To the Editor:

In the article "Diffusion Under Pore Saturaton Conditions", Lettat et al.[1] presents a model to describe mixture diffusion in MFI zeolite under conditions of pore saturation. As a motivation for developing their model they remark "the classical adsorbed-phase diffusion models based on the Maxwell-Stefan (M-S) equation cannot represent correctly multicomponent diffusion close to saturation", citing a variety of articles published prior to 2005.[2–5] In this Letter, we take issue with this remark. We also have reservations about the modifications that they have introduced in reformulating M-S equations, based on their perceived shortcomings of our published work in this area.

An important point of contention with the approach taken by Lettat et al.[1] concerns the exchange coefficients $Đ_{ij}$ defined in the M-S equations [2–9]

$$-\phi \frac{c_i}{RT}\nabla\mu_i = \sum_{\substack{j=1\\j\neq i}}^{n} \frac{c_j N_i - c_i N_j}{c_i Đ_{ij}} + \frac{N_i}{Đ_i}; \qquad i = 1,2,..n \tag{1}$$

where ϕ represents the fractional pore volume of the microporous crystalline material, and the concentrations c_i are defined in terms of moles per m^3 of accessible pore volume. The fluxes N_i are defined in terms of the cross-sectional area of the microporous crystalline framework. The $Đ_i$ characterize species i - wall interactions in the broadest sense. At the molecular level, the $Đ_{ij}$ reflect how the facility for transport of species *i correlates* with that of species *j*.

The M-S equations[2–9] can be rewritten to evaluate the fluxes N_i explicitly by defining a matrix (Δ)

$$N_i = -\phi \sum_{j=1}^{n} \Delta_{ij} \frac{c_j}{RT}\nabla\mu_j; \quad i = 1,2..n \tag{2}$$

The elements Δ_{ij} can be explicitly determined from information on the $Đ_i$, and $Đ_{ij}$. In several articles published since 2005,[5–14] we had used molecular dynamics (MD) simulations for a wide variety of guest molecules in zeolites, metal organic frameworks (MOFs), covalent organic framework (COFs), zeolite imidazolate frameworks (ZIFs), and carbon nanotubes (CNTs) to show that the exchange coefficients $Đ_{ij}$ decrease with increasing concentrations c_i.

In the limit of low-pore concentrations $c_i \to 0$, correlation effects are negligible, i.e., $Đ_{ij} \to \infty$, yielding

$$\Delta_{ii} = Đ_i; \quad \Delta_{ij}(i \neq j) = 0; \qquad \text{correlations negligible} \tag{3}$$

The degree of correlations, defined by the ratio $Đ_i/Đ_{ij}$ is found to increase with increasing c_i.[5–14] This is a physically rational result; correlation effects become stronger because there are progressively fewer vacant sites available for molecules to jump to. At pore saturation conditions, we should expect correlation effects to be at their strongest.

For a scenario in which correlation effects are considered to be dominant, i.e. $Đ_i/Đ_{ij} \gg 1$, we had derived explicit expressions for Δ_{ij} in our article on Onsager coefficients published in 2008.[7] This scenario yields the following expressions for Δ_{ij}

$$\Delta_{ij} = \frac{c_i}{\frac{c_1}{Đ_1} + \frac{c_2}{Đ_2} + \ldots.. + \frac{c_n}{Đ_n}}; \quad i,j = 1,2 = 1,2,..n; \quad \text{correlation dominant} \tag{4}$$

For the special case of equimolar mixture mixtures, with $c_1 \;\; c_2 \;\; .. \;\; c_n$ Eq. (4) simplifies further to yield

$$\Delta_{ii} = \Delta_{ij}; \quad i,j = 1,2,\ldots n; \quad \text{correlations dominant, equimolar mixture} \tag{5}$$

All the elements of the matrix [Δ] are equal to one another, and there is just one characteristic diffusivity. This is an intuitively rational result; when correlations are dominant, the differences in the diffusivities get washed out. Contrary to the Lettat claim, the *correlations dominant* scenario offers the correct description of the mixture diffusion behavior under pore saturation conditions. It appears that Lettat et al.[1] have not taken due cognizance of the correlations dominant scenario that was derived and discussed in three articles,[7–9] all of which were available for scrutiny before their article was submitted to the AIChE J. The validity of the expression (Eq. 4) under conditions of pore saturation has been established with the aid of MD simulations for an extremely wide variety of guest molecules in a different host structures.[7–10] The correlations dominant scenario is particularly relevant in describing diffusion in microporous materials used in CO_2 capture processes.[11]

The approach taken by Lettat et al.[1] in developing their diffusion model for pore saturation conditions is fundamentally different to the one we have adopted.[7–10] A key assumption they make is $Đ_{ij} \to \infty$. This assumption is not supported by the extensive MD simulation data for binary mixture diffusion of a variety of mixtures in MFI zeolite, the main focus of their attention.[10] Coupling effects in the Lettat model are entirely thermodynamic in character. Their approach is fraught with danger and will lead to erroneous results and conclusions in a variety of situations. Consider diffusion of a binary mixture of tagged and untagged species, corresponding to experiments on self-diffusivity in a unary system. For self-diffusion, thermodynamic nonideality effects are absent and there is no thermodynamic coupling. The M-S equations (1) can be used to derive the following expression for the self-diffusivity[9]

$$\frac{1}{D_{i,self}} = \frac{1}{Đ_i} + \frac{1}{Đ_{ii}} \tag{6}$$

As the loading increases correlation effects become increasingly important because the tagged species will have to return to recently vacated sites and most molecular jumps will be unsuccessful. The net result is that the self-diffusivity $D_{i,\mathrm{self}}$ will fall progressively below $Đ_i$ with increasing c_i. This is shown both experimentally[15,16] and by MD simulations.[5–14] Because of their assertion that, the application of the Lettat model for this situation, will yield the conclusion $D_{\mathrm{i,self}} \;\; Đ_i$ not just for unary diffusion, but also for the general case of n-component diffusion. For diffusion of a mixture of alkane isomers in MFI zeolite, for example, their model will not be able to explain why the self-diffusivity of the linear isomer falls dramatically as the concentration of the branched isomer reaches a value of 4 molecules per unit cell.[16–18]

It is worth pointing out that we have applied the M-S equations with success to describe the performance of fixed-bed catalytic reactors for alkylation and ethylation of benzene under conditions that approach pore saturation.[19,20]

Notation

c_i	pore concentration of species i, mol m^3
$Đ_i$	M-S diffusivity of species i, m^2 s^1
$Đ_{ij}$	M-S exchange coefficient, m^2 s^1
n	number of components in mixture, dimensionless
N_i	molar flux of species *i* defined in terms of the cross-sectional area of the crystalline framework, mol m^2 s^1
R	gas constant, 8.314 J mol^1 K^1
T	absolute temperature, K

Greek letters

Δ_{ij}	diffusivities defined by Eq. (2), m^2 s^1
ϕ	fractional pore volume of microporous material, dimensionless
μ_i	molar chemical potential, J mol^1

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