

## Reply to the Comment on “Computer Simulation of Incommensurate Diffusion in Zeolites: Understanding Window Effects”

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We would like to thank Professor Ruthven for highlighting some experimental difficulties in determining the diffusion coefficients in zeolites. We would like to clarify the two points raised in the comment.

### (1) Diffusivities for Linear Alkanes in LTA-Type Zeolite.

In the book of Kärger and Ruthven<sup>1</sup> and ref 2, it is stated that the lack of anomalies in 5A provides no evidence for the incommensurate diffusion (a window effect) in LTA-type zeolites. Our simulations show that in the cation free form of 5A (LTA) the onset of incommensurate diffusion is not to be expected until alkanes are as long as C<sub>20</sub>. In the C<sub>8</sub>–C<sub>20</sub> range, the diffusion rate is nearly constant. Accordingly, simulations indicate that the alleged lack of anomalies in the experimental data for alkanes shorter than C<sub>17</sub> has no bearing on incommensurate diffusion in LTA-type zeolites.

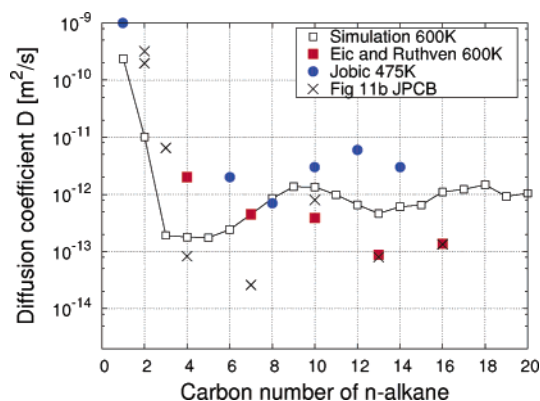
In our original publication, we used the experimental data as compiled by Kärger and Ruthven<sup>1</sup> and extrapolated these to the temperature of the simulations. In his comment, Professor Ruthven states that only the experimental data on large crystals are reliable. This data set shows a decrease of the diffusion coefficient in 5A with chain length. Figure 1 shows the data we have used previously together with recent data from Jobic et al.<sup>3</sup> In addition, we have clearly indicated the large crystal data points. The agreement between simulated and experimental data remains remarkable, especially if one considers that (1) we have obtained the parameters for our model from the adsorption of alkanes in MFI-type silica and (2) we simulate LTA-type silica, and not the mixed calcium and sodium form of the zeolite. More importantly, none of the experimental or simulated data suggests any incommensurate diffusion, irrespective of (the reliability of) the data points.

In his comments, Professor Ruthven stresses that the variation of the diffusion rate with alkane chain length shows no anomalies for LTA-type zeolites. We are inclined to disagree. In our opinion, the nearly constant diffusion rate in the C<sub>8</sub>–C<sub>20</sub> range is anomalous, for usually diffusion rates decrease with increasing *n*-alkane chain length. In addition, a more detailed inspection of our simulation data suggests that there is a small increase in diffusion for C<sub>5</sub>–C<sub>10</sub>. This local maximum is related to a cage effect; that is, at C<sub>5</sub>–C<sub>10</sub>, the molecule starts to feel the limitations of the cage, whereas the nearly constant diffusion coefficient in the C<sub>8</sub>–C<sub>20</sub> range is a consequence of the cage–window structure of LTA.

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**Figure 1.** Diffusivities for linear alkanes in LTA-type zeolite as a function of carbon number. The simulations are compared to the experimental results of Eic and Ruthven.<sup>1,2</sup> For reference, the disputed data of Figure 11b (ref 4) and the new experimental data of Jobic et al.<sup>3</sup> are included.

Very recently, experimental data were published by Jobic et al.<sup>3</sup> that support the two anomalies predicted by our simulations. These new data do not agree with the data mentioned in the comment of Ruthven, but do support our conclusion that the diffusion coefficient shows a local maximum near C<sub>10</sub> or C<sub>12</sub> (depending on the loading, temperature, and amount of cations) due to a cage effect.

**(2) The “Window Effect” in Zeolite T.** One could say that “zeolite T” denotes a complex family of materials comprising a myriad of possible intergrowths between OFF- and ERI-type zeolites. Goring reported that the potassium form of one of the zeolite T family members exhibited incommensurate diffusion. Reproducing Goring’s diffusion coefficients for “zeolite T” by modern methods proved to be a challenge. Since Goring’s diffusion measurements do not meet contemporary standards, the existence of incommensurate diffusion in zeolites has become controversial. In our view, evaluating the relevance to zeolites of incommensurate diffusion requires samples better defined than zeolite T. Our simulations predict that ERI-type silica and, by extension, AIPO-17 exhibit incommensurate diffusion. Very recently, a paper was published that reports a periodic dependence of the diffusion coefficient on the number of carbon atoms in *n*-alkanes in MTW- and LTL-type zeolites. The paper relates the diffusion coefficient to the degree to which the shape of a molecule and the shape of the channels are (in)commensurate.<sup>5</sup> To the best of our knowledge the diffusion coefficients were obtained using contemporary experimental techniques and validation criteria. In addition to this recent report on incommensurate diffusion, Jobic et al. found experimental evidence of an increase in diffusion due to an innercage reorganization of a molecule as predicted by our work.<sup>4</sup> This illustrates an important observation, namely that a diffusion coefficient in a zeolite can increase as a function of chain length.

### References and Notes

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# COMMENTS

## Comment on “Computer Simulation of Incommensurate Diffusion in Zeolites: Understanding Window Effects”

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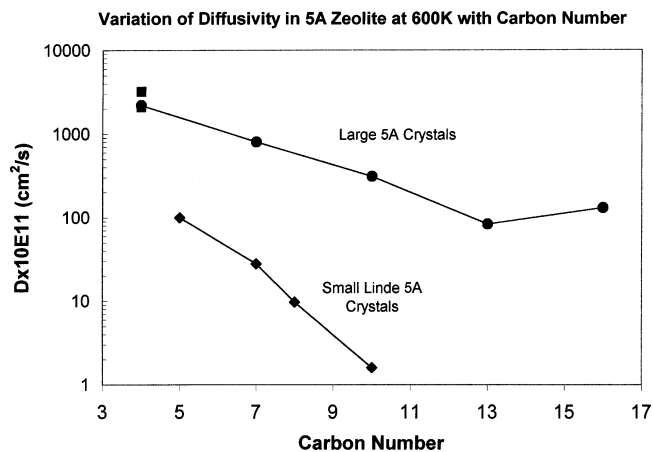
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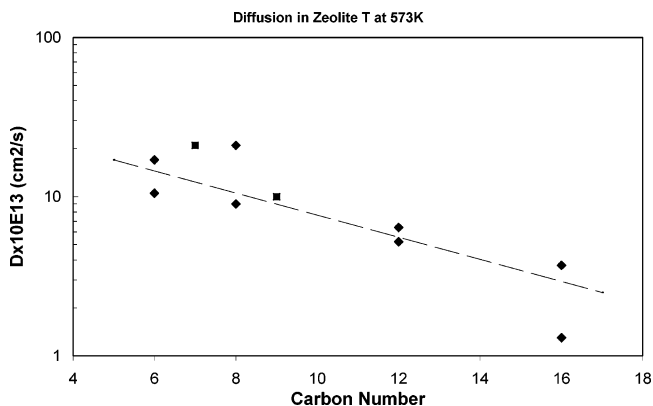
This paper<sup>1</sup> presents an interesting example of the power of molecular simulations to predict the diffusivities of sorbate molecules in zeolite adsorbents under sterically restricted conditions. There are, however, two major points which should not be allowed to pass without comment.

(1) **Diffusivities for Linear Alkanes in 5A Zeolites.** Figure 11b, which purports to show the experimental data of Eic and Ruthven<sup>2</sup> extrapolated to 600 K, indicates a clear maximum in the plot of diffusivity vs carbon number at C<sub>10</sub>. This is in accordance with the molecular simulation results which also suggest a maximum at C<sub>10</sub>, leading the authors to state: “The agreement between simulated data on a cation-free LTA type sieve and the experimental data on a cation-loaded LTA type zeolite is remarkable.” In fact the experimental data of Eic and Ruthven, which are reproduced in Figure 1, show a monotonic decline in diffusivity with carbon number. There is no evidence of a maximum in the diffusivity at C<sub>10</sub>. It should be noted that the ZLC measurements reported by Eic and Ruthven were made using several different samples of relatively large (7.3–55 μm) laboratory synthesized crystals of 5A zeolite. Earlier gravimetric data for small (3–4 μm) commercial Linde 5A crystals obtained by Loughlin, Derrah, Doetsch, and Vavlitis<sup>3–5</sup> were included for comparison. As may be seen from Figure 1, the two data sets are quite distinct with the reported diffusivities for the commercial material being substantially smaller and showing a steeper decrease with carbon number. We now suspect that the low diffusivity values observed for the commercial material reflect a surface resistance resulting from the severe conditions used in the initial dehydration step, as suggested by Kondis and Dranoff many years ago.<sup>6</sup> However, neither data set shows any evidence of a maximum in diffusivity at C<sub>10</sub>. The plot shown in Figure 11b of the paper by Dubbeldam and Smit is misleading and could only have been obtained by a judicious selection of data points from the two different data sets.

(2) **The “Window Effect” in Zeolite T.** The 1973 paper by Goring<sup>7</sup> in which the idea of a “window effect” was first introduced is probably one of the most frequently cited references in zeolite science. Unfortunately, because the reported effect appears novel and interesting the validity of Goring’s experimental data has often been accepted without critical reexamination. He used very large (5 gm) samples of small (micron sized) zeolite crystals and made integral gravimetric measurements between zero loading and one atmosphere of sorbate pressure. Only adsorption measurements were made and neither the mass of the sample nor the pressure step was changed to check for system linearity. Anyone with practical experience of this kind of measurement would realize that it would be



**Figure 1.** Variation of corrected diffusivity ( $D_0$ ) with carbon number for linear alkanes in 5A zeolites at 600K. ■,▲; gravimetric data of Yucel obtained with 3 different samples of large 5A crystals.<sup>10</sup> ●, ZLC data of Eic and Ruthven<sup>2</sup> for large laboratory synthesized 5A crystals. ◆, gravimetric data of Doetsch<sup>3</sup> and Vavlitis<sup>5</sup> for small (3–4 μm) commercial 5A crystals.



**Figure 2.** Variation of diffusivity with carbon number for linear alkanes in Zeolite T at 573K. ■, Data of Magalhaes et al.;<sup>9</sup> ◆, data of Cavalcante et al.<sup>8</sup> ( $D_0$ ).

virtually impossible to obtain reliable intracrystalline diffusivity data from such experiments. The results would almost certainly have been impacted by nonlinearity, extracrystalline diffusion and heat transfer effects. Such considerations led two independent research groups to attempt to reproduce these measurements using more modern experimental techniques.<sup>8,9</sup> This is not straightforward since zeolite T is a poorly defined material being an intergrowth of erionite and offretite. Cavalcante et al.<sup>8</sup> therefore used two different materials containing different proportions of offretite and erionite. Their results are shown, together with the data of Magalhaes et al.<sup>9</sup> in Figure 2. Although the data show considerable scatter the two data sets are remarkably consistent and suggest a monotonic decline in diffusivity with carbon number. There is no evidence to suggest that the minimum and maximum reported by Goring (at C<sub>8</sub> and C<sub>12</sub> respectively) are genuine.

Although, on the basis of this evidence, it would be presumptuous to state that the “window effect” does not exist,

I believe that it is reasonable to assert that there are, as yet, no *reliable* macroscopic measurements that show the existence of such an effect.

#### References and Notes

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