

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

D. Dubbeldam,<sup>\*,†</sup> T. L. M. Maesen,<sup>‡</sup> and B. Smit<sup>†</sup>

Department of Chemical Engineering,  
University of Amsterdam, Nieuwe Achtergracht 166,  
1018 WV Amsterdam, The Netherlands, and ChevronTexaco,  
Energy Technology Company, Chevron Way 100,  
Richmond, California 94802-0627

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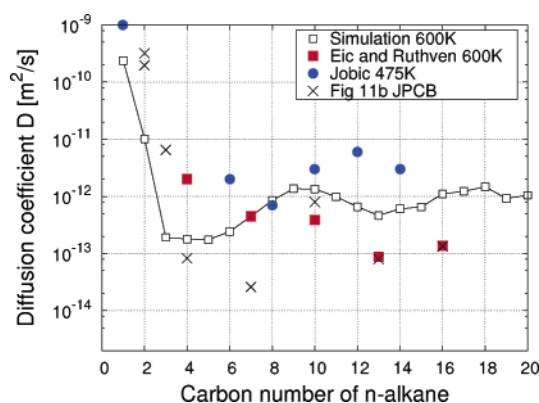
We would like to thank Professor Ruthven for highlighting some experimental difficulties in determining the diffusion coefficients in zeolites. We would like to clarify the two points raised in the comment.

## (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.



**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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\* To whom correspondence should be addressed. E-mail: dubbelda@science.uva.nl.

<sup>†</sup> University of Amsterdam.

<sup>‡</sup> ChevronTexaco.