

Response to “Comment on ‘Normal, single-file, and dual-mode diffusion of binary adsorbate mixtures in AIPO 4 -5 ’” [J. Chem. Phys. 109, 5691 (1998)]

David S. Sholl and Kristen A. Fichthorn

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Response to "Comment on 'Normal, single-file, and dual-mode diffusion of binary adsorbate mixtures in $\text{AlPO}_4\text{-5}$ ' "

[J. Chem. Phys. 109, 5691 (1998)]

David S. Sholl

Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

Kristen A. Fichthorn

Departments of Chemical Engineering and Physics, The Fenske Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802

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In Ref. 1, we provided a general classification of the types of diffusion possible for multicomponent adsorbate mixtures in one-dimensional pores. The diffusion of mixtures of Ne and CF_4 in $\text{AlPO}_4\text{-5}$ pores was examined as an example of "dual-mode diffusion." We offer here a brief discussion of the thoughtful comments by Hahn and Kärger² regarding our Ne+ CF_4 / $\text{AlPO}_4\text{-5}$ results.

One complication with directly comparing our simulated CF_4 mobilities with experimental data is that the temperature of our simulations was $T=100$ K, while experimental data is only available at 180 K (Ref. 3) and 293 K.⁴ Our simulations cannot be directly extended to higher T because the use of smart Monte Carlo for computing dynamical information is limited to temperatures where transition state theory is valid.⁵ To directly compare the behavior of our atomically-detailed model to the available experimental data, we have simulated the diffusion of single CF_4 molecules in $\text{AlPO}_4\text{-5}$ using standard molecular dynamics (MD). In our MD simulations, we allow ensembles of CF_4 molecules to evolve independently by removing the intermolecular forces between the molecules and control the temperature of these ensembles using the Nosé–Hoover thermostat.⁶ The details of the adsorbate–pore interactions were identical to Ref. 1. We analyzed the diffusion of 200 independent molecules, each for 3 ns. For the temperatures discussed below, the typical displacement of an adsorbate during these simulations is 13–20 nm. To compare our results with the experimentally observed single-file mobilities, we converted the experimental values to infinite dilution tracer diffusivities, D_{id} , using^{2,3}

$$D_{\text{id}} = \pi \frac{F^2}{\sigma^2} \frac{\theta^2}{(1-\theta)^2}. \quad (1)$$

Here, $\sigma=0.47$ nm is the nominal diameter of CF_4 and θ is the pore occupancy relative to a perfect one-dimensional arrangement of adsorbates.² This approach is useful because the direct measurement of single-file mobilities from MD simulations requires very large scale simulations.^{1,7} Equation (1) cannot be exact in general, since simple models are known where it is not precisely obeyed.⁸ Concerted motion of multiple adsorbates may also complicate the relationship between F and D_{id} .⁹ Nonetheless, Eq. (1) has proven to

provide a useful expression for relating single particle diffusion and single-file mobilities at finite pore loadings.^{2,3} We calculated tracer diffusivities of $3 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ at 180 K and $6 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ at 293 K. We checked that these results are insensitive to the relaxation time of the Nosé–Hoover thermostat. The experimental diffusivities are $3\text{--}11 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ at 180 K (Ref. 3) and $1 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ at 293 K.⁴ These results confirm that the transport rates predicted by our simulations are substantially smaller than experimentally observed rates. We concur with Hahn and Kärger that the origin of this discrepancy is difficult to explain. In light of the fact that the experimental results are among the highest intracrystalline diffusivities that have been reported for adsorbate transport in zeolites^{3,4} and the observation that quantitative agreement between experimental and MD results has been achieved for diffusion in other zeolites,¹⁰ we suggest that this discrepancy is an interesting issue for further study.

Hahn and Kärger correctly point out that for the results with low CF_4 loadings in Fig. 2 of Ref. 1, the diffusing Ne molecules only pass one or two CF_4 molecules, on average, on the time scale of our simulations. We point out that our data with high CF_4 loadings, and of course the data point with $\theta_{\text{CF}_4}=0$, do not suffer from this difficulty. Even if we ignore the data with $\theta_{\text{CF}_4}=0.069$ and 0.139 (in the notation of Ref. 2), it is very clear from our results that the diffusivity of Ne is strongly reduced by the presence of CF_4 . We also note that Eq. (4) in Ref. 2 cannot hold as $\theta \rightarrow 0$, the same limit in which it is difficult to achieve complete convergence in our simulations. As a result, we feel that analyzing our data based on Eq. (4) of Ref. 2 does not provide a sound basis for determining the rate-limiting step for Ne diffusion. Thus, while a fully quantitative description of the diffusion of Ne at all CF_4 loadings is not currently available, our simulations conclusively demonstrate that the presence of CF_4 greatly reduces the diffusivity of Ne in $\text{AlPO}_4\text{-5}$ pores. Finding detailed descriptions of single-file mobilities and tracer diffusivities for binary adsorbate mixtures undergoing dual-mode diffusion remains a challenge for future work.

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