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Diffusion of binary mixtures in zeolites: molecular dynamics simulations versus Maxwell–Stefan theory

R. Krishna*

Department of Chemical Engineering, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

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Abstract

The Maxwell–Stefan formulation of diffusion in multicomponent mixtures is used to obtain explicit formulae for calculating the diffusivities of binary mixtures within a zeolite matrix. The theoretical development allows the estimation of the mixture diffusivities on the basis of the pure component diffusivities at zero loadings. The applicability of the Maxwell–Stefan model is demonstrated by comparison with published molecular dynamics simulations for mixtures of methane–perfluoromethane, methane–xenon, and methane–n-butane in silicalite. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The proper description of diffusive transport within zeolitic materials is of considerable importance in practice because of the many applications in catalytic reaction and separation processes [1–3]. A variety of models and techniques have been used to describe diffusion within zeolites, ranging from phenomenological models such as the Fick's law of diffusion [1,2] and the Maxwell–Stefan (MS) formulation [4–7] to Monte Carlo (MC) simulations [8–11] and molecular dynamics (MD) [12,13]. In recent years, increasing attention has been paid to the description of diffusion of mixtures [14–18] using MD techniques. The computational expense involved in the use of MD techniques for mixtures is considerable. In this Letter, we show that the published MD simulation results for mixture diffusivities obey simple mixture rules which can be derived from MS diffusion formulation that has its roots in the theory of non-equilibrium thermodynamics [4].

2. Maxwell–Stefan theory of diffusion in zeolites

The essential concepts behind a general constitutive relation for diffusion in multicomponent mixtures were already available more than a century ago following the pioneering works of James Clerk Maxwell [19] and

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* Fax: +31-20-5255604; e-mail: krishna@its.chem.uva.nl

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Josef Stefan [20]. These ideas have been applied to describe diffusion of n species within a zeolite matrix using the following set of equations [4,5]:

$$-\rho\frac{\theta_i}{RT}\nabla\mu_i = \sum_{\substack{j=1\\ j\neq i}}^{n}\frac{\Theta_j\boldsymbol{N}_i - \Theta_i\boldsymbol{N}_j}{\Theta_{i,\mathrm{sat}}\Theta_{j,\mathrm{sat}}\text{Đ}_{ij}} + \frac{\boldsymbol{N}_i}{\Theta_{i,\mathrm{sat}}\text{Đ}_i}; \quad i = 1,2,\ldots n \tag{1}$$

where ρ is the zeolite matrix density expressed as unit cells per m^3, Θ_i represents the loading expressed in molecules of sorbate per unit cell of zeolite, $\Theta_{i,\mathrm{sat}}$ is the saturation loading of species i, R is the gas constant and T is the temperature. $\nabla\mu_i$ is the gradient of the chemical potential of species i, which is the fundamental driving force for diffusion. The fractional occupancy θ_i of the sorbate within the zeolite matrix is defined as

$$\theta_i \equiv \Theta_i/\Theta_{i,\mathrm{sat}}; \quad i = 1,2,\ldots n. \tag{2}$$

In general, the saturation loadings of the various species $\Theta_{i,\mathrm{sat}}$ in the mixture will be different from one another. The $\boldsymbol{N}_i$ are the molecular fluxes expressed in terms of molecules transported per square meter per second.

In the MS formulation for zeolite diffusion (Eq. (1)), we have to reckon in general with two types of MS diffusivities: Đ_{ij} and Đ_i. The Đ_i are the diffusivites which reflect interactions between species i and the zeolite matrix. Mixture diffusion introduces an additional complication due to sorbate–sorbate interactions. This interaction is embodied in the coefficients Đ_{ij}. We can consider this coefficient as representing the facility for counter-exchange, i.e. at a sorption site the sorbed species j is replaced by the species i. The net effect of this counter-exchange is a slowing down of a faster moving species due to interactions with a species of lower mobility. Also, a species of lower mobility is accelerated by interactions with another species of higher mobility.

The MS formulation of single component diffusion, can be derived from Eq. (1) by setting $n = 1$:

$$\boldsymbol{N}_1 = -\rho\Theta_{\mathrm{sat}}\text{Đ}_1\left(\frac{\theta_1}{RT}\nabla\mu_1\right) \tag{3}$$

where μ_1 is the chemical potential of the sorbed species 1. Assuming equilibrium between the sorbed species and the bulk fluid phase we have the following relationship for the chemical potential μ_1

$$\mu_1 = \mu_1^0 + RT\ln(f_1) \tag{4}$$

where μ_1^0 is the chemical potential in the chosen standard state and f_1 is the fugacity. For not too high system pressures the component partial pressure, p_1, can be used in place of the component fugacity, f_1, i.e. $f_1 \approx p_1$. The chemical potential gradients may be expressed in terms of the gradients of the fractional occupancy, $\nabla\theta_1$,

$$\frac{1}{RT}\nabla\mu_1 = \frac{1}{\theta_1}\Gamma\,\nabla\theta_1; \Gamma \equiv \theta_1\frac{\partial\ln p_1}{\partial\theta_1} \tag{5}$$

where Γ is the thermodynamic correction factor. Introducing Eq. (5) into Eq. (3) we obtain

$$\boldsymbol{N}_1 = -\rho\Theta_{1,\mathrm{sat}}D_1\nabla\theta_1 = -\rho\Theta_{1,\mathrm{sat}}\text{Đ}_1\Gamma_1\nabla\theta_1 \tag{6}$$

where D_1 is termed the transport or Fick diffusivity. Đ_1 is variously called the MS, 'corrected' or 'jump' diffusivity [1,4]. These two diffusivities are inter-related:

$$D_1 = \text{Đ}_1\Gamma. \tag{7}$$

Often in experiments and simulations, the self-diffusivity of species 1 is determined under conditions where there is no net gradient, $\nabla\theta_1 \equiv 0$. The self diffusivity shows a decreasing trend with molecular loading; see Fig. 1a,b for MD simulation results of CH_4, CF_4 and Xenon in silicalite. MC simulations have been used recently to show the inter-relationship between self-, MS and transport diffusivities (see Fig. 1c). The self-diffusivity is

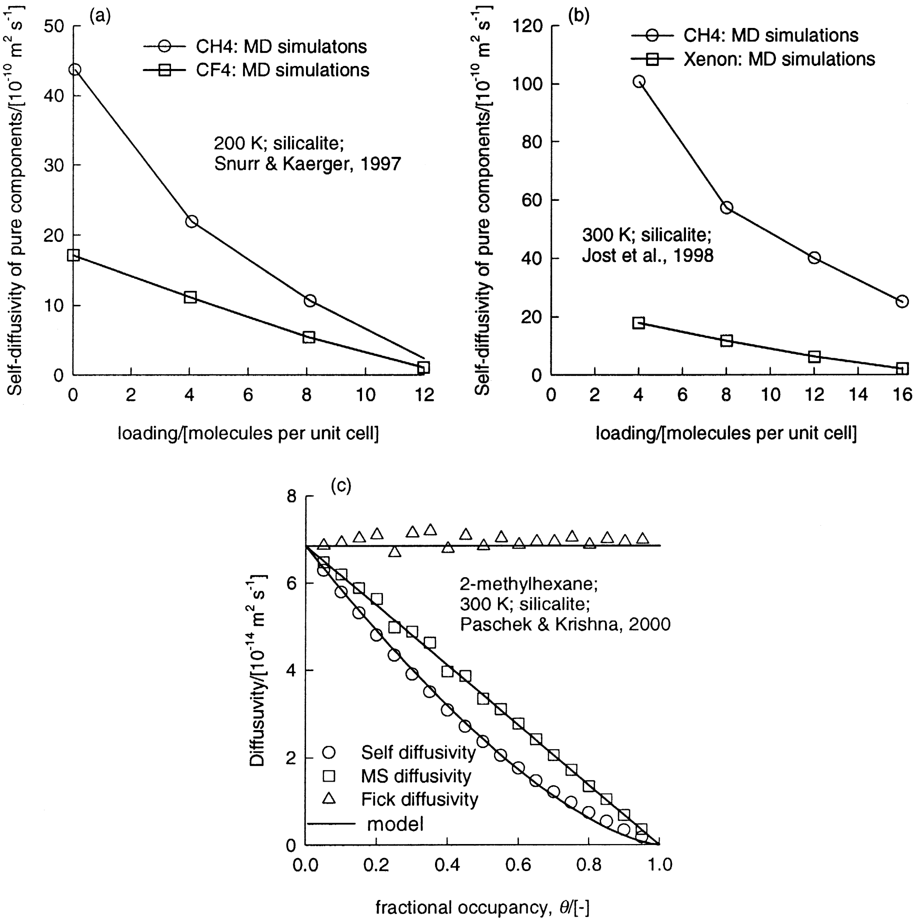

Fig. 1. (a) Self-diffusivities of pure components CH_4 and CF_4 in silicalite-1 at 200 K. MD simulations of Snurr and Kärger [14]. (b) Self-diffusivities of pure components CH_4 and xenon in silicalite-1 at 300 K. MD simulations of Jost et al. [15]. (c) MC simulations of self-, MS and Fick diffusivities of 2-methylhexane in silicalite at 300 K [11]. The saturation capacity of 2MH is 4 molecules per unit cell.

influenced by correlation effects whereas such correlation effects do not affect the MS and Fick diffusivities. We note that the MS diffusivities follow the simple linear relationship:

$$\text{Đ}_1 = \text{Đ}_1(0)(1-\theta_1) \qquad (8)$$

where Đ_1 (0) represents the MS diffusivity in the limit of zero loading. At zero loading, all three diffusivities, self-, MS and Fick equal one another. This zero loading diffusivity can be determined experimentally or by use of transition state theory [21].

Kärger and Pfeifer [22] have shown that experimental data on pure component diffusivities can exhibit five different types of loading dependencies; the model described by Eq. (8) represents one such behaviour. The mixture relations to be derived below are valid for all the five cases described by Kärger and Pfeifer [22], provided the loading dependence of the MS diffusivity can be described by a functional relation $\text{Đ}_1 = \text{Đ}_1(0)f(\theta_1)$.

For a binary mixture, $n = 2$, Eq. (1) may be cast into 2-dimensional matrix notation to give

$$(\boldsymbol{N}) = -\rho[\Theta_{\mathrm{sat}}][B]^{-1}[\Gamma]\nabla(\theta) = -\rho[\Theta_{\mathrm{sat}}][D]\nabla(\theta) \tag{9}$$

where $[D]$ is the two-dimensional Fick diffusvity matrix and $[\Theta_{\mathrm{sat}}]$ is a diagonal matrix with the saturation loadings $\Theta_{i,\mathrm{sat}}$. The matrix $[B]$ has the elements

$$B_{ii} = \frac{1}{Đ_i} + \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{\theta_j}{Đ_{ij}}; \quad B_{ij} = -\frac{\theta_i}{Đ_{ij}}; \quad i,j = 1,2 \ldots n. \tag{10}$$

Taking the inverse of matrix $[B]$ and denoting this as $[R]$, we obtain

$$[B]^{-1} \equiv [R] = \frac{1}{\left(1 + \theta_1 \frac{Đ_2}{Đ_{12}} + \theta_2 \frac{Đ_1}{Đ_{12}}\right)} \begin{bmatrix} Đ_1 + \theta_1 \frac{Đ_1 Đ_2}{Đ_{12}} & \theta_1 \frac{Đ_1 Đ_2}{Đ_{12}} \\ \theta_2 \frac{Đ_1 Đ_2}{Đ_{12}} & Đ_2 + \theta_2 \frac{Đ_1 Đ_2}{Đ_{12}} \end{bmatrix}. \tag{11}$$

A procedure for the estimation of the counter-exchange coefficient $Đ_{12}$ has been suggested by Krishna and Wesselingh [4]:

$$Đ_{12} = [Đ_1]^{\frac{\theta_1}{(\theta_1 + \theta_2)}} [Đ_2]^{\frac{\theta_2}{(\theta_1 + \theta_2)}}. \tag{12}$$

The matrix $[\Gamma]$ is the thermodynamic correction factor matrix, which can be determined from the mixture isotherm

$$\Gamma_{ij} \equiv \left(\frac{\Theta_{j,\mathrm{sat}}}{\Theta_{i,\mathrm{sat}}}\right) \frac{\Theta_i}{p_i} \frac{\partial p_i}{\partial \Theta_j}; i,j = 1,2 \ldots n. \tag{13}$$

When the saturation loadings of the two components, $\Theta_{i,\mathrm{sat}}$, are equal to each other, and the isotherms of the pure components can be described by a single-site Langmuir isotherm, the matrix of thermodynamic correction factors can be determined from

$$[\Gamma] = \begin{bmatrix} \Gamma_{11} & \Gamma_{12} \\ \Gamma_{21} & \Gamma_{22} \end{bmatrix} = \frac{\begin{bmatrix} 1 - \theta_2 & \theta_1 \\ \theta_2 & 1 - \theta_1 \end{bmatrix}}{1 - \theta_1 - \theta_2}. \tag{14}$$

In the general case, when the saturation loadings of the two components are different we must use the 'ideal adsorbed solution' theory to calculate the mixture isotherms [5].

We could force-fit Eq. (9) for the two fluxes $\boldsymbol{N}_i$ into the form of Fick's law for each species with effective diffusivities:

$$\boldsymbol{N}_i = -\rho\Theta_{\mathrm{sat}} D_{i,eff} \nabla\theta_i; \quad i = 1,2 \tag{15}$$

where the effective Fick diffusivities of components 1 and 2 are given by

$$D_{1,\mathrm{eff}} = D_{11} + D_{12} \frac{\nabla\theta_2}{\nabla\theta_1}, \tag{16}$$

$$D_{2,\mathrm{eff}} = D_{21} \frac{\nabla\theta_1}{\nabla\theta_2} + D_{22}. \tag{17}$$

For self-diffusivity measurements or simulations, the sum of the gradients vanishes, i.e.

$$\nabla\theta_1 + \nabla\theta_2 = 0 \tag{18}$$

and therefore the expression for the self diffusivities of components 1 and 2 simplify to

$$\begin{pmatrix} D_{1,\mathrm{eff}} \\ D_{2,\mathrm{eff}} \end{pmatrix} = \begin{pmatrix} D_{11} - D_{12} \\ D_{22} - D_{21} \end{pmatrix} = \begin{pmatrix} R_{11}\Gamma_{11} + R_{12}\Gamma_{21} - R_{11}\Gamma_{12} - R_{12}\Gamma_{22} \\ R_{21}\Gamma_{12} + R_{22}\Gamma_{22} - R_{21}\Gamma_{11} - R_{22}\Gamma_{21} \end{pmatrix}. \tag{19}$$

For the situation in which Eq. (14) applies, Eq. (19) further simplifies, yielding

$$\begin{pmatrix} D_{1,\mathrm{eff}} \\ D_{2,\mathrm{eff}} \end{pmatrix} = \begin{pmatrix} R_{11} - R_{12} \\ R_{22} - R_{21} \end{pmatrix} = \frac{1}{\left(1 + \theta_1 \dfrac{\text{Đ}_2}{\text{Đ}_{12}} + \theta_2 \dfrac{\text{Đ}_1}{\text{Đ}_{12}}\right)} \begin{pmatrix} \text{Đ}_1 \\ \text{Đ}_2 \end{pmatrix}. \tag{20}$$

Eq. (20) represents a remarkably simple result which shows that the self-diffusivities in a binary mixture are not affected by thermodynamic factors and can be determined purely from knowledge of Đ_1, Đ_2 and Đ_{12}. Extending Eq. (8) to binary mixtures we take

$$\text{Đ}_1 = \text{Đ}_1(0)(1 - \theta_1 - \theta_2); \quad \text{Đ}_2 = \text{Đ}_2(0)(1 - \theta_1 - \theta_2) \tag{21}$$

and use Eq. (12) for determination of the counter-exchange coefficient Đ_{12}.

3. Verification of Eq. (20) using MD mixture simulations

We first consider the MD simulations of Snurr and Kärger [14] for CH_4 (1) and CF_4 (2) at 200 K in silicalite at a total mixture loading of 12 molecules per unit cell. The pure component self-diffusivities are shown in Fig. 1a. Methane being a smaller molecule has a higher saturation loading than that of CF_4; we therefore take $\Theta_{1,\mathrm{sat}} = 22$ and $\Theta_{2,\mathrm{sat}} = 12$ on the basis of information on mixture isotherms [23]. The pure component diffusivites at zero loading are estimated from Fig. 1a as $\text{Đ}_1(0) = 6 \times 10^{-9}$ m^2/s, $\text{Đ}_2(0) = 3 \times 10^{-9}$ m^2/s. The calculations of the diffusivites $D_{1,\mathrm{eff}}$ and $D_{2,\mathrm{eff}}$ using Eqs. (20), (21) and (12) show excellent agreement with the MD simulations of Snurr and Kärger [14] (see Fig. 2).

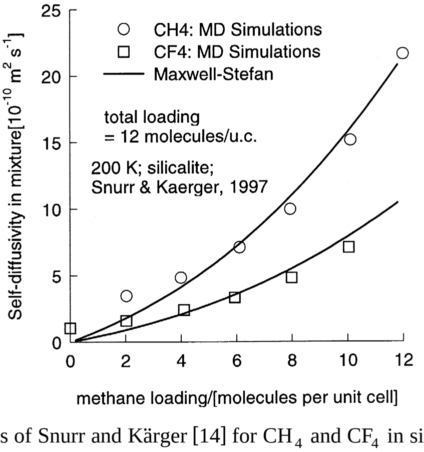

Fig. 2. Comparison of MD mixture simulations of Snurr and Kärger [14] for CH_4 and CF_4 in silicalite-1 at 200 K with estimations using Eq. (20).

Jost et al. [15] have published MD simulations for CH_4 (1) and Xenon (2) at 300 K in silicalite at total mixture loadings of 4, 8, 12 and 16 molecules per unit cell (see Fig. 3a–d). The pure component self-diffusivities are shown in Fig. 1b. The saturation loadings are estimated as $\Theta_{1,\mathrm{sat}} = 22$ and $\Theta_{2,\mathrm{sat}} = 16$. The pure component diffusivites at zero loading are estimated from Fig. 1b as $Đ_1(0) = 12 \times 10^{-9}$ m²/s, $Đ_2(0) = 4 \times 10^{-9}$ m²/s. The calculations of the diffusivites $D_{1,\mathrm{eff}}$ and $D_{2,\mathrm{eff}}$ show good agreement with the MD simulations of Jost et al. [15] for the whole range of total loadings studied (see Fig. 3).

Gergidis and Theodorou [17] have performed two sets of MD simulations for the mixture of CH_4 (1) and n-butane (2) at 300 K in silicalite (see Fig. 4a,b). The saturation loadings are estimated as $\Theta_{1,\mathrm{sat}} = 22$ and $\Theta_{2,\mathrm{sat}} = 12$. The pure component diffusivites at 300 K are taken as $Đ_1(0) = 11 \times 10^{-9}$ m²/s and $Đ_2(0) = 5 \times 10^{-9}$ m²/s. The calculations of the diffusivites in the mixture, $D_{1,\mathrm{eff}}$ and $D_{2,\mathrm{eff}}$, show excellent agreement with the MD simulations of Gergidis and Theodorou [17] for the both sets of simulations reported (see Fig. 4a,b). More recent MD simulations were carried out by these authors for the same mixture at 200 K [18]. Taking pure component diffusivites at 200 K to be $Đ_1(0) = 4.5 \times 10^{-9}$ m²/s and $Đ_2(0) = 1.5 \times 10^{-9}$ m²/s, the effective

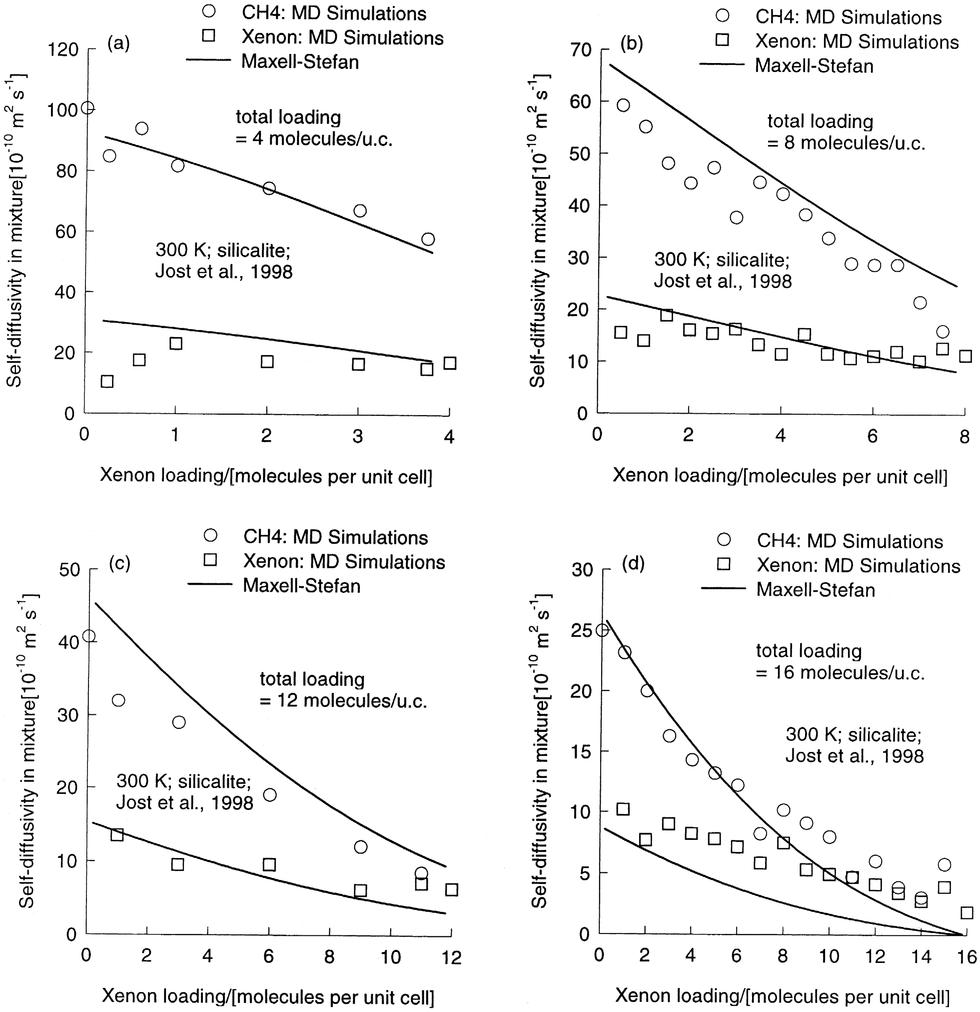

Fig. 3. Comparison of MD mixture simulations of Jost et al. [15] for CH_4 and Xenon in silicalite at 300 K with estimations using Eq. (20).

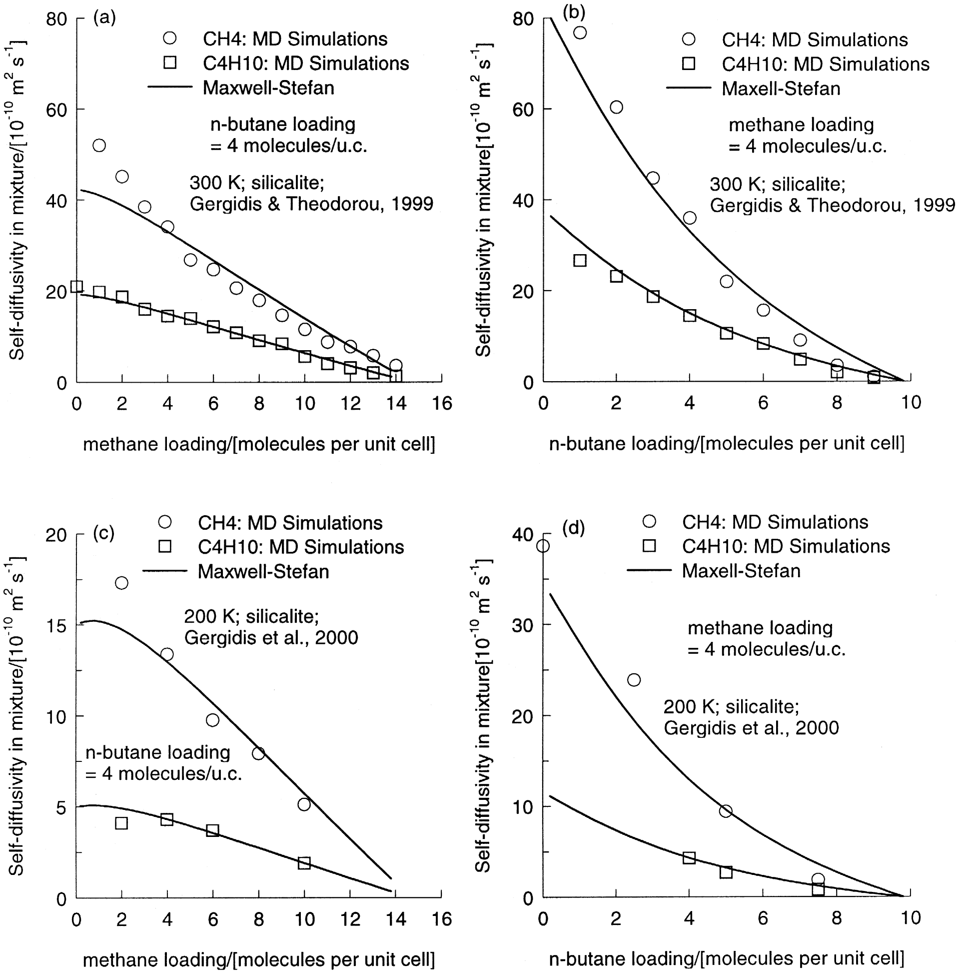

Fig. 4. Comparison of MD mixture simulations of Gergidis and Theodorou [17,18] for the mixture of CH_4 (1) and n-butane (2) in silicalite with estimations using Eq. (20). The data in (a) and (b) are at 300 K. The data in (c) and (d) are at 200 K.

diffusivities can be calculated in the mixture. Comparison of the MD simulation results with the estimations of the MS theory are shown in Fig. 4c,d. Again the agreement is excellent.

4. Conclusions

Using the MS theory for binary mixture diffusion in zeolites we have developed explicit formulae, Eqs. (16) and (17), for calculation of the diffusivities of the components in the mixture. For situations in which the sum of the gradients of the two species is maintained as zero, these expressions simplify considerably to yield Eq. (20) which, when used in conjunction with Eq. (12) for estimation of the counter-exchange coefficient $Đ_{12}$, allows the estimation of the mixture diffusivities purely on the basis of the zero-loading diffusivities $Đ_i(0)$. The validity of the Eq. (20) has been demonstrated by comparing with published MD mixture simulations for mixtures of methane–xenon, methane–perfluoromethane and methane–n-butane in silicalite.

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