đ}_{ij}} \\ B_{ij} &= -\theta_i\left(\frac{1}{\text{Đ}_{ij}} - \frac{1}{\text{Đ}_{iV}}\right) \end{aligned} \tag{2}$$

and the matrix of thermodynamic factors

$$\Gamma_{ij} = \theta_i \frac{\partial \ln(f_i)}{\partial \theta_j} \tag{3}$$

with f_i the fugacity of component i in the bulk phase, determining the surface chemical potential

$$\mu_i = \mu^0 + R_g T \ln(f_i). \tag{4}$$

These relations are the basis of the continuum GMS theory and with this result the different diffusion processes can be described.

Single-File Diffusion

The connection between the Monte Carlo simulations of surface diffusion, in channel-type zeolites, and the GMS formulation is made through the single-file diffusion approach. In the applied Monte Carlo method and surface structures considered molecules are likely to move in a single-file. The simulated diffusion processes correspond to mass transfer in channel-type zeolites, for example mordenite and silicalite, where sorbed molecules are not able to pass one another.

Based on a lattice-gas model a number of previous workers have described surface diffusion phenomena, making use of the quasi-chemical approximation to determine the surface chemical potential.

One-component diffusion. For one-component surface diffusion Reed and Ehrlich (*3*) and Zhdanov (*9*) have derived the following expression for the Fick diffusion coefficient, by taking the chemical potential the driving force for mass transfer

$$D_{1V}(\theta) = \frac{z}{4}\lambda^2\nu(\theta)\frac{\partial(\mu/R_gT)}{\partial \ln \theta}, \tag{5}$$

with λ a constant displacement, the distance between two adjacent sites, and ν the jump frequency of the sorbed molecules. In terms of the GMS formulation this reads for the one-component diffusion coefficient

$$D_{1V}(\theta_1) = \text{Đ}_{1V}(\theta_1)\Gamma, \tag{6}$$

with the discrete GMS diffusion coefficient given by

$$\text{Đ}_{1V}(\theta_1) = \frac{z}{4}\lambda^2\nu_1(\theta_1). \tag{7}$$

As a result of the dependence of the jump frequency on the surface occupancy, the thermodynamics of the adsorbed phase has an influence on the surface migration. In the case of Langmuir adsorption the jump frequency at an arbitrary occupancy can be written in terms of the jump frequency for one molecule on an empty lattice. The GMS diffusion coefficient then becomes

$$\begin{aligned}\text{Đ}_{1V}(\theta_1) &= \frac{z}{4}\lambda^2\nu_1(0)(1-\theta_1)\\ &= \text{Đ}_{1V}(0)\theta_V\end{aligned} \tag{8}$$

Two important extensions can be made; first, inclusion of interactions between adsorbed species, and second the description of multicomponent adsorbed species.

To include interactions between adsorbed mixture components the chemical potential must be modified; to indicate deviations from the Langmuir model we write

$$\mu_i = \mu^0 + R_gT\mu_{i,\mathrm{L}} + R_gT\mu_{i,\mathrm{I}}, \tag{9}$$

with L and I denoting the contribution from the Langmuir model and the interactions, respectively.

The Fick diffusion coefficient then reads

$$D_{1V}(\theta_1) = \frac{z}{4}\lambda^2\nu_1(\theta_1)\left(\frac{1}{1-\theta_1} + \frac{\partial(\mu_{1,\mathrm{I}}/R_gT)}{\partial \ln \theta_1}\right), \tag{10}$$

which is identical to Eq. (6), with a modified thermodynamic factor. For the Monte Carlo simulations the thermodynamic factor can be determined with Eq. (3).

In Eq. (10) the jump rate $\nu(\theta)$ is also affected by the interactions. The influence of the interactions between molecules adsorbed on nearest-neighbour sites on the jump rate and the chemical potential can be evaluated by use of the quasi-chemical approximation [see, for example, Reed and Ehrlich (*3*)].

Multicomponent diffusion. The description of multicomponent surface diffusion in the single-file diffusion approach is based on the zero-coverage diffusion coefficients [see, for example, Sundaresan and Hall (*6*), Zhdanov (*10*), and Qureshi and Wei (*20*)]. Starting with different models the same expression for the binary Fick diffusion coefficient matrix, Eq. (11), has been derived.

For a ternary system with Langmuir adsorption the Fick diffusion coefficient matrix, in the single-file diffusion model, is given by

$$[D] = \begin{pmatrix} \text{Đ}_{1V}(0) & 0 \\ 0 & \text{Đ}_{2V}(0) \end{pmatrix} \begin{pmatrix} 1-\theta_2 & \theta_1 \\ \theta_2 & 1-\theta_1 \end{pmatrix} \tag{11}$$

Extension to a system with an arbitrary number of components ($n > 3$) is straightforward. This result will be used to compare the results obtained from the Monte Carlo simulations of multicomponent mass transfer in channel-type zeolites with theory.

The Fick diffusion matrix in the case of the single-file diffusion model can also be derived from the GMS theory. From Eq. (1) it follows that the Fick diffusivity is a combination of Maxwell–Stefan diffusivities and thermodynamic effects. The Maxwell–Stefan diffusion coefficient has the meaning of an inverse drag coefficient. Comparing Eq. (1) for the Fick diffusion coefficient, with the dependence of the GMS diffusion coefficients on the surface occupancy given by Eq. (2), with Eq. (11) it follows that the single-file diffusion model uses only zero-coverage diffusivities of the individual components, represented by $Đ_{iV}$. The dependence of the one-component diffusivities on the surface occupancy and the contribution of the counter-exchange coefficient, $Đ_{ij}$, are not taken into account in the single-file diffusion model. Equation (11), for the Fick diffusion coefficient matrix, follows from the GMS equations by taking $\theta_i \rightarrow 0$ $(i \neq V)$; this means that $\theta_V \rightarrow 1$, in Eq. (2) and use of Eq. (8). As a consequence the counter-exchange coefficient $Đ_{12}$ drops out of the equations. We see that the dependence of the one-component GMS diffusion coefficients on the surface occupancies cancels against a part of the thermodynamic effects. In other words if we take the B matrix, Eq. (2), independently of the surface occupancy of the adsorbed components, a single-file diffusion model is obtained. In the single-file diffusion model the mixture components exert no or very little drag on one another, due to the pore size, and the Fick diffusion coefficient matrix is independent of the vacancy θ_V.

Equation (11) is the single-file diffusion matrix as presented by Qureshi and Wei (cf. Eq. (6) of Ref. (*21*)). However, no information is given about this choice of the diffusion coefficient matrix in relation to the type of zeolite.

Tracer diffusion. A special case of binary diffusion is given by tracer diffusion. Applying the single-file diffusion model to tracer diffusion the following relation, in the case of Langmuir adsorption, is obtained

$$\begin{aligned} D^* &= D_{11} - D_{12} \\ &= Đ_{1V}(\theta) \end{aligned} \tag{12}$$

with the use of relation (8). In the single-file diffusion model with Langmuir adsorption the tracer diffusion coefficient decreases linearly with increasing surface occupancy. This has been derived before by Riekert (*1*). For the general case this can be extended by use of equation (10).

Monte Carlo Method

Using Monte Carlo simulations sorption and diffusion phenomena in microporous media, representing zeolitic channel structures, have been studied. The simulations have been performed for two different surface structures and two different adsorption models.

The surface structures used are a one-dimensional pore structure and a two-dimensional square lattice. The adsorption sites are uniformly distributed and in the case of the lattice placed at the channel intersections, forming an energetically homogeneous surface with respectively two and four nearest-neighbour sites. The bulk phase is represented in the same way by localized sites, which can be considered as an extension of the lattice. Adsorption from the bulk phase takes place only at the sites at the boundaries of the surface. For the square lattice the approach has been used that for a number of zeolites the most stable sites are localized at the channel intersections.

To investigate the influence of thermodynamics on surface diffusion two different models have been used for the description of the adsorption processes. The rates of adsorption and desorption can be expressed in terms of probabilities in the following way:

Model 1:	rate of adsorption	$1 - \theta_1$
	rate of desorption	θ_1.
Model 2:	rate of adsorption	$1 - \theta_1^z$
	rate of desorption	θ_1.

The probability of a site being occupied is given by the fractional surface occupancy θ_1.

The first model corresponds to the Langmuir adsorption model. The probability of finding one empty nearest-neighbour site, which is equal to the probability of performing a jump, is given by the vacancy, $1 - \theta_1$.

The second model states that an activated molecule will always perform a jump unless all the nearest-neighbour sites are occupied. The probability for an activated molecule to have at least one empty nearest-neighbour site depends in this model on the lattice coordinate number z and is equal to $1 - \theta_1^z$, with z equal to 2 or 4 corresponding to the pore and the square lattice structure, respectively. The second model corresponds to a model of localized adsorption with repulsive interaction. The movement of an activated molecule is always in a direction away from the occupied sites. For this model also an interaction parameter, ε, must be taken into account. The interaction parameter vanishes in the case of Langmuir adsorption.

The chemical potential for the Langmuir adsorption model can, for one-component sorption, be written as

$$\frac{\mu_1}{R_g T} = \frac{\mu^0}{R_g T} + \ln\left(\frac{\theta_1}{1 - \theta_1}\right). \tag{13}$$

The chemical potential for model 2 in the quasi-chemical approximation can be written as

$$\frac{\mu_1}{R_g T} = \frac{\mu^0}{R_g T} + \ln\left(\frac{\theta_1}{1 - \theta_1}\right) + \frac{z}{2}\ln\left(\frac{(\beta - 1 + 2\theta_1)(1 - \theta_1)}{(\beta + 1 - 2\theta_1)\theta_1}\right) \tag{14}$$

with β given by

$$\beta = \left(1 - 4\theta_1(1 - \theta_1)\left(1 - \exp\left(-\frac{\varepsilon}{R_g T}\right)\right)\right)^{1/2} \tag{15}$$

and z the lattice coordinate number equal to 1, 2, or 4 describing, respectively, the Langmuir model (model 1; $\varepsilon = 0$) and the pore and the square lattice (model 2) [see, for example, Reed and Ehrlich (*3*)].

We see that the Langmuir adsorption model gives always the same contribution to the chemical potential, regardless of the dimension of the lattice. The Langmuir model corresponds to the situation where the activated molecules have the possibility to go to only one nearest-neighbour site.

Equations (13) and (14) are used to calculate the thermodynamic factor, for comparison of the results of the Monte Carlo simulations with theory.

In the Monte Carlo method the adsorption and diffusion process in molecular sieves is modelled as a sequence of elementary events. Inside the adsorbent the molecules are in the force field of the surface, at all times. The migration of the molecules is assumed to take place in the adsorbed phase only; there is no gas phase inside the micropores. The adsorbed molecules are exposed to a periodic potential field, with the adsorption sites representing the minima of this field. Simulated are two experimental methods used to study mass transfer phenomena in zeolites. Uptake experiments, where the bulk gas phase is maintained at the equilibrium surface occupancy values, and tracer diffusion experiments, where only the behaviour of the molecules on the lattice is considered.

For the Monte Carlo simulations, based on the random walk principle, this gives the following elementary steps and conditions:

—A molecule is activated to execute a jump and a nearest-neighbour site is selected, both at random.

—This molecule cannot move to an already occupied nearest-neighbour site:

Model 1: If the move in the selected direction is not possible a new molecule is activated, at random.

Model 2: If the move to the selected nearest-neighbour site is not possible a new direction, for the same molecule, is selected. If all the nearest-neighbour sites are occupied a new molecule is randomly activated.

—There are no multiple jumps possible.

—The final concentration on the surface is given by the concentration of the bulk.

Putting all the conditions together the

Monte Carlo method can be applied to obtain a solution of the time evolution of the system under consideration, for a given set of initial and boundary conditions.

In the following sections the results of the Monte Carlo simulations for several cases will be examined. In the simulation two different parameters are used, namely, the jump frequency corresponding to an empty lattice and the surface occupancies at the beginning of the experiment and the surface occupancy at equilibrium. In the simulations of one-component and tracer diffusion the jump frequency is set equal to unity (in arbitrary units). This is also done in the case of multicomponent mass transfer for the jump frequency of the slowest moving component. This means that the GMS diffusion coefficient $Đ_{1V}$ becomes equal to unity.

The Monte Carlo simulations have been performed on an IBM ES/9000-270.

RESULTS AND DISCUSSION

One-Component and Tracer Diffusion

The GMS theory and Monte Carlo simulations are combined to evaluate one-component Fick diffusion, GMS or intrinsic diffusion, tracer diffusion, and counter-sorption coefficients on one- and two-dimensional surface structures. To display the results obtained from the Monte Carlo simulations a time-scale must be introduced. In the following we use an arbitrary time-scale defined by the number of activations per site, which is equivalent to the inverse of the jump frequency.

One-component. The dependence on surface occupancy of the one-component surface diffusion coefficient can be determined from uptake experiments. The solution for a constant Fick diffusion coefficient with constant boundary conditions in terms of the surface occupancy is given for small times by

$$\frac{\theta(t) - \theta(t_0)}{\theta(t_\infty) - \theta(t_0)} = \alpha \sqrt{\frac{D_{1V} t}{l^2}} \qquad (16)$$

with α a numerical factor depending on the surface structure [cf. Crank (*25*)]. From simulations with different initial surface occupancies the diffusion coefficient as a function of the square root of time can be evaluated. From the slope of this linear graph the diffusion coefficient is readily obtained with Eq. (16). To provide the same driving force in all the one-component uptake simulations a difference of 0.05 between the bulk and the surface occupancy is used as initial condition. Furthermore, to be able to compare the results obtained with the different models the diffusion coefficients have been normalized on the diffusion coefficient for an empty surface.

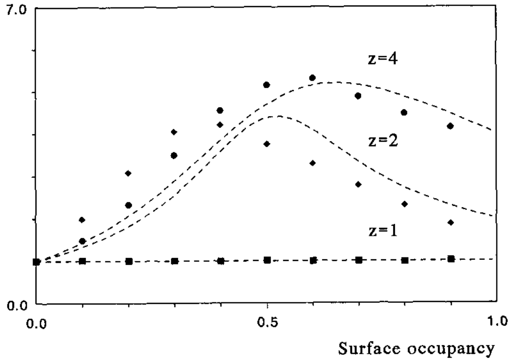

FIG. 1. Dimensionless one-component Fick diffusion coefficient as function of the surface occupancy. Results obtained from uptake simulations in a pore of 1000 sites and on a square lattice of 250 × 250 sites, with: (■) model 1, pore and lattice; (●) model 2, pore; (◆) model 2, lattice. Dashed lines are fit with quasi-chemical approximation.

Pore. The results of the one-component uptake simulations, for both adsorption models ($z = 1$ and $z = 2$), in the pore structure are shown in Figure 1. The dimensionless Fick diffusion coefficient as a function of the surface occupancy is plotted. The results are obtained for a pore of 1000 sites, the pore being open at both ends.

Square lattice. In Fig. 1 are also shown the results of the dimensionless one-component Fick diffusion coefficient as a function of the surface occupancy, as found on a square lattice of 250 × 250 sites for $z = 1$ and $z = 4$. On the square lattice the one-component Fick diffusion coefficient shows the same behaviour as for the pore. From the Monte Carlo simulations it can be concluded that the one-component Fick diffusion coefficient depends weakly on the lattice coordinate number or, equivalently, the dimension of the lattice. For the Langmuir adsorption the Fick diffusion coefficient is independent of surface occupancy.

For the one-component diffusion behaviour with the Langmuir adsorption (model 1 or $z = 1$), for both the pore and the square lattice, the jump rate decreases by the same amount as the thermodynamic factor increases [Eqs. (6) and (8)]. For model 2 the mobility of the adsorbed molecules on the square lattice first increases, due to the repulsive interaction. At high occupancies the mobility decreases as a consequence of the decrease of the number of empty sites [Eqs. (10) and (14)]. Also shown are the results of the quasi-chemical approximation.

Tracer. The influence of the surface occupancy on tracer flow can be studied by monitoring the mean square displacement of labelled molecules. The tracer diffusion coefficient for z nearest-neighbours can be determined from the mean square displacement with the Einstein relation

$$D^* = \frac{\langle R^2(t)\rangle}{zt}. \tag{17}$$

To exclude boundary effects in the Monte Carlo simulations of the mean square displacement only a number of molecules in the center of the surface are tagged.

Due to the differences between the tagged and untagged molecules tracer diffusion requires the same approach as a binary mixture. Therefore, the surface chemical potential must be modified to describe the sorption process of a binary mixture. Analogously to Eq. (14) we can write, for a binary mixture in the case of Langmuir adsorption, for the chemical potential of component 1

$$\frac{\mu_1}{R_gT} = \frac{\mu^0}{R_gT} + \ln\left(\frac{\theta_1}{1 - \theta_1 - \theta_2}\right) \tag{18}$$

and a similar relation for component 2.

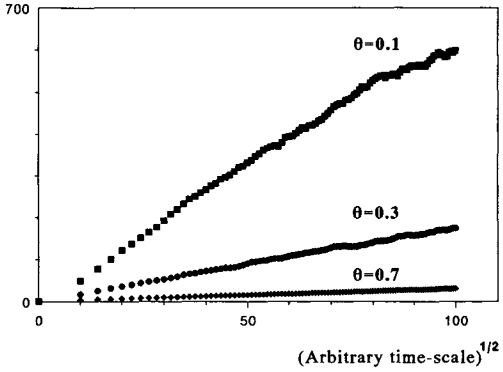

FIG. 2. Mean square displacement versus root of arbitrary time-scale for different surface occupancies, with: (■) $\theta = 0.1$; (●) $\theta = 0.3$; (◆) $\theta = 0.7$. Tracer diffusion, obtained with model 1, in a pore with 1000 sites.

From Eq. (18) the following relation between the elements of the thermodynamic factor matrix, Eq. (3) can be derived:

$$\begin{aligned}\Gamma_{11} &= 1 + \Gamma_{12}\\ \Gamma_{22} &= 1 + \Gamma_{21}.\end{aligned} \tag{19}$$

Combining relation (19) with the expression for the elements of the matrix of inverted GMS diffusion coefficients, given by relation (2), the GMS theory gives the following relation for the tracer diffusion coefficient

$$\begin{aligned}D^* &= D_{11} - D_{12}\\ &= \left(\frac{\theta_1 + \theta_2}{\mathrm{Đ}_{12}} + \frac{\theta_V}{\mathrm{Đ}_{1V}}\right)^{-1}.\end{aligned} \tag{20}$$

This relation for tracer diffusion is also independent of the dimension of the lattice. If we take in Eq. (20) $\mathrm{Đ}_{12}$ equal to $\mathrm{Đ}_{1V}$, Eq. (12) is obtained again.

Pore. In Fig. 2 the mean square displacement of tagged molecules for three different surface occupancies, in the one-dimensional pore structure, versus the square root of time is displayed. The linear dependence of the mean square displacement on the square root of time means that the tracer diffusion coefficient, for this system, cannot be obtained from the Einstein relation. With model 2 the same effect is found; the results

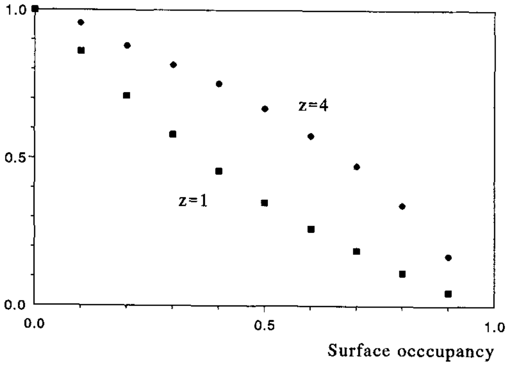

FIG. 3. Dimensionless tracer diffusion coefficient as function of the surface occupancy, on a square lattice of 250 × 250 sites, with: (■) model 1; (●) model 2.

are not presented. Due to the higher mobility of the molecules described by model 2, as compared to model 1, the mean square displacement of tagged molecules at a given time is larger than for model 1.

Square lattice. Figure 3 shows the tracer diffusion coefficient as a function of surface occupancy, for the two adsorption models. For both adsorption models ($z = 1$ and $z = 4$) the tracer diffusion coefficient decreases with increasing surface occupancy. For tracer diffusion with the Langmuir adsorption isotherm ($z = 1$) the diffusion coefficient decreases faster than $(1 - \theta)$. On the other hand, the tracer diffusion coefficient for model 2 ($z = 4$) decreases more slowly than $(1 - \theta)$.

The result of the Monte Carlo simulations with the Langmuir adsorption model (model 1) for tracer diffusion in the one-dimensional pore and on the two-dimensional square lattice are in good agreement with Monte Carlo results obtained by Tsikoyiannis and Wei (*14*). These results are, however, in contradiction with results reported by Rajadhyaksha *et al.* (*26*), who also found that the mean square displacement on a square lattice is a nonlinear function of time.

The behaviour of tracer diffusion obtained with model 1, Langmuir adsorption on the square lattice, has also been found experimentally. Using the NMR pulse field gradient technique, Caro *et al.* (*27*) and Kärger and Pfeifer (*28*) have measured tracer diffusion of a number of *n*-paraffins in silicalite. The experimental results show the same behaviour of the tracer diffusion coefficient as obtained from simulations with model 1. For example, the tracer (or self-) diffusion coefficient of methane in ZSM-5 type zeolites (silicalite) decreases in almost a linear manner on a logarithmic scale with increasing occupancy (cf. Fig. 1a of Ref. (*27*)).

Counter-exchange and corrected diffusion coefficient. Combining the results for the one-component Fick diffusion coefficient with the results for the tracer diffusion coefficient we can proceed in two ways. It is possible to describe tracer diffusion in terms of a corrected diffusion coefficient or by using a counter-exchange coefficient.

In Eq. (21) the tracer diffusion coefficient is expressed in terms of a corrected diffusion coefficient

$$D^* = D_0(1 - \theta_1^z) \qquad (21)$$

In Fig. 4 is displayed the corrected diffusion coefficient D_0 for $z = 1$ and $z = 4$, as the ratio of the tracer diffusion coefficient D^*, obtained from the Monte Carlo simulation, and the probability of performing a jump $(1 - \theta^Z)$. From the linear relation be-

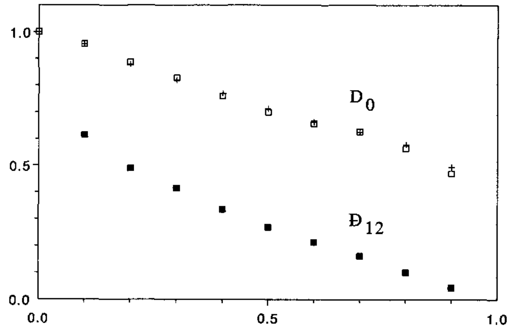

FIG. 4. Diffusion coefficient D_0, obtained from relation (21), and $Đ_{12}$, obtained from relation (20), as function of surface occupancy, with: (□) D_0 model 1; (+) D_0 model 2; (■) $Đ_{12}$ model 1.

TABLE 1

Input Conditions for Counterdiffusion Experiments

	Case A			Case B		
Component	$\theta_i(t_0)$	$\theta_i(t_\infty)$	$Đ_{iV}(0)$	$\theta_i(t_0)$	$\theta_i(t_\infty)$	$Đ_{iV}(0)$
$i = 1$	0.00	0.70	1	0.70	0.00	1
$i = 2$	0.70	0.00	20	0.00	0.70	20

tween the corrected diffusion coefficient D_0 and the surface occupancy found for both models on the square lattice it can be concluded that tracer diffusion can be described by one parameter, which is a function of the total surface occupancy.

However, in the single-file model the tracer diffusion coefficient, for Langmuir adsorption, decreases linearly with increasing surface occupancy [Eqs. (8) and (12)]. The deviation from the linear dependence can be ascribed to drag effects between sorbed molecules, represented by the counter-exchange coefficient $Đ_{12}$. This coefficient can be determined from relation (20). In Fig. 4 is also plotted the GMS counter-exchange coefficient $Đ_{12}$ as a function of surface occupancy, for the Langmuir model. The counter-sorption diffusivity decreases with increasing surface occupancy.

From Figs. 1 and 3 it can be concluded that model 1, the Langmuir isotherm, applied to the square lattice is consistent with a number of experimental results of mass transfer in channel-type zeolites.

Counterdiffusion of a Binary Mixture

For separation applications the behaviour of mixtures with large differences between the individual properties is of great interest. In the following, the results obtained from the Monte Carlo simulations of multicomponent surface diffusion on the square lattice are discussed.

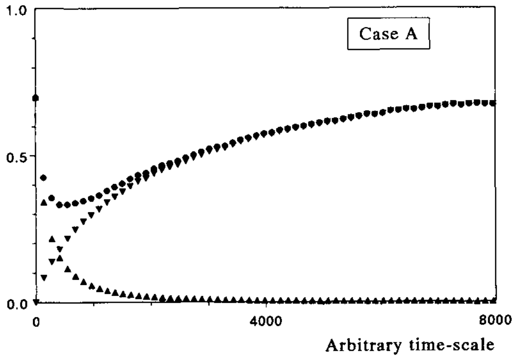

FIG. 5. Uptake profiles for transient counterdiffusion as function of arbitrary time-scale on a square lattice of 25 × 25 sites. Data of case A, with: (▼) component 1; (▲) component 2; (●) total surface occupancy (component 1 + 2).

In the case of binary counterdiffusion two different situations can be distinguished, adsorption of the component with the highest intrinsic or GMS diffusion coefficient from the bulk phase on the lattice replacing the other component with the smaller coefficient, which then desorbs into the bulk and, of course, the reverse situation.

The results of the counterdiffusion simulations, with the data of Table 1, are shown in Figs. 5 and 6. The transient uptake profiles are plotted as a function of an arbitrary time-scale.

The surface coverage profiles obtained from the simulations show that the counterdiffusion process is not symmetrical. This holds as well for the individual components

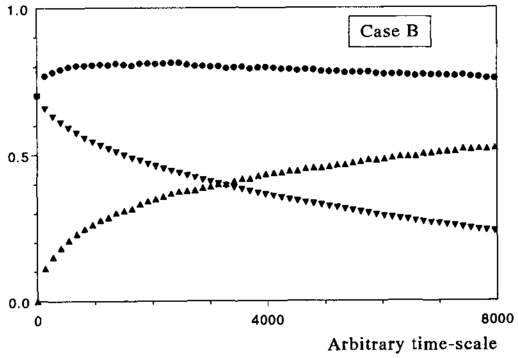

FIG. 6. Uptake profiles for transient counterdiffusion as function of arbitrary time-scale on a square lattice of 25 × 25 sites. Data of case B, with: (▼) component 1; (▲) component 2; (●) total surface occupancy (component 1 + 2).

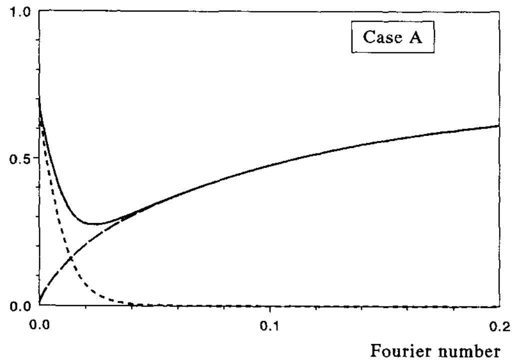

FIG. 7. Analytical result for a plane sheet obtained with the single-file diffusion matrix for uptake profiles in the case of transient counterdiffusion, as function of Fourier number. Data of case A, with: (———) component 1; (-----) component 2; (———) total surface occupancy (component 1 + 2).

as for the profiles of the total amount adsorbed.

An analytical solution for the uptake profiles of mixtures can be obtained from the GMS theory combined with the linearized theory of multicomponent mass transfer [see Krishna and Standart (*23*) and Krishna (*22*)]. Analytical results of transient profiles as a function of the Fourier number, Fo = $Đ_{1V}t/l^2$, for the two counterdiffusion processes are given in Figs. 7 and 8, with the same conditions as in cases A and B. The profiles are obtained by using the single-file diffusion matrix, Eq. (11), and the solution for a plane sheet with a constant surface concentration [cf. Crank (*25*)]

$$\frac{\theta(t)-\theta(t_0)}{\theta(t_\infty)-\theta(t_0)} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty} \frac{1}{(2n+1)^2}\exp\left(-\frac{(2n+1)^2\pi^2 D_{1V}t}{l^2}\right). \tag{22}$$

The same has been done with the complete GMS theory for a cage type zeolite, by Krishna, for a particle with a spherical geometry (cf. Fig. 10 of Ref. (*22*)).

From the different figures for counterdiffusion, Figs. 5–8 and Fig. 10 of Ref. (*22*), it is clear that the approach to equilibrium of the components depends on the surface structure. The single-file diffusion model predicts the same behaviour as the Monte Carlo simulations. For the approach to equilibrium, in channel-type structures, we see that the desorption process is faster than the adsorption process, for the same component. In cage-type structures the opposite holds.

The effect of the influence of the direction of mass transfer on the rates of adsorption and desorption for different types of zeolites has been measured experimentally. Results of counterdiffusion for the system benzene/toluene/ZSM-5 are presented by Tsikoyiannis and Wei (*29*) and results for counterdiffusion of liquid hydrocarbons in zeolite NaY are presented by Moore and Katzer (*30*). The experimental results for the channel-type structure ZSM-5 confirm the outcome displayed in Figures 5–8.

The difference in the uptake behaviour for different surface structures can be explained in terms of a different contribution of the counter-exchange coefficient $Đ_{ij}$ in the Fick diffusion coefficient matrix. In channel-type structure the counter-exchange between the sorbed molecules is more restricted, due to blockage by the sorbent structure and other adsorbed molecules, than in cage-type structures. From the analytical results it fol-

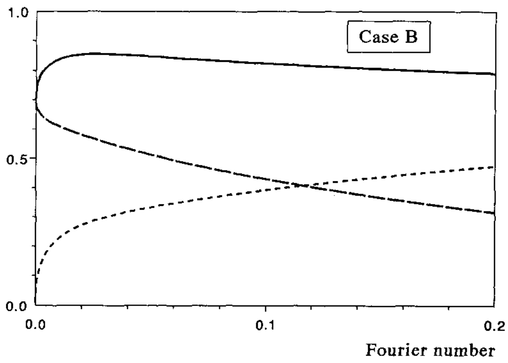

FIG. 8. Analytical result for a plane sheet obtained with the single-file diffusion matrix for uptake profiles in the case of transient counterdiffusion, as function of Fourier number. Data of case B, with: (———) component 1; (-----) component 2; (———) total surface occupancy (component 1 + 2).

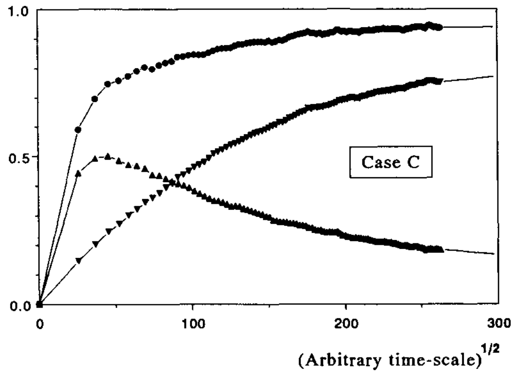

FIG. 9. Transient uptake profiles for binary sorption as function of the square root of arbitrary time-scale. Data of case C on a square lattice of 25 × 25 sites, with: (▼) component 1; (▲) component 2; (●) total surface occupancy (component 1 + 2).

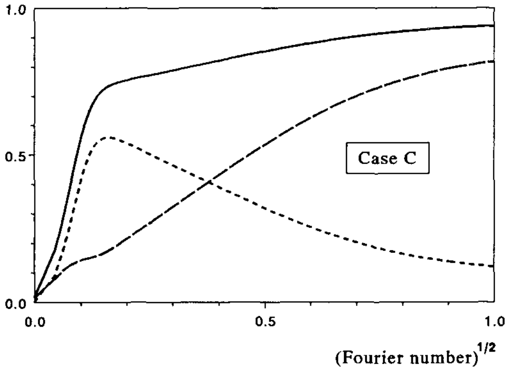

FIG. 10. Analytical result for a plane sheet obtained with the single-file diffusion matrix for transient uptake profiles of a binary mixture as function of the square root of Fourier number. Data of case C, with: (———) component 1; (-----) component 2; (———) total surface occupancy (component 1 + 2).

lows that the cross-coefficients D_{ij} in the single-file diffusion matrix, Eq. (11), are always positive; however, in the complete GMS diffusion matrix given by Eqs. (1)–(3) the cross-coefficients can be positive as well as negative.

Transient Uptake of Binary and Ternary Mixtures

Two multicomponent uptake experiments have been simulated (see Table 2). Case C is an example of a binary mixture with a fast-moving less-strongly-adsorbed component and a slow-moving more-strongly-adsorbed component. In Fig. 9 the binary uptake profiles and the total amount sorbed are shown. In case D simultaneous uptake of three components on the lattice is considered. The ternary uptake profiles are shown in Fig. 11. The analytical solutions for the two cases are displayed in Figs. 10 and 12.

For the case of binary transient uptake Monte Carlo simulations give a maximum in the profile of the faster-moving less-strongly-adsorbed component (component 2). The maximum value in the surface occupancy is considerably higher than the value at equilibrium. The uptake profile of the slow-moving more strongly adsorbed component (component 1) increases monotonously, during which the weakly adsorbed component is being replaced, after some time.

This binary behaviour has also been observed experimentally. For example, binary uptake profiles for the system methane/nitrogen/chabazite have been measured by Habgood (*31*) and for the system *n*-heptane/benzene/zeolite NaX by Kärger *et al.* (*32*) and Kärger and Bülow (*33*).

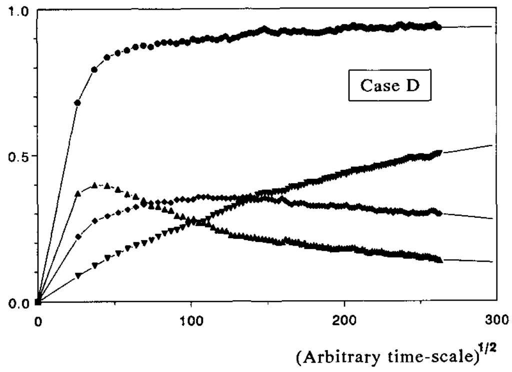

FIG. 11. Transient uptake profiles for ternary sorption as function of the square root of arbitrary time-scale. Data of case D on a square lattice of 25 × 25 sites, with: (▼) component 1; (◆) component 2; (▲) component 3; (●) total surface occupancy (component 1 + 2 + 3).

TABLE 2

Input Conditions for Transient Uptake Experiments

	Case C			Case D		
Component	$\theta_i(t_0)$	$\theta_i(t_\infty)$	$Đ_{iV}(0)$	$\theta_i(t_0)$	$\theta_i(t_\infty)$	$Đ_{iV}(0)$
$i = 1$	0.00	0.85	1	0.00	0.65	1
$i = 2$	0.00	0.10	50	0.00	0.20	10
$i = 3$				0.00	0.10	50

In the case of ternary uptake two maxima are observed. Both the maxima in the surface occupancies are higher than the values at equilibrium. The uptake profile of the component with the lowest diffusion coefficient increases monotonically with increasing time.

Experimental results for the uptake profiles of a ternary mixture, toluene, *p*-xylene, and *n*-propyl benzene, in H-ZSM-5 have been reported by Choudhary *et al.* (*34*). They have found a total of two maxima, one in every uptake profile of the two fastest-moving species. The slowest-moving most-strongly adsorbed species has no maximum in its uptake profile.

Furthermore, from the binary uptake profiles it is clear that there are two points important for separation applications. These are the conventional equilibrium selectivity process and a new diffusive selectivity process requiring a much shorter residence time.

The results from the Monte Carlo simulations are in good agreement with analytical results for a plane sheet obtained from the single-file diffusion model (Figs. 10 and 12). The theoretical uptake curves for multicomponent mixture are quantitatively in good agreement with experimental results. For small times the uptake profiles are linear with the square root of time, or the square root of Fourier number. Furthermore, the uptake process in channel type structures, as described by the single-file diffusion model, is much slower than the uptake process in cage type structures, as described by the complete GMS theory. The maximum value in the surface occupancy, in the case of the binary uptake, of component 2 predicted with the single-file diffusion model occurs at about (1/50)th of the time to reach the equilibrium values.

For a cage-type structure, described with the complete GMS theory, the maximum in the uptake profile of the faster-moving less-strongly-adsorbed component is reached at about a sixth of the time it takes to reach equilibrium (cf. Fig. 8 of Ref. (*22*)).

The Monte Carlo simulations and the analytical results clearly demonstrate the coupling between the surface fluxes of the sorbed molecules. From the theoretical considerations, the Monte Carlo simulations and the GMS theory, it is clear that the properties of the fast-moving species are the most affected by the presence of other sorbed species. The slowest-moving species in the mixture shows an uptake behaviour similar to one-component mass transfer. Comparing the single-file diffusion model with the GMS model, diffusion takes place at a rate five to ten times higher when counter-exchange is important.

Transient uptake of multicomponent mixtures have also been simulated with adsorp-

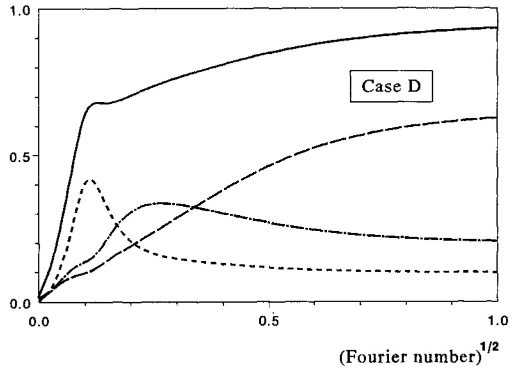

FIG. 12. Analytical result for a plane sheet obtained with the single-file diffusion matrix for transient uptake profiles of a ternary mixture as function of the square root of Fourier number. Data of case D, with: (———) component 1; (—-—) component 2; (-----) component 3; (———) total surface occupancy (component 1 + 2 + 3).

tion model 2. However, the uptake profile with this model for both the counter- and the co-diffusion processes are similar to the profiles obtained with model 1. In general the uptake with model 2 is faster than in the case of model 1.

CONCLUSIONS

Using the transient uptake technique, diffusion of multicomponent mixtures in molecular sieve materials has been studied theoretically. With the Monte Carlo method transient uptake profiles of one- and multicomponent systems have been simulated. Also tracer diffusion has been simulated. The Monte Carlo simulations are based on a model where adsorbed molecules jump between nearest-neighbour sites. The results of the Monte Carlo simulations have been compared with theoretical models for multicomponent diffusion and some published experimental results.

From the theoretical and computational results it can be concluded that a surface diffusion model can be applied to describe diffusion of mixtures in molecular sieve materials. In this work we have showed that several features of multicomponent mass transport in zeolites can be described and predicted by a surface diffusion model, based on one-component mass transport data.

Two theoretical models, the GMS formulation and a single-file diffusion model, for the concentration dependence of the Fick diffusion coefficient matrix are compared. The uptake profiles for multicomponent diffusion obtained from Monte Carlo simulations are in good agreement with results predicted with an analytical single-file diffusion model.

The single-file diffusion matrix can be regarded as a limiting case of the GMS theory. However, the assumptions made in the derivation need some extra investigation, especially, on the relation between the counter-exchange coefficient and the type of adsorbent structure.

From the results of the Monte Carlo simulations a new effect has been indicated, namely, that the type of adsorbent structure (molecular sieve carbon and cage-type (or large port) zeolites vs channel-type (or small port) zeolites) has an influence on the time dependence of both tracer diffusion and the uptake profiles in the case of multicomponent mixtures. If counter-exchange is absent diffusion takes place at a rate 5 to 10 times higher, depending on the specific conditions.

Simulations of uptake profiles clearly show the coupling between surface fluxes of mixture components. A combination of the analytical and computational approach can help to determine the concentration dependence of the Fick diffusion coefficient.

The major advantages of a Monte Carlo method are clear; a systematic approach can be followed to study macroscopic diffusion phenomena of mixtures in micropores. However, a careful comparison between the theoretical and computational results on the one hand and experimental observations on the other hand is necessary. The comparisons made in this work confirm the potency of both the GMS and the Monte Carlo approach.

APPENDIX: NOTATION

$[B]$	matrix of GMS diffusion coefficients ($m^2\,s^{-1}$)
$[D]$	matrix of Fick diffusion coefficients ($m^2\,s^{-1}$)
D^*	tracer diffusion coefficient ($m^2\,s^{-1}$)
D_0	corrected diffusion coefficient ($m^2\,s^{-1}$)
D_{1V}	one-component Fick diffusion coefficient ($m^2\,s^{-1}$)
$Đ_{ij}$	GMS diffusion coefficient (i,j = 1 . . . (n + 1)) ($m^2\,s^{-1}$)
Fo	Fourier number ($= Đ_{1V}t/l^2$)
f	fugacity ($N\ m^{-2}$)
l	length (m)
n	number of components in mixture
R	displacement (m)
R_g	gas constant ($J\ mol^{-1}\ K^{-1}$)
t	time (s)
T	temperature (K)
z	lattice coordinate number

Greek Letters

α	numerical factor ($= 2/\pi^{1/2}$, for a plane sheet)
β	function of the interaction energy, defined in equation (15)
ε	interaction energy (J mol^{-1})
$[\Gamma]$	matrix of thermodynamic correction factors
λ	displacement, distance between two adjacent sites (m)
μ	chemical potential (J mol^{-1})
ν	jump frequency (s^{-1})
θ	fractional surface occupancy

Subscript

I	refers to interaction contribution in the surface chemical potential
i,j	components i,j
L	refers to the Langmuir contribution in the surface chemical potential
$n + 1$	vacancy ($= V$)
0	initial condition at time $t = 0$
∞	final, or equilibrium, condition at time $t \to \infty$
V	vacancy ($= n + 1$)

Superscripts

0	refers to standard state

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